# Formation and reactions of radicals during pyrolysis of acetone and reaction of hydrogen atoms with ethane

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by

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for the degree of Doctor of Philosophy

at

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# List of important reactions

Part 1	number
$CH_3COCH_3 \rightarrow CH_3CO + CH_3$	(1)
$CH_3CO \rightarrow CH_3 + CO$	(2)
$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$	(3)
$CH_2COCH_3 \rightarrow CH_2CO + CH_3$	(4)
$2 \text{ CH}_3 \rightarrow \text{C}_2\text{H}_6$	(5)
$CH_2COCH_3 + CH_3 \rightarrow C_2H_5COCH_3$	(6)
$2 \text{ CH}_2\text{COCH}_3 \rightarrow (\text{CH}_2\text{COCH}_3)_2$	(7)
Part 2	
$H + C_2H_6 \rightarrow H_2 + C_2H_5$	(21)
$H + C_2H_5 \rightarrow 2 \ CH_3$	(28)
$H + C_2H_5 \rightarrow H_2 + C_2H_4$	(2 9)
$H + CH_3 + M \rightarrow CH_4 + M$	(2 10)
$CH_3 + C_2H_5 \rightarrow C_3H_8$	(211)
$H + C_2 H_4 \rightarrow C_2 H_5$	(2 13)
$2 \text{ C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$	(2 14)
$H + wall \rightarrow 1/2 H_2$	(2 17)
$H + C_2H_5 + M \rightarrow C_2H_6 + M$	(2 21)
$H + H + M \rightarrow H_2 + M$	(2 36)

# List of important equations

Part 1 number

$$k/k_{\infty} = F_{LH} F^{SC} F^{WC}$$
(35)

$$\log k = \log \left( \frac{\delta k_{\rm B} T \Gamma B_{\rm tr} B_{\rm e} B_{\rm v} B_{\rm IR} B_{\rm r}}{h} \right) - \left( \frac{E_0}{2.303 \,\rm RT} \right)$$
(74)

$$t = \left(\frac{pv}{RT}\right) \left(\frac{1}{\frac{\Delta n_b}{\Delta t}}\right)$$
(84)

$$k_{1} = (R_{e}^{ss} + R_{b}^{ss} + R_{h}^{ss})/[A]$$
(85)

$$k_3 = R_m^{ss} k_5^{1/2} / ((R_e^{ss})^{1/2} [A])$$
(86)

$$(k_3 k_4 / k_6) = (R_m^{ss})^2 / (R_b^{ss} \times [A])$$
(87)

$$R_{b}^{ss} = m(R_{e}^{ss} R_{h}^{ss})^{1/2}$$
(90)

$$\frac{R_{\rm m}^{\rm app}}{R_{\rm m}^{\rm ss}} = 1 - \frac{\tau_{\rm h}}{t} \tag{91}$$

$$\kappa = \lambda / (C_0 C_p) \tag{93}$$

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$$\frac{\mathbf{R}_{\mathrm{m}}^{\mathrm{app}}}{\mathbf{R}_{\mathrm{m}}^{\mathrm{ss}}} = \frac{\tau_{\mathrm{c}}}{\mathrm{tln}\,2} \ln\!\left(\cosh\!\left(\frac{\mathrm{tln}\,2}{\tau\,\mathrm{c}}\right)\right) \tag{103}$$

$$\tau_{\rm c} = \left(\frac{1}{k_3} + \frac{[A]}{k_4}\right) \left(\frac{1}{2k_1[A]^2}\right) R_{\rm m}^{\rm ss} \times \ln 2 \tag{106}$$

$$\frac{1}{k_4} = \frac{2\tau_c k_1[A]}{\ln(2) R_M^{ss}} - \frac{1}{k_3[A]}$$
(117)

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$$\frac{1}{\mathbf{k}_{6}} = \left(\frac{\Phi}{\mathbf{k}_{3}}\right) \left(\frac{2\tau_{c} \mathbf{k}_{1}[\mathbf{A}]}{\ln(2) \mathbf{R}_{\mathbf{M}}^{\mathbf{ss}}} - \frac{1}{\mathbf{k}_{3}[\mathbf{A}]}\right)$$
(119)

Part 2

11

$$[H] = \frac{k_{w}}{\frac{\exp(k_{w}t)(k_{w}+2k_{236}[M][H_{0}])}{[H_{0}]} - 2k_{236}[M]}$$
(238)

$$[H] = \frac{k_{w} + nk_{21}[C_{2}H_{6}]}{\frac{e xp(k_{w} + nk_{21}[C_{2}H_{6}])(t + \delta t)(k_{w} + nk_{21}[C_{2}H_{6}] + 2k_{236}[M][H_{0}])}{[H_{0}]} - 2k_{236}[M]}$$
(2 54)

$$[H] = \frac{k_{w} + nk_{21}[C_{2}H_{6}]}{\frac{e xp(k_{w} + nk_{21}[C_{2}H_{6}])(t - \delta t))(k_{w} + nk_{21}[C_{2}H_{6}] + 2k_{236}[M][H_{0}])}{[H_{0}]} - 2k_{236}[M]}$$
(2.55)

$$n = \frac{[H]_{consumed}}{0.5[CH_4] + [C_2H_4] + 1.5[C_3H_8] + 2[C_4H_{10}] + [C_2H_6]}$$
(2.57)

### **Abstract**

The kinetics of two reaction systems have been studied.

In the first part, the pyrolysis of acetone in a flow system has been investigated during its induction period. In that study gas chromatography and infra-red spectroscopy were used to identify and measure the products. The Troe method was used to study the fall-off behavior of the rate constant for the decomposition of acetone to  $CH_3$  and  $CH_3CO$ . The limiting high pressure Arrhenius parameters for the decomposition of acetone,  $\log_{10}$  $(A/s^{-1})= 17.9 \pm 0.8$  and  $E_A = 353 \pm 14$  kJ mol<sup>-1</sup>, were calculated for the first time in the temperature range 825 to 940 K. A transition state theory model was used to study the transition state properties of the reaction of  $CH_3$  with  $(CH_3)_2CO$ . It has been shown that the Arrhenius plot for this reaction is curved. The effective activation energy,  $46 \pm 1 \text{ kJ}$ mol<sup>-1</sup>, the characteristic tunneling temperature,  $375 \pm 17$  K, and the average transitional vibrational term value,  $279 \pm 8$  cm<sup>-1</sup>, in the transition state were calculated for this reaction. The limiting high pressure Arrhenius parameters for the decomposition of the acetonyl radical, CH<sub>3</sub>COCH<sub>2</sub>  $\rightarrow$  CH<sub>3</sub> + CH<sub>2</sub>CO, log<sub>10</sub> (A/s<sup>-1</sup>) = 15.58 ± 0.26 and E<sub>A</sub> =  $184.1 \pm 4.4$  kJ mol<sup>-1</sup>, were found for the first time. The geometry and frequencies of the acetonyl radical and the activated complex for this reaction were investigated at the HF/6-31G<sup>\*\*</sup> level of theory. This information was used to investigate the fall-off behavior for the rate constant of this reaction using RRKM theory. A value for the rate constant for the cross-combination reaction of methyl and acetonyl radicals of  $1.5 \pm 0.3 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> has been measured for the first time. A value for the rate constant for the recombination reaction of acetonyl radicals of  $3.0 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> has been determined for the first time in this temperature range

The second part of this thesis reports a study of the reaction of hydrogen atoms with ethane at 295 to 516 K and 4.1 to 8.6 Torr in a flow system. ESR and gas chromatography were used to measure the concentrations of H atoms and of the products, respectively. Computer simulation was performed to determine the main reactions and also to optimize the rate constants for the reaction of hydrogen atoms with ethyl radicals to produce methyl radicals and ethylene. The number of hydrogen atoms removed per ethane molecule reacted was calculated to be  $4.3 \pm 0.4$  at room temperature and to approach 3.1 at 516 K. The Arrhenius parameters for the reaction of hydrogen atoms with ethane, log<sub>10</sub>  $(A/L \text{ mol}^{-1}\text{s}^{-1}) = 10.38 \pm 0.09$  and  $E_A = 33.4 \pm 0.7 \text{ kJ mol}^{-1}$ , were calculated. The branching ratio for the reactions of hydrogen atoms with ethyl radicals to produce ethylene or methyl radicals was determined to be  $0.18 \pm 0.05$ . Also the ratio of the rate constant for the reaction of hydrogen atoms with ethyl radicals to produce methyl radicals, k<sub>2.8</sub>, to the rate constant for the reaction of hydrogen atoms with methyl radicals to produce methane,  $k_{2.10}$ , was found to be  $(2.9\pm0.4)\times10^{-4}$  mol L<sup>-1</sup>. Using this ratio and a value from the literature for  $k_{2,10}$ , a value of  $1.3 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> was found for  $k_{2,8}$ . A value of  $(3\pm 1) \times 10^{9}$ L mol<sup>-1</sup>s<sup>-1</sup> was found for the rate constant for the reaction of hydrogen atoms with ethyl radicals to produce ethylene.

### **List of Abbreviations**

- B magnetic field strength
- $\beta$   $\beta$  in Morse potential function
- $\beta_c$  collision efficiency
- $\beta_m$  Bohr magneton
- d collision diameter
- D diffusion coefficient
- $\delta$  reaction path degeneracy
- E<sub>0</sub> thresholu energy per mole
- $\epsilon_0$  threshold energy per molecule
- F<sup>SC</sup> strong collision broadening factor
- F<sup>WC</sup> weak collision broadening factor
- g g factor
- $\Gamma$  tunnel factor
- h Planck constant
- $I_{at}$  integrated intensity of atom in ESR
- J total angular momentum
- k<sub>B</sub> Boltzmann constant
- k, rate constant for reaction i
- κ thermal diffusivity
- $\kappa(\varepsilon)$  transmission probability
- $\lambda$  thermal conductivity
- M modulation factor in ESR
- M<sub>J</sub> component value of total angular momentum
- me mass of electron
- m<sub>I</sub> component value of nuclear spin
- m<sub>s</sub> component value of electron spin
- $\mu$  reduced mass
- n number of moles

- v frequency
- p<sub>b</sub> pressure in the storage bulb
- Q partition function
- Q<sub>at</sub> calibration factor in ESR
- R gas constant
- R<sub>i</sub> rate of formation of I
- s vibrational degrees of freedom
- S<sub>z</sub> spin operator
- $\sigma$  cross section
- t time
- T<sup>\*</sup> characteristic tunneling temperature
- T<sub>b</sub> temperature of the storage bulb
- $\tau_h$  heat transfer induction period
- $\tau_c$  chemical induction period
- $\theta$  mean free path
- v<sub>b</sub> volume of the storage bulb
- V Flow velocity
- $V_H$  flow rate of the hydrogen atoms
- W power in ESR
- ω bending term value
- Z collision number

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Part one

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The pyrolysis of acetone

#### **1. Introduction**

#### 1-1. General introduction and mechanism

The pyrolysis and photolysis of acetone are complex processes which are composed of several elementary reactions and are believed to occur by free radical chain mechanisms. A survey of the literature reveals that in the last three decades the photolysis of acetone has been much more frequently investigated than the pyrolysis of this compound. According to a review<sup>1</sup> the photolysis of acetone is the most studied reaction in gas kinetics. However, these studies have been limited to the temperature range of 300 to 750 K.

It is the objective of the present study to simultaneously examine the initiation and termination steps, which are mostly investigated in pyrolysis studies, and the propagation reactions, which were of concern in the photolysis experiments, in order to have a better picture of how this system works. It will also be an objective to calculate the individual rate constants for different steps involved in this reaction. We will study this reaction in a flow system over a temperature range of 825 to 940 K and a pressure range of 10 to 180 Torr in the early stages of the reaction where conversion is less than 3%. Low conversion of acetone at low residence times prevents interference by secondary reactions.

The thermal decomposition of acetone has been studied in a less detailed way since the 1920's. In 1926 Hinshelwood and Hutchinson<sup>2</sup> measured the rate of decomposition of acetone vapour in a quartz bulb maintained at temperatures of 773-873 K. They reported that the decomposition is a homogeneous first order reaction with carbon monoxide, methane, ethylene and hydrogen as major products.
Rice and Vollrath<sup>3</sup> observed that, when acetone is passed through a heated glass tube, methane and ketene result. They suggested that at high temperatures the ketene undergoes a bimolecular decomposition and converts to  $C_2H_4$  and CO.

In 1934 Rice and Herzfeld<sup>4</sup> studied the thermal decomposition of some organic compounds. In that study they considered the mechanism of the thermal decomposition of acetone. They proposed that the reaction proceeds almost entirely by a free radical mechanism, as follows

$$(CH_3)_2CO \rightarrow CH_3 + CH_3CO \tag{1}$$

$$CH_3CO \rightarrow CH_3 + CO$$
 (2)

$$CH_3 + (CH_3)_2 CO \rightarrow CH_4 + CH_3 COCH_2$$
(3)

$$CH_3COCH_2 \rightarrow CH_2 = CO + CH_3$$
 (4)

$$2CH_3 \rightarrow C_2H_6 \tag{5}$$

$$CH_3 + CH_3COCH_2 \rightarrow CH_3COC_2H_5 \tag{6}$$

$$2CH_3COCH_2 \rightarrow (CH_3COCH_2)_2 \tag{7}$$

They suggested that the concentration of CH<sub>3</sub>COCH<sub>2</sub>, one of the main carriers of the chain, is proportional to the concentration of acetone because it is produced by a collision of methyl radicals with acetone. In a later theoretical article, Rice, Rodowskas and Lewis<sup>5</sup> wrote that the main products in the early stages are methane and ketene and that the overall decomposition of acetone may be represented by the equation

$$(CH_3)_2CU \rightarrow CH_4 + CH_2 = CO \tag{8}$$

Winkler and Hinshelwood<sup>6</sup> in an experimental study on the thermal decomposition of acetone vapour mentioned that after a time ketene is decomposed as rapidly as it is formed.

They showed that acetone pyrolysis is first order in acetone in the pressure range of 120-200 Torr. They reported CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, ketene and an unsaturated compound as products for 12 to 98% acetone decomposition. They reported ethane as product only at 98% conversion at 873K.

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McNesby, Davis and Gordo  $1^7$  in 1954 studied the pyropsis of a mixture of acetone and acetone-d<sub>6</sub> in the temperature range from 739 to 797 K. They agreed that a Rice-Herzfeld mechanism, equations (1) to (7), is consistent with the facts. They found ethane and 2,5hexanedione, the products of reactions (5) and (7), but were unable to find butanone, the product of reaction (6). They suggested that the presence of ethylene and ketene as well as large amounts of CO indicated that ketene decomposition also occurred. Using Winkler and Hinshelwood's<sup>5</sup> data they suggested that acetone pyrolysis is first order in acetone only in the pressure range of about 120-300 Torr at 875 K and it is more likely that the reaction order is 3/2 in the pressure range 3.5-120 Torr. They suggested the activation energy for the reaction (3) as 40.1 kJ/mol.

In 1961 Brinton<sup>8</sup> studied the photolysis of acetone in the range of 473 to 748 K. He proposed a mechanism consisting of reactions (9), (3), (5), (6) and (7).

$$(CH_3)_2CO + h\nu \rightarrow 2CH_3 + CO \tag{9}$$

He recommended the following mechanism for the photolysis below 373 K

$$(CH_3)_2CO + h\nu \rightarrow CH_3CO + CH_3 \tag{10}$$

$$CH_3CO \rightarrow CH_3 + CO$$
 (2)

$$CH_{3}CO + CH_{3} \rightarrow CH_{4} + CH_{2} = CO$$
(11)

 $2CH_3-CO \rightarrow CH_3CHO + CH_2=CO$ (12)

$$2CH_3-CO \rightarrow (CH_3-CO)_2 \tag{13}$$

He reported CH<sub>4</sub>, CO,  $C_2H_4$ ,  $C_2H_6$ , ketene, butanone, methyl vinyl ketone and 2,5-hexanedione as products. He also suggested the following reaction as an additional source for ethane

$$CH_3 + (CH_3)_2 CO \rightarrow C_2 H_6 + CO + CH_3$$
(14)

Brinton also studied the dark reaction, but he was not able to detect butanone and 2,5hexanedione, products of reactions (6) and (7), in the dark reaction experiments

# 1-2. Previous studies on each of the individual reactions and the objective of the present study

#### 1-2-1. Dissociation of acetone to CH<sub>3</sub>CO and CH<sub>3</sub>, reaction (1)

Winkler and Hinshelwood<sup>6</sup> in their study on the pyrolysis of acetone suggested an Arthenius expression for reaction (1) as

$$\log k_1 (s^{-1}) = 10^{1491} \exp \left(-284 \ 2 \ \text{kJ mol}^{-1} \ / \ \text{RT}\right)$$
(15)

In 1955 Szwarc and Taylor<sup>9</sup> studied the co-pyrolysis of acetone and toluene They observed CO,  $CH_4$ ,  $C_2H_6$ ,  $CH_2CO$  and  $C_6H_5CH_2CH_3$  as the products They suggested that the initial step, equation (1), was first order and unimolecular Using the measured CO concentrations, they wrote the rate constant for this reaction as

$$k (s^{-1}) = 2.4 \times 10^{14} \exp(-301 \text{ kJ mol}^{-1}/\text{RT})$$
 (16)

Clark and Pritchard<sup>10</sup>, using the same technique, measured  $E_A$  for reaction (1) equal to 296 4 kJ/mol with the same pre-exponential factor as Szwarc and Taylor They also measured CO to monitor the extent of the reaction

In 1976 Ernst and Spindler<sup>11</sup> studied the thermal decomposition of acetone behind reflected shock waves in the temperature range 1350 to 1650 K Using ultra-violet absorption by acetone, they reported the rate constant of reaction (1) as

$$k_1 (s^{-1}) = 10^{1643} \exp(-342 (\pm 13) \text{ kJ mol}^{-1}/\text{RT})$$
 (17)

In the present study the Troe factorization method is used to investigate the pressure dependency of  $k_1$  and also to calculate the low- and high-pressure limiting values for this rate constant over the present temperature range. The reaction is studied at low conversion of acetone to prevent possible secondary reactions

# 1-2-2. Acetyl radical decomposition, reaction (2)

Bencsura, Knyazev, Slagle, Gutman and Tsang<sup>12</sup> in 1992 studied the weak collision effects in reaction (2) over the temperature range 420 to 500 K In that study they reported the Arrhenius expression for the high pressure limiting value for the rate constant of reaction (2) as  $k (s^{-1}) = 10^{13 40} exp(-68 54 kJ mol^{-1}/RT)$  (18)

A survey of the literature<sup>13</sup> shows a relatively good agreement between different studies on reaction (2) The activation energy for reaction (2) reported by Bencsura *et al*<sup>12</sup> is about one-fourth of the activation energy for reaction (1) reported by different workers  $^{\circ 10,11,13}$ 

In the present study it was assumed that the big difference between the activation energies for reactions (1) and (2) causes the  $CH_3CO$  concentration to reach its steady state very fast Reaction (2) is the major consumer of acety! radicals at low conversions

## 1-2-3. Hydrogen abstraction by CH<sub>3</sub> from an acetone molecule, reaction (3)

Reaction (3) has mostly been studied in the photolysis of acetone<sup>1</sup> The lowest temperature photolysis experiments on this reaction in the literature were reported by Dorfman and Noyes in 1948 for 300 to 395 K<sup>14</sup> They reported their results as  $k_3/k_5^{1/2}$  and suggested 27 2 kJ mol<sup>-1</sup> as the activation energy for reaction (3)

Trotman-Dickenson and Steacie<sup>15</sup> in a study of the photolysis of acetone in a temperature range of 423-523 K noticed the pressure dependence of  $k_3/k_5^{1/2}$  and expressed their results at 24 Torr as

$$k_3/k_5^{1/2}$$
 (L mol<sup>-1</sup> s<sup>-1</sup>)<sup>1/2</sup> =10<sup>701</sup> exp(-40 6 kJ mol<sup>-1</sup> / RT) (19)

They found the pre-exponential factor for this ratio changed by 0 06 log unit from 24 to 100 Torr For deuterated acetone they calculated  $E_3$ - $E_5/2$  to be 43 1 kJ/mol They suggested that the activation energy,  $E_5$ , for the methyl-methyl reaction is equal to zero

Nicholson<sup>16</sup> in 1951 studied the photolysis of acetone over the temperature range 300-480 K He reported his results as  $k_3/k_5^{1/2}$  He suggested 40 1 kJ mol<sup>-1</sup> as the activation energy for reaction (3)

In 1954 Mandelcorn and Steacie<sup>17</sup> photolyzed acetone over a temperature range of 557-712 K They suggested that formation of ethylene, a minor product, became more important at higher temperatures They reported rates of formation of methane, ethane, ethylene, and carbon monoxide They did not mention observation of ketene, the product of reaction (4), as a product They also reported values for the ratio of the rate constants for reaction (3) and reaction (5),  $k_3/k_5^{1/2}$ , at two different pressures using the relationship

$$\frac{k_3}{k_5^{1/2}} = \frac{R_m}{R_e^{1/2}[A]}$$
(20)

Here  $R_m$  and  $R_e$  are the rates of formation of methane and ethane and [A] is the concentration of the acetone.

In 1968 Gray and Herod<sup>18</sup> studied the abstraction of a hydrogen atom from acetone by a methyl radical in a chain propagation step, reaction (3), in the photolysis of acetone. Using Shepp's<sup>19</sup> value for the rate constant,  $k_5$ , they calculated the temperature dependence of the rate constant for reaction (3) as

$$k_3 (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{846 \pm 0.07} \exp (-40.3 (\pm 0.3) \text{ kJ/mol} / \text{RT})$$
(21)

Shapiro and Weston<sup>20</sup>, in a study of kinetic isotope effects in the reaction of methyl radicals with H<sub>2</sub> and D<sub>2</sub>, measured the activation energy for reaction (3). In that work they assumed that the Arrhenius plot for the reaction of methyl radicals with H<sub>2</sub> and D<sub>2</sub> is linear Using this assumption they reported their value for the activation energy of reaction (3) This assumption is in contrast with the report by Furue and Pacey<sup>21</sup> that showed a non-linear Arrhenius plot for the reaction of methyl radicals with H<sub>2</sub>. Reaction (3) is a hydrogen abstraction reaction.

A survey of the literature<sup>13</sup> shows that the reported Arrhenius parameters for reaction (3) in the temperature range of 400-700 K are almost all the same, with the exception of the activation energies of 65.2 kJ mol<sup>-1</sup> reported by Brinton<sup>8</sup> from photolysis experiments. Brinton noticed that the Arrhenius plot for  $k_5/k_3^2$  appeared to start to curve in the temperature range 638 to 708 K The Arrhenius parameters for reaction (3) from different references are shown in Table 1 1

T (K)	$\log (A / L mol^{-1}s^{-1})$	E ( $kJ mol^{-1}$ )
473-748 <sup>8</sup>		65 2
300-395 <sup>14</sup>		27 2
290-470 <sup>16</sup>		40.1
423-523 <sup>15</sup>	701	40 6
557-712 <sup>17</sup>		41 0
403-523 <sup>18</sup>	8 46 ± 0 07	$40.3 \pm 0.3$
393-523 <sup>22</sup>	<b>8</b> 50 ± 0 10	$40.3\pm0.8$
398-718 <sup>20</sup>	8 51	40 3
393-518 <sup>23</sup>	8 61 ± 0 05	$40.5 \pm 0.5$
390-517 <sup>24</sup>	$853\pm0.02$	40 6 ± 0 2
398-522 <sup>25</sup>	8 54 ± 0 02	$40.0 \pm 0.2$

Table 1.1 Experimental values of the Arrhenius parameters for reaction (3)

Reaction (3) could provide some information on the tunnel effect if data is available in a wide range of temperature The present study extended the temperature range for this reaction up to 940 K in order to investigate the tunnel effect

#### 1-2-4. Decomposition of CH<sub>3</sub>COCH<sub>2</sub> radicals, reaction (4)

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This reaction is a unimolecular reaction and is expected to be pressure dependent Because of the complexity of the mechanism of the pyrolysis or photolysis of acetone it was difficult to find Arrhenius parameters for reaction (4) independently Rice and Herzfeld<sup>4</sup> in their study on the pyrolysis of acetone compared the difference and summation of the activation energies for reactions (3) and (4) and reported an activation energy for reaction (4) equal to 201 kJ mol<sup>-1</sup> Brinton<sup>8</sup> in an acetone photolysis experiment has measured the ratio of  $k_d/k_7^{1/2}$ and plotted the logarithm of this ratio versus temperature and reported an activation energy for reaction (4) as 171 kJ mol<sup>-1</sup> It is expected that the activation energy for a recombination reaction like reaction (7) is zero In the present study the high-pressure value of  $k_4/k_6$  has been calculated. By using information from measurements of the induction periods it has been possible to find a value for  $k_4$  or  $k_6$  at 876 K. The fall-off behaviour of  $k_4$  has also been investigated using the Troe method and RRKM method. To use RRKM theory the necessary parameters have been calculated theoretically at the semi-empirical level of AM1 and also at HF/3-21G and HF/6-31G\*\* levels of ab initio theory.

# 1-2-5. Recombination of methyl radicals, reaction (5)

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The recombination of methyl radicals, reaction 5, plays a significant role in pyrolysis and combustion. It is also important in experimental gas kinetics as a reference reaction in competitive studies of  $CH_3$  radical-molecule reactions, and as a model system on which to test unimolecular rate theory.<sup>26</sup>

Most of the early measurements on this reaction were carried out by means of the rotating sector(r.s.) technique. Using an improved version of sector theory, Shepp<sup>19</sup> recalculated the rate constant for this reaction, and obtained the value  $2.2 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup>. Similar results were later obtained in flash photolysis (f.p.),<sup>27</sup> and molecular modulation spectroscopy(m.m.s.)<sup>28</sup> experiments. High-temperature shock tube<sup>29</sup> (s.t.) studies yielded somewhat lower values. The agreement between the r.s., f.p., and m.m.s. values led Baulch and Duxbury<sup>30</sup>, in their evaluation of the literature until 1978, to recommend  $2.4 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> as the best value for the rate constant near the high-pressure limit in the temperature range 250-450 K.

In 1980 Pacey and Wimalasena<sup>31</sup>, in a study of the pyrolysis of neopentane, reported a value of  $(2.2\pm0.5) \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> at 823 K for this reaction.

In 1986 Arthur and Biordi<sup>32</sup> suggested  $(2.8\pm0.4) \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> as the best value for the rate constant for CH<sub>3</sub> radical recombination in the temperature range 295-450 K, and compared the rate constant for recombination, measured directly, with the value  $2.8 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> deduced from the rate constant of the reverse reaction, the thermal decomposition of C<sub>2</sub>H<sub>6</sub>, at different temperatures.<sup>20,33</sup>

Wagner and Wardlaw<sup>34</sup> studied the temperature and pressure dependence of this reaction theoretically and suggested the high-pressure limiting rate constant expression as  $k_5 (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{13.96} (\text{T})^{-1.18} \exp(-2.74 \text{ kJ mol}^{-1}/\text{RT})$  (22)

In 1989 Darvesh, Boyd, and Pacey<sup>35</sup> by ab initio calculation found a rate constant for this reaction equal to  $5 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> at 300 K, decreasing with increasing temperature

In the present study the expression reported for  $k_5$  by Wagner and Wardlaw, equation (22), has been used to substitute in the measured  $k_5/k_3^2$  ratio to calculate  $k_3$ 

# 1-2-6. Reaction of methyl radicals with acetonyl radicals, reaction (6)

The present study is the first study to report a value for the rate constant of reaction (6) using the measured induction period data for the formation of methane during the pyrolysis of acetone In the present study, assuming a steady state, it was possible to calculate the ratio of the rate constants for reactions (4) and (6) Having the data obtained from the induction period measurements made it possible to calculate the value of  $k_6$ 

## 1-2-7. Recombination of acetonyl radicals, reaction (7)

To the best of the author's knowledge there is only one paper in the literature which reported a value for the rate constant of reaction (7) Cox, Munk, Nielsen, Pagsberg and Rataczak,<sup>36</sup> in a study of the ultra-violet absorption spectra and kinetics of acetonyl

and acetonylperoxy radicals, reported a value of  $2.88 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> for k<sub>7</sub> at room temperature. In the present work the ratio of  $k_7k_5/k_6^2$  has been measured and, using a value for k<sub>5</sub> from the literature and the value of k<sub>6</sub> calculated in the present study, it was possible to calculate k<sub>7</sub> in the temperature range 825 to 940 K.

#### 2. Theoretical background

In this chapter the history of unimolecular reactions will be presented The RRKM and Troe methods to calculate the fall-off behavior of unimolecular reactions will be discussed. A model to calculate transition state properties will be shown. The method used for the ab initio calculations for reaction (4) will be discussed. To end the chapter, the Bond Energy Bond Order method will be presented.

## 2-1. Unimolecular Reactions

Molecularity specifies the number of reactants or atoms that are involved in a particular reaction step. If a reactant spontaneously decomposes or isomerises to products in a single reaction step, the reaction is said to be unimolecular In such a reaction the activated complex contains the same atoms as the reactant molecule. Perrin<sup>37</sup> proposed in 1919 that reactant molecules acquire energy by absorbing radiation from the walls of the reaction vessel. This theory is called the radiation hypothesis

# 2-1-1. The Lindemann Theory

In 1922 Lindemann<sup>38</sup> proposed a general theory which forms the basis for the current theory of thermal unimolecular rates He proposed that molecules become energised by bimolecular collisions These energised molecules could then undergo a decomposition reaction - or deactivating collisions According to these concepts, the mechanism for a unimolecular reaction may be written as

$$A + M \xrightarrow{k_1} A^* + M$$
$$A^* + M \xrightarrow{k_2} A + M$$
$$A^* \xrightarrow{k_3} \text{ products}$$

The net rate of production of the short-lived intermediate A<sup>\*</sup> is equal to

$$\mathbf{R}_{A^{\bullet}} = \mathbf{k}_1 \, [\mathbf{A}] [\mathbf{M}] - \mathbf{k}_2 [\mathbf{A}^{\bullet}] [\mathbf{M}] - \mathbf{k}_3 [\mathbf{A}^{\bullet}] \tag{23}$$

By using the steady-state assumption, the rate of production of  $A^*$  is equal to the rate of consumption, thus  $R_{A^*}$  equals zero. Then the overall rate of reaction becomes

rate = 
$$k_{uni}[A] = k_3[A^*] = \frac{k_1k_3[A][M]}{k_2[M] + k_3}$$
 (24)

Clearly, the reaction rate is first order at high pressures, where [M] approaches  $\infty$ , and second order at low pressures, where [M] approaches zero.

## 2-1-2. The Hinshelwood Modification

In 1927 Hinshelwood<sup>39</sup> proposed that in addition to the translational energy the vibrational degrees of freedom, s, can contribute to the threshold energy,  $E_0$ . Then the probability that a molecule contains energy greater than or equal to  $E_0$  clearly increases with the number of internal degrees of freedom. According to the Hinshelwood-Lindemann theory the high-pressure rate constant is given by<sup>40</sup>

$$k_{\infty} = \frac{k_1 k_3}{k_2} = \frac{k_3}{(s-1)!} \left(\frac{E_0}{RT}\right)^{s-1} \exp\left(\frac{E_0}{RT}\right)$$
(25)

In Hinshelwood's modification, equation (25), the critical energy  $E_0$  in Figure 2-1 is involved but both  $k_2$  and  $k_3$  are treated as independent of the amou<sup>-+</sup> of energy,  $E^*$ , in the energised molecule.

# 2-1-3. The RRK Theory

Rice and Ramsperger<sup>41</sup> and, independently, Kassel<sup>42</sup> proposed theories in which both  $k_2$  and  $k_3$  were treated as dependent on the energy E<sup>\*</sup> contained within an individual energised molecule. These theories are referred to jointly as RRK theory. In this theory an amount of energy E<sup>\*</sup> is distributed among the normal modes of vibration and, because these normal modes



Figure 2-1. Energy Scheme for Lindemann, Hinshelwood, and RRK mechanism

are coupled loosely, it is possible that a critical amount of energy  $E^*$  associates with a particular normal mode and reaction can occur. The contributions of Rice, Ramsperger and Kassel were directed towards the development of expressions for the energy-dependence of  $k_3$ .

$$A+ M \xrightarrow{\delta k_{1}(E \to E+\delta E)} A^{*}_{(E \to E+\delta E)} + M$$
$$A^{*}_{(E \to E+\delta E)} + M \xrightarrow{k_{2}} A + M$$
$$A^{*}_{(E^{*})} \xrightarrow{k_{3}(E)} \text{ products}$$

The RRK theories assume that the rate constant for conversion of energised molecules to products is proportional to a finite statistical probability that the critical energy,  $E_0$ , will be found in the relevant part of the molecule. An expression is derived for the energy dependence of  $k_3$ ,

$$k_{3}(E) = B\left(\frac{E-E_{0}}{E}\right)^{s-1}$$
 (26)

where B is the proportionality constant and  $((E-E_0)/E)^{s-1}$  is the probability that some energy equal to or greater than  $E_0$  is allocated to one chosen oscillator. The rate constant expression for a unimolecular reaction according to these theories is written as

$$k_{uni.} = \int_{E_0}^{E^*} \frac{B\left(\frac{E^* - E_0}{E^*}\right)^{s-1} \frac{1}{(s-1)!} \left(\frac{E^*}{RT}\right)^{s-1} \frac{1}{RT} \exp\left(\frac{E^*}{RT}\right)}{1 + \frac{B}{k_2[M]} \left(\frac{E^* - E_0}{E^*}\right)^{s-1}} dE$$
(27)

In this expression B is the rate constant corresponding to the free passage of the system through the dividing surface. When [M] is very large, that is, at the high-pressure, first-order limit, this expression reduces approximately to

$$k_{\text{uni},\infty} = \text{Bexp}\left(\frac{-E_0}{RT}\right)$$
(28)

This theory would predict a pre-exponential factor of about  $10^{13}$  s<sup>-1</sup> for all unimolecular reactions. This is true for some reactions, but for many the values are very much greater than this. RRK theory provides no explanation for such high values. Also this theory could not predict the best value for s

## 2-1-4. The RRKM theory

In 1952 Marcus<sup>43</sup> extended the RRK theory by using transition state theory concepts. This theory now is known as the RRKM theory and in this theory the individual vibrational frequencies of the energised species and activated complexes are considered explicitly. According to this theory the mechanism of a unimolecular reaction is written as

$$A + M \xrightarrow{\delta_{k_1}(E^* \to E^* + \delta E^*)} A_{(E^* \to E^* + \delta E^*)} + M$$
$$A_{(E^* \to E^* + \delta E^*)} + M \xrightarrow{k_2} A + M$$
$$A_{(E^*)}^* \xrightarrow{k_3(E^*)} \text{ products}$$

There are essentially two new principles involved in the RRKM treatment. Firstly, the energization rate constant,  $k_1$ , is evaluated as a function of energy by a quantum-statisticalmechanical treatment instead of the classical treatment used in the RRK. The de-energization rate constant  $k_2$  is considered as in that theory to be independent of energy, and is often assumed to be the collision number Z or  $\beta_c Z$  where  $\beta_c$  is a collisional deactivation efficiency. The second major feature of RRKM theory is the application of absolute rate theory to the calculation of  $k_3(E^*)$ . For this purpose the third step in this mechanism is written in terms of two steps as

$$A_{(E^*)}^* \xrightarrow{k_a(E^*)} A^+ \xrightarrow{k^+} \text{products}$$
(29)

Here a careful distinction has been made between the energised molecule,  $A^*$ , and the activated complex,  $A^+$ . Figure 2-2 shows the energy scheme for the RRKM theory.

In this theory the total energy contained in the energised molecule is classified as either active or inactive (also referred to as adiabatic). The inactive energy is the energy that remains in the same quantum state during the course of reaction and that therefore cannot contribute to the breaking of bonds. It is assumed that the various normal modes of vibration and rotation contribute to reaction although in some calculations the rotational modes are also treated as inactive modes. Figure 2-2 shows the energy scheme for the RRKM mechanism. The expression for  $k_{uni}$  according to this theory is given as

$$k_{\text{uni.}} = \int_{E^*=E_0}^{\infty} \frac{k_a(E^*) \frac{d k_1(E^* \to E^* + dE^*)}{k_2}}{1 + \frac{k_a(E^*)}{k_2[M]}}$$
(30)



Figure 2-2. Energy scheme for the RRKM mechanism.

A particularly satisfactory point in this theory is that it leads to the same expression for the limiting high-pressure, first-order rate constant as is given by conventional transition-state-theory,

$$k_{\infty} = \Gamma\left(\frac{\mathbf{k}_{\mathrm{B}}\mathbf{T}}{\mathbf{h}}\right) \,\delta\left(\frac{\mathbf{Q}_{*}}{\mathbf{Q}_{i}}\right) \,\exp\!\left(\frac{-\mathbf{E}_{0}}{\mathbf{R}\mathbf{T}}\right) \tag{31}$$

where  $Q_{\bullet}$  and  $Q_{i}$  are the total partition functions for activated and initial states, respectively. Thus, the theory can explain the abnormally high pre-exponential factors that are sometimes obtained because one or more vibrations in the reactant change to rotations or hindered rotations in the activated complex.

In the present study a program written by Hase and Bunker<sup>44</sup> has been used to apply the RRKM theory to reaction (4). The program originally was able to calculate  $k_a(E^*)$ , the rate constant for the conversion of an energised molecule to the activated complex. To calculate  $k_{uni}$ , the unimolecular rate constant for the reaction, the program is modified according to Robinson and Holbrook<sup>45</sup> using the following expression

$$k_{uni} = \delta \frac{Q_*}{Q_i} \exp\left(\frac{-E_0}{RT}\right) \Delta E^+ \sum_{i=1}^{i_{max}} \left[\frac{\{\Sigma p(E_{vr}^+)\} \exp\left(\frac{-E^+}{RT}\right)}{1 + \frac{k_a(E^*)}{Zp\beta_c}}\right]_i$$
(32)

Here  $\delta$  is the reaction path degeneracy, Q• and Q<sub>i</sub> are the total partition functions for activated and initial states, respectively, E<sup>+</sup> is the total non-fixed energy of activated complex and  $\Delta E^+$  is the energy step-size. The quantities  $p(E_{vr}^+)$  and  $k_a(E^*)$  are the number of vibrational and rotational states i and the rate constant for converting the energised reactant species to the activated complex, respectively, both are the output of the original program. E<sub>0</sub> is the threshold energy, the difference between the sum of electronic and the zero point energies in the activated complex and the reactant The term  $Zp\beta_c$  is the collisional deactivation rate constant, where p is the pressure,  $\beta_c$ , the collisional deactivation efficiency and Z, the collision number, defined as

$$Z = (\sigma^2 N_A / R) (8\pi N_A k_B / T\mu)^{1/2}$$
(33)

Here  $\sigma$  is the collision diameter, N<sub>A</sub> Avogadro's number and  $\mu$  is the reduced mass defined as follows

$$\mu = m_A m_B / (m_A + m_B) \tag{34}$$

This program was used to calculate the fall-off behaviour and also the low- and highpressure limiting values for  $k_4$ . The geometries and frequencies of the acetonyl radical and the activated complex were calculated theoretically (See Section 5-6)

#### 2-2. Troe method to calculate low- and high-pressure limits of rate constants

Another method to study the fall-off behavior and also to calculate the low- and high-pressure limits of rate constants is a factorization method introduced by Troe <sup>46</sup> This method is simpler than the RRKM method In this study the Troe method is used to find the low- and high-pressure limiting values for the rate constants  $k_1$ ,  $k_4$ , and  $k_5$  The factorization method of Troe<sup>44</sup> is based on the following equation

$$\mathbf{k}/\mathbf{k}_{\infty} = \mathbf{F}_{LH} \mathbf{F}^{SC} \mathbf{F}^{WC} \tag{35}$$

where

$$F_{LH} = (k_0[M]/k_{\infty})/(1 + k_0[M]/k_{\infty})$$
(36)

Here  $k_{\infty}$  and  $k_0$  are the limiting high-pressure unimolecular and limiting low-pressure bimolecular rate constants, respectively, for reactions (1) and (4) Parallel expressions are

available for reaction (5), but the rate constants are bimolecular and termolecular, respectively. The strong collision broadening factor,  $F^{SC}$ , corrects for strong collision effects and can be calculated using the following expression.

$$\log F^{SC} = \frac{\log F_{cent}^{SC}}{1 + \left[\frac{\log(k_0 / k_{\infty})}{N^{SC}}\right]}$$
(37)

Here

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$$N^{SC} \cong 0.75 - 1.27 \log F_{cent}^{SC}$$
(38)

$$F_{\text{cent}}^{\text{SC}} = F_1 + F_2 \exp\left(\frac{B_T}{195}\right) + (1 - F_1 - F_2) \exp\left[2.3\left(\frac{B_T}{F_3}\right)^{1.5}\right]$$
(39)

$$F_1 = 1.32 \exp(-S_T / 4.2) - 0.32 \exp(-S_T / 1.4)$$
(40)

$$F_2 = 1 - \exp(-S_T / 30) \tag{41}$$

$$F_3 = 7.5 + 0.43S_T \tag{42}$$

The effective number of vibrational modes,  $S_T$ , could be calculated using the following expression

$$S_T = 1 + \sum_{i=1}^{s-1} \frac{\frac{hv_i^*}{kT}}{\exp\left(\frac{hv_i^*}{kT}\right) - 1}$$
(43)

Here s is the total number of vibrational modes and  $v^*$  represents the activated complex vibrational frequencies. One can calculate B<sub>T</sub> using the following expression

$$B_T = \left(\frac{S_T - 1}{s - 1}\right)^{1.6} \left(\frac{E_0 + aE_z}{kT}\right) \tag{44}$$

Here  $E_0$  is the dissociation energy,  $E_z$ , the zero point energy,  $k_B$  the Boltzmann constant and T the temperature The constant,  $\alpha$ , could be calculated from

$$\alpha = 1 - \beta \omega \tag{45}$$

Here  $\omega \cong$  - 1 0506(E/E<sub>7</sub>)<sup>0 25</sup> and  $\beta$  could be calculated as

$$\beta \approx \frac{(s-1)^2 \sum_{I=1}^{s} v_I}{s \left(\sum_{I=1}^{s} v_I\right)^2}$$
(46)

Here v is a vibrational frequency and s is the total number of vibrational degrees of freedom

The effective number of vibrational modes,  $S_T$ , was calculated for reaction (1) and (5) from experimental vibrational frequencies of acetone<sup>47</sup> and ethane<sup>48</sup>, listed in Table 2-1  $S_T$  was calculated for reaction (4) from the vibrational frequencies calculated for the activated complex, to be presented in Table 5-77 in Chapter 5

.

acetone		ethane		
description	frequency (cm <sup>-1</sup> )	description	frequency (cm <sup>-1</sup> )	
C-H stretch	3018	C-H stretch	2985	
C-H stretch	3018	C-H stretch	2985	
C-H stretch	3018	C-H stretch	2969	
C-H stretch	2970	C-H stretch	2969	
C-H stretch	2963	C-H stretch	2954	
C-H stretch	2944	C-H stretch	2896	
C=O sym stretch	1730	CH <sub>3</sub> deg deform	1472	
CH <sub>3</sub> deg deform	1454	CH <sub>3</sub> deg deform	1472	
CH <sub>3</sub> deg deform	1435	CH <sub>3</sub> deg deform	1469	
CH <sub>3</sub> deg deform	1426	CH <sub>3</sub> deg deform	1469	
CH <sub>3</sub> deg deform	1410	CH <sub>3</sub> sym deform	1388	
CH <sub>3</sub> sym deform	1364	CH <sub>3</sub> sym deform	1379	
CH <sub>3</sub> sym deform	1364	CH <sub>3</sub> rock	1206	
C-C stretch	1216	CH <sub>3</sub> rock	1206	
CH <sub>3</sub> rock	1091	C-C stretch	995	
CH <sub>3</sub> rock	1066	CH <sub>3</sub> rock	821	
CH <sub>3</sub> rock	891	CH <sub>3</sub> rock	821	
CH <sub>3</sub> rock	877	CH <sub>3</sub> torsion	289	
C-C asym stretch	787			
C=O bend	527			
C-C-C deform	385			
CH <sub>3</sub> torsion	109			
CH <sub>3</sub> torsion	105			

Table 2.1 Vi	brational frequencie	s used to calculate	$S_{T}$ for re	actions (1) and (5	5)
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Troe reported a value for  $\alpha$  equal to 0 932 for the ethane molecule <sup>49</sup> In the present study the values of  $\alpha$  for acetone and the acetonyl radical were calculated to be equal to 0 87

 $F_C^{WC}$  corrects for weak collision effects and is a function of the collisional efficiency,  $\beta_c$  It could be calculated using the following equations

$$\log F^{WC} \cong \frac{\log F_{cent}^{WC}}{1 + \left[\frac{\log(k_0 / k_\infty) + c}{N^{WC} - d\{\log(k_0 / k_\infty) + c\}}\right]^2}$$
(47)

The weak collision broadening factor at the centre is defined as

$$\log F_{\rm cent}^{\rm WC} \cong 0.14 \log \beta_c \tag{48}$$

N<sup>WC</sup> is the width of broadening, calculated as

$$N^{WC} \cong 0.7 + 0.3S_{T} + 0.25\log\beta_{L}$$
(49)

The asymmetry broadening terms c and d are functions of the collisional efficiency,  $\beta_c$ , as

$$\mathbf{c} \cong 0.085 \mathbf{S}_{\mathrm{T}} - 0.17 \log \beta_{\mathrm{c}} \tag{50}$$

$$\mathbf{d} \cong -0 \ 2 - 0 \ 12 \log \beta_c \tag{51}$$

For the calculations it was possible to select a value for  $\beta_c$  and examine its effect on the low- and high-pressure values of the rate constants Table 2.2 shows the calculated parameters for k<sub>1</sub>, k<sub>4</sub>, and k<sub>5</sub> at different temperatures Table 2-2. Calculated parameters used in Troe method to estimate the high pressure limiting values for  $k_1$ ,  $k_4$  and  $k_5$ 

reaction	ST	$\mathbf{B}_{\mathbf{T}}$	F <sup>SC</sup>
		928 K	
(1)	9 290	13 866	0 303
(4)	9 170	10 800	0 368
(5)	7 810	16 300	0 312
		876 K	
(1)	8 858	13 660	0 315
(4)	8 850	10 730	0 377
(5)	7 590	16 400	0 320
		834 K	
(4)	8 590	10 680	0 384
(5)	7 410	16 500	0 325

# 2-3. Calculation of transition state properties

To calculate transition state or activated complex properties we can fit a transitionstate theory (TST) model to the kinetic data by non-linear least squares. For this purpose it is necessary to use a proper equation in which those properties are included. We can write the general equation for TST as follows<sup>50</sup>

$$\mathbf{k} = \Gamma\left(\frac{\mathbf{k}_{\mathbf{B}} \mathbf{T}}{\mathbf{h}}\right) \delta\left(\frac{Q^*}{Q_a Q_b}\right) \exp\left(\frac{\varepsilon_0}{\mathbf{k}_{\mathbf{B}} \mathbf{T}}\right)$$
(52)

Here Q is the partition function with symmetry factors deleted,  $\delta$  is the reaction path degeneracy, which is equal to the number of different suitable pathways by which reactants could approach each other to react, and  $\Gamma$  represents the tunnel factor<sup>51</sup> The translational, rotational, vibrational, and electronic partition functions might be treated separately The translational partition function is given by the equation

$$B_{\rm tr} = h^3 \left(\frac{m^*}{2\pi \,k_{\rm B} T \,m_a \,m_b}\right)^{\frac{3}{2}}$$
(53)

where  $m^*$ ,  $m_a$ , and  $m_b$  are masses of transition state species and reactants a and b, respectively. The overall rotational contribution for non-linear species is

$$B_{r} = \frac{h^{3} \left[ (I_{x} I_{y} I_{z})_{TS} \right]^{1/2}}{8 \pi^{2} (2\pi k_{B} T)^{1/2} (I_{x} I_{y} I_{z})_{a}^{1/2} (I_{x} I_{y} I_{z})_{b}^{1/2}}$$
(54)

Here  $B_r$  is the ratio of the rotational partition functions for the activated complex to the reactants.  $I_x$ ,  $I_y$  and  $I_z$  are the moments of inertia around each of the x, y, and z axes. The partition function for internal rotation is

$$Q_{IR} = \frac{(8\pi^3 k_B I_{IR} T)^{1/2}}{h}$$
(55)

 $I_{I\!R}$  is the reduced moment of inertia for an internal rotation, calculated by the method introduced by Pitzer<sup>52</sup> as follows

$$I_{\rm IR} = A_m - \sum_{i} \left[ \frac{(a_m^{iy} U_m)^2}{M} + \frac{(J_m^i)^2}{I_i} \right]$$
(56)

Here the summation is over the principal axes and  $I_i$  is the principal moment of inertia around axis i, M is the total molecular mass,  $\alpha_m^{iy}$  is the element of the direction cosines determinant and  $j_m'$  is a function of masses and distances

$$j_{m}^{i} = \alpha_{m}^{iz} A_{m} - \alpha_{m}^{ix} Bm - \alpha_{m}^{iy} C_{m} + U_{m} (\alpha_{m}^{i-1,y} r_{m}^{i+1} - \alpha_{m}^{i+1,y} r^{i-1})$$
(57)

Here

$$A_{m} = \sum_{i} m_{i} \left( x_{i}^{2} + y_{i}^{2} \right)$$
(58)

$$\mathbf{B}_{m} = \sum_{i} m_{i} \mathbf{x}_{i} \mathbf{z}_{i}$$
(59)

$$\mathbf{C}_{\mathbf{m}} = \sum_{i} \mathbf{m}_{i} \mathbf{y}_{i} \mathbf{z}_{i} \tag{60}$$

$$\mathbf{U}_{\mathbf{m}} = \sum_{i} \mathbf{m}_{i} \mathbf{x}_{i} \tag{61}$$

In equation (57)  $r_m^{i}$  is the component of the vector of the distance of the centre of gravity of the whole molecule from the origin of the coordinates on the ith axis.

For the product of vibrational partition functions we can write

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$$Q_{v} = \prod_{i=1}^{s} \left[ 1 - \exp\left(\frac{-i\nu_{i}}{k_{B}T}\right) \right]^{-1}$$
(62)

A polyatomic molecule has s equal to 3N-6 vibrational modes if it is nonlinear N is the number of atoms in the molecule. We define the vibrational partition function in the activated complex as<sup>53</sup>

$$(\mathbf{Q}_{\mathbf{v}})_{\mathrm{TS}} = \left[1 - \exp\left(-\frac{\mathrm{hc}\omega_{\mathbf{b}}}{\mathrm{k}_{\mathrm{B}}\mathrm{T}}\right)\right]^{-s}$$
(63)

Here, s is the number of vibrations involved, h is Planck's constant and c is the speed of light  $\omega_b$  is the average of the low frequency bending term values involved in the transition state The overall vibrational partition function ratio for the reaction can be written as

$$B_{v} = \frac{(Q_{v})_{TS}}{(Q_{v})_{a} (Q_{v})_{b}}$$
(64)

The electronic partition function is given by

$$Q_{e} = \sum_{l} g_{l} \exp\left(\frac{-\varepsilon_{l}}{k_{B}T}\right)$$
(65)

Here the summation is over electronic states,  $\varepsilon_i$  and  $g_i$  are the electronic energy and degeneracy, respectively, of the ith electronic state. Nearly all electronically excited states of stable molecules are high enough in energy to be neglected except at very high temperatures If the zero of energy is chosen to be the ground electronic state, then the electronic partition function is unity. A number of species have relatively low-lying excited electronic energy levels,

while others, for example radicals, are degenerate in their ground states and for these species the electronic partition function must be calculated.

The tunnelling factor,  $\Gamma$ , is defined as the ratio of the quantum mechanical to the classical mechanical barrier crossing rate<sup>51, 54</sup>

$$\Gamma(T) = \frac{\int_{0}^{\infty} \kappa(\varepsilon) \exp\left(\frac{-\varepsilon}{k_{\rm B}T}\right) d\varepsilon}{\int_{\varepsilon 0}^{\infty} \exp\left(\frac{-\varepsilon}{k_{\rm B}T}\right) d\varepsilon}$$
(66)

or

$$\Gamma(T) = \exp\left(\frac{\varepsilon_0}{k_B T}\right) \int_0^\infty \frac{\kappa(\varepsilon) \exp\left(\frac{-\varepsilon}{k_B T}\right)}{k_B T} d\varepsilon$$
(67)

where  $\kappa(\varepsilon)$  is the transmission probability for a particle with energy,  $\varepsilon$ , approaching a barrier<sup>55</sup> and  $\varepsilon_0$  is the barrier height.

For a symmetrical barrier  $\kappa(\epsilon)$  could be related to the barrier height  $\epsilon_0 as^{51, 54}$ 

$$\kappa(\varepsilon) = \frac{\cosh\left[\left(\varepsilon \varepsilon_{0}\right)^{1/2} \left(h\omega^{*}\right)^{-1}\right] - 1}{\cosh\left[4\pi(\varepsilon \varepsilon_{0})^{1/2} \left(h\omega^{*}\right)^{-1} + \cosh\left[\pi\left[16\varepsilon_{0}^{2} \left(h\omega^{*}\right)^{-2} - 1\right]^{1/2}\right]}$$
(68)

 $\omega^*$  is the term value for vibration in a well created by inverting the barrier and  $\varepsilon$  is the energy of the particle. For an unsymmetrical barrier the expression  $\kappa(\varepsilon)$  might be written as follows<sup>56</sup>

$$\kappa(\varepsilon) = \frac{\cosh \pi \left( \left[ \frac{\varepsilon + E_1}{C} \right]^{1/2} + \left[ \frac{\varepsilon + E_2}{C} \right]^{1/2} \right) - \cosh \pi \left( \left[ \frac{\varepsilon + E_1}{C} \right]^{1/2} - \left[ \frac{\varepsilon + E_2}{C} \right]^{1/2} \right)}{\cosh \pi \left( \left[ \frac{\varepsilon + E_1}{C} \right]^{1/2} + \left[ \frac{\varepsilon + E_2}{C} \right]^{1/2} \right) + D}$$
(69)

$$\mathbf{D} = \cosh(4\alpha_1\alpha_2 - \pi^2)^{1/2} \text{ if } (4\alpha_1\alpha_2 - \pi^2) > 0$$
(70)

or

$$\mathbf{D} = \cos(|4\alpha_1\alpha_2 - \pi^2|)^{1/2} \text{ if } (4\alpha_1\alpha_2 - \pi^2) < 0$$
(71)

$$\mathbf{C} = (1/8)(\pi \hbar \omega^* / k_{\rm B} T)(\alpha_1^{-1/2} + \alpha_2^{-1/2})^2$$
(72)

Here  $\alpha_I = 2\pi E_i / h\omega^*$ , where i = 1, 2,  $E_i$  is the barrier height for the forward, i=1, and for the reverse, i=2, reaction.

The characteristic tunnelling temperature,  $T^*$ , is defined as<sup>57</sup>

$$T^* = \frac{hc\omega^*}{2\pi k_B}$$
(73)

The final model obtained through the use of TST and its various assumptions is

$$\log k = \log \left( \frac{\delta_{kB} T \Gamma B_{tr} B_{e} B_{v} B_{IR} B_{r}}{h} \right) - \left( \frac{E_{0}}{2.303 RT} \right)$$
(74)

Three parameters,  $E_0$ ,  $\omega_b$ , and  $T^*$ , could be fitted to experimental data by nonlinear least squares.

# 2-4. Computational study of the dissociation reaction of the acetonyl radical, reaction (4)

To apply the Rice-Ramsperger-Kassel-Marcus (RRKM) theory to calculate the rate constant of the dissociation reaction of the acetonyl radical, reaction (4), it was necessary to have some knowledge of the geometry and frequencies of the reactant and activated complex. The optimized geometry and frequencies of the acetonyl radical and the activated complex were calculated using the semi-empirical AM1 method and also using quantum mechanical methods at the rafe/3-21G and HF/6-31G\*\* levels. The Gaussian 92 package program was used in these calculations.<sup>58</sup> The AM1 method was able to detect a stationary point which was a transition state for the isomerization of the radical

$$CH_2COCH_3 \leftrightarrow CH_3CH_2CO$$
 (75)

To find the transition state for reaction (4) the distance between the carbon in the  $CH_3$  group and the carbonyl carbon in the acetonyl radical was kept constant at different distances. The program was allowed to optimize the other geometric variables In this way the program was able to find the minimum energy path along the reaction coordinate.

#### 2-5. Bond Energy Bond Order (BEBO) method

Johnston developed a semi-empirical method to predict the activation energy, critical configuration and frequencies of transition species.<sup>50</sup> This method is applicable for those reactions in which a hydrogen atom is transferred between the two reactants. It relies on two empirical rules proposed by Pauling. The first relates bond length, r, and bond order, n, as  $r = r_s - 0.26 \ln n$  (76)

Here  $r_s$  is the single-bond length for a bond connecting a hydrogen atom to another atom in the reactant.

The second rule might be expressed as

$$\mathbf{E} = \mathbf{E}_{1s} \, \mathbf{n}^{\boldsymbol{\rho}} \tag{77}$$

Here E is the bond energy of the bond which could be calculated from the single-bond energy, E<sub>s</sub>,  $\rho$  is a constant related to the nature of the bond and is 1 087 for a C-H bond <sup>50</sup> For reaction AH + B->A + HB it is possible to extend this rule as

$$E = E_{1s} (1 - n_1^{\rho}) - E_{2s} (1 - n_1)^{q} - E_{3s} B(n_1 - n_1^{2})^{\gamma}$$
(78)

where again q is a parameter and  $\gamma = 0.26$  Å  $\beta$  and  $B = 1/2 \exp(-\beta \Delta R_s)$ ,  $\Delta R_s = r_{1s} - r_{2s} - r_{3s}$ , and subscripts 1, 2, and 3 are related to the A-H, H-B, and A-<sup>*r*</sup> bonds, respectively Here  $\beta$  is from the Morse potential function

$$V(R) = E \{1 - \exp[-\beta(R - R_c)]\}$$
(79)

Here E is the depth of the potential minimum  $\beta$  is equal to 1 78 Å<sup>-1</sup> for a C-H bond and 1 94 Å<sup>-1</sup> for a C-C bond <sup>50</sup>

It is possible to calculate the exothermicity of a reaction from

$$D_{\min} = (ZPE_{TS} - ZPE_{r})$$
(80)

Here ZPE stands for zero point energy and TS and r for transition state and reactants The exothermicity of the reaction was found to be  $27 \text{ kJ mol}^{-1}$ 

This method was used to calculate the geometry and the frequencies of the activated complex is searction (3)

#### 3. Derivation of equations to carry out experimental calculations

In this chapter the expressions used to calculate the rate constants for elementary reactions in the pyrolysis of acetone and their ratios will be discussed Also the expressions used for the induction period will be presented

# **3-1.** Calculation of reactor residence time (t)

The present study on the pyrolysis of acetone has been carried out in a flow system Reactant ...as passed at a constant measured flow rate and controlled pressure through a heated cylindrical reactor Products were sampled and analyzed This procedure is suitable for fast reactions, for example the high temperature pyrolysis of acetone The reactor residence time, t, can be calculated using the reactant flow rate and the temperature of the storage bulb and reactor

If the volume  $(v_b)$ , pressure  $(p_b)$ , and temperature  $(T_b)$  of the storage bulb were measured then the number of moles of gas in the storage bulb can be calculated using the ideal gas law

$$n_{b} = \frac{p_{b}v_{b}}{RT_{b}}$$
(81)

The molar flow rate can be calculated by

$$\frac{\Delta n_{b}}{\Delta t} = \left(\frac{\Delta p_{b}}{\Delta t}\right) \left(\frac{v_{b}}{RT_{b}}\right)$$
(82)

 $(\Delta p_b/\Delta t)$  is the rate of pressure drop in the storage bulb If n is the number of moles of gas in the reactor, the residence time of gas in the reactor can be calculated as

$$t = \frac{n}{\left(\frac{\Delta n_b}{\Delta t}\right)}$$
(83)

Assuming ideal gas behavior, the reactor residence time can be measured by substituting equation (81), the pressure(p), volume(v), and temperature (T) of the reactor and the number of moles of gas in equation (83)

$$\mathbf{t} = \left(\frac{\mathbf{pv}}{\mathbf{RT}}\right) \left(\frac{1}{\frac{\Delta \mathbf{n}_{\mathbf{b}}}{\Delta \mathbf{t}}}\right)$$
(84)

The effective length of the reactor can be calculated by means of a computer program<sup>59</sup> from the temperature profile of the reactor. The program is also able to calculate the average temperature in the reaction zone.

The residence time calculated by means of equation (84) involves some assumptions We should consider potential difficulties which arise from these assumptions

# 3-1-1. Effect of volume expansion

In some reactions, because of a net increase in the number of moles of gas, the volume increases at constant pressure This volume expansion forces the gas molecules out of the reaction zone at a faster rate This effect would be negligible at low conversion

# 3-1-2. Effect of mass transfer

To derive equation (84) it was assumed that each molecule spends the same length of time in the reaction zone As reaction proceeds in the reactor the concentration of the reactant decreases This decrease in reactant concentration along the reactor creates a concentration gradient, which causes the reactant molecules to diffuse towards the exit Therefore, the actual residence time should be less than the value calculated from equation (84) Furue and Pacey<sup>60</sup> studied the interaction of mass and heat transfer with chemical reactions They showed that for mass transfer the fractional error is approximately equal to  $kr^2 / (48D) + kDt^2/l^2$  Here k is the true rate constant, r the reactor radius, D the diffusion coefficient and 1 the reactor length They concluded that this error in the residence time is small at low conversion

# 3-1-3. Neglecting reactions between the reactor and sampling point for gas chromatography

To calculate the reaction time in equation (84) it was assumed that the temperature of the gas at the outlet of the reactor drops very fast to freeze the reaction. This could be investigated by the temperature profile measurement at the outlet of the reactor. At the conditions of the present s<sup>+</sup> 'dy it has been found that the gas at the outlet of the reactor reaches room temperature: after 0.04 s at lower flow rates,  $t \cong 2.5$  s, and  $2 \times 10^{-4}$  s at higher flow rates,  $t \cong 0.01$  s. This delay in the cooling causes an error of less than 2% in the calculation of residence time

## 3-2. Derivation of the rate constant expressions

In this section derivation of those expressions which were used to calculate the rate constants or their ratio would be discussed

Applying the steady state approximation to the radicals in the mechanism proposed by Rice and Herzfeld<sup>4</sup>, reactions (1) to (7), the rate of the initiation reaction, step (1), would be equal to the sum of the rates of the termination reactions, steps (5), (6), and (7) This assumption would allow the calculation of the rate constant,  $k_1$ , for reaction (1) as

$$k_1 = (R_e^{ss} + R_b^{ss} + R_h^{ss})/[A]$$
(85)

Here [A] is the total acetone concentration and  $R_e^{ss}$ ,  $r_b^{ss}$ , and  $R_h^{ss}$  are the steady state rates of formation of the termination products, ethane, butanone, and 2,5-hexanedione, respectively

We were interested to calculate the other rate constants involved in this system For this reason we tried to examine the ratios of the rates of formation of different products to find suitable expressions for the rate constants or a ratio of them In this way we were able to find the ratios of  $k_3/k_5^{1/2}$  and  $k_3k_4/k_6$ 

Applying the steady state approximation, k<sub>3</sub> may be calculated as

$$k_3 = R_m^{ss} k_5^{1/2} / ((R_e^{ss})^{1/2} [A])$$
(86)

where  $R_m^{ss}$  is the steady state rate of formation of methane This equation has been the basis of the determination of  $k_3$  in most photolysis experiments Reaction (5) has been studied many times, and the pressure and temperature dependence of its rate constant are reasonably well known<sup>61</sup>

The ratio of  $k_3k_4/k_6$  could be calculated by the steady state approximation as

$$(k_3 k_4/k_6) = (R_m^{ss})^2 / (R_b^{ss} \times [A])$$
(87)

It is expected that only  $k_4$  would be strongly pressure dependent in this quotient of rate constants In this study we will attempt to apply equations (85), (86), and (87) to the pyrolysis of acetone for the first time

The collision number,  $Z_{AB}$ , the total number of collisions per unit time per unit volume, for two unlike molecules A and B, of masses  $m_A$  and  $m_B$ , is as follows<sup>62</sup>

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$$Z_{AB} = N_A N_B d^2 (8\pi k_B T/\mu)^{1/2}$$
(88)

Where N is the number of molecules, d, the collision diameter,  $r_A+r_B$ ,  $k_B$ , Boltzmann constant, T, the temperature and  $\mu$ , the reduced mass defined in equation (34)

The collision number for two molecules of A might be written as

$$Z_{AA} = N_A^2 d_A^2 (8\pi k_B T/\mu)^{1/2}/2$$
(89)

For equal masses and diameters, it is possible to conclude that  $Z_{AB}$  could be greater than  $Z_{AA}$  by a factor of 2.

According to this simple collision theory, at high pressures the steady state rate of formation of the cross-combination product, butanone, should be approximately twice the square root of the product of the other two termination rates <sup>63,64</sup> At lower pressures, this relationship could be generalized as follows.

$$\mathbf{R}_{b}^{ss} = \mathbf{m} \left( \mathbf{R}_{c}^{ss} \mathbf{R}_{h}^{ss} \right)^{1/2}$$
(90)

This relationship made it possible to estimate the rate of formation of one of these termination rates in conditions where direct measurements were not possible. To estimate the high-pressure values of m at 876 and 928 K, the Troe expression, equation (35), was fitted to the inverse of m squared,  $1/m^2$ , which is proportional to  $k_5$
## 3-3. The induction period expressions

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The present experiments employed a flow reactor system Acetone entered the reactor cold, and the steady rates of product formation would only have been achieved after a delay,  $\tau_h$ , in transferring heat to the flowing gas and after a delay,  $\tau_c$ , as reactions (1) and (2) increased the concentration of CH<sub>3</sub> toward its steady-state value

The physical meaning of the induction period could be described as the time necessary for the reaction to establish steady state conditions. This delay in time is referred to as the induction period. There are two possible sources for the induction period. The first is incomplete radial heat transfer, time is needed so that the temperature throughout the gas reaches the wall temperature. The second is the chemical induction period, the time necessary for the rate of consumption of the intermediates to equal their rate of formation.

## 3-3-1. The induction period caused by delay in heat transfer

During the delay caused by incomplete radial heat transfer, the observed chordal or average rate of methane formation,  $R_m^{app}$  (=[CH<sub>4</sub>]/t), would have been given by the following expression<sup>65</sup>

$$\frac{\mathbf{R}_{m}^{app}}{\mathbf{R}_{m}^{ss}} = 1 - \frac{\tau_{h}}{t}$$
(91)

The induction period,  $\tau_h$ , for heat transfer might be calculated as follows<sup>65</sup>

$$\tau_{\rm h} = r^2 \left[ 0.577 + \ln \left( 0.58 E_{\rm A} \left( T_{\rm w} - T_{\rm t} \right) / (R T_{\rm w}^2) \right] / (3.658 \, \kappa)$$
(92)

Here the coefficient of thermal diffusivity could be calculated as

$$\kappa = \lambda / (C_0 C_p) \tag{93}$$

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where  $C_0$  is the initial concentration of the reactant,  $C_p$ , the heat capacity of reactant, and  $\lambda$ , the thermal conductivity of the reactant.

Wimalasena<sup>66</sup> has calculated a minimum residence time,  $t_{min}$ , which could be employed without unacceptable error due to incomplete radial heat transfer

$$t_{min} = n / 0.1 \text{ mole per hr}$$
(94)

Here n is the number of moles of reagent in the reactor. To observe an induction period from another cause,  $t_{min}$  must be less than this induction period.

 $R_m^{\ s_s}$  and  $\tau_h$  can be taken as parameters to fit equation (91) to experimental data.

## 3-3-2. Lack of establishment of the steady state

To calculate the chemical induction period,  $\tau_c$ , it is necessary to integrate the sum of the concentration of the radicals, CH<sub>3</sub>, CH<sub>3</sub>CO and CH<sub>3</sub>COCH<sub>2</sub> during the initial stages of the reaction as

# $d([CH_3]+[CH_3CO]+[CH_3COCH_2])/dt =$

$$k_1[A]+k_2[CH_3CO]-2(k_5[CH_3]^2-k_6[CH_3COCH_2][CH_3]-k_7[CH_3COCH_2]^2)$$
 (95)

As pointed out in the introduction the rate of formation of  $CH_3CO$  by reaction (1) is about five orders of magnitude slower than consumption of this radical by reaction (2), so the concentration of  $CH_3CO$  reaches its steady state value much faster than the other two radicals. According to the proposed mechanism, reactions (1) to (7), and also the long chain assumption, the rate of formation of  $CH_3COCH_2$  in reaction (3) is equal to its rate of consumption in reaction (4). According to the long chain assumption, it was expected that reaction (4) was more important than reactions (6) and (7). It is possible to write the rate of formation and consumption of acetonyl radicals as follows

$$d[CH_{3}COCH_{2}]/dt = k_{3}[CH_{3}][A] - k_{4}[CH_{3}COCH_{2}]$$
(96)

Integration of equation (96) for reaction times greater than 0.003 s gives the same results as the steady state assumption for reaction (3) and (4) as

$$[CH_3COCH_2] = \left(\frac{k_3[CH_3][A]}{k_4}\right)$$
(97)

On substitution of the steady state approximation for CH<sub>3</sub>CO, (= $k_1[A]/k_2$ ), and equation (97) into equation(95), one may obtain this equation

 $(d [CH_3]+d[CH_3](k_3[A]/k_4))/dt =$ 

$$2(k_{1}[A]-k_{5}[CH_{3}]^{2}-(k_{6}k_{3}/k_{4})[A][CH_{3}]^{2}-k_{7}(k_{3}/k_{4})^{2}[A]^{2}[CH_{3}]^{2})$$
(98)

Integration of equation (98) yields the concentration of CH<sub>3</sub> as

$$[CH_3] = X \tanh(qt/2)$$
 (99)

Here

$$\mathbf{X} = (2\mathbf{k}_1[\mathbf{A}])^{1/2} / (2\mathbf{k}_5 + (2\mathbf{k}_6\mathbf{k}_3/\mathbf{k}_4) [\mathbf{A}] + 2\mathbf{k}_7(\mathbf{k}_3 / \mathbf{k}_4)^2 [\mathbf{A}]^2)^{1/2}$$
(100)

and

$$q = 4 (k_1[A])^{1/2} (k_5 + (k_6k_3/k_4) [A] + k_7(k_3 / k_4)^2 [A]^2)^{1/2} / (1 + k_3 [A] / k_4)$$
(101)

The rate of formation of methane might be written as

$$d [CH_4]/dt = k_3 [A] [CH_3]$$
(102)

Substitution of  $CH_3$  in equation (99) into the expression for the rate of formation of methane, equation (102), and then integration of the equation would give an expression similar to that proposed by Pacey and Wimalasena<sup>67</sup> as

$$\frac{R_{\rm m}^{\rm app}}{R_{\rm m}^{\rm ss}} = \frac{\tau_{\rm c}}{t \ln 2} \ln \left( \cosh(\frac{t \ln 2}{\tau_{\rm c}}) \right) \tag{103}$$

Here

$$\tau_{c} = (1 + k_{3} [A] / k_{4}) \ln 2 / 2 \{ (k_{1}[A])^{1/2} (k_{5} + (k_{6}k_{3}/k_{4}) [A] + k_{7}(k_{3} / k_{4})^{2} [A]^{2} \}^{1/2} \}$$
(104)

It is possible to derive the same expression for  $\tau_c$ , equation (104), using the method introduced by Come, Large, and Rondeau.<sup>68</sup> In their method the steady state concentration of radicals is used to derive the expression for  $\tau_c$ .

Assuming a steady state for formation  $f CH_3$ , one may obtain the steady rate of formation of methane as

$$\mathbf{R}_{m}^{ss} = k_{3} [\mathbf{A}] (k_{1} [\mathbf{A}]) / (k_{5} + (k_{3}k_{6}[\mathbf{A}]/k_{4}) + k_{7}(k_{3}[\mathbf{A}]/k_{4})^{2})^{1/2}$$
(105)

Substitution of equation (105) into equation (104) would result in a simpler expression for  $\tau_c$  as

$$\tau_c = \left(\frac{1}{k_3} + \frac{[A]}{k_4}\right) \left(\frac{1}{2k_1[A]^2}\right) \mathbf{R}_m^{ss} \times \ln(2)$$
(106)

 $R_m^{ss}$  and  $\tau_c$  can be taken as parameters to fit equation (103) to experimental data. The steady state rate of formation of methane could also be calculated by fitting equation (91) to experimental data. Knowing  $\tau_c$  and  $R_m^{ss}$  from fitting equation (103) to the experimental data and knowing  $k_1$  and  $k_3$  from equations (85) and (86) makes is possible to calculate  $k_4$  in equation(106) Also one might calculate  $k_6$  using equation (87). Knowing  $k_5$  and  $k_6$  one may calculate  $k_7$  through equation (90).

## 4. Experimental

In this chapter the flow system and the procedure used to study the pyrolysis of acetone will be described.

## 4-1. Apparatus and materials

Acetone of 99.9% purity (Burdick & Jackson,) was used in this study. Methane and ethane of 99% purity (Matheson CP Grade) in nitrogen (Linde, 99%) were used to prepare a mixture to calibrate the gas chromatograph. To prepare the standard mixture a known pressure of ethane was added to a known pressure of methane, then this standard mixture was diluted using nitrogen. The mole fractions of methane and ethane in the prepared calibration gases were about  $2\times10^{-2}$  and  $1.4\times10^{-3}$ , respectively. For those experiments in which ethylene was measured, a calibration mixture consisting of methane, ethane and ethylene (Matheson CP Grade, 99%) was prepared. The mole fractions of ethane and ethylene were almost the same and were about 10% of the mole fraction of methane. Butanone (Fisher) and 2,5-hexanedione (Eastman Kodak Co.), with less than 1% acetone as impurity, were used individually for calibration. A mixture of carbon monoxide (Matheson CP Grade, 99%) with mole fraction of  $1.9\times10^{-3}$  in argon (Linde, 99%) was used to calibrate the zirconia sensor<sup>69</sup> to measure the CO concentration in the reaction mixture.

A calibration gas bulb was used to introduce the standard mixture to the gas chromatograph. Figure 4-1 shows the linearity of the gas chromatograph for methane within the experimental pressure range. The slope of the graph was found to be  $1.01\pm0.02$ .



Figure 4-1. Linearity of the gas chromatograph within the experimental pressure range.

The flow system, Figure 4-2, was similar to those used previously in this laboratory.<sup>65, 57</sup> The pressures in the storage bulb (13 L) and reactor were monitored by two pressure transducers (Bell & Howell, type 4-366-0006-03Mo, 0-50 and 0-15 psi) The flow rate into the reactor was controlled by a needle valve (Edwards, Model LBIB)

Three one-meter cylindrical quartz reactors were used, two with inside thermocouple wells and 0 376 and 0 157 cm<sup>2</sup> cross sections, and the third with an outside thermocouple compartment and a 0 064 cm<sup>2</sup> cross-section The surface to volume ratios (s/v) for these reactors were calculated to be 10 3, 20 4, and 14 0 cm<sup>-1</sup>, respectively During an experiment, a 43-cm-long section was heated by a resistive furnace The reactor temperature was controlled by a platinum/platinum-13%-rhodium thermocouple An automatic controller, which consisted of a pressure transducer (MKS-122AA-01000AB), a programmable temperature controller (Omega CN 2000) and an outlet solenoid valve (MKS-0248A-50000SY), were used to control the pressure in the reactor The average residence time, t, of molecules in the reactor was calculated from the measured pressure, temperature, and effective cross-section of the reactors and from the acetone flow rate

A six-way linear gas sampling valve (Varian 57-000034-00) was used to take samples in a 10 cm<sup>3</sup> sample loop and a gas chromatograph (Tracor 550) was used to analyze the samples Methane, ethane, and ethylene were separated on a one-meter silica gel column (mesh 100/120) at room temperature, CO and hydrogen, on a 1 2 meter alumina column (type F1) at 0°C, butanone, on a 1 2 meter Porapak column (type Q) at



- Teflon value

Figure 4-2. Schematic diagram of the apparatus for the pyrolysis of the acetone.

160°C, and 2,5-hexanedione. on a 1 0 meter 10% carbowax-20M on chromosorb column at 110° C Nitrogen was used as carrier gas A flame ionization detector was used to detect the hydrocarbon and ketone products, and a zirconia sensor<sup>69</sup> was used to detect CO and hydrogen Ketene peaks at 2150 cm<sup>-1</sup> were detected with a (Nicolet, 510P FT-IR) spectrometer with a 4 cm<sup>-1</sup> resolution A mass spectrometer (Consolidated Electrodynamics, 21-104) was used to detect any m/e larger than 72

## 4-2. Procedure

Acetone was degassed by condensing with liquid nitrogen It was then placed in the storage bulb, shown in Figure 4-2, by evaporation and was again degassed in li · id nitrogen The storage bulb was covered with aluminum foil to prevent photolysis of the acetone The vapor pressure of acetone could be controlled by maintaining an appropriate temperature of the storage bulb and could be measured by the transducer The needle valve controlled the flow rate of the acetone vapor Acetone was heated by a pre-heater to 200 °C below the temperature of reaction and then passed through the main furnace The reactor was made from a quartz tube, which was situated in a brass tube to smooth the temperature profile These tubes were in the middle of the main furnace which was electrically heated with nichrome wire The reactor temperature was monitored by a platinum-10% rhodium thermocouple It was very important to keep the temperature along the reactor constant The temperature profile was measured several times during each run

The outlet gases were exhausted from the system by the mechanical pump The pressure in the reactor was controlled by the pressure controller. The ability of the

controller to maintain a desired pressure was measured to be equal to  $\pm 2\%$ . The pressure transducer sensed the pressure in the inlet to the gas chromatograph. The six-way linear gas sampling valve was used for sampling the outlet gases and introducing the sample to the gas chromatograph

Before the experiment the acetone was degassed in liquid nitrogen and checked for any impurity of methane or ethane by analysis of the acetone vapor in the gas chromatograph. There was less than 0 05% of accualdehyde in the acetone as an impurity. There was not any measurable amount of either product in the acetone.

The mass spectrometer was used to seek heavier compounds like butanone and 2,5-hexanedione To collect the sample for mass spectrometry a 100 cm<sup>3</sup> bulb was used It was possible to connect the bulb to the outlet of the reactor beside the six-way linear gas sampling valve, used to take samples for the gas chromatograph. The filled bulb was taken to the mass spectrometer room, while kept frozen in liquid nitrogen. In the mass spectrum we found a peak with m/e equal to 72, which is the molecular weight of butanone. We couldn't find any peak at m/e larger than 72 in the reaction mixture. This was also true even with a calibration mixture with 1% of 2,5-hexanedione in acetone This could be the result of low volatility of 2,5-hexanedione The same procedure was performed to take samples in a 10 cm long infra-red sampling bulb for the infra-red spectroscopy.

#### 5. Results

The reaction was studied in the temperature range of 825 to 940 K and the pressure range 10 to 180 Torr The main products observed were methane and ketene and the minor products were hydrogen, carbon monoxide, ethylene, ethane, propylene, propane, butanone, and 2,5-hexanedione. The measured concentrations of products were divided by corresponding values of residence times to give chordal rates of formation of methane ( $[CH_4]/t$ ), carbon monoxide, ethylene, ethane, butanone, and 2,5-hexanedione. Values at several temperatures and pressures in three reactors are given in Tables 5-1 to 5-65.

For methane there was an initial rise in the rate, followed by a plateau at longer times. Both equations (91) and (103) were fitted by nonlinear least squares<sup>70</sup> to the methane data from those experiments in which an induction period was observed. The difference between the steady state rates obtained from one set of data with the two equations was always less than 5%. Figures 5-1 to 5-15 show the establishment of the steady state rate of formation of methane. At conditions where no induction period was observed, the average rate of formation of methane in the plateau region was taken as the steady state rate of formation.

**Table 5-1.** Chordal rates of formation of methane ( $[CH_4]/t$ ) and ethane ( $[C_2H_6]/t$ ) during pyrolysis of acetone at 15 5 Torr and 940 K in reactor 1

t (ɛ)	$R_{m} \times 10^{5} \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$	$R_{e} \times 10^{6} \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
0 055	4 16	2 23
0 064	4 27	2 25
0 071	4 34	2 30
0 104	4 41	2 32
0 174	4 42	2 42
0 278	4 45	2 52
0 419	4 44	2 51
0 715	4 33	2 53
1 200	3 65	2 31
1 739	3 28	2 03

**Table 5-2.** Chordal rates of formation of butanone during pyrolysis of acetone at 15 5Torr and 940 K in reactor 1

t (s)	$R_b \times 10^6 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
0 318	1 04
0 618	1 05
1 096	1 16
1 216	0 74
1 587	0 73

**Table 5-3.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at 15 5Torr and 940 K in reactor 3

t (s)	$R_{h} \times 10^{8} (mol L^{-1} s^{-1})$
0 625	8 95
0 963	9 86
1 550	9 46
1 855	9 20

 Table 5-4. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 15 5 Torr and 897 K in reactor 1

t (s)	$R_{m} \times 10^{6} (mol L^{-1} s^{-1})$	$R_{c} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 053	7 59	2 08
0 078	8 37	2 15
0 122	8 50	2 37
0 254	8 80	2 48
0 358	9 04	2 56
0 470	9 08	2 84
0 <b>798</b>	9 10	2 81
1 016	9 13	2 89
1 863	8 64	2 64

**Table 5-5.** Chordal rates of formation of butanone during pyrolysis of acetone at 15 5Torr and 897 K in reactor 1

t (s)	$R_{\rm b} \times 10^7 ({\rm mol} \ {\rm L}^{-1} \ {\rm s}^{-1})$
0 515	1 42
0 870	2 08
1 555	1 92
2 061	2 04

 Table 5-6. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 15 5 Torr and 854 K in reactor 1

t (s)	$R_{m} \times 10^{6} (mol \ L^{-1} \ s^{-1})$	$R_e \times 10^8 (mol \ L^{-1} \ s^{-1})$
0 050	1 01	
0 062	1 17	
0 094	1 20	1 52
0 187	1 36	1 68
0 361	1 40	1 72
0 665	1 55	181
1 088	1 59	1 96
1 575	1 72	1 97
2 211	1 65	1 97

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t (s)	$R_b \times 10^8 (mol \ L^{-1} \ s^{-1})$
0.920	3 39
1.699	3.34
1.267	3.48
1.517	3.57
1.942	2.98

**Table 5-8.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 15.5 Torr and 825 K in reactor 1.

t (s)	$R_{m} \times 10^{7} (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{9} (\text{mol } \text{L}^{-1} \text{ s}^{-1})$
0 067	1.73	
0 086	2.06	
0 175	3 10	2.13
0 350	3 59	2.27
0 605	3.87	2.31
0 883	4 18	2.50
1 166	4 46	2.86
1 692	4 20	3.27
2.47	4 11	3.13

**Table 5-9.** Chordal rates of formation of butanone during pyrolysis of acetone at 15.5Torr and 825 K in reactor 1.

t (s)	$R_b \times 10^8 (mol \ L^{-1} \ s^{-1})$
0.837	1 03
1.095	1.05
1.641	1.07
1.813	1.10

 Table 5-10. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 10 3 Torr and 876 K in reactor 1

t (s)	$R_{\rm m} \times 10^6 ({\rm mol} \ {\rm L}^{-1} \ {\rm s}^{-1})$	$R_{c} \times 10^{8} (mol \ L^{-1} \ s^{-1})$
0 036	1 20	3 20
0 051	1 47	3 30
0 105	1 74	3 47
0 175	1 90	3 64
0 276	2 01	3 89
0 402	2 12	3 95
0 771	2 28	3 93
1 286	2 28	3 99
3 856	1 29	4 05

**Table 5-11.** Chordal rates of formation of butanone during pyrolysis of acetone at 10 2Torr and 876 K in reactor 1

t (s)	$R_b \times 10^8 (mol \ L^{-1} \ s^{-1})$
0 994	3 93
1 212	4 1 1
2 041	3 82

 Table 5-12. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at ^0 6 Torr and 876 K in reactor 1

$\mathbf{R}_{\mathbf{m}} \times 10^{6} (\text{mol } \text{L}^{-1} \text{ s}^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
4 10	0 58
4 75	0 70
5 35	082
5 67	0 91
5 92	0 97
6 13	1 08
6 16	1 05
6 27	1 10
6 25	1 18
	$R_{m} \times 10^{6} (mol L^{-1} s^{-1})$ 4 10 4 75 5 35 5 67 5 92 6 13 6 16 6 27 6 25

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**Table 5-13** Chordal rates of formation of butanone during pyrolysis of acetone at 20 6Torr and 876 K in reactor 1

t (s)	$R_b \times 10^8 (mol \ L^{-1} \ s^{-1})$
1 033	7 30
1 365	8 24
1 842	8 11
2 248	7 54

**Table 5-14.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 30 7 Torr and 876 K in reactor 1

t (s)	$R_m \times 10^5 (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 069	0 77	1 10
0 130	0 94	1 42
0 256	0 96	1 46
0 319	0 99	1 53
0 541	1 00	1 61
0 735	1 01	1 63
1 062	1 01	1 73
1 194	1 09	1 91
1 333	1 07	1 89
2 866	0 66	1 10

**Table 5-15.** Chordal rates of formation of butarone during pyrolysis of acetone at 31 0Torr and 876 K in reactor 1

t (s)	$R_b \times 10^7 (mol \ L^{-1} \ s^{-1})$
1 143	1 00
1 295	1 15
1 491	1 23
2 266	0 95

 Table 5-16. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 41 2 Torr and 876 K in reactor 1

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t (s)	$R_m \times 10^6 (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 077	1 00	1 15
0 086	1 09	1 26
0 140	1 30	1 60
0 274	1 39	184
0 499	1 40	181
0 782	1 42	1 94
1 114	1 43	2 00
1 420	1 46	2 15
2 018	1 47	2 24

**Table 5-17.** Chordal rates of formation of butanone during pyrolysis of acetone at 41 3Torr and 876 K in reactor 1

t (s)	$R_b \times 10^7 (mol \ L^{-1} \ s^{-1})$
1 075	1 49
1 189	1 54
2 012	1 59

**Table 5-18.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 20 5 Torr and 876 K in reactor 2

$R_{\rm m} \times 10^6 ({\rm mol} \ {\rm L}^{-1} \ {\rm s}^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
4 06	
5 02	
5 19	
5 52	0 85
5 76	0 96
5 78	1 04
5 83	1 05
6 1 1	1 15
6 14	1 16
6 22	1 21
	$R_{m} \times 10^{6} (mol \ L^{-1} \ s^{-1})$ 4 06 5 02 5 19 5 52 5 76 5 78 5 83 6 11 6 14 6 22

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t (s)	$R_{m} \times 10^{6} (mol \ L^{-1} \ s^{-1})$	$R_e \times 10^7 (\text{mol } L^{-1} \text{ s}^{-1})$
0.036	7.60	0.93
0.051	8.30	1.17
0.086	8.78	1.09
0.131	8.98	1.27
0.191	9.17	1.22
0.368	9.18	1.30
0.490	9.38	1.29
0.725	9.49	1.41
0.967	9.69	1.39
1.203	9.70	1.45
1.450	10.10	1.52
1. <b>761</b>	9.92	1.47

**Table 5-20.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 41.1 Torr and 876 K in reactor 2.

t (s)	$R_m \times 10^5 (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0.052	1.30	
0.064	1.34	1.10
0.115	1.42	1.50
0.228	1.46	1.76
0.405	1.47	1.81
0.533	1.49	1.85
0.627	1.49	2.00
0.874	1.50	2.15
1.300	1.49	2.16
1.510	1.50	2.16
1.846	1.53	2.25

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t (s)	$R_b \times 10^7 (mol \ L^{-1} \ s^{-1})$
1 562	1 58
2 089	1 61
2 159	1 56

**Table 5-22.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 82 0 Torr and 876 K in reactor 2

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t (s)	$R_m \times 10^5 (mol L^{-1} s^{-1})$	$R_{c} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 074	2 90	2 00
0 0° 0	2 98	2 05
0 150	3 03	2 30
0 355	3 12	2 75
0 579	3 21	2 94
0 822	3 23	3 08
i 075	3 26	3 27
1 378	3 31	3 47
1 696	3 25	3 67

**Table 5-23.** Chordal rates of formation of butanone during pyrolysis of acetone at 82 1Torr and 876 K in reactor 2

t (s)	$\mathbf{R}_{b} \times 10^{7} (\text{mol } \mathrm{L}^{-1} \mathrm{s}^{-1})$
1 550	3 60
1 756	3 96
2 283	3 74

**Table 5-24.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 20 6 Torr and 876 K in reactor 3

t (s)	$R_m \times 10^6 (mol L^{-1} s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 009	1 92	
0 013	2 40	
0 021	3 22	0 47
0 029	4 20	0 62
0 044	4 94	0 75
0 077	5 24	0 86
0 093	5 46	0 89
0 109	5 49	0 92
0 166	5 68	0 97
0 221	5 78	1 00
0 260	6 11	1 08
0 552	6 16	1 10
0 921	6 26	1 13
1 721	6 09	1 20

**Table 5-25.** Chordal rates of formation of methane and ethane during pyrolysis of acetoneat 41 2 Torr and 876 K in reactor 3

t (s)	$R_{m} \times 10^{5} (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 017	0 78	0 64
0 019	0 83	0 64
0 023	0 98	0 95
0 039	1 18	1 26
0 060	1 25	1 42
0 099	1 35	1 52
0 201	1 36	1 68
0 403	1 39	1 76
0 60 <b>8</b>	1 49	1 92
0 934	1 55	2 18
1 137	1 52	2 26
1 640	1 64	2 77

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 Table 5-26. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 81 3 Torr and 876 K in reactor 3

t (s)	$R_{\rm m} \times 10^5 ({\rm mol} \ {\rm L}^{-1} \ {\rm s}^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 037	2 69	1 75
0 059	3 20	2 55
0 097	3 38	2 76
0 205	3 56	3 33
0 386	3 5	3 50
0 553	3 58	3 60
0 808	3 69	3 84
0 992	3 71	4 00
1 347	3 74	4 21
1 722	3 87	4 74
2 235	3 85	5 13

 Table 5-27. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 124 3 Torr and 876 K in reactor 3

t (s)	$R_{m} \times 10^{5} (mol L^{-1} s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
0 721	5 88	3 72
1 329	5 93	4 04
1 565	6 12	4 57
1 753	6 2 1	5 56
2 025	6 24	6 25
2 577	5 79	6 79

**Table 5-28.** Chordal rates of formation of butanone during pyrolysis of acetone at 124 3Torr and 876 K in reactor 3

t (s)	$R_b \times 10^7 (mol \ L^{-1} \ s^{-1})$
1 635	5 58
2 025	5 28
2 501	5 64

 Table 5-29. Chordal rates of formation of methane and ethane during pyrolysis of acetone

 at 176 2 Torr and 876 K in reactor 3

t (s)	$R_m \times 10^4 (mol \ L^{-1} \ s^{-1})$	$R_{e} \times 10^{7} (mol \ L^{-1} \ s^{-1})$
1 104	0 92	5 85
1 335	1 08	6 01
1 350	0 96	6 83
1 800	1 06	7 00
2 126	1 06	7 25
2 567	1 06	8 26
3 252	0 96	9 25

**Table 5-30.** Chordal rates of formation of butanone during pyrolysis of acetone at 176 2Torr and 876 K in reactor 3

t (s)	$R_b \times 10^7 (mol \ L^{-1} \ s^{-1})$
1 690	8 90
1 870	8 80
2 937	8 71

**Table 5-31.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at10 3 Torr and 876 K in reactor 3

t (s)	$R_{h} \times 10^{8} (mol L^{-1} s^{-1})$
1 323	0 55
1 598	0 78
2 806	0 43

**Table 5-32.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at20 6 Torr and 876 K in reactor 3

t (s)	$R_{h} \times 10^{8} (mol \ L^{-1} \ s^{-1})$
1 6 <b>8</b> 0	0 92
1 920	0 91
2 024	0 75

**Table 5-33.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at41 2 Torr and 876 K in reactor 3

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t (s)	$R_h \times 10^8 (\text{mol } L^{-1} \text{ s}^{-1})$
1 560	2 13
1 860	2 33
2 03 1	2 08
2 522	1 99

**Table 5-34.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at81 2 Torr and 876 K in reactor 3

t (s)	$R_h \times 10^8 (\text{mol } L^{-1} \text{ s}^{-1})$
1 499	0 99
1 605	1 06
1 955	1 10

**Table 5-35.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at125 0 Torr and 876 K in reactor 3

t (s)	$R_{\rm h} \times 10^8 ({\rm mol} \ {\rm L}^{-1} \ {\rm s}^{-1})$
1 680	1 76
1 962	1 86
2 152	1 83
2 563	1 59

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**Table 5-36.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at177 0 Torr and 876 K in reactor 3

t (s)	$R_{h} \times 10^{8} (mol \ L^{-1} \ s^{-1})$
1 456	2 89
1 861	2 92
2 065	2 92
2 860	2 86

**Table 5-37.** Chordal rates of formation of methane and ethane during pyrolysis of acetone at 10 3 Torr and 927 3 K in reactor 2

t (s)	$R_{m} \times 10^{5} \text{ (mol } L^{-1} \text{ s}^{-1} \text{ )}$	$R_e \times 10^7 \text{ (mol } L^{-1} \text{ s}^{-1} \text{ )}$
1 103	1 15	6 36
0 682	1 35	7 26
0 446	1 37	7 06
0 319	1 36	6 90
0 207	1 39	6 96

Table 5-38. Chordal rates of formation of methane and ethane during pyrolysis of acetone at 20 9 torr and 927 8 K in reactor 2

t (s)	$R_{\rm m} \times 10^5$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_e \times 10^6 \text{ (mol } L^{-1} \text{ s}^{-1} \text{ )}$
1 967	2 97	1 35
1 240	3 39	1 53
1 042	2 54	161
0 815	3 45	161
0 519	3 64	161
0 228	3 68	1 54
0 120	3 58	1 39

**Table 5-39.** Chordal rates of formation of butanone during pyrolysis of acetone at 10 3 torr and 928 6 K in reactor 2

t (s)	$R_b \times 10^7 \text{ (mol } L^1 \text{ s}^{-1} \text{ )}$
1 500	2 1 1
0 714	3 35
0 405	3 06

**Table 5-40.** Chordal rates of formation of butanone during pyrolysis of acetone at 20 8 torr and 928 6 K in reactor 2

t (s)	$\mathbf{R}_{b} \times 10^{7} \pmod{L^{-1} s^{-1}}$
1 782	5 67
1 932	7 03
0 659	6 54
0 474	7 28

**Table 5-41.** Chordal rates of formation of methane, ethane and ethylene during pyrolysis of acetone at 41 4 torr and 928 3 K in reactor 2

t (s)	$R_{m} \times 10^{4} \text{ (mol } L^{-1} \text{ s}^{-1} \text{ )}$	$R_e \times 10^6$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_{en} \times 10^6$ (mol L <sup>-1</sup> s <sup>-1</sup>
			)
1 766	080	3 15	1 70
1 089	1 04	3 92	1 94
0 898	1 08	3 93	1 60
0 764	1 13	4 07	1 60
0 639	1 05	3 68	1 12
0 312	1 14	3 85	0 70
0 166	1 18	3 92	0 48

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**Table 5-42.** Chordal rates of formation of methane, ethane and ethylene during pyrolysis of acetone at 82 4 torr and 928 3 K in reactor 2

t (s)	$R_{\rm m} \times 10^4 ({\rm mol}\;{\rm L}^{-1}\;{\rm s}^{-1})$	$R_e \times 10^6 (\text{ mol } L^{-1} \text{ s}^{-1})$	$R_{en} \times 10^{6}$ (mol L <sup>-1</sup> s <sup>-1</sup>
			)
2 424	1 82	7 39	10 60
1 755	1 99	7 41	8 41
1 1 1 9	2 2.4	7 41	5 72
0 749	2 31	7 04	3 95
0 509	2 55	7 33	2 99
0 277	2 58	7 23	1 96

**Table 5-43.** Chordal rates of formation of methane, ethane and ethylene during , prolysis of acetone at 125 6 torr and 927 1 K in reactor 2

t (s)	$R_{m} \times 10^{4} ( \text{ mol } L^{-1} \text{ s}^{-1} )$	$R_e \times 10^5$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_{en} \times 10^5$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1 776	3 07	1 06	0 77
1 220	3 84	1 23	0 68
1 015	3 97	1 21	0 56
0 662	4 34	1 16	
0 460	4 50	1 02	
0 279	4 88	1 12	
0 176	4 71	0 98	

**Table 5-44.** Chordal rates of formation of methane, ethane and ethylene during pyrolysis of acetone at 182 0 torr and 927 1 K in reactor 2

t (s)	$R_{\rm m} \times 10^4$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_e \times 10^5$ ( mol L <sup>-1</sup> s <sup>-1</sup> )	$R_{en} \times 10^5$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1 858	4 42	1 51	2 27
1 417	5 41	1 74	2 02
1 111	6 05	181	161
0 945	6 31	181	1 32
0 683	6 35	161	0 62
0 497	7 54	1 50	0 28
0 301	7 74	1 62	
0 189	7 57	1 71	

**Table 5-45.** Chordal rates of formation of butanone during pyrolysis of acetone at 41 4 torr and 927 5 K in reactor 2

t (s)	$R_b \times 10^6$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1 657	1 14
1 069	1 52
0 513	1 74

**Table 5-46.** Chordal rates of formation of butanone during pyrolysis of acetone at 82 6 torr and 927 5 K in reactor 2

t (s)	$R_b \times 10^6 (\text{ mol } L^{-1} \text{ s}^{-1})$
2 326	2 69
1 462	3 22
0 882	3 96
0 512	3 92

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Table 5-47. Chordal rates of formation of butanone during pyrolysis of acetone at 126 2

torr and 927 7 K in reactor 2

t (s)	$R_b \times 10^6$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1 344	4 80
1 064	6 68
0 467	8 04
0 240	8 18

Table 5-48. Chordal rates of formation of butanone during pyrolysis of acetone at 181 5

torr and 927 7 K in reactor 2

u (s)	$R_{b} \times 10^{5}$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1 413	0 77
0 744	1 18
0 562	1 03
0 303	1 05

Table 5-49. Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at

10 2 Torr and 928 K in reactor 3

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t (s)	$R_h \times 10^8 (mol \ L^{-1} \ s^{-1})$
1 066	1 88
1 356	1 78
1 980	1 50
2 002	1 66

**Table 5-50.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at21 0 Torr and 928 K in reactor 3

t (s)	$R_h \times 10^8 \pmod{L^{-1} s^{-1}}$
1 250	4 86
1 562	4 56
1 868	4 96
2 560	3 09

**Table 5-51.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at41 0 Torr and 928 K in reactor 3

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t (s)	$R_h \times 10^7 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
1 025	1 12
1 436	1 33
1 655	1 20
2 000	0 99

**Table 5-52.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at83 0 Torr and 928 K in reactor 3

t (s)	$P_n \times 10^7 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
1 100	4 10
1 450	3 89
1 880	4 22
2 402	3 65

**Table 5-53.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at125 3 Torr and 928 K in reactor 3

t (s)	$R_{h} \times 10^{6} \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
1 650	1 23
1 754	1 12
1 923	1 50
2 1 1 1	1 00

**Table 5-54.** Chordal rates of formation of 2,5-hexanedione during pyrolysis of acetone at181.2 Torr and 928 K in reactor 3.

t (s)	$R_h \times 10^6 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
1.566	1.84
1. <b>777</b>	1 60
1. <b>978</b>	1 68
2.698	1.56

**Table 5-55.** Chordal rates of formation of CO during pyrolysis of acetone at 85.1 torr and 927 K in reactor 2.

t (s)	$R_{CO} \times 10^5 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
0.265	3.61
0.338	4.03
0.667	4.63
0.860	3.81
1.185	3.86

**Table 5-56.** Chordal rates of formation of CO during pyrolysis of acetone at 41.5 torr and 925 K in reactor 2.

t (s)	$R_{CO} \times 10^6 \text{ (mol } L^{-1} \text{ s}^{-1}\text{)}$
0.118	9.24
0 208	9.57
0 443	11.90
0 629	9.03
1 133	6.71

**Table 5-57.** Chordal rates of formation of methane and ethane during pyrolysis of acetone at 10.3 torr and 834.7 K in reactor 2.

t (s)	$R_{m} \times 10^{7} ( mol L^{-1} s^{-1} )$	$R_{e} \times 10^{9} ( \text{ mol } L^{-1} \text{ s}^{-1} )$
3.184	3.78	3.64
1.745	3.96	3.92
1.358	3.98	3.99
0.767	3.85	3.87
0.366	3.35	3.75

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**Table 5-58.** Chordal rates of formation of methane and ethane during pyrolysis of acetone at 21.0 torr and 834.7 K in reactor 2.

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t (s)	$R_{m} \times 10^{7} ( mol L^{-1} s^{-1} )$	$R_{e} \times 10^{9} ( \text{ mol } L^{-1} \text{ s}^{-1} )$
2.813	9.05	6.58
1.299	9 41	6.69
1.055	9. <b>80</b>	7.19
0 774	9.87	7.13
0.431	8.56	6,60
0.190	8.12	6.26

**Table 5-59.** Chordal rates of formation of methane and ethane during pyrolysis of acetone at 41.5 torr and 834.7 K in reactor 2.

t (s)	$R_{m} \times 10^{6}$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_{e} \times 10^{8} ( \text{ mol } \text{L}^{-1} \text{ s}^{-1} )$
2.034	2.33	1 24
1.426	2.36	1 21
0. <b>847</b>	2.38	1 24
0.532	2.42	1 22
0.326	2.23	1 12
0.209	2.08	1 06

**Table 5-60.** Chordal rates of formation of methane and ethane during pyrolysis of acetone at 80.5 torr and 834.5 K in reactor 2.

t (s)	$R_{m} \times 10^{6} ( mol L^{-1} s^{-1} )$	$R_{e} \times 10^{8} ( \text{ mol } \text{L}^{-1} \text{ s}^{-1} )$
2.232	4.25	1 52
1.330	4.44	1 64
0.877	4.64	1 70
0.649	4.45	2 39
0.364	4.43	1 65
0.251	4.44	1 56

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2.013 9 24 2.77	
1.318 8.88 2.37	
1.107 8.61 2.30	
0 852 8.96 2.38	
0.420 9.01 2.41	
0.301 9 12 2 37	

**Table 5-62.** Chordal rates of formation of methane, ethane and ethylene during pyrolysis of acetone at 183.7 torr and 834.5 K in reactor 2

t (s)	$R_{m} \times 10^{5}$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_e \times 10^8$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R_{en} \times 10^9$ (mol L <sup>-1</sup> s <sup>-1</sup> )
2 001	1 26	3.40	3 54
1.609	1 32	3.45	1 83
1 334	1 46	3.66	0 55
0 988	1 44	3.51	
0 765	1 48	3.72	

**Table 5-63.** Chordal rates of formation of butanone during pyrolysis of acetone at 11.0 torr and 834.6 K in reactor 2.

t (s)	$R_b \times 10^9$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1.435	8 66
1.862	8.75
2 341	8.30

**Table 5-64.** Chordal rates of formation butanone during pyrolysis of acetone at 21.1 torr and 834 6 K in reactor 2.

t (s)	$R_b \times 10^8$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1.560	2.03
1.778	1.83
2.797	0.85

**Table 5-65.** Chordal rates of formation of butanone during pyrolysis of acetone at 41.1 torr and 836.1 K in reactor 2.

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t (s)	$R_b \times 10^8$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1.467	3.24
1.662	3.20
1.970	3.23



Figure 5-1. Establishment of the steady state rate of formation of methane at 15.5 Torr and 940 K in reactor 1: ( $\blacksquare$ ) experimental, (---) least-squares fit to equation (91), (-) least-squares fit to equation (103). The last four points were not included in the fitting.



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Figure 5-2. Establishment of the steady state rate of formation of methane at 15.5 Torr and 897 K in reactor 1: ( $\bullet$ ) experimental, (---) least-squares fit to equation (91), (-) least-squares fit to equation (103). The last point was not included in the fitting.



Figure 5-3. Establishment of the steady state rate of formation of methane at 15.5 Torr and 854 K in reactor 1: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103).



Figure 5-4. Establishment of the steady state rate of formation of methane at 15.5 Torr and 825 K in reactor 1: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103)



Figure 5-5. Establishment of the steady state rate of formation o `.nethane at 10 Torr and 876 K in reactor 1. (•) experimental, (-) least-squares fit to equation (103)

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Figure 5-6. Establishment of the steady state rate of formation of methane at 20 Torr and 876 K in reactor 1: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103).



Figure 5-7. Establishment of the steady state rate of formation of methane at 30 Torr and 876 K in reactor 1. ( • ) experimental, ( - ) least-squares fit to equation (103)



Figure 5-8. Establishment of the steady state rate of formation of methane at 40 Torr and 876 K in reactor 1: ( $\blacksquare$ ) experimental, (-) least-squares fit to equation (103).



Figure 5-9. Establishment of the steady state rate of formation of methane at 20 Torr and 876 K in reactor 2: ( $\blacksquare$ ) experimental, (-) least-squares fit to equation (103).



Figure 5-10. Establishment of the steady state rate of formation of methane at 30 Torr and 876 K in reactor 2: ( $\blacksquare$ ) experimental, ( $\neg$ ) least-squares fit to equation (103). The last three point were not included in the fitting.



Figure 5-11. Establishment of the steady state rate of formation of methane at 40 Torr and 876 K in reactor 2: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103).



Figure 5-12. Establishment of the steady state rate of formation of methane at 80 Torr and 876 K in reactor 2: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103). The last three points were not included in the fitting.



Figure 5-13. Establishment of the steady state rate of formation of methane at 20 Torr and 876 K in reactor 3: ( $\blacksquare$ ) experimental, (---) least-squares fit to equation (91), (-) least-squares fit to equation (103).



Figure 5-14. Establishment of the steady state rate of formation of methane at 40 Torr. and 876 K in reactor 3: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103). The last point was not included in the fitting.



Figure 5-15. Establishment of the steady state rate of formation of methane at 80 Torr and 8% K in reactor 3: ( $\bullet$ ) experimental, (-) least-squares fit to equation (103). The last two points were not included in the fitting.

Figure 5-16 shows the infra-rea spectrum of the reaction mixture at 85.3 Torr and 929 K. Figure 5-17 shows the absorbance by ketene at 2164 cm<sup>-1</sup> as a function of residence time at 131 Torr and 928 K. This shows ketene is a primary product.

Tables 5-66 to 5-71 show the absorbance by ketene at 2164 cm<sup>-1</sup> as a function of residence time at several temperatures and pressures. The molar absorption coefficient was calculated from the Beer-La.nbert law, assuming the steady rates of formation of methane, reaction (3), and ketene, reaction (4), were equal, as predicted by the mechanism. To calculate the average molar absorption coefficient, the data at 1.190 and 2.356 s in Table 5-69 were not included. The absorbance of ketene at these conditions were less accurate, probably because of experimental error. The average molar absorption coefficient of ketene was calculated to be  $561 \pm 22 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ .

Hydrogen, ethylene, propane, and propylene were secondary products, with yields proportional to the square of the residence time. Only ethylene was determined quantitatively. At longer residence times, the amount of ethylene exceeded the amount of ethane formed, as listed in Tables 5-41 to 5-44 and 5-62. Hydrogen was detected in clean reactors only at pressures higher than 80 Torr, but was also detected at lower pressures when the reactor surface was partially covered by carbon.



Figure 5-16. Infrared spectrum of the reaction mixture

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t (s)	ketene absorbance	molar absorptivity $(L \text{ mol}^{-1} \text{ cm}^{-1})$
0.29	0.43	575
0.48	0.68	556
0.95	1.20	564
1.43	1.78	593
3.21	3.45	537

Table 5-66 Absorbance by ketene formed in an experiment at 85.3 torr and 929 K in reactor 2.

Table 5-67. Absorbance by ketene formed in an experiment at 131 torr and 928 K reactor 2.

t (s)	ketene absorbance	molar absorptivity $(L \text{ mol}^{-1} \text{ cm}^{-1})$
0.159	0.42	561
0.217	0.60	557
0.545	1.41	575
0.839	2.09	579
1.193	2.78	509

Table 5-68. Absorbance by ketene formed in an experiment at 125 torr and 876 K in reactor 2.

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t	ketene absorbance	molar absorptivity
(s)		$(L \text{ mol}^{-1} \text{ cm}^{-1})$
0.721	0.24	566
1.820	0.67	593
2.686	0.83	534

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ketene absorbance	molar absorptivity
	$(L \text{ mol}^{-1} \text{ cm}^{-1})$
0 29	551
0 58	477
1 11	470
	ketene absorbance 0 29 0 58 1 11

Table 5-70. Absorbance by ketene formed in an experiment at 124 torr and 834 K in reactor 2

t	ketene absorbance	molar absorptivity
(s)		$(L \text{ mol}^{-1} \text{ cm}^{-1})$
3 123	0 16	555

**Fable 5-71.** Absorbance by ketene formed in an  $\epsilon$  periment at 176 torr and 834 K in reactor 2

t (s)	ketene absorbance	molar absorptivity
3 652	0 26	565



Figure 5-17. Absorbance by ketene as a function of time in an experiment at 85.3 Torr and 929 K in reactor 2.

Tables 5-72 and 5-73 show the steady state rates of formation of methane, ethane, butanone, and 2,5-hexanedione and the calculated rate constants The standard deviation of each rate quoted in Tables 5-72 and 5-73 was between 1 and 3% The last digit in the rates is the first digit of the standard deviation In those experiments where the induction period was observed, equation (103) was used to estimate the steady state rates of formation of methane

Experiments were carried out in the three reactors at 876 K to search for any surface reaction Carbon deposition on the reactor wall increased the yield of ethylene but, as Table 5-72 shows, with clean quartz reactors at identical pressures, there was no trend evident in the steady-state rates of formation of methane, ethane, and butanone on changing surface-to-volume ratio

The butanone and 2,5-hexanedione peaks appeared in the tail of the acetone peak and could not be detected at some experimental conditions, represented by blanks in Tables 5-72 and 5-73 Where peaks could be reliably measured for all three termination products, equation (90) was applied to calculate values of the cross combination quotient m Tables 5-72 and 5-73 show the value of  $1/m^2$ , (=  $k_5k_7/k_6^2$ ), at different conditions

For conditions where one termination product could not be measured, a value of m determined at a similar temperature and pressure was inserted in equation (90), which was then solved for the missing rate For example the values of m at 928 K were equal to 2 67, and 2 57 at 10 3 and 20 9 Torr, respectively The average of 2 67 and 2 57 was used as the value for m at 15 5 Torr This average value of m was used to calculate the rate of formation of 2,5-hexanedione at 897 K

Table 5-72 Steady state rates and rate constants from experiments at several pressures and temperatures in three reactors.

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  $R_m \times 10^5$   $R_e \times 10^7$   $R_b \times 10^7$   $R_5/k_3^2 \times 10^4$   $k_1 \times 10^4$   $k_4k_3/k_6$   $k_5k_7/k_6^2$  

 Torr
 mol L<sup>-1</sup>s<sup>-1</sup>
 mol L<sup>-1</sup>s<sup>-1</sup>
 mol L<sup>-1</sup>s<sup>-1</sup>
 mol L<sup>-1</sup>s<sup>-1</sup>
 s<sup>-1</sup>
 s<sup>-1</sup>

928 K,  $s/v = 20.4 \text{ cm}^{-1}$ 

10.3	1.37	7.0	3.2	0.21	1.18±0.08	58±2	3.3±0.2	0.14±0.01
20.9	3.67	15.8	7.2	0.49	1.53±0.08	65±1	5.2±0.3	0.15±0.01
41.4	11.0	39	16.3	1.23	1.65±0.07	79±2	10.4±0.6	0.1 <b>8±0</b> .01
82.2	25.7	73	39.4	4.1	2.23±0.2	82±2	11.8±0.8	0.19±0.02
126.0	46	107	81	12.0	2.37±0.2	92±2	12.1±0.8	0.20±0.02
182.0	76	161	109	17.0	2.75±0.2	91±1	17±1	0.23±0.02

876 K, s/v = 10.3 cm<sup>-1</sup>

10.3	0.22	0.40	0.41	2.0±0.3	4.6±0.2	0.63±0.04	0.14±0.01
20.6	0.62	1.08	0.78	3.0±0.2	5.2±0.1	1.31±0.08	0.16±0.01
30.6	1.00	1.62	1.13	5.2±0.3		1.6±0.1	
41.3	1.40	1.81	1.54	5.3±0.2	4.7±0.1	1.7±0.1	0.17±0.01

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20 5	0 61	1 05		4 0±0.4			
30 8	0.95	1 33		4.7±0 3			
41.0	1 49	1 89	1 60	4 8±0 1	4.9±0.1	1 9±0.1	0.16±0.01
82.0	3.27	2 92	37	6.1±0 2	5 1±0.1	1.9±0.1	0 22::0.02

876 K, s/v = 20.4 cm<sup>-1</sup>

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# $876 \pm 2$ K, s/v = 14.0 cm<sup>-1</sup>

10.3				0.059				
20 6	0 62	1 13		0 090	4 2±0 8			
41 3	1 43	1 79		0 223	5 0±0.2			
81 4	3 70	33		1 03	5 4±0 2			
124.0	59	3 9	55	181	5 7±0 2	4 9±0 1	2 8±0 2	0.23±0.02
176.0	95	59	88	2 92	6 8±0 3	5.5±0 1	3 2±0 2	0.22±0.02

10 3	0 039	0 039	0 087	10 <del>±</del> 2	0 81± 04	0 10±0 01
21 0	0 098	0 072	0 190	13±1	0 84± 03	0 13±0 01
41 5	0 24	0 122	0 323	14±2	0 74± 02	0 23±0 02
80 6	0 44	0 163		20±2		
126 9	0 88	0 238		18±2		
183 6	1 46	0 361		21±2		

R<sub>m</sub>, R<sub>e</sub>, R<sub>en</sub>, R<sub>b</sub>, and R<sub>h</sub> are the rates of formation of methane, ethane, ethylene, butanone, and 2,5-hexanedione, respectively

 $834 \pm 2$  K, s/v = 20.4 cm<sup>-1</sup>

<b>Aubic C</b> for account of some experiments carried out at 15.5 1 of at universite temperatures in a reactor with bit in 10.5 one
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Т	$R_m \times 10^{-6}$	$R_{c} \times 10^{-8}$	$R_b \times 10^{-8}$	$R_h \times 10^{-8}$	$k_{5} / k_{3}^{2}$	k <sub>1</sub>	k4k3/k6	k5k7/k6 <sup>2</sup>
К	mol L <sup>-1</sup> s <sup>-1</sup>	mol L <sup>-1</sup> s <sup>-1</sup>	mol L <sup>-1</sup> s <sup>-1</sup>	mol $L^{-1}s^{-1}$	mol s L <sup>-1</sup>	s <sup>-1</sup>	s <sup>-1</sup>	
940	45 4	230	108	94	7 8×10 <sup>-5</sup>	1 31×10 <sup>-2</sup>	7 2±0 4	0 18±0 01
897	9 23	28 5	18 7		2 57×10 <sup>-4</sup>	1 77×10 <sup>-3</sup>	1 6±0 1	
854	1 63	1 97	3 35		6 3×10 <sup>-4</sup>	2 12×10 <sup>-4</sup>	0 27±0 02	
825	0 44	0 32	1 06		1 49×10 <sup>-3</sup>		0 06±0 01	

## 5-1. Calculation of the rate constant for reaction (1)

The decomposition of acetone, reaction (1), is unimolecular. Its rate constant was calculated using the sum of the yields of termination products as in equation (8) The results for this rate constant listed in Table 5-72 reveal a dependence on pressure at 928 K and a slight dependence at 876 K. The Troe expression, equation (35), was fitted to the experimental data at 928 and 876 K by nonlinear least-squares<sup>70</sup> to estimate the low and high pressure limits,  $k_{1,0}$  and  $k_{1\infty}$  The results showed that  $k_{1\infty}$  was not sensitive to  $F^{WC}$  and that changing  $\beta_c$ , the collision efficiency, from unity to 0.1 again changed  $k_{1\infty}$  by only 15%. In these fittings the values of  $k_{1,0}$  were found to be  $(1.0 \pm 0.2) \times 10^3$  and  $(1.3 \pm 1.8) \times 10^3$  L mol<sup>-1</sup> s<sup>-1</sup> at 928 and 876 K, respectively. The results of these fits are shown in Figure 5-18. The resulting high-pressure limits for  $k_1$  are given in Table 5-74.

To calculate  $k_{1\infty}$  at 940 K the value of  $k_1$  at 15.5 Torr was multiplied by 1.8, the ratio of  $k_{1\infty}$  to the  $k_1$  calculated at 15.5 Torr at 928 K.  $k_1$  was assumed to be independent of pressure at temperatures lower than 876 K. No value of  $k_{1\infty}$  is listed at the lowest experimental temperature because of uncertainty regarding the yield of 2,5-hexanedione.

An Arrhenius plot for  $k_{1\infty}$  is shown in Figure 5-19. The Arrhenius expression for this rate constant was found by least squares to be

$$k_{1\infty} (s^{-1}) = 10^{179 \pm 0.8} \exp(-353 \pm 14 \text{ kJ mol}^{-1}/\text{ RT})$$
(107)

### 5-2. Calculation of the rate constant for reaction (3)

Equation (86) was used to calculate the values of  $k_5/k_3^2$  for different conditions. Figure 5-20 shows the pressure and temperature dependence of this quotient. The value of  $k_5$  is known to be affected by changing the pressure.



Figure 5-18. Dependence of  $k_1$  on acetone concentration at 876 and 928 K;  $\blacksquare$ , experimental data; ---, nonlinear least-squares fit of equation (35) to the data,  $\beta_C=1.0.$  (a); 928 K, (b); 876 K

Т	k <sub>1</sub>	$k_{5}/k_{3}^{2} \times 10^{4}$	k <sub>3</sub> ×10 <sup>-6</sup>	k3k4/k6	$k_4/k_6 \times 10^6$	$k_4 \times 10^4$	k5k7/k62	$k_{6} \times 10^{10}$	k <sub>7</sub> ×10 <sup>9</sup>
Κ	s <sup>-1</sup>	mol s L <sup>-1</sup>	Lmol <sup>-1</sup> s <sup>-1</sup>	s <sup>-1</sup>	mol L <sup>-1</sup>	s <sup>-1</sup>		Lmol <sup>-1</sup> s <sup>-1</sup>	Lmol <sup>-1</sup> s <sup>-1</sup>
940	(2.4±0.2)×10 <sup>-2</sup>	2.2±0.2	9.5±0.5	138±20	15±3	22±2			
928	$(1.2\pm0.1)\times10^{-2}$	3.7±0.3	7.4±0.3	81±12	11±2	17±2	0.1 <del>9±</del> 0.01		
897	(2.7±0.2)×10 <sup>-3</sup>	7.4±0.6	5.3±0.2	27±4	5±1	7.5±0.9			
876	(5.8±0.3)×10 <sup>-4</sup>	9.3±0.5	4.8±0.1	14±2	2.9±0.5	4.3±0.5	0.19±0.02	1.5±0.3	3.0±0.7
854	(2.5±0.1)×10 <sup>-4</sup>	17±1	3.6±0.1	3. <del>9±</del> 0.6	1.1±0.2	2.0±0.2			
834	(8.8±0.6)×10 <sup>-5</sup>	29±3	2.8±0.2	2.3±1.2	0.8±0.5				
825		39±4	2.4±0.2						

 Table 5-74. High pressure limiting rate constants at different temperatures

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Figure 5-19. Dependence of the high pressure limit of  $k_1$  on temperature.



**Figure 5-20.** Dependence of the ratio,  $k_5/k_3^2$ , on temperature and acetone concentration: **a**, experimental data; a, 834 K; b, 876 K; c, 928 K; —, nonlinear least squares fit of equation (35) with unit collision efficiency to the data

To calculate the high-pressure limit for 'his quotient of rate constants, the Troe expression (35) was fitted to the data by nonlinear least squares <sup>70</sup> The high-pressure limits for this quotient at each temperature were affected by only 15% on changing  $\beta_c$  from unity to 0 1 The low pressure limits for  $k_5/k_3^2$  were calculated to be 8 8 ± 1 9, 24 8 ± 2 9, and 65 5 ± 15 9 L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup> at 928, 876, and 834 K, respectively, for unit  $\beta_c$  The high pressure limits for this quotient with unit collision efficiency are presented in Table 5-74 The ratios of  $(k_5/k_3^2)_{\infty}$  to  $k_5/k_3^2$  at 15 5 Torr were calculated to be 2 75, 2 66, and 2 62 at 928, 876, and 834 K respectively Values of  $(k_5/k_3^2)_{\infty}$  at 940, 897, 854, and 825 K were calculated by multiplying the values of  $k_5/k_3^2$  at 15 5 Torr in Table 5-73 by the ratios at the nearest temperature in the preceding sentence

The expression of Wagner and Wardlaw,<sup>34</sup>  $k_{5\infty}(L \text{ mol}^{-1} \text{ s}^{-1}) = 9.05 \times 10^{13} (\text{T/K})^{-1.18}$ exp(-2 74 kJ mol<sup>-1</sup>/RT), was used to calculate  $k_{5\infty}$  at different temperatures. The values of  $k_3$  in Table 5-74 were calculated by substituting these values of  $k_{5\infty}$  into the high pressure limiting values of  $k_5/k_3^2$  at each temperature. The results are shown in Figure 5-21. The Arrhenius expression for this reaction was calculated by linear least squares to be  $k_3$  (L mol<sup>-1</sup> s<sup>-1</sup>) =  $10^{10.9 \pm 0.2} \exp(-71.9 \pm 3.5 \text{ kJ mol}^{-1}/\text{RT})$  (108)

# 5-3. Calculation of the quotient, k4k3/k6

The decomposition of the  $CH_3COCH_2$  radical, reaction (4), is a unimolecular reaction Its rate constant is expected to be strongly pressure dependent in the present pressure and temperature range It was possible to calculate the ratio of  $k_3k_4/k_6$  by way of equation (87) It was expected that  $k_3$  would be independent of pressure and that  $k_6$  could be slightly pressure dependent at 928 K only, based on  $k_1$ 



Figure 5-21. Dependence of  $k_3$  on temperature.

The dependence of  $k_6$  on pressure is expected to be less than that for  $k_3$  or  $k_1$  Figure 5-22 shows the pressure dependence of  $k_3k_4/k_6$  at 834, 876 and 928 K The Troe method, equation (35), was fitted to the experimental data to calculate the low- and high-pressure limits of  $k_4k_3/k_6$  at 834, 876, and 928 K The low-pressure limiting values at these temperatures were found to be  $(8.6\pm3.6)\times10^2$ ,  $(6.7\pm1.4)\times10^3$ , and  $(3.1\pm0.6)\times10^4$  L mol<sup>-1</sup> s<sup>-2</sup>, respectively, with unit collision efficiency,  $\beta_c$  The high-pressure values of this quotient with unit collision efficiency are listed in Table 5-7.4 The high-pressure values of this quotient were affected by 35% on changing the collision efficiency from unity to 0.1

The values of  $k_3k_4/k_6$  at 940, 897, 854, and 825 K were only measured at 15 5 Torr, as listed in Table 5-73 The ratios of  $(k_3k_4/k_6)_{\infty}$  to  $k_3k_4/k_6$  at 15 5 Torr at 834, 876, and 928 K were calculated to be 13.4, 15 0 and 18 6, respectively It was possible to plot an Arrhenius plot for these ratios and, using the resulting parameters, to calculate this ratio at 825, 854, 897 and 940 K The resulting Arrhenius parameters were found to be

$$\ln \left( \frac{\left(\frac{k_{3}k_{4}}{k_{6}}\right)_{\infty}}{\left(\frac{k_{3}k_{4}}{k_{6}}\right)_{15\,5}} \right) = 5\,85 - 2\,72 \left(\frac{1000}{T}\right)$$
(109)

Equation (109) was used to calculate the ratio of  $(k_3k_4/k_6)_{\infty}$  to  $k_3k_4/k_6$  at 15 5 torr at 854, 897 and 940 K. The values of  $k_3k_4/k_6$  at 15 5 Torr in Table 5-73 were multiplied by the corresponding ratio and the resulting high-pressure limits of  $k_3k_4/k_6$  are listed in Table 5-74. The value of  $k_3$  calculated at each temperature in the previous section was used to calculate the high-pressure limit of the  $k_4/k_6$  ratio, listed in Table 5-74



Figure 5-22. Pressure dependence of  $k_3k_4/k_6$ , (a); 834 K, (b); 876 K, (c); 928 K, —; nonlinear least squares fit of equation (35) with unit collision efficiency to the experimental data.

Figure 5-23 shows an Arrhenius plot for  $k_4/k_6$ . A linear least-squares fit to the high-pressure limiting values of  $k_4/k_6$  resulted in Arrhenius parameters as follows

$$k_4/k_6 \text{ (mol } L^{-1}) = 10^{721 \pm 0.70} \exp(-217.2 \ (\pm 11.7) \text{ kJ mol}^{-1} / \text{RT})$$
 (110)

A possible source for the high pre-exponential value could be the inaccurate calculated high-pressure value of  $k_3k_4/k_6$  at 834 K. It was possible to measure the value of  $k_3k_4/k_6$  only at three pressures, 10, 20 and 40 Torr, at 834 K. This limited number of measured values for this quotient at low pressures led to a relatively large uncertainty, 60%, in the calculated low- and high-pressure limiting values of this quotient at 834 K

To investigate the accuracy of the calculated Arrhenius parameters for  $k_4/k_6$ , the data at 15 5 Torr were fitted linearly to calculate the Arrhenius parameters at 15 5 Torr. To calculate the value of  $k_3k_4/k_6$  at 15 5 Torr at 928, 876 and 834 K, the average of this quotient at 10 and 20 Torr was calculated at each of these temperatures All the values of  $k_3k_4/k_6$  at each temperature were divided by corresponding values of  $k_3$  at each temperature to calculate the values of  $k_4/k_6$ . The resulting Arrhenius plot is shown in Figure 5-24 and the Arrhenius parameters for  $k_4/k_6$  at 15 5 Torr were found as follows

$$k_4/k_6 \text{ (mol } L^{-1}) = 10^{4.36 \pm 0.66} \exp(-187.6 (\pm 11.1) \text{ kJ mol}^{-1} / \text{ RT})$$
 (111)



Figure 5-23. Dependence of the high pressure limit of  $k_4/k_6$  on temperature.



Figure 5-24. Dependence of  $k_4/k_6$  at 15 5 Torr on temperature.

# 5-4. Calculation of the quotient, $k_5k_7/k_6^2$ (=1/m<sup>2</sup>)

Equation (90) was used to calculate the value of  $k_5k_7/k_6^2$  (=1/m<sup>2</sup>). It is expected that  $k_5$  would be the major pressure dependent rate constant in this quotient. To calculate low- and high-pressure limits for this ratio of termination rate constants at 876 and 928 K the Troe method, equation (35), was fitted to 1/m<sup>2</sup>. The low-pressure values of 1/m<sup>2</sup> were found to be 1 9×10<sup>4</sup> and  $2.3\times10^4$  L mol<sup>-1</sup> at 876 and 928 K, respectively. The highpressure values are listed in Table 5-74. The high-pressure values were not sensitive to the collision efficiency. Changing  $\beta_c$  from unity to 0.1 changed the high pressure values by less than 15%. The pressure and temperature dependence of m<sup>-2</sup> is shown in Figure 5-25.

## 5-5. The measured induction periods

The chemical induction period,  $\tau_c$ , is expected to be independent of reactor radius, as in equation (104), whereas the thermal induction period,  $\tau_h$ , is expected to be a function of reactor radius squared times pressure, as in equation (92). The induction periods determined by fits to data showed elements of both sorts of behavior, especially at higher temperatures in reactor one, indicating that both  $\tau_c$  and  $\tau_h$  contributed to the measured induction periods. It is generally more difficult to reach very low residence times as the reactor radius increases or pressure increases. Equations (91) and (103) have been fitted to the rates of formation of methane at different conditions to estimate the steady rate of formation of methane and the thermal diffusivity,  $\kappa$ , or the chemical induction period,  $\tau_c$ .



Figure 5-25. Dependence of the ratio,  $k_5k_7/k_6^2$  (=1/m<sup>2</sup>), on temperature and acetone concentration: **II**, experimental data; a, 876 K and c, 928 K, —, nonlinear least squares fit of equation (35) with unit collision efficiency to the data

The results are shown in Table 5-75. The steady rates of formation of methane estimated by both equations (91) and (103) are in agreement. The observed induction period estimated by equation (103) increases as the temperature decreases. It was possible to calculate the thermal diffusivity of the acetone using equation (93). The heat capacity,  $C_{p}$ , for acetone<sup>71</sup> at 825, 854, 876, 897 and 940 K is equal to 148, 149, 152, 154 and 156 J mol<sup>-1</sup> $K^{-1}$ , respectively. The thermal conductivity of acetone at these temperatures was found to be  $6.8 \times 10^{-4}$ ,  $7.2 \times 10^{-4}$ ,  $7.7 \times 10^{-4}$ ,  $8.0 \times 10^{-4}$  and  $8.6 \times 10^{-4}$  J cm<sup>-1</sup>s<sup>-1</sup>K<sup>-1</sup>, respectively, from extrapolation of the data reported by Gallant<sup>66</sup> to the higher temperatures. The thermal diffusivity calculated via equation (93) is shown in the last column of Table 5-75. The thermal diffusivity estimated at 940 K was comparable with the calculated thermal diffusivity, which indicates that the observed induction period at 940 K was mostly caused by incomplete radial heat transfer. As Table 5-75 shows when the temperature decreases, the thermal diffusivity estimated from experiment decreases sharply and no longer is comparable with the calculated thermal diffusivity. This behavior of the thermal diffusivity shows that the major contributor to the observed induction periods at lower temperatures was chemical.

p (Torr)	reactor	$R_m \times 10^5 (eq \ 103)$ (mol L <sup>-1</sup> s <sup>-1</sup> )	τ <sub>obs</sub> ×10 <sup>2</sup> (s) 940 K	$R_{m} \times 10^{5} (eq 91)$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$\kappa^{a}$ (cm <sup>2</sup> s <sup>-1</sup> )	κ <sup>b</sup> (cm <sup>2</sup> s <sup>-1</sup> )
15 5	1	4 54 ± 0 06	0 39±0 08 897 K	4 46 ± 0 04	21 3±7 0	20 8
15 5	1	0 92 ± 0 02	0 90±0 08 876 K	0 91 ± 0 01	7 40±1 4	186
10 <b>3</b>	1	$0~22\pm0~02$	1 90±0 2	$0\ 22\pm 0\ 01$	2 96±0 23	27 5
20 6	1	0 62 ± 0 01	<b>1 80±</b> 0 1	0 64 ± 0 01	2 93±0 13	13 8
30 6	1	$1 \ 90 \pm 0 \ 03$	1 80±0 2	1 06 ± 0 02	2 81±0 32	93
41 3	1	$1 40 \pm 0 02$	2 30±0 2	$1\ 48\pm 0\ 02$	2 23±0 14	69
20 5	2	$0.61 \pm 0.01$	0 97±0 15	0 61 ± 0 01	0 <b>87±</b> 0 06	13 8
30 8	2	$0.95\pm0.02$	0 76±0 08	$0.97\pm0.01$	0 99±0 09	93
41 0	2	1 49 ± 0 03	0 71±0 20	1 51 ± 0 01	1 10±0 05	69
82 0	2	3 27 ± 0 03	0 76±0 09	$3\ 27 \pm 0\ 02$	0 92±0 10	35
20 6	3	$0.62 \pm 0.02$	1 02±0 05	0 60 ± 0 92	2 37±0 14	13 8
41 3	3	$143 \pm 0.03$	0 <b>87</b> ±0 06	$151 \pm 003$	1 99±0 12	69
81 4	3	3 70 ± 0 04	0 95±0 08 854 K	$3\ 76\pm 0\ 03$	1 65±0 13	3 5
15 5	1	0 16 ± 0 01	1 85±0 21 825 K	0 16 ± 0 01	2 57±0 31	16 5
15 5	1	0 04 ± 0 01	5 42±0 40	0 04 ± 0 01	1 13±0 06	15 2
(a), fr	om fitting	equation (96) to the	experimental	l data, (b), from the	rmal conducti	vity and

Table 5-75.	The results of	fitting equations	(91) and	(103) to the	experimental	data

 $\mathbf{C}_{\mathbf{p}}$
# 5-6. Results of the computational study of the dissociation reaction of the acetonyl radical, reaction (4)

The theoretical study of reaction (4) was carried out using the Gaussian 92 program. To find the transition state for reaction (4) the distance between the carbon in the CH<sub>3</sub> group and the carbonyl carbon in the acetonyl radical was kept constant at 16 different distances. The AM1 program was allowed to optimize the other geometric variables to find the minimum energy path along the reaction coordinate. A saddle point along the reaction path was detected when the two carbon atoms were 2.1 Å from each other. The same approach was used at twelve different C-C distances between 1.7 and 2.5 Å to detect the saddle point at the HF/3-21G level. Figure 5-26 shows the potential energy barrier for reaction (4) calculated at the HF/3-21G level. To save computer time only six points from 2.07 to 2.2 Å were calculated at the HF/6-31G\*\* level. At the AM1 level the output of the program had two imaginary frequencies in the saddle point region. One was for movement along the reaction coordinate. This was imaginary only in the saddle point region and was real before and after that point. The second imaginary frequency was for rotation of the CH<sub>3</sub> group. This stayed negative for a distance after the saddle point region. The calculations at the HF/3-21G and HF/6-31G\*\* levels of theory gave only one imaginary frequency in the saddle point region.

The activation energy for reaction (4) at the HF/3-21G and HF/6-31G\*\* levels was found to be 217 and 233 kJ mol<sup>-1</sup>, respectively. There was not any experimental or theoretical data about the frequencies of the acetonyl radical in the literature but it was possible to compare the calculated ketene and methyl radical frequencies with the

experimental frequencies. A summary of the results of these calculations for the reactant and the activated complex and the products are presented in Figure 5-27 and Tables 5-76 to 5-79.



Figure 5-26. The potential energy barrier for reaction (4).



Figure 5-27. HF/6-31G\*\* optimized geometry of the acetonyl radical.

**Table 5-76.** Geometry of the acetonyl radical calculated at the HF/6-31G<sup>\*\*</sup> level of theory for the reactant and activated complex. Distances, r, in Angstrom and angles,  $\angle$ , in degrees. Atoms are numbered according to Figure 5-27.

Dimension	reactant	activated complex
r (C <sub>1</sub> -C <sub>2</sub> )	1.43	1.32
r (C <sub>2</sub> -C <sub>3</sub> )	1.51	2.10
r (H-C <sub>1</sub> ) (2)	1.07	1.07
r (H-C <sub>3</sub> ) (3)	1.09	1.08
r (C=O)	1.23	1 18
$\angle$ (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )	119.4	105 0
∠ (C <sub>3</sub> -C <sub>2</sub> -O)	120.9	98.5
$\angle$ (H-C <sub>1</sub> -C <sub>2</sub> )	119.8	1198
∠ (H-C₃-C₂)	110.3	100.9
$\angle H_1$ -C <sub>1</sub> -C <sub>2</sub> -O (dihedral)	0.1	0 0
$\angle H_2$ -C <sub>1</sub> -C <sub>2</sub> -O (dihedral)	-180.0	-180.0
$\angle$ H <sub>3</sub> -C <sub>3</sub> -C <sub>2</sub> -O (dihedral)	-120.2	-118.8
$\angle H_4$ -C <sub>3</sub> -C <sub>2</sub> -O (dihedral)	120.5	120.8
$\angle H_5$ -C <sub>3</sub> -C <sub>2</sub> -O (dihedral)	0.2	10

description	AM1	HF/3-21G	HF/6-31G**
	Acetonyl radical (	reactant)	
CH <sub>3</sub> rotation	74	21	65 (59)
CH <sub>3</sub> rock	205	420	408 (367)
CH <sub>2</sub> rotation	400	531	449 (404)
C-C-C bend	525	533	544 (490)
C-C-C bend	536	574	561 (505)
CH <sub>2</sub> bend	813	858	757 (681)
C-C stretch	968	<b>88</b> 0	883 (795)
CH <sub>3</sub> rock	1035	1046	1004 (904)
CH <sub>2</sub> bend	1052	1089	1123 (1011)
CH <sub>3</sub> sym. bend	1110	1165	1144 (1030)
CH <sub>3</sub> bend, CH <sub>2</sub> rock	1369	1339	1348 (1213)
CH <sub>3</sub> bend, CC stretch	1371	1422	1531 (1378)
CH <sub>3</sub> asym. bend	1381	1569	1548 (1393)
CH <sub>3</sub> deform	1420	1626	1605 (1445)
CH <sub>2</sub> bend	1464	1647	1609 (1448)
CO stretch	1920	1660	1621 (1459)
CH stretch	3060	3204	3189 (2870)
CH stretch	3068	3254	3248 (2923)
CH stretch	3155	3297	3301 (2971)
CH stretch	3215	3329	3317 (2985)
CH stretch	3226	3433	3430 (3087)

**Table 5-77.** Calculated frequencies in  $cm^{-1}$  for the acetonyl radical and the activated complex. Frequencies in parentheses are scaled by 0.9.

# Table 5-77 continued

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description	AM1	3-21G	6-31G**			
	Activated complex					
reaction coordinate	150i	735i	625i (563)			
CH <sub>3</sub> rotation	83i	56	35 (32)			
CCO bend	107	289	300 (270)			
CH <sub>2</sub> hindered rotation	236	416	389 (350)			
CCO bend	432	418	425 (383)			
CH <sub>3</sub> rock & CH <sub>2</sub> rotation	444	579	521 (469)			
CCC bend	537	697	667 (600)			
CH <sub>3</sub> rock	619	726	698 (628)			
CH <sub>2</sub> bend	906	940	781 (703)			
CH <sub>3</sub> sym bend	<u> </u>	966	987 (888)			
CH3 bend, CH2 rock	1077	1153	1128 (1015)			
CH <sub>3</sub> bend, CC stretch	1297	1181	1222 (1099)			
CH <sub>3</sub> asym. bend	1346	1564	1543 (1389)			
CH <sub>3</sub> deform	1348	1586	1564 (1408)			
$CH_2$ bend	1440	1627	1590 (1431)			
CO stretch	2329	1932	2035 (1831)			
CH stretch	3195	3258	3255 (2930)			
CH stretch	3208	3365	3362 (3026)			
CH stretch	3211	3413	3420 (3078)			
CH stretch	3218	3415	3421 (3079)			
CH stretch	3234	3453	3463 (3117)			

**Table 5-78.** Comparison of the calculated frequencies in  $\text{cm}^{-1}$  for ketene at different theoretical levels with the experimental frequencies<sup>72</sup>. Frequencies in the parentheses are scaled

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description	AM1	3-21G	6-31G**	experimental
CCO bend	406	532	490 (441)	438
CCO bend	461	651	622 (560)	528
CH <sub>2</sub> wag	883	892	724 (651)	588
CH <sub>2</sub> deform	1035	1176	1104 (994)	977
CC stretch	1277	1271	1262 (1136)	1118
CH <sub>2</sub> rock	1439	1590	1558 (1402)	1388
CO stretch	2423	2330	2378 (2140)	2152
CH stretch	3190	3364	3360 (3024)	3071
CH stretch	3230	3453	3465 (3119)	3166

**Table 5-79.** Comparison of the calculated frequencies in cm<sup>1</sup> for the methyl radical at different theoretical levels with the experimental frequencies<sup>73</sup>. Frequencies in the parentheses are scaled

by 0.9.

by 0.9.

description	AMĭ	3-21G	6-31G**	experimental
CH <sub>3</sub> out of plane bend	778	423	341 (307)	580
CH <sub>3</sub> in plane bend	1348	1544	1529 (1376)	1396
CH <sub>3</sub> in plane bend	1348	1544	1529 (1376)	1396
CH stretch	3249	3252	3260 (2934)	3044
CH stretch	3249	3429	3441 (3097)	3162
CH stretch	3252	3429	3441 (3097)	3162

#### 6. Discussion

#### 6-1. Other possible reactions

It is necessary to consider whether reactions in addition to (1) to (7) could have contributed to the observed products. A possible competitor to the initiation reaction (1) is the rupture of a carbon-hydrogen bond in acetone. However, the bond dissociation enthalpy for this bond is 411 kJ mol<sup>-1</sup>,<sup>74</sup> 72 kJ mol<sup>-1</sup> greater than that calculated for reaction (1). Such a difference would lead to a ratio of four orders of magnitude in the exponential factor at the present experimental temperatures.

It is also necessary to consider possible competing termination reactions. It has been suggested by Darwent *et al*<sup>75</sup> that there is a disproportionation reaction as follows

$$CH_3 + CH_3COCH_2 \rightarrow CH_4 + CH_2COCH_2$$
(112)

with a rate about one quarter the rate of reaction (6). However, one of the products in reaction (112) was a diradical, which seems improbable.

Another reaction suggested by Brinton<sup>8</sup> was

$$CH_3 + CH_3COCH_2 \rightarrow CH_4 + C_2H_4 + CO$$
(113)

This reaction can be ruled out because  $C_2H_4$  was not a primary product in the present study. The CH<sub>3</sub>CO radical could participate in termination as in the following reaction

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2$$
 (114)

Using a value for  $k_2$  from the literature,<sup>12</sup> it was estimated that the concentration of this radical is always about four orders of magnitude less than that of CH<sub>3</sub> under the present experimental conditions.

Addition of  $CH_3$  to acetone would produce the  $(CH_3)_3CO$  radical. Using reported rate constants for the forward and reverse processes,<sup>76,77</sup> it is possible to predict that the concentration of this radical would be several orders of magnitude lower still.

The theoretical study on reaction (4) by the semi-empirical AM1 method showed a stationary point which corresponded to the transition state for the isomerization of the acetonyl radical, reaction (75). This isomerization produces a new radical,  $CH_3CH_2CO$ , which could react with other radicals such as  $CH_3$  or another acetonyl radical to pro<sup>-1</sup>uce butanone or a diketone. A survey in the literature<sup>78</sup> shows that the enthalpy of formation of the  $CH_3CH_2CO$  radical,  $43\pm4$  kJ mol<sup>-1</sup>, is 67 kJ mol<sup>-1</sup> more than the enthalpy of formation of the acetonyl radical, -23 kJ mol<sup>-1</sup>. This would suggest that, if such an isomerization reaction occurs during the pyrolysis of acetone, the concentration of the  $CH_3CH_2CO$  radical would be much less than the acetonyl radical concentration.

Variation, like that observed in Figure 5-20, of the quotient,  $k_5/k_3^2$ , with changing acetone concentration has previously been observed in photolysis experiments. Brinton<sup>8</sup> performed the most detailed study, and criticized previous investigations, particularly those at temperatures above 600 K. In order to explain values of m as low as 0.3 and variation of  $k_5/k_3^2$  by a factor of seven with only a four-fold pressure change (but a 25-fold photolysis intensity change), he postulated the following additional reaction

•.

$$CH_3 + (CH_3)_2 CO \rightarrow C_2 H_6 + CH_3 + CO$$
(115)

It is necessary to carefully consider the pressure dependence of m and  $k_5/k_3^2$  to determine whether reaction (15) could have an effect under the present conditions

The values of  $p_{1/2}$ , the pressure at which  $k_5$  has fallen to half its high pressure limiting value, were found from  $k_5/k_3^2$  to be 39, 42, and 49 Torr at 834, 876, and 928 K, respectively, and, from m<sup>-2</sup>, to be 12 and 10 Torr at 876 and 928 K, respectively These may be compared with a value of 17 Torr found for reaction (5) at 822 K,<sup>79</sup> and values between 10 and 60 Torr in the present temperature range from a survey of the literature for the reverse reaction <sup>80</sup>

To investigate the possibility of reaction (115) occurring, an equation derived by Brinton<sup>8</sup>, equation (116), was fitted to the results for  $R_e[A]^2 / R_m^2$  at different pressures, from the third column in Table 5-72

$$(\mathbf{R}_{e}[\mathbf{A}]^{2} / \mathbf{R}_{m}^{2}) = (\mathbf{k}_{5\infty} / \mathbf{k}_{3}^{2}) (\mathbf{k}_{5} / \mathbf{k}_{5\infty}) + X (\mathbf{R}_{h}^{2} [\mathbf{A}] / \mathbf{R}_{b})$$
(116)

Here X is a combination of rate constants including the rate constant for reaction (115),  $k_{115}k_6 / k_3^2 k_7$  The ratio of  $k_5 / k_{5\infty}$  was calculated from the literature<sup>71,72</sup> and  $k_{5\infty}/k_3^2$  and X were selected as parameters The fitted rates of reaction (115) were small enough to affect the quoted values of  $k_3$  by 5% or less

#### 6-2. Rate constant of reaction (1)

The values of Arrhenius parameters for  $k_1$  reported in the present study,  $log_{10}$ A=17 9 ± 0.8 and  $E_A$ =353 ± 14 kJ mol<sup>-1</sup>, are in agreement with the values reported by Ernst and Spindler<sup>11</sup> from shock tube experiments,  $log_{10}$  A=16 4 and  $E_A$ =342±12 kJ mol<sup>-1</sup> The pre-exponential factors,  $\log_{10} A = 144$ , and 141, reported<sup>9,10</sup> from toluene carrier experiments, are lower than expected for a unimolecular decomposition reaction

Assuming the temperature dependence of the reverse of reaction (1) is between  $\pm$  RT/2, its activation energy would be 0  $\pm$  4 kJ mol<sup>-1</sup> Combining this with the present activation energy for reaction (1), we obtain 353  $\pm$  15 kJ mol<sup>-1</sup> as the internal energy change for reaction (1) and 360  $\pm$  15 kJ mol<sup>-1</sup> as the enthalpy change Taking heat capacities from the literature, the latter value may be adjusted to 358  $\pm$  15 kJ mol<sup>-1</sup> at 298 K Combining this with the heats of formation of acetone<sup>81</sup> and CH<sub>3</sub><sup>48</sup>, we obtain -6±15 kJ mol<sup>-1</sup> as the heat of formation of CH<sub>3</sub>CO This may be compared with the following values reported in the literature, -9 kJ mol<sup>-1</sup> from a study of CH<sub>3</sub>CO→CH<sub>3</sub> + CO<sup>82</sup>, -22  $\pm$  4 kJ mol<sup>-1</sup> from a study of CH<sub>3</sub>CO + HI,<sup>83</sup> -19  $\pm$  8 kJ mol<sup>-1</sup> from a study based on ionization phenomena,<sup>84</sup> -22 6  $\pm$  9 kJ mol<sup>-1</sup> in an electron affinity determination study,<sup>85</sup> -10 0  $\pm$  1 2 kJ mol<sup>-1</sup> in reaction of CH<sub>3</sub>CO + HBr<sup>86</sup> and -24 2 $\pm$  1 7 kJ mol<sup>-1</sup> calculated from a bond dissociation energy calculation<sup>87</sup>

# 6-3. Cross combination reaction, reaction (6)

The value of  $1.9 \pm 0.1$  found in this work for the cross-combination quotient of CH<sub>3</sub> and CH<sub>3</sub>COCH<sub>2</sub> radicals is similar to the values of 2.4, 2.0,  $1.8 \pm 0.1$ ,  $1.9 \pm 0.2$ , and  $2.4 \pm 0.2$  found in photolysis experiments<sup>8</sup> at temperatures of 473, 523, 578, 638, and 708 K It is also similar to values of 1.86 to 2.08 determined for various alkyl radicals at room temperature <sup>63,64</sup>

#### 6-4. Calculation of k4 using the measured induction period data

As Table 6-1 shows the measured induction periods at 876 K in reactor one were larger than those measured in reactors two and three at the same pressures According to equation (92) it is expected that in larger reactors the contribution of  $\tau_h$  would be larger than in smaller reactors It was possible to calculate  $\tau_h$  using equations (92) and the calculated thermal diffusivity listed in Table 5-75 The calculated  $\tau_h$  are shown in Table 6-1 One might calculate  $\tau_c$  by subtraction of the calculated  $\tau_h$  from the observed induction periods As Table 6-1 shows the resulting  $\tau_c$  in reactors two and three are relatively close to each other but different from  $\tau_c$  calculated in reactor one

There are two possible sources for this difference. One possibility could be the surface termination reactions which decrease the required time for the establishment of the steady state condition in smaller reactors where the surface-to-volume ratio is larger. This could be ruled out because as Table 5-72 showed no evidence was found for the surface reaction. The second possibility might be an error in the measured induction period in reactor one. This could be the source of error. As Tables 5-2 to 5-72 show, because of the larger size of reactor one it was difficult to reach very low residence times in this reactor. At higher pressures and very fast flow rates, the rate of vaporization of acetone was not fast enough to produce a constant pressure in the supply bulb before the reactor.

It was also possible to calculate  $\tau_c$  from extrapolation of the measured induction periods in reactors two and three to zero radius Because of the possibility of error, the measured induction periods in reactor one were not included From equation (104), $\tau_c$ should be independent of reactor radius The values of  $\tau_c$  found in this way are listed in the fifth column in Table 6-1. The slopes of these graphs agreed with the slopes of the calculated  $\tau_h$  versus squares of the reactor radius plots. As Table 6-1 shows, in reactor two 94% and 80% of the measured induction periods at 20 and 40 Torr, respectively, came from the chemical induction period. The average of 87 5% was taken as the contribution of the chemical induction period to the measured induction period at 30 torr. Also Table 6-1 shows that 70% of the observed induction period in reactor 2 is from the chemical induction period at 80 Torr.

The calculated  $\tau_h$  at 854 K was found to be  $3 \times 10^{-3}$  s. Comparing this value of  $\tau_h$  with the measured induction period reported in Table 6-1 at 854 K shows that the major source for the measured induction period at this temperature was the delay in the establishment of the steady state. The measured induction periods at 897 and 940 K were more affected by incomplete radial heat transfer.

р	$\tau_{obs} \times 10^2$	$\tau_h \times 10^2$	$\tau_{obs}$ - $\tau_h \times 10^2$	$\tau_c \times 10^3$	$k_4 \times 10^{-3}$	$k_{4\infty} \times 10^{-4}$
				from $\tau$ vs $r^2$		
(Torr)	(s)	(s)	(s)	(s )	(s <sup>-1</sup> )	(s <sup>-1</sup> )
			reactor 1, s/v,	876 K		
10 3	19±02	0 201	16			
20 6	<b>18</b> ±01	0 402	14			
30 6	$18\pm02$	0 600	12			
41 3	$2\ 3\pm 0\ 2$	0 801	15			
			reactor 2, s/v,	876 K		
20 5	0 97±0 15	0 057	0 91	0 91	3 6±0 3	44
30 8	0 76 ±0 08	0 086	0 70		4 1±0 2	39
41 0	0 71±0 20	0 115	0 60	0 57	5 0±0 8	42
82 0	0 76±0 09	0 229	0 53	0 59	4 5±0 5	27
			reactor 3, s/v,	876 K		
20 6	1 02±0 05	0 122	0 90		3 6±0 2	44
41 3	0 87±0 06	0 244	0 63		5 0±0 3	43
814	0 95±0 08	0 485	0 47		7 1±0 5	43
			reactor 1, s/v,	854 K		
15 5	1 85±0 21	0 300	1 55		1 36±0 10	20
			reactor 1, s/v,	825 K		
15 5	5 42±0 40	0 304	5 12		0 19±0 03	

Table 6-1. The measured induction period and calculated  $\tau_h$  and  $\tau_c$  and  $k_4$ 

One might rearrange equation (106) for  $1/k_4$  as follows

$$\frac{1}{k_4} = \frac{2\tau_c k_1[A]}{\ln(2) R_m^{ss}} - \frac{1}{k_3[A]}$$
(117)

The calculated values of  $\tau_c$  from  $\tau_{obs} - \tau_h$  were used to calculate k<sub>4</sub> using equation (117). The calculated values of k<sub>4</sub> are presented in Table 6-1. The quoted errors were calculated using the method of propagation of errors.

From Figure 5-22 in Chapter 5,  $k_4$  is expected to be strongly pressure dependent. The same procedure was followed to calculate  $\tau_c$  and  $k_4$  at lower temperatures.

The ratios of the high-pressure values of  $k_4k_3/k_6$  to the values of this quotient at 10, 20, 30, 40 and 80 Torr at 876 K were calculated from Table 5-74 to be 12.2, 9.7, 8.3 and 6.1, respectively. The ratios were used to calculate the high-pressure values of  $k_4$  at 876 K. The resulting values of  $k_{4\infty}$  are shown in Table 6-1. To calculate the average value of  $k_{4\infty}$  at 876 K the calculated high-pressure value of this rate constant at 80 Torr in reactor two was eliminated. To calculate the high-pressure values of  $k_4$  at 854 K the calculated  $k_4$  at 15.5 Torr was multiplied by 14.4, calculated from equation 109. The resulting high-pressure values of  $k_4$  are listed in Table 6-1 and 5-74. The high-pressure value of  $k_4$  at 825 K was not calculated because of uncertainty in the extrapolation of the value of  $k_4$  to the high-pressure limit at this temperature.

#### 6-5. Calculation of rate constants for reactions (6) and (7)

It was possible to substitute the calculated value of  $k_{4\infty}$ ,  $4.2 \times 10^4$ , at 876 K in the high pressure value of  $k_4/k_6$  in Table 5-74 to calculate  $k_6$ . In this way a value of  $1.5 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> was found for  $k_6$  at 876 K.

To calculate  $k_7$  equation (90) was used. A value of  $1.9\pm0.1$  was accepted for m Using the calculated value for  $k_6$ ,  $1.5\times10^{10}$ , and a value of  $k_5$  calculated from reference 34, a value of  $3.0\times10^9$  L mol<sup>-1</sup>s<sup>-1</sup> was found for  $k_7$  at 876 K

#### 6-6. Calculation of k4m at other temperatures

It is expected that the rate constants for recombination reactions like reaction (6) and (7) would be almost constant within the present temperature range This allows one to assume the same values for the rate constant,  $k_6$ , at other temperatures and to calculate  $k_{4\infty}$  at these temperatures. In this way, using the ratios of  $(k_4/k_6)_{\infty}$  in Table 5-74, the calculated high-pressure values of  $k_4$  were found to be  $1.7 \times 10^4$ ,  $7.5 \times 10^4$ ,  $16.5 \times 10^4$  and  $21.8 \times 10^4$  s<sup>-1</sup> at 854, 897, 928 and 940 K, respectively. Because of uncertainty in the high-pressure extrapolation, the high-pressure values of  $k_4$  at 825 and 834 K were not calculated. The calculated  $k_{4\infty}$  at 854 is less than the corresponding value of  $k_{4\infty}$  in Table 6-1 by only 15%.

The values of  $k_{4\infty}$  at different temperatures are listed in Table 5-74 To calculate the Arrhenius parameters the calculated values of  $k_{4\infty}$  at 854, 876, 897, 928 and 940 K in Table 5-74 were used and the results are shown in Figure 6-1 The calculated Arrhenius parameters for this reaction are as follows

$$k_{4\infty} (s^{-1}) = 10^{1558 \pm 0.26} \exp \left(-1841 \pm 4 \text{ kJ mol}^{-1} / \text{RT}\right)$$
(118)



Figure 6-1. Dependence of the high pressure limit of  $k_4$  on temperature.

#### 6-7. Calculation of $k_6$ directly from the measured induction period data

It was possible to calculate  $k_6$  directly from the measured induction periods One might substitute  $k_4k_3/k_6$  from Tables 5-72 and 5-73 into equation (117) and solve the equation for  $k_6$  as

$$\frac{1}{k_6} = \left(\frac{\Phi}{k_3}\right) \left(\frac{2\tau_c k_1[A]}{\ln(2) R_m^{ss}} - \frac{1}{k_3[A]}\right)$$
(119)

Here  $\Phi$  represents the values of  $k_4k_3/k_6$  at different conditions in Tables 5-72 and 5-73 The values of  $k_6$  calculated using equation (119) are listed in Table 6-2. The quoted errors were calculated using the method of propagation of errors

Т	р	reactor	$\mathbf{k}_{6}$
(k)	(Torr)		$(L \text{ mol}^{-1}\text{s}^{-1}) \times 10^{-10}$
876	20 5	2	1 9±0 2
876	30 8	2	1 4±0 1
876	41 0	2	1 6±0 2
876	82 0	2	1 2±0 1
876	20 6	3	1 <b>8</b> ±0 1
876	41 3	3	1 3±0 1
876	81 4	3	1 5±0 1
854	15 5	1	1 7±0 1
825	15 5	1	0 <b>8</b> ±0 1

**Table 6-2**. Calculated values of  $k_6$  at different conditions using equation (119)

It was possible to compare the accuracy of the calculated values of  $k_6$  in Table 6-2 with the accuracy of  $k_4$  in Table 6-1. The calculated values of  $k_6$  in Table 6-2 at 876 K in reactors two and three were relatively close to each other. The average value of  $k_6$  in reactors two and three was found to be  $(1.5 \pm 0.3) \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> at 876 K. This value could be compared with the value of  $1.5 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> calculated in section 6-5 from  $k_4$ in Table 6-1 and  $k_4/k_6$  in Tables 5-72 and 5-73. This agreement was also an indication of the validity of the high pressure extrapolation for  $k_4/k_6$ . The value of  $k_6$  at 854 also agreed with the calculated average value of  $k_6$  ...t 876 K within the estimated experimental uncertainty. It was expected that the observed induction periods at higher temperatures were largely caused by incomplete radial transfer and therefore no values of  $k_6$  were shown in Table 6-2.

The results for  $k_6$  in section 6-5 and this section confirm a value of  $(1.5\pm0.3) \times 10^{10}$ L mol<sup>-1</sup>s<sup>-1</sup> for  $k_6$  at the conditions of the present study.

#### 6-8. The results of RRKM calculations for k4

The geometry and frequencies of the acetonyl radical and of the activated complex for reaction (4) were calculated by the semi-empirical AM1 method and at the HF\3-21G and HF\6-31G\*\* levels of ab initio theory, as described in section 5-6. The frequencies calculated at the HF/6-31G\*\* level of theory, listed in Table 5-77, were corrected to be used in the RRKM calculations for reaction (4). A summary of the inputs to the unimolecular RRKM program for reaction (4) is given in Table 6-3. The program calculated k<sub>4</sub> at eight pressures from 10 to 190 Torr and also calculated the low- and highpressure limiting values at 876 K.

-Reactant-
------------

$\begin{array}{llllllllllllllllllllllllllllllllllll$	frequencies of $CH_3COCH_2$ (cm )	3087, 2985, 2971, 2923, 2870, 1621, 1445,
795, 681, 505, 490, 404, 367moments of inertia (g Ų mol <sup>-1</sup> )97 8, 45 56, 45 56reduced moment of inertia (g Ų mol <sup>-1</sup> )2 94symmetry number3 0threshold energy (kJ mol <sup>-1</sup> )171 0cross section (Ų) and collision efficiency6 4, 0 2-Activated complefrequencies of CH <sub>3</sub> COCH2 (cm <sup>-1</sup> )3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,		1445, 1393, 1378, 1213, 1030, 1011, 904,
moments of inertia (g Ų mol <sup>-1</sup> )97 8, 45 56, 45 56reduced moment of inertia (g Ų mol <sup>-1</sup> )2 94symmetry number3 0threshold energy (kJ mol <sup>-1</sup> )171 0cross section (Ų) and collision efficiency6 4, 0 2-Activated complefrequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> )3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,		795, 681, 505, 490, 404, 367
reduced moment of inertia (g Ų mol <sup>-1</sup> )2 94symmetry number3 0threshold energy (kJ mol <sup>-1</sup> )171 0cross section (Ų) and collision efficiency $6 4, 0 2$ -Activated complefrequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> )3117, 3079, 3078, 3026, 2930, 1832, 1431,1408, 1389, 1100, 1015, 888, 703, 628,	moments of inertia (g $Å^2$ mol <sup>-1</sup> )	97 8, 45 56, 45 56
symmetry number 3 0 threshold energy (kJ mol <sup>-1</sup> ) 171 0 cross section (Å <sup>2</sup> ) and collision efficiency -Activated comple frequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> ) 3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,	reduced moment of inertia (g $Å^2$ mol <sup>-1</sup> )	2 94
threshold energy (kJ mol <sup>-1</sup> )       171 0         cross section (Å <sup>2</sup> ) and collision efficiency       6 4, 0 2         -Activated comple         frequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> )       3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1389, 1100, 1015, 888, 703, 628, 1408, 1408, 1389, 1100, 1015, 888, 703, 628, 1408,	symmetry number	3 0
cross section (Å <sup>2</sup> ) and collision efficiency $64, 02$ -Activated comple frequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> ) 3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,	threshold energy (kJ mol <sup>-1</sup> )	171 0
-Activated comple frequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> ) 3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,	cross section ( $Å^2$ ) and collision efficiency	6 4, 0 2
frequencies of $CH_3COCH_2$ (cm <sup>-1</sup> ) 3117, 3079, 3078, 3026, 2930, 1832, 1431, 1408, 1389, 1100, 1015, 888, 703, 628,	-Activated	d comple
1408, 1389, 1100, 1015, 888, 703, 628,	frequencies of CH <sub>3</sub> COCH <sub>2</sub> (cm <sup>-1</sup> )	3117, 3079, 3078, 3026, 2930, 1832, 1431,
		1408, 1389, 1100, 1015, 888, 703, 628,
600, 200, 191, 175, 135		600, 200, 191, 175, 135
moments of inertia (g $Å^2$ mol <sup>-1</sup> ) 118 6, 91 3, 30 8	moments of inertia (g $Å^2$ mol <sup>-1</sup> )	118 6, 91 3, 30 8
reduced moment of inertia (g $Å^2$ mol <sup>-1</sup> ) 3 02	reduced moment of inertia ( $g Å^2 mol^{-1}$ )	3 02
symmetry number 3 0		
symmetry number 3 0		

For the calculated fall-off behavior to agree with the experimental data, it was necessary to use a collision efficiency of 0.2 Such a collision efficiency was reported before for molecules like methylcyclopropane at 764 K.<sup>88</sup> The cross section of the acetonyl radical was assumed to be the same as the cross section of acetone<sup>89</sup>, 6.4 Å<sup>2</sup> For good agreement between the pre-exponential factors calculated by the RRKM program and the experimental data the smallest vibrational frequency in the activated complex, for the rotation of the methyl group around the reaction coordinate axis, was treated as a free rotation. The four next smallest frequencies calculated at the HF/6-31G\*\* level were decreased by half. The moments of inertia of the reactant and the activated complex were calculated using the method introduced by Thompson.<sup>90</sup> The reduced moment of inertia for the internal rotation of the CH<sub>3</sub> top in the reactant and activated complex was calculated using the Pitzer<sup>52</sup> method. For good agreement among the fall-off behaviors of the Troe method, the experimental data and the RRKM method, the threshold energy was chosen to be 171 kJ mol<sup>-1</sup>.

The low- and high-pressure values of  $k_4$  calculated at 876 K according to these parameters were found to be  $6.0 \times 10^7$  L mol<sup>-1</sup>s<sup>-1</sup> and  $3.8 \times 10^4$  s<sup>-1</sup>, respectively. To compare the fall-off behavior calculated by the RRKM theory with the experimental data and the Troe curve estimated from the fitting of equation (35) to the experimental data, the value of  $k_4$  at each pressure calculated by RRKM was multiplied by the value of  $k_3/k_6$ calculated at 876 K in the present work The results are shown in Figure 6-2 The Arrhenius expression for  $k_4$  calculated by the RRKM program was as follows

$$k_4 (s^{-1}) = 10^{1552} \exp(-1832 \text{ kJ mol}^{-1} / \text{RT})$$
 (120)



Figure 6-2. The pressure dependence of  $k_4k_3/k_6$  at 876 K. experimental, ( $\blacksquare$ ); least-squares fit of equation (35) to the data with  $\beta_c=1.0$ , (---), with  $\beta_c=0.1$ , (+); RRKM theory with  $\beta_c=0.2$ , (----).

These Arrhenius parameters are in agreement with the Arrhenius parameters calculated from the induction period data,  $log_{10}(A/s^{-1})=15.58\pm0.26$  and  $E_A=184.1\pm4.4$  kJ mol<sup>-1</sup> in equation (118). The heat capacity of activation was calculated to be 4.8 J mol<sup>-1</sup>K<sup>-1</sup>.

There is not any data on the rate constant or on the Arrhenius parameters for reaction (4) in the literature. The experimental values of the Arrhenius parameters, stated in the previous paragraph, and the rate constant,  $4.3 \times 10^5$  s<sup>-1</sup>, calculated for reaction (4) at 876 K in the present study, from Table 5-74, might be compared with the corresponding values of the Arrhenius parameters and the rate constant for the dissociation reaction of n-propyl radicals. A survey in the Chemical Kinetics Data Base<sup>13</sup> reveals that the reported values of the Arrhenius parameters for the dissociation reaction of n-propyl radical. A survey in the Chemical Kinetics Data Base<sup>13</sup> reveals that the reported values of the Arrhenius parameters for the dissociation reaction of n-propyl to a methyl radical and ethylene lie between 13.0 and 14.48 for  $\log_{10} (A/s^{-1})$  and between 137.6 and 139.0 kJ mol<sup>-1</sup> for E<sub>A</sub>, respectively. The corresponding value of the rate constant calculated at 876 K in the above Arrhenius parameters is between 3 3×10<sup>5</sup> and 1.5×10<sup>6</sup> s<sup>-1</sup>. The value of  $\Delta ri$  for reaction (4) was calculated to be 122.4 kJ mol<sup>-1</sup> while that for the dissociation reaction of n-propyl is 101.0 kJ mol<sup>-1</sup>.<sup>74</sup> These values indicate that the dissociation reaction of n-propyl to methyl and ethylene should have higher rate constants and a lower activation energy than reaction (4).

#### 6-9. Calculation of transition state properties for reaction (3)

The value found for the pre-exponential factor for  $k_3$  was larger than those reported in photolysis experiments by two orders of magnitude and the activation energy was also larger than reported values by about 30 kJ mol<sup>-1</sup>. It is difficult to think of an alternative source for the CH<sub>4</sub> observed in the present experiments, except for disproportionation reactions, which would be expected to be slower than the combination reactions, which are two orders of magnitude slower than the rate of formation of  $CH_4$ 

-2

Higher Arrhenius parameters at higher temperatures have been observed previously in a number of reactions involving hydrogen transfer  $^{91,92,93}$  For similar reactions it has been possible to fit a transition-state-theory model, equation (74), to the experimental data  $^{90}$ 

The reaction path degeneracy is twelve for reaction (3) since there are six equivalent hydrogen atoms with an equal probability of being transferred to the methyl radical and there are two different faces on each methyl radical

The tunneling factor,  $\Gamma$ , was calculated<sup>51,54</sup> for passage through an unsymmetrical Eckart barrier with height V<sub>b</sub> in the forward direction and V<sub>b</sub> plus the measured exoergicity in the reverse direction, V<sub>br</sub> The thickness of the barrier can be described by a characteristic tunneling temperature, T<sup>\*</sup>, which is the temperature at which the average reacting molecule has energy approximately equal to  $\frac{h_2h}{h}$  ine barrier height

The translational, rotational, and vibrational partition functions were treated separately

For the transition state the moments of inertia were calculated from the results of a semi-empirical bond energy-bond order (BEBO) calculation <sup>50</sup> The exoergicity,  $V_{br} - V_{b}$ , of the reaction was taken as 27 kJ mol<sup>-1</sup> The vibrational term values,  $\omega$ , for acetone and methyl radical are given in Tables 2-1 and 5-79, respectively By the BEBO method the bond length and bond order for the CH<sub>3</sub>----H in the TS were estimated to be equal to 1 33 A and 0 4, respectively For CH<sub>3</sub>COCH<sub>2</sub>----H the bond length was estimated to be 1 22 Å

The barrier height was calculated to be  $51.4 \text{ kJ mol}^{-1}$  Reduced moments of inertia,  $I_{IR}$ , for the TS were calculated making use of the scheme of reference 52 and are listed in Table 6-4. The term values for the symmetric stretch, 565 cm<sup>-1</sup>, for the reaction coordinate, 975i cm<sup>-1</sup>, and for bending, 464 cm<sup>-1</sup>, in the transition state were also calculated according to the BEBO method.

To determine the vibrational contribution to the reaction rate, the vibrations in the reactants were compared to those in the transition state. In CH<sub>3</sub> there are 6 vibrational frequencies, all of which were assumed to be unchanged between the reactant and the transition state. Two CH<sub>3</sub> tumbling rotations would change to two H---C---H bending (rocking) motions in the transition state. The CH<sub>3</sub> rotation about the three-fold axis would become a free internal rotation in the transition state. In acetone there are 24 vibrational degrees of freedom, only two of which were assumed to change significantly during the reaction. One C-H stretch becomes the symmetric C---H---C stretch in the transition state. One CH<sub>3</sub> hindered internal rotation at 105 cm<sup>-1</sup> would change its moment of inertia substantially when the reactant CH<sub>3</sub> radical attaches to one hydrogen. One of the acetone overall rotations would change to an overall rotation of the TS The other two overall rotations in the TS would arise from relative translational motions of the two reactants Two other acetone rotations would become two C---H---C bends

$\omega_{b1}, \omega_{b2} (cm^{-1})$	2969 0, 105 0
$I_{x}I_{y}I_{zA}$ (g <sup>3</sup> Å <sup>6</sup> mol <sup>-3</sup> )	2 04×10 <sup>5</sup>
$I_x I_y I_{zCH3}$ (g <sup>3</sup> Å <sup>6</sup> mol <sup>-3</sup> )	12 46
$I_x I_y I_{zTS}$ (g <sup>3</sup> Å <sup>6</sup> mol <sup>-3</sup> )	2 28×10 <sup>6</sup>
$I_{\mathbb{R}}$ (g Å <sup>2</sup> mol <sup>-1</sup> )	3 21

In summary, in the TS we should consider eight new degrees of freedom, consisting of motion along the reaction path, a free internal rotation, one symmetric stretch, a hindered internal rotation in the acetonyl group, two C---H---C bends and two CH<sub>3</sub> rocking motions The six vibrational term values (including the hindered internal rotation) were averaged to give  $\omega_b$  In this case the vibrational partition function of the transition state was given by

$$\mathbf{q}_{\mathbf{v},\mathrm{TS}} = [1 - \exp(-\mathrm{hc}\omega_{\mathrm{b}}/\mathrm{k_{\mathrm{B}}}\mathrm{T})]^{-6}$$
(122)

Assuming only two frequencies in acetone were changed, the reactant vibrational partition function was given by

$$q_{v,A} = [1/(1 - \exp(-hc\omega_{b1}/k_BT))] \times [1/(1 - \exp(-hc\omega_{b2}/k_BT))]$$
(123)

For the reduced moment of inertia for the internal rotation of the three hydrogen atoms on the methyl radical about the C-H-C axis combined with the rotation of the CH<sub>2</sub>COCH<sub>3</sub> group about the same axis, the mom\_nts of inertia, I<sub>1</sub> and I<sub>2</sub>, of the rotating fragments were used to calculate the reduced moment of inertia by the Pitzer method <sup>48</sup> The bond lengths and angles for acetone<sup>74</sup> were C-H 1 103 Å, C-C 1 52 Å, C=O 1 213 Å, C-C-C 116 0, H-C-H 108 5 For CH<sub>3</sub> the bond length was 1 079 Å and the geometry was planar

A summary of the parameters used as input to the TST calculations is given in Table 6-4

The experimental data for  $k_3$  from Fable 5-74 were combined with data at lower temperatures from the literature in Figure 6-3 The results of photolysis experiments in the temperature range 400-550 K reported by different groups are mostly similar. See Table 1-1, so only three such studies have been included Between 550 and 750 K, only the data from the most detailed study<sup>8</sup> have been included We have not included the results from reference 20 which measured the rate constant for reaction (3) relative to that for other hydrogen or deuterium atom abstractions, since such studies assumed the reference reactions had linear Arrhenius plots, something which now seems unlikely At low temperature, data from references 14 and 16 were included in the fitting

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**Figure 6-3.** Overall temperature dependence of  $k_3$ ,  $\blacksquare$ , this work,  $\forall$  reference 25, x reference 22,  $\Delta$  reference 15,  $\bullet$ , reference 14,  $\Box$  reference 16,  $\nabla$ , reference 8, —, nonlinear least-squares fit of equation (74) to the experimental data.

The three parameters  $V_{b,}$ , T<sup>\*</sup>, and  $\omega_{b}$ , in equation (74) were fitted to the experimental data by nonlinear least squares The three parameters were found to be equal to 46 0 ± 1 0 kJ mol<sup>-1</sup>, 375 ± 17 K, and 279 ± 8 cm<sup>-1</sup>, respectively

These results could be compared with those for reaction of CH<sub>3</sub> with H<sub>2</sub>, 61 0 ± 1 5 kJ mol<sup>-1</sup>, 460 ± 41 K, and 772 ± 37  $\pm$  1<sup>1</sup>, reaction of NH<sub>2</sub> with H<sub>2</sub>, 60 kJ mol<sup>-1</sup>, 406 K and 975 cm<sup>-1</sup>, reaction of CH<sub>3</sub> with HCl, 7 6 ± 0 8 kJ mol<sup>-1</sup>, 111 ± 60 K and 789 ± 71 cm<sup>-1</sup> in reference 90, with those for reaction of CH<sub>4</sub> with H, 63 ± 1 kJ mol<sup>-1</sup>, 500 ± 30 K and 640 ± 30 cm<sup>-1</sup> in reference 91 and with those of reaction NH<sub>3</sub> with OH, 8 5 ± 0 5 kJ mol<sup>-1</sup>, 130 ± 32 K and 660 ± 20 cm<sup>-1</sup> in reference 92, respectively

The average term value in the transition state for reaction (3) is expected to be lower than those for the reactions quoted in the previous paragraph, because of the heavier  $CH_3COCH_2$  replacing a hydrogen atom and because of the contribution of a hindered internal rotation in the TS for reaction (3) The characteristic tunneling temperatures are in agreement within their estimated uncertainties, except for reactions of  $CH_3$  with HCl and NH<sub>3</sub> with OH

#### 6-10. Summary

In the first part of this thesis the pyrolysis of acetone was studied during its induction period over the temperature range 825 to 940 K. Gas chromatography and infrared spectroscopy were used to identify and measure the products The main products were methane and ketene and the minor products were hydrogen, carbon monoxide, ethylene, ethane, propylene, propane, butane, butanone and 2,5-hexanedione. The rate constant for reaction (1) in the present temperature range was calculated for the first time. In the present study the temperature range for the hydrogen abstraction by a methyl radical from an acetone molecule, reaction (3), was extended Combining the present data with the data in the literature, it has been shown that the Arrhenius plot for reaction (3) is curved. The Arrhenius parameters for the decomposition of the acetonyl radical, reaction (4), were calculated for the first time. Theoretical RRKM calculations on reaction (4) have been carried out. For the first time a value for the rate constant for the cross-combination reaction of methyl and acetonyl radicals has been introduced Also for the first time a value in this temperature range for the rate constant for the recombination reaction of acetonyl radicals, reaction (7), has been calculated.

Part two

Reaction of hydrogen atoms with ethane

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# 7. Introduction

The reaction of hydrogen atoms with ethane, reaction (2.1), has been studied since the 1940s.

$$H + C_2 H_6 \rightarrow H_2 + C_2 H_5 \tag{2.1}$$

Previous works normally investigated either the consumption of a reactant, hydrogen atoms or ethane, or the formation of products. In this system it is possible for hydrogen atoms to react with ethane and also with other species which are produced. Therefore, to find the rate constant for reaction (2.1), it is necessary to evaluate the stoichiometric number n, the number of hydrogen atoms used per ethane molecule reacted. For this reason this reaction should be studied by simultaneously monitoring the consumption of one of the reactants, hydrogen atoms, and the formation of different products; this is the intention of the present study. This system could also be used to investigate the relatively unknown branching ratio for the reactions of hydrogen atoms with ethyl radicals to produce ethylene or methyl radicals We will study this reaction in a flow system.

In 1948 Trost and Steacie<sup>94</sup> studied abstraction of a hydrogen atom from an ethane molecule, reaction (2 1), by a hydrogen atom. They produced hydrogen atoms by a microwave discharge and measured their concentration by means of two Wrede gauges, one in the entrance and one at the exit of the vessel. The products were identified quantitatively by combustion analysis of the individual fractions. They were able to identify methane as the product and reported an activation energy of 28 ° kJ mol<sup>-1</sup> for reaction (2.1).

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In 1953 Berlie and Le Roy<sup>95</sup> reported their results on this reaction in a flow system over the temperature range 353 to 436 K They measured the hydrogen concentration by using a platinum or tungsten detector on which hydrogen atoms recombined with the liberation of a measurable quantity of heat per unit time They were able to detect only methane as a product of the reaction They followed the changes in the concentrations of the hydrogen and ethane during the reaction and reported a rate constant for reaction (2 1) as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{9.53} \exp(-28.4 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.2)

They also reported that the stoichiometric number, n, was equal to 4

In 1969 Azatyan and Filippov<sup>96</sup> studied reaction (2 1) They produced hydrogen atoms by discharge and used ESR to determine the rate constant for reaction (2 1) over the temperature range of 290 to 579 K The Arrhenius expression reported for reaction (2 1) was

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{1105} \exp(-389 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.3)

They also reported a stoichiometric number of 4

In 1962 Gorban and Nalbandyan<sup>97</sup> studied reaction (2 1) in a mixture of  $H_2$  and  $O_2$ in the presence of 0 6% of ethane in the temperature range 670 to 820 K They reported Arrhenius parameters for reaction (2 1) as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{1153} \exp(-510 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.4)

They did not discuss the stoichiometric number n

In 1963 Fenimore and Jones<sup>98</sup> in a study of the decomposition of ethylene and ethane in a flame, reported Arrhenius parameters for this reaction as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{1114} \exp(-406 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.5)

In 1964 Baldwin and Melvin<sup>99</sup> combined the data from different studies and reported an expression for the rate constant of reaction (2.1) as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{1112} \exp(-406 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.6)

Clark and Dove<sup>100</sup> noted the possibility of a non-linear Arrhenius plot for reaction (2 1) and calculated the rate constant for this reaction by means of the BEBO and transition state theory methods in the temperature range 300 to 1800 K They predicted the rate constant for reaction (2 1) to be

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{-0.27} \text{ T}^{3.5} \exp(-21.74 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.7)

In 1974 Camilleri, Marshall and Purnell<sup>101</sup> studied the reaction of H atoms with ethane in detail in a flow-discharge system in the temperature range 503 to 753 K and pressure range 8 to 16 Torr They suggested the following mechanism for the reaction of hydrogen atoms with ethane

$$H + C_2 H_6 \rightarrow H_2 + C_2 H_5 \tag{21}$$

$$H + C_2 H_5 \rightarrow 2 C H_3 \tag{28}$$

$$C_{2}H_{5} + H \rightarrow H_{2} + C_{2}H_{4}$$

$$(2 9)$$

$$H + CH_{3} + M \rightarrow CH_{4} + M$$

$$(2 10)$$

$$C_2H_5 + CH_3 \rightarrow C_3H_8 \tag{211}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2.12}$$

$$H + C_2 H_4 \rightarrow C_2 H_5 \tag{2 13}$$

$$2C_2H_5 \rightarrow C_4H_{10} \tag{214}$$

$$2C_{2}H_{5} \rightarrow C_{2}H_{4} + C_{2}H_{6}$$

$$(2 15)$$

$$C_{2}H_{5} \rightarrow H + C_{2}H_{4}$$

$$(2 16)$$

$$H + Wall \rightarrow 1/2 H_2$$
 (2 17)

They used a gas chromatograph to detect methane, ethylene, propane, and butane as products To monitor the hydrogen atom concentration they applied the ethylene titration method. They suggested the stoichiometric number is 4 at room temperature and approaches 2.8 at temperatures higher than 430 K. They indicated that the Arrhenius plot for reaction (2.1) is linear and reported their expression as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{1127 \pm 0.13} \exp(-40.9 \pm 1.6 \text{ k! mol}^{-1} / \text{RT})$$
(2.18)

In 1977 Jones, Morgan, and Purnell<sup>10°</sup> studied the reaction of H atoms with ethane over the temperature range 357-544 K at a constant pressure of 4 Torr using a flowdischarge system linked to a mass spectrometer. They confirmed the mechanism proposed by Camilleri *et al*<sup>101</sup> They reported Arrhenius parameters for reaction (2 1) as follows  $k_{21}$  (L mol<sup>-1</sup>s<sup>-1</sup>) = 10<sup>11 03±0 27</sup> exp (-38 6±2 6 kJ mol<sup>-1</sup> / RT) (2 19)

They also considered the stoichiometric number n and suggested it must lie between 2 and 4 and they showed a plot of n versus temperature and suggested a quasi-Arrhenius expression for n as  $\log_{10} (n) = -0.57 + 439/T$  They suggested that  $k_{21}$  is linear over a wide range of temperature

.4

In 1978 Lede and Villermaux<sup>103</sup> studied reaction (2 1) in the temperature range 281 to 347 K They generated hydrogen atoms by electrical discharge and studied the reaction in tubular and stirred open reactors They measured the absorption of Hg atoms released in the reaction of H with HgO to determine the concentration of hydrogen atoms They reported a stoichiometric number of four They determined the Arrhenius parameters for reaction (2 1) as  $\log_{10} (A/L \text{ mol}^{-1}\text{s}^{-1})=107\pm06$  and  $E_A=380\pm25$  kJ mol<sup>-1</sup>

7. 31

In 1986 Cao and Back<sup>104</sup> studied reaction (2 1) in the temperature region of 876 to 1016 K In that study they looked at the rate of conversion of ethane to ethylene in the presence of hydrogen and suggested the reaction proceeds by a mechanism such as

$$H_2 \rightarrow 2 H \tag{2.20}$$

$$H + C_2 H_6 \rightarrow H_2 + C_2 H_5 \tag{21}$$

$$H + C_2 H_5 \rightarrow C_2 H_6 \tag{2.21}$$

$$C_2H_5 \rightarrow H + C_2H_4 \tag{2.16}$$

$$C_2H_5 + H_2 \rightarrow H + C_2H_6 \tag{2.22}$$

They predicted a value of  $5.0 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> for reaction (2.21) according to collision theory and also reported an Arrhenius expression for the rate constant of reaction (2.1) as  $k_{2.1}$  (L mol<sup>-1</sup>s<sup>-1</sup>) =  $10^{11.72}$  exp (-53.5 kJ mol<sup>-1</sup> / RT) (2.23)

They reported a curved Arrhenius plot for  $k_{21}$ 

In 1992 Baulch *et al*<sup>105</sup> in an extensive literature review concluded reaction (2 1) has a curved Arrhenius plot and suggested an expression for  $k_{21}$  as

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{6.16} \text{ T}^{1.5} \exp(-31.01 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.24)

# 7-1. Other important reactions in this system

# 7-1-1. Reaction of hydrogen atoms with ethyl radicals

This reaction is important in the combustion of hydrocarbons Different products might be expected from this reaction, depending on the condition of the reaction. One might suggest three possible paths for the reaction of H atoms with ethyl radicals,

$$H + C_2 H_5 \rightarrow 2 C H_3 \tag{28}$$

$$H + C_2 H_5 \rightarrow H_2 + C_2 H_4 \tag{29}$$

$$H + C_2H_5 + M \rightarrow C_2H_6 + M \tag{2.21}$$
It is expected that reactions (2.8) and (2.9) are more important than reaction (2.21), especially at low pressures. In the present study reaction (2.21) was treated as a third body reaction Reaction (2.9) is one of the simplest organic disproportionation reactions

In 1970 Halstead, Leathard, Marshall and Purnell<sup>106</sup> studied reaction (2.8) following the reaction of H atoms with ethylene over the pressure range 8 to 16 Torr at 290 K in a flow-discharge system They reported methane and ethane as the major products and propane and n-butane as the minor products They concluded that the main source of the ethane was methy! recombination and that the rate of recombination of a hydrogen atom with an ethyl radical was negligible in comparison with the cracking reaction which produces two methyl radicals They estimated that the ratio of  $k_{221} / k_{28}$  was two times the ratio  $[C_2H_6] / [CH_4]$  at  $[C_2H_4] = 0$  and in this way they concluded  $k_{221}/k_{28}$  should be equal to  $0.04\pm0.02$  They did not include reaction (2.9) in their proposed mechanism In that study they reported a value for the rate constant for reaction (2.8) equal to  $5 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup>.

In 1972 Teng and Jones<sup>107</sup> in a study of the reaction of H atoms with ethylene and vinyl fluoride in a flow-discharge system over the temperature range 303 to 603 K at 1 2 Torr reported an expression for  $k_{2.8}$  as

$$k_{28} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{1103} \exp(-3.64 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.25)

In 1974 Camilleri, Marshall and Purnell<sup>101</sup> reported a value for  $k_{2\,8}$  as 3 72×10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup>

Pratt and Veltman<sup>108</sup> in 1976 studied the reaction of H atoms with ethyl radicals following the reaction of hydrogen atoms with ethylene over the temperature range 321 to 521 K at 8 Torr They used a mass spectrometer to analyze the products They reported an expression for  $k_{2.8}$  as

$$k_{28} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{1081} \exp(-0.93 \text{ kJ mol}^{-1}/\text{ RT})$$
 (2.26)

In 1984 Pratt and Wood<sup>109</sup> studied the reaction of methyl radicals with oxygen over the temperature range 230 to 568 K and the pressure range 2 to 10 Torr In that study they produced methyl radicals by means of the reaction of hydrogen atoms with ethylene They used a gas chromatograph to measure the products and reported Arrhenius parameters for reaction (2 8) as

$$k_{28} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{10.68} \exp(-1.06 \text{ kJ mol}^{-1} / \text{ RT})$$
 (2.27)

In 1992 Baulch *et al*<sup>105</sup> in an extensive literature review recommended a value of  $3.61 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> for reaction (2.8) over the temperature range 300 to 2000 K

It was one of the purposes of the present study to investigate the rate constants for reactions (2 8) and (2 9)

### 7-1-2. Reaction of H atoms with ethylene

The reaction of H atoms with ethylene, reaction  $(2 \ 13)$ , has been studied more often than reaction  $(2 \ 1)$  It was not the intention of this study to find a rate constant for reaction  $(2 \ 13)$ , therefore a value from the literature was selected for this rate constant to calculate the other rate constants in this system

In 1970 Halstead, Leathard, Marshall and Purnell<sup>106</sup> studied the reaction of hydrogen atoms with ethylene from 8 to 16 Torr at 290 K They reported a value for  $k_{2,13}$ 

as  $1.17 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> They used Ar as bath gas They reported that the ratio of  $[C_3H_8] / ([C_2H_6] [C_4H_{10}])^2$  was constant with an average value of 2 05±0 50

Barker, Keil, Michael and Osborne<sup>110</sup> in 1970 compared three different experimental techniques to study reaction (2 13) and reported a value of 2  $33 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> for k<sub>2 13</sub> at room temperature and in the pressure range 0 4 to 5 1 Torr in He bath gas

In 1973 Michael, Osborne and Suess<sup>111</sup> studied the effects of pressure and the nature of the bath gas on the reaction of the hydrogen atoms with ethylene They followed the concentration of hydrogen atoms by Lyman  $\alpha$  photometry They reported the high-pressure value of  $k_{2 13}$  as 9 70×10<sup>8</sup> L mol<sup>-1</sup>s<sup>-1</sup>

In 1987 Lightfoot and Pilling<sup>112</sup> studied the temperature and pressure dependence of  $k_{2\,13}$  over the temperature range of 285 to 604 K and a pressure range of 50 to 600 Torr in He as bath gas They reported low- and high-pressure expressions for  $k_{2\,13}$  The low-pressure Arrhenius expression for reaction (2 13) was

$$k_{2 13,0} (L^2 \text{ mol}^{-2} \text{ s}^{-1}) = 10^{12 70} \exp(-4.67 \text{ kJ mol}^{-1} / \text{RT})$$
 (2.28)

and the high-pressure expression for k<sub>2 13</sub> was

$$k_{2\,13,\infty} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{10\,42} \exp \left(-9.04 \text{ kJ mol}^{-1} / \text{ RT}\right)$$
(2.29)

In the present study the termolecular expression for  $k_{2\,13}$  reported by Lightfoot and Pilling was used

# 7-1-3. Reactions involving methyl and ethyl radicals

There are two possible paths for the reaction of a methyl radical with an ethyl radical, reaction (2 11) and also reaction (2 30)

$$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4 \tag{2.30}$$

In this study the rate constant for reaction (2.11) was calculated from the cross combination relationship

$$k_{211} = 2 \left( k_{212} k_{214} \right)^{1/2}$$
(2.31)

Here,  $k_{2\,12}$  is the rate constant for methyl radical recombination and has been discussed in part I. A value for  $k_{2\,14}$ , the rate constant for ethyl radical recombination, was chosen as  $9.75 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>, as reported by Dobis and Benson<sup>113</sup>

Anastasi and Arthur<sup>114</sup> suggested that the rate constant for reaction  $(2 \ 30)$  is 4% of that for reaction  $(2 \ 11)$ 

Another possible reaction involving ethyl radicals is the disproportionation reaction

$$2 C_2 H_5 \rightarrow C_2 H_6 + C_2 H_4 \tag{2.32}$$

Kutschke, Wijnen and Steacie suggested<sup>115</sup> the rate constant for reaction (2 32) should be 14% of that for the etixel radical recombination reaction

# 7-1-4. Reaction of a methyl radical with an ethane molecule

This reaction was also slow relative to other reactions

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{2.33}$$

Baulch *et al*<sup>105</sup> in a literature review suggested an expression,  $k_{2,33}=1.51\times10^{-10}$  (L mol<sup>-1</sup>s<sup>-1</sup>) T<sup>6</sup> exp (-25 30 kJ mol<sup>-1</sup> / RT), for the rate constant for this reaction This expression is used in this study

# 7-1-5. Reaction of hydrogen atoms with propane

This reaction is a hydrogen abstraction from a propane molecule by a hydrogen atom and is not expected to be pressure dependent

$$H + C_3 H_8 \rightarrow H_2 + C_3 H_7 \tag{2.34}$$

Marshall, Purnell and Sheppard<sup>116</sup>, in a study of reaction of H atoms with propane in the temperature range of 298 to 534 K at 5 Torr, reported an Arrhenius expression for this reaction as

$$k_{2.32} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{10.81} \exp(-28.8 \text{ kJ mol}^{-1}/\text{ RT})$$
 (2.35)

Because of the low concentration of propane in this study, this reaction did not play an important role. The above Arrhenius expression was chosen to be used in this study

### 7-1-6. H atom recombination

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This reaction was important in removing hydrogen atoms especially at lower temperatures and was able to compete with reactions (2 1), (2.8), (2.9), (2 10), and (2.17).

$$H + H + M \rightarrow H_2 + M \tag{2.36}$$

Here M is the bath gas. Baulch *et al* in an extensive literature review<sup>117</sup> suggested an expression for this reaction over the temperature range 100 to 5000 K at low pressure with H<sub>2</sub> as bath gas as  $k_{2.34}$  (L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>) =  $10^{10.99}$  T<sup>-0.6</sup>. In that review, it was possible to find that H<sub>2</sub> is more efficient as bath gas than He by a factor of almost 1.4. In this study the expression given by Baulch *et al* was divided by 1.4 to correct for the bath gas effect.

## 7-1-7. Wall reaction, reaction (2.17)

This reaction also was important in consuming hydrogen atoms in the system, especially at higher temperatures. To decrease this rate constant the reactor wall was covered by phosphoric acid. A value for this rate constant at different conditions was calculated from the present results and is shown in the Result section From this point on the rate constant for the wall reaction will be shown as  $k_w$ .

## 7-2. Objective of the present study

The present study on reaction (2.1) is the first to monitor the consumption of the reactant, hydrogen atoms, and the formation of the products as a function of time in a flow system. In this way it is expected that more accurate results would be obtained in the calculation of the stoichiometric number for hydrogen atoms. It has been suggested by some workers<sup>100</sup> that the Arrhenius plot for reaction (2 1) should be curved It was also the objective of the present study to investigate the Arrhenius parameters for reaction (21) at temperatures lower than 500 K It was intended to calculate the branching ratio,  $k_{29}/(k_{29}+k_{28})$ , experimentally There is only one study which has discussed this ratio in the literature.<sup>101</sup> Investigation of this ratio would provide a better understanding of energy transfer in the reaction of hydrogen atoms with ethyl radicals. In the present study we also seek an experimental ratio for  $k_{28}/k_{210}$  A value for  $k_{210}$  from the literature is used to calculate  $k_{28}$  Computer simulation is a useful tool to find values of  $k_{28}$  and  $k_{29}$  It was intended to compare the value of the branching ratio calculated directly from experimental results with the value of this ratio calculated from rate constants used in optimizing the computer simulation

# 8. Derivation of expressions for the rate constants

In this chapter the equations used for the calculation of the initial hydrogen atom concentrations and also for the calculation of  $k_w$  and  $nk_{2.1}$  will be discussed. A derivation to obtain the branching ratio  $k_{2.8}/(k_{2.9}+k_{2.8})$  at room temperature will be shown. In the last section of this chapter the computer simulation will be discussed.

# 8-1. Wall reaction rate constant, k<sub>w</sub>

In the absence of ethane there were two sources for hydrogen atom consumption, reactions (2.17) and (2.36). Reaction (2.17) is a unimoleular reaction while reaction (2.35) is a termolecular reaction. Yerrick and Russell<sup>118</sup> have derived an equation for a system in which a reactant disappears by first- and second-order reactions simultaneously, as hydrogen atoms disappear by reactions (2.17) and (2.36).

$$\frac{[H_0](k_w + 2k_{2.36}[M][H])}{[H](k_w + 2k_{2.36}[M][H_0])} = \exp(k_w t)$$
(2.37)

Here  $[H_0]$  is the initial hydrogen atom concentration and [H] is the hydrogen atom concentration at time t, [M] is the total concentration and  $k_w$  is the rate constant for the wall reaction, reaction (2.17). It is possible to rearrange equation (2.37) for [H] as follows

$$[H] = \frac{k_{w}}{\frac{\exp(k_{w}t)(k_{w}+2k_{2.36}[M][H_{0}])}{[H_{0}]} - 2k_{2.36}[M]}$$
(2.38)

Equation (2.38) was fitted to the experimental data obtained in the absence of ethane to calculate the  $[H_0]$  and  $k_w$  at different pressures and temperatures. A value from

the literature, discussed in Section 7-1-6, was chosen for  $k_{236}$  To calculate  $nk_{21}$  in the presence of ethane,  $k_w$  in equation (2 38) was replaced by  $k_w + nk_{21}[C_2H_6]$  and the equation was fitted to the experimental data to find  $nk_{21}$ 

## 8-2. Branching ratio for reactions (2.8) and (2.10)

Methane is the only measurable product at room temperature The rate of formation of methane could be calculated as

$$\mathbf{R}_{m} = \mathbf{k}_{2 \ 10} [\mathbf{H}] [\mathbf{M}] [\mathbf{CH}_{3}]$$
(2 39)

Making the steady state approximation and considering only reactions 2 1, 2 8, 2 9 and 2 10, it was possible to calculate the concentration of methyl radicals as

$$[CH_3] = \frac{2k_{28}[C_2H_5]}{k_{210}[M]}$$
(2 40)

Using the steady state approximation, the concentration of ethyl radicals could be written as follows

$$[C_2H_5] = \frac{k_{21}[C_2H_6]}{k_{28}+k_{29}}$$
(2.41)

Substitution of the  $[CH_3]$  concentration from equation (2 40) and the  $[C_2H_5]$  concentration from equation (2 41) into equation (2 39) gives the rate of formation of methane as a function of ethane and hydrogen concentration

$$\frac{d[CH_4]}{dt} = \frac{2k_{21}k_{28}}{k_{28}+k_{29}}[C_2H_6][H]$$
(2.42)

To calculate the concentration of methane in a particular reaction time t it was possible to integrate equation (2 42) over time, taking [H] from equation (2 38)

$$[CH_4] = \frac{2k_{21}k_{28}}{k_{28}+k_{29}} [C_2H_6]k_w Z$$
(2.43)

Here  $k_w$  is the rate constant for the wall reaction and Z is

$$Z = -\frac{t}{2k_{236}[M]} + \frac{\ln\left(\frac{(k_{w} + 2k_{236}[M][H_{0}])\exp(k_{w}t)}{k_{21}[H_{0}]} - \frac{2k_{236}[M]}{k_{21}}\right)}{2k_{236}[M]k_{w}}$$
(2 44)  
$$-\left(\frac{\ln\left(\frac{(k_{w} + 2k_{236}[M][H_{0}])}{k_{21}[H_{0}]} - \frac{2k_{236}[M]}{k_{21}}\right)}{2k_{236}[M]k_{w}}\right)$$

Equation (2 43) could be useful to determine the branching ratio for  $k_{28}$  and  $k_{29}$ 

### 8-3. Computer simulation

The proposed mechanism for the reaction of H atoms with ethane consisted of several steps At room temperature only reactions (2 1), (2 8), (2 10), (2 17) and (2 36) were important, but as temperature increased the other reactions also became important One possible approach to determine the rate constants at any condition is the simulation of the reactions on a computer A program was written for such a simulation and is given in the Appendix In this program all possible reactions were included and the rate constants of all reactions except reactions (2 1), (2 8), (2 9) and (2 17) were assumed to be relatively well known and were taken directly from the literature. The program was designed to be able to estimate the rate constants for the above reactions by trial and error and by comparing the calculated concentrations with the measured concentrations of these species at different conditions. To calculate the stoichiometric number n in the simulation program the ratio of the hydrogen atoms consumed by different reactions, reaction (2 1), (2 8), (2 9), (2 10) and (2 13), ( except wall reaction and gas phase H recombination) to

the hydrogen atoms consumed by reaction (2 1) alone,  $\Phi_{21}$ , was calculated The flow chart of the program is shown in Figure 8-1 Euler's rule was used in the program for the integration To perform the integration the reaction time was divided into small time steps,  $t_s$  In the flow chart  $t_f$  stands for the final time or the reaction time In the program it was found that a time step equal to  $5 \ 0 \times 10^{-6}$  s was a proper value A value smaller than  $5 \ 0 \times 10^{-6}$  s increased the computer time without any effect on the results

# 8-3-1. Reactions included in the computer simulation

The following reactions and rate constants were included in the program

The rate constants for reaction (2 1) calculated directly from the experiments at different conditions in the present study were used in the computer simulation. Values of  $nk_{21}$  were estimated by fitting equation 2 38 to the experimental data. To calculate  $k_{21}$  the estimated values of  $nk_{21}$  at different conditions were divided by the corresponding values of n. Values of n from experiment and values of n calculated by the computer simulation were combined to find an optimum value of n at each condition. Reactions (2 8) and (2 9) were included in the simulation and it was one of the goals of this study to measure the rate constants for these reactions. The temperature dependence reported by Cobos and Troe<sup>119</sup> for reaction (2 10) was used to calculate the rate constant for this reaction at different conditions.

$$k_{2 10} (L^2 \text{ mol}^{-2} \text{s}^{-1}) = 3.09 \times 10^{18} (\text{T})^{-1.8}$$
(2.45)





The rate constant for the methyl radical recombination reaction was calculated from the expression reported by Wagner and Wardlaw <sup>34</sup> To correct for the fall-off behavior this rate constant was divided by 1 3.<sup>120</sup> A v-lue reported by Dobis and Benson<sup>113</sup>, 9 75×10<sup>9</sup> L mol<sup>-1</sup>s<sup>-1</sup>, was used for the rate constant of the ethyl radical recombination

To calculate the rate constant for reaction (2 11) the cross combination relation,  $k_{2 11} = m (k_{2 12} \times k_{2 14})^{1/2}$ , was used

Reaction (2 13) removed ethylene and also increased the value of n The expression reported by Lightfoot and Pilling<sup>112</sup> was used to calculate the rate constant for this reaction To correct for the fall-off behavior the rate constant was divided by 2 3

The Arrhenius expression reported by Marshall, Purnell and Sheppard<sup>116</sup>, equation (2 35), was chosen to calculate the rate constant for reaction (2 34) at different temperatures

Another minor reaction included in the program was the disproportionation reaction of two ethyl radicals to produce ethylene and ethane, reaction (2 31) It has been proposed by Kutschke and coworkers<sup>115</sup> that the rate constant for this reaction is about 14% of  $k_{2.14}$ 

Reaction (2 33) was included in the simulation program and the expression reported by Baulch *et al*<sup>105</sup> was chosen for the rate constant of this reaction

It has been suggested by Anastasi and Arthur<sup>114</sup> that a methyl radical is able to abstract a hydrogen atom from an ethyl radical to produce methane and ethylene, reaction (2 30) They suggested the rate constant for this reaction should be about 4% of the rate constant for reaction (2 11)

Another reaction included in the mechanism was the termolecular reaction of hydrogen atoms with ethyl radical to produce ethane, reaction (2.21) According to Halstoad, Leathard, Marshall and Purnell<sup>104</sup> the rate of this reaction was about 4% of reaction (2.8) In the present study this reaction was treated as third order

The hydrogen atom recombination reaction, reaction (2 36) was included in the simulation program. The expression recommended by Baulch *et al*<sup>117</sup> tor H<sub>2</sub> bath gas was used to calculate the rate constant for this reaction. To correct the expression for He bath gas the expression was divided by 1.4. This ratio could be concluded from the comparison of the reported data for the two different bath gases in that review.

The last reaction included was the wall reaction, reaction (2 17) The values of  $k_w$  measured in the present study, as discussed in Section 8-1, were used in the calculations

#### 9. Experimental

In this chapter the concept of electron spin spectroscopy will be discussed. The electron spin spectrum of hydrogen atoms will be presented. Also in this chapter the flow system and the procedure used to carry out the experiments on the reaction of hydrogen atoms with ethane will be presented. At the end of the chapter, the method used to calculate the absolute hydrogen atom concentration will be discussed.

### 9-1. Electron spin resonance (ESR) spectroscopy

A static magnetic field is able to interact with the unpaired electron spin moment and split the energy levels (Zeeman effect) in molecules, radicals and ions which have unpaired electrons. A transition between these states occurs by applying a microwave frequency. The Zeeman Hamiltonian for the interaction of the magnetic field with an electron is given by<sup>121</sup>

$$H = g \beta_m B S_z \tag{2.46}$$

Here g is called the g factor which, for an electron, is equal to 2.0023193,  $\beta_m$  is the Bohr magneton,  $eh/4\pi m_e$ , which is equal to  $9.27402 \times 10^{-24}$  J tesla<sup>-1</sup>, B is the applied magnetic field strength, and  $S_z$  is the spin operator. In this way the transition energy is given by

$$\Delta \mathbf{E} = \mathbf{g} \,\beta_{\mathrm{m}} \mathbf{B} \tag{2.47}$$

In practice it is generally easier to work at a fixed microwave frequency and a changing magnetic field.

#### 9-2. ESR spectrometer

In this experiment an X-band spectrometer, Varian E-106, was used. In this kind of spectrometer the microwave frequency is about 9.5 GHz, and a magnetic field strength of 3400 Gauss is applied for the spectrum of the H atom. The microwave source in an ESR spectrometer is usually a klystron which is a vacuum tube well known for its lownoise characteristics. The output of a klystron is a function of frequency and may be monitored on an oscilloscope. A waveguide, which normally is a brass pipe, could be used to transmit microwave frequency to and from the klystron. A cavity called the resonator holds the sample and is connected to the klystron via the waveguide. To have a good resonance in the cavity holding the sample there is an attenuator to adjust the level of the microwave power reaching the sample and a circulator which is a device to direct the microwave power to the cavity and simultaneously to direct the power reflected from the cavity to the detector.

The frequency characteristics of the resonator can be shown on an oscilloscope by sweeping the voltage on the klystron. The microwave energy is coupled into the cavity through an adjustable iris hole which could be varied by the iris screw.

A phase-sensitive detector is used in the ESR spectrometer. To improve the sensitivity of the spectrometer it is possible to modulate the magnetic field at 100 kHz. The advantages of this modulation are (a) the amplification of the ESR signal, (b) elimination of most of the noise-contributing components, and (c) the increased resolution of the spectrum. The signal from the resonator is transmitted to the detector by the same waveguide which brings the frequency from the klystron to the resonator. The circulator is able to separate the incident wave from the exit wave and send the exit wave from the resonator to the detector. The detector in an ESR spectrometer usually is a silicon crystal in contact with a tungsten wire.

corresponds to an average incident microwave power level of about 1 mW. The detector current varies as the square root of the power. Saturation occurs when the rates of upward and of downward transitions are equalized; then no net energy is transferred between the excitation source and the spin system. If the sample is saturated, the output signal of the detector is no longer proportional to the square root of the power, and one must use the attenuator to reduce the power received from the klystron by the resonator to remove the saturation. When saturation occurs, the area under the absorption curve is no longer a valid measure of spin concentration in the sample. A silicon crystal detector produces an inherent noise that is inversely proportional to the frequency of the detected signal. The reason for the use of 100 kHz magnetic field modulation frequency is because at this modulation frequency the detector noise is less than that from other causes. The output signal of the detector appears approximately as the first derivative (the slope) of the absorption signal when plotted against the strength of the magnetic field.

#### 9-3. Hydrogen spectrum

The ESR spectrum of the hydrogen atom, which consists of only one electron and one proton, is one of the simplest spectra. The spin energy level in a hydrogen atom splits to two energy levels with  $m_s -1/2$  and +1/2 in a static magnetic field. The nuclear moment in the hydrogen atom also interacts with the external magnetic field and its degeneracy is removed to split into two energy levels with  $m_I + 1/2$  and -1/2. The lower state of the nuclear moment is  $m_I = +1/2$  which is of opposite sign to and also smaller in magnitude than the lower electronic spin energy level ( $m_s = -1/2$ ). The interaction of nuclear and electron spin states creates four energy levels which are shown in Figure 9-1. The usual

selection rules in ESR are  $\Delta m_I = 0$  and  $\Delta m_S = \pm 1$ , which produces two absorption lines in the ESR spectrum of the hydrogen atom. The approximate field position B(v) of the two hydrogen lines could be calculated from the following equations.<sup>122</sup>

$$B(v)_1 \approx (0.3568 v + 275) \times 10^{-4} \text{ tesla}$$
 (2.48)

$$B(v)_2 \approx (0.3568 v - 275) \times 10^{-4}$$
 tesla (2.49)

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Here v is the frequency in MHz. Figure 9-2 shows the spectrum of the hydrogen atom. In the present study the hydrogen atom line at the lower magnetic field, equation (2.49), was used to measure the hydrogen atom concentration in the system.



Figure 9-1. Energy diagram of a hydrogen atom in a magnetic field



Figure 9-2. ESR hydrogen atom spectrum

#### 9-4. Experimental

This study is carried out in a flow system. Hydrogen was mixed with He as bath gas and introduced to a microwave discharge to produce hydrogen atoms. Hydrogen atoms then were mixed with ethane in the reactor. It was possible to study the reaction at different reaction times. The concentration of hydrogen atoms was measured at the end of the reactor by ESR and the concentrations of products were measured with a gas chromatograph.

The flow system consisted of four sections, gas supply, main reactor, pressure controller and pumping system, and gas chromatograph.

# 9-4-1. Gas supply

Figure 9-3 shows this section of the flow system. Four 13 L bulbs were filled with gases, two with He gas (Atlantic Oxygen Ltd., 99.996%), one with H<sub>2</sub> gas (Linde, UHP, CH<sub>4</sub>, H<sub>2</sub>O < 10ppm), and the last one with C<sub>2</sub>H<sub>6</sub> gas (Matheson, Research Grade, 99.99%). Volumes of the four bulbs and the tubing between these bulbs are listed in Table 9-1. The pressures in the bulbs were measured using a common pressure transducer (Bell and Howell, model CEC 1000, pressure range 0-50 psi) shown in the Figure. One of the He gases, bulb B in Figure 9-3, was used as a source to produce H atoms; normally there is some hydrogen gas as impurity in He. The H<sub>2</sub> gas, bulb D in Figure 9-3, was used to increase the H<sub>2</sub> concentration in the He. The flow rates of these two gases were controlled by two needle valves (Whitey, catalogue number SS 21RF2). By adjusting each of these needle valves it was possible to control the ratio of H<sub>2</sub> to He.





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Figure 9-3. Gas supply section of the flow system.

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The flow rates of the He bath gas, bulb A in Figure . 3, and the  $C_2H_5$ , bulb C in Figure 9-3, were controlled by two flow controllers (MKS, 11593-00500SV, 500 sccm), which were connected to a 4-channel readout (MKS, 247C). A rotary vacuum pump (Welch Duo-Seal, 1400) and a glass oil diffusion pump were connected to this section of the flow system for evacuation.

**Table 9-1.** Volumes of the four bulbs in Figure 9-3. The values in the parentheses are the volumes of the glass tubing connecting each bulb to the corresponding needle value.

Bulb number	nber volume (L)	
Α	13.18	(0.0345)
В	13.40	(0.0396)
С	13.10	(0.0326)
D	13.31	(0.0304)

### 9-4-2. Main reactor

The main reactors are shown in Figures 9-4 and 9-5. In this study two different reactors were used which are indicated as reactor (a), Figure 9-4, and reactor (b), Figure 9-5.

Reactor (a) consisted of two sections, a moveable quartz injector and the main reactor. The moveable injector was constructed of two sections, a side tube of 18 mm i d. which connected to a one-meter-long tube of 7 mm id. To generate hydrogen atoms a microwave discharge cavity (240 watt, Microtron 200, Electro-Medical Supplies) was mounted around the large diameter section of the injector. The mixture of H<sub>2</sub> and He from the gas supply section was connected to this tube The reactor was 100 cm long and 20 mm i d. The effective cross-section of reactor (a) was  $2.975 \text{ cm}^2$  The He bath gas and the ethane from the gas supply section were connected to this tube. To reduce the surface reaction the interior surface of the injector and reactor were washed with 20% HF, and with distilled water and coated with 85% phosphoric acid (Fisher). To probe the temperature of the reactor a 10-cm-long well was constructed near the outlet of the reactor. Another thermocouple, placed in a 50-cm moveable quartz tube between the furnace and the main reactor, was used to probe the temperature along the reactor from both ends of the reactor. The exit of the reactor was connected to a 40-cm quartz tube, 19 mm i.d., coated with Teflon, prepared previously in this laboratory.<sup>91</sup> The cross-section of the Teflon-coated tube was 2.813 cm<sup>2</sup>. This tube was placed in an ESR cavity (E-235 large-access, cylindrical) part of the Varian E-1096, X-band spectrometer.

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reactor (a)

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G.C. Gas chromwlograph

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Figure 9-4. Main reactor (a)



reactor (b)

Figure 9-5. Main reactor (b)

Using a movable injector in reactor (a) was a source of a problem at higher tomperatures. The wall reaction inside the injector was a function of temperature. In those experiments carried out at temperatures higher than 430 K, the difference between the wall reactions at room and high temperature was significant. In this way as the injector moved inside the reactor, changing from room temperature to the temperature of the reactor, the concentration of hydrogen atoms coming out of the injector decreased because of an increase in the wall reaction inside the injector. For this reason another type of reactor, reactor (b), was designed, as will be explained in the following paragraph. In reactor (b) no moveable part was used.

Reactor (b) was constructed of two sections The main part consisted of a Py.ex manifold connected via five Tef.on valves to five quartz tubes of 3.0 mm i d The lengths of these five tubes were different, 4.5 cm, 53.5 cm, 69.5 cm, 74.5 cm, and 80.5 cm. By choosing different tubes it was possible to change the reaction time or contact time between H atoms and ethane gas. The He bath gas and ethane from the output of the gas supply section were connected to the manifold The main reactor was a one-meter quartz tube, 2.7 cm i.d. with a side arm tube made of 18 mm i d quartz. The output of the mixture of H<sub>2</sub> and He from the gas supply section was connected to this tube. The microwave discharge cavity was mounted around this side arm tube to produce H atoms. The effective cross-section for reactor (b) was different at different positions because of the five quartz tubes inside the reactor. The effective cross-sections from the entrance of reactor (b) weie 2.565, 2.732, 2.775, 2.813 and 2.784 cm<sup>2</sup> The lengths of these crosssections were, 50 5, 16 0, 5 0, 6 0 and 6 0 cm The end of the reactor was connected to the Teflon-coated tube in the ESR cavity

To maintain the temperatures of the reactors, an 80-cm long, 3-cm od copper pipe, wrapped with mullite paper and with nichrome heating ribbon was used A copperconstantan thermocouple was placed in the thermocouple well in the main reactor to monitor the temperature of the reactor The other thermocouple, Chromel-Alumel, Omega Engineering model 199, was placed into the 50-cm quartz tube to observe the temperature profile along the furnace

## 9-4-3. Pumping system and gas chromatograph

A 70-cm Pyrex tube, 25-mm i d, connected the end of the Teflon-coated tube in the ESR cavity to a pressure controller system This system consisted of a 100 Torr pressure transducer (MKS, Baratron type 122A) and an Omega pressure controller (model CN-2000) which controlled an MKS (model 248A/B) controller valve The exit of the controller valve was connected to a rotary pump (Precision, D25) To monitor the reactor pressure another pressure transducer (Bell and Howell, model CEC 1000, pressure range 0-15 psi) was also used

To analyze the reaction mixture a six-way linear gas sampling valve (Varian 57-000034-00) was connected to the end of the 70-cm-long tube A one-meter-long Porapak column, mesh 100-120, was used at  $60^{\circ}$ C to separate the methane, ethylene, ethane and propane and a flame ionization detector was used as detector To measure the butane the column temperature was raised to  $130^{\circ}$ C The pressure in the gas chromatograph inlet was monitored by a pressure transducer (Bell and Howell, model CEC 1000, pressure range 0-15 psi). A rotary pump (Vac Torr, 25) was used to evacuate this section.

### 9-5. Procedure

To carry out an experiment in reactor (a) the following procedure was followed. Before each experiment the whole system was evacuated to decrease the chance of any impurity in the system. All gases were dried using a 40-cm-long tubes, 1 cm i.d., containing silica gel, before introduction to the bulbs. One of the He gas streams was conducted to the injector and passed through the microwave cavity to generate H atoms. The H atom concentration was increased by adding  $H_2$  to the He before the microwave cavity. Normally to have a maximum H atom peak height in the ESR cavity the number of moles of H<sub>2</sub> gas was about 0.2% of that of He gas. Excessive amounts of H<sub>2</sub> caused a decrease in the H atom concentration. The He was introduced to the reactor via one of the MKS mass flow meters. After flow stabilization the concentration of H atoms were measured by the intensity of the ESR spectrum. The injector was pulled out to increase the distance between the end of the injector, where the H atoms were introduced to the reactor, and the ESR cavity. The intensity, H<sub>0</sub>, of the H atom spectrum was recorded and then ethane was introduced to the reactor. To keep the same flow conditions, the flow rate of the He decreased by an amount equal to the ethane flow rate. Because of the reaction between the H atoms and ethane, the intensity, H, of the H atom peak in the ESR decreased and was recorded. To monitor the concentration of hydrocarbon products the gas chromatograph and flame ionization detector were used. The above procedure was carried out at three different pressures at the same position of the injector and then the

injector was allowed to be pulled in towards the ESR cavity by the vacuum and the procedure was repeated until the injector tip reached the end of the furnace

A similar procedure was also followed for reactor two Instead of moving the injector in, the small tubes with different lengths were used to introduce the He bath gas and ethane into the reactor to mix with H atoms at different points along the reactor

During each experiment the intensity of the H atom peak changed because of wall and gas phase reactions. Therefore, it was necessary to use different gain factors to have measurable peaks. The linearity of the gain factor was tested and the results are given in Figure 9-6. The intercept of the plot was found to be  $0.12\pm0.13$  and the slope was found to be  $0.0233\pm0.0003$ 



Figure 9-6. The linearity of the ESR gain factor.

### 9-6. Calculation of flow rate and reaction time

To calculate the reaction time in this study it was necessary to know the total linear flow rate (LFR) of all the gases in the reactor One might calculate the molar flow rate of each gas from the storage bulbs by measuring the pressure drop using equation (82) in Chapter 3 The summation of the molar flow rates for all the gases gives the total molar flow rate  $(\Delta n/\Delta t)_t$  The linear flow rate (LFR) in the reactor could be calculated as follows

$$LFR = \frac{\left(\frac{dn}{dt}\right)_{t} \left(\frac{RT_{r}}{p_{r}}\right)}{S}$$
(2.50)

Here S is the reactor cross-section and  $T_r$  and  $p_r$  are the temperature and pressure of gas in the reactor The unit of LFR is cm s<sup>-1</sup>

To calculate the reaction time in the first reactor the calculated LFR at each condition was divided by the distance between the mixing point of ethane with hydrogen atoms and the end of the reactor In reactor two there are five different cross-sections and therefore the LFR for each part was different To calculate the total reaction time in reactor two the sum of the individual reaction times in each part of the reactor involved was calculated At higher temperatures the concentration of hydrogen atoms at the end of the reactor was less than 10% of the initial hydrogen atom concentration For this reason the contribution of the reaction at room temperature between the end of the reactor and the ESR cavity was negligible At room temperature the reaction time was calculated from the mixing point of the hydrogen atoms and ethane up to the ESR cavity

#### 9-7. Hydrogen atom concentration

The concentration of hydrogen atoms could be determined as an absolute or relative quantity. To find the absolute hydrogen atom concentration, a calibration gas containing a species with unpaired electrons could be used. Oxygen molecules in the air were used to calibrate the absolute H atom concentration.

The ESR spectrum of  $O_2$  is relatively complex. The nuclear spin angular momentum I is zero for <sup>16</sup>O and there are two unpaired electrons in  $O_2$ . Due to the coupling between the molecular rotation angular momentum and electron spin, the spectrum consists of many lines. There are some strong transitions which could be used as standards to calibrate the hydrogen atom concentration. Each of these lines are identified by a letter.

In this study C, F, and G lines were used for the calibration. These lines belong to transitions  $J,M_J \rightarrow J',M_J'$  of  $1,-1 \rightarrow 1,0, 2,0 \rightarrow 2,1$  and  $6,-2 \rightarrow 4,-1$ , respectively. To calibrate the H atom concentration with each of these lines the following equation was used<sup>123</sup>

$$[\mathbf{H}] = \left[\mathbf{O}_{2}\right] \times \mathbf{Q}_{at} \times \left(\frac{\mathbf{M}_{O2}}{\mathbf{M}_{at}}\right) \times \left(\frac{\mathbf{W}_{O2}}{\mathbf{W}_{at}}\right)^{1/2} \times \left(\frac{\mathbf{I}_{at}}{\mathbf{I}_{O2}}\right)$$
(2.51)

Here  $[O_2]$  is the oxygen concentration, which could be calculated from the air pressure in the ESR cavity,  $Q_{at}$  is the calibration factor, which is different for each oxygen line,  $1.96 \times 10^{-2}$  for the C line,  $5.48 \times 10^{-2}$  for the F line and  $1.63 \times 10^{-2}$  for the G line.<sup>123</sup> M<sub>O2</sub> and  $W_{O2}$  are the modulation amplitude and power level used for the oxygen sample and M<sub>at</sub> and  $W_{at}$  are those for the hydrogen atom sample. In this equation, I is the integrated intensity of the ESR signal, which could be calculated as

$$\mathbf{I} = \sum_{i=1}^{n} (\mathbf{B}_{i} - \mathbf{B}_{0}) \mathbf{S}_{a} d\mathbf{B}$$
(2.52)

I could be calculated from the recorded signal for each species. The spectrum was divided into n increments. The origin of the magnetic field ,  $B_0$ , was taken to be the resonance point in the spectrum.  $S_a$  was the amplitude for each increment. dB was the spacing between increments I should be calculated at the same Gain in the ESR for oxygen and for hydrogen atoms.

To calculate the field position, B(v), of each of the oxygen lines at different magnetic field strengths Westenberg<sup>124</sup> proposed the following equation

$$B(v) = B(9477) - (v - 9477)/(dv/dB)$$
(2.53)

Here B(9477) is the magnetic field strength in tesla when the microwave frequency is equal to 9477 MHz, v is the microwave frequency used in the experiment and (dv/dB) is a constant in MHz/tesla given in reference 123. Table 9-2 shows the calculated field positions for the C, F and G oxygen lines at 9432 MHz. Table 9-3 shows the results of calculations of the absolute concentration of hydrogen atoms for a 10-cm peak height at setting conditions in Table 9-4.

O <sub>2</sub> ESR lines	B at 9477 MHz	dv/dB	B at 9432 MHz
	(tesla) $\times 10^4$	(MHz / tesla) $\times 10^{-4}$	(tesla) $\times 10^4$
С	5584	1.96	5561
F	6710	1.42	6678
G	6509	1.74	<b>5483</b>

Table 9-2. Field position B(v) at 9432 MHz calculated from equation (2.53).

**Table 9-3.** Calibration of H atom concentration, mol  $L^{-1}$ , corresponding to a 10-cm peak height at the standard setting given in Table 9-4 using different ESR oxygen lines in reactor one.

p air (Torr)	C line	F line	G line
	[H]×10 <sup>7</sup>	[H]×10 <sup>7</sup>	[H]×10 <sup>7</sup>
0.9	0.99	1.14	
1.0		1.07	1 02
2	1.07	1.20	1.10

.

	hydrogen atom	oxygen molecule
Magnetic field (B)	3091 ×10 <sup>-4</sup> tesla	6761 ×10 <sup>-4</sup> tesla
Scan range	$8 \times 1 \times 10^{-4}$ tesla	$80 \times 10^{-4}$ tesla
Time constant	1 s	4 s
Modulation Amplitude	$0.2 \times 10^{-4}$ tesla	$40 \times 10^{-4}$ tesla
Modulation frequency	100 kHz	100 kHz
Phase	90°	90°
Field sweep	2.0	2.0
Scan time	4 min	4 min
Microwave frequency	9.43? GHz	9.432 GHz
Klystron Power	0.8 mW	0.8 mW
Gain	(6 - 600) × 100	160 × 100

 Table 9-4. The ESR experimental conditions to record the hydrogen atom spectrum and oxygen molecule F-line spectrum.

#### **10. Results and calculations**

The reaction was studied in the temperature range 295 to 516 K at 4.0, 6.6, and 8.6 Torr. The reaction was monitored at different reaction times at each condition. At each reaction time the intensity of the hydrogen peak was observed by ESR and the concertations of different products were measured using the gas chromatograph. At room temperature the only detectable product was methane. At higher temperatures ethylene and propane were detectable. Butane was measurable only at high temperatures and high ethane concentration. The other expected product was ethane, which could not be monitored because of the presence of a relatively high concentration of ethane as reactant.

Table 10-1 shows the hydrogen atom wall and gas phase recombination reaction with the Teflon-coated tube placed in the ESR cavity to connect the end of the reactor to the pressure controller and gas chromatograph. For this purpose a longer injector, 130 cm long, was used to extend the tip of the injector into the Teflon-coated tube. LFR was defined in equation (2.50). In Table 10-1,  $[H]_0$  is the hydrogen atom concentration in the ESR cavity in the absence of ethane.
t	[H]₀
(s)	mol $L^{-1} \times 10^{-7}$
0 428	081
0 351	0 82
0 241	084
0 186	0 91
0 132	0 99
0 1 1 0	1 04
0 077	1 07
0 055	1 09
0 044	088

**Table 10-1.** Wall reaction measurement with the Teflon-coated tube placed in the ESR cavity at 6 6 Torr at room temperature, LFR=91.2 cm s<sup>-1</sup>, with reactor one

To calculate the initial concentration of hydrogen atoms it was necessary to know the wall reaction rate constant in the Teflor tube To calculate  $k_w$  in the Teflon tube equation (2 38) was fitted to the [H]<sub>0</sub> data in Table 10-1 while  $k_w$  and [H<sub>0</sub>] were chosen as parameters It was noticed that when the injector coated with phosphoric acid was placed in the ESR cavity the intensity of the H atom peak decreased In the fitting, the point at 0 044 s in Table 10-1 was not included, because of the interference of phosphoric acid with the ESR The resulting  $k_w$  and [H<sub>0</sub>] were found to be 0 75±0 13 s<sup>-1</sup> and J 12 ×10<sup>-7</sup> mol L<sup>-1</sup>, respectively

Tables 10-2 to 10-43 show the results of the reactions at different conditions The standard deviation of the quoted hydrogen concentrations was found to be 7%, from Table 9-3, and, for the products, 1 to 3% In these Table, the first column shows the time for the hydrogen atoms to reach the ESR cavity from the tip of the injector in reactor one This is also equal to the contact time between the hydrogen atoms and ethane before the

ESR cavity. In reactor two the quoted times are the contact times between hydrogen atoms and ethane. The second column is the hydrogen concentration in the ESR cavity in the absence of ethane and the third column is the hydrogen atom concentration in the ESR cavity in the presence of ethane. The fourth column is the difference between the second and third columns corrected for the wall and gas phase hydrogen recombination reactions The concentration of hydrogen atoms in column 2, [H]<sub>0</sub>, is not the concentration of hydrogen atoms at the tip of the injector. To know how much hydrogen is consumed we should calculate the difference between the hydrogen concentration at the tip of the injector and the hydrogen concentration in column 3. This would include hydrogen atoms consumed in the reaction with ethane and in the wall and gas phase hydrogen recombination reactions. To estimate the concentration of hydrogen atoms consumed in the reaction with ethane, equation (238) was fitted to the difference between the concentrations in columns two and three to estimate [H<sub>0</sub>]. The program used to calculate [H]<sub>consumed</sub> in reactors one and two and a sample of input and output of the program are given in Appendix B.

The concentrations of ethane shown in Tables 10-2 to 10-43 are measured at the corresponding temperatures.

**Table 10-2.** Results at 295 K, 4 1 Torr,  $[C_2H_6]=3$  7×10<sup>-6</sup> mol L<sup>-1</sup>, LFR = 136 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^{7}$
0 236	2 99	1 62	1 67	0 57
0 310	2 79	1 39	1 78	0 62
0 384	2 73	1 35	1 83	0 70
0 457	2 70	1 31	189	0 72
0 531	2 65	1 22	2 10	0 75

**Table 10-3.** Results at 295 K, 6 6 Torr,  $[C_2H_6]=6.0\times10^{-6}$  mol L<sup>-1</sup>, LFR = 82 cm s<sup>-1</sup>, in

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$
0 389	3 10	1 60	2 16	1 04
0 511	<b>2 8</b> 0	1 35	2 33	1 10
0 632	2 43	1 08	2 4.	1 15
0 754	2 38	0 9 <b>8</b>	2 60	1 28
0 <b>87</b> 6	2 19	0 86	2 87	1 36

**Table 10-4.** Results at 295 K, 8 6 Torr,  $[C_2H_6]=7 8 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 63 cm s<sup>-1</sup>, in reactor one

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH₄]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$
0 507	2 70	1 35	2 37	13
0 666	2 33	1 04	2 50	15
0 824	2 07	0 82	3 68	16
0 983	188	0 68	2 85	16
1 141	1 76	0 54	3 33	18

**Table 10-5.** Results at 362 K, 4 1 Torr,  $[C_2H_6]=2 4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 188 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^{10}$
0 170	2 66	1 72	1 09	0 73	
0 223	2 59	0 81	2 18	0 85	
0 276	2 36	0 59	2 26	1 17	
0 329	2 34	0 47	2 50	1 27	
0 382	2 26	0 37	2 65	1 43	2 02

**Table 10-6.** Results at 362 K, 6 6 Torr,  $[C_2H_6]=3 8 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 117 cm s<sup>-1</sup>, in

[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$
$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mcl/L) \times 10^7$	$(mol/L) \times 10^{10}$
2 80	1 70	1 38	12	
2 53	0 64	2 66	14	
2 39	0 44	3 00	19	
2 30	0 28	3 27	20	15
2 12	0 17	3 40	21	3 5
	[H]₀ (mol/L)×10 <sup>7</sup> 2 80 2 53 2 39 2 30 2 12	$[H]_0$ $[H]$ $(mol/L) \times 10^7$ $(mol/L) \times 10^7$ 2 801 702 530 642 390 442 300 282 120 17		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

[H]<sub>0</sub> [H] t [H]<sub>consumed</sub>  $[CH_4]$  $[C_2H_4]$  $(mol/L) \times 10^{10}$  $(mol/L) \times 10^7$  $(mol/L) \times 10^7$  $(mol/L) \times 10^7$ (s)  $(mol/L) \times 10^7$ 0 3 5 6 2 49 1 47 1 46 13 0 467 2 2 5 0 66 2 63 16 0 579 2 04 0 32 3 12 19 14 0 690 188 0 16 3 33 21 30 0 800 1 74 0 04 3 56 23 46

**Table 10-7.** Results at 362 K, 8 6 Torr,  $[C_2H_6]=5 0 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 90 cm s<sup>-1</sup>, in reactor one

**Table 10-8.** Results at 401 K, 4 1 Torr,  $[C_2H_6]=25 \times 10^{-6}$  mol L<sup>-1</sup>, LFR = 187 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 171						
0 187	2 10	0 75	1 57	07		
0 225	2 12	0 45	2 02	08		
0 278	1 98	0 23	2 26	09		12
0 332	1 87	0 14	2 35	14	15	14
0 385	1 79		2 56	12	15	16

**Table 10-9.** Results at 401 K, 6 6 Torr,  $[C_2H_6]=4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 116 cm s<sup>-1</sup>, in

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	(mol/L)×10 <sup>9</sup>	$(mol/L) \times 10^9$
0 276	2 17					
0 302	2 00	0 50	2 06	09		13
0 362	1 98	016	2 75	09		14
0 448	1 75	0 04	2 89	10	18	15
0 534	1 51	0 01	2 80	12	30	22
0 621	1 43		2 99	14	32	23
0 448 0 534 0 621	1 75 1 51 1 43	0 04 0 01	2 89 2 80 2 99	1 0 1 2 1 4	1 8 3 0 3 2	15 22 23

t (s) 0 359	[H]₀ (mol/L)×10 <sup>7</sup> 1 93	[H] (mol/L)×10 <sup>7</sup>	[H] <sub>consumed</sub> (mol/L)×10 <sup>7</sup>	[CH <sub>4</sub> ] ×10 <sup>7</sup> (mol/L)×10 <sup>7</sup>	[C <sub>2</sub> H <sub>4</sub> ] (mol/L)×10 <sup>9</sup>	[C <sub>3</sub> H <sub>8</sub> ] (mol/L)×10 <sup>9</sup>
0 393	1 73	0 37	2 11	09		
0 471	1 70	0 08	2 92	12	15	21
0 584	1 45	0 01	3 04	12	28	24
0 696	1 20		2 91	13	36	26
0 808	1 06		2 99	13	41	24

**Table 10-10.** Results at 401 K, 8 6 Torr,  $[C_2H_6]=5 3 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 89 cm s<sup>-1</sup>, in reactor one

**Table 10-11.** Results at 430 K, 4 1 Torr,  $[C_2H_6]=2.0 \times 10^6 \text{ mol } L^{-1}$ , LFR = 228 cm s<sup>-1</sup>, in

reactor one

t	[ <b>H</b> ]₀	[H]	[H] <sub>consumed</sub>	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 140	2 14					
0 158	2 12	0 41	2 10	06	07	17
0 193	1 77	0 23	2 01	08	16	17
0 228	1 70	0 11	2 22	08	24	20
0 280	1 39	0 03	2 17	09	61	24
0 324	1 63	0 02	2 66	1 12	61	34

**Table 10-12.** Results at 430 K, 6 6 Torr,  $[C_2H_6]=3 2 \times 10^6 \text{ mol } L^{-1}$ , LFR = 142 cm s<sup>-1</sup>, in

t	[H] <sub>0</sub>	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]	$[C_2H_4]$	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \sim 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 226	2 31					
0 254	2 26	0 27	2 78	09	07	20
0 3 1 1	181	0 07	2 71	11	24	2 5
0 367	1 72	0 02	2 92	11	40	28
0 452	1 25	0 01	2 53	11	61	40
0 523	1 50		3 43	14	81	47

t (s) 0 294	[H]₀ (mol/L)×10 <sup>7</sup> 2 21	[H] (mol/L)×10 <sup>7</sup>	[H] <sub>consumed</sub> (mol/L)×10 <sup>7</sup>	[CH <sub>4</sub> ] (mol/L)×10 <sup>7</sup>	[C <sub>2</sub> H <sub>4</sub> ] (mol/L)×10 <sup>9</sup>	[C <sub>3</sub> H <sub>8</sub> ] (mol/L)×10 <sup>9</sup>
0 331	2 12	01	2 98	10	09	29
0 404	1 70	0 02	2 93	11	36	32
0 478	1 58		3 14	11	46	36
0 588	1 11		2 75	11	61	41
0 6 <b>8</b> 0	1 23		3 81	16	8 7	50

**Table 10-13.** Results at 430 K, 8 6 Torr,  $[C_2H_6]=42 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 109 cm s<sup>-1</sup>, ir. reactor one

**Table 10-14.** Results at 454 K, 4 1 Torr,  $[C_2H_6]=1.8 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 245 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[CH <sub>4</sub> ]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 130	1 30	0 58	07		
0 163	1 44	0 05	10	30	31
0 195	1 15	0 03	11	53	4 2
0 228	1 50	0 02	12	61	3 5
0 260	1 20		11	3 5	36
0 293	1 13		13	73	4 5

**Table 10-15.** Results at 454 K, 6 6 Torr,  $[C_2H_6]=2 4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 186 cm s<sup>-1</sup>, in

reactor one

;

t	[H]₀	[H]	[CH4]	$[C_2H_4]$	$[C_3H_8]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 172	1 32	0 60	08		30
0 215	1 43	0 03	12	43	3 5
0 258	1 15	0 01	13	66	42
0 301	1 19		14	80	46
0 344	1 12		14	75	53
0 387	1 04		15	83	54

<b>EXAMPLE 10</b> IN THE ALL AND A
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reactor one

t	[H]₀	[H]	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 224	1 30	0 57	10		40
0 280	1 37	0 01	10	58	52
0 336	1 05		14	83	56
0 392	1 16		14	90	62
0 448	0 98		14	86	62
0 504	0 90		14	93	63

**Table 10-17.** Results at 485 K, 4 1 Torr,  $[C_2H_6]=2 \ 1 \times 10^{-6} \ \text{mol } L^{-1}$ , LFR = 224 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	$[C_3H_8]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 143	1 11	0 47	03	0 5	26
0 170	0 94	0 03	04	66	31
0 197	0 99	0 03	04	77	41
0 233	0 99	0 01	0 5	96	50
0 277	0 92		0 5	108	64
0 322	0 92		05	110	5 5

**Table 10-1**<sup>**\***</sup>. Results at 485 K, 6 6 Torr,  $[C_2H_6]=35 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 139 cm s<sup>-1</sup>, in

reactor one

1

t	[H]₀	[H]	[CH4]	$[C_2H_4]$	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$
0 230	1 03	0 24	0 5	0 07	47
0 273	0 99	0 01	0 7	0 99	77
0 3 1 6	0 93		07	1 25	89
0 374	0 99		07	1 35	10 3
0 446	0 96		07	1 40	10 0
0 518	0 93		07	1 44	10 2

**Table 10-19.** Results at 485 K, 8 6 Torr,  $[C_2H_6]=4.6 \times 10^{-6} \text{ mol } L^{-1}$ . LFR = 107 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^8$
0 300	0 74	0 13	05	01	0 5
0 356	0 75	0 01	07	11	08
0 413	0 74		07	13	10
0 488	0 81		07	15	11
0 581	0 80		07	15	12
0 675	0 76		07	15	11

**Table 10-20.** Results at 485 K, 6 6 Torr,  $[C_2H_6]=22 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 221 cm s<sup>-1</sup>, in

reactor one

t	[H]₀	[H]	[CH <sub>4</sub> ]	$[C_2H_4]$	$[C_3H_8]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 145	1 29	1 13			
0 171	123	0 04	08		
0 199	1 25	0 02	08		
0 235	1 41		09		
0 326	1 27		10		

**Table 10-21.** Results at 485 K, 8 6 Torr,  $[C_2H_6]=2.8 \times 10^{-6}$  mol L<sup>-1</sup>, LFR = 170 cm s<sup>-1</sup>, in

t	[H]₀	[H]	[CH <sub>4</sub> ]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 189	1 08	0 68			
0 223	0 98	0 01	10		
0 260	1 17		11		
0 307	1 27		11		
0 425	1 13		11		

Table	10-22.	Wall	reaction	measurements	at 298	K at	different	pressures	in	reactor	two
LFR =	66, 42	and S	53 cm s <sup>-1</sup>	at 4 1, 6 6 and	86 To	rr, re	spectively	,			

4 1 (Torr)		6	6 (Torr)	8 6 (Torr)		
t	[H]₀	[H] <sub>0</sub> t		t	[H]₀	
(s)	$(mol/L) \times 10^7$	<b>(s)</b>	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	
0 810	1 63	1 304	1 20	1 147	1 06	
0 994	1 44	1 601	0 93	1 305	0 93	
1 058	1 37	1 704	088	1 360	0 90	
1 079	1 33	1 737	087	1 377	089	
1 105	1 31	1 777	0 85	1 398	087	

**Table 10-23.** Wall reaction measurements at 461 K at different pressures in reactor two LFR = 213, 133 and 102 cm s<sup>-1</sup> at 41, 66 and 86 Torr, respectively

4 1 (Torr)		6	6 (Torr)	8 6 (Torr)		
t [H] <sub>0</sub>		t [H] <sub>0</sub>		t	[H] <sub>0</sub>	
(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	
0 345	1 56	0 556	1 58	0 724	1 36	
0 395	1 51	0 636	1 44	0 829	1 24	
( <sup>1</sup> 413	1 49	0 664	1 42	0 866	1 21	
0 419	1 48	0 672	1 41	0 878	1 19	
0 426	1 47	0 683	1 39	0 892	1 <b>17</b>	

Table 10-24. Wall reaction measurements at 486 K at different pressure in reactor two

LFR = 224, 140 and 107 cm s<sup>-1</sup> at 4 1, 6 6 and 8 6 Torr, respectively

41 (Torr) 66		6 (Torr)	8	6 (Torr)	
t	[H] <sub>0</sub>	t	[H] <sub>0</sub>	t	[H] <sub>0</sub>
(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$
0 329	1 55	0 527	1 51	0 687	1 28
0 376	1 50	0 603	1 39	0 787	1 13
0 392	1 48	0 630	1 34	0 822	1 08
0 397	1 47	0 638	1 33	0 833	1 07
0 403	1 46	0 649	1 31	0 846	1 05

Table 10-25. Wall reaction measurements at 515 K at different pressures in reactor two LFR = 238, 148 and 114 cm s<sup>-1</sup> at 41, 66 and 86 Torr, respectively

4 1 (Torr)		6	6 6 (Torr)		8 6 (Torr)	
t [H]0		t	[H]₀	t	[H]₀	
(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	(s)	$(mol/L) \times 10^7$	
0 309	1 39	0 498	1 00	0 649	0 51	
0 354	1 29	0 570	0 86	0 743	0 39	
0 369	1 27	0 595	0 80	0 775	0 36	
0 374	1 26	0 602	0 78	0 785	0 34	
0 380	1 25	0 612	0 75	0 797	0 33	

**Table 10-26.** Results at 299 K, 4 1 Torr,  $[C_2H_6]=3.9 \times 10^{-6}$  mol L<sup>-1</sup>, LFR = 131 cm s<sup>-1</sup>, in

reactor two

t	[H]0	[H]	[H] <sub>consumed</sub>	[CH4]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$
0 000	2 35	1 67	080	04
0 047	2 37	1 58	0 96	05
0 086	2 37	1 46	1 15	05
0 208	2 43	1 30	1 55	06
0 559	2 52	0 80	3 17	10

**Table 10-27.** Results at 299 K, 6 6 Torr,  $[C_2H_6]=6 3 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 82 cm s<sup>-1</sup>, in

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH <sub>4</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$
0 000	1 66	1 04	083	06
0 076	1 67	0 95	1 02	07
0 138	1 69	0 87	121	07
0 335	1 72	0 69	180	10
0 900	182	0 44	4 16	21

**Table 10-28.** Results at 299 K, 8.6 Torr,  $[C_2H_6] \approx 8.2 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 63 cm s<sup>-1</sup>, in reactor two.

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$
0.000	1.27	0.65	0.92	0.6
0.099	1.27	0.58	1.10	0.7
0.180	1.28	0.54	1.27	0.7
0.436	1.30	0.41	1.94	1.0
1.172	1.37	0.23	4.91	2.4

**Table 10-29.** Results at 459 K, 4.1 Torr,  $[C_2H_6]=2.1\times10^{-6}$  mol L<sup>-1</sup>, LFR = 239 cm s<sup>-1</sup>, in

reactor two.

t	<b>[H]</b> ₀	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0.000	3.08	1.46	1.90	1.2		
0.026	3.10	0.79	2.81	1.9	1.1	
0.047	3.10	0.45	3.31	2.1	2.4	2.0
0.114	3.12	0.05	4.13	2.1	5.9	2.6
0.307	3.15		5.14	2.5	10.1	3.1

**Table 10-30.** Results at 459 K, 6.6 Torr,  $[C_2H_6]=3.4\times10^{-6}$  mol L<sup>-1</sup>, LFR = 149 cm s<sup>-1</sup>, in

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH₄]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	(mol/L)×10 <sup>9</sup>	$(mol/L) \times 10^9$
0.000	2.56	1.03	2.04	1.8		
0.042	2.57	0.27	3.34	2.4	1.1	
0.076	2.58	0.05	3.87	2.4	4.2	3.2
0.184	2.62		4.62	2.4	9.4	4.0
0.495	2.68		6.76	3.4	11.7	4.9

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 000	2 03	0 68	2 01	18		
0 054	2 05	0 06	3 35	21	24	16
0 099	2 05	0 01	3 64	21	71	26
0 24	2 09		4 56	23	113	47
0 645	2 1 5		7 60	37	117	54

**Table 10-31.** Results at 459 K, 8 6 Torr,  $[C_2H_6]=4 4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 114 cm s<sup>-1</sup>, in

**Table 10-32.** Results at 459 K, 6 6 Torr,  $[C_2H_6]=1.7 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 149 cm s<sup>-1</sup>, in

reactor two

reactor two

t	[H] <sub>0</sub>	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 000	2 56	1 18	1 83	11		
0 042	2 57	0 64	2 74	20		
0 076	2 58	0 36	3 33	23		
0 184	2 62	0 03	4 62	2 5	28	
0 495	2 68		6 76	32	52	16

**Table 10-33** Results at 459 K, 8 6 Torr,  $[C_2H_6]=2 2 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 114 cm s<sup>-1</sup>, in

t	[H] <sub>0</sub>	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	$[C_{3}H_{8}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	(mol/L)×10 <sup>9</sup>	$(mol/L) \times 10^9$
0 000	2 03	1 02	1 47	13		
0 054	2 05	0 42	2 64	20		
0 099	2 05	0 1 1	3 42	22	12	
0 240	2 09	0 01	4 56	23	47	
0 645	2 1 5		761	35	68	16

**Table 10-34.** Results at 486 K, 4 1 Torr,  $[C_2H_6]=2 0 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 254 cm s<sup>-1</sup>, in

reactor two

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	[C <sub>3</sub> H <sub>8</sub> ]
(s)	(mol/L)×10 <sup>7</sup>	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$
0 000	2 36	1 08	1 49	07	01	
0 025	2 38	0 38	2 43	10	01	15
0 045	2 39	0 16	280	10	02	2 0
0 108	2 39	0 01	3 23	09	10	47
0 290	2 40		4 11	11	13	66

**Table 10-35.** Results at 486 K, 6 6 Torr,  $[C_2H_6]=3 2 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 158 cm s<sup>-1</sup>, in

reactor two

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^8$
0 000	2 36	0 57	2 42	12	01	
0 039	2 37	0 05	3 41	13	04	
0 071	2 36	0 01	3 60	12	08	08
0 173	2 39		4 25	12	13	09
0 466	2 45		6 79	17	15	12

**Table 10-36.** Results at 486 K, 8 6 Torr,  $[C_2H_6]=42 \times 10^{-6}$  mol L<sup>-1</sup>, LFR = 121 cm s<sup>-1</sup>, in

t	[H] <sub>0</sub>	[H]	[H] <sub>consumed</sub>	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^8$
0 000	1 96	0 21	2 71	13	02	01
0 051	1 96	0 01	3 31	1 20	07	07
0 093	1 96		3 53	12	12	08
0 226	2 00		4 49	14	14	09
0 608	2 04		6 72	19	15	12

t (s)	[H]₀ (mol/L)×10 <sup>7</sup>	[H] (mol/L)×10 <sup>7</sup>	[H] <sub>consumed</sub> (mol/L)×10 <sup>7</sup>	$[CH_4]$ (mol/L)×10 <sup>7</sup>	$[C_2H_4]$ (mol/L)×10 <sup>9</sup>	$[C_{3}H_{8}]$ (mol/L)×10 <sup>9</sup>
0.000	2 36	0 96	1 85	09		
0 039	2 37	0 30	2 99	14		
0 071	2 36	0 10	3 45	14	23	
0 173	2 39	0 01	4 24	14	68	09
0 466	2 45		6 72	18	91	27

**Table 10-37.** Results at 486 K, 6 6 Torr,  $[C_2H_6]=1.6 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 158 cm s<sup>-1</sup>, in

**Table 10-38.** Results at 486 K, 8 6 Torr,  $[C_2H_6]=2 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 121 cm s<sup>-1</sup>, in

reactor two

reactor two

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	$[C_3H_8]$
(s)	$(mol/L) \times 10^7$	(mol/L)×10	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^9$	$(mol/L) \times 10^9$
0 000	1 96	0 67	1 91	1 01	0 50	
0 051	1 96	0 07	3 18	1 41	14	
0 093	1 96	0 02	3 43	1 42	2 27	
0 226	2 00		4 40	14	7 72	1 83
0 608	2 04		6 72	2 14	9 08	6 39

**Table 10-39.** Results at 516 K, 4 1 Torr,  $[C_2H_6]=2 \ 1 \times 10^{-6} \ \text{mol } L^{-1}$ ,  $LFR = 250 \ \text{cm s}^{-1}$ , in

t	[H] <sub>0</sub>	[H]	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	$[C_3H_8]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$
0 000	2 01	0 51	1 78	11	02	
0 027	2 00	0 09	2 46	12	04	22
0 049	2 03	0 03	2 72	11	09	34
0 1 1 8	2 05		3 3 5	11	18	67
0 3 1 7	2 07		5 75	16	19	73

**Table 10-40.** Results at 516 K, 6 6 1 orr,  $[C_2H_6]=3 4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 155 cm s<sup>-1</sup>, in

reactor two

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>3</sub> H <sub>8</sub> ]
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$
0 000	1 39	1 28	2 00	14	03	
0 043	1 41		2 25	12	11	34
0 078	1 44		<b>2</b> 51	12	14	56
0 189	1 49		3 34	13	20	89
0 606	1 58		7 29	22	22	95

**Table 10-41.** Results at 516 K, 8 6 Torr,  $[C_2H_6]=4 4 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 119 cm s<sup>-1</sup>, in

t	[H]₀	[H] <sub>consumed</sub>	[CH4]	$[C_2H_4]$	$[C_{3}H_{8}]$	$[C_4H_{10}]$
(s)	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^8$	$(mol/L) \times 10^8$	$(mol/L) \times 10^9$
0 000	0 51	0 <b>78</b>	13	03		
0 056	0 61	1 34	11	13	04	
0 102	0 65	180	11	16	07	
0 247	0 68	3 47	13	20	10	
0 664	0 77	4 04	25	23	11	22

2 64×10<sup>-5</sup> mol  $L^{-1}$  in reactor two

0 206 0 77 1 1 4 1 2 6 6 4  

$$[C_2H_6] = 2.64 \times 10^{-5} \pmod{L^{-1}}$$

**Table 10-43.** Results at 485 K, 8 6 Torr,  $4 \ 2 \times 10^{-5}$  mol L<sup>-1</sup> C<sub>2</sub>H<sub>6</sub>, and 6 6 Torr, 3  $5 \times 10^{-5}$  mol L<sup>-1</sup> C<sub>2</sub>H<sub>6</sub>, LFR = 173 6 and 226 3 cm/s, respectively, in reactor one

[CH<sub>4</sub>]  $[C_{3}H_{8}]$  $[C_4H_{10}]$ t [H]<sub>0</sub>  $[H]_{consumed}$  $[C_2H_4]$  $(mol/L) \times 10^7$  $(mol/L) \times 10^7$   $(mol/L) \times 10^8$  $(mol/L) \times 10^8$  $(mol/L) \times 10^7$  $(mol/L) \times 10^8$ (s) 86 (Torr) 06 22 02 0 2 3 0 1 62 14 66 (Torr) 0 177 1 88 04 14 11 02

## 10-1. Wall reaction rate constant

To calculate the hydrogen atom wall reaction rate constant, k<sub>w</sub>, in reactor one at each temperature, the natural logarithm of the hydrogen peak height at zero ethane concentration, [H]<sub>0</sub>, at different positions was plotted versus the corresponding time calculated from the measured LFR at each injector position. Tables 10-22 to 10-25 were used in a similar way to calculate  $k_w$  in reactor two. In the experiments quoted in Tables 10-22 to 10-25, the substitute He added to the main flow was higher by a factor of 5 than in those experiments k, which the reaction with ethane was studied. To determine  $k_w$  at different temperatures in reactor two, the LFR was changed by introducing the substitute He from different small tubes in the reactor, and in this way the time which hydrogen atoms spent in the reactor was different By increasing the amount of the substitute He in the main flow, the difference between times would increase. The natural logarithm of the recorded hydrogen atom peak height at each LFR was plotted versus the corresponding calculated time. The calculated wall reaction rate constants, kw, at each condition are presented in Tables 10-44 and 10-45 As is expected, the wall reaction rate constant increased at higher temperatures, which means the activity of the phosphoric acid increased at higher temperatures.

Another sink for H atoms was the gas phase third body recombination of hydrogen atoms, which was more important at lower temperatures. The results show that both gas phase and wall reactions removed hydrogen atoms along the reactor tube. To take this into account equation (2 38) was fitted to the  $[H]_0$  data at different conditions to find k<sub>w</sub> and  $[H_0]$  as the parameters while a value for k<sub>2 34</sub> was chosen from the literature. The results are shown in Figures 10-1 to 10-8 and the calculated values of  $k_w$  are listed in Tables 10-46 and 10 47

Table 10-44. Wall reaction rate constants calculated at different conditions in reactor one from the slope of  $\ln[H]_0$  vs t

T (K)	$k_w$ (s <sup>-1</sup> ) at 4 1 Torr	$k_w (s^{-1})$ at 6 6 Torr	$k_w (s^{-1})$ at 8 6 Torr
295	$0.4 \pm 0.1$	07±01	$0.68\pm0.06$
362	$08\pm01$	0 76 ± 0 07	$0 81 \pm 0 03$
401	$0 9 \pm 0 1$	$1\ 2\pm 0\ 1$	$1\ 3\pm 0\ 1$
430	$2\ 0\pm 0\ 6$	$18\pm05$	$18 \pm 03$
454	$0.9\pm0.9$	$1\ 3\pm 0\ 4$	$14 \pm 04$
485	$08\pm04$	0 3 ± 0 1	

Table 10-45. Wall reaction rate constant calculated at different conditions in reactor two

from the slope of  $ln[H]_0$  vs t

.

T (K)	$k_w$ (s <sup>-1</sup> ) at 4 1 Torr	$k_w (s^{-1})$ at 6 6 Torr	$k_w$ (s <sup>-1</sup> ) at 8 6 Torr
298	$0.74 \pm 0.04$	0 74 <sup>,</sup> ± 0 05	$0\ 77\pm 0\ 03$
461	$0\ 87\pm 0\ 04$	0 99 ± 0 07	$0\ 87\pm 0\ 04$
486	$0.79\pm0.05$	$1 16 \pm 0.03$	$1\ 24\pm 0\ 02$
515	$1\ 49\pm 0\ 07$	$25 \pm 02$	$29 \pm 01$



Figure 10-1. Determination of wall reaction rate constant at 295 K in reactor one.  $\blacksquare$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least- squares fit of equation (2.38) to the experimental data.



**9**2

Figure 10-2. Determination of wall reaction rate constant at 299 K in reactor two. **••**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr — least-squares fit of equation (2.38) to the experimental data.



Figure 10-3. Determination of wall reaction rate constant at 362 K in reactor one. **••**, 8 6 Torr,  $\Delta$ ; 6 6 Torr, O; 4 1 Torr — least-squares fit of equation (2.38) to the experimental data.



Figure 10-4. Determination of wall reaction rate constant at 401 K in reactor one. **•**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equation (2.38) to the experimental data.



Figure 10-5. Determination of wall reaction rate constant at 430 K in reactor one. **•**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. -- least-squares fit of equation (2.38) to the experimental data.



Figure 10-6. Determination of wall reaction rate constant at 459 K in react Jr two. **•**; 8.6 Torr,  $\Delta$ ; 6 6 Torr, 0; 4.1 Torr — least-squares fit of equation (2.38) to the experimental data



Figure 10-7. Determination of wall reaction rate constant at 486 K in reactor two.  $\blacksquare$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equation (2.38) to the experimental data.



Figure 10-8. Determination of wall reaction rate constant at 515 K in reactor two.  $\blacksquare$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equation (2.38) to the experimental data.

**Table 10-46.** Wall reaction rate constants in reactor one from non-linear least squares fits of equation (2 38) to the  $[H]_0$  data The quoted  $[H_0]$  values are multiplied by  $10^7$ 

	4 1 Torr		6 6 Torr		86 Torr	
Т	kw	$[H_0]$	k <sub>w</sub>	[H <sub>0</sub> ]	k <sub>w</sub>	[H <sub>0</sub> ]
(K)	(s <sup>-1</sup> )	(mol L $^1$ )	(s <sup>-1</sup> )	$(mol L^{-1})$	(s <sup>-1</sup> )	(mol L <sup>-1</sup> )
295	0 21±0 07	3 77±0 05	0 25±0 09	5 18±0 16	0 18±0 02	5 83±0 03
362	0 65±0 13	3 17±0 06	0 67±0 07	3 70±0 06	0 47±0 02	4 06±0 01
401	0 77±0 12	2 56±0 04	1 09±0 11	2 92±0 06	1 22±0 10	2 97±0 08
430	1 89±0 62	2 37±0 15	1 76±0 48	2 90±0 24		

Table 10-47. Wall reaction rate constants in reactor two from non-linear least squares fits

of equation (2 38) to the  $[H]_0$  data The quoted  $[H_0]$  values are multiplied by  $10^7$ 

	4 1 Torr		6 6 Torr		8 6 Torr	
Т	k.,	[H <sub>0</sub> ]	ίκ <sub>w</sub>	[H <sub>0</sub> ]	$\mathbf{k}_{\mathbf{w}}$	[H <sub>0</sub> ]
(K)	(s <sup>-1</sup> )	$(mol L^{-1})$	(s <sup>-1</sup> )	(mol L <sup>-1</sup> )	(s <sup>-1</sup> )	$(mol L^{-1})$
299	0 23±0 04	3 30±0 10	0 20±0 04	4 30±0 29	0 19±0 03	3 46±0 13
460	0 61±0 03	2 22±0 03	0 90±0 05	3 61±0 11	0 <b>80±</b> 0 03	3 96±0 12
<b>48</b> 6	0 79±0 05	2 23±0 04	1 09±0 02	3 60±0 05	1 20±0 04	4 61±0 15
515	1 43±0 07	2 45±0 07	2 43±0 15	4 35±0 40	2 97±0 05	<b>4 87±</b> 0 18

It was not possible to fit equation (2 38) to the  $[H]_0$  results in reactor one at 454 and 485 K in Tables 10-14 to 10-19 to find the initial hydrogen atom concentration and value of  $k_w$  This could be due to a systematic error As the injector moved into the hot zone in the reactor, the wall reaction inside the injector would increase and therefore fewer H atoms would have been introduced to the reactor The surface-to-volume ratio in the injector is much higher than that in the reactor tube Therefore, the change in the hydrogen atom concentration as the injector moved into the reactor was not linear In reactor two such a systematic error did not exist The wall reaction rate constant increased as temperature increased The measured wal! reaction at 516 K in reactor two might be not as accurate, because phosphoric acid starts to dimerize and become more active at about 500 K

## 10-2. Calculation of nk<sub>21</sub>

Two different methods were used to calculate nk<sub>21</sub>

The first method<sup>122</sup> was to make a plot of  $\ln([H]_0/[H])$  versus time at each condition The slope was calculated and divided by the ethane concentration at that particular condition In these calculations it was assumed that the ethane concentration was constant during the reaction and also that the first order rate constant for combined wall reaction and gas phase hydrogen atom recombination was the same in the presence and absence of ethane The concentration of H atoms ranged from  $1 \times 10^{-7}$  to  $8 \times 10^{-7}$  and the concentration of ethane from  $1.5 \times 10^{-6}$  to  $7.8 \times 10^{-6}$  in different experiments From the stoichiometric number n, it was expected that hydrogen atoms were consumed 3 to 4

times faster than the ethane. The experimental data show that the hydrogen atom concentration was less than 10% of the ethane concentration.

The second method to calculate  $nk_{2.1}$  was to fit a modified form of equation (2.38) to the [H] data in the third column of Tables 10-2 to 10-41. The wall reaction rate constant,  $k_w$ , in equation (2.38) was replaced by  $k_w + nk_{2.1}$ . To take into account the time for hot gas from the end of the reactor to cool down and reach room temperature, t in equation (2.38) was replaced by  $t + \delta t$  in the reactor and by t -  $\delta t$  in the Teflon part. The modified forms of equation (2.38) are equations (2.54) and (2.55) for the reactor and Teflon-coated tube, respectively.

$$[H] = \frac{k_{w} + nk_{2.1}[C_{2}H_{6}]}{\frac{exp((k_{w} + nk_{2.1}[C_{2}H_{6}])(t + \delta t))(k_{w} + nk_{2.1}[C_{2}H_{6}] + 2k_{2.36}[M][H]_{0})}{[H]_{0}} - 2k_{2.36}[M]}$$
(2.54)

$$[H] = \frac{k_{w} + nk_{2.1}[C_{2}H_{6}]}{\frac{exp((k_{w} + nk_{2.1}[C_{2}H_{6}])(t - \delta t))(k_{w} + nk_{2.1}[C_{2}H_{6}] + 2k_{2.36}[M][H]_{0})}{[H]_{0}} - 2k_{2.36}[M]}$$
(2.55)

Equations (2.54) and (2.55) were fitted to the experimental data at room temperature, where  $\delta t$  was zero, to find  $nk_{2.1}$  and  $[H_0]$  as the parameters. In reactor one, it was necessary to use equations (2.54) and (2.55) at the same time, equation (2.54) for the reactor region with its calculated  $k_w$  and then equation (2.55) for the Teflon-coated tube, with its value of  $k_w$  at room temperature. The values of  $[H_0]$  at 295 K in reactor one were found to be 2.2±0.2, 6.0±0.3 and 4 7±0.3 × 10<sup>-7</sup> mol L<sup>-1</sup> and at 299 K in reactor two, were found to be 47±01, 60±03 and  $83\pm03 \times 10^{-7}$  mol L<sup>-1</sup> at 41, 66 and 86 Torr, respectively

At higher temperatures  $nk_{21}$  and  $\delta t$  were chosen as parameters In reactor one it was assumed that the concentration of hydrogen atoms which exited from the tip of the injector at each condition was constant. This assumption was not true for reactor two, where the concentration of hydrogen atoms decreased along the reactor as the gas moved toward the ESR cavity. In reactor two it was necessary to use equation (2.38) and equations (2.54) and (2.55) in the fitting program. To calculate the concentration of hydrogen atoms at t = zero, equation (2.38) was used and then this calculated initial hydrogen concentration was used as  $[H_0]$  in equation (2.54). The results are shown in Figures 10-9 to 10-16 and calculated values of  $nk_{21}$  and  $\delta t$  are listed in Tables 10-48 and 10-49. Input files used to calculate  $nk_{21}$  and  $\delta t$  for reactors one and two are given in Appendix C

Figure 10-17 shows the variation of  $nk_{21}$  with temperature The Arrhenius parameters for this plot were found to be

$$nk_{21} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{10.47 \pm 0.10} \exp(-29.9 \pm 0.7 \text{ kJ mol}^{-1} / \text{ RT})$$
(2.56)



Figure 10-9. Consumption of hydrogen atoms in the reaction with ethane at 295 K in reactor one.  $\blacksquare$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equations (2.54) and (2-55) to the experimental data.



Figure 10-10. Consumption of hydrogen atoms in the reaction with ethane at 299 K in reactor one. **•**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, 0, 4.1 Torr — least-squares fit of equations (2.54) and (2-55) to the experimental data.



Figure 10-11. Consumption of hydrogen atoms in the reaction with ethane at 362 K in reactor one.  $\blacksquare$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr, 0; 4.1 Torr. — least-squares fit of equations (2.54) (2.55) to the experimental data.



Figure 10-12. Consumption of hydrogen atoms in the reaction with ethane at 401 K in reactor one. **•**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equations (2 54) and (2.55) to the experimental data.



Figure 10-13. Consumption of hydrogen atoms in the reaction with ethane at 430 K in reactor one. **•**; 8.6 Torr,  $\Delta$ ; 6.6 Torr, O; 4.1 Torr. — least-squares fit of equations (2.54) and (2.55) to the experimental data.


Figure 10-14. Consumption of hydrogen atoms in the reaction with ethane at 459 K in reactor two. **•**; 8.6 Torr,  $\Box$ ; 8.6 Torr,  $\Delta$ , 6.6 Torr,  $\Delta$ ; 6.6 Torr, 0; 4.1 Torr. — least-squares fit of equations (2.54) and (2.55) to the experimental data.



Figure 10-15. Consumption of hydrogen atoms in the reaction with ethane at 486 K in reactor two. **•**; 8.6 Torr,  $\Box$ ; 8.6 Torr,  $\Delta$ ; 6.6 Torr,  $\Delta$ ; 6.6 Torr, 0; 4.1 Torr. — least-squares fit of equations (2.54) and (2.56) to the experimental data.



Figure 10-16. Consumption of hydrogen atoms in the reaction with ethane at 516 K in reactor two. O; 4.1 Torr. — least-squares fit of equations (2.54) and (2.55) to the experimental data.

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Table 10-48. Values of $nk_{21}$ and $\delta t$ calculated at different conditions in reactor one from
non-linear least squares fits of equations (2 54) and (2 55) to the values of [H] and t

	4 1 To	rr	6 6 Tc	rr	86 Te	orr
Т	nk <sub>2 1</sub>	δt	<b>n</b> k <sub>2 1</sub>	δt	<b>nk</b> <sub>2 1</sub>	δt
(K)	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s) $\times 10^{2}$	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s) $\times 10^{2}$	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s)× $10^{2}$
295	1 41±0 03	0 0	1 47±0 07	0 0	1 40±0 08	0 0
362	11 1±0 6	25±3	10 <b>8</b> ±0 5	6±2	9 2±0 8	0 70±0 03
401	<b>42</b> ±3	8±1	43±2	5 6±0 8	43±3	2 5±1 2
430	73±2	10±1	67 0±0 6	7 2±0 2		

Table 10-49. Values of  $nk_{21}$  and  $\delta t$  calculated at different conditions in reactor two from

non-linear least squares fits of equations (2 54) and (2 55) to the values of [H] and t

Т	nk <sub>2 1</sub>	δt	nk <sub>2 1</sub>	δt	nk <sub>2 1</sub>	δt
(K)	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s) $\times 10^{2}$	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s) $\times 10^{2}$	L mol <sup>-1</sup> s <sup>-1</sup> ×10 <sup>5</sup>	(s) $\times 10^{2}$
299	3 9±0 1	0 0	1 99±0 07	0 0	1 55±0 02	0 0
459	124±4	2 7±0 2	121±13	1 5±0 7	107 8±0 8	1 73±0 06
459ª			129±8	2 6±0 8	115±5	1 8±0 6
486	206±3	1 4±0 1	<b>187</b> ±13	2 1±0 5		
486 <sup>b</sup>			185±30	4±1	201±10	2 4±0 4
516	298±19	2 7±0 3				

a, from the data in Tables 10-32 and 10-33, b, from the data in Tables 10-37 and 10-38



Figure 10-17. Arrhenius plot of nk<sub>2.1</sub>

#### 10-3. Calculation of the stoichiometric number n

The stoichiometric number, n, the number of hydrogen atoms used per ethane molecule reacted, is needed to calculate  $k_{21}$  At room temperature it was expected that only reactions (2 1), (2 8) and (2 10) were important and that n should be close to 4 At higher temperatures, where the other products were formed and hydrogen atoms could react with some products like ethylene, it was difficult to find n easily from the experimental data and the computer simulation was used to calculate n

At room temperature and at 352 K, where methane was the only detectable product, n was equal to twice the ratio of the hydrogen atoms consumed, in the fourth column of Tables 10-2 to 10-43, to the methane produced At higher temperatures, because of involvement of other reactions, it was not possible to calculate n in this way The program used to calculate [H]<sub>consumed</sub> is shown in Appendix B To calculate n at higher temperatures the following equation might be used

$$n = \frac{[H]_{consumed}}{0.5[CH_4] + [C_2H_4] + 1.5[C_3H_8] + 2[C_4H_{10}] + [C_2H_6]}$$
(2.57)

The factors quoted for each product in equation  $(2\ 57)$  are the ratio of the number of hydrogen atoms consumed in reaction  $(2\ 1)$  to the number of molecules of that particular species formed if it were the only product As reactions  $(2\ 1)$ ,  $(2\ 8)$  and  $(2\ 10)$ indicate, to produce two molecules of methane, four hydrogen atoms were necessary One hydrogen atom is consumed in reaction  $(2\ 1)$  to produce two molecules of methane. Thus a factor of 0 5 was selected for methane Reactions  $(2\ 1)$  and  $(2\ 9)$  were involved in the formation of ethylene. Two hydrogen atoms (one for reaction  $(2\ 1)$  and one for reaction  $(2\ 9)$ ) were necessary for the formation of each ethylene molecule, thus a value of one was selected as the ethylene factor in equation  $(2\ 57)$  Reactions  $(2\ 1)$ ,  $(2\ 8)$ ,  $(2\ 9)$  and  $(2\ 11)$  were involved in the formation of propane To produce two molecules of propane, three hydrogen atoms were reacted in reaction  $(2\ 1)$  Then the ratio of the hydrogen atoms consumed in reaction  $(2\ 1)$  to form one propane molecule should be  $1\ 5$  Reactions  $(2\ 1)$ ,  $(2\ 8)$  and  $(2\ 12)$  were involved in the formation of ethane Two hydrogen atoms were necessary to produce two methyl radical via reactions  $(2\ 1)$  and  $(2\ 8)$  to then form one ethane molecule in reaction  $(2\ 12)$  Thus the number of the hydrogen atoms reacted in reaction  $(2\ 1)$  to produce one ethane molecule was 1 Reactions  $(2\ 1)$  and  $(2\ 14)$  were involved in the form one butane molecule via reaction  $(2\ 14)$  Then a value of 2 was chosen as the factor for the number of the hydrogen atoms reacted in reaction  $(2\ 1)$  to form a butane molecule

To calculate n using equation (2-57) the results at the longest reaction time at each condition were chosen. It was not possible to calculate n at room temperature using equation (2-57), because of the distance between the ESR cavity and the place where the sample was taken for gas chromatography. At room temperature, there was still a high percentage of the hydrogen atoms left to react with ethane beyond the ESR cavity. At higher temperatures a relatively small portion of the hydrogen atoms remained to react with ethane. The values of n calculated from the experimental results are listed as  $n_{exp}$  and the values of n predicted by the computer simulation are listed as  $n_{sum}$  in Tables 10-50 and 10-51.

Т	р	n <sub>exp</sub>	n <sub>sım</sub>	k <sub>2 1</sub>
(K)	(Torr)			$(L \text{ mol s}^{-1}) \times 10^5$
295	41	4 3±0 4	43	0 32
295	66	4 2±0 4	44	0 36
295	86	4 2±0 4	44	0 33
362	41	3 8±0 4	43	27
362	66	3 8±0 4	43	28
362	86	3 9±0 4	44	2 5
401	41	3 9±0 4	41	10 4
401	66	3 9±0 4	41	10 2
401	86	4 1±0 4	42	10 6
430	4 1	4 0±0 4	39	177
430	66	4 0±0 4	40	168

Table 10-50. Calculated values of  $n_{exp}$ ,  $n_{sim}$  and  $k_{21}$  in reactor one To calculate  $k_{21}$  corresponding values of  $n_{k_{21}}$  in Table 10-48 were divided by corresponding values of  $n_{exp}$ 

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**Table 10-51.** Calculated values of  $n_{exp}$ ,  $n_{sim}$  and  $k_{21}$  in reactor two To calculate  $k_{21}$  at temperatures below 486 K the corresponding values of  $nk_{21}$  in Table 10-49 were divided by  $n_{exp}$  At 486 and 516 K the values of  $nk_{21}$  were divided by  $n_{sim}$ 

Т	р	n <sub>exp</sub>	n <sub>sım</sub>	k <sub>2 1</sub>
(K)	(Torr)			$(L \text{ mol s}^{-1}) \times 10^{5}$
299	41	8 3±0 8	42	0 47
299	66	4 4±0 4	43	0 45
299	86	4 4±0 4	43	0 35
459	41	3 7±0 4	39	31 8
459	66	3 8±0 4	39	31 0
459	<b>8</b> 6	4 0±0 4	39	27 6
459	66	3 7±0 4	38	33 1
459	86	4 0±0 4	39	29 5
486	41	5 3±0 5	36	57 2
486	66	5 9±0 6	35	52 0
486	66	6 7±0 6	36	51 4
486	86	6 8±0 6	35	57 4
516	4 1	5 2±0 6	3 1	96 1

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### 10-4. Computer simulation

To calculate  $k_{28}$  and  $k_{29}$  and to review the values of n at different conditions it was possible to simulate the reaction on the computer using the program discussed in section 8-3 The rate constants for all reactions, except for reactions (2 1), (2 8), (2 9) and the wall reaction, were taken from the literature The program is listed in Appendix A Table 10-52 shows the results of the computer simulations at two temperatures This table corresponds to the experimental conditions in Tables 10-4 and 10-36

Values of  $k_{28}$  and  $k_{29}$  were adjusted to provide good agreement between the experimental concentrations of methane, ethylene, propane and hydrogen at different reaction times The optimum values of  $k_{28}$  and  $k_{29}$  were found to be  $1.2 \times 10^{10}$  and  $2.3 \times 10^{9}$  L mol<sup>-1</sup>s<sup>-1</sup>, respectively, independent of temperature Values of  $n_{sim}$  calculated by the program were listed in Tables 10-50 and 10-51 in the previous section. It was found that the values of n calculated at room temperature were in good agreement with the experimental values of n. The values of n calculated via equation (2.57) at higher temperatures seem higher than the values expected from the simulation

$$n = \frac{[H]_{consumed}}{0.5[CH_4] + [C_2H_4] + 1.5[C_3H_8] + 2[C_4H_{10}] + [C_2H_6]}$$
(2.57)

This could be due to the fact that equation  $(2\ 57)$  does not take into account the reactions of hydrogen atoms with the products, like reactions  $(2\ 13)$  and  $(2\ 34)$  Also to calculate the values of n using equation  $(2\ 57)$  the formation of ethane is neglected. To examine the effect of reactions  $(2\ 12)$ ,  $(2\ 13)$  and  $(2\ 34)$  the value of n was calculated by computer

t	[H]	[CH <sub>4</sub> ]	[C <sub>2</sub> H <sub>4</sub> ]	$[C-H_6]_{formed}$	[C <sub>3</sub> H <sub>8</sub> ]	[C <sub>4</sub> H <sub>10</sub> ]
(s)	(mol L <sup>-1</sup> )×10 <sup>7</sup>	(mol L <sup>-1</sup> )×10 <sup>7</sup>	(mol L <sup>-1</sup> )×10 <sup>8</sup>	(mol L <sup>-1</sup> )×10 <sup>8</sup>	(mol L <sup>-1</sup> )×10 <sup>8</sup>	(mol L <sup>-1</sup> )×10 <sup>9</sup>
	[H	$[0] = 5 8 \times 10^{-7} \text{ mc}$	ol $L^{-1}$ and $[C_2H_6]_0$	$_{0} = 4.2 \times 10^{-6} \text{ mol I}$	<sup>1</sup> at 295 K	
0 5	15	08	0 01	0 0003	0 0006	0 0004
11	07	14	0 03	0 0007	0 001	0 0007
$[H_0] = 6.7 \times 10^{-7} \text{ mol } L^{-1} \text{ and } [C_2H_6]_0 = 4.2 \times 10^{-6} \text{ at } 486 \text{ K}$						
0 01	32	12	11	20	05	03
0 10	0 03	18	16	47	16	19
0 50	0 001	19	17	52	17	21

10-52. The output of the computer simulation at 295 and 486 K at 8 6 Torr

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simulation excluding these reactions In this way the values of  $n_{sum}$  at higher temperatures increased Also it was possible to calculate n in Table 10-52 at 486 K using equation (2 57) but ignoring [C<sub>2</sub>H<sub>6</sub>], as in the experimental results The calculated value of n was found to be 5 0 Including [C<sub>2</sub>H<sub>6</sub>] decreased the calculated value of n from Table 10-52 to 3 5, the same value calculated in the program For this reason the values of n calculated from equation (2-57),  $n_{exp}$  in Tables 10-50 and 10 51, were used to calculate k<sub>21</sub> at temperatures lower than 486 K and the values estimated by computer simulation,  $n_{sim}$  in Table 10 51, were used to calculate k<sub>21</sub> at 486 and 516 K

Calculated values of  $k_{21}$  at different conditions are listed in Tables 10-50 and 10-51 The Arrhenius plot for  $k_{21}$  is shown in Figure 10-18 and the Arrhenius expression is as follows

$$k_{21} (L \text{ mol}^{-1} \text{s}^{-1}) = 10^{10 \, 11 \pm 0.06} \exp \left(-31.6 \pm 0.5 \text{ k J mol}^{-1} / \text{RT}\right)$$
(2.58)

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Figure 10-18. Arrhenius plot for k<sub>2.1</sub>

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### 11. Discussion

The results in the present study, Tables 10-2 to 10-49, show that the main product at lower temperatures was methane while at higher temperatures ethylene and propane became important. At the highest temperatures the concentrations of ethylene and propane approached 20 to 50% of the concentration of methane

To check for the possibility of any metastable He or other reactive species in the system, two different injectors with different lengths, 100 and 130 cm, were used. Because the time which gas spends in the latter was longer than the time for the shorter injector, it was expected that in the 130 cm-long injector the reactive species would have disappeared to a greater extent. We did not notice any trend in the results of the experiments carried out with each of these injectors. Table 11-1 shows the results of an experiment carried out at room temperature at 6 6 Torr in reactor one, using the longer injector The results in Table 11-1 might be compared with the results in Tables 10-2 to 10-4, in which the shorter injector was used The value of n calculated from twice the ratio of the slope of  $[H]_{consumed}$  to the methane produced in Table 11-1 was found to be 4 3 This value agrees with the values of n at room temperature in Tables 10-50 and 10-51 The value of nk<sub>21</sub> in Table 11-1 was found to be 1  $56 \times 10^5$  L mol<sup>-1</sup> s<sup>-1</sup>

t	[H]₀	[H]	[H] <sub>consumed</sub>	[CH4]
(s)	$(mol/L) \times 10'$	$(mol/L) \times 10^7$	$(mol/L) \times 10^7$	$(mol/L) \times 10^{-1}$
0.185	3 21	2 01	1 45	0 90
0.243	3 01	1 70	1 66	0 9 <b>8</b>
0 319	2 95	1 63	1 73	1 02
0 400	2 85	1 46	1 77	1 08
0 470	2 68	1 27	1 97	1 14
0 551	2 63	1 16	2 14	1 18

**Table 11-1.** Results at 297 K, 6 6 Torr,  $[C_2H_6]=62 \times 10^{-6} \text{ mol } L^{-1}$ , LFR = 140 cm s<sup>-1</sup>, in reactor one, using a 130-cm injector

Near the point where the hydrogen atoms mixed with ethane the concentration of ally Jrogen atoms decreased because of fast consumption. This would cause the hydrogen atoms to diffuse to those areas where their concentration was lower. In this way there should have been a decrease in the apparent rate constant for reaction (2.1) Kaufman<sup>125</sup> showed a simplified expression used by Krongelb and Strandberg<sup>126</sup> to correct for the back diffusion effect as follows

$$k=k'(1+k'D/V^2)$$
 (2 59)

Here k is the true rate constant and k' is the apparent first-order rate constant For the reaction of hydrogen atoms with ethane k' is equal to  $nk_{21}[C_2H_6]$ , D is the diffusion coefficient of hydrogen atoms in He and V is the flow velocity in cm s<sup>-1</sup> Khouw, Morgan and Schiff<sup>127</sup> measured the diffusion coefficient for hydrogen atoms in He at room temperature They suggested a value of 1 94 Å for the rigid-sphere collision diameters of H atoms in He This value was used to calculate the mean free path for hydrogen atoms in He using the following equation <sup>128</sup>

$$\theta = 1/(2^{1/2} \pi d^2 [M])$$
(2.60)

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Here d is the collision diameter,  $\theta$  is the mean free path and [M] is the total concentration in the reactor. The diffusion coefficient for hydrogen atoms was calculated using equations (2.60) and (2.61).

$$D = (1/3) \theta (8 k_B T / \pi m_H)$$
(261)

Here  $m_H$  is the mass of the hydrogen atom The values of D at different temperatures and pressures were calculated and are listed in Table 11-2.

Equation (2.59) was applied to the values of  $k_{21}$  calculated in the present work to correct for diffusion The results are shown in Table 11-2 This correction was small at lower temperatures, where the values of  $nk_{21}$  were small, and approached a factor of 1 33 at 486 K

The corrected values of  $k_{21}$  listed in Table 11-2 can be compared with the values of  $k_{21}$  listed in Tables 10-50 and 10-51 Figure 11-1 shows the Arrhenius plot for the corrected values of  $k_{21}$  in Table 11-2 Using these values of  $k_{21}$  the Arrhenius parameters for reaction (2 1) increased as

$$(k_{21})_{\text{corrected}} (L \text{ mol}^{-1}\text{s}^{-1}) = 10^{10 \ 38 \pm 0 \ 09} \exp(-33 \ 4\pm 0 \ 7 \ \text{kJ mol}^{-1})$$
(2 62)

Another consideration is the heat which is released by the reaction at higher temperatures. To find the temperature increase at the tip of the injector the following equation was used.<sup>129</sup>

$$T = T_{w} + \frac{V_{H} \Delta H}{4\pi\lambda} \left[ \frac{1}{r_{i}} (1 - \exp(-\Psi r_{i})) - \frac{1}{r_{w}} (1 - \exp(-\Psi r_{w})) \right]$$
(2.63)

Here T is the corrected temperature,  $T_w$  is the temperature of the outer wall of the reactor,  $\Delta H$  is the enthalpy of the reaction,  $4H+C_2H_6\rightarrow 2CH_4+H_2$ ,  $V_H$  is the flow rate of the hydrogen atoms in mol s<sup>-1</sup>,  $\lambda$  is the thermal conductivity,  $r_1$  is the radius of the injector and  $r_w$  is the radius of the reactor  $\Psi$  is a function of  $nk_{21}$ , the concentration of ethane and the diffusion coefficient, as follows

$$\Psi^2 = nk_{21}[C_2H_6]/D \tag{2.64}$$

Т	р	D	$[C_2H_6]$	$1+k'D/V^2$	<b>k</b> <sub>2 1</sub>
(K)	(Torr)	$(cm^2 s^{-1})$	(mol L) ×10 <sup>-6</sup>		$(L \text{ mol}^{-1}\text{s}^{-1}) \times 10^{5}$
516	41	859	2 1	1 28	123
486	41	785	20	1 14	65 2
486	66	487	32	1 33	69 2
486	66	487	16	1 16	59 6
486	86	374	21	1 31	75 2
459	4 1	722	21	1 09	34 7
459	66	448	34	1 23	38 1
459	86	344	44	1 33	37 0
459	66	448	17	1 11	36 7
459	86	344	22	1 15	34 5
430	4 1	653	2 0	1 07	18 9
430	66	406	32	1 11	18 7
401	4 1	589	2 5	1 04	10 8
401	66	366	41	1 11	11 3
401	86	281	53	1 20	12 7
362	4 1	505	24	1 01	2 7
362	66	314	38	1 02	29
362	86	241	50	1 04	26
295	4 1	372	37	1 00	0 32
295	66	231	60	1 01	0 36
295	86	177	78	1 01	0 34

**Table 11-2.** Values of  $k_{21}$  corrected for back diffusion using equation (2 59)



Figure 11-1. Arrhenius plot of  $k_{2.1}$ ;  $\Box$ , apparent;  $\blacksquare$ , corrected for diffusion.

Equation (2.63) was used to estimate the temperature correction at our conditions. A value of  $3.0 \times 10^{-3}$  J K<sup>-1</sup>cm<sup>-1</sup>s<sup>-1</sup> was used for the thermal conductivity of He<sup>130</sup> at 486 K. Values of r<sub>i</sub> and r<sub>w</sub> were 0.35 and 1 cm, respectively, and D was calculated from reference 127. The corrected temperature T in equation (2.62) was found to be higher than T<sub>w</sub> at 486 K by less than 1 K and therefore the effect was not important.

## 11-1. Stoichiometric number

The present study is the first study of the reaction of hydrogen atoms with ethane which monitored the consumption of hydrogen atoms, using the ESR, and the formation of the products, using the gas chromatograph. This was useful for a better understanding of the ratio of the amount of hydrogen consumed and the formation of different products, except ethane, the product of reactions (2.12) and (2.32).

The values of n calculated in the present study, listed in Tables 10-50 and 10-51, could be compared with the values reported in the literature. Camilleri, Marshall and Purnell<sup>101</sup> suggested a value of 4 for n at room temperature, dropping to 2.8 at temperatures higher than 430 K. Our results in Table 10-51 show that the value of n is equal to 3.1 at 516 K. They proposed that ethyl radicals directly dissociate to produce an ethylene molecule and a hydrogen atom.

$$C_2H_5 \to H + C_2H_4 \tag{2.65}$$

Reaction (2 65) would produce more hydrogen atoms in the system and reduce the consumption of hydrogen atoms to produce ethylene by reaction (2.9) A survey in the literature<sup>13</sup> reveals that the proposed rate constants for this reaction at 516 K are between

 $1 45 \times 10^{-3}$  and  $3 14 \times 10^{-4}$  s<sup>-1</sup> Computer simulation shows that the concentration of ethyl radical should be about  $1 \times 10^{-8}$  mol L<sup>-1</sup> Using these values, the rate of reaction (2 65) was found to be  $1 45 \times 10^{-11}$  to  $3 14 \times 10^{-22}$  mol L<sup>-1</sup>s<sup>-1</sup> The rate of reaction (2 9) is calculated to be  $1 2 \times 10^{-5}$  mol L<sup>-1</sup>s<sup>-1</sup> at a hydrogen atom concentration of  $5 \times 10^{-7}$  mol L<sup>-1</sup>, using a value of  $2 3 \times 10^{9}$  L mol<sup>-1</sup>s<sup>-1</sup> for the rate constant of reaction (2 9) calculated in the present study. Computer simulation also gives the same value for the rate of reaction (2 9) These calculations show that reaction (2 65) is not an important source for ethylene at our conditions

Other workers<sup>95, 96, 102, 103</sup> used a value of 4 for n to calculate their values of  $k_{21}$  over the temperature range 280 to 579 K An analysis of the accepted mechanism, reactions (2 1), (2 8), (2 9). (2 10), (2 11), (2 12), (2 13), (2 14), (2 15), (2 17), (2 30), (2 32) and (2 33), and the results of the computer simulation suggests a value of 4  $3\pm0.4$  for n at room temperature, as discussed in Section 10-3 Equation (2 57), deduced from the mechanism, predicts a reasonable value for n at lower temperatures where reaction (2 12) and the reactions of hydrogen atoms with products, like reactions (2 13) and (2 33), were still not important The values of n calculated in the computer simulation at temperatures lower than 486 K were in agreement with the values of n calculated using equation (2-57) At temperatures higher than 486 K, reactions (2 12) and (2 13) became more important and caused an increase in the calculated value of n Table 10-52 shows that at higher temperatures the concentration of newly formed ethane is about 3 times higher than the concentration of ethylene.

10-51 Also the consumption and production of ethyl radicals in reactions (29), (212),

(2 13) and (2 34) could increase the value of n as discussed in section 10-4

# 11-2. The rate constant for reaction (2.1)

The Arrhenius parameters for reaction (2 1) calculated in this study can be compared with the values reported in the literature Table 11-3 lists the values of Arrhenius parameters for reaction (2 1) reported by different workers

Reference	T (K)	log <sub>10</sub> ( A /(L mol <sup>-1</sup> s <sup>-1</sup> ))	$E_A (kJ mol^{-1})$
94	295		28 0±4 2
103	281-347	10 7± 0 6	38 0±2 5
95	353-436	9 53	28 42
this work	295-516	10 38±0 09	33 4± 0 7
96	290-579	11 05	38 9
102	357-544	11 03±0 27	38 6± 2 6
101	503-753	11 27±0 13	40 9±1 6
97	673-823	11 53	51 04
104	876-1016	11 72±0 05	53 5±0 8
98	1050-1350	11 15	40 6

Table 11-3. Arrhenius parameters for reaction (2 1) reported by different workers

Our value of the activation energy is about 5 kJ mol<sup>-1</sup> higher than the values reported by Trost<sup>94</sup> and Berlie and Le Roy<sup>95</sup> but about 5 kJ mol<sup>-1</sup> lower than the values reported in references 96, 102 and 103 The pre-exponential factor calculated in this study is also in the range of the values at lower temperatures reported by the groups in Table 11-3

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The Arrhenius parameters calculated from the present study are lower than the Arrhenius parameters from the most detailed previous study on this system by Camilleri, Marshall and Purnell<sup>101</sup> They studied the reaction at higher pressures, 8 to 16 Torr in Ar, than the present study They were not able to monitor the concentration of hydrogen atoms during the reaction Also they mentioned that reaction (2.9) does not play an important role, suggesting the rate constant for reaction (2.9) should be about 5% of the rate constant for reaction (2.8)

To have a better comparison between the values of  $k_{21}$  from the present work and the values published in the literature, an overall Arrhenius plot is shown in Figure 11-2 The data in this graph have been chosen from those workers who corrected their reported values of  $k_{21}$  for n

Our values of  $k_{21}$ , the solid squares, at room temperature are higher than the values reported by others in Figure 11-2 In our calculations to find the initial hydrogen concentration, [H<sub>0</sub>], using equation (2 38), the hydrogen wall reaction (2 17) and the gas phase hydrogen recombination reaction (2 36) were included The present experimental results and the computer simulation show that reaction (2 36) is an important sink for hydrogen atoms and should be included at lower temperatures. Our results show that the values of  $nk_{21}[C_2H_6]$  at room temperature are about 0 5 to 1 5 s<sup>-1</sup>



Figure 11-2. Overall temperature dependence of  $k_{2.1}$ ;  $\blacksquare$ , this work;  $\blacktriangle$ , reference 95;  $\blacktriangledown$ , reference 96;  $\Box$ , reference 98;  $\bullet$ , reference 101; O, reference 102;  $\nabla$ , reference 103;  $\Delta$ , reference 104.

These values are about three times bigger than the values of kw listed in Tables 10-46 and 10-47. The computer simulation in Appendix A shows that the rate of the gas phase hydrogen atom recombination reaction is comparable with the rate of the wall reaction at room temperature, especially at early stages where the concentration of hydrogen atoms is high. At room temperature neglecting reaction (2 36) decreased the calculated initial concentration of hydrogen  $[H_0]$  by a factor of 1.6 This would decrease the value of ln  $([H_0]/[H])$  by a factor of 2 Berlie and Le Roy<sup>95</sup> only considered a first order gas phase recombination reaction to remove hydrogen atoms They did not include reaction (2 17) in calculating the initial concentration of hydrogen atoms Azatyan and Filippov<sup>96</sup> neglected both reactions (2 17) and (2 36) Jones, Morgan and Purnell<sup>102</sup> and Lede and Villermaux<sup>103</sup> considered the wall reaction (2.17) but did not take into account reaction (2.36) Neglecting both reactions (2 17) and (2 36) or one of these reactions would result in a lower value for the initial hydrogen atom concentration by a factor of 1 5 to 2. It was not possible from their data to calculate the concentrations of hydrogen atoms. If their concentrations of hydrogen atoms are comparable with ours, the values of  $k_{21}$  reported by these workers at room temperature should rise by a factor of 1 5 to 2 The effect of reaction (2 36) is not very important at higher temperature

Our values of  $k_{21}$  corrected for diffusion are in line with the values reported by Camilleri *et al*<sup>101</sup> at their lower temperatures Their values of  $k_{21}$  at higher temperatures are more than two times higher than the values predicted by our Arrhenius parameters corrected for diffusion Applying our value of n at 516 K, 3 1, to the data reported by them would decrease their values of  $k_{21}$  by 11% Another possible source of error at higher temperatures is the increase in the temperature because of heat released by the reaction, according to equation (2 63) If this is the case then their values of  $k_{21}$  at higher temperatures should be shifted to even higher temperatures. It was not possible to find the total flow rate or concentrations of reactants and products from their data

Values of  $k_{21}$  reported by Cao and Back<sup>104</sup> over the temperature range 376-1016 K do not follow the overall trend of the graph, as they indicated in their paper In their calculation of  $k_{21}$  they neglected reactions (2.9) and (2.10) Taking into account these reactions would increase their calculated values of k21 Also they assumed that the initiation reaction in their system is gas-phase dissociation of hydrogen, but at their conditions the rate of diss\_ iation of ethane to methyl radicals is about six orders of magnitude higher than the rate of dissociation of hydrogen This would affect the rate constant for reaction (21) To reduce the effect of the heterogeneous reaction on the surface they extrapolated the calculated values of  $k_{21}$  to a ratio of surface area to volume of zero We believe the extrapolation should be made to a ratio of surface area to volume of infinity to keep the order of the reaction one with respect to the concentration of ethane This correction would change their reported Arrhenius parameters to A(L mol<sup>-1</sup>s<sup>-1</sup>) =  $(7.6 \pm 2.3) \times 10^{11}$  and E<sub>A</sub>= 48.4±6.6 kJ mol<sup>-1</sup> This would increase their reported values of  $k_{21}$  by a factor of 4, the  $\Delta$  points shown in Figure 11-2, bringing them into line with the values of k<sub>21</sub> reported by Camilleri et al<sup>101</sup>

It was possible to calculate the overall Arrhenius parameters for reaction (2 1) in Figure 11-2 as follows

$$k_{21} (L \text{ mol}^{-1} \text{ s}^{-1}) = 10^{10.9 \pm 0.1} \exp(-37.6 \pm 0.4 \text{ kJ mol}^{-1} / \text{RT})$$
(2.66)

Clark and Dove<sup>100</sup> suggested a nonlinear Arrhenius plot for reaction (2 1) To investigate the possibility of curvature of the Arrhenius plot more studies at temperatures below room temperature and higher than 1000 K are necessary

## 11-3. Calculation of the value of $k_{2.8}/(k_{2.8}+k_{2.9})$

It was possible to rearrange equation (2 43) as follows to calculate the value of  $k_{2,8}/(k_{2,8}+k_{2,9})$  at room temperature

$$\frac{k_{28}}{k_{28}+k_{29}} = \frac{[CH_4]}{2k_{21}[C_2H_6]k_{217}Z}$$
(267)

Z was defined in equation (2 44) Substitution of the experimental values for  $[CH_4]$ ,  $k_{21}$ ,  $[C_2H_6]$  and  $[H_0]$  at a specific time t from those experiments carried out at room temperature gives an average value for  $k_{28}/(k_{28}+k_{29})$  of 0 86±0 05 This value could be compared with the value 0 84 calculated from the values of 1 2×10<sup>10</sup> for  $k_{28}$  and 2 3×10<sup>9</sup> L mol<sup>-1</sup>s<sup>-1</sup> found in the computer simulation The value of this ratio was found to be 0 84 from the results of computer simulation at 295 K given in Table 10-52

## 11-4. Calculation of the value of $k_{2.9}/(k_{2.8}+k_{2.9})$

We were interested to find more information about the reactions of hydrogen atoms with ethyl radicals Knowledge about the branching ratio,  $k_{2.9}/(k_{2.9}+k_{2.8})$  would lead to a better understanding of energy distribution in the reaction of hydrogen atoms with ethyl radical The value of  $\Delta H$  for reaction (2.8) is calculated to be -47 kJ mol<sup>-1</sup> and for reaction (2.9) was calculated to be -287 kJ mol<sup>-1 74</sup> Reaction (2.9) is the sir iplest organic disproportionation reaction, so knowledge of its kinetics would help in understanding other disproportionation reactions It has been found that the rate of formation and consumption of ethylene can be used to find the branching ratio,  $k_{29}/(k_{28}+k_{29})$ . Reactions (2 9), (2 30) and (2 32) are the sources of formation of ethylene and reaction (2 13) is the only sink for ethylene. The results of the computer simulation, listed in Appendix A, reveal that the main reactions involving C<sub>2</sub>H<sub>4</sub> were reactions (2 9) and (2 13) As discussed in Section 11-1, the rate for reaction (2 9) at our conditions is about 10<sup>6</sup> times faster than the rate of reaction (2 65) Reaction (2 65) would produce more hydrogen atoms in the system. We also know that some of the ethylene would react with hydrogen atoms to produce the ethyl radical, by reaction (2 13)

According to these results it was possible to find the steady rate of formation of  $C_2H_4$  as follows

$$\frac{d[C_2H_4]}{dt} = k_{29}[H][C_2H_5] - k_{213}[H][C_2H_4][M]$$
(2.68)

Here [M] is the total concentration According to the computer simulation, major reactions involving ethyl were reactions (2 1), (2 8) and (2 9) Equation (2 41) gives the steady state concentration of ethyl radicals Substitution of equation (2 41) into equation (2 67) and integration gave the concentration of ethylene as follows

$$[C_{2}H_{4}] = \frac{k_{21}k_{29}[C_{2}H_{6}]}{k_{213}[M](k_{28}+k_{29})}Y$$
(2 69)

Here Y is

$$Y = 1 - \exp\left[-\left(\frac{k_{213}[H_0][M]}{nk_{21}[C_2H_6]}\right) (1 - \exp(-nk_{21}[C_2H_6]t))\right]$$
(2 70)

It is possible to rearrange equation (2 69) for  $k_{29}/(k_{28}+k_{29})$  as follows

$$\frac{k_{29}}{k_{28}+k_{29}} = \frac{k_{213}[C_2H_4][M]}{k_{21}[C_2H_6]Y}$$
(271)

The value of  $k_{2,13}$  in equation (2 71) was calculated from the low-pressure Arrhenius expression given by Lightfoot and Pilling<sup>112</sup> and divided by 2 3, as discussed in Section 8-3-1 To calculate this branching ratio the data at the longest reaction times in Tables 10-2 to 10-41 were used The values of  $k_{2,9}/(k_{2,8}+k_{2,9})$  calculated at different conditions are listed in Table 11-4 The calculated average value of the  $k_{2,9}/(k_{2,8}+k_{2,9})$  ratio in Table 11-4 was found to be 0 18±0 02 Using the data at early stages of the reaction would decrease the average value of this ratio to 0 14 Using the values of  $k_{2,8}$ , 1 2×10<sup>10</sup> L mol<sup>-1</sup>s<sup>-1</sup> and  $k_{2,9}$ , 2 3×10<sup>9</sup> L mol<sup>-1</sup>s<sup>-1</sup>, estimated in the computer simulation, the  $k_{2,9}/(k_{2,8}+k_{2,9})$  ratio was found to be 0 16 It was possible to calculate this ratio using the data obtained from the output of computer simulation at 486 K in Table 10-52 The calculated value of  $k_{2,9}/(k_{2,8}+k_{2,9})$  using equation (2 71) was found to be 0 19 at 0 1 and 0 5 s

In these calculations the value of  $k_{213}$  was divided by 2 3 to have better agreement between experimental results and simulation results The value of  $k_{213}$  used in this study when multiplied by the total concentration at 8 6 Torr, 2  $0 \times 10^8$  L mol<sup>-1</sup>s<sup>-1</sup>, is higher than the value of 1  $17 \times 10^8$  L mol<sup>-1</sup>s<sup>-1</sup> for  $k_{213}$  at room temperature reported by Halstead, Leathard, Marshall and Purnell<sup>106</sup> in Ar at 8 to 16 Torr and smaller than the value of 3  $7 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> at 486 K reported by Teng and Jones <sup>107</sup> Teng and Jones measured their Arrhenius parameters for reaction (2 13) over the temperature range of 303 to 603 K and pressure range of 1 2 to 2 Torr in H<sub>2</sub> In the present study He was used as bath gas

Т	р	reactor	[C <sub>2</sub> H <sub>6</sub> ]	k <sub>2 9</sub> /(k <sub>2 8</sub> +k <sub>2 9</sub> )
(K)	(Torr)		$(mol L^{-1}) \times 10^{6}$	
430	41	1	20	0 19
430	66	1	32	0 23
430	86	1	4 2	0 16
459	41	2	21	0 18
459	66	2	34	0 20
459	86	2	44	0 19
459	66	2	17	0 16
459	86	2	22	0 21
486	41	2	20	0 18
486	66	2	32	0 17
486	86	2	4 2	0 17
486	66	2	16	0 17
486	86	2	21	0 17
516	41	2	21	0 17
516	66	2	34	0 17
516	86	2	4 4	018

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Table 11-4. Values of  $k_{29}/(k_{28}+k_{29})$  calculated at different conditions, using equation (2 71)

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To compensate for the bath gas efficiency, value of  $3.7 \times 10^{8}$ L mol<sup>-1</sup>s<sup>-1</sup> reported by Teng and Jones<sup>107</sup> in H<sub>2</sub> might be divided by 1 4, as discussed in Section 7-6-1 This would reduce their value of k<sub>213</sub> to  $2.7 \times 10^{8}$  L mol<sup>-1</sup>s<sup>-1</sup> Using values of  $1.17 \times 10^{8}$  L mol<sup>-1</sup>s<sup>-1</sup> reported by Halstead *et al*<sup>106</sup> and  $2.7 \times 10^{8}$  L mol<sup>-1</sup>s<sup>-1</sup> reported by Teng and Jones<sup>107</sup> would change the branching ratio of k<sub>29</sub>/(k<sub>28</sub>+k<sub>29</sub>) to 0.15 and 0.23, respectively Taking into account these values for the branching ratio, it was possible to report the value of k<sub>29</sub>/(k<sub>29</sub>+k<sub>28</sub>) as 0.18±0.05

These values could be compared with the ratio of 0 04 calculated from the values of  $k_{28}$ ,  $3.7 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup>, and  $k_{29}$ ,  $1.9 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> reported by Camilleri *et al* <sup>101</sup> Our results at higher temperatures show that the concentration of ethylene is between 7 to 11% of the concentration of methane. Therefore, the value of  $k_{29}$  should be at least 14 to 22% of the value of  $k_{28}$  to produce enough ethylene, as reaction (2.8) produces two methyl radicals from a hydrogen atom and an ethyl radical. Using the value of  $1.9 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> proposed by Camilleri *et al*<sup>101</sup> for  $k_{29}$  in the simulation program at 516 K would produce only 3% ethylene relative to methane. In this way it is possible to conclude that our value for this branching ratio is more reasonable. Underestimation of reaction (2.9) would affect the calculation of the consumption of hydrogen atoms and also the value of n by 11%. Both of these could cause an error in the rate of reaction (2.1)

It was possible to run the computer simulation program using the expression (2 28) given by Lightfoot and Pilling<sup>112</sup>, not divided by 2 3, and instead multiply the value of  $k_{29}$  by 2 3 to increase  $k_{29}$  to 5 3 × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup> This caused a decrease in the concentration of hydrogen atoms, methane and butane but did not have any significant

effect on the concentration of ethylene and propane The output concentrations of hydrogen, methane, ethylene, ethane, propane and butane at 8 6 Torr and 486 K at 0 5 s were found to be  $1.7 \times 10^{-9}$ ,  $1.6 \times 10^{-7}$ ,  $1.7 \times 10^{-8}$ ,  $4.1 \times 10^{-8}$ ,  $1.8 \times 10^{-8}$  and  $1.8 \times 10^{-9}$  mol L<sup>-1</sup> These values could be compared with the results in Table 10-52 This also would increase the branching ratios by  $^{-1}$  factor of two in Table 11-3 and increase  $k_{2.9}$  to 44% of  $k_{2.8}$  which does not agree with our results for the ratio of the concentrations of ethylene to methane which is between 7 to 11%

Using the value of  $k_{21}$  corrected for diffusion in Table 11-1 at 8 6 Torr and 486 K in the computer simulation at the conditions in Table 10-52, the concentration of propane increased to as much as twice the concentration of ethylene. The concentrations of hydrogen, methane, ethylene, ethane, propane and butane at 0 5 s were found to be 1 ×  $10^{-11}$ , 1 8×10<sup>-7</sup>, 1 2×10<sup>-8</sup>, 6 4×10<sup>-8</sup>, 3 1×10<sup>-8</sup> and 3 7×10<sup>-9</sup> mol L<sup>-1</sup>. These results are not in agreement with the experimental results in Table 10-36

### 11-5. Calculation of the value of k<sub>28</sub>/k<sub>210</sub>

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It has been found that it is possible to calculate the ratio  $k_{2.8}/k_{2.10}$  using the ratio of the concentration of propane to butane This ratio could lead us to calculation of the rate constant for reaction (2.8), which is an important reaction in systems in which hydrogen atoms and hydrocarbons are present and also in combustion chemistry The rate of formation of propane could be written as

$$\frac{d[C_3H_8]}{dt} = k_{211}[CH_3][C_2H_5]$$
(272)

The results of the computer simulation also indicated that the main source of methyl radicals was reaction (2.8) and the main sink for this radical was reaction (2.10) These

results allow the use of equation (2.40) for the steady state concentration of methyl radicals. Substitution of equation (2.40) into equation (2.72) yields the rate of formation of propane as

$$\frac{d[C_{3}H_{8}]}{dt} = \frac{2k_{2.11}k_{2.8}[C_{2}H_{5}]^{2}}{k_{2.10}[M]}$$
(2.73)

It was possible to express the rate of formation of butane as

$$\frac{d[C_4H_{10}]}{dt} = k_{2.14}[C_2H_5]^2$$
(2.74)

Using equations (2.73) and (2.74) made it possible to calculate the ratio of propane to butane as follows

$$\frac{[C_3H_8]}{[C_4H_{10}]} = \frac{2k_{2.11}k_{2.8}}{k_{2.10}k_{2.14}[M]}$$
(2.75)

Equation (2.75) could be rearranged to calculate the quotient of  $k_{2.8}/k_{2.10}$  as

$$\frac{\mathbf{k}_{2.8}}{\mathbf{k}_{2.10}} = \frac{\mathbf{k}_{2.14} [C_3 H_8] [M]}{2 \mathbf{k}_{2.11} [C_4 H_{10}]}$$
(2.76)

To calculate  $k_{2.8}/k_{2.10}$  it was necessary to choose a value for  $k_{2.14}$ , the rate constant for the recombination of ethyl radicals, and a value for  $k_{2.11}$ , the rate constant for the cross combination of methyl and ethyl radicals. A value of  $9.8 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> reported by Dobis and Benson<sup>113</sup> was chosen for  $k_{2.14}$ . A value of  $2.83 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> proposed by Baulch *et al*<sup>105</sup> was chosen for  $k_{2.11}$ . The calculated values of  $k_{2.8}/k_{2.10}$  are listed in Table 11-5.

Т	р	reactor	$[C_2H_6]$	$(k_{2 8}/k_{2 10})$
(K)	(Torr)		$(mol L^{-1}) \times 10^5$	$(mol L^{-1}) \times 10^4$
486	66	1	3 5	27
486	86	1	4 2	3 5
516	86	2	04	26
516	86	2	18	3 0
516	86	2	26	24
516	86	2	26	29

**Table 11-5.** Calculated values of  $k_{2.8}/k_{2.10}$  at different conditions

The amount of butane at temperatures lower than 486 K was so small that it was not possible to deter: and measure it Table 11-5 shows consistent values for the ratio of  $k_{28}/k_{210}$  at different conditions The average of the calculated values of  $k_{28}/k_{210}$  in Table 11-5 was found to be  $(2.9\pm0.4) \times 10^{-4}$  mol L<sup>-1</sup> Computer simulation was carried out at 516 K at the same conditions as in Table 10-42 at 8.6 Torr The concentrations of methane, ethylene, ethane, propane and butane were found to be  $9.5 \times 10^{-8}$ ,  $4.1 \times 10^{-8}$ ,  $1.1 \times 10^{-7}$ ,  $6.6 \times 10^{-8}$  and  $1.0 \times 10^{-8}$  mol L<sup>-1</sup> respectively. Using the ratio of propane to butane from these data, the value of  $k_8/k_{10}$  was found to be  $3.1 \times 10^{-4}$  mol L<sup>-1</sup>. Using the data listed in Table 10.52 at 486 K the ratio of  $k_{2.8}/k_{2.10}$  was found  $4.0 \times 10^{-4}$  mol L<sup>-1</sup>. Using the data in the output file given in Appendix A at 459 K the calculated value of this ratio was found to be  $3.1 \times 10^{-4}$  mol L<sup>-1</sup>. Using the value of  $k_{2.8}$  used in computer simulation,  $1.2 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup>, and the values of  $k_{10}$  calculated at 4.59, 486 and 516 K from equation (2.45), this ratio was found to be  $2.4 \times 10^{-4}$ ,  $2.7 \times 10^{-4}$  and  $3.0 \times 10^{-4}$  mol L<sup>-1</sup>, respectively

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It was possible to calculate  $k_{28}$  by substitution of a value of  $k_{210}$  from the literature into the calculated ratios of  $k_{28}/k_{210}$  listed in Table 11-5 Using the expression given by Cobos and Troe<sup>119</sup>, equation (2 45), it was possible to calculate a value of  $4.5 \times 10^{13} L^2$ mol<sup>-2</sup> s<sup>-1</sup> for  $k_{210}$  Accepting this value for  $k_{210}$ , the calculated average value of  $k_{28}$  was found to be  $1.3 \times 10^{10} L$  mol<sup>-1</sup>s<sup>-1</sup> This value could be compared with the values of  $k_{28}$ reported in the literature in Table 11-6

Reference	Т	k <sub>28</sub>
	(K)	$(L \text{ mol}^{-1}\text{s}^{-1}) \times 10^{10}$
106	290	5 1
107	303-603	4 35
101	503-753	3 72
108	321-521	5 13
109	230-568	3 68
105	300-2000	3 61

Table 11-6. Values of  $k_{28}$  reported in the literature at 486 K

Reference 106 in Table 11-6 calculated k<sub>28</sub> using collision theory and the ratio of  $k_{221}/k_{28}$  Reference 107 reported their Arrhenius parameters for reaction (2.8) in a study of the reaction of hydrogen atoms with ethylene They did not discuss how they measured  $k_{28}$  at three different temperatures. Reference 101 used a computer simulation to calculate  $k_{28}$  Reference 108, in a study of the reaction of hydrogen atoms with ethylene used a least-squares procedure to fit the rate constants to their results and in this way they calculated k<sub>28</sub> Reference 109 reported their Arrhenius expression also from a study of the reaction of hydrogen atoms with ethylene Reference 105 is a review of reaction (28) References 106, 107, 108 and 109 in their proposed mechanisms ignored reaction (29) They studied reaction of hydrogen atoms with ethylene and therefore it was not possible to determine the newly-formed ethylene Ignoring reaction (29) in their system would cause them to use a higher limit for  $k_{28}$  to remove ethyl radicals Reference 101 reported their values in a study of hydrogen atoms reacting with ethane, but they underestimated reaction (29) and suggested reaction (265) as another source for ethylene in their study At our conditions reaction (265) was not a major source for ethylene, as discussed Section 11-1

It was also possible to calculate the value of  $k_{28}$  using an equilibrium constant for the reverse and forward reaction (28) and the values of the rate constant for the reverse reaction (-28)

$$2 \operatorname{CH}_3 \to \mathrm{H} + \mathrm{C}_2 \mathrm{H}_5 \tag{-2.8}$$

In 1990 Hidaka, Nakamura, Tanaka, Inami and Kawano<sup>131</sup> studied the pyrolysis of methane in a shock tube over the temperature range 1400 to 2200 K and pressure range

1750 to 2812 Torr Pyrolysis of methane produces considerable quantities of methyl radicals Under these conditions they studied reaction  $k_{28}$  and suggested the Arrhenius parameters for reaction (-2 8) as

$$k_{-28} = 10^{1045} L \text{ mol}^{-1} \text{s}^{-1} \exp(-564 \text{ kJ mol}^{-1}/\text{RT})$$
(277)

In 1994 Lim and Michael<sup>132</sup> studied reaction (-2 8) in reflected shock waves over the temperature range 1224 to 2520 K They reported the Arrhenius parameters for reaction (-2 8) as

$$k_{-28} = 10^{10.50} \text{ L mol}^{-1} \text{s}^{-1} \exp(-61.4 \text{ kJ mol}^{-1}/\text{RT})$$
(2.78)

Baulch *et al*<sup>61</sup> in a review in 1992 recommended an Arrhenius expression for reaction (-2 8) as

$$k_{-28} = 10^{1049} L \text{ mol}^{-1} \text{s}^{-1} \exp(-565 \text{ kJ mol}^{-1}/\text{RT})$$
(279)

Also they recommended the equilibrium constant for reaction (-2.8) and the reverse reaction as

$$K_{p} = 2.21 \times 10^{-4} T^{0.741} \exp(-39.8 \text{ kJ mol}^{-1} / \text{RT})$$
(2.80)

It was possible to calculate  $k_{28}$  at 516 and 486 K from equations (2 77), (2 78), (2 79) and (2 80) The calculated values of  $k_{28}$  are listed in Table 11-7

Some values of  $k_{28}$  in Table 11-5 agree with the value of  $2.2 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> chosen in the computer simulation but some are more than twice the average value  $1.3 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> calculated from equation (2.76) and from the value for  $k_{2.10}$  from the literature. The value of  $3.6 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> recommended by Baulch *et al*<sup>61</sup> is different from the values calculated from their expression for the equilibrium constant and  $k_{-2.8}$ , listed in Table 11-7
Reference	Т	k <sub>2 8</sub>
	(K)	$(L \text{ mol}^{-1}\text{s}^{-1}) \times 10^{10}$
131	486	2 1
131	516	26
132	486	07
132	516	09
61	486	23
61	516	26

**Table 11-7.** Calculated values of  $k_{28}$  using the values of the rate constant for the reverse reaction and the equilibrium constant

Accepting the value of  $1.3 \times 10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> for k<sub>2.8</sub> calculated in the present study, it was possible to calculate the value of k<sub>2.9</sub>, using a ratio of  $0.18\pm0.05$  for the branching ratio of k<sub>2.8</sub>/(k<sub>2.8</sub>+k<sub>2.9</sub>) A value of ( $2.9\pm1.0$ )  $\times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> was found for k<sub>2.9</sub> This value is 22% of the value for k<sub>2.8</sub> calculated in the present study This value could be compared with the value of  $1.9\times10^9$  L mol<sup>-1</sup>s<sup>-1</sup> reported by Camilleri *et al*<sup>101</sup> Our results, Table 10-2 to 10-49, show that the concentration of ethylene in the present study is about 7 to 11% of the concentration of methane As reaction (2.8) produces two methyl radicals, we expected the rate of formation of ethylene in reaction (2.9) be more than 14 to 22% of the rate of formation of methyl radicals in reaction (2.8) Here we neglected the formation of propane, the concentration of which was always less than 8% of the concentration of methane

1

Using the experimental values of  $k_{28}$  and  $k_{29}$ ,  $1.3 \times 10^{10}$  and  $2.9 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup>, respectively instead of the values of  $1.2 \times 10^{10}$  and  $2.3 \times 10^9$  L mol<sup>-1</sup>s<sup>-1</sup>, determined in the computer simulation, decreases the rate of consumption of hydrogen atoms by 20% ir. the early stages but does not change the concentration of products effectively A sample output with experimentally determined values of  $k_{28}$  and  $k_{29}$  at 459 K is shown in Appendix A to compare with the output of the program using the values of  $k_{28}$  and  $k_{29}$ determined in the computer simulation

#### 11-6. Summary

The reaction of hydrogen atoms with ethane was studied in a flow system over the temperature range 295 to 516 K and the pressure range 4 1 to 8 6 Torr The consumption of hydrogen atoms was monitored by ESR and the formation of products was determined by gas chromatography. Methane was the only detectable product at temperatures lower than 400 K. The other products were ethylene and propane at higher temperatures. Butane was detectable only at the highest temperatures and ethane concentrations. Computer simulation was performed to determine the main reactions and also to optimize the temperatures of hydrogen atoms with ethyl radicals to produce methyl radicals and ethylene, reactions (2.8) and (2.9). The program was also able to calculate values of the stoichiometric coefficient n at different conditions. In the present study the stoichiometric number was found to be 4.3 at room temperature and to approach 3.1 at 516 K. The Arrhenius expression for the reaction of hydrogen atoms with ethane, reaction (2.1), was found to be  $k_{2.1}$  (L. mol<sup>-1</sup>s<sup>-1</sup>) =  $10^{10.38 \pm 0.09}$  exp (33.4±0.7 kJ mol<sup>-1</sup> / RT ). The average value of  $k_{2.9}$  / ( $k_{2.8} + k_{2.9}$ ) was found to be 0.18±0.05 and the average value of

 $k_{28}/k_{210}$  was found to be  $(29\pm02)\times10^{-4}$  mol L<sup>-1</sup> Using this ratio and a value from the literature for  $k_{210}$ , a value of  $1.3\times10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> was found for  $k_{28}$  A value of  $(3\pm1)\times10^{9}$  L mol<sup>-1</sup>s<sup>-1</sup> was found for  $k_{29}$  Computer simulation yielded a value of  $1.2\times10^{10}$  L mol<sup>-1</sup>s<sup>-1</sup> for the rate constant of reaction (2.8) and a value of  $2.3\times10^{9}$  L mol<sup>-1</sup>s<sup>-1</sup> for the rate constant of reaction (2.9)

# Appendix A:

Program ESR FOR to perform the computer simulation

\*\*\*\*\*\*\*

program ESR implicit real\*8(a-h,o-z) dimension rc(20), rate(20) double precision rc open(unit=2, file='ESRinp') read(2,\*)p,c2h6,cH,rcw,temp,ts,tf,rc(1),rc(2),rc(3) open (unit=5, file='ESRout') ct=p/temp/62 364 Hvd1o=cH t=0.0c2h4=0 0 ch4=0.0c3h8=00c4h10=00 dc2h6--00 c2h5=0 0 ch3=00c2h6t=0 0 h2=00dch=00 c2h6i=c2h6 c Calculation of the rate constants h+c2h6 = h2+c2h5С rc(1) = as input

h+c2h5 = 2ch3С

С



- c rc(2)= as input
- c h+c2h5 = h2+c2h4
- c rc(3)= as input
- c h+ch3+m=ch4
- c rc(4)=(3.09e18\*(temp\*\*(-1.8)))

rc(4)=6.44e17\*(temp\*\*(-1.8))

- c ch3+c2h5 = c3h8
- c rc(5) = see later
- c ch3+ch3 = c2h6 rc(6)=9.05e13\*(temp\*\*(-1.18))\*exp(-2735/8 314/temp)
- c h+c2h4 = c2h5

rc(7)=ct\*(5.05e12\*exp(-4673/8.314/temp))

- c 2 c2h5 = c4h10rc(8)=(1.3e10) rc(5)=2 0\*(sqrt(rc(6)\*rc(8)))
- c h+c3h8 = h2+c3h7rc(9)=6 46e9\*exp(-21820/8.3.4/temp)
- c 2 c2h5 = c2h6+c2h4

rc(10)=0.14\*rc(8)

- c ch3+c2h6 = ch4+c2h5 rc(11)=1.51e-10\*(temp\*\*6)\*exp(-25.3e3/8.314/temp)
- c ch3+c2h5 = ch4+c2h4

rc(12)=0.04\*rc(5)

c H+H+M = H2 + M

rc(13)=9.69e10\*(temp\*\*(-0.6))

-

- c rc(13)=6.53e11\*(temp\*\*(-1))
- c rc(13)=0.0
- c H + c2h5 + m = c2h6 + m

rc(14)=4e10

c H + wall = 1/2 H2

rc(15)=rcw

- c Calculation of changes in the concentration of reactants, intermediates and products

- c during a time step st

```
20 cHH=(rcw+rc(1)*c2h6+rc(2)*c2h5+rc(3)*c2h5+rc(4)*ch3*ct
 1 + rc(7)*c2h4+rc(9)*c3h8+2.0*rc(13)*cH*ct+rc(14)*c2h5*ct)*ts
 cHt=cH*(EXP(-cHH))
 c2h5t=c2h5+(rc(1)*cH*c2h6+rc(7)*cH*c2h4-rc(2)*cH*c2h5
 1 -rc(3)*cH*c2h5-2.0*rc(8)*c2h5**2-rc(12)*ch3*c2h5-rc(14)*cH
 2 *c2h5*ct-2.0*rc(10)*c2h5**2-rc(5)*c2h5*ch3+rc(11)*ch3*c2h6)*ts
 ch3t=ch3+(2.0*rc(2)*cH*c2h5-rc(4)*cH*ch3*ct-rc(5)*ch3*c2h5
 1 -2 0*rc(6)*ch3**2-rc(12)*ch3*c2h5-rc(11)*ch3*c2h6)*ts
 c2h4t=c2h4+(rc(3)*cH*c2h5-rc(7)*cH*c2h4+rc(10)*c2h5**2
 1 + rc(12) * ch3 * c2h5) * ts
 ch4t=ch4+(rc(4)*cH*ch3*ct+rc(11)*ch3*c2h6+rc(12)*ch3*c2h5)*ts
 c3h8t=c3h8+(rc(5)*ch3*c2h5-rc(9)*cH*c3h8)*ts
 c2h6tt=c2h6t+(rc(6)*ch3**2+rc(10)*c2h5**2+rc(14)*cH*c2h5*ct)*ts
 c4h10t=c4h10+(rc(8)*c2h5**2)*ts
 cH2=H2+(rc(1)*cH*c2h6+rc(3)*cH*c2h5+rc(9)*cH*c3h8+rc(13)*ct
 1 *cH*cH)*ts
 dc2h6t=dc2h6+(rc(1)*cH*c2h6)*ts
 dc2h6=dc2h6t
 c2h6=c2h6-(rc(1)*cH*c2h6+rc(11)*ch3t*c2h6-rc(6)*ch3**2
 1-rc(10)*c2h5**2-rc(14)*ch*c2h5*ct)*ts
 dcHH = (rc(1)*c2h6+rc(2)*c2h5+rc(3)*c2h5+rc(4)*ch3*ct
 1 + rc(7)*c2h4+rc(9)*c3h8+rc(14)*c2h5*ct)*ts
 dcHtt=cH*(EXP(-dcHH))
 dcHt=dcH+cH-dcHtt
 dcH=dcHt
```

```
cHwt=cHw+rcw*cH*ts
```

```
dnc2h6t=dnc2h6t+(rc(1)*cH*C2H6*ts)
```

I

# Storage of the concentration of reactants, intermediates and products

c2h5=c2h5t

С

ch3=ch3t ch4=ch4t

c2h4=c2h4t

c3h8==c3h8t

c2h6t=c2h6tt

c4h10=c4h10t

cH=cHt

H2=cH2

cHw=cHwt

if (cH. lt. 1.0e-11) go to 40

dnc2h6=dnc2h6t

ti=0.0

t=t+ts

if (t.lt. tf) go to 20

```
c Calculation of n
```

```
c 40 cnt=dcH/(dnc2h6-c2h6i)
```

40 cm=rc(1)\*c2h6+(rc(2)+rc(3)+rc(14)\*ct)\*c2h5+rc(4)\*ch3\*ct

cnt=(cnt+rc(7)\*c2h4+rc(9)\*c3h8)/(rc(1)\*c2h6)

write(5,\*)' T t-initial t-step size t-END'

write(5,15)temp,ti,ts,t

write(5,\*)' p ct c(C2h6) cH'

```
write(5,14)p,ct,c2h6,hydro
```

14 format(4e13.3,(/))

```
15 format(4e13.3,(/))
```

write(5,16)' C2H5',c2h5

write(5,16)' CH3',ch3

write(5,16)' H',cH

write(5,16)' CH4',ch4

-

- write(5,16)' C2H4',c2h4
- write(5,16)' C2H6',c2h6t
- write(5,16)' C3H8',c3h8
- write(5,16)' C4H10',c4h10
- write(5,16)' H2',H2
- write(5,16)' Hw',cHw
- write(5,16)' c2h6',c2h6
- write(5,16)' n ',cnt
- 16 format(A,T10,e12.3)
- c if (t.lt tf) go to 20
  - rate(1)=rc(1)\*C2H6\*cH
  - rate(2)=rc(2)\*c2h5\*cH
  - rate(3)=rc(3)\*cH\*c2h5
  - rate(4)=rc(4)\*cH\*ch3\*ct
  - rate(5)=rc(5)\*ch3\*c2h5
  - rate(6)=rc(6)\*ch3\*ch3
  - rate(7)=rc(7)\*cH\*c2h4
  - rate(8)=rc(8)\*c2h5\*c2h5
  - rate(9)=rc(9)\*cH\*c3h8
  - rate(10)=rc(10)\*c2h5\*c2h5
  - rate(11)=rc(11)\*ch3\*c2h6
  - rate(12)=rc(12)\*ch3\*c2h5
  - rate(13)=rc(13)\*cH\*cH\*ct
  - rate(14)=rc(14)\*ch\*c2h5\*ct
  - rate(15)=rc(15)\*cH
  - do 10 i=1,15, 1
  - write(5,6) ' rate constant and rate (',i,')'
  - write(5,7) rc(i), rate(i)
  - 6 format(A,T27,i2,A)
  - 7 format(2e12.3,(/))

10 continue

stop

end

```
*******
                                                ******
The output of ESR FOR program at 8 6 Tori and 295 K in reactor one
*****
         Т
              t-initial
                       t-step size
                                 t-END
  0 295E+03 0 000E+00 0 500E-05
                                0 120E+01
                       c(C2h6)
                                  cH
               ct
     р
 0 860E+01 0 467E-03 0 773E-05 0 580E-06
Concentrations of different species at time 1 2 s in mol L^{-1}
 C2H5
           0 119E-10
 CH3
           0 101E-10
 Η
           0 579E-07
 CH4
           0 146E-06
 C2H4
           0 344E-09
 C2H6
           0 634E-10
 C3H8
           0 557E-11
 C4H10
           0 241E-11
 H2
           0 168E-06
 Hw
           0 479E-07
 c2h6
           0 773E-05
           0 437E+01
 n
rate constant and rate (1)
 0 340E+05 0 152E-07
rate constant and rate (2)
 0 220E+11 0 152E-07
rate constant and rate (3)
 0 440E+10 0 304E-08
rate constant and rate (4)
 0 111E+15 0 304E-07
rate constant and rate (5)
```

```
0.380E+11 0.460E-11
rate constant and rate (6)
0.278E+11 0.286E-11
rate constant and rate (7)
0.153E+09 0.304E-08
rate constant and rate (8)
0.130E+11 0.185E-11
rate constant and rate (9)
0.884E+06 0.285E-12
rate constant and rate (10)
0 182E+10 0.259E-12
rate constant and rate (11)
0.330E+01 0.258E-15
rate constant and rate (12)
0 152E+10 0.184E-12
rate constant and rate (13)
0.228E+10 0.357E-08
rate constant and rate (14)
0.400E+11 0.129E-10
rate constant and rate (15)
0.180E+00 0.104E-07
```

\*\*\*\*\*\*\*\*\*\*\*\*\*

The output of ESR FOR program at 8 6 Torr and 459 K in reactor two

\*\*\*\*\*\*\*

T	t-initial	t-step size	t-END
0.459E+03	0.000E+00	0.500E-05	0.200E+00
р	ct	c(C2h6)	cH
0.860Е+01	0.300E-03	0.422E-05	0.760E-06

0.237E-09
0.229E-09
0.279E-09
0.328E-06
0.112E-07
0.513E-08
0.282E-08
0.478E-09
0.224E-06
0.113E-07
0.422E-05
0.399E+01
and rate (1)
0.339E-08
and rate (2)
0.146E-08
and rate (3)
0.291E-09
and rate (4)
0.960E-09
and rate $(5)$
105E08
0.195E-08
and rate $(6)$
$0.129F_{-}08$
0.1272-00
and rate (7)
0 607E-09
0.00712 07
and rate (8)
0.733E-09
and rate (9)
0.167E-10
and rate (10)
0.10 <b>3E-09</b>

•

-

```
rate constant and rate (11)

0.186E+04 0.180E-11

rate constant and rate (12)

0.14.2.+10 0.779E-10

rate constant and rate (13)

0.175E+10 0.409E-13

rate constant and rate (14)

0.400E+11 0.796E-12

rate constant and rate (15)

0.750E+00 0.209E-09
```

The output of ESR.FOR program at 8.6 Torr and 459 K in reactor two, using experimentally determined values of  $k_{2.8}$  and  $k_{2.9}$ .

\*\*\*\*\*\*

Т	t-initial	t-step size	t-END
0.459E+03	0.000E+00	0 500E-05	0.100E+00
р	ct	c(C2h6)	cH
0.860E+01	0.300E-03	0.421E-05	0 805E-06
C2H5	0.649E-09		
CH3	0.777E-09		
Н	0.782E-08		
CH4	0.339E-06		
C2H4	0.121E-07		
C2H6	0.416E-08		
C3H8	0.382E-08		
C4H10	0 836E-09		
H2	0.238E-06		
Hw	0 129E-07		
c2h6	0.421E-05		
n	0 399E+01		
rate constant and rate (1)			
0.280E+07	0 921E-07		

rate constant and rate (2)

```
0.130E+11 0.659E-07
rate constant and rate (3)
0.290E+10 0.147E-07
rate constant and rate (4)
0.500E+14 0 911E-07
rate constant and rate (5)
0.411E+11 0.207E-07
rate constant and rate (6)
0.246E+11 0.148E-07
rate constant and rate (7)
0.194E+09 0.184E-07
rate constant and rate (8)
0.130E+11 0.547E-08
rate constant and rate (9)
0.212E+08 0.634E-09
rate constant and rate (10)
0.182E+10 0.766E-09
rate constant and rate (11)
0.186E+04 0.610E-11
rate constant and rate (12)
0.164E+10 0.829E-09
rate constant and rate (13)
0.175E+10 0.321E-10
rate constant and rate (14)
0.400E+11 0.610E-10
rate constant and rate (15)
0.800E+00 0.625E-08
```

I

......

## Appendix B:

#### \*\*\*\*\*\*\*\*

The program 2HCON FOR to calculate the [H]<sub>consumed</sub> in Table 10-4. In this program time is the reaction time in the reactor, timet is the time which reactants spend in the Teflon tube, akone is  $k_w$ , aktwo is  $k_{36}$ , ctotal is the total concentration in the reactor and ctotalt is the total concentration in the Teflon tube.

\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

program initial H concentration

- C calculates the H atom concentration at zero time with wall and
- C recombination reactions

write(5,\*) ' pressure, [H], time, timet, kone ='

read(5,\*) p,hcon,time,timet,akone

temp=401

aktwo=1.91e9

ctotal=p/62.364/temp

ctotalt=p/62.364/300.

ak1t=0 75

c=exp(ak1t\*timet)

cc=ak1t+2\*2.2e9\*hco1i\*ctotalt

bb=hcon\*aklt\*c/(cc)

a=(2\*2.2e9\*hcon\*ctotalt\*c/cc)

bbb=bb/(1-a)

15 A

```
d=exp(akone*time)
dd akone+2*aktwo*bbb*ctotal
ee=bbb*akone*d/(dd)
cH=ee/(1-(2*aktwo*ctotal*bbb*d/dd))
write(5,*) ' [H] consumed = '
write(5,*)cH
stop
end
```

A sample of input and output for program ZHCON FOR at 295 K in reactor one For the third row in Table 10-4

input

٩

86 129×10<sup>-7</sup> 0317 0507 02

output [H]<sub>consumed</sub> in mol L<sup>-1</sup>

 $250 \times 10^{-7}$ 

## Appendix C:

In the following files aktwo and aktwot stand for the hydrogen atom recombination rate constant in the reactor and in the Teflon tube, respectively, and p1 and p2 are the parameters to be fitted

\*\*\*\*\*\*\*

The input file used for the nonlinear least-squares fit of equation (2 38) to the values of  $[H]_0$  and t to estimate the values of the wall reaction rate constant, p1, and the initial hydrogen atom concentration, p2, at different conditions

\*\*\*\*\*\*

- /PROBLEM TITLE IS 'CURVE FITTING'
- /INPUT VARIABLES ARE 2

FILE IS'Hcon DAT'

FORMAT IS FREE

/VARIABLE NAMES ARE t, H

/REGRESS DEPEND IS H

PARAMETERS ARE 2

/PARAMETER INITIAL ARE 0 5, 5 0

MAXIMUM ARE 10 0e6, 100 0e6

MINIMUM ARE 0 03e-5, 0 03e-5

/FUN pressure=8 6



/END

#### \*\*\*\*\*\*\*

The input file used for the nonlinear least-squares fit of equations (2 54) and (2 55) to the values of [H] and t to estimate the values of  $nk_{21}$ , p1, and  $\delta t$ , p2, in reactor one at different conditions

\*\*\*\*\*

/PROBLEM	TITLE IS 'CURVE FITTING'
/INPUT	VARIABLES ARE 2
	FILE IS'Hcon DAT'
	FORMAT IS FREE
/VARIABLE	NAMES ARE t, H
/REGRESS	DEPEND IS H
	PARAMETERS ARE 2
/PARAMETER	INITIAL ARE 8 0e6, 0 02
	MAXIMUM ARE 10 0e7, 10 0e8
	MINIMUM ARE 0 05e-5, 0 05e-7

/FUN pr=5 1

```
ctotal=pr/62 364/454 0

ctotalt=pr/300 0/62 364

aktwo=1 76e9*ctotal

cethane=1 79e-6

ee=2 5+p1*cethane

aktwot=2 1e9*ctotalt

b=exp(ee*(t+p2))*(ee+2*aktwo*2 64e-7)/(2 64e-7)

c=(ee/(b-2*aktwo))

eee=0 75+1 5e5*1 43*cethane

bt=exp(eee*(0 13-p2))*(eee+2*aktwot*c)/c

f=ln((eee/(bt-2*aktwot)))

/PLOT VARIABLE IS t

SIZE = 25, 25
```

/END

\*\*\*\*\*\*\*\*\*\*\*\*

The input file used for the nonlinear least-squares fit of equations (2 54) and (2 55) to the values of [H] and t to estimate the values of  $nk_{21}$ , p1, and  $\delta t$ , p2, in reactor two at different conditions

\*\*\*\*\*\*\*\*\*\*\*\*

/PROBLEM TITLE IS 'CURVE FITTING'
 /INPUT VARIABLES ARE 3

 FILE IS'Hcon DAT'
 FORMAT IS FREE

 /VARIABLE NAMES ARE t, th, H
 /REGRESS DEPEND IS H

 PARAMETERS ARE 2

# /PARAMETER INITIAL ARE 3 0e7, 0 02 MAXIMUM ARE 10 0e8, 10 0e8 MINIMUM ARE 0 03e-5, 0 03e-7

```
/FUN
          pr=4 1
       ctotal=pr/62 364/516 0
       ctotalt=pr/62 364/300 0
        aktwo=1 63e9*ctotal
       akwp=1 5
       cethane=2 12e-6
       aktwot=2 2e9*ctotalt
       a=exp((akwp)*(th+p2))*(akwp+2*aktwo*6 2e-7)/(6 2e-7)
       aa=(akwp)/(a-2*aktwo)
       ee=akwp+p1*cethane
       b=exp(ee*(t+p2))*(ee+2*aktwo*aa)/aa
       c=(ee/(b-2*aktwo))
       eee=0 75+1 5e5*1 7*cethane
       bt=exp(eee*(0 189-p2))*(eee+2*aktwot*c)/c
       f=ln(eee/(bt-2*aktwot))
/PLOT
             VARIABLEs are t, th
             SIZE = 25, 25
```

/END

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