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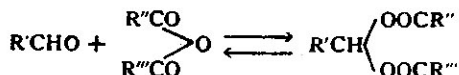## Nova Scotian Institute of Science[*]

STUDIES ON ANHYDRIDE — ALDEHYDE — ESTER SYSTEMS; THE RATE OF FORMATION OF BUTYLIDENE DIACETATE.

C. C. Coffin and Pauline A. Miller,
Dept. of Chemistry, Dalhousie Univ., Halifax, N. S.

ABSTRACT.

The series of liquid phase reactions represented by the general equation

$$R'CHO + \begin{matrix} R''CO \\ \diagup \\ R'''CO \end{matrix}\!\!>O \rightleftarrows R'CH\begin{matrix} OOCR'' \\ \diagdown \\ OOCR''' \end{matrix}$$

has been found to be very suitable for the test of previously outlined ideas regarding the effect of molecular attractive forces on the velocity of chemical change. This paper deals with the uncatalysed reaction in the liquid state between acetic anhydride and butyraldehyde to form butylidene diacetate. The reaction velocity and the equilibrium concentrations have been determined by a "bulb method" for equimolecular mixtures from 138 to 180°. The reaction is proved to be strictly homogeneous, reversible and free from side reactions. It is catalysed by traces of mineral acids and by acetic acid at concentrations above about 2% so that the materials must be carefully purified and the apparatus thoroughly cleaned in order to obtain reproducible results. The freezing point curve of the system shows the existence of a highly associated 1:1 molecular compound melting at —20°. The existence of this compound at higher temperatures is indicated by the fact that at 20° there is a large negative heat of mixing although the chemical reaction itself is exothermic. No measurable reaction occurs after 6 months at room temperature. The significance of the results are discussed and the scope of future work in this connection is indicated.

INTRODUCTION.

During the past few years O. Maass and his students have collected a considerable amount of experimental data

indicating that the physical forces of attraction between molecules play a large part in determining the velocity of chemical reactions and suggesting that in general the explanation of the highly specific nature of reaction rate is to be looked for in mechanisms involving the interplay of such molecular attractive forces.[1]   As the effect of these forces on the physical properties of a system increases with the total concentration it is to be expected that their influence on reaction velocity will likewise increase with concentration and so be most readily observed in reactions in liquids and highly compressed gases.   An example will facilitate the presentation of the ideas underlying the experimental work in this connection and will serve to indicate the nature of the effects to be expected.

In an apparently homogeneous liquid mixture of two potentially reactive molecules A and B there exist three attractive forces, viz., A to A, B to B, and A to B.   If either of the first two is greater than the third, then at any point the actual composition of the solution may be far from that indicated by its analysis or preparation and the velocity constant of the reaction will be diminished since the acquisition of activation energy by a molecule surrounded only by its own kind cannot result in reaction.   On the other hand if the attraction between A and B predominates the solution will be more truly homogeneous and the concentration will be more uniformly equimolecular with the obvious result that the velocity of the reaction will be increased since the chances are that a greater proportion of the molecules in possession of energy of activation will be spatially in positions favorable for reaction.

Where the forces A to A or B to B are very large compared to the force A to B, like molecules will associate to an extent sufficient to "squeeze out" unlike molecules and the system will separate into two layers, i.e., the rate of the homogeneous reaction will be zero.   Where the attraction A to B is large enough to form a highly associated molecular compound the great majority of the molecules can be considered as being

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1.   For bibliography, etc. see Coffin and Maass, *J. Am. Chem. Soc.*, **50**, 1427, (1928); *Can. J. of Research* **3**,526 (1930); **3**,540, (1930).
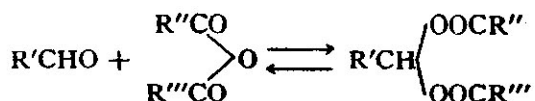
involved in "perpetual collisions" and the rate of reaction will be determined solely by the rate of activation.   Between these two extremes every gradation is possible and a quantitative investigation of the actual part played by such forces in determining reaction velocity necessitates some measure of their magnitude.

While Van der Waals "a" is theoretically the most direct measure of the forces of attraction between like molecules its determination is difficult and its meaning is obscure in the case of liquid mixtures.   A more convenient but strictly relative estimate of the forces between the molecules of, for instance, two different series of compounds is afforded by a comparison of those physical properties of the pure substances and their mixtures which according to kinetic theory are the consequences of intra molecular attraction.   For example from the complete freezing point diagram of a two component system (usually to be obtained at temperatures so low that the velocity of the chemical reaction is negligible) the extent of association or dissociation of one substance in the other as well as the occurrence composition and comparative stability of molecular compounds can be determined.   Thus from the freezing point and reaction velocity curves for mixtures of different members of two series of compounds any parallelism between molecular attractive forces and reaction rate may be noted.   For the interpretation and the general theoretical significance of any such parallelism it is highly desirable to be able to determine the order and probable mechanism of the reaction.

So unsuitable is the vast majority of chemical reactions for profitable quantitative study in this connection that one of the most important parts of such an investigation is the choice of the system on which to work.   That is, the reaction to be studied must possess certain simplifying "ideal" characteristics if velocity and equilibrium data of any real theoretical value are to be obtained.   It must of course proceed at a measurable and reproducible velocity under experimentally attainable conditions of temperature and pressure and be of such a nature that its progress may be readily followed and

its equilibrium concentrations determined. It should be simple, uncatalysed, strictly homogeneous and free from complicating side reactions over a wide range of temperature and concentration in both the liquid and gaseous states. A further necessary feature and one practically confined to organic reactions is that the character of the reaction should remain unchanged throughout a series of compounds so that various molecular attractive forces, which can be changed only by changing molecular structure, may be obtained.

The formation of esters from aldehydes and acid anhydrides according to the equation

$$R'CHO + \begin{matrix} R''CO \\ \diagup \\ R'''CO \end{matrix}\!\!\!\!\!\!\diagdown O \rightleftarrows R'CH \begin{matrix} OOCR'' \\ \diagup \\ \diagdown \\ OOCR''' \end{matrix}$$

has been found to satisfy the above criteria remarkably well. The reactions so far investigated are strictly homogeneous and take place at a reproducible and measurable velocity in the absence of catalysts over a wide temperature range in both the liquid and gaseous states. Except at high temperatures in the gaseous state no side reaction occurs so that the determination of only one component (the anhydride analysis is most convenient) is necessary to completely define the concentration of the system. In the liquid phase the equilibrium does not in general lie too far to any one side and experimentally may be approached from either direction. In the gaseous state the equilibrium as written above appears to be shifted completely to the left at all temperatures—a result of considerable significance from several points of view. These gaseous ester decompositions, which are homogeneous and monomolecular,[2] are being discussed in a series of papers in the "Canadian Journal of Research". As far as physical properties are concerned preliminary experiments on several different aldehyde-anhydride systems indicate that highly associated 1:1 molecular compounds exist at low temperatures and that a relative estimate of the "A to B" attraction at

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2. Coffin, *J. Am. Chem. Soc.*, **53**, 3905, (1931).

higher temperatures can be obtained from the heats of mixing which are negative and of the order of several hundred calories per mol.

The present paper deals with the velocity of the reaction in the liquid state between equimolecular quantities of butyraldehyde and acetic anhydride to form butylidene diacetate.

EXPERIMENTAL.

Velocity Measurements. The velocity of the reaction was determined by heating known weights of an equimolecular mixture of aldehyde and anhydride at definite temperatures for various lengths of time and analysing for unreacted anhydride. Since the vapor pressure of the mixture is considerable at temperatures at which the reaction attains a measurable rate all experiments were carried out in sealed pyrex glass tubes which were made large enough to contain about 1 gram of the mixture in order that analytical errors would not be augmented by the use of too small a quantity of material. These tubes were simply 10 cm. lengths of 5 mm. i.d. tubing drawn down at each end to a heavy capillary ending in a bell mouth to which rubber pressure tubing could be attached for filling and evacuating. They were cleaned with hot chromic acid solution, thoroughly dried, labeled with turns of aluminium wire and weighed. One end of the tube was then immersed in a freshly prepared and analysed reaction mixture and the liquid was drawn up into it by suction at the other end which was then sealed off. The tube was then inverted in a solid CO_2 ether mixture and as soon as the contents had frozen was evacuated through the remaining capillary which was likewise sealed off. A second weighing of the tube plus the two sealed off ends gave the weight of the mixture taken. Care was taken throughout the manipulation to prevent the loss of either component by evaporation and to protect the mixtures from contact with the moisture of the air—a very necessary precaution in experiments involving acetic anhydride. In filling each tube an effort was made to take a quantity of the mixture such that the tube would be very nearly full of liquid at the temperature of the experiment

in order that complications due to a different equilibrium or reaction velocity in the gaseous phase would not occur. After a little practice it was easy to estimate this quantity quite closely. As preliminary experiments had proved that the reaction velocity at room temperature was negligible the filled bulbs could be kept indefinitely and the rate measurements and analyses carried out at leisure.

In the actual experiments, which were always carried through in duplicate, the filled tubes bound in pairs to glass rods were plunged into a thermostat at the desired temperature. From time to time a pair was removed and quickly cooled in running water. The tip of each capillary was then cut off and the tube contents was carefully washed with a large quantity of distilled water into a flask for analysis. After standing for half an hour (to allow the anhydride to reach equilibrum with the water) the free acid was titrated with standard baryta in the presence of phenolphthalein. From this figure the amount of anhydride reacted (= amount of aldehyde reacted = amount of ester formed) was calculated.

The homogeneity of the reaction was tested by carrying out several experiments exactly as described above except that the glass surface in contact with the liquid was enormously increased by loosely filling the tubes with finely crushed pyrex glass. As pointed out below the fact that the rate remained unchanged proves that the reaction takes place homogeneously throughout the liquid. It is worth emphasizing that all the reactions took place in the liquid phase only and in the absence of air, moisture, and catalysts.

Except at 138°, where a xylene vapour bath was used, constant temperatures were obtained by means of an electrically heated and vigorously stirred oil bath provided with a bi-metallic thermoregulator. By continually tapping the regulator with a device actuated by the stirring motor the temperature could be kept constant within about 0.2° for many hours at a time. Temperatures were measured on a mercury thermometer graduated in 0.2° and calibrated against Reichenstalt standards.

Analyses. As already stated the contents of the reaction tubes were analysed by allowing the anhydride to react with a large excess of water and titrating the acetic acid formed with standard baryta. In determining the amount of acetic acid in the reaction mixtures and in the original anhydride recourse was had to the well known analine method of Menschutkin in which the anhydride present reacts with the dry analine to form equimolecular quantities of acetanalide and acetic acid the latter of which can then be titrated with alkali to obtain half the anhydride plus the acid originally present. From these data together with the figure for all the anhydride plus the acid the amount of each in the original sample can be calculated. The same baryta solution was used throughout, a 10 l. lot having been made up and standardized at the beginning of the work. Its concentration (0.284N) was checked from time to time.

In order to obtain definite proof that the ester formed was equivalent to the anhydride lost many attempts were made to devise a saponification procedure by which the amount of ester present could be determined. As it was at length evident that the erratic results first obtained were in all probability due to the absorption of caustic by the resinification of the liberated butyraldehyde the final saponifications were carried out in low wide mouthed glass jars kept in a water bath at temperatures somewhat above the boiling point of butyraldehyde. Small quantities of alkali were run in from a burette from time to time until the smallest possible excess had been added. After cooling to room temperature the excess alkali was titrated with standard HCl. This method though tedious gives quite good results presumably on account of the fact that the butyraldehyde can escape from the solution as it is liberated and is not at any time in the presence of a large excess of caustic.

Purification of Materials. The butyraldehyde (Eastman's C. P.) was dried for several weeks over a large quantity of $CaCl_2$ from which it was removed by distillation on a water bath. It was then fractionated twice through a 4 foot glass column and the middle third used for the velocity experiments

Several kilograms of 85% acetic anhydride (Eastman's Technical) was repeatedly fractionated through a large glass column of special design until the acetic acid content was reduced to about 1%. A few hours' refluxing with a large excess of metallic sodium and a final fractionation gave a very pure sample of anhydride.[3]

Pure butylidene diacetate was prepared by refluxing equimolecular quantities of butyraldehyde and acetic anhydride with about 0.1% sulphuric acid as catalyst. When after several hours the boiling point had become constant (140° at 760 mm.) the catalyst was neutralized with a calculated excess of sodium acetate and the whole was fractionated several times in vacuo. The final ester fraction was washed with dilute $Ba(OH)_2$ solution until free from acid, dried with $CaCl_2$ and again fractionated. Saponifications, carried out as described above, as well as cryoscopic molecular weight determinations in benzene proved beyond all doubt that the compound formed was butylidene diacetate. That it was of a high degree of purity was indicated by the constancy of the physical properties of the fractions obtained in the final distillation. The following physical constants were determined.

B. P.   760 mm.   195°
B. P.   2 mm.   90°
M. P.   −6.5°

RESULTS.

In Figure I are plotted the experimental results at 160° (curve B.O●⊕) and 180° (curve AΔ). As is to be expected equilibrium is reached more rapidly at the higher temperature and corresponds to an ester concentration of 24 mole % at 180° as against 28 mole % at 160°. Thus rise of temperature shifts the equilibrium in the direction of ester decomposition in accordance with the fact that the latter is the endothermic reaction. The "time to half value" at 160° is seen to be approximately 8 hours as compared with 3 hours at 180°.

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3.   Edwards and Orton.   *J. Chem. Soc.*, **99**, 1181, (1911).

The open circles of curve B were obtained with reaction mixtures made from anhydride containing 0.6% acetic acid while the solid circles represent experiments in which the original anhydride analysed 2% acid. It is to be noted that both sets of points fall fairly well on the same curve showing that acetic acid at these low concentrations exerts no appreciable catalytic effect. That such is not the case at higher concentrations of acetic acid was evinced by a series of experiments (not plotted in Figure I) made with anhydride containing 5% acid. The curve obtained in this case leads to the same equilibrium concentrations but the reaction velocity is much
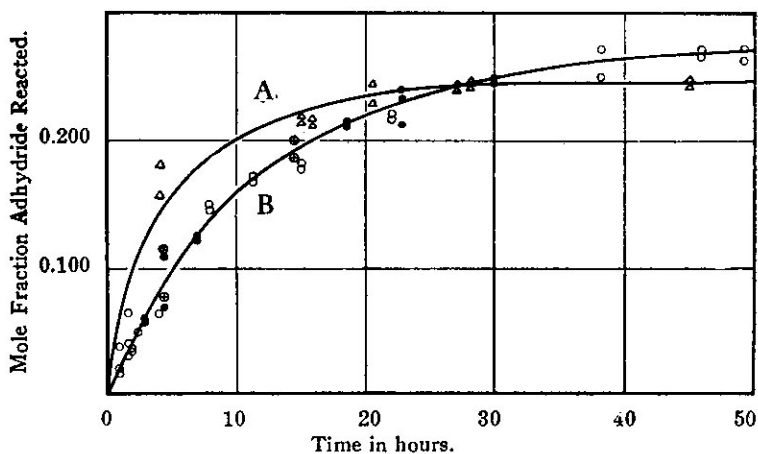

Fig. I.

increased, the "time to half value" being 4 hours as compared with the 8 hours of curve B. Curve A was obtained from anhydride analysing 0.6% acid and is therefore directly comparable to curve B. At 138° the "time to half value" for mixtures made from anhydride containing 5% acetic acid is about 20 hours.

The points ⊕ of curve B were obtained with the bulbs in which the glass surface in contact with the reaction mixture was increased by the addition of powdered glass. The reaction

is seen to be definitely homogeneous, no increase of rate being evident in these experiments.

The reality of the equilibrium was definitely established by experiments in which it was found that the same final concentrations could be reached from either side. Thus after a few hours' refluxing with 0.1% H_2SO_4 an equimolecular mixture of aldehyde and anhydride was indistinguishable as regards both analyses and physical properties from a quantity of ester given the same treatment. At atmospheric pressure the final temperature in each case was 140° at which the ester concentration was 35 mole % When no catalyst was employed about a week's refluxing was necessary to reach equilibrium.

Application of the van't Hoff isochore to the three equilibrium points obtained gives a heat of reaction of about 6,400 cal. per mole of ester formed and indicates that the latter under equilibrium conditions is about 80% dissociated at 195° where ordinarily it distils unchanged. Experiments to be reported in detail elsewhere have shown that in the gaseous state at 210° dissociation is practically complete. It would seem therefore that change of state has but little effect on the equilibrium.

A pronounced maximum in the freezing point curve of the system indicates the existence of a highly associated 1:1 molecular compound the melting point of which is -20°,—50° higher than that of the anhydride and 80° higher than that of the aldehyde. That such "A to B" attraction is appreciable at still higher temperatures is shown by the fact that while both liquids are of the normal unassociated type their heat of mixing has a negative value of several hundred calories per mole at 20°. The vapour pressure curves of the mixtures are likewise highly abnormal and give promise of affording convenient comparisons of the molecular forces involved in the various aldehyde anhydride systems.

That a measurable homogeneous reaction does take place in the liquid state between molecules which exhibit an attraction of the order indicated in the preceding paragraph is qualitatively in harmony with the ideas outlined in the above introduction. Any quantitative conclusions must await the investigation of other aldehyde anhydride systems.