

CURVED ARROWS AND THE ELECTRONIC THEORY OF ORGANIC CHEMISTRY*

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The historical genesis of the curved arrow in organic chemistry is described during the debate in the pages of *Chemistry and Industry* (Review Section) from 1923 to 1926 between Robert Robinson, Christopher Ingold and others. Following Ingold's article in *Chemical Reviews* in 1934, the gradually increasing use of the curved arrow, first in advanced research level books on physical organic chemistry and then in entry level organic chemistry textbooks, is discussed.

La genèse historique de la flèche courbée en chimie organique est le sujet de débat sur les pages de *Chemistry and Industry* (Review Section) depuis 1923 jusqu'à 1926 entre Robert Robinson, Christopher Ingold et d'autres. On discute de l'usage progressivement accroissant de la flèche courbée d'abord dans les livres au niveau de recherche en chimie physico-organique et ensuite dans les manuels de chimie organique de première année d'études universitaires.

Introduction

In the preface of a recently published textbook for teaching organic reaction mechanisms (Weeks, 1992), the author remarks, "At the introduction of resonance or mechanisms, the professor begins using little arrows that resemble fish-hooks.* Using these arrows, electrons are moved around molecules and appear - is if by wizardry - precisely where the professor needs them. The penchant for moving electrons has earned organic chemists the pejorative *electron pusher* that .. we wear proudly." In agreement with this statement, the curved arrow has been called "the most important symbol in twentieth-century organic chemistry" (Brock, 1992). In another text (Scudder, 1992), the author warns, "We use the concept of electron flow together with rigorous use of curved arrows as an electron book-keeping device. The use of curved arrows without mechanistic constraint has been rightfully criticized. Because a process can be drawn with arrows has no bearing on its correctness. It often seems that novice "electron pushers" are just trying to rearrange the lines and dots of reactant structure into the lines and dots of product structure with a minimum number of intermediates.... There is much less tendency to write nonsense with arrows if you are assembling proven mechanistic units, the electron flow pathways."

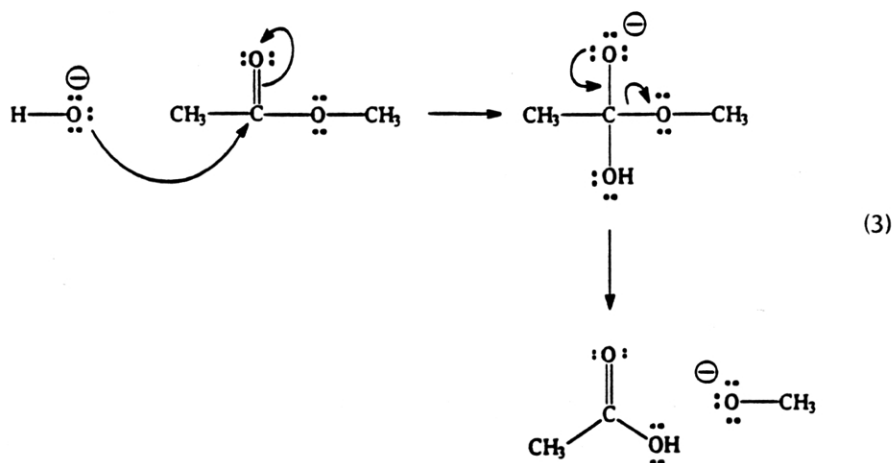
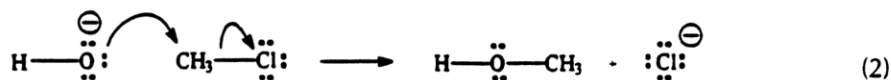
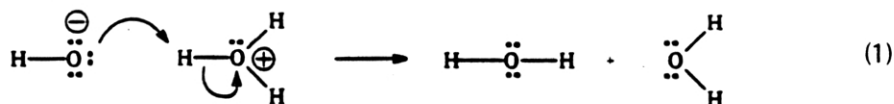
Three examples of the use of these arrows for reaction steps, as they would appear in modern introductory organic chemistry texts, are presented. The tail of the arrow shows where the reactive electron pair is and the head shows where it is going. The curved arrows then generate new structures that appear as product(s).

Equation 1 shows the neutralization of a base (HO^-) by an acid (H_3O^+). In the Brønsted definition, the acid is a proton donor and the base is a proton acceptor. In the Lewis definition, the base is an electron-pair donor and the acid an electron pair acceptor. For the latter definition, electron flow is clearly illustrated by the curved

* Dedicated to the memory of Walter J. Chute.

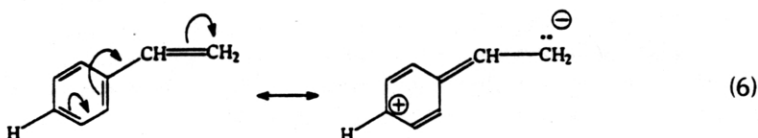
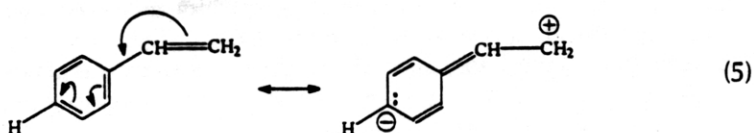
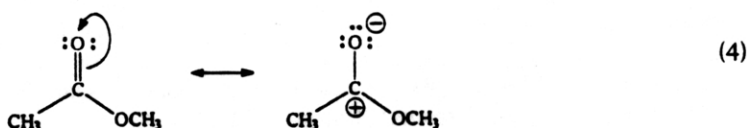
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* This term is normally used to indicate homolytic bond cleavage and formation. In this paper double headed arrows represent motion of electron pairs, i.e. heterolytic bond formation and cleavage



arrows which are book-keepers of the charge. As electron density moves from negative hydroxide ion to positive hydronium ion, the oxygens of both become neutral. Equation 2, an S_N2 substitution, also shows the Lewis base acting as an electron-pair donor; hydroxide ion (HO^-) is now called a nucleophile because it reacts with an electron deficient carbon-centered acid called an electrophile; i.e. an electron pair acceptor or Lewis acid. The saponification of an ester (Equation 3), shows how the curved arrow method can be applied to a two-step reaction. The rate-determining step, reaction of the hydroxide ion (nucleophile) with the carbonyl carbon (electrophile), leads to an intermediate which then rapidly decomposes to the products.

It is often possible to draw more than one resonance structure for a compound or reaction intermediate (a double headed arrow defining contributing resonance forms) and curved arrows can be used to illustrate which electron pairs change position when a new structure is generated. In Equation 4, because oxygen is more electronegative than carbon, there is no ambiguity about the polarity of the bond represented by the charge-separated resonance form. This polarity indicates why the carbon should react with nucleophiles and the oxygen with electrophiles. In Equation 5, the charge-separated form suggests that the methylene group will react with nucleophiles, while Equation 6 infers that it will react with electrophiles. These examples illustrate that although curved arrows can be drawn for two possibilities, one must understand which makes more chemical sense. In this case, styrene reacts rapidly with electrophiles (Equation 6) but not with nucleophiles (Equation 5).



This interpretation of reactions by the movement of electrons, represented by curved arrows or sometimes more colloquially “curly arrows”, is now a ubiquitous part of the thinking of organic chemists, but most practitioners of this field have little knowledge of how these concepts of the electronic theory came to dominate organic chemistry.

The history of the development of the electronic theory of organic reactions

The birth of this electronic theory and the accompanying curved arrow is one of the more colorful episodes in the history of organic chemistry. The theory of organic reactions developed over about three decades, and started just before the beginning of the twentieth century, with two publications by Thiele (1899) in which he postulated “an affinity residue or partial valency”. Flürscheim (1902) used these publications and Werner’s theory of variable valency to develop his own theory of alternate affinity to explain the *ortho/para* to *meta* ratios of the products of aromatic substitution reactions. He continued the development of his theory for the rest of his career and was never able to accept the concept of the electron pair in covalent bonding and organic reactions. This concept of a chemical bond was introduced by Lewis (1916), but it took several years, and Irving Langmuir, who “was to act as publicist for the shared pair immediately after the First World War” (Brock, 1992, p 477) to impress its importance on the organic chemist.

About 1916, Arthur Lapworth, one of the first chemists to elucidate mechanisms of organic reactions, put forward the theory of alternating polarities. Robert Robinson, who was a colleague of Lapworth’s at Manchester University, began using this theory in his interpretation of reactions at about the same time, though Lapworth did not publish his theory until 1920 (Lapworth, 1920). By 1922, Robinson had picked up the electron pair theory of bonding and then he began writing organic reactions in these terms, using a curved arrow to denote the movement of electron pairs in a molecule (Kermack and Robinson, 1922). Arrows had appeared in the earlier literature, but this was the first use made of them to indicate the movement of electrons. These ideas began to appear in advanced texts almost immediately (Cohen, 1923) although a review of them was not encouraging: “This is perhaps the least satisfactory portion of

the book, because it is doubtful whether any useful purpose is served by burdening the students' mind with a mass of theoretical and practical detail much of which is non-proven and all of which is highly controversial. Its intrusion at the present time is apt to lead to confusion if only because its many votaries seem incapable of reaching agreement among themselves" (Thorpe, 1923).

No doubt the modern theory of organic reactions would have assumed, more or less, its present form even had the leisurely pace of advance continued. However, it was given a volcanic upheaval in the mid-1920's. This extraordinary episode in the development of the theory of physical organic chemistry was played out at the monthly meetings of the Chemical Society in London, in the reports of those meetings and in the letters to the editor in the review section of *Chemistry and Industry*. Over the course of about three years, the debate led to a transformation of the pre-electronic theories of organic chemistry of Thiele, Flürscheim and Lapworth to the beginnings of the modern view of organic reactions based on Ingold's terminology and concepts.

"It also left Robert Robinson feeling that his contribution to the new theory had been unacknowledged and that Ingold, in fact, had stolen his ideas. He carried this grievance for the rest of his 88 years and was still calling "Stop thief!" from beyond the grave, since he renewed the cry in his autobiography, which was published posthumously, the year following his death. "... these ideas constituted, in the writer's [Robinson] opinion, his most important contribution to knowledge..." (Robinson, 1976). There were many who felt that this grievance caused Robinson, in later years, to block the award of the Nobel Prize to Ingold. There is, however, no evidence that Robinson ever did more than fail to support Ingold's nominations for the prize.

There were five principal players in the debate, the oldest of whom was Lapworth, 51 years old in 1923. Next was T. Martin Lowry, 49 years old and professor of physical chemistry at Cambridge. Both of these men had been taught by H.E. Armstrong in London. Third was Bernard Flürscheim, a chemist of independent means, born in Baden Baden, and who had studied at the University of Geneva, and then worked at Zurich under Werner and at Strasbourg with Thiele. He obtained his Ph.D. in 1901 at Heidelberg and in 1905 settled at Fleet in Hampshire, U.K., where he built his own laboratory. He remained there for the rest of his life, except for a few temporary paid positions and First World War work. The other two protagonists were younger - Robinson, at 37 had just become Professor of Chemistry at Manchester, junior to Lapworth, and Christopher Ingold, 30, was a Lecturer at Imperial College under J.F. Thorpe. Others, such as Thorpe and Boyd, contributed to the debate from time to time, the subject and emphasis of which often changed, making for an involved and confusing series of events. The main players frequently misunderstood and misinterpreted each other, so that other workers, not actually involved but trying to follow the developments, sometimes broke into print themselves to express their exasperation with the principal participants.

The older men were essentially defending their theories. By contrast Robinson, at the peak of his intellectual powers, and Ingold - who had recently won two Meldola medals and who was in a phase of extreme career acceleration - were both willing to change and develop their ideas. In the end it came down to a conflict between these two.

The dispute initially broke out upon the presentation of a paper at the Chemical Society meeting on June 21, 1923 (Baker, Ingold and Thorpe, 1923) which was one of a series on ring-chain tautomerism in the mutarotation of sugars. It presented evidence that there was no hydrated intermediate in this reaction, contrary to the theory held by Lowry. The argument was not resolved but it can be seen with hindsight that Ingold was arguing that the water molecule was not involved in the rate determining step of

the reaction, whereas Lowry was arguing that water was involved somewhere in the overall reaction. They were, in fact, both right; the differences expressed were academic and Lowry signed Ingold's nomination proposal for election to the Royal Society.

However, in June 1924 the controversy began in earnest with a paper by Boyd (1924) entitled "Hydrolysis and the theory of induced polarities" which cited results in direct conflict with the theories of Lapworth and Robinson. Robinson responded vigorously, claiming that Boyd had wrongly interpreted his examples. Lowry maintained that there was no justification for the assumption of alternate polarities in the case of saturated compounds. Flürscheim agreed with Boyd, and G.T. Morgan expressed his exasperation with a theory whose proponents continually shifted their ground. Ingold moved to support Boyd's paper "as a much needed protest against *ex cathedra* utterances relating to polarity theory, and the chosen evidence by which it was widely upheld; moreover, the type of criticism employed was very widely applicable". During his discourse, Ingold wrote the formula of styrene as $^+\text{Ph.C}^+\text{H}:\text{CH}_2^+$ (note Equation 5).

In the July 1924 issue of *Chemistry and Industry*, Lowry published a letter (1924b) objecting to this formula of styrene apparently carrying a positive charge as if it were a univalent cation like NH_4^+ . He wrote "There is no need for me to defend the theory of induced alternate polarities, which is quite secure in its Manchester stronghold. My own responsibility has been incurred in suggesting an electronic mechanism, which makes the phenomenon inevitable in conjugated systems undergoing chemical change, but has also the effect (fortunate or unfortunate) of limiting it to conjugated systems - except, perhaps, in those cases where a single bond can be ionized or activated in the same way as the double bonds of a conjugated system".

Thus, Lowry demonstrated that he had a clear concept of how the theory of organic reactions was developing. Despite this, his letter triggered vigorous responses. The first came from Lapworth (1924) who claimed that, historically, the + and - signs had been used, "to indicate the *kind* of electrification, and this therefore had priority over the quantitative application. It seems to me undesirable to restrict the significance of the older signs, and the onus of finding new signs with a quantitative meaning such as Professor Lowry requires for his electro-covalent double bonds rests with him". Lapworth's historical argument was, rejected by chemists and the + and - signs were retained only for full charges. Another terminology, $\delta+$ and $\delta-$, was invented by the Ingolds (Christopher and Hilda, his wife) for fractional charges and was introduced two years later (Ingold and Ingold, 1926). In modern presentations, the better texts do not use $\delta+$ and $\delta-$, instead, partial charges are described by resonance contributors (forms) and the charges on those with charge separation are called "formal charges". Thus in Equation 4, the charges on the right hand structure are formal charges on a resonance "form" but the overall charge on the molecule is zero.

Further letters were exchanged between Lowry and Lapworth into the summer of 1924 and additional contributions to the debate made by Boyd and H.G. Rule, extended into the autumn of that year. Ingold's next statement came on October 16, 1924 in response to a paper presented at the Chemical Society on "The nitration of 2-phenylglyoxime and its carboxylic acids" (Pyman and Stanley, 1924). These authors invoked the theory of induced alternate polarities to explain their results, to which Ingold responded by claiming "equality of consideration for the alternate polarity theory and Flürscheim's theory of variable affinity in cases where the experimental results could be explained equally satisfactorily by the latter as by the former".

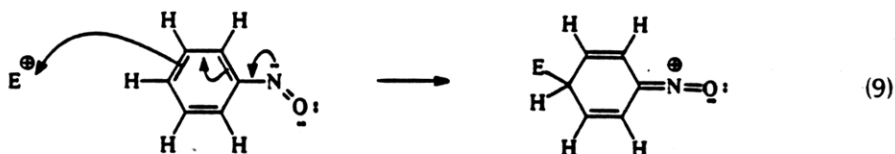
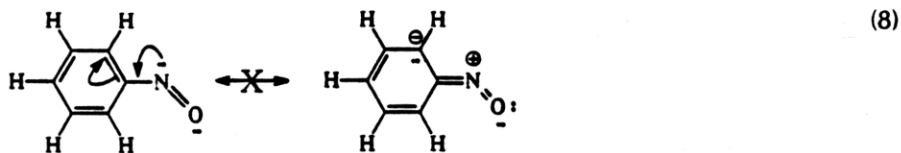
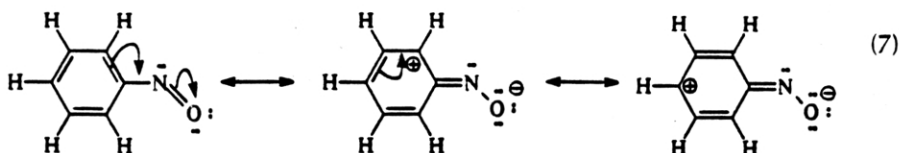
This discussion of the mechanism of nitration of 2-phenylglyoxime focused attention on the problem of the orientation of a second substituent when an aromatic compound

e.g. chlorobenzene, underwent further substitution. Obviously reaction could occur at either the 2-(*ortho*), 3-(*meta*) or 4-(*para*) position and the challenge was to develop a theory which could predict the relative proportions of the three products for any given mono-substituted benzene.

At the December 18, 1924 meeting of the Chemical Society, Ingold (1924) presented a paper on the "Directing influence of the nitroso group in aromatic substitution", stating that "the results are in better harmony with the view that the alternation along a carbon chain is an alternation in the quantity, rather than in the electropolar quality, of the residual affinity". Robinson was not at this presentation but sent a letter (Robinson 1924) that was read by the Secretary and explained why the nitroso group led to *ortho/para* substitution products. This included a diagram using curved arrows to show the flow of electrons in a molecule during a chemical reaction. Although Kermack and Robinson (1922) had used curved arrows two years earlier, this was the first effective use of them in the substitution debate. Robinson wrote, "Representing an electron pair by a line, the following exhibits the covalency change leading to the negatively charged *para* position:



Polar activation and valency redistribution occur simultaneously and are not, as Professor Ingold seems to imply irreconcilable hypotheses".



In retrospect, the nitroso substituent is one for which a prediction of its ability to donate or withdraw electrons by the resonance effect is not obvious. As shown in Equation 7, the nitroso group is electron withdrawing because the π bond of the NO group is conjugated to the π bonds of the aromatic ring. The *ortho* and *para* carbons will be electron deficient. The nitroso group cannot be an electron pair donor because

the lone pair on nitrogen is not conjugated to the benzene π bonds but occupies the orthogonal σ plane (Equation 8). Although the nitroso group could possibly stabilize the *ortho* and *para* intermediate (*para* shown in Equation 9) of electrophilic aromatic substitution by changing its geometry from bent (sp^2 hybridized) to linear (sp hybridized), the experimental observations are that the nitroso group is strongly electron withdrawing (Equation 7) and only activates the ring towards nucleophilic aromatic substitution (Boyer, 1969).

Perhaps because Robinson was not at the meeting, his argument did not capture the audience. Professor G.T. Morgan "disclaiming any knowledge of this plus and minus business" was on the whole inclined to prefer Flürscheim's theory. Flürscheim thought that Robinson was "trying to make on the swings what he had lost on the roundabouts". Ingold reacted uncharacteristically by making no effort to rebut Robinson or to win the debate - he merely said "that his paper was primarily intended to publish a new experimental fact; he found great difficulty in understanding the views expressed by Professor Robinson". Ingold was not a person who frequently had difficulty understanding chemical arguments. At this point he quietly relinquished the position of standard bearer for Flürscheim's theory and concluded the discussion by saying that "The issue could only be settled by crucial experiments in some dozens of suitable cases". Thus 1924 closed with relations between Robinson and Ingold still quite harmonious.

In 1925 Ingold was still searching for the definitive experiment. When he thought that he had it he wrote again to *Chemistry and Industry* (Ingold 1925a) pointing out that Robinson had said that $\text{PhCH}_2\text{N}^+\text{H}_3$, $\text{PhCH}_2\text{NHCOMe}$ and $\text{PhCH}_2\text{NEtPh}$ would all react to give *meta*-substituted products according to the alternating polarity theory. Ingold had found, experimentally, that the first two gave *ortho*- and *para*-substituted products. The third compound was, as yet, untested. However, he did not repeat his indiscretion of the previous year and claim that the polar theory was wrong but emphasized the triumph of experimental results over debate. "That the facts .. though agreeing with Dr. Flürscheim's theory, are opposed to Professor Robinson's predictions, is perhaps an appropriate answer to Professor Lapworth's contention that it is impossible, by experiments on aromatic substitution, to distinguish between polar and non-polar theories of directive action". But Lapworth replied that "the real question was :- do such experiments prove that any of these directive effects are non-polar? - the only truthful answer is in the negative". Ingold eventually had to concede that point.

At the June 18, 1925 meeting of the Chemical Society, Robinson presented a paper "The relative directing powers of groups of the form RO- and RR'N- in aromatic substitutions. Part IV. A discussion of the observations recorded in Parts I, II and III". The paper (Allan, Oxford, Robinson and Smith, 1926) summarized his experimental results and interpreted them in the light of his most recently developed theory. The theory was attacked by Flürscheim in the discussion but Ingold was a lot more cautious saying, "The value of Professor Robinson's theory as a stimulant to research depended on its freedom from ambiguity and the definiteness of its consequences, matters on which it was difficult to form an opinion until the theory had been published. The principle of starting with an *ortho*- compound and considering only substitution on the other side of the ring ... appeared sound and was being employed at Leeds to compare the directive powers of different atoms". Robinson expressed appreciation of Professor Ingold's remarks.

Ingold was still trying to find the definitive experiment to test the two theories, but this was not possible until a final form of the alternating polarities theory was settled. His exasperation with Robinson's "adjustments" began to show in a letter of June 20,

1925 (Ingold, 1925b) which concluded "[Robinson's] letters make it clear that either the verification or the non-verification of Professor Robinson's predictions would constitute evidence in favour of his theory, and that Professor Lapworth holds his opinions with great tenacity".

On August 14, 1925, the first long letter of the debate from Ingold (Ingold, 1925c) appeared, discussing the relative tendencies of trivalent nitrogen, bivalent oxygen and fluorine to set up alternations which control aromatic substitution. Ingold quoted extensively from Robinson's papers tracing the adjustments which Robinson made to his theory to change the sequence from $F > O > N$ to $N > O > F$, the experimentally observed result. The letter concludes "The recent 'adjustment' of polarity theories lends support to Professor Lapworth's denial of the possibility of testing any theory of the origin of directing effects by experiments on aromatic substitution; and I regret that I ever expressed a different opinion on that point. Naturally if the investigated consequences of a theory can be inverted by a change of emphasis, that theory cannot be tested. It remains true, however, that such experiments can *yield information* about the origin of directive power, and may form a *check* on any theory sufficiently precise to be so treated".

Robinson (1925) replied in September, again denying that he had altered his views but admitting that he "had found it necessary to adjust the earlier view of the parts played by conjugation and the general electrical effect respectively". This distinction was one Ingold was unable to see and he replied, briefly to that effect. The continuous barrage of letters debating intricate points of theory and detailed experimental results was completely incomprehensible to many chemists and even to most of those who had some interest in the subjects under discussion. Even the participants had trouble understanding each other and Armstrong's patience ran out about the middle of October when he tabled a motion at a meeting of the Council of the Chemical Society, in his own inimitable style: "that henceforth the absurd game of chemical noughts and crosses be taboo within the Society's precincts and that, following the practice of the press in ending a correspondence, it be an instruction to the officers to give notice 'That no further contributions to the mystics of polarity will be received, considered or printed by the Society'". His challenge was not accepted because no one would second the motion. Nevertheless, a stalemate had been reached and there was a lull in the activities of the antagonists as 1925 drew to a close. Armstrong had never had any time for electronic interpretations of organic chemistry "No one", he said, "would hang him in chains, conjugated or otherwise" He dismissed Robinson's curved arrow with "A bent arrow never hit the mark" (Robinson, 1958).

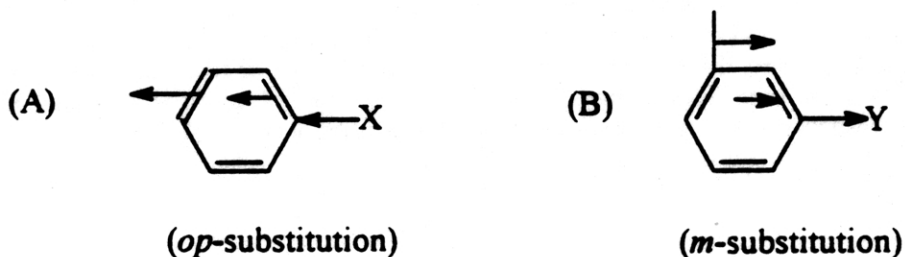
The stalemate was broken when Robinson (1926a) announced new experimental results (Robinson and Ing, 1926) on the nitration of benzylamines, where *meta,meta*-dinitrobenzylamine was obtained from benzylamine - exactly the opposite result to that reported by Holmes and Ingold (1925). Other experiments showed conclusively that amine salts gave *meta* products and free amines gave *ortho/para* products. These results were clearly those predicted by Robinson on the basis of the alternate polarity theory and contrary to Flürscheim's alternate affinity theory. Now it was Ingold's turn to wriggle and he did so in his reply (Ingold, 1926a): "This paper, being a preliminary survey of a wide field ... described in each case the main product and by-products *isolated*; it was not stated that nothing else was *present*". Also, "It is true that our results were described as consistent with Flürscheim's theory, but this does not mean they are inconsistent with *general* polarity - the only form of polarity recognized by that theory". Flürscheim also wrote in the same issue, with more detailed argument and an account of experiments in progress with Holmes, who was now working with him. He got in

one last jab with, "In view of Professor Robinson's many conflicting statements...it is scarcely surprising that, whereas Holmes and Ingolds' results (1925) contributed important and fresh evidence in favour of alternate polarities and a wonderful contribution to the same, Professor Robinson's partly conflicting results are held to be a confirmation of the same theory". Nevertheless, the game was clearly over when Ingold confirmed that his work with Holmes had been in error and that Robinson's results were correct. No doubt the fact that Ingold had published 34 papers in 36 months meant that his supervision of laboratory work was not as close as turned out to be necessary. At this point the Editor of *Chemistry and Industry* closed the correspondence column to this topic with the statement "Discussion of alternate polarities and kindred topics is of great importance, and we hope the letters we have published in these columns have cleared away a considerable mass of misapprehensions. We are, however, obliged to wait for a period before dealing with the subject again; a proportion of our readers fail to understand the whole arguments without a mental effort which is made unwillingly".

The hope expressed was a long shot because surely in most readers' minds "the considerable mass of misapprehensions" had completely swamped them and the mental effort required to clear it away was not so much made unwillingly as entirely beyond their abilities. However, one person had the will and the ability to profit from it, and that person was Ingold.

Ingold had received from Robinson manuscript copies of some of the latter's papers and he returned them with a seven-page covering letter. The letter begins "I return your papers. Thank you for letting me see them. They represent in my opinion a very fine effort, especially on the theoretical side, and the theory is certainly one of Organic Chemistry and not of aromatic substitution only". At the bottom of page 5 of his letter, Ingold says "I am glad to hear your benzylamine paper is shortly to be published. I shall also publish again on the subject but am not ready just yet. When I do I shall turn right around. I do not care two straws what the public in general...". Robinson lost page 6 of this letter, but its absence does not prevent the conclusion that Ingold had now abandoned Flürscheim's theory in favour of an electronic view of organic chemistry.

Chemistry and Industry continued to report Chemical Society Proceedings and on March 18 recorded Robinson and Ing's (1926) paper on the nitration of benzylamines. At the meeting Ingold said "that his view, which agreed in principle points with Robinson, was based on accurate determinations by Dr. Goss ...the ion directed *meta* to the extent of more than 80% and the uncharged molecule almost wholly *ortho/para*". At a subsequent meeting (May 6, 1926), Ingold presented six different papers including "The nature of the alternating effect in carbon chains." Parts IV, V, VI and VII (Ingold 1926c). It was part V (Ingold and Ingold, 1926) with Hilda Ingold, which most clearly set his path by applying a single set of principles to different types of organic reactions. For aromatic substitution he talked about "electronic strain" transmitted from the



directing group through the benzene ring resulting in either a relaxation or constraint upon electrons, without actual transference.

"(A) represents an electronic interpretation of Flürscheim's mechanism for the development of partial valencies, and the strain directions correspond with Robinson's electron-transference paths...This combination of postulates appears to retain all the advantages and avoids the more obvious inconsistencies and difficulties of the theories recently published and discussed". In other words this was a new theory, i.e. Ingold's theory. It may be noted that he avoided using curved arrows although he had previously used them in private correspondence with Robinson and in published papers.

Robinson was not present at this meeting but sent a communication noting that by courtesy of Professor Ingold he had had the opportunity to read the papers presented. He wrote (Robinson, 1926b), "The views now adopted by Ingold and his collaborators differed in no fundamental respect from those already advanced at various times by Lapworth and himself. The advocacy of non-polar theories of alternation, so characteristic a feature of Parts I, II and III of this series, have now been abandoned and this development was welcomed". In reply, Ingold said "The authors preferred their own view....and that in formulating it much benefit had been derived from consideration both of Flürscheim's theory and Robinson's. Since many important principles of Flürscheim's theory had now been reproduced in electronic language, it could not be sweepingly described as having been abandoned" (Ingold, 1926d).

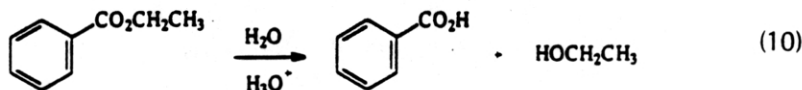
This essentially concluded the great debate on the theory of organic reactions. It was not an attack by Ingold on Robinson, nor was it an exercise in exchanging insults as some light-hearted accounts have alleged. It was a serious scientific debate in which the participants were seeking the truth. They occasionally became irritated with each other but in general they kept their tempers remarkably well. Robinson and Ingold, both changed their views in the light of their experiments and worked to find the correct theory which could be applied to all organic reactions. In fact, they were sorting out the two major effects of a substituent, called in modern terms inductive and resonance effects, and, at the same time, the structure and reactivity of electrophiles and nucleophiles. In this they were successful. However, whereas Robinson basically disliked argument and debate and was worn down by it, Ingold loved it and was vitalized by it. When the debate was over, Robinson went back to his natural product chemistry.

In contrast, Ingold continued to recast the electronic theory of organic chemistry in his own terms and supported it with a prolific flow of research papers. In 1926, he reversed the sign of the inductive effect of the methyl group from negative, as it had been denoted by Robinson, to positive. The reason he gave for this change was quintessential Ingold, "The electron releasing effect of the methyl group in toluene increases the electron density in the aromatic nucleus, and the differential coefficient of an increasing quantity is positive" (Shoppee, 1984).

In 1932 Ingold was forced to interrupt his research work because of problems with his eyes. The cure took the form of an extended visit to California where he wrote a review "Principles of electronic theory of organic reactions" (Ingold, 1934). This quickly became the seminal source on the theory of organic reactions for research workers on both sides of the Atlantic. From this source, Ingold's terminology and Robinson's curved arrows moved into the mainstream of chemical thought.

The assimilation of the electronic theory and curved arrows into the teaching of organic chemistry

An inspection of modern text books used for teaching introductory organic chemistry will reveal detailed multi-colour graphics of organic reaction mechanisms. An example is shown (without the colours) for the acid-catalyzed hydrolysis of an ester, Equation 10 and Fig 1*, from the book currently used at Dalhousie University (Ege, 1994).



One of the reasons that this text was selected is the clarity of the schemes: complete Lewis structures with all lone pairs of each intermediate in the step-by-step mechanism and careful use of curved arrows to show all bonds formed and broken. As well, there is continuous qualitative discussion of reaction rate as a function of the structure of both substrates and reagents. In good modern textbooks (Carey, 1992), curved arrows are introduced as soon as possible. For reactions; "*Curved arrow notation* is used to show the electron pair of the base abstracting a proton from the acid. The *pair* of electrons in the H-A bond becomes an unshared pair in the anion, :A⁻. Curved arrows track electron movement, not atomic movement." (p 124).

For resonance; "What we try to show by the resonance formulation of ozone is the delocalization of the lone-pair electrons of one oxygen and the electrons in the double bond over the three atoms of the molecule. Organic chemists often use curved arrows to show this electron delocalization" (p 24).

The pedagogical reason for this approach is obvious. With practice, students do not have to rely entirely on memorizing reactions and mechanisms. They learn to predict what steps make chemical sense by a logical understanding of acids, bases, electrophiles, nucleophiles and formal charges. This approach attempts to minimize the problem as expressed by Conant in 1928 (Wheeler and Wheeler, 1982): "It is generally conceded that in order to teach any subject effectively, it is first necessary to arouse an interest in it. This is not easy in the elementary course in organic chemistry because of the bewildering array of facts and formulae which confront the beginner."

Conversion of text books to this modern standard was a slow process after the development of the concepts in the 1920's and 30's. Probable reasons for this delay were both the expense and difficulty, until recently, of producing graphics of this quality. However, the major reason was surely intellectual. Many years were required to convince academics that the ideas of the electronic theory were essential to understanding organic chemistry even at the research level, let alone at the introductory undergraduate level.

An interesting observation is the contrast in the use of curved arrows to describe resonance forms (electron density distribution in a molecule) as opposed to reaction steps (making and breaking of bonds). The first curved arrows used (Kermack and Robinson, 1922) describe how resonance in a triene leads to reaction by addition at the terminal ends. By 1926, Robinson was systematically using curved arrows for reaction steps. For instance, his description of the mechanism for the bromination of anisole is reproduced below where the arrows, labelled a, represent the first step

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† Note equation 1.

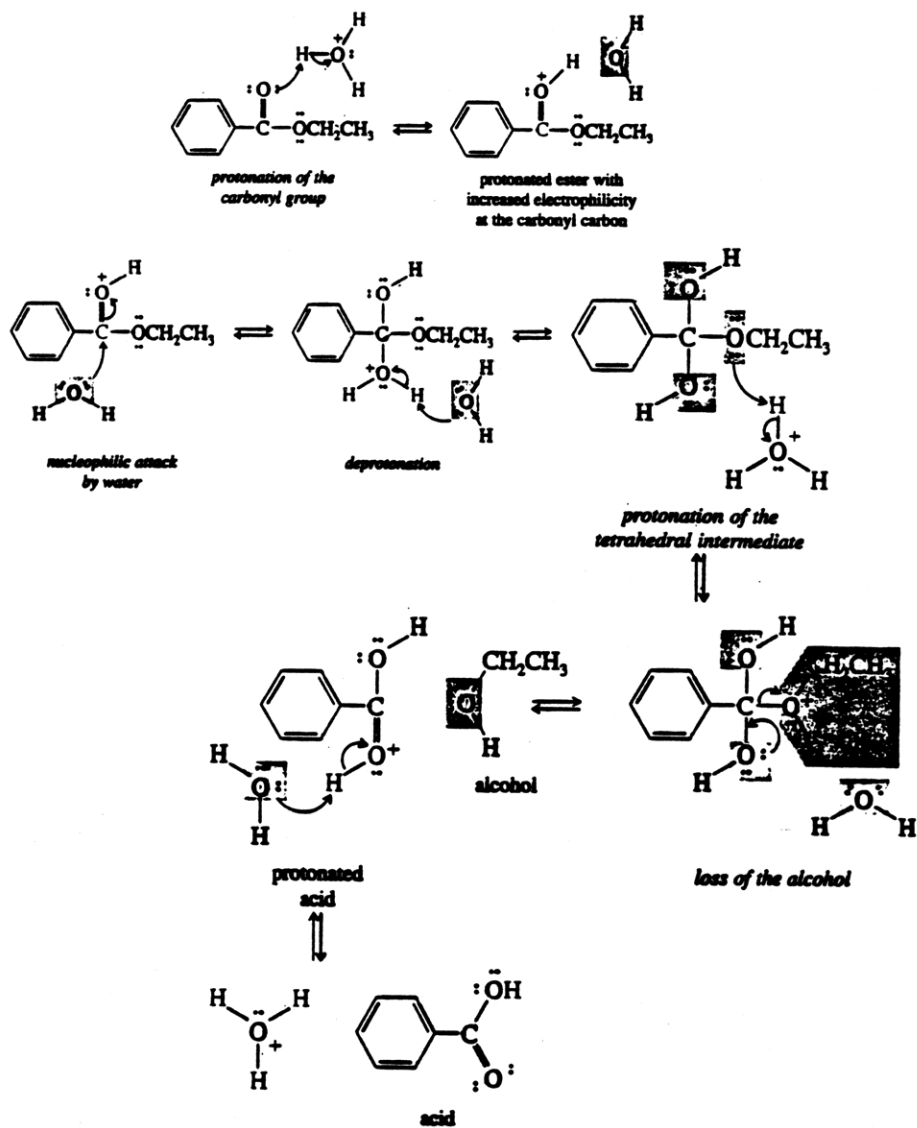
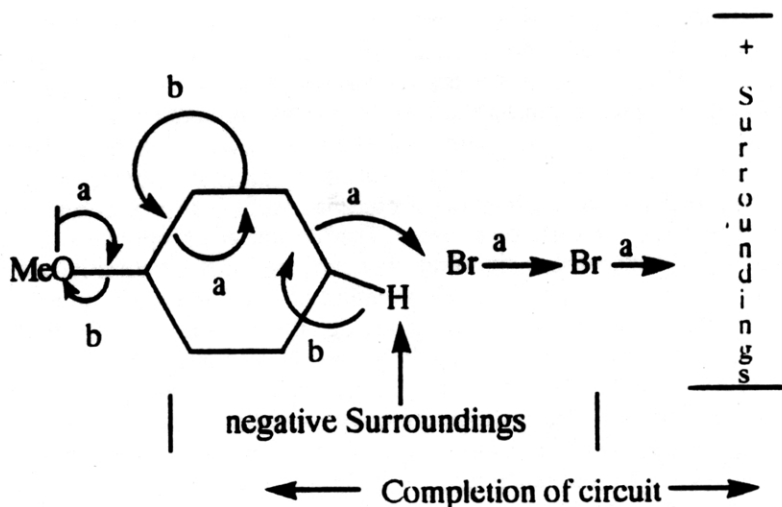


Fig 1 Acid-catalyzed Hydrolysis of an Ester.



showing the *para* directing ability of a CH_3O group (the vertical line on the oxygen represents a lone pair of electrons) (Robinson, 1941 citing *Chem. News*, 133: 3455; 1926). The arrows, labelled b, describe the second step, deprotonation at the *para* position. The diagram provides an interesting analogy to an electrical circuit.

By contrast, in his 1934 review, Ingold only uses curved arrows for the interconversion of resonance forms. In 1953, Ingold wrote his definitive text (as a consequence of the Baker Lectureship at Cornell University in the fall of 1950) summarizing the advances in the electronic theory over some thirty years of his scientific career. Even by that time, he used curved arrows to describe reaction steps only sporadically. In the modern introductory text examples used above, Ege uses curved arrows for reaction steps, but not for resonance forms, and Carey uses them for both.

The original ideas of the electronic theory led to the development of the subject specialty called physical organic chemistry, first by Hammett (Hammett, 1940). Recent reviews (Saltzman, 1986; Tarbell and Tarbell, 1986; Brock, 1992) emphasize that although this subject developed from the ideas and research of the English school in the 1920's and 30's, the modern quantitative detail of physical organic chemistry was mainly American. The major thrust of organic chemistry in England continued to be synthesis and natural products, Ingold's and his collaborators' research groups being one exception.

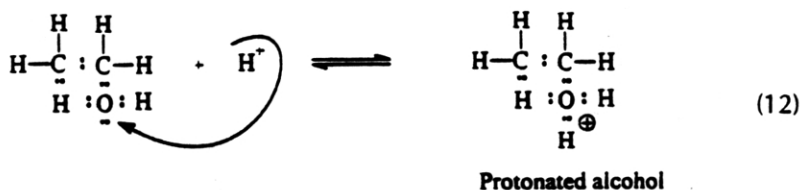
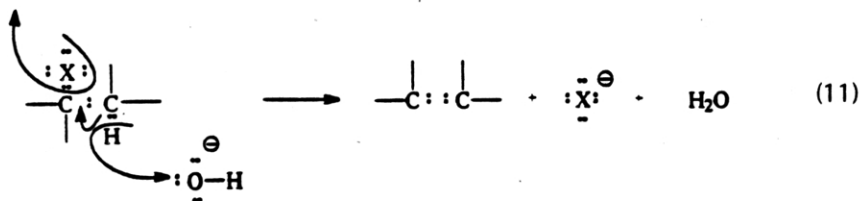
Although research level books in both physical and synthetic organic chemistry finally began to include the electronic theory and the mechanistic approach, they did not adopt curved arrows. Thus, over a period of fifty years a series of physical organic books (Hammett, 1940, 1970, p 332; Remick, 1949, p 413; Alexander, 1950, p 224; Ingold, 1953, p 779; Gould, 1959, p 318; Hine, 1962, p 277; Wiberg, 1964, p 443; Lowry and Richardson, 1987, p 720; Carey and Sundberg, 1990, p 466) discusses the mechanism of ester hydrolysis using schemes devoid of curved arrows as well as the lone pairs required for Lewis structures. It is as if the "pure" physical organic chemists' approach was to avoid the descriptive crutch of the curved arrow. These books do use the curved arrow notation, at least sporadically, for other reactions and some (Remick, 1949; Alexander, 1950; Ingold, 1953) use them very consistently for resonance forms.

The conversion of introductory text books to the mechanistic/curved arrow approach was also a slow process. For instance, the book (Kipping and Kipping, originally Perkin and Kipping) used by the father of one of us (JAP) at the University of Manitoba

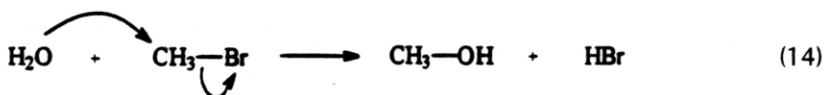
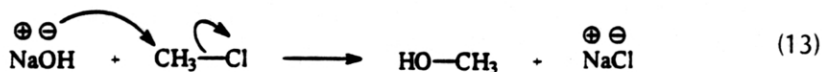
in 1935 went through numerous editions, the first in 1894 and the last, more than fifty years later, in 1948. It used the classical approach which simply catalogued and described the numerous reactions of the various organic functional groups. As was traditionally done, it also separated aliphatic (Part I) from aromatic (Part II) chemistry. By this time, of course, Ingold had written his definitive review, but not a word of the theory is incorporated into this popular text book of the time. As described above, the effect of substituents in directing electrophilic aromatic substitution reactions was a key to the understanding of the electronic theory. The Kipping and Kipping text states very clearly (p. 384) that if one wants *p*-chloronitrobenzene, one must nitrate chlorobenzene, but to obtain *m*-chloronitrobenzene, chlorination of nitrobenzene is required. No explanation of the reasons for this is given although the importance of Crum Brown's empirical rule as an aid in remembering these and similar facts is stressed (p. 382).

In 1952, one of us (KTL) studied introductory organic chemistry at University College, London with E.D. Hughes, Ingold's long-time collaborator. The text used was Finar (Finar, 1951) and the use of curved arrows is introduced on page 15 for generation of two charge separated resonance forms of carbon monoxide in a discussion of the polarity of the C-O bond. However, presentation of reaction mechanisms is limited and curved arrows seldom appear. In the section on aromatic chemistry, the electronic theory of substitution is briefly reviewed (p. 413-421) and curved arrows are used to show resonance effects of substituents. Some curved arrows are included in the discussion of ester hydrolysis (p. 148).

In 1962 Morrison and Boyd's (1959) textbook, which at one time commanded 90% of the American market, was used by the other of us (JAP) at the University of Manitoba. This book was heralded because it consistently used a mechanistic approach to the learning of organic chemistry. This learning process was hung on a framework of electronic theory and did not require committing a catalogue of organic reactions to memory. However, the book did not use curved arrows consistently to describe electron flow. For instance, in the first edition, curved arrows are used on p 113 for an E2 elimination reaction as reproduced in Equation 11 - the arrow on the right violates the electron movement convention, which was not defined. Another example (p. 117, Equation 12) may be compared with the currently accepted arrows in Equation 1 for a proton transfer step.

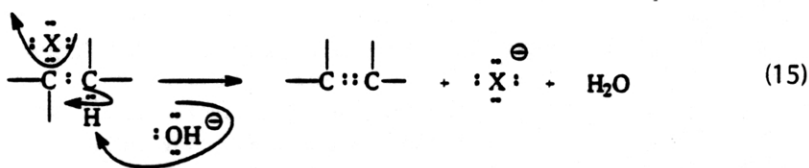


Another novel book (Cram and Hammond, 1959) emphasized reaction types grouped by mechanisms as opposed to the usual functional group approach, but the use of curved arrows was omitted for the generation of resonance forms. They were used for chemical reactions and were introduced for nucleophilic substitution on p. 199, "in order to indicate the direction of flow of electrons in equations, curved arrows are frequently added to the formulas". Surprisingly, the next sentence reads, "The arrows do not imply anything about the detailed mechanism of the reaction, which may be very complex". The S_N2 mechanism is shown (p. 199; Equation 13)

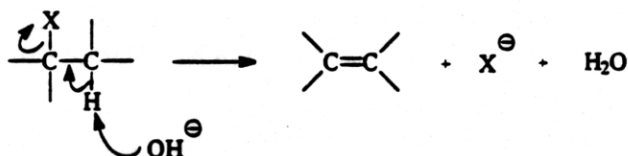


and later (p. 203), in a section on solvolysis reactions the conversion of methyl bromide to methyl alcohol is shown as reproduced in Equation 14. This is also an S_N2 reaction but is stated to be very slow because of the weakness of water as a nucleophile. The next two examples of solvolysis reactions in the book are S_N1 reactions involving a mechanism of rate-determining cation formation but no distinction is made at this point between the two mechanisms. In fact, the details (and Ingold's terms, S_N1 and S_N2) are only introduced in the next chapter and, again curved arrows are not used for reaction steps. Why the authors, who are internationally famous physical organic chemists, did not take the logical step of using curved arrows to describe the individual steps of these reaction mechanisms is not clear. The mechanism of acid catalysed ester hydrolysis is not given, though the initial protonation step is shown (p. 304), albeit without curved arrows.

In 1973, the introductory organic chemistry class at Dalhousie was using the third edition of Morrison and Boyd (1973). In this text curved arrows are first introduced on p. 157 in a rather elaborate style (Equation 15), which is similar to the style used in the



Represented as



*where arrows show the
direction of electron shift*

first edition (Equation 10), but now in accord with electron movement convention. The next equation in the text shows less elaborate arrows, as would be used in a current text, but with the lone pairs of electrons removed. The acid catalysed ester hydrolysis (p. 681) is still shown without arrows or lone pairs.

From 1975 until the present there has been a continuous stream of books, by more than a dozen authors, published for use in the standard full year (two semester) course in introductory organic chemistry. The standard of these books is uniformly high and selection of one by a given University is a difficult task. During this period, the quality of drawings, including the use of curved arrows and complete Lewis diagrams, has continuously evolved and improved. The mechanistic approach as derived from electronic theory is firmly entrenched.

Thus, a fundamental pedagogical tool in the modern approach to organic chemistry had a difficult and contentious birth, followed by a long and confused upbringing over a period of about 60 years, before it finally reached the sophisticated and elegant presentations exemplified by Fig 1 (Ege, 1994).

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