

## THE PROGRESS OF PHYSICAL ORGANIC CHEMISTRY AS MIRRORED IN THE FARADAY SOCIETY DISCUSSIONS OF 1923, 1937, AND 1941

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The Faraday Society Discussion of 1923 titled "The Electronic Theory of Valency" was a stellar affair (1). It was prompted by the 25th anniversary of the "discovery" of the electron and J. J. Thomson himself was in the chair. The opening address was given by G. N. Lewis whose classic contribution to "the ephemeral literature of science," *Valence and the Structure of Atoms and Molecules*, was at the proof stage (2). Other participants included R. H. Fowler, N. V. Sidgwick, W. A. Noyes, W. H. Bragg and, on the organic side, T. M. Lowry (the convener), A. N. Lapworth, Robert Robinson, B. Flurschheim, and J. F. Thorpe. The absence of Thorpe's former student and then colleague, C. K. Ingold, is explained by the fact that he had been married the previous week and was away on his honeymoon in Wales (3). That physicists should be interested in the nature of the chemical bond in those pre-Heitler/London days was not unusual. On August 6, 1922, for instance, Max Born wrote to Albert Einstein(4):

A short notice in *Naturwissenschaften* about the H<sub>2</sub> molecule contains some results of interest to connoisseurs. But the more unequivocal these turn out to be, the crazier the whole system seems. I am not yet on the right track as questions of principle go.

Early in 1923, Born again wrote to Einstein(5):

Then I am going to put this subject into cold storage until the question of homeopolar binding forces between atoms has been solved from Bohr's point of view. Unfortunately every attempt to clarify the concept fails. I am fairly sure though that in reality it must all be very different from what we think now.

The Discussion opened with a few rather perfunctory remarks by Sir Joseph followed by G. N. Lewis' key-

note address. As H. B. Watson was later to observe in the preface to his pioneering *Modern Theories of Organic Chemistry* (6):

Professor G. N. Lewis's conception of the sharing of one or more electron pairs by two atoms gave a new and illuminating picture of the bonds which link carbon atoms into chains and rings, and set organic chemists the task of interpreting the reactions of carbon compounds of various types in terms of the electronic structure of molecules.

In the event Lewis' address was rather low-key, by no means a call-to-arms(7):

Since it is the purpose of such a discussion as the present one to attempt to secure agreement between conflicting opinions, or at least to secure better mutual understanding of divergent points of view, it seems to me that the introduction might well consist merely of a sketch of a few of the more controversial topics chosen from the many which our subject suggests.

Lewis here reiterated his famous statement that "I proposed to represent every [chemical] bond as a pair of electrons held jointly by two atoms." He adumbrates his "magnetochemical" theory of the chemical bond, a theory that was to prove one of the few "ephemeral" parts of his monograph in press (8). He gives no credence to alternating polarity, a matter that was to remain one of the "divergent points of view" at the close of the Discussion.

Lewis, together with Lowry and Thorpe, addressed the difficulty of pinning down some substances to a single electron structure (9):

Rather we may state that no one of the formulae given above expresses the average state of ethylene. Some

molecules may at times approximate to any one of these and possibly other states but the average properties of ethylene would be somewhere between those corresponding to the three formulas, and I think we may state that the great majority of molecules must be nearest to the first structure, as shown by the prevalence of that stereoisomerism which can be ascribed to the lack of free rotation about the double bond.

and further (10):

I hope that Professor Thorpe will present to us in this discussion some of his extremely convincing evidence that there are tautomeric substances which are not to be interpreted by an oscillation between two distinct structures, but rather as a single loose structure of intermediate character which cannot be represented by our existing graphical methods.

These musings would seem to represent the first glimmerings of mesomerism and resonance theory.

In two papers Lowry advocated his semi-polar double bond, even for the case of the symmetrical ethylene molecules, but this came under ironic attack in the Discussion (11) and elsewhere:

The remark that *a double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency is*, with its double qualification, unexceptionable, being no more than a restatement of the fact that unsaturated compounds undergo polar additive reactions - sometimes.

Bond polarity (alternating or not) was a major point of dispute. Thus we find Thorpe pontificating (12):

Organic chemistry is, however, the most exact of sciences, because the organic chemist can build models of his compounds, ask them questions and obtain answers....In the case of the polarity theory, the main point is that its supporters are not yet agreed among themselves, and until they are there is no point in bringing forward any evidence against them. The polarity theory explains everything and predicts nothing.

To which Robert Robinson rather ingenuously replied (13):

The difficulty was that prediction and verification were usually published in the same paper and the reader could not tell which really came first, and in order to show good faith in the theory he would predict the results of some experiments now being carried out by Mr. Oxford in Manchester....

Although he was not one of the invited speakers, the most trenchant voice was that of Bernard Flursheim

(14), a rather shadowy figure whose obituary Ingold was to write in 1956 (15):

Since organic molecules contain atoms with substantially different volumes and total number of electrons it requires courage to assume that they all share the preference shown by many authors for the number 8; and that, to gratify this preference, they will set aside the fundamental laws of electrostatics. ...To summarize, organic facts can be concordantly coordinated on the basis of varying affinity demand in conjunction with general polarity and steric hindrance. Electronic bonds, however, are confronted with serious difficulties by the facts of organic chemistry as well as by the postulates of physics.

In spite of Ingold's absence, this meeting can be viewed as the birth pangs of what Remick was later to call "The Electronic Theory of the English School" (16). In the evolution of this far from homogenous, indeed highly disputatious, "school", Lapworth, Robinson, and Lowry were at first the principal figures. But by the mid-1920's Ingold (with his idiosyncratic ally, Flursheim) was in the thick of the fray. The lively epistolary battles that ensued, mainly in the indulgent correspondence columns of *Chemistry and Industry*, have been described elsewhere (17-20). There was to be no victor and no vanquished at this time, and when Ingold moved to University College London in the summer of 1930 he was briefly the colleague of Robert Robinson, who was about to move on to the Waynflete Chair of Organic Chemistry at Oxford. There are no reports of rancor.

Such was probably not the case in 1934 when Ingold published his magisterial review, "Principles of Electronic Theory of Organic Reactions" (21). This "reads like a legal brief as to how God should have fashioned physical organic chemistry if only He had listened to the best advice" (22). The review opens with the passage:

The electronic theory of organic reactions has now developed to a stage at which it seems desirable to give a connected statement of its principles. Actually these principles have emerged piece-meal in connection with various separate applications of the theory; but the presentation of the subject on a corresponding plan has the disadvantage that the common viewpoint tends to become obscured in what at the outset constitutes a mass of undesired detail.

Among the "undesired detail" would seem to have been much sense of historical fairness. Parts of Lapworth and Robinson's classification of reagents are silently subsumed, and their curly arrows are appropriated. The terms "kationoid" and "anionoid" are dismissed in a

footnote and the more felicitous "electrophilic" and "nucleophilic" introduced in their place. Nonetheless the review does make manifest Ingold's originality and his genius for codification, rationalization, and speculation. In his discussion of mesomerism he marshals evidence from polarizabilities, dipole moments, infrared spectroscopy, and the emerging quantum mechanics. This was an early example of Ingold's ability to bring a wide range of physical insight to bear on the problem of organic structure and reactivity. Surprisingly, there is no mention of chemical kinetics.

Not everyone was pleased by these remarkable developments. Early on H. S. Fry had protested that "the structural formula of the organic chemist is not the canvas on which the cubist artist should impose his drawing which he alone can interpret (23)" while that glorious old curmudgeon Henry Armstrong complained about 'jargonthropos' and slyly observed that "bent arrows never hit their marks (24)."

The three-day Faraday Society Discussion of September, 1937, was titled "Reaction Kinetics" (25). It was divided into two parts: Part I. - General: On the Theoretical Methods of Treating Activation Energy and Reaction Velocity and Part II. - Some Experimental Evidence Bearing on the Discussion of Part I. The program led off with talks by Henry Eyring, M. G. Evans and Michael Polanyi, and Eugene Wigner, who between them had just laid the foundations of quasi-thermodynamic and statistical mechanical transition state theory. This Discussion illustrates the Faraday Society's long-time gift for spotlighting "hot" and controversial topics. The inclusion of extensive verbatim accounts of the spoken and written discussion that ensued provides a fine sense of important science in the making.

The experimental Part II contains papers by C. N. Hinshelwood, Louis P. Hammett, and Ingold's bright young proteges: Christopher L. Wilson and Edward D. Hughes. Strangely, Ingold himself did not make a formal presentation (though he participated in the Discussion) but his Svengali-like presence can be sensed in Wilson's paper on the "Rate of Ionisation Part I. Ionisation of C-H Bonds" and in Hughes' two papers on the "Rate Of Ionisation. Part II. Ionisation of C-Hal Bonds" and on "Aliphatic Substitution and the Walden Inversion."

There is a singular appropriateness in the marriage of reaction kinetics and physical organic chemistry found in this Discussion. Although Lapworth (26, 27) and others had already made shrewd mechanistic use of kinetic rate laws, it was Hughes and Ingold who largely consummated the union. By 1937 Ingold's mechanistic sym-

bolism:  $S_N2$ ,  $S_N1$ ,  $S_E2$ ,  $S_E1$ ,  $E2$ ,  $E1$ , etc., was established, at least in the English literature (28), and many of his neologisms had become standard. In the course of the Discussion that followed Hughes' second paper he makes a seemingly impromptu addition to the list (29):

I hold that new words, like falsehoods, should be invented sparingly, but if chemists as a whole feel one of the former to be necessary here, then I would suggest that we may as well have two and be done with it: *viz.*, "heterolysis" and "homolysis" defined as follows:



Here the dots represent electrons, whilst charges on A & B are subject to the balancing of the equations but are otherwise designedly unspecified. Be it understood I do not *advocate* this step .....

The disclaimer notwithstanding, the coinage quickly joined the others already in the literature.

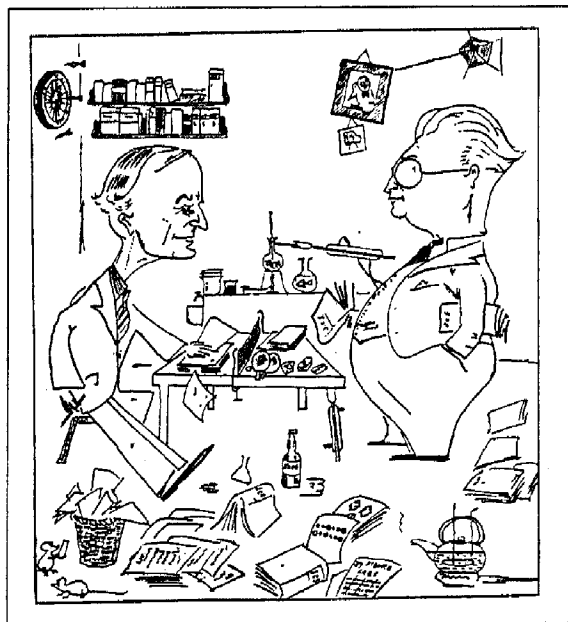
Not everyone was enraptured by Ingold's proliferating nomenclature and symbolism. In the US, where activity in physical organic chemistry was already at a high, if not yet dominant, level, little notice was given to it until the appearance of Remick's *Electronic Interpretations of Organic Chemistry* in 1943 (16). In the preface to Branch and Calvin's *The Theory of Organic Reactions* published in 1941 we find (30):

C. K. Ingold, whose contributions to electronic structural theory are second to none, has developed a language to express his ideas. We have given scant recognition to his language, and have even taken liberties with it. Actually, we are in very close agreement with Professor Ingold's theories.

A surprising number of Ingold's coinages have survived, though few students (and even junior faculty) are aware of their provenance.

Mention has been made of Ingold's two bright young proteges, Ted Hughes and Chris Wilson. Since the writer was the student of one and later, in Columbus, Ohio, a friend of the other, perhaps he may be permitted a few personal comments. Ted Hughes was a taciturn Welshman and, to this student at least, a rather dour figure. Undergraduates knew little of his ribaldry, his capacity for beer, and his love of greyhounds and dog racing. I took his course "Kinetics and Mechanisms of Some Organic Reactions." I still have my notes and they bring back grim memories. The lectures were meticulously prepared, and their substance was simply copied on the board with every comma and full stop firmly in

place. It was like learning chemistry from an un-droll Victor Borge. However, a vast amount of insight was packed into very few words and, retrospectively, I am grateful. When Hughes was elected to The Royal Society in 1949, I was one of many who shouldered the not inconsiderable burden of carrying him in triumph to a nearby pub.



Ingold and Hughes, ca. 1948  
(cartoon by J. D. H. Mackie)

At the beginning of my graduate work I was assigned the topic of aromatic sulfonation by Ingold. I was to meet with him only two or three times more in the ensuing three years. Meanwhile Hughes was still at the University of Wales, and about once a month he came riding down from Bangor (though not on an Eastern train!) to visit at University College London. The interviews were brief (so often were the progress reports) and Hughes' comments were terse and noncommittal. Finally he would say "Well then, Davenport, carry on." It was research direction by benign neglect, and it seems only appropriate that my thesis work was never to be published (31).

In comparison with Ingold's brilliance both as lecturer and researcher, Ted Hughes seemed to me at that time something of a plodder. How wrong that impression was can be gauged from the two obituary notices Ingold wrote after Hughes' premature death (32, 33). Close to a third of Ingold's papers have Hughes as a co-author, though from internal evidence it would seem that Ingold did virtually all of the writing. Ingold's hand is even apparent when his name does not appear, as in the

magnificent paper on the Walden Inversion and substitution in secondary octyl iodide. Chris Wilson always claimed that Ingold was not a particularly adroit experimentalist, while allowing that Hughes' experimental skills were exceptional (34). What is clear is that Ingold's intuitively brilliant intellectual framework for organic reaction mechanisms could not have been constructed without the buttressing provided by the rock-solid kinetic rate data supplied by Hughes and his coworkers.

By comparison with Hughes, Chris Wilson, a far from taciturn Yorkshireman, had a chameleon-like charm and brilliance, coupled with a sly sense of humor. It is not surprising that at one time Ingold wrote "...he [Wilson] seems to be quite the best student I have ever had (35)." Wilson was more restless and ranged more widely than did Hughes and unlike Hughes he found Ingold's overwhelming intellectual presence at times somewhat suffocating. In spite of his steady progress through the ranks at UCL he felt he had to get away (36). World War II served to direct Wilson to ICI in Manchester, where one of his assignments was to develop expanded plastics and polymeric adhesives for the largely wooden Mosquito aircraft then under development for the R.A.F. This early experience in industrial polymers was to become a principal interest after his post-war emigration to the U.S. After stints at the University of Notre Dame and The Ohio State University, where he worked primarily in organic electrochemistry, he set up his own company and left the academic world. One can only speculate as to what might have happened had he stayed on at UCL, but somehow "Wilson and Ingold" sounds as strange to the ear as does "Burnand and Sullivan."

By comparison with the international character of the 1937 Faraday Discussion, the one held in September, 1941 was, understandably, a somewhat parochial affair (37). This was not a propitious time for an international meeting in London. It was held at the Hotel Rembrandt in South Kensington, and Professor Emeleus is thanked "for providing the epidiascope and other conveniences." The somewhat cart-before-the-horse title of the Discussion is "Mechanism and Chemical Kinetics of Organic Reactions in Liquid Solution." Besides Hughes and Ingold, only Michael Polanyi was a carry-over author from the 1937 Discussion, though Chris Wilson took a lively part in many of the discussions. The total assimilation of transition state theory in the intervening four years is everywhere apparent. Most of the authors were colleagues, or former colleagues, of Ingold who was the organizer of the Discussion. In his "Introductory Remarks" Ingold states:

We may note with gratification that all the papers have avoided, on the one hand, the tendency to be observed among physical chemists to drift obscurely into the misty regions of the general theory of reaction rate; and, on the other, the still surviving tendency among organic chemists towards that picturesque but only pseudo-physical type of speculation, which fifteen years ago might have been justifiable, but today is an anachronism.

Ingold also pays generous tribute to Kennedy Orton, one of the pioneers of detailed studies of the kinetics of reactions in solution, five of whose students participated in the program.

There is little need for specific comment on the individual papers in the 1941 Discussion. Hughes gave a classic summary of "Mechanism and Kinetics of Substitution at a Saturated Carbon" while Hughes and Ingold rendered the same service to "Mechanism and Kinetics of Elimination Reactions" and Day and Ingold to "Mechanism and Kinetics of Carboxylic Ester Hydrolysis and Carboxyl Esterification." Ingold's nomenclature, particularly his symbolism, is on full, indeed effulgent, display. It is almost a relief to find free radicals and radical cations creeping into some of the later papers. With the publication of this 1941 Discussion the Ingold school effectively shut up shop for the remainder of the war.



C. K. Ingold, E. D. Hughes, and E. H. (Hilda) Ingold

Only three papers were published, one of which was, in the mean spirit of the times, a rather savage attack on work by Jander (38).

There were to be no more Faraday Society Discussions on physical organic chemistry, recently so-named by Louis Hammett (39). The topic was no longer "hot" and was soon to enter the mainstream. It might have entered the mainstream even earlier if Ingold's plan to

write a defining textbook had not been delayed by the war. I clearly remember, sometime in 1952, Chris Wilson's showing me a substantial typescript (no doubt typed by Mrs. Ingold) from the late 1930's. He led me to understand that he had collaborated with Ingold on parts of this. There is no mention of this aborted effort (or of Chris Wilson) in the preface to Ingold's magnum opus, *Structure and Mechanism in Organic Chemistry*, published by Cornell University Press in 1953. That book is the capstone of an extraordinary era in the development of a new chemical discipline. It serves as Christopher Kelk Ingold's true memorial. By 1953, however, the center of activity had ineluctably moved across the Atlantic and the appearance, in 1969, of a second edition of *Structure and Mechanism* was, if not anachronistic, at least something of an anticlimax. But then so had been the appearance of the third edition of Linus Pauling's *Nature of the Chemical Bond* in 1960.

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### ABOUT THE AUTHOR

Derek Davenport was a student at University College London from 1945 to 1950. Since 1953 he has been associated with Purdue University, where he is now Professor Emeritus. His interests have been primarily in chemical education and the history of chemistry, and he has served as chair of both the ACS Divisions of Chemical Education and the History of Chemistry. The present symposium is the sixth in a series he has organized over the years.

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