

C. K. INGOLD'S DEVELOPMENT OF THE CONCEPT OF MESOMERISM

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Charles W. Shoppee, in his obituary notice for Sir Christopher Kelk Ingold (1893-1970), wrote(1):

..he was a chemical genius, an excellent physicist, and a talented mathematician, able to employ and to combine all aspects of organic, inorganic, and physical chemistry.

Ingold's enormous output totaling 443 papers covered a vast array of subjects and set the research agenda for physical organic chemistry for several decades. His *Chemical Reviews* paper "Principles of an Electron Theory of Organic Reactions(2)" published in 1934 was for many years the only source for understanding the pioneering work he and other British chemists had done on the interpretations of reactions mechanisms. This paper will deal with one aspect of his work: his anticipation of a development of the concept of mesomerism, which he derived from both physical and chemical evidence. Linus Pauling (1901-1995), using quantum mechanics, developed resonance theory at the same time.

Ingold realized that the Lewis theory was a first step in relating structure and reactivity, but that it did not go far enough. As Ingold wrote(3):

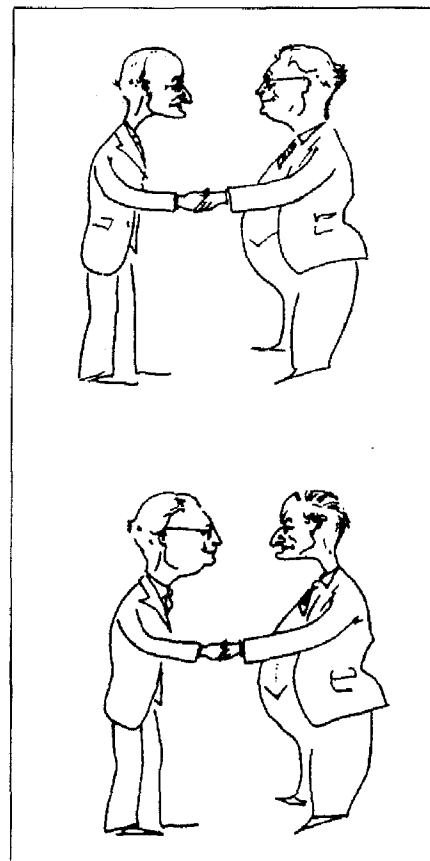
Lewis discovered the material constitution of the covalent bond. But he could not describe the forces involved, because they were of a nature unknown in classical physics.

Lewis's pioneering paper "The Atom and the Molecule(4)" appeared in 1916; just a decade later Ingold was questioning whether certain types of structures represented by the Lewis theory were adequate.

G. N. Lewis (1875-1946) provided little leadership to the organic chemical community in how to apply his

ideas to the problems of structure, reactivity, and mechanism. In

1919 Irving Langmuir (1881-1957) elaborated upon the foundation established by Lewis and introduced the octet and covalent bond concept into chemical thinking. Through his many papers and lectures Langmuir was to have more of an impact than G. N. Lewis on organic chemists. In the US there were only isolated attempts by chemists such as James Bryant Conant (1893-1978) and Howard Lucas (1885-1963) to use Lewis theory. The most fertile ground for the



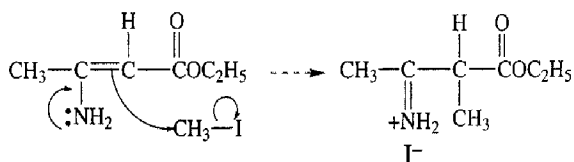
Mesomerism: Ingold metamorphoses into E. D. Hughes. (cartoon by J. D. H. Mackie)

Lewis-Langmuir theory, however was in Great Britain. Langmuir lectured on his work at a British Association meeting in Edinburgh in 1921, and in 1923 Lewis attended a symposium sponsored by the Faraday Society at Cambridge devoted to the use of the electron pair and octet theory.

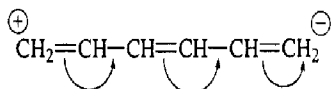
Major strides in the use of the Lewis-Langmuir theory were made in the early 1920's by Thomas Martin Lowry (1874-1936), Arthur Lapworth (1873-1941), and—most importantly—by Robert Robinson (1886-1973). Not until approximately 1925 did Ingold begin to make use of the Lewis-Langmuir theory in his work. Even though his was a somewhat late and shaky start, because of a bitter polemic with Robinson(5), he easily surpassed his rivals in his understanding and use of the new theory.

The positive attitude of the British toward electronic theory may be attributed to several factors. One is the history of the consistent success in attempting to utilize electronic theory in organic chemistry, whereas the American chemical community had been plagued with failures. The second factor is the type of problems that British chemists initially chose to study. Much of the focus was on understanding conjugated systems in general and aromatic systems in particular, for the chemistry of these systems was a "hot" subject in the 1920's. Finally, there was an accepted tradition of theoretical speculation in British organic chemistry and of an openness to new ideas.

Robinson introduced the concept of the mobility of electron pairs in conjugated systems in 1926 (6). For example, he represented the reaction of methyl iodide with an aminocrotonic ester as follows:



An often cited example is the ionic reaction of hexatriene, which is represented as the following doubly charged structure:



Ingold was later to name this the "electromeric effect," the term being borrowed from the American chemist Harry Shipley Fray (1878-1949). In 1926 Robinson published a detailed general theory of reactivity in conjugated systems. He not only invoked the use of electromeric ef-

fects but also suggested how polar effects can influence substitution in conjugated systems.

By 1923 Lowry had already introduced a concept of the double bond as one containing both covalent and ionic attributes or a mixed bond to account for its reactivity in various systems(8). He believed that the polarization was only of a temporary nature and existed at the time of reactions. Lowry was also the first person to realize that formal positive and negative charges must be included in the structures of certain molecules, such as amine oxides.

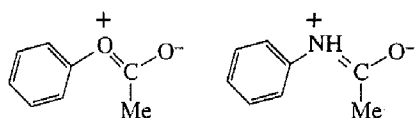
Colin Russell, in his classic study of valence, summarizes the contributions made by Robinson and Lowry(9):

Thus the covalent bond was no longer conceived as a rigid entity with two electrons symmetrically shared between the atoms. A molecule was subject to strains and stresses unimagined twenty years previously, and the valency bonds were more dynamic than static, responding to the demand of a reagent to assist a reaction.

Ingold's late start in this field was due to his use of the concept of partial affinity as being the major determinant in the course of reactions. Between 1924 and early 1926, Ingold relied upon the theoretical framework as developed by Bernard Flurschheim (1874-1955), who had studied with Johannes Thiele (1865-1918) and Alfred Werner (1866-1919). He advocated the use of residual affinity as the basis of his theories. A substituent could exert a strong or weak affinity demand on the carbon to which it was bonded, and this effect would be carried along a chain in an alternating manner. Implicit in Flurschheim's theoretical framework was the notion that affinity was continuously divisible and was partly bound and partly free. In 1924 Ingold was a rising star in British chemistry, having just been made a Fellow of the Royal Society and appointed Professor of Organic Chemistry at Leeds University. He may have sought to enhance his stature by engaging in studies of aromatic substitution, a subject of intense interest. His interpretation was contrary to that of Robinson; and over a period of approximately two years Ingold and Robinson engaged in bitter and at times personal polemics concerning the mechanism of aromatic substitution. By late 1925 Ingold knew that Robinson was correct and started to use many of Robinson's ideas concerning the mobility of the electron pair in conjugated systems. The 1926 paper (10), "The Nature of the Alternating Effect in Carbon Chains, Part V," which Ingold published with his wife Edith Hilda (1898-1988) as the co-author, was

to be the beginning of the series of events which shall form the major focus of this paper.

Ingold attempted to place himself into the mainstream of chemical science by showing that his previous theoretical framework for interpreting aromatic substitution was compatible with the views of Robinson. In this paper several insights are presented that had been previously overlooked by others. For example, in discussing the depressive effect of the acylated substituent as compared to an alkyl group with regard to *o,p*-directive power, he proposed the following structures for the acyloxy and carboxyamido groups and commented(10):



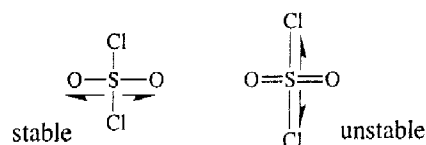
...a modernized interpretation of which would involve the recognition of a betaine-like phase (or a condition corresponding with partial conversion into such a phase), the bond joining the oxygen atoms being an electrovalency. In the carboxylamide group, the nitrogen atom will necessarily constitute the positive end of the betaine linking, and thus forms arise which...would be expected to diminish the tendency to *o,p*-substitution.

Thus, we can see from this quotation the crucial idea that polarization by the electromeric effect may have a permanent aspect. The actual state of the molecule may be intermediate between the two structures, an anticipation of the concept of mesomerism and resonance.

Ingold also offered a rationalization for why certain reagents such as phosphorus pentachloride, iodine trichloride, and sulfuryl chloride will produce a positive chlorine ion in aromatic substitution, whereas we usually expect a negative chloride ion from these reagents. To understand this, Ingold proposed that the chlorine in these compounds separates as a neutral or positive group that would then seek a negative center. As Ingold pointed out, "...phosphorus pentachloride readily chlorinates anisole in the *p*-position, but has no action on nitrobenzene(10)."

In a footnote Ingold indicated that measurement of the conductivity of phosphorus pentachloride in nitrobenzene produces such a low value that it would not be compatible with an ionic structure such as $(\text{PCl}_4)^+(\text{Cl})^-$. In describing the structure of phosphorus pentachloride he stated "the bonds by which the labile chlorine atoms are held might be termed semi-polar single bonds and written to avoid use of signs such as $1/2^+$ and $1/2^-$ (10)." The semi-polar bond idea had been developed by Lowry, although Lowry's use of it was

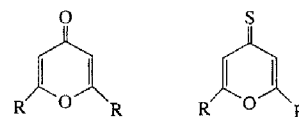
not well understood by his contemporaries. Structures for sulfuryl chloride incorporating these ideas are reproduced below(10):



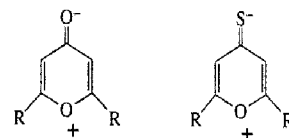
Sulphuryl chloride may be regarded as having two electromeric forms, the stable one containing two semipolar double bonds (X), and the other only one semipolar double bond and the two semipolar single bonds (Y). It is the latter which contains the labile chlorine, and it would be in this form rather than the first which is concerned in chlorination by sulphuryl chloride.

Polarization in conjugated systems may have a permanent aspect. The molecule as it was represented by the Lewis structure up to this point may not be the "normal" state. Ingold was to refer to this as "electronic strain," an entirely novel idea in 1926. The inductive effect had been previously described in 1923 by Lewis (11) and applied by Lucas(12) in 1924 and 1925 to problems of orientation in alkenes; but the idea that permanent polarization could exist in conjugated molecules had not been proposed before 1926.

Fritz Arndt (1885-1969) in many ways anticipated Ingold's concept of mesomerism through his analysis of the properties of pyrones and thiopyrones, first published in 1924. The Lewis structures for these molecules do not explain their characteristic reactions.



Arndt proposed that an additional zwitterionic dipolar structure (below) could be written for these molecules. The actual state of the molecule was an intermediate or Zwischenstufe, as Arndt termed it.



Campaign(13) has presented an excellent account of Arndt's work and the reasons for the general lack of recognition of this early anticipation of the resonance(mesomerism) theory. A letter to Campaign by Arndt in 1957 contains the following statement(13):

It should be noted that Sir Robert Robinson, one of the first pioneers of electronic theory, formulated in 1925..the potential shifts in pyrones and similar systems..In doing so he made a more detailed use of electronic theory than I had at first done; but he did not speak of a definite intermediate state of the molecule.

There are no references to Arndt's work in the early Ingold papers; whether Ingold knew of his work is a matter of conjecture. Ingold probably independently conceived of the idea of intermediate states.

A hallmark of Ingold's work was the use of physical methods to substantiate his theoretical speculations. Having presented the possibility of conjugate polarization, he proposed in the *Annual Reports* of the Chemical Society for 1926 a test of his hypothesis. This test was to measure dipole moments of certain molecules, a technique that had recently been developed by Peter Debye (1884-1966). Ingold proposed that, if a dipole moment were to be found for dimethylaniline, it would confirm permanent polarization existed in this molecule. Nitrogen in the dimethylamino group should have a weak inductive effect, drawing electron density from the aromatic ring; but it should also exert a stronger "tautomeric electron-repulsion," as Ingold termed it. In 1934 Ingold wrote(2):

...it then had to be shown by the use of vector addition principle that the direction of electric moment associated with the saturated aliphatic linking of the group becomes reversed in the corresponding aromatic combination:



The first test of this kind was completed (for the group NH_2) in 1928 by K. Hogendahl...with definitely positive results.

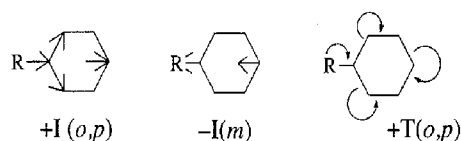
There are two orienting effects in aromatic substitution, according to Ingold "originating in the combinations of inductively propagated electronic strain (I,--->) and tautomeric or electromeric transformations (T, \curvearrowright)(2). Ingold sought to determine how these effects would influence reactivity in various positions, i.e., *o,p*- versus *m*-. At that time it was known from experimental observation that, whatever the substituent effect, it was most prominent at the *o*- and *p*-positions. To understand fully what these effects were, Ingold realized that he must know not only the isomer distribution but "relative velocities of the total substitutions (*o* + *m* + *p*) of different

substances(2)." Since such data was not available, Ingold and Shaw in 1927(14) derived partial rate factors for aromatic substitution which they termed "coefficients of activation." The method of competitive reactions was used to obtain the data for the rate factors. An analysis was presented for the four possible cases: +I-T; -I-T; -I+T; +I+T. The most interesting are the latter two, where the inductive and tautomeric effects compete in one case and reinforce each other in the other. Ingold assumed that in the -I+T case, as for example the halobenzenes, the *o*- and *p*-deactivation is less pronounced than that for the *meta* position. Thus, by default, the *o*- and *p*-positions become more susceptible to attack, though at a slower rate, than would be found in the pure +T case. That tautomeric effect in this instance is very weak but, coupled with enhanced deactivation of *m*-positions, leads to the observed outcome.

In another case of -I+T, i.e., the phenoxide ion, we find some of Ingold's most original thinking. Perhaps the most important statement concerning this case is as follows(14):

..that whilst inductive effects give rise to an essentially permanent not necessarily constant, molecular condition, the tautomeric effect (apart, possibly, from a small permanent residuum) is essentially temporary in character, assuming much greater importance at the moment of attack by a reagent than in the quiescent period preceding it.

These remarks were accompanied by the following representations:



Further clarification of the inductive effect in aromatic substitution was made by Ingold and Vass in 1928 (15). They proposed that there was operating, in addition to the I effect, what he called a direct effect D(15).

Since its genesis is also that of the inductive effect (-I), its variation as between different directing atoms will be the same as that of the inductive effect. Because, however, it is propagated, not through the bonds, but through space, its distribution in the ring will be, not in the order *o,p* > *m*, but in the order *o* > *m* > *p*.

The following nitration data was presented to substantiate the argument.

	PhF	PhCl	PhBr	PhI
<i>ortho</i>	12.7	30.1	37.6	41.1
<i>para</i>	87.4	69.9	62.1	58.9

Iodine having the largest +T and smallest -I, it followed that -D would favor more of the *o*- than the *p*- product. In the case of fluorobenzene, fluorine having the smallest +T and largest -I, the -D effect will result in least favored attack at the *o*-position. To Ingold's mind the inductive effect was transmitted both through bonds and through space.

By 1928 Ingold had almost completed his assessment of electronic effects in aromatic substitution. He would later classify some of these as permanent or polarization effects and some as temporary or polarizability effects. This is summarized in a table Ingold included in his 1934 *Chemical Reviews* paper (2).

Electronic Mechanism	Electrical Classification	
	Polarization	Polarizability
Chemical inductive ($\text{---}\rightarrow$) (I)	Inductive	Inductomeric *
Tautomeric (\curvearrowright) (T)	Mesomeric	Electromeric

While Ingold was developing his ideas, a concurrent revolution was occurring in physics: the development of quantum mechanics. This revolution in physics would rapidly become the basis for theoretical chemistry and the whole new field of chemical physics in the 1930's. How these ideas related to the problems that organic chemists were grappling with seemed totally incomprehensible to most organic chemists. There were, however, a few exceptions, these being Ingold and his fellow countryman Neville Sidgwick (1873-1952). M. J. S. Dewar in his 1949 text *The Electronic Theory of Organic Chemistry* sums up the problem best(16):

The application of the new quantum mechanics of Heisenberg and Schrödinger to chemistry in general, and organic chemistry in particular, has been hampered by two facts. Firstly, the mathematicians and physicists who have devised and elaborated the new theory have naturally had little or no knowledge of chemistry, and they have, moreover, been mainly interested in the quantitative application of the theory in a few simple problems and not in its qualitative application to more complex cases. Secondly, chemists have felt that the new theory must be unintelligible without a more detailed knowledge of mathematics than they possess, and many have also clung

to the older ideas of atomic structure because they found them easier to visualize.

Quantum mechanics provided a theoretical justification for the Lewis theory, which, in turn, fostered the initial impetus for the mechanistic revolution in organic chemistry. A passage from a letter of Linus Pauling to G. N. Lewis written on March 7, 1928, shows this connection(17).

You have no doubt seen London's recent paper in the *Zeitschrift für Physik* and have observed that the results which he derives from the quantum mechanics regarding the sharing of electrons are in the main equivalent to the rules which you had previously postulated. It is, of course, your prerogative to point this out; but, in the belief that you would probably not do so, I have taken the liberty of referring to the fact in the first part of a note concerning some further developments of the theory which has been sent to the *Proceeding of the National Academy* (a copy is enclosed).

Ingold realized that quantum mechanics was to play an important role in organic chemistry. As Shoppee has indicated, Ingold possessed the skill to gain an understanding of the subject which he did in 1932 while on leave at Stanford University, recovering from a serious illness. A letter dated April 2, 1932, from Ingold to Lewis written on Stanford stationery indicates that Ingold was planning to visit Lewis at Berkeley and was prepared to present, as Ingold phrased it, an "informal talk" during his visit (18). Ingold had first met Lewis in 1922 in London, when Ingold was a lecturer at Imperial College in the department headed by his mentor J. F. Thorpe (1872-1940). Ingold described this meeting to Lewis in a letter of April 12, 1927, "...though I do not think either of us realized what a large influence you would have on our chemical lives (19)." Ingold was now prepared to try to translate some of his ideas on a quantum mechanical basis.

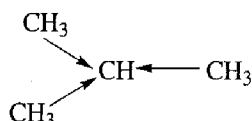
An anticipation of what would come later can be seen in a 1929 paper in which he discussed the reasons for the existence of stable free radicals. Ingold proposed that it is the result of the ability to distribute charge and made the following apocryphal statement as to why this charge is redistributed(20).

To this the best answer we can make is to refer to the microphysical equivalent (the exclusion principle) of the macrophysical law, which militates against the continued existence of intense, highly localised charge. In our view, this is also the ultimate cause of tautomeric change.

The first significant use of wave mechanics was made by Ingold in 1933. In a paper (21) entitled "Significance of Tautomerism and of the Reactions of Aromatic Compounds in the Electronic Theory of Organic Reactions" Ingold returned to a discussion of the general inductive and tautomeric effects with regard to which is time-dependent and which is time-independent. In this paper the inductomeric effect, the time-dependent inductive effect, was introduced. This type of polarizability, Ingold argued, occurs during the course of a reaction(21).

On the other hand, a general inductive effect of the same kind persists even in hydrocarbons when the practical issue is reactivity towards an electrophilic reagent, as illustrated by the orientation rules (Markovnikoff) for the nitration of paraffins. Clearly, the polarisability of carbon is the important factor here, and thus, despite a zero moment, a condition such as the following may obtain during reaction:

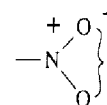
In dealing with the time-independent tautomeric effect Ingold introduced the term mesomerism, which he equated with "between the parts." Why does the mesomeric effect exist? Ingold considered this by analysis of all of the possible types of structures for a molecule, for example, such as in enamines. Two unperturbed states are presented and then a third state which was "expected to have lower energy than the unperturbed states, and therefore to correspond to the most stable condition of the system."



Where there is an exact equivalence of unperturbed states, the degenerate state must be symmetrically related to the unperturbed states, whilst in other cases the relationships, although not identical, must be similar; hence, the term mesomeric = between the parts...

Ingold offered evidence for his views from observations that had been made of the chemical properties of certain systems. Various physical measurements such as dipole moments and spectroscopy were readily available by the 1930's. An example cited was that of the nitro group, in which, if the Lewis structure $-\text{N}^+(\text{=O})-\text{O}^-$ were the correct representation, one would expect "a large dipole moment oriented perpendicular to the line of the nitroxyl groups just as have quinol ethers (21)." The actual measurement is a value close to zero. This is

what would be predicted if the nitro group has a mesomeric structure which Ingold represented as



Spectroscopic evidence reported in 1933 showed that in sulfur dioxide the two oxygen atoms are equivalent, a result that could only be rationalized by mesomerism. A further insight by Ingold is given by this statement near the end of the paper(21).

In general, the fall in energy arising from a degeneracy of given order will be increased when the order of degeneracy is raised by the participation of further unperturbed states.

An example is provided by the case Ingold had examined in 1929 of the stability of the triphenylmethyl radical, where "owing to the large number of possible positions for the free valency, the energy of degeneracy becomes comparable with the energy of the homopolar linking (20)." Aromaticity was also interpreted in terms of this wave mechanical degeneracy.

Ingold had developed his ideas by a combination of deductions from chemical and physical measurement as well as from ideas from wave mechanics. In a series of papers appearing in the premier volume of *The Journal of Chemical Physics*, Linus Pauling and his coworkers George W. Wheland and J. Sherman introduced the resonance theory(22) which they based on both chemical and physical data, as well as on quantum mechanics. As Ingold stated in 1934, "Pauling describes the phenomenon under the name resonance, which as is well known, is based on the mathematical analogy between mechanical resonance and the behavior of wave functions in quantum mechanical exchange phenomena(2)." Ingold's mechanical presentation of the concept of mesomerism led to confusion as to what he meant by mesomeric states. In the minds of some of his contemporaries these mesomeric states, equated with tautomeric structures, would interconvert much more quickly than would ordinary tautomers. The use of structural formulas created the problem that these were thought by many to be real states of the molecules. Ingold argued that "they are of the nature of intellectual scaffolding, and only the mesomeric state is real"(23).

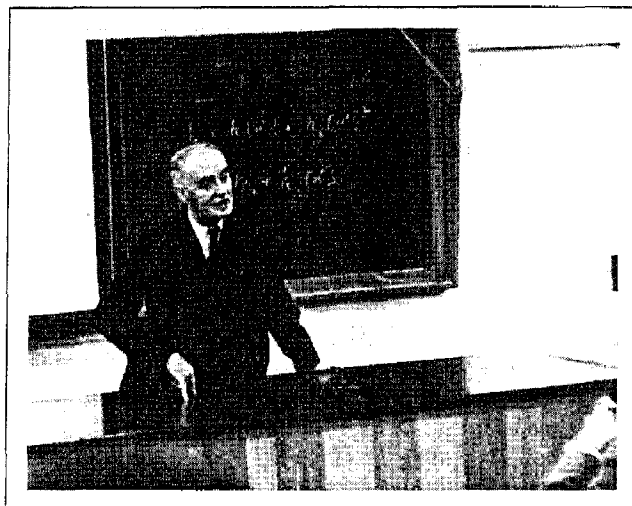
As an example Ingold cites the reduced basicity of aniline by a factor of 106 over that of aliphatic amines. The confusion that arises is the misconception that the reduced basicity can be accounted for by postulating that

there is a tautomerism occurring between the uncharged and the three dipolar structures.

The uncharged structure would exhibit a basicity of the same magnitude as that of the aliphatic amines, whereas the dipolar structures would show no basicity at all. Tautomerism would require that aniline must exist almost entirely in the betaine form to account for the lower basicity, something Ingold viewed to be an untenable state of affairs. The only rationale is to discard altogether the idea of unperturbed forms as molecular states and to adopt in its place the concept of a state distinct in properties from any of those originally assumed. Thus, mesomerism and tautomerism are different, and one must ascribe to the mesomeric state something more than a titular position in the physics and chemistry of unsaturated structures (23). This confusion Ingold hoped to dispel indicates a problem for the modern reader of his papers. Indeed this situation is best seen from a footnote in D. Stanley Tarbell's essay on valence in organic chemistry(24):

One of us, as a graduate student in 1934-1937, remembers clearly the reaction of some classical organic chemists to the "new-fangled theories" of Ingold and others; these were considered not entirely respectable intellectually, and it was said that the Ingold nomenclature was difficult and obscure. This was not confirmed by a reading of Ingold's *Chem. Rev.* article in 1934, although the presentation was more formalistic than seemed necessary. Ingold's presentations improved with time, the 2nd ed. of *Structure and Mechanism* being the best.

C. K. Ingold was the dominant figure in physical organic chemistry during the decades of the 1930's, 1940's, and 1950's. His work was the most frequently cited in the first generation of physical organic textbooks. For example, Waters' *Physical Aspects of Organic Chemistry* from 1925 contains 45 citations to Ingold's work(25). In Watson's *Modern Theories of Organic Chemistry* of 1937 there are 14 references(26). In Hammett's *Physical Organic Chemistry* of 1940(27) there are 51 references—six more than from Hammett's own work. Finally, Remick's *Electronic Interpretation of Organic Chemistry* of 1943 (28) contains 83 Ingold references. Even on the basis of this one small aspect of Ingold's work, there is little doubt of the greatness of the man, who almost single-handedly revolutionized the interpretation of structure, function, and mechanism in organic chemistry.



The Lecturer

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