PHYSICAL ORGANIC TERMINOLOGY, AFTER INGOLD

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The preeminence of Christopher Ingold in physical organic chemistry during its formative quarter century, say, 1925-1950, was based in part on his experimental contributions but even more on his perception and organization of principles and his communication of the new knowledge to his fellow chemists. That communication, in *Annual Reports of the Chemical Society* for several consecutive years in the late 1920's, in review articles published notably in 1929, 1934, and 1941, and in a major book(1), as well as in experimental papers, required the employment of good terminology for lucid expression of those principles.

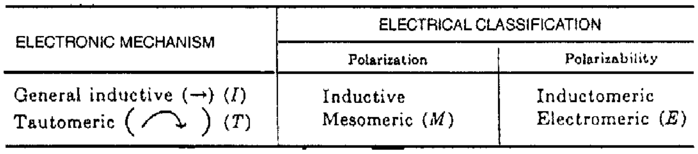
My present purposes are: to recognize characteristic Ingold terminology; to discern the origin of his terms, whether original or adopted; and to recognize why some terms endure in the working language of chemists while others wither, drawing in part on my own experience in the invention of terms. I do not claim to present an exhaustive catalog of Ingold's terms.

The intellectual foundation of physical organic chemistry, as it developed under Ingold's leadership, was G. N. Lewis' recognition, in 1916, that a covalent bond consists of a pair of electrons shared between the atoms joined by that bond. Acceptance of his ideas was slow, no doubt in part because Berkeley was then two weeks in travel time distant from England, where Ingold and the other principal founders of the field were located. At an influential 1923 Faraday Society discussion, Lewis apparently convinced a number of other participants of the validity of his concepts in his role as lead-off speaker and perhaps as well in informal discussions at that meeting. His book on chemical bonding (2) gave guidance and inspiration to all persons seriously interested in organic mechanisms and reactivity.

Before 1925 significant insights were published, notably by Arthur Lapworth, Thomas M. Lowry, and Robert Robinson, while Ingold was busily at work in other areas, especially small ring chemistry, but also certain physico-chemical phenomena(3). Ingold's attention to chemistry of the sort most often associated with his name might be said to start with a 1925 paper(7) on the directive influence of the nitroso group in aromatic substitution. That and some of his other early studies were however interpreted in terms of then-current alternate polarity theory (8).

Terms for Electronic Effects

These effects were characterized as "electronic strain" in Ingold's early recognition of them(9,10). His understanding of electronic effects materialized gradually. In his 1934 review(11) they were presented in a table reproduced here as Figure 1. Virtually the same table appears in both the 1953 and 1969 editions of his book.



ELECTRONIC MECHANISM	ELECTRICAL CLASSIFICATION	
	Polarization	Polarizability
General inductive (→) (*I*)	Inductive	Inductomeric
Tautomeric (↷) (*T*)	Mesomeric (*M*)	Electromeric (*E*)

Figure 1. "The four polar effects, their electrical classification, and their electronic mechanism," as outlined in Ingold's 1934 review(11).

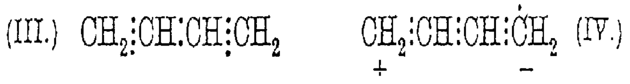
The two "electrical classification" categories, polarization and polarizability, refer to what today would generally be called ground state and transition state effects, respectively.

***Inductive* effects.** What we today term the through-bond inductive effect was clearly recognized by G. N. Lewis in his 1923 book(12), but he did not use the word "induce" or any variant thereof in discussing it. Lewis took the decreasing acid strength in the series chloroacetic, β-chloropropionic, γ-chlorobutyric, and δ-chlorovaleric acids as evidence that the effect is dampened as it passes through a saturated chain. Ingold, in 1926 papers(9,10,13), utilized the idea in discussion of experimental data, but also without using "induce" or any variant of it. It appears that he first employed the term "inductive effect," together with the symbols +I and -I, in his section of the *Annual Reports* for 1926(14).

The term *inductive effect* was more an adoption than an invention. Lapworth in 1922 published "A Theoretical Derivation of the Principle of Induced Alternate Polarities"(8). He(15,16) and Robinson(17) used variants of *induce* in additional papers, with meaning somewhat like that intended by Ingold. Thus Ingold's *inductive effect* resembled usage current at that time.

In Lewis' discussion(12) of what Ingold later called the inductive effect, he acknowledged that the effect might be transmitted in part through space, as well as through bonds. In 1929, Ingold(18) recognized explicitly the through-space possibility, calling it the *direct effect (±D)*. Like Lewis, he said "the operation of this effect seldom becomes obvious." The direct effect does not appear in his 1934 table of electronic effects (Fig. 1) but is discussed in nearby text(11). Since Ingold's death in 1969, experimental evidence indicating operation of what is now generally termed the *field effect* has been obtained(19). The effect as recognized today is however not quite the same as that postulated by Lewis or as originally conceived by Ingold. They visualized that an electronegative substituent, such as chlorine, would exert a through-space attraction of electrons so as, for example, to increase the dissociation constant of a carboxylic acid by stabilization of the negative charge of the carboxylate ion. Recent evidence(19) indicates, rather, that the effect stems from the interaction of the dipole of the substituent-to-carbon bond with an electrical charge or dipole generated during formation of the final or transition state(20). In certain carboxylic acids of rigid structure having the negative end of a C-Cl dipole closer than the positive end to the carboxyl group, a chlorine substituent is actually acid-weakening(19).

***Tautomeric* effects.** In my first earnest study of Ingold's scheme of electronic effects (Fig. 1), I was surprised by his characterization as "tautomeric" effects that had more to do with resonance than with tautomerism, as the latter had been taught to me. From Professors Leland Pence at Reed College and Ralph Helmkamp at the University of Rochester, I had learned in the early 1940's that tautomerism was a condition of facile interconversion of isomers, sometimes isolable, sometimes constantly in equilibrium with each other. I had also learned about the phenomenon of resonance(21), and particularly that a "resonance hybrid" is steadily in-between the canonical forms, *not* oscillating back and forth.



$$\text{(III.)}\quad \mathrm{CH_2\vdots CH{:}CH\vdots CH_2} \qquad \mathrm{\underset{+}{CH_2}{:}CH{:}CH{:}\underset{-}{\dot{C}H_2}}\quad \text{(IV.)}$$

Figure 2. Polarized and nonpolarized forms of butadiene, from Robinson (1922)(17)

In the 1920's the distinction between tautomerism as we now know it and the yet-to-be recognized resonance was not clearly perceived. Thus Kermack and Robinson(17) wrote in 1922, referring to the electron-dot structures III and IV for 1,3-butadiene shown in Fig. 2,

> in III ... the system is probably an oscillating one, the terminal carbon atoms becoming in turn feebly electropositive and electronegative ...We suppose ... that the reactant takes advantage of these momentary manifestations of polarity ...

The following year Lowry(22) described the anion from acetoacetic ester as a "tautomeric ion." He also discussed the "tautomeric" ions of carboxylic acids, in which "the distinction between the single and double bonds disappears"(23). G. N. Lewis said, in his address at the 1923 Faraday Society Discussion(24):

> While there can be no question that tautomerism often represents a rapid equilibrium between two or more distinct substances, to each of which an orthodox formula may be assigned, apparently this is not always true. I hope that Professor Thorpe will present to us ... 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 a single loose structure of intermediate character ...

In view of the widespread description as *tautomerism* of systems more or less recognized to be in a condition that we now call resonance, it is not surprising that Ingold(14) chose to call a mode of electronic interaction of a substituent group with a reacting system, in which an electron pair of a double bond between two atoms shifts so as to become an unshared pair on one of the atoms so joined, or the reverse, a *tautomeric* "type of disturbance." He retained the term *tautomeric* in writing his 1934 review(11) and even in his 1953 book(1). In the second edition of the book, however, *conjugative (K)* succeeded *Tautomeric (T)* of his earlier writings.

Other electronic effects. Ingold and Shaw wrote, in 1927:

> 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 views were repeated in 1928(25) and 1929(26). It will be noted that, despite a nearly rigid I/T permanent/transient distinction, he sensed that each might obtain to some extent in the time domain assigned to the other. In his 1934 review(11) two virtually new categories of electronic effect were introduced: *mesomeric (M)* for initial-state conjugative interaction of groups with an unsaturated system and *inductomeric (I)* for inductive-type electron shifts in response to the demands of attacking reagents (Fig. 1). Also, what had been termed *tautomeric* was renamed *electromeric (E),* with *tautomeric* being used to designate conjugative shifts both in the initial state and at reagent demand.

Fry(27), an American chemist, attempted in 1921 to explain numerous phenomena in terms of electronic tautomerism, defined as tautomerism involving electromers in dynamic equilibrium. One might liken that to resonance between canonical forms, but Fry's electromers were vastly different from canonical forms that might be proposed today. In his 1927 *Annual Reports* article(25), Ingold discussed "tautomeric (electromeric) transformations," acknowledging Fry. His utilization of *electromeric* was therefore precedented.

In 1934 Ingold employed an apparently novel term, *mesomeric* effect, to designate a molecular condition that had previously been recognized, although he had not emphasized it. The term is well-conceived; literally, a *mesomer* is a molecule in an intermediate state, or in more recent usage, a resonance hybrid. Some authors today use *mesomerism* for a condition of resonance. *Inductomeric* was also a late arrival in Ingold's set of electronic effects.

In discussing the inductive as contrasted to the inductomeric effect, Ingold wrote(11):

> The terms 'polarization' and 'polarizability' have quantitative meaning in relation to a molecule, since each may be measured by certain accurately definable magnitudes.

Those were stated to be respectively dipole moment, μ, and polarizability, α, as evaluated from optical measurements. His inductomeric effect pertained however to through-bond electron shifts, whereas polarizability as evaluated from optical measurements relates to the general phenomenon of distortion, by a nearby ion or dipole, of an electron cloud somewhat loosely associated with its nucleus or nuclei. Intermolecular attraction due to dispersion forces is largely dependent on the polarizabilities of the molecules or ions involved. Deep in his 1934 review(28) Ingold acknowledged this point.

Synartetic Acceleration **versus** ***Anchimeric Assistance.*** Wagner-Meerwein rearrangements had attracted Ingold's attention even in the 1920's(18) and received significant experimental attention in his laboratories. In 1950-51, he proposed the terms *synartetic acceleration* and *synartetic ion(29-31).* The former pertained to acceleration of solvolysis in substrates such as isobornyl chloride, attributed to participation by the electrons of a suitably juxtaposed C-C single bond in loosening the C-Cl bond, and the latter to the nonclassical ion so formed. Soon thereafter, Winstein(32) proposed *anchimeric assistance* for the same meaning as *synartetic acceleration.* Inasmuch as in the 'fifties and 'sixties the study of solvolyses was fashionable, especially in the US, and the research of the charismatic Winstein was the paradigm for the fashion, Winstein's term prevailed. In my judgment, Ingold's term was a good one, Winstein's unnecessary

Lapworth(33) in 1925 suggested the terms *anionoid* and *kationoid* for the meanings now conveyed by *nucleophilic* and *electrophilic,* respectively. *Anionoid* and *kationoid* were utilized in succeeding papers by Robinson(34) and by Lapworth and Robinson(35), to cite two examples. Ingold was doubtless aware of those terms, but he did not use them. He regarded classification on the basis of similarity to cations or anions to be unsound(36).

In a 1929 presentation of "the principles of aromatic substitution(26), Ingold used the term *electron-seeking reagent,* not so much to distinguish such a reagent from others but rather in a context in which it was pretty much taken for granted that species effecting aromatic substitution were electron-seeking. The understood presumption that aromatic substitution was facilitated by electron supply to the site of reagent attack prevailed in other Ingold papers in those years, without being specifically stated. A 1934 Ingold paper(37) on modes of addition to conjugated systems, however, included the term *electrophilic* for a reagent that "demands a centre of high electron-availability." By 1935, Hughes and Ingold(38) were writing of *nucleophilic* and *electrophilic* reagents without special explanation.

Reactions. The familiar reaction descriptions, *substitution* and *elimination*, gained their present connotations surprisingly late. As late as 1933, in reports on the decomposition of

$$\{\mathrm{R^1R^2CH{\cdot}CR^3R^4{\cdot}NR'R''R'''}\}^+\mathrm{X^-} \longrightarrow \mathrm{R^1R^2C{=}CR^3R^4 + NR'R''R''' + HX} \qquad \text{(A)}$$

$$\{\mathrm{R{\cdot}NR'R''R'''}\}^+\mathrm{X^-} \longrightarrow \mathrm{RX + NR'R''R'''} \qquad \text{(B)}$$

Figure 3. Ingold's representation of reactions both called *elimination*(39)

quaternary ammonium salts(39) (Fig. 3) and tertiary sulfonium salts(40), Ingold and coworkers characterized as "elimination reactions" two competing routes that we know today as elimination and substitution. Evidence was presented that both modes of reaction might occur either by bimolecular reaction of X^- with the 'onium ion (pathway A2 or B2) or by unimolecular heterolysis of the 'onium ion to form a carbocation, which then coordinates with X^- to form RX (B1) or cedes a β-H to X^- to form the alkene (A1). The numerals 1 and 2 in these descriptions were intended to symbolize reaction molecularity(39).

Two years later, papers by Hughes and Ingold(38,41-43) utilized, without special comment, the terms *substitution* and *elimination* with their modern connotation as well as the now familiar symbols S_N1, S_N2, S_E1, S_E2, E1, and E2. The symbols used in 1933 mainly to delineate within one research paper different reaction mechanisms were transformed into symbols that served, besides that purpose, as general representations of reaction type and mechanism: A1 became E1; A2 became E2; B1 became S_N1; and B2 became S_N2.

With respect to both reagents and reactions, the change in terminology between 1933 and 1935 is remarkable. What factor was chiefly responsible? Did the new terms result from increasing influence by Hughes? Did conversations with American chemists in California(44) stimulate formulation of the new definitions and symbols?

The convenient and widely used terms, *heterolysis* and *homolysis*, were suggested by Ingold(45,46), seemingly as an afterthought following a Faraday Society Discussion. Ingold also proposed sensible nomenclature for the reverse of these processes, presenting the following diagrams:

$$\mathrm{A\cdot + B\cdot} \xrightleftharpoons[\text{homolysis}]{\text{colligation}} \mathrm{A{:}B}$$

$$\mathrm{A + B{:}} \xrightleftharpoons[\text{heterolysis}]{\text{co-ordination}} \mathrm{A{:}B}$$

Of the two terms for combination of species, *co-ordination* is familiar from inorganic chemistry and is utilized by Ingold for essentially the same meaning. *Colligation* is novel, a convenient, logical term, but one little used by radical chemists(47), even by C. K. Ingold's radical son Keith, who uses *combination* instead(48).

Symbols for Mechanisms

The genesis of E1, E2, S_N1, and S_N2 has already been discussed. Another group of Ingold mechanism symbols pertains to ester hydrolysis and related reactions, which had been of interest to him from the 1920's. That carboxylic esters may be hydrolyzed by action of either aqueous acid or alkali was common knowledge. Research in his laboratories and from other sources showed that the carbon-oxygen bond broken might be either

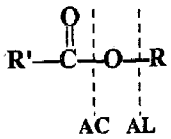


Figure 4. Alternative C-O bond cleavage in ester hydrolysis

that from the bridging oxygen to the carbonyl carbon (AC) or to the first carbon of the alkyl group (AL), as shown in Fig. 4. Moreover, the actual breaking of that bond might occur either unimolecularly in the ester or its conjugate acid, or bimolecularly thru attack of hydroxide ion or water on the relevant carbon atom. Unimolecular acyl-oxygen fission forms an acylium ion intermediate, while unimolecular alkyl-oxygen fission generates an alkyl carbocation.

In a 1941 review Day and Ingold(49) used a newly-devised set of symbols to represent the various possibilities. The symbols started with A or B, for acidic or basic, and ended with 1 or 2, for unimolecular or bimolecular. In between was a single or double prime (′ or ″), the single prime indicating acyl-oxygen scission and the double prime alkyl-oxygen scission. Thus, common saponification (which involves bimolecular attack of hydroxide ion at acyl carbon) was symbolized by B′2, while unimolecular scission of the alkyl-oxygen bond of the ester conjugate acid was respresented as A″1, etc. This system allowed eight mechanism types to be represented by compact symbols, and facilitated representation of the various mechanisms in discussions. (For $B''2$, there was at that time no known example.)

In his 1953 book(l) Ingold modified these symbols to increase their clarity. The single prime was replaced by subscript AC and the double prime by subscript AL. Thus, $B'2$ became $B_{AC}2$, and $A''1$ became $A_{AL}1$, and so forth. In their 1953 form, the symbols relieve one from having to remember whether single or double prime stands for acyl-oxygen scission.

Some Other Terms

Of career-long interest to Ingold were rearrangements that he called, as many others do, *prototropic* and *anionotropic* rearrangements. Lowry wrote of *prototropy* in a 1923 paper(23) and, according to Ingold(50), in 1925 spoke *of ionotropy,* which implies *anionotropy* as well as *cationotropy.*

A convenient term frequently used in treatment of rate data for electrophilic aromatic substitution is *partial rate factor.* It is the part of the total rate constant for a substrate with more than one reactive site that pertains to reaction at one particular site; for example, one-sixth the total rate constant for nitration of benzene is the partial rate factor for one benzene carbon atom. It was introduced in a paper co-authored by Ingold, Lapworth, Rothstein, and Ward(51). Which co-author was principally responsible for initiating the term is unclear.

Related Terms, Proposed by Others, that Did Not Survive

In 1920, Lapworth(52) proposed words to describe the effects of substituent groups on acid dissociation constants:

> The writer would propose the term 'basylous' for a group such as $-NH_2$ which tends to lower the acidity of a molecule of which it forms but a part, and the term 'acylous' for a group such as CH_3CO which has the opposite effect.

These terms were used in 1923 by Lowry(53), but Lapworth did not make much if any use of his own invention in subsequent papers. For example, they were not used in a 1927 discussion(35) of the *ortho-para* ratio in aromatic substitutions; substituents were instead treated with respect to their "attraction on electrons." Lapworth was, in the early 1920's, much more interested in his "principle of induced alternate polarities"(8).

Lapworth proposed(33) in 1925 the terms *anionoid* and *kationoid* for reagents of opposite polar character, for the meanings now generally conveyed by *nucleophilic* and *electrophilic,* respectively. I must confess to finding these terms attractive when I first encountered them in the 1940's. Ingold eschewed them on grounds that they overemphasized the charge character of reagents(36). Without denying the validity of that criticism, I suggest that *nucleophilic* is defective to a similar extent in that it implies nucleus-seeking whereas a nucleophile actually seeks an atom with a real or virtual empty valence-shell orbital.

In a 1925 paper, Robinson(54) proposed terms related to the capacities of substituent groups to contribute or accept what we now call π-electrons to or from an unsaturated system; see Fig. 5. The terms are *crotenoid* for a system in which the substituent has contributed π-electrons to the unsaturated system, and *crotonoid* for the opposite. The structures in Fig. 5 are those of Robinson, in a newer notation, but intellectually equivalent to his. These terms were used to some extent by others(55) as well as by Robinson(34); indeed, he extended that terminology style to embrace *butadienoid, quinonoid, semi-crotonoid* and *allyloid.* Bearing in mind that he also characterized reagents as *anionoid* or *kationoid,* one speculates that some readers may have been annoyed. The ideas expressed by *crotenoid* and *crotonoid* could also be conveyed in Ingold's terms for electronic effects, which prevailed. In modern usage, *quinonoid appears* now and then, and perhaps *butadienoid.*

Crotenoid

Crotonoid

Figure 5. Robinson's 1925 depiction of *crotenoid* and *crotonoid* systems.

Some Terms Suggested by Bunnett

The following experiences will aid in the assessment of what characteristics in a newly proposed term contribute to its longevity in the language of chemists. Some of mine survived, whereas others died.

Names for Charge-Carrying Substituent Groups. Incidental to a review of aromatic nucleophilic substitution reactions(56), Roland Zahler and I introduced the term *ammonio* for the $-NH_3^+$ substituent group, and suggested that substituted ammonio groups be named according to the same principle. In a later article(57), the proposal was extended to substituted sulfonio groups, for example, *dimethylsulfonio* for $-S(CH_3)_2^+$. In April, 1954, this suggestion, as well as the one below on naming substitution reactions, was submitted to Mary Alexander, Chair of the Committee on Nomenclature of the American Chemical Society Division of Organic Chemistry. She passed it on to Austin M. Patterson, who had in those times a regular column on nomenclature in *Chemical and Engineering News.* He reported it benignly(58). Shortly thereafter, H. J. Barber(59) disclosed that he had independently proposed the same nomenclature. *Ammonio* and *sulfonio* are now recommended by the IUPAC Commission on Nomenclature of Organic Chemistry(60).

Cine-Substitution. Zahler and I recognized(61) several kinds of substitution reactions that surprisingly introduced the entering group at a position *ortho* to the leaving group. These included prominently the von Richter reaction and some reactions of aryl halides with strong bases that we now recognize to occur via aryne intermediates. For such reactions, we proposed the term *cine-substitution,* from the Greek *cine,* to move. This term has gained wide usage.

Names for Substitution Reactions. My proposal, published by Patterson(62) in October, 1954, was that the name of a substitution reaction comprise these parts: the name of the incoming group, the syllable "de," the name of the departing group, and the suffix "ation," with occasional elision of vowels or introduction of consonants as occasionally necessary for euphony. I used this terminology in my own papers on aromatic nucleophilic substitution, but probably more important to its acceptance was reproduction of my proposal, with favorable comment, in the 1954 Editorial Report on Nomenclature of The Chemical Society(63). Also helpful were utilization of such names in an important monograph(64) and recommendation of them by IUPAC(65). These names are now widely used, and even abused(66).

The $S_{RN}1$ Mechanism. In 1970, Jhong Kook Kim and I(67) found evidence that certain reactions that might appear to be aromatic nucleophilic substitutions actually occur by a radical mechanism previously recognized for aliphatic reactions by other chemists(68). Inasmuch as a characteristic step in this then-unusual mechanism is the fragmentation of the radical anion of the substrate, to form an aryl radical, we suggested the mechanism be symbolized $S_{RN}1$, by analogy with the well-known S_N1. (The step, $ArX^{\bullet}$ — —> $Ar^{\bullet} + X^{-}$, resembles the rupture step of S_N1, except that the reactant and the organic product are one electron richer.) Since 1970 there has been quite a bit of study of such reactions, for which the symbol $S_{RN}1$ is generally used.

Names for E2 Transition States. In a 1962 review of bimolecular olefin-forming elimination reactions(69), I presented arguments that the E2 transition state need not be synchronous, in that rupture of the C_β–H bond may be much more advanced than of the C_α–X bond, or *vice versa.* In an extreme case of the former, C_β has much carbanion character, while at the other extreme C_α has much carbonium ion(70) character. I called these extremes *nearly carbanion* and *nearly E1.*

That concept received favorable attention from mechanisms chemists in the 1960's. In a review written in 1967(71), I advocated, on the indirect advice of a classical scholar at the University of Canterbury, New Zealand(72), for the transition state extremes instead the terms *paenecarbanion* and *paenecarbonium,* these being derived from the Latin *paene,* "almost." These terms have received little use, however. A major reason is that my concept of a variable E2 transition state was subsumed into a more general variable transition state theory proposed in 1970 by More O'Ferrall(73), which is now widely employed. The terms themselves may, however, have been defective, as I speculate below.

The Usual Mechanism of Aromatic Nucleophilic Substitution. In 1951, Zahler and I(74) proposed that the usual mechanism involves two steps: the nucleophile attaches to the site of substitution, and then the leaving group departs. However, we passed up the opportunity to propose a special name or symbol for this mechanism. Later, Parker(75,75) proposed for it the convenient symbol S_NAr, which is now generally used(77).

Treatment of Acid/Base Equilibria in Moderately Concentrated Sulfuric Acid *via* Linear Free Energy Relationships. Hammett's H_0 acidity function(78) was a pioneering achievement, but his method actually was accurate for but a limited range of bases. As other acidity functions were evaluated for other classes of bases, the field became complicated. In 1966 Olsen and I showed, however, that H_0 alone was sufficient for accurate treatment of such equilibria for bases in general, if it were employed in a new way(79), which was of the character of a linear free energy relationship (LFER). Our treatment involved plotting data against the parameter $(H_0 + \log [H^+])$. A few years later Cox and Yates(80) developed another LFER, related in principle but different in approach; in their method, data were plotted against parameter X. In magnitude, X and $(H_0 + \log [H^+])$ are, however, very similar(81). Perhaps because their parameter is simpler(82), and also because they were diligent in publishing a series of papers on their treatment, their modification is today more often used than our original method.

***Attachment* and *Detachment*.** For several years I was a member of the IUPAC Commission III.2, on Physical Organic Chemistry, the main concern of which was terminology in the field. In developing a general system for naming transformations(65), we limited the term *addition* to its common use in describing the bonding of *two* moieties, e.g., to an alkene or a carbene, and advocated that the bonding of *one* moiety to a single site be called *attachment*. Conversely, *elimination* connotes the release of two moieties, and *detachment* for the release of one from a single site. These usages have not yet become general; thus, the S_NAr is still sometimes referred to as an *addition/elimination* mechanism; it is better called an *attachment/detachment* mechanism.

***Hydron*.** Commission III.2 also dealt with a common irregularity in the language of physical organic chemists, namely, that *proton* was used both for $^1H^+$ and for H^+ of whatever isotopic nature. That led to such nonsensical concepts as the kinetic isotope effect in proton transfer reactions. Rigorously, the proton is H^+ of mass unity, and no isotope effect is measurable if all atoms of an element are of the same isotope. Accordingly, Commission III.2 proposed(83) *hydron* as the term for H^+ of whatever isotope, restricting *proton* to $^1H^+$. Chemists, have however, been slow to relinquish the familiar if irregular use of *proton* for all monohydrogen cations.

Perspectives

Ingold's numerous contributions to the terminology of physical organic chemistry tell us something about Ingold the scientist. Another aspect is what significance they had for the development of the field. Finally, from consideration of Ingold's contributions to terminology as well as those of others, including my own lesser efforts, we may gain some insight into what factors determine whether a new term will become part of the basic language of the field or will wither on the page.

What Ingold's Terms Tell about Ingold. First, an orderly mind is revealed. One senses that from his study of various questions, he was able to discern features he wished to stake out in his mind, somewhat as a prospector might mark a discovery of gold. For that purpose, attaching definitive labels was helpful. It appears that his terms first served that private purpose. Some of those "private" labels appear in early publications on various topics; for example, A1, A2, B1 and B2 pathways for decomposition of quaternary ammonium salts *(vide supra)*.

Second, they indicate something of his quality as a teacher. Often he perceived dichotomies and chose terms or symbols that would effectively contrast differing behaviors. Thus, *inductive* vs. *tautomeric*, *nucleophilic* vs. *electrophilic*, S_N1 vs. S_N2, and E1 vs. E2. For his purposes as a teacher, introducing terms that effectively contrast one feature from another was useful. Relabeling A1 as E1, B1 as S_N1, etc., as mentioned, served pedagogical purposes.

We have also seen that Ingold often chose terms that were part of the current language of the field, giving them however more precise definitions. *Inductive, tautomeric, electromeric,* and *prototropy* are examples. Noteworthy, however, is his introduction of *nucleophilic* and *electrophilic* in place of *anionoid* and *kationoid,* which had been proposed years earlier(33) for the same meanings. *Elimination* and *substitution* had been in the language of chemists for many years, but Hughes and Ingold(41,43,84) in effect redefined them in the way we understand them today.

Significance of Ingold's Terminology. Its significance can be evaluated with respect to two standards: how valuable were his terms in years immediately following their development, and what use do they enjoy in the current language of scientists?

Ingold's terms were indeed important in the former sense. Besides his original research contributions, Ingold was an intellectual systemizer and a teacher. In times when many others had only murky perceptions of new developments, he got them straight in his own mind and repeatedly offered his understanding to his fellow chemists in review articles as well as in research papers. He was a teacher not only to traditional students, but also to his contemporaries. He became the effective leader in reconstruction of the intellectual outlook of organic chemists; terminology that helped organic chemists in the classical tradition to grasp the new concepts was important to his mission.

Now about the endurance of his terms: of those in Fig. 1, *inductive effects* are part of the standard language of physical organic chemistry. *Mesomerism is* considerably used to designate conditions of resonance. The others are seldom used today. Why? In large part because two structures of theory that were little known in the years 1926-34, transition state theory and quantum mechanics, are now foundations to the field. Those other terms no longer seem needed.

Most of the rest of the Ingold terms that I have discussed are central to modern physical organic chemistry, in both the thinking of chemists and in their language. As mentioned above, *synartetic acceleration* did not however survive. *Colligation* has not been much used, nor are Ingold's symbols for the various carboxylic ester hydrolysis mechanisms.

Factors That Affect Whether a New Term Will Endure. The following thoughts are based mainly on consideration of Ingold's terms, as well as the few that I have suggested.

That it represent a new substance or concept. Examples include several terms introduced by Woodward and Hoffmann(85) in connection with orbital symmetry principles, as well as benzyne, ferrocene, and, it appears, fullerene. From Ingold's terminology contributions, S_N1, S_N2, E1, and E2 endure in part for the same reason. Prior to 1933(39), what we now call aliphatic nucleophilic substitution reactions and olefin-forming eliminations were all more or less assumed to be of bimolecular character.

That it state concisely an idea otherwise cumbersome to express. A good example is S_NAr(75) to designate what I had been calling the intermediate complex mechanism of aromatic nucleophilic substitution. Another is $S_{RN}1$, which seems more efficient than longer terms such as "substitution reactions which proceed via radical anion intermediates"(86). Terms of that sort had been used by Kornblum, who continued to use them, eschewing $S_{RN}1$, long after the latter had come into general use(86,87).

That it replace an existing term generally regarded as deficient. Ingold's set of electronic effects (Fig. 1) might be cited in this regard, although they supplanted not only the terminology but also the concepts of alternate polarity theory.

That it be uncomplicated, easy to remember, pronounce, and spell. That *synartetic acceleration* did not survive was perhaps due in minor part to this factor; I have trouble remembering how to spell *synartetic*. Possibly the seemingly greater acceptance of the Cox-Yates than of the Bunnett-Olsen LFER stems in part from the seemingly greater simplicity of X than (H_O + log [H^+]).

That terms in a set to contrast two or more concepts be quickly distinctive. Nucleophilic vs. electrophilic is a good example, as also are S_N1 vs. S_N2, and E1 vs. E2. Deficient in this regard are *paenecarbanion vs. paenecarbonium;* although intended to represent extremes, the first three syllables, which receive the main accent, are identical. Robinson's *crotenoid* and *crotonoid* are deficient in much the same way.

Diligence in employment of the term, a very important factor. One reason so many of Ingold's terms are part of the modern language of physical organic chemistry is that he used them repeatedly in experimental reports and reviews. (It also helped that his experimetal reports were scientifically substantial.) That caused them frequently to enter the minds of scientists keeping abreast of modern developments. Lapworth was not diligent in using his *acylous* and *basylous,* even in his own later publications. Robinson was more faithful in using *crotenoid* and *crotonoid,* as well as *anionoid* and *kationoid,* which he favored; but Robinson turned his research focus away from reaction mechanisms toward synthetic chemistry. After 1930, he published little in physical organic chemistry. Here, as elsewhere, the principle "out of sight, out of mind" is relevant.

Official adoption. That my scheme for naming substitution reactions *(vide supra)* was generally adopted was no doubt assisted by its endorsement by The Chemical Society(63). On the other hand, IUPAC recommendation of schemes for naming elimination, addition and insertion transformations(65) has had little apparent effect. Systems (not discussed above) recommended by Commission III.2 for naming transformations of those types have found little use. Official adoption had nothing to do with furthering use of the numerous terms proposed by Ingold.

Fashion. This is a major factor. That *anchimeric assistance* prevailed over *synartetic acceleration* in the usage of the throng of American solvolysis chemists of the third quarter of this century was considerably the outcome of fashion; Winstein was in vogue with that crowd; Ingold was not, as discussed above. Fashion powerfully influences the choices chemists make as to what to study and what language to use in reporting their results.

Epilog

In studying and evaluating with the wisdom of retrospection the vocabulary, and to some extent the scientific contributions, of great figures like Lewis, Lapworth, Lowry, Robinson, and Ingold, one feels more than usual humility. Had I been a scientist at the time, would I have been able to make even one of the conceptual advances that they made?

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COMING EVENTS

ACS National Meeting, April 13–17, San Francisco, CA. [see *Chem Eng. News* for more details]

ACS Great Lakes Regional Meeting, May 28-30, Loyola University, Chicago, IL. History of Chemistry Symposium, Dr. Elsa L. Gonzalez, Chair.

ACS National Meeting, September 7–11, Las Vegas NV.