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Hammett Deserved a Nobel Prize

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Abstract

Louis P. Hammett is hereby nominated for a "Posthumous Nobel Prize" in Chemistry for his discovery of the quantitative relation between rate constants and acidity constants of benzoic acids.

Vital Statistics

Louis Plack Hammett (Figure 1) was born on 7 April 1894 in Wilmington DE and died at the age of 92 on 9 February 1987 in Medford NJ. He was the oldest of three children. His middle name was a family name, originally from Germany, on his mother's side.

Figure 1. Louis P. Hammett (1894-1987),

from Shorter, *Progr. Phys. Org. Chem.* **1990**, 17, p. 2, © by John Wiley & Sons.

Hammett grew up in Portland ME and followed his father to college at Harvard, from which he graduated *summa cum laude* in 1916. At Harvard he came under the influence of Gregory Baxter, E. P. Kohler, and James Bryant Conant. At graduation he won a Sheldon Traveling Fellowship from Harvard. Even while World War I was raging, he used it to work on hydrazones in the Zurich lab of Hermann Staudinger, who had been recommended by Kohler.

In 1917 he returned to the U.S. and took a job at the National Bureau of Standards, where he investigated paints and varnishes that were used to coat airplane wings. A supervisor there was Hal Beans, who returned to Columbia University after the war. In 1920 Beans offered Hammett an instructorship to teach qualitative analysis at Columbia, a position that also allowed him to enter the university as a graduate student. There he did research under Beans on the hydrogen electrode, which had recently been developed for measurement of pH, and he received his Ph.D. in 1923.

In 1924 Hammett was appointed as an Assistant Professor at Columbia. He taught graduate and undergraduate courses in analytical chemistry, in physical chemistry, and in what became known as physical organic chemistry. He wrote a textbook, *Solutions of Electrolytes, with Particular Application to Qualitative Analysis* ⁽¹⁾, published by McGraw-Hill in 1929, and reviewed in the *Journal of Chemical Education* ⁽²⁾. A second edition of the book was published in 1936. It covered the general principles of electrolytes in solution, including strong electrolytes, the solubility product, weak electrolytes, hydrolysis, compounds, and oxidation-reduction, with problems for students and a group of laboratory exercises. Later he wrote another textbook, *Introduction to the Study of Physical Chemistry* ⁽³⁾, published by McGraw-Hill in 1952, and reviewed in *Science* ⁽⁴⁾. Among the topics included were gases, dilute solutions, thermodynamics, quantum principles, chemical equilibrium, reaction rates, conductivity, and reactions of ions, with an appendix on mathematical techniques and on the Boltzmann equation.

Hammett remained at Columbia until 1961, when he became Mitchell Professor Emeritus, a position he held until 1973. Among the honors he received were membership in the National Academy of Sciences (1943), the Priestley Medal and the Willard Gibbs Medal of the American Chemical Society (both in 1961), and the James Flack Norris Award in Physical Organic Chemistry (1966). In 1967 he was awarded the National Medal of Science by President Lyndon Baines Johnson, and he received the Barnard Medal for Meritorious Service to Science in 1975.

Hammett and the Nobel Prize

According to the will of Alfred Nobel (Figure 2), the Nobel Prize in Chemistry is awarded "to the person who shall have made the most important chemical discovery or improvement". Hammett did receive several official nominations. In 1962 he was nominated by two Columbia colleagues, George K. Fraenkel and Thomas I. Taylor. In 1963 he was nominated by Albert Bruylants, a Belgian organic chemist and President of IUPAC. In 1964 he was nominated by William H. Powers and Robert W. Taft, from Penn State. In 1965 he was nominated by Tadeusz Urbanski, an explosives expert from Warsaw who also nominated R. B. Woodward, the winner that year. Later records are not yet available from the Nobel Foundation. Despite those nominations, Hammett was never selected for the Prize.

Figure 2. Alfred Nobel (1833-1896). Image provided by the Nobel Foundation.

In 1944 Hammett did nominate UC Berkeley's G. N. Lewis, also unsuccessfully. (See the chapter on G. N. Lewis by William Jensen elsewhere in this book.) Hammett said "I think one of the great tragedies of American Science is that Lewis never got the Nobel Prize and that it was given to Langmuir for inventing Lewis's valence theories. I think Langmuir deserved the prize for his surface work but he was given the prize for valence theory when everything he added to Lewis's original ideas was wrong" ⁽⁵⁾.

In my own opinion, Hammett deserved the Nobel Prize in Chemistry. This posthumous nomination of Louis Hammett for the Nobel Prize is a personal account, because Hammett was one of my scientific grandfathers. Frank Westheimer was a post-doctoral scholar with Hammett, and I received my Ph.D. under Westheimer's direction.

The Hammett Equation

This nomination of Louis P. Hammett for a posthumous Nobel Prize in Chemistry is based on the discovery of the quantitative relation (Hammett equation) between rate constants and acidity constants of benzoic acids. This discovery was presented in an article entitled "The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives" ⁽⁶⁾.

The Hammett equation is applicable to the effect of a substituent in the meta or para position of a benzene ring on the rate or equilibrium of a chemical reaction. It is shown as eq 1, where k_X or K_X is the rate constant or equilibrium constant of the reaction of interest for the substituted derivative, and k_H or K_H is the rate constant or equilibrium constant of the reaction of interest for the unsubstituted derivative. A key feature is the separation into two parameters, σ , dependent on the substituent, and ρ , dependent on the reaction (and on the medium and the temperature).

$$\log k_X = \log k_H + \rho\sigma_X \quad \text{or} \quad \log K_X = \log K_H + \rho\sigma_X \quad (1)$$

The parameter ρ is defined as 1 for the reference reaction, namely the acid-ionization equilibrium of benzoic acids in water at 25°. It is thus possible to empirically evaluate σ_X ,

defined as $\log(K_a^X/K_a^H)$, for a large number of substituents X. Then, for another reaction, a plot of $\log k_X$ or of $\log K_X$ vs. σ_X , according to eq 1, should be a straight line with slope ρ and with intercept $\log k_H$ or $\log K_H$. Indeed, in 1937 Hammett successfully correlated rates and equilibria of 39 reactions with an average error of $\pm 17\%$ in k or K .

The Hammett equation (eq 1) is an example of reasoning by analogy. It compares the conversion of functional group Y to functional group Y' with the ionization of benzoic acid (Scheme 1). To the extent that the reaction of interest is analogous to the ionization of a benzoic acid, a plot of the data of eq 1 will fit well to a straight line. Scheme 1 illustrates the analogy. In the ionization of the benzoic acid, ArCOOH , a negative charge is generated in the carboxylate group. If substituent X is electron-withdrawing, it will stabilize the negative charge and increase the acidity of ArCOOH and the value of K_a^X . On the other hand, if substituent X is electron-donating, it will destabilize the negative charge and decrease the acidity of ArCOOH and the value of K_a^X . Therefore σ_X is > 0 for electron-withdrawing substituents, and it is < 0 for electron-donating ones. If the functional group Y' in the product differs from the group Y in the reactant by an additional negative charge (or by loss of a positive charge), then electron-withdrawing X will stabilize Y' and increase k_H or K_H , and electron-donating X will have the opposite effect. Alternatively, if the functional group Y' differs from Y by an additional positive charge (or by loss of a negative charge), then electron-withdrawing X will destabilize Y' and decrease k_H or K_H , and electron-donating X will have the opposite effect. The result will be a Hammett plot whose slope ρ represents the sensitivity of the reaction to substituent effects.

Scheme 1. Analogy between reaction of ArY and ionization of a substituted benzoic acid ArCOOH .

This description can be bewildering in the abstract. It is much clearer with a specific example. However, if one searches the web for an image of a Hammett plot, Figure 3 may result.

Figure 3. Example of a Hammett plot. Reprinted by permission of mptvimages.com.

Figure 4 shows a plot of eq 1. This is for the specific example of the ionization equilibrium of anilinium ions, ArNH_3^+ (7, 8). Electron-withdrawing substituents, with $\sigma_X > 0$, increase not only the acidity of benzoic acids but also the acidity of anilinium ions. Meta and para substituents are fit separately in Figure 4, but the slopes, 2.91 and 3.15, respectively, are very similar. The point at $\sigma_X = 0.78$ is discussed below.

Figure 4. Plot of the acidity constants of anilinium ions, ArNH_3^+ , vs. σ_X for acidities of ArCOOH (x = meta substituents, + = para substituents). Data from Refs. 7-8.

The historical significance of the Hammett equation was that it established organic chemistry as a quantitative science with predictable regularities, rather than only a collection of observations and preparations. As Hammett wrote, "To many physical chemists in the 1920's and early 1930's, the organic chemist was a grubby artisan engaged in an unsystematic search for new compounds. ... I had, however, developed a strong hunch that the organic chemists' basic rule, that like changes in structure produce like changes in reactivity, could be made quantitative" (9). In my opinion this discovery is what warrants a Nobel Prize for Hammett.

Currently the major utility of the Hammett equation is for drawing mechanistic inferences. If ρ is > 0 , the reaction is accelerated by electron-withdrawing substituents, and the aromatic ring in

the transition state bears negative charge (strictly, a greater negative charge than borne in the reactant). In contrast, if ρ is < 0 , the reaction is accelerated by electron-donating substituents, and the aromatic ring in the transition state bears positive charge (strictly, a greater positive charge than borne in the reactant).

A nontrivial example is the solvolysis of benzoyl chlorides in ethanol, to form the corresponding ethyl benzoate (Scheme 2). The rates of this reaction can be correlated by the Hammett equation, with slope $\rho = 1.529$. The positive value means that negative charge develops in the transition state. This result excludes a dissociative mechanism, via $\text{ArC}\equiv\text{O}^+$. Instead the reaction involves association with a lone pair on the ethanol oxygen, which isolates the aromatic ring from the electron-withdrawing COCl group and increases the electron density felt by the aromatic ring.

Scheme 2. Solvolysis of benzoyl chlorides.

Although such mechanistic insights are examples of the explanatory power of the Hammett equation, a stronger test of any scientific theory is its predictive power. Recently Perrin (my son, not me) and coworkers studied the stability to hydrolysis of organotrifluoroborates RBF_3^- (¹⁰). The rate-limiting step is the heterolysis of a first B-F bond (Scheme 3). The substituent effect of the R group ought to be analogous to its substituent effect on the protonation equilibrium of RCO_2^- , in that both reactants are losing a negative charge. Indeed, for a series of 12 different RBF_3^- a plot of $-\log k$ is linear in the $\text{p}K_a$ of RCOOH , as shown in Figure 5. (It should be noted that the plot is vs. $\text{p}K_a$, not the σ of eq 1, because R is not restricted to aryl.) From the rate constant for $\text{PhS}^+(\text{CH}_3)\text{CH}_2\text{BF}_3^-$ on this plot it was possible to predict that the

pK_a of $\text{PhS}^+(\text{CH}_3)\text{CH}_2\text{COOH}$ is 0.98, and this was confirmed by titration to be 1.1. It was also possible to predict that $t_{1/2} = 10.4$ years for CF_3BF_3^- . Moreover, the ability to predict stability toward hydrolysis then permitted the development of ^{18}F -labeled bioconjugates suitable for positron emission tomography (PET scans) (¹¹).

Scheme 3. Hydrolysis of organotrifluoroborates.

Figure 5. Plot of $-\log k$ for hydrolysis of RBF_3^- vs. pK_a of corresponding RCOOH , from Ref 10.

Linear free-energy relationships

Eq. 1 has the form of a linear-free energy equation. Replacing σ_X by $\log(K_a^X/K_a^H)$ for benzoic acids, changing $\log_{10}$ to $\ln$, and multiplying by $-RT$ converts eq 1 to eq 2, where the extra subscript in ΔG_0° refers to the acidity of benzoic acids. Alternative forms are given in eq 3, where the constant C contains the terms for the unsubstituted derivative. Thus a plot of the free energy of activation or of the standard free energy of reaction vs. the standard free energy of ionization of the substituted benzoic acid should be linear, with slope ρ .

$$\Delta G^\ddagger_X = \Delta G^\ddagger_H + \rho(\Delta G_0^\circ_X - \Delta G_0^\circ_H) \quad \text{or} \quad \Delta G^\circ_X = \Delta G^\circ_H + \rho(\Delta G_0^\circ_X - \Delta G_0^\circ_H) \quad (2)$$

$$\Delta G^\ddagger_X = C + \rho \Delta G_0^\circ_X \text{ or } \Delta G^\circ_X = C + \rho \Delta G_0^\circ_X \quad (3)$$

Hammett acknowledged that an inspiration for the Hammett equation (eq 1) was Brønsted's catalysis law relating rate constants of proton transfer, k_{HA} , and equilibrium acidity constants, K_{a}^{HA} , as expressed in eq 4, where k_0 and K_{a}^0 are rate constant and acidity constant, respectively, for a reference acid. The alternative form, eq 5, is a linear free-energy relationship between the free energy of activation for proton transfer and the standard free energy of that proton transfer.

$$\log k_{\text{HA}} = \log k_0 + \alpha(\log K_{\text{a}}^{\text{HA}} - \log K_{\text{a}}^0) \quad (4)$$

$$\Delta G^\ddagger_{\text{HA}} = C + \alpha \Delta G^\circ_{\text{HA}} \quad (5)$$

Hammett noted: "The idea that there is some sort of relationship between the rate of a reaction and the equilibrium constant is one of the most persistently held and at the same time most emphatically denied concepts in chemical theory. Many organic chemists accept the idea without question and use it, frequently with considerable success, but practically every treatise on physical chemistry points out that such a relationship has no theoretical basis and that it is in fact contradicted in many familiar cases" (¹²). Yet the contradictory cases (such as the violent combustibility of potassium even though its oxidation is less exothermic than that of charcoal) are readily apparent as lacking analogy, and the cases where reactions are analogous do provide guidance and insight into reactivity.

Hammett's extension of Brønsted's linear free-energy relationship is especially remarkable in its generality and scope. Eq 4-5 relate the kinetics of a proton transfer to the equilibrium constant for ionization of that same acid. The two reactions are very similar. Eq 1-3 are more general. They can relate the kinetics of a reaction to the equilibrium constant for a different reaction, the ionization of benzoic acids. All that is necessary is that the two reactions be analogous.

The Hammett equation can be generalized still further, to what are called quantitative structure-activity relations, part of a broad field of study sometimes called correlation analysis (¹³, ¹⁴, ¹⁵). These relations are not limited to rate constants of chemical reactions. They can correlate the effects of substituents on boiling points, biological activity, toxicity, pharmacokinetics, and drug

activity. All that is needed are molecular and solvent parameters such as molecular weight, water-octanol partition ratio, hydrogen-bond donor/acceptor ability, solvent polarity, and/or steric effects.

Deviations from the Hammett equation are also informative. The circle at $\sigma_X = 0.78$ in Figure 4 is for *p*-nitro. Its positive deviation is evidence that the analogy between the acidities of anilines and the acidities of benzoic acids is imperfect. A *p*-nitro group on an anilinium ion (**1**) is more electron-withdrawing than would be expected from its electron-withdrawing power on a benzoic acid. This is a consequence of the additional resonance form (**2**) available to *p*-nitroaniline, which enhances the electron-withdrawing power of the nitro group.

Eventually success with the Hammett equation became too routine. Chemists delighted in observing deviations, which showed the limitations of analogy. Besides, those deviations allowed the observers to define other substituent parameters, which often could be published in a more prestigious journal. Among these are σ^+ , σ^- , F , R , σ^* , E_s , σ_X , σ_α , σ_F , and σ_R (¹⁶). Thus, in a study of the polarographic reduction of substituted benzyl chlorides we found that the half-wave potentials, which measure the rate of the electron-transfer reaction in Scheme 4, follow the Hammett equation with $\rho \sim 1.45$, consistent with an electron-rich transition state as expected from adding an electron (¹⁷). However, the correlation is not good. In particular, the positive deviation of *p*-CH₃S is extreme, consistent with an increased ability of this substituent to stabilize a radical, as expressed by the second resonance form for the transition state in Scheme 4. At the time of that study there were too few data to justify defining a new substituent constant, $\sigma^\bullet$, reflecting radical stabilization, but eventually such scales were devised (¹⁸).

Scheme 4. Polarographic reduction of benzyl chlorides.

Other contributions by Hammett

The Curtin-Hammett Principle is a general statement about the kinetics of a reaction with two reactants, A and B, and two products, C, and D, as in Scheme 5 (¹⁹). The two reactants must equilibrate rapidly compared to the rate of the chemical reaction, and the two products must be stable to equilibration. Usually A and B are conformers (conformational isomers), but they could also be tautomers. The observed rate constant for this kinetic scheme is given in eq 6, and the product ratio is given in eq 7. Notice that the product ratio is not equal to the equilibrium ratio K_e .

Scheme 5. Reaction with two reactants and two products, subject to the Curtin-Hammett Principle.

$$k_{\text{obs}} = \quad (6)$$

$$= \quad (7)$$

The Curtin-Hammett Principle is an Uncertainty Principle about such kinetics. It is clear that the measurement of k_{obs} and product ratio is insufficient to specify the three parameters k_A , k_B , and K_e , because there are only two equations in three unknowns.

Another conclusion from the Curtin-Hammett Principle can be drawn from the energy diagram in Figure 6. Although k_A and k_B are governed by the activation free energies $\Delta G_A^\ddagger$ and $\Delta G_B^\ddagger$, it can be shown that the product ratio is governed by the relative energies, $G_C^\ddagger$ and $G_D^\ddagger$, of the two transition states.

Figure 6. Energy Diagram for Curtin-Hammett kinetics

Another contribution of Hammett's to fundamental chemistry is the Hammett acidity function H_0 (pronounced "aitch-nought"), defined in eq 8 (²⁰). It uses a series of indicator bases B, for which the ratio $[BH^+]/[B]$ can be measured colorimetrically. In practice, the bases are substituted anilines, but acidity functions have been extended to other kinds of indicators. In dilute aqueous solution H_0 is defined as equal to pH and is then extended to weaker bases and more acidic solutions by a relay (step) method. Thus H_0 in 100% H_2SO_4 is found to equal -10.6 (a negative value) corresponding to a 4×10^{10} -fold increased acidity over 1M H_2SO_4 . Subsequently George Olah extended acidity functions to "superacids" (²¹), media that are even more acidic than 100% H_2SO_4 , a development that won him the 1994 Nobel Prize in Chemistry.

$$H_0 = pK_a^{BH^+} - \log([BH^+]/[B]) \quad (8)$$

The acidity function H_0 can be used to correlate reactivity in strong acid. Often it is found that rate constants follow eq 9, where k_{obs} is the observed rate constant in an acidic medium and where dividing by $[H^+]$ corrects the pseudo-first-order rate constant to a second-order one. The success of this correlation depends on the extent to which the transition state is analogous to an anilinium ion. An apt example is the hydrolysis of sucrose, via unimolecular heterolysis of the protonated substrate (²²).

$$\log(k_{obs}/[H^+]) = -H_0 \quad (9)$$

If the analogy does not hold, it might be possible to generalize eq 9 to eq 10, with a sensitivity parameter α , analogous to ρ in eq 1. An example is the iodination of acetophenone, where the rate increase is simply linear in $[H^+]$, so that $\alpha \sim 0$, because the rate-limiting step is C-H

deprotonation of the *O*-protonated substrate by water (²³). However, it must be admitted that such generalizations are not very useful.

$$\log(k_{\text{obs}}/[\text{H}^+]) = -\alpha H_0 \quad (10)$$

The augmentation of acidity, as expressed by H_0 , can be understood in terms of the thermodynamic activity of water (²⁴). If an acid-base reaction is expressed as eq 11, then the equilibrium will lie further to the right as the activity of water is reduced. Indeed, the excess acidity can be defined as $-H_0 - \log[\text{H}^+]$, where the second term reflects the increase of acidity due simply to the molarity of acid. A plot of the excess acidity vs. the logarithm of the water activity is adequately linear, with slope = 4, consistent with a formula of $\text{H}(\text{OH}_2)_4^+$ for hydronium ion, although over a wider range of acid concentrations a variable slope is observed (²⁵). The interpretation of these observations is simple: The excess acidity of strong acids is due to the liberation of n molecules of water upon protonation of the base B.

The activity of water also correlates the kinetics of the mercuration of benzene (Scheme 6). It was observed that the reaction is accelerated by acids, especially perchloric and nitric, and by their anionic salts (²⁶). The acceleration had been ascribed to formation of a reactive complex HgA^+ , in which the anion A^- is a better leaving group than H_2O . However, the kinetic isotope effect, $k_{\text{C}_6\text{H}_6}/k_{\text{C}_6\text{D}_6}$, is 6.75 in dilute solution and 4.68 in 6.65 *M* HClO_4 (²⁷), so that the rate-limiting step in Scheme 6 must be the deprotonation of the intermediate, whose rate is independent of that leaving-group ability. Moreover, the acceleration by perchloric acid and its salts does not correlate with H_0 (or with another acidity function H_{R}). Therefore this is not a case of acid catalysis.

Scheme 6. Mercuration of benzene.

To describe this behavior a new acidity function, Hg_0 , was defined, as in eq 12, where k_2 is the second-order rate constant for reaction of benzene with Hg^{++} . This is analogous to eq 9, except that it applies to a Lewis acid, and an excess Lewis acidity can be defined as $-Hg_0 - \log[Hg^{++}]$. Moreover, both Hg_0 and the excess acidity were found to depend only on water activity. The slope of the plot of excess acidity against the logarithm of the water activity is ~ 15 in dilute solution and decreases to ~ 4 in 8 M $HClO_4$. The interpretation of these observations is also simple: If the mercuration reaction is expressed as eq 13, analogous to eq 11, the excess acidity in strong acids is due to the liberation of n molecules of water upon formation of the transition state in Scheme 6.

$$\log(k_2/[Hg^{++}]) = -Hg_0 \quad (12)$$

Frank Westheimer was delighted with these results. He had been a post-doc with Hammett, who assured him that the H in H_0 refers to hydrogen, not to Hammett. Now we had a new acidity function, which we should call W_0 , where he assured me that the W would refer to water, not to Westheimer. He was disappointed that the proper designation is Hg_0 .

Physical Organic Chemistry

The influence of Hammett's pioneering research was reinforced with his book, *Physical Organic Chemistry* (²⁸), which defined the field. It is a designation that Hammett had arrived at in the 1930's. Table 1 lists its contents. The overlap with his earlier textbook, "Solutions of Electrolytes", is clear. This book goes further and presents known reaction mechanisms and the methodology for determining additional mechanisms. Chapter 7 features both the Hammett equation (eq 1) and the Brønsted catalysis law (eq 4). Chapter 9 presents the acidity function H_0 (eq 8). A second edition was published in 1970 (²⁹), but it was more idiosyncratic, less successful, and certainly less influential.

Table 1. Table of Contents of Hammett's *Physical Organic Chemistry*.

I. Structural Theory: Nonelectrolytes	VII. The Effect of Structure on Reactivity
II. Electrolytes	VIII. Enolization and Related Reactions
III. Equilibrium and Energy of Reactions	IX. The Quantitative Study of Acids and Bases
IV. Reaction Rates and Mechanisms: Energies, Free Energies, and Entropies of Activation	X. Carbonium-Ion Reactions
V. The Displacement Reaction	XI. Carbonyl-Addition Reactions
VI. Stereochemistry of the Displacement Reaction	XII. Atom and Radical Reactions: Other Redox Reactions

Another influential book in the area of physical organic chemistry was *Structure and Mechanism in Organic Chemistry* ⁽³⁰⁾, by Christopher K. Ingold (Figure 7). (See the chapter on C. K. Ingold by John H. Ridd elsewhere in this book.) Ingold was professor at University College, London from 1930 to 1961 and was knighted in 1958. He too did much to develop the theory of organic reaction mechanisms, and he was the first winner, in 1965, of the James Flack Norris Award in Physical Organic Chemistry, ahead of Hammett, who was second.

Figure 7. Sir Christopher K. Ingold (1893-1970), from

Above I expressed the opinion that Hammett deserved the Nobel Prize in Chemistry. The question remains: Why did he *not* win it? A possible answer is that it might have been appropriate for him to share it with Ingold for their separate but reinforcing contributions to the development of the field of physical organic chemistry. Indeed, there were 68 nominations for Ingold between 1940 and 1965 (far more than the nominations of Hammett in that period), and no doubt additional ones thereafter, but later records are not yet available. Ingold's candidacy was probably blocked by Sir Robert Robinson, a Nobel Laureate who was influential with the Nobel Committee and who harbored a grudge against Ingold (³¹). Alternatively, Derek Davenport has focused on Ingold's adoption of the "invective effect" (³²). Another explanation is that the judges were simply misinformed, as I inferred many years ago from a conversation with a member of the Nobel Committee for Chemistry, who thought that Bob Taft (who had nominated Hammett) deserved the prize more than Hammett did.

Summary

In my opinion Louis P. Hammett deserved a Nobel Prize for his discovery of the quantitative relation between rate constants and acidity constants of benzoic acids. This discovery established organic chemistry as a science with regularities, rather than only a collection of observations and preparations. The resulting ability to understand and predict reactivity across a wide range of processes represents a powerful advance of science and a benefit to humanity.

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