

The centenary of the birth of Louis Hammett

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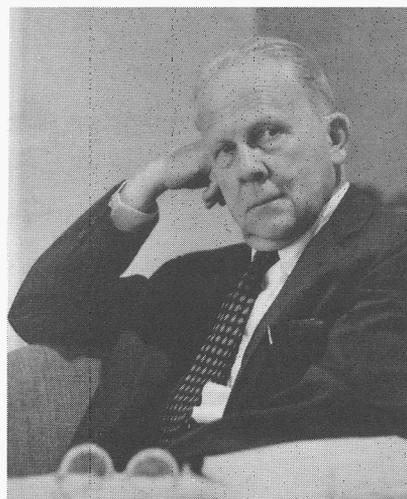
Abstract - Louis Plack Hammett was born on 7th April 1894. He is commonly regarded as one of the founding fathers of physical organic chemistry. This is partly by virtue of his original contributions to quantitative structure-reactivity relationships (the Hammett equation) and to the study of solutions of organic compounds in concentrated acids, particularly strong acids (the Hammett acidity function). He also exerted a major influence, however, through his book Physical Organic Chemistry, published in 1940, with a new edition in 1970.

Louis Plack Hammett was born in Wilmington, Delaware on 7th April 1894 and died in his 93rd year at Medford, New Jersey on 23rd February 1987. Thus the Twelfth International Conference on Physical Organic Chemistry took place five months after the centenary of Hammett's birth, so a centenary tribute seemed appropriate. I gave a Hammett Memorial Lecture at the Fourth International Conference on Correlation Analysis in Organic Chemistry in Poznań in 1988. A somewhat expanded version of the text of this was later published in Progress in Physical Organic Chemistry (1). This centenary tribute is a greatly abbreviated version of the earlier lecture and article.

Hammett was awarded his BS from Harvard University in 1916 and his PhD from Columbia University, New York in 1923, there being an interval between his studies for these degrees during which he worked in Zürich under Staudinger and engaged in wartime scientific activities and briefly in industrial research. From 1921 to 1961 he was on the chemistry faculty of Columbia University and thereafter was Professor Emeritus.

Hammett is commonly regarded as one of the founding fathers of physical organic chemistry. Actually this term only began to be widely used after Hammett employed it for the book he published in 1940 (2). By that year the foundations of his own original contributions to the subject had been laid. These were the equation for summarizing the effects of meta- and para-substituents on the rate or equilibrium constants for side-chain reactions of benzene derivatives and the study and applications of concentrated solutions of acids, in particular strong acids, through the acidity function. Hammett's pre-eminent connection with these is indicated by the commonly used terms: the Hammett equation and the Hammett acidity function, a usage he did not himself encourage. The second edition of his book appeared in 1970 and it contains much evidence of the way in which the first edition and his own original contributions had influenced the development of physical organic chemistry in the intervening thirty years (2). Hammett retained his interest in the subject through his quarter century of retirement: indeed he was 76 years of age when the second edition of the book appeared.

In background, experience and outlook Hammett was very different from most physical organic chemists, who tend to regard themselves as primarily organic chemists, who use physico-chemical techniques to attack problems of structure, mechanism and reactivity. I think this would be true of most of those attending ICPOC 12. Hammett regarded himself as a physical chemist, who found his research outlet in studying organic compounds and their reactions. When Hammett received the Norris Award in Physical Organic Chemistry in 1966, he gave an address entitled "Physical Organic Chemistry in Retrospect" (4). In this he described the influences which had made him as he was.



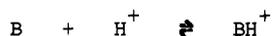
Louis Hammett ca. 1960

Hammett characterized as "ambiguous" the way in which his own research experience developed from 1916 and through the 1920s. He meant that he responded to very varied influences and in consequence developed interests covering a wide range of chemistry. This process began at Harvard and continued in his work with Staudinger and in his wartime activities and post-war industrial research. But it was at Columbia that the most important developments occurred. He was much influenced by several senior colleagues towards interests in both physical and organic chemistry. He chose to pursue his doctoral studies under the analytical chemist H. T. Beans, in examining the factors that affect the reliability of the hydrogen electrode (5). The discharge of hydrogen ions at platinum and other metals and related matters such as catalytic properties and over-voltage, continued to interest Hammett for many years (6).

As a young Instructor and later Assistant Professor, Hammett taught qualitative inorganic analysis. This led to his first book, published in 1929, and entitled Solutions of Electrolytes, with the sub-title With Particular Application to Qualitative Analysis (7). The book was no mere handbook of recipes for systematic qualitative analysis. Its emphasis was on the physical chemistry underlying the analytical procedures. Hammett's activities in analytical chemistry included a research collaboration with his colleague George Walden in the early 1930s. This led to the introduction of the ortho-phenanthroline-ferrous ion complex as a high potential indicator for redox titrations (8). If you require any further convincing that Hammett was a physical chemist and regarded himself as such, I simply mention that he wrote a textbook of physical chemistry, which was published in 1952 (9).

The most important influences on Hammett that led ultimately to his status as one of the founders of physical organic chemistry were the papers of Alfred Werner, G. N. Lewis, J. N. Brønsted, and A. R. Hantzsch. The influence of the first three no doubt contributed to Hammett's general interest in electrochemistry. The influence of Hantzsch was also in connection with electrochemistry, which appears odd at first sight, because Hantzsch is generally thought of as a great German organic chemist of the late 19th and early 20th centuries (10). But much of Hantzsch's work had physico-chemical aspects, unusual at the time. The part of Hantzsch's work that appealed to Hammett was his investigations of acids and bases in non-aqueous solutions, particularly in anhydrous sulfuric acid (11). In the light of the then recent advances in the theory of acids and bases through the work of Brønsted and of Lewis, Hammett saw the behaviour of organic compounds in solution in highly acidic media as a promising field of research. Thus around 1928 Hammett began the studies which led to one of his major contributions to physical organic chemistry, the acidity function.

In work with his student Deyrup, Hammett came to define the acidity function H_0 in terms of the equilibrium between a suitable indicator B and its protonated form BH^+ in a given solution (12). Thus:



$$H_0 = pK_{BH^+} - \log (C_{BH^+}/C_B)$$

where C_{BH^+}/C_B is the directly observable concentration ratio of the indicator in its two differently coloured forms. Hammett and Deyrup (12) developed a series of indicators whereby H_0 could be measured for any solution in the range from dilute aqueous sulfuric acid to 100% sulfuric acid by the so-called step method. At that time the only instrument available was a simple visual colorimeter and this greatly restricted the choice of indicators, which were mainly nitroanilines. Actually this was fortunate in that it led to a fairly simple pattern of results. A wider choice of indicators might well have led to such bewildering results that serious doubts might have been cast on the value of the entire enterprise.

From the start Hammett envisaged two possible types of application of the acidity function. One was the determination of the strengths of bases and of acids, too weak and too strong, respectively, to permit measurements in aqueous solutions. The other was the interpretation of velocity data obtained for reactions carried out in concentrated solutions of acids. Hammett pursued research in this general area throughout the 1930s with several collaborators, leading to around twenty papers. From 1934 a crude form of spectrophotometer was used. Hammett's work with Paul (13) on the hydrolysis of sucrose and with Zucker (14) on the iodination of acetophenone was particularly influential in the development of the field. This part of Hammett's work involved ideas that have become known as the "Zucker-Hammett hypothesis", and they initiated a long saga in physical organic chemistry, leading ultimately to the work of Bunnett and Olsen in the 1960s (15).

Hammett's work in this area largely ended with World War II, with minor exceptions. He himself took no part in the proliferation of acidity functions, which has led to the definition of over 400 different varieties (16). It had probably been Hammett's hope that H_0 would describe the behaviour of a wide range of substrates in highly acidic media. However, in the first edition of his *Physical Organic Chemistry* in 1940, he did define the function H_- for the tendency to transfer a proton to a base with a single negative charge, and he recognized that for a given medium H_0 and H_- might have very different values (17).

I have already mentioned that Hammett was much influenced by the papers of Brønsted. These included that of Brønsted and Pedersen (18) in 1924 on the decomposition of nitramide catalysed by general bases, in which for a series of bases the values of the logarithm of the rate constant plotted against values of the logarithm of the dissociation constant of the conjugate acid of the base gave a straight line of negative slope. This was the first example of the type of relationship that was generalized by Brønsted to include acid catalysis in 1926 (19). Hammett became interested in the possibility of finding analogous relationships for other types of reaction. The initial stage of this interest was his starting of experimental studies in kinetics in the 1930s. His first kinetics paper, published with Pfluger in 1933, was a study of the reactions of methyl esters with trimethylamine in methanol, which showed that there was a linear relationship between the logarithms of the rate constants for the reactions and the logarithms of the ionization constants of the corresponding carboxylic acids in water (21). (Fig. 1)

As the 1930s advanced, Hammett became increasingly aware that there were already many data in the literature that conformed to logarithmic relationships analogous to the Brønsted equation. In particular, around 1935 he became aware of the work of G. N. Burkhardt at Manchester University. Burkhardt and his collaborators, independently of Hammett, found a widespread conformity to logarithmic relations for the rate or equilibrium constants of the side-chain reactions

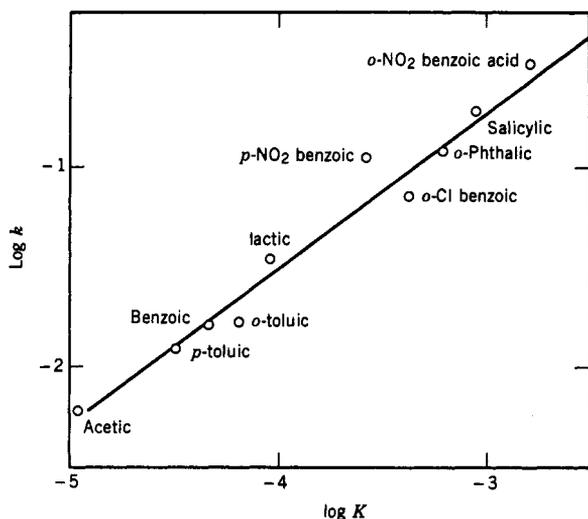
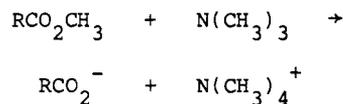


Fig. 1 Correlation between values of $\log k$ for the reactions of trimethylamine with methyl esters of carboxylic acids in methanol at 100°C and values of $\log K$ for the ionization of the carboxylic acids in water, extrapolated to 100°C.



(Fig. 1 is reproduced by courtesy of the American Chemical Society.)

of meta- or para-substituted benzene derivatives (21). Burkhardt's contributions have been rather overlaid by Hammett's, although Hammett was always very careful to give Burkhardt due credit. Undoubtedly the reason why Hammett rather than Burkhardt is commonly remembered in this connection is because Hammett went on to develop the delightfully simple relation that we know as the Hammett equation.

Hammett's paper on "The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives." was received by the American Chemical Society on November 7th 1936, and was published in the January 1937 issue of their journal (22). In this paper Hammett put forward the equations:

$$\log k = \log k^{\circ} + \rho\sigma \text{ for rates}$$

$$\log K = \log K^{\circ} + \rho\sigma \text{ for equilibria}$$

to summarize the effects of meta- or para-substituents on the rate constants or the equilibrium constants of side-chain reactions of benzene derivatives, in terms of substituent constant σ and reaction constant ρ . The presentation of the equation was of course accompanied by the famous diagram reproduced as Fig. 2, the first published Hammett plots.

In later life Hammett was rather surprised by what his eight page paper had started. He himself made little contribution to refining and extending the Hammett equation. The $\rho\sigma$ relation did, of course, feature a year or two later in Hammett's book Physical Organic Chemistry (2) as part of Chapter VII, "The Effect of Structure on Reactivity". I have the feeling that great interest in the Hammett equation was slow to develop until Jaffé gave it extensive exposure in his "Re-examination of the Hammett Equation", published in Chemical Reviews in 1953 (23), which presented the application of the equation to about 400 reaction series. At about the same time, Robert W. Taft, who had done post-doctoral work with Hammett in the late 1940s began to publish work on systems for which no simple Hammett-type treatment had been found to apply, notably the reactions of aliphatic systems and ortho-substituted benzene derivatives. Taft's success in this area became well known after it was featured in Newman's book on steric effects in 1956 (24). Thus the 1950s saw the real flowering of what Hammett had started in structure-reactivity relationships: the refinement of the Hammett equation through the proliferation of different types of sigma value, notably σ^+ and σ^- ; the dissection into σ_I and σ_R ; the separation of polar, steric and resonance effects through σ^* and E_S ; the treatments proposed by Wepster and by Yukawa and Tsuno; the dual-substituent parameter equation; the application of Hammett-type treatments to spectroscopic data, notably NMR and IR; and so on (25). But in all of this Hammett was content to be an observer, duly recording what went on up to about 1970 in the second edition of his Physical Organic Chemistry (3). We may recall, however, Hammett's recognition in 1937 that the

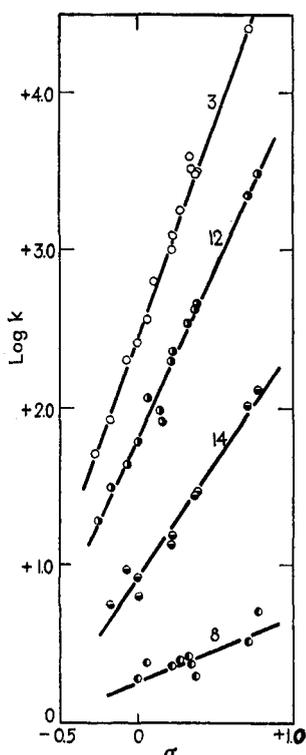


Fig. 2. The first published Hammett plots of $\log k$ or $\log K$ versus σ for various reactions. The numbered lines correspond to the following reactions: 3 - ionization of substituted anilinium ions in water at 25°C; 8 - bromination of substituted acetophenones in acetic acid-water-sodium acetate at 25°C; 12 - ionization of substituted phenylboric acids in 25% ethanol at 25°C; 14 - solvolysis of substituted benzoyl chlorides in methanol at 25°C. The position of the scale of ordinates is arbitrary.

(Fig. 2 is reproduced by courtesy of the American Chemical Society.)

para-nitro group required on occasion an exalted sigma value (later designated σ^-), thereby indicating one of the directions in which the $\rho\sigma$ equation would be further developed (2, 22).

During World War II, like many senior scientists of the time, Hammett was engaged in war work, particularly in connection with explosives and rocket propellants. After the war, as far as experimental research was concerned, he appears to have sought topics that would be largely fresh and stimulating to him but within the general area of solution kinetics. These included the acid-catalysed hydration of olefines and the hydrolysis of esters catalysed by cation exchange resins. A further area of research was essentially concerned with developing techniques for studying faster reactions than could be examined by the kinetic methods of the times. Thus Hammett studied several reactions by means of a stirred flow reactor, including the alkaline bromination of acetone and the alkaline hydrolyses of methyl and ethyl formate and of diethyl succinate. All this work shows very clearly Hammett's interest in carrying out elegant experimental studies (26).

In 1961 Hammett retired from Columbia University. During the next ten years he delivered many lectures and seminars as a guest at various universities and other institutions. In this period he prepared the second edition of *Physical Organic Chemistry* (3). From the early 1950s to the 1970s he accumulated the responsibilities and awards that come to those who are recognized as elder statesmen in their particular disciplines. Thus in the late 1950s he was a member and later chairman of the important Committee on Professional Training of the American Chemical Society. He received the James Flack Norris Award of the A.C.S. twice, in 1960 and 1966. He also received the Priestley Medal - the supreme A.C.S. award - and many other lesser awards; he became an Honorary Fellow of the Royal Society of Chemistry.

I would like to conclude this outline of Hammett's life and work by quoting the words with which Hammett closed his Norris Award address (4) in 1967 (when he was 73 years of age), since they express an attitude and a confidence which I hope is shared by all those who attended ICPOC 12. Hammett said, "So, for many years to come, I am sure that physical organic chemistry will continue to be fun, as it has been all the time I have been a chemist."

References and Notes

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