

## THE PREHISTORY OF THE HAMMETT EQUATION

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Dedicated to Professor Dr. Otto Exner on the occasion of his 75th birthday, in recognition of his outstanding contributions to physical organic chemistry and especially the application of correlation analysis thereto.

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On November 7th 1936 the American Chemical Society received a short paper entitled “The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives.” The author was the physical chemist Louis P. Hammett (1894–1987) of Columbia University in New York City. In those days publication was often very rapid and Hammett’s paper appeared in the January 1937 issue of the *Journal of the American Chemical Society*<sup>1</sup>. It was just eight pages long. In this paper Hammett presented the equation:

$$\log K = \log K^0 + \rho\sigma \quad (1)$$

to summarize the effects of *meta*- or *para*-substituents on the rate constants or equilibrium constants of side-chain reactions of benzene derivatives. The symbol  $K^0$  denotes the statistical quantity (intercept term) approximating to  $K$  for the “parent” or “unsubstituted” compound<sup>2</sup>. The substituent constant  $\sigma$  is a measure of the electronic effect of replacing H by a given substituent (in the *meta* or *para* position) and is, in principle, independent of the nature of the reaction. The reaction constant  $\rho$  depends on the nature of the reaction (including conditions such as solvent and temperature) and is a measure of the susceptibility of the reaction to the electronic effects of substituents. With  $\rho$  defined as unity for the ionization of substituted benzoic acids in water at 25 °C, Hammett was able to tabulate  $\sigma$  values for 14 substituents (including that for H as zero) and for a further 17 substituents by including secondary values derived from correlations of data for various reactions by applying the primary  $\sigma$  values. Hammett found in the literature some 38 reaction series on which to test the equation. He concluded that the verification of the equation was satisfactory.

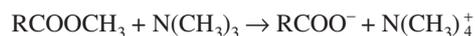
Hammett presented an updated version of the treatment in his book published in 1940 (Ref.<sup>3</sup>). The number of  $\sigma$  values tabulated had increased to 44 and the number of reaction series to 51.

The story of the applications, modifications, and extensions of the  $\rho\sigma$  or Hammett equation is well known and has been told in outline or in detail in numerous articles and books<sup>4,8</sup>. The background to Hammett’s paper of 1937 is not so well known, although there is an outline of this by Hammett himself<sup>9</sup> and the matter has been touched on briefly in various pla-

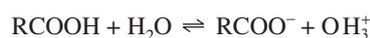
ces<sup>5,6</sup>. It is the aim of the present article to give a somewhat more detailed account of the prehistory of the Hammett equation.

In his article “Physical Organic Chemistry in Retrospect”, written in 1966 (Ref.<sup>9</sup>), Hammett describes how in the early 1920s he was much influenced by reading the papers of several prominent chemists including J. N. Brønsted (1879–1947)<sup>10,11</sup>. Hammett thus became familiar with the Brønsted equation. In his recollections over thirty years later of the consequences of his interest in the Brønsted equation, Hammett wrote as follows under the heading of “Correlations of Structure and Reactivity”<sup>9</sup>:

“The parent of all relationships of this kind is the discovery by Brønsted and Pedersen<sup>10,11</sup> of general acid and base catalysis and of the rule that the logarithms of the rate constants of the catalyzed reactions are linearly related to those of the acidity constants of the catalyzing acid or base. Pedersen<sup>12</sup> in 1931 clearly recognized that this is a relationship between the rates and the equilibria of the same series of reactions, i.e. the proton transfer process. In 1933 Pfluger and I<sup>13</sup> extended the idea by finding a linear relation between the logarithms of the specific rates of the reactions



and those of the equilibrium constants of the reactions



i.e., a relation between the rate constants of one reaction and the equilibrium constants of a different but closely related reaction. And in 1935 both Burkhardt<sup>14</sup> and I<sup>15</sup> found a whole flock of linear free energy relationships in the reactions of substituted benzene derivatives.”

Hammett’s summary of the situation in the early 1930s merits considerable expansion and clarification.

### Hammett and Pfluger (1933)

Hammett and Pfluger’s paper<sup>13</sup> appeared in the October 1933 issue of the *Journal of the American Chemical Society*, having been received on June 27th. The paper records that it is based upon a dissertation submitted by Pfluger at Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May 1933. It seems likely that the experimental work on “The Rate of Addition of Methyl Esters to Trimethylamine” had been commenced sometime in 1931, but possibly earlier. Clearly this work was started as part of a search for other kinds of reaction which would conform to logarithmic relationships of the type found by Brønsted to apply to general acid and base catalysis. There is, however, no clear indication in the paper as to why this particular reaction was selected for study. According to Hammett and Pfluger, the alkylation of tertiary amines by esters was discovered in 1902 by Willstätter and Kahn<sup>16</sup>, “who worked without solvent, and merely demonstrated the formation of a large yield of tetraalkylammonium salt. We have found that the reaction

goes cleanly and at a suitable rate for measurement in methyl alcoholic solution at 100 °C". No other reference to earlier work on the reaction is cited.

This was Hammett's first research involving rate measurements. The experimental procedures are described in detail and the work was manifestly carried out very carefully. The selection of a temperature about 35 °C above the normal boiling point of methanol necessitated the use of sealed ampoules throughout the work. The progress of the reaction was followed by determining the concentration of trimethylamine which remained after definite intervals of time. Even at the elevated temperature used, the experiments with the less reactive esters lasted one to two weeks, and with the more reactive esters, a day or two. Good second-order kinetics were usually obtained.

The opening sentence of the paper reads as follows: "We have found that the rate of methylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is determined by the strength of the acid in a fashion which is without parallel in recorded ester reactions but is very similar to the general acid catalysis equation of Brønsted." Later in the paper it is apparent that by "recorded ester reactions" the authors had particularly in mind the alkaline hydrolysis of the ethyl esters of carboxylic acids, for which they show the 7 point scatter diagram, reproduced as our Fig. 1, and based on data from the literature. It would in fact have been possible for many more points to have been plotted on this graph. If several more points for *meta*- or *para*-substituted systems had been included, it would have become apparent that such systems were conforming to their own straight line; this is barely discernible for the three such points actually plotted. It seems that at this stage Hammett was looking only for a relationship as general as a Brønsted plot, involving both aliphatic and aromatic systems, including *ortho*-substituted systems. Such a general relationship he considered he had found for the ester-amine reaction.

The graphs which Hammett and Pfluger presented in support were subject to certain limitations and it will be better to show now a diagram in the form used by Hammett in his 1935 article<sup>15</sup>, which is undoubtedly very impressive as a linear free energy relationship, particularly in its contrast to the scatter diagram of Fig. 1. Much of the discussion section of Hammett and Pfluger's paper is devoted to this contrast, which the authors attribute to an important difference in mechanism as between alkaline ester hydrolysis and the reaction of the ester with tertiary amine. In the former the attack by the OH<sup>-</sup> is on the carbon of the carbonyl of RCOOC<sub>2</sub>H<sub>5</sub>, while in the latter the attack by the tertiary amine is on the carbon of the methyl group of RCOOCH<sub>3</sub>. Hammett was well aware "that any substitution, of whatever electrochemical nature, in the immediate neighborhood of the carboxyl group tends to decrease the hydrolysis rate," although he seems to have had reservations about the explanation of this in terms of "steric hindrance". This feature underlies the scatter of points in Fig. 1, while the clearer relationship in Fig. 2 arises because the point of attack is more remote from R.

Hammett and Pfluger do not claim that they embarked on the study of this reaction because they predicted that it would have the characteristics which they later found it to possess. Neither did Hammett make any such claim three decades later<sup>9</sup>. One is left with the feeling that whatever their reason

may have been for selecting the reaction, it was a fortunate choice in that it gave such a remarkable linear free energy relationship. This no doubt increased Hammett's confidence that the search for relationships of this type was a worthwhile pursuit and led him to follow the road which led ultimately to his paper of 1937 (Ref.<sup>1</sup>). This road involved examining the literature rather than undertaking further experimental studies.

### Hammett (1935)

During the early 1930s Hammett became aware that the literature already contained a great deal of data that conformed to logarithmic relationships. He drew attention to this in a talk given<sup>15</sup> in a one-day Symposium on "Kinetics of Reaction" held in the Division of Physical and Inorganic Chemistry at the 89th National Meeting of the ACS in New York City in

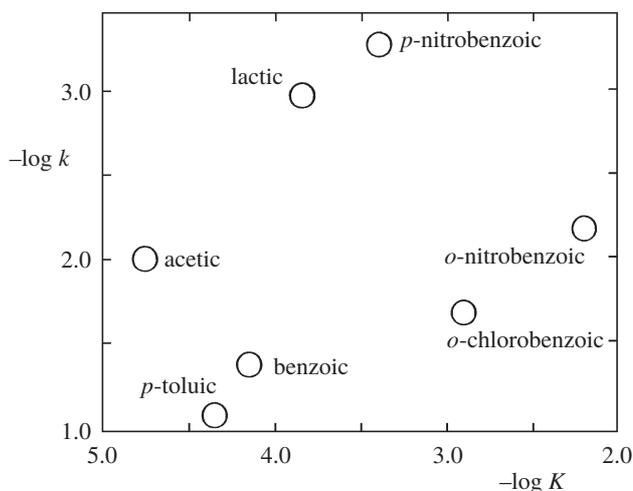


Fig. 1. Lack of correlation between the rate constants for the alkaline hydrolysis of ethyl esters of carboxylic acids and the ionization constants of the acids. Redrawn from Ref.<sup>13</sup>

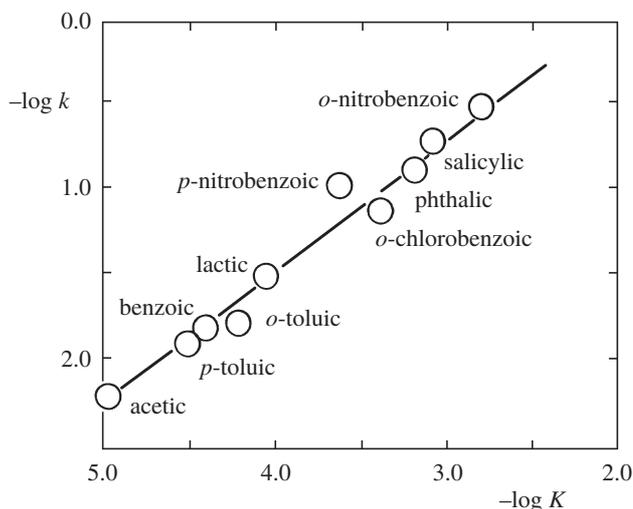


Fig. 2. Correlation between the rate constants for the reactions of trimethylamine with the methyl esters of carboxylic acids at 100 °C and the ionization constants of the acids at 100 °C. Redrawn from Ref.<sup>15</sup>

April 1935. Articles based on the various talks subsequently appeared in *Chemical Reviews*.

Hammett's paper was entitled "Some Relations between Reaction Rates and Equilibrium Constants". He was well aware that many physical chemists were sceptical about any claimed relationship between rates and equilibria, so he was careful to agree that "there is no universal and unique relation between the rate and equilibrium of a reaction." He went on to assert, however, "that there frequently is a relation between the rates and equilibrium constants of a group of closely related reactions. It is the purpose of this paper to review the known examples of this kind of relationship, to point out the quantitative form which it assumes, and to state certain limitations to its application."

Hammett's first example concerns reactions showing general acid or base catalysis and the Brønsted equation; the second is the methyl ester + trimethylamine reaction, as already discussed above. Next he presents data from the literature for rate constants of *meta*- or *para*-substituted aromatic amines reacting with various reagents, the relationships shown being to the equilibrium constants for ionization of the same or closely related amines. Thus linear logarithmic plots are presented for the rate constants of *meta*- or *para*-substituted anilines reacting with 2,4-dinitro-1-chloro-naphthalene versus the ionization constants of the substituted anilines, and correspondingly for the reactions of substituted anilines with benzoyl chloride.

Graphs were also presented for the alkaline hydrolysis of *meta*- or *para*-substituted ethyl benzoates versus the ionization constants of the corresponding substituted benzoic acids and for the alkaline hydrolysis of similarly substituted ethyl phenylacetates versus the ionization constants of the corresponding substituted phenylacetic acids. Hammett points out that the *ortho*-substituted systems cannot be incorporated in such relationships and comments: "It is an obvious generalization that correlations of this sort between the reaction rates and the equilibrium constants of a series of reactants will succeed only when the substitutions take place in a part of the molecule sufficiently removed from the point at which the reaction occurs."

The importance of *meta*- and *para*-substituted aromatic systems in the further development of linear free energy relationships was clearly now apparent to Hammett.

Hammett includes brief reference to rate-equilibrium relationships for oxidation-reduction reactions which he had come across in the literature. Barron (1932)<sup>17</sup> had found a linear relationship between the logarithms of the time required for 50 % oxidation by oxygen of the reduced forms of various dyes and the molar oxidation potentials of the dyes. Hammett refers also to an extensive series of investigations by Otto Dimroth (1933)<sup>18</sup> in which a similar relation holds for the reactions of a series of quinone derivatives with an organic reducing agent<sup>19</sup>.

### Burkhardt (1935)

The paper based on Hammett's talk at the ACS meeting in April 1935 was received in the *Chemical Reviews* office on June 20th. It appeared in the August issue. Unbeknown to Hammett, G. N. Burkhardt of the University of Manchester in England was working independently on rather similar lines<sup>20</sup>. For the past year or two he and two students, W. G. K. Ford

and E. Singleton, had been studying the kinetics of the acid-catalysed hydrolysis of potassium arylsulphates in water, and were comparing their results with those of other studies of substituent effects. They had found a widespread occurrence of logarithmic relationships involving rate or equilibrium constants for the side-chain reactions of *meta*- or *para*-substituted benzene derivatives. Burkhardt considered that these findings were sufficiently important to justify writing a letter to *Nature*, a commonly used means of rapid preliminary publication, pending the preparation and publication of a full paper. Burkhardt sent such a letter on September 29th 1935; it appeared<sup>14</sup> in the issue of *Nature* dated October 26th.

The letter was headed "Influence of Substituents on Organic Reactions: a Quantitative Relationship." After a brief mention of certain literature dealing with substituent effects in aromatic systems, Burkhardt refers to the work of Hammett and Pfluger<sup>13</sup> and then comes to the main reason for writing the letter:

"It now appears that this last quantitative relationship is more general. Plotting the logarithms of the dissociation constants of a number of *m*- or *p*-substituted benzoic acids as a reference series and, against them, the logarithms of the velocity constants of a number of side-chain reactions involving substances containing the same *m*- or *p*- substituents, one obtains a series of linear relationships. For example, a straight line is obtained for the alkaline hydrolysis of the various substituted ethyl benzoates, another for the substituted benzamides, and others for the solvent hydrolysis of the benzyl chlorides, the acid catalysed hydrolysis of the potassium arylsulphates, the alkaline hydrolysis of the ethyl cinnamates and so on. The logarithms of dissociation constants other than those of the substituted benzoic acids (for example, those of the phenylacetic acids) can be similarly related to the same reference series. The choice of this is quite arbitrary and the relationships of course hold between the different phenomena as well as between them and the reference series".

A footnote to the citation of Hammett and Pfluger<sup>13</sup> reads: "Since this letter was passed for press, a further paper by Hammett<sup>15</sup> has been received, which extends greatly the application of the linear relationship to the reactions of pairs of closely related substituted substances." Presumably the August issue of *Chemical Reviews* had reached the UK in early October.

Thus Hammett and Burkhardt had certainly been working independently on very similar lines. It may justly be claimed that the idea of using the ionization of substituted benzoic acids as a reference series came first from Burkhardt.

### Burkhardt, Ford, and Singleton (1936)

The full publication of the material summarized in the letter to *Nature* was "The Hydrolysis of Arylsulphuric Acids. Part I." It was received by the Chemical Society on October 19th 1935, and appeared in the January 1936 issue of the *Journal of the Chemical Society*<sup>21</sup>.

Potassium phenylsulphate is readily hydrolysed by boiling dilute mineral acid:



and the authors found that the reactions of a series of substituted arylsulphates in water could be conveniently followed at

48.6 °C and 78.7 °C by titration of samples with alkali. The reaction is of the first order with respect to substrate, with the rate coefficients being proportional to the hydrogen ion concentration<sup>22</sup>, but the kinetics were slightly complicated by an autocatalysis due to the production of bisulphate ion. In addition to potassium phenylsulphate itself, the hydrolysis of 4 *meta*-, 5 *para*-, and 4 *ortho*-substituted compounds was studied. The results for the *meta*- and *para*-substituted compounds were presented as a linear logarithmic plot against the dissociation constants of the corresponding substituted benzoic acids. As indicated in the letter to *Nature* (see above)<sup>14</sup>, corresponding results from the work of various authors for other side-chain reactions were also represented through similar logarithmic plots, giving, in all, nine such plots. One of the diagrams from the paper is redrawn as Fig. 3. The quality of the linearity of the plots was not uniformly good: there were some deviant points. This elicited some comments from Burkhardt and his colleagues, who also discussed their attempts to include *ortho*-substituted systems and various issues which they considered pertinent. Some features of the plots foreshadow features which emerged as important later in the development of linear free energy relationships.

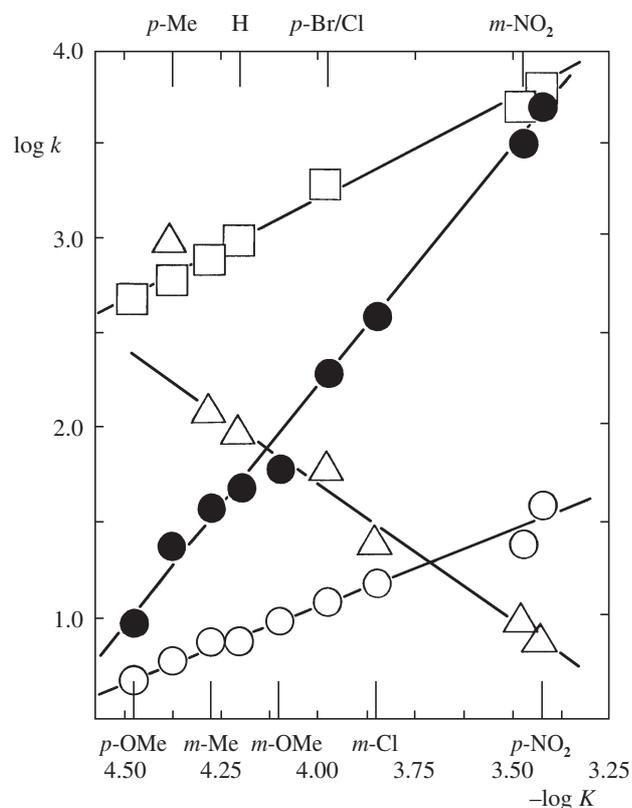


Fig. 3. Correlation between the rate constants for the side-chain reactions of *meta*- or *para*-substituted benzene derivatives and the ionization constants of the corresponding substituted benzoic acids. Redrawn from Ref.<sup>21</sup>. The position of the scale of ordinates is arbitrary; ○  $\log k$  for acid-catalysed hydrolysis of substituted potassium phenylsulphates in water at 48.6 °C, ●  $\log k$  for alkaline hydrolysis of substituted ethyl benzoates in aqueous ethanol at 30 °C, □  $\log k$  for alkaline hydrolysis of substituted benzamides in water at 100 °C, △  $\log k$  for hydrolysis of substituted benzyl chlorides in aqueous ethanol at 83 °C

Hammett's article in *Chemical Reviews*<sup>15</sup> is referred to in a more extended footnote than appeared in the letter to *Nature*<sup>14</sup>.

"Since this paper was written and a summary published<sup>14</sup>, Hammett<sup>15</sup> has extended the scope of the relationship observed by him and Pfluger<sup>13</sup> to include a wide variety of pairs of closely related phenomena, including, as one pair, the logarithms of the dissociation constants of the substituted benzoic acids against the logarithms of the rates of hydrolysis of the benzoic esters. Since he stresses closely related phenomena, the present extension to include reactions less clearly related on *a priori* grounds is largely complementary to his, and requires a still wider explanation."

The work of Burkhardt and colleagues on the hydrolysis of arylsulphuric acids was continued in two later papers<sup>23</sup>. Part IV (Ref.<sup>23</sup>) is of particular interest in connection with structure-reactivity and linear free energy relationships, since it deals with "(a) Conjugation between the Benzene Nucleus and Unsaturated Side Chains, and (b) Steric Effects and the Influence of Alkyl Groups." These later Parts were received by the *Chemical Society* on May 5th and appeared in the November 1936 issue of the *Journal*.

Burkhardt's contributions have rather been overlaid by Hammett's, although Hammett in his later publications was always very careful to give Burkhardt due credit and to acknowledge his own indebtedness to Burkhardt's work<sup>24,25</sup>. Undoubtedly the reason why Hammett rather than Burkhardt is commonly remembered in connection with linear free energy relationships is because Hammett went on to develop the delightfully simple summarizing relation that we know as the Hammett Equation.

Data in the last Burkhardt paper (Part IV<sup>23</sup>) were actually the basis of values for 11 new substituents in the expanded version of Hammett's Table of  $\sigma$  constants which is in the account of the Hammett equation in the 1940 book<sup>3</sup>.

### Hammett (1936)

There is one other paper by Hammett which should be mentioned as relevant to the background of the Hammett equation<sup>26</sup>. The September 1936 issue of the *Journal of Chemical Physics* contains a short paper (just over 4 pages) by Hammett, which had been received on June 1st. It was entitled "The Effect of Structure Upon the Reactions of Organic Compounds. Temperature and Solvent Influences". It is interesting that the first part of the title is exactly the same as that of the 1937 paper on the  $\rho\sigma$  equation. The reactions are, in fact, mainly the ionization of formic acid and 6 other aliphatic carboxylic acids and of benzoic acid and 10 substituted benzoic acids, the data considered (from the literature) being substituent induced changes in free energy, enthalpy, and entropy of ionization, with formic/benzoic acid as reference. The discussion involves various thermodynamic/electrostatic equations, in which the substituent effects are modelled in terms of dipole moments, and solvent effects in terms of the dielectric constant, which is temperature dependent. As might be expected for such work done at that time, not a great deal is accomplished in the paper, although there are some interesting comments. There is one regarding the differing sensitivities of various reactions to the effects of *para*- or *meta*-substituents, and this is accompanied by a footnote: "This is one of

a large number of simple linear relations between the effects of substituents upon various reactions of benzene derivatives. Attention to some of these has previously been called by myself<sup>15</sup> and by Burkhardt, Ford, and Singleton<sup>21</sup>. This subject will be discussed in detail in another paper.”

The discussion in the paper works towards an equation for the free energy change:

$$\Delta F = (A/r^2)(1/D + B) \quad (3)$$

where  $r$  is the distance from the substituent dipole to the carboxyl group, and  $D$  is the dielectric constant of the solvent. “The quantity  $A$  is characteristic of a given substituent and position and is independent of temperature...  $B$  is of the nature of a function of the polarizabilities of the linkages being made and broken in the reaction. It is independent of temperature and medium.”

The reason for mentioning the above equation in the present article is that it plays a part in Hammett’s 1937 paper<sup>1</sup>. In fact the discussion which leads to the  $\rho\sigma$  equation begins with the putting forward of an equation which is an elaboration of the above, namely:

$$-RT \ln K + RT \ln K^0 = \Delta F = (A/d^2)(B_1/D + B_2) \quad (4)$$

This equation is almost immediately rearranged to the familiar form:

$$\log K = \log K^0 + \rho\sigma \quad (5)$$

where  $\sigma = -A/2.303 R$  and  $\rho = (1/d^2T)(B_1/D + B_2)$

It is not intended in this article to examine further the content of the 1937 paper, except to say that Hammett appears to have attached great importance to the more elaborate equation (4). After the establishment of the  $\sigma$  scale and its application as outlined at the beginning of the present article, a fair amount of the discussion is in terms not of the  $\rho\sigma$  equation, but of equation (4).

*This article is based on a talk given at the Fifth Conference on Chemometrics held at the Masaryk University, Brno, 30th August to 2nd September, 1999.*

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- Otto Dimroth (1872–1940). German organic chemist; Professor at Würzburg 1918–1940. At the time of his death in 1940, Dimroth bequeathed to his son Karl (later Professor of Chemistry at Marburg) a large volume of unpublished material on relationships between reaction velocities and oxidation–reduction potentials for quinone systems and asked him to have it published. For various reasons this was never found to be practicable. [Personal communications to J. S. by Professor K. Dimroth (1984) and Dr. Peter Dimroth (1999).] There is no doubt that Otto Dimroth did extensive pioneering work on rate–equilibrium relationships. If he had been more assiduous in publishing his work, it would certainly have played a more significant role in the development of linear free energy relationships.
- George Norman Burkhardt (1900–1991), devoted his entire professional life to the University of Manchester and its Chemistry Department. He was a pupil of Arthur Lapworth (1872–1941), who was a pioneer in the study of organic reaction mechanisms. Burkhardt worked in physical organic chemistry until World War II, but thereafter devoted himself mainly to teaching and administration.
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**J. Shorter** (*Department of Chemistry, University of Hull, Hull, U.K.*): **The Prehistory of the Hammett Equation**

The evolution of linear free energy relationships is traced from the Brönsted equation for general acid–base catalysis (1924) to the Hammett  $\rho$ – $\sigma$  equation for the effects of meta or para substituents on the rate or equilibrium constants of side-chain reactions of benzene derivatives (1937). In addition to a natural emphasis on Louis P. Hammett’s own contributions, those of G. N. Burkhardt and his colleagues are also described, along with the extent to which these two authors interacted.