Number 33 August 15, 1977

Citation Classics

Jaffé, Hans H. A reexamination of the Hammett equation.
Chemical Reviews 53:191-261, 1953.

Since the publication of Hammett's book,[1] which proposed an empirical relation on the parallelism of the effects of substituents on the rate or equilibrium constants in many different sidechain reactions of benzene derivatives, many additional reactions have been investigated which permit the application of Hammett's equation. One of the aims of this review is to gather together and thus render accessible all material pertinent to the Hammett equation. The equation is reexamined for its range of application, usefulness, and precision. [The *SCI*® indicates that this paper was cited 1,667 times in the period 1961-1975.]

Dr. Hans H. Jaffé
Department of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221

January 25, 1977

"In a major lecture at the 1951 Organic Mechanism Conference at Swarthmore, Pennsylvania, C. Gardner Swain said that if he just had a collection of some 3,000 pieces of data permitting application of the Hammett equation, he would like to undertake a statistical reevaluation of the σ constants. A brash young graduate student stuck up his hand and bragged that he had such a collection. After the lecture, H.C. Brown took self-same young man aside to tell him that such a collection should be made available to the scientific community. Next morning this same student just accidentally found a seat next to Professor Hammett, related the conversation with Professor Brown, and intimated that an invitation from a journal such as *Chemical Reviews* (on whose editorial board Professor Hammett was just serving), would make it infinitely easier for a government employee to prepare such a publication.

"The result of the events, coupled with much subsequent literature work and calculator punching led to the paper 'A Re-examination of the Hammett Equation' in *Chemical Reviews*. An interesting sidelight of this publication is the widespread use of the correlation coefficient in physical organic chemistry, which, it appears, was first introduced into this field in that paper.

"A further sidelight–Swain never did the statistical study he had suggested. We later attempted such a study, and after many nights on an IBM 650, concluded that the results are not sufficiently stable to be meaningful. The results change too much by addition or omission of a single data set, sometimes even of a single data point. We thus concluded that the values of McDaniel and Brown[2] are the most acceptable set of values."

1. **Hammett L P.** *Physical Organic Chemistry.* New York: McGraw-Hill Book Company, Inc., 1940.
2. **McDaniel D H & Brown H C.** An extended table of Hammett substituent constants based on the ionization of substituted benzoic acids. *Journal of Organic Chemistry* 23:420, 1958.