CC/NUMBER 24
JUNE 17, 1985

This Week's Citation Classic®

Ritchie C D & Sager W F. An examination of structure-reactivity relationships. *Prog. Phys. Org. Chem.* **2**:323-400, 1964.
[State University of New York, Buffalo, NY and George Washington University, Washington, DC]

The origins, applications, and interrelationships of the various substituent constants used in the Hammett and Taft equations are reviewed and examined for self-consistency. Recommendations are made to standardize notation and to correct some inconsistencies. [The *SCI*® indicates that this paper has been cited in over 445 publications since 1964.]

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April 16, 1985

My interest in the Hammett equation began with a PhD thesis under the direction of W.F. Sager, and expanded through a year of postdoctoral work with E.S. Lewis. During the postdoctoral year at Rice University, R.W. Taft visited Houston and was gracious in giving me an opportunity to talk with him at length. That meeting between a giant in the area of structure-reactivity relationships and an eager, but green, postdoc led to a long continued exchange of ideas in diverse areas of physical organic chemistry. Not long after our meeting, Taft asked if I might be interested in writing an article for *Progress in Physical Organic Chemistry*. Encouraged by Lewis, and with the agreement of Sager to collaborate, I accepted the invitation. The article was one of the first ones that I wrote after taking a position at the State University of New York at Buffalo.

Hans Jaffé's classic review[1] of the Hammett equation,[2] appearing in 1953, had been followed by massive development, primarily by Roberts,[3] Taft,[4] and Brown,[5] of linear free-energy relationships. By 1963, there were enough different sigma scales and modifications of the Hammett and Taft equations to confuse even the initiates in the field. In short, the time was right for a review.

The primary aim of the article was to present a logical analysis of the basic concepts of linear free-energy relationships. I suspect, however, that the major reason for the popularity of the work lies in the extensive table of substituent constants that were gleaned from the primary literature, rather than in the incisiveness of the logic. The ideas formalized by Hammett,[2] and extended by Roberts[3] and Taft,[4] were, and continue to be, of such importance and wide applicability that a timely review could not fail to attract citation—particularly if published in a medium that had already gained a high reputation.

For a recent review, see reference 6.

1. **Jaffé H H.** A reexamination of the Hammett equation. *Chem. Rev.* **53**:191-261, 1953. [See also: **Jaffé H H.** Citation Classic. *Current Contents* (33):9, 15 August 1977.]
2. **Hammett L P.** Some relations between reaction rates and equilibrium constants. *Chem. Rev.* **17**:125-36, 1935. (Cited 180 times since 1955.)
3. **Roberts J D & Moreland W T, Jr.** Electrical effects of substituent groups in saturated systems. Reactivities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids. *J. Amer. Chem. Soc.* **75**:2167-73, 1953. (Cited 240 times since 1955.)
4. **Taft R W, Jr.** Separation of polar, steric and resonance effects in reactivity. (Newman M S, ed.) *Steric effects in organic chemistry*. New York: Wiley, 1956. p. 556-675.
5. **Brown H C & Okamoto Y.** Electrophilic substituent constants. *J. Amer. Chem. Soc.* **80**:4979-87, 1958. (Cited 970 times.)
6. **March J.** *Advanced organic chemistry: reactions, mechanisms, and structure*. New York: Wiley-Interscience, 1985. p. 243-50.

