

Hammond G S. A correlation of reaction rates.

J. Amer. Chem. Soc. 77:334-8, 1955.

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In this paper several examples are presented of the application of a simple postulate by which one can decide whether reactants or products or neither are good structural models for estimating the influence of structural variations on the free energies of transition states. [The *SCI*® indicates that this paper has been cited in over 1,400 publications since 1955.]

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August 6, 1985

I began thinking about the subject of this paper while I was still in graduate school at Harvard and later during the year that I spent in postdoctoral work in Saul Winstein's lab at UCLA.

I realized that there were many series of related reactions in which there was a reasonable and intuitively attractive correlation between reaction rates and the strengths of bonds made or broken in the reaction process. Many proton transfer reactions fall into this category. On the other hand, many show no such obvious kinetic-thermodynamic relationships. Good examples are S_N2 reactions involving halide ions as entering or leaving groups. It was fine to note that iodide was the most reactive group in leaving a saturated carbon center because C-I bonds are the weakest of the C-X group. However, this thinking did not lead one to anticipate that the rates of nucleophilic attack by I^- , to form weak C-I bonds, would be faster than similar reactions of the other halide ions. Furthermore, I was downright irritated to learn that fluoride is by far the most reactive of the halides in departing from an unsaturated carbon atom. There are other similar puzzles, including several from aromatic substitution, a favorite topic for discussion of structure-reactivity relationships.

As I pondered the facts, it appeared that one could divide the systems that were not correlated by simplistic thermodynamic concepts into two groups: (1) those in which polarizability of the groups involved in bond making and breaking was an important predictor of rates and (2) those in which it was not.

At the time, organic chemists were switching their language for discussion of reactivity relationships from that of the Robinson school to a formal-

ism based upon the transition-state concept. It was a great concept, and still is. You can explain anything with the theory. All one has to do is to formulate hypothetical transition-state structures until one is found that seems to account for the relative values of free energies of activation in the series of reaction rates being compared.

Not surprisingly, I turned to the universally accountable theory for help with my dilemma and was well rewarded. It seemed reasonable that reactions in which an old bond was nearly completely broken in the transition state would show reasonable correlation with the energy of that bond. Conversely, reactions in which rates do not correlate with bond energies must involve transition states in which bond making and breaking are quite incompleting. This, of course, agreed well with common concepts concerning transition states in S_N2 reactions at saturated centers. The behavior of both electrophilic and nucleophilic substitution at unsaturated centers seems well accommodated by the presumption that the transition states usually resemble adducts in which the atom being attacked is strongly bonded to both entering and leaving groups.

The foregoing paragraph is all there is to the "Hammond" postulate. I did try to formulate a few rules for identification of the satisfying transition-state model. Those rules contain conceptual weaknesses, perhaps the most egregious of which is the tacit assumption that there is a basic similarity among the potential functions for stretching and contracting all bonds. I realized this problem and was led thereby to the view that an easy way to find deviations from the "principle" would be to look at reactions involving large variations in polarizability of substrates and reagents.

Many papers published since 1955 have shed light of a more profound nature on the problems with which I dealt in a simplistic manner. There are too many to mention, but I do wish to note that my thoughts about the correlation of reaction rates prepared me well to appreciate both the approach and the wisdom of Ralph Pearson's paper on hard and soft acids and bases.¹

One reason for the frequent citation of my paper is its simplicity. Another is the previously mentioned fact that one can make transition-state theory explain almost everything, if one is willing to abuse the theory without limit. Frankly, I wish that some of the citations had been omitted because there have been occasions when well-meaning authors have distorted transition-state theory beyond what seem to be reasonable limits while attributing to me the authority to do so.

1. Pearson R G. Hard and soft acids and bases. *J. Amer. Chem. Soc.* 85:3533-9, 1963. [See also: Pearson R G. Citation Classic. *Current Contents/Physical, Chemical & Earth Sciences* 20(23):12, 9 June 1980.]