

From Robert Ellis and Denny Gullick, *Calculus with Analytical Geometry*
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HAMMOND POSTULATE

1955 paper used transition-state theory to explain structure-reactivity relationships

DURING THE 1940S AND 1950S, physical organic chemists were struggling to explain why subtle changes in the structure of reactants affect the rate of chemical reactions and their product distributions. Competing theories and confusion reigned.

George S. Hammond, then a young associate professor of organic chemistry at Iowa State College, thought he could do better by thinking about organic reactions in terms of their transition states as well as their reactants and products. In 1955, he suggested that transition-state theory—which had previously been the domain of physical chemists—could be used in a qualitative manner to explain structure-reactivity relationships in a variety of organic reactions.

Hammond laid out his postulate in a *Journal of the American Chemical Society* paper that ranks among the 125 most cited in *JACS* history [77, 334 (1955)]: “If two states, as for example, a transition state

and a reactant, are similar in energy, the transition state closely resembles the reactant; in highly endothermic ones, the product is a better model for the transition state.

Hammond managed to identify those reactions or reaction steps in which the transition state can be assumed to be reasonably approximated by the structure of either the reactant, intermediate, or product. He cautioned that doing so is only acceptable when the two species' energies are similar. In highly exothermic reactions, the transition state closely resembles the reactant; in highly endothermic ones, the product is a better model for the transition state.

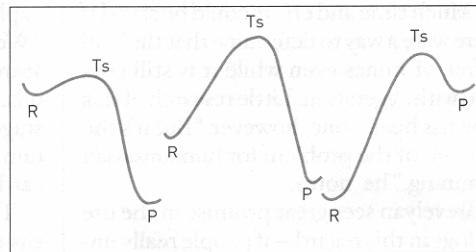
The energy of a transition state relative to that of a reactant, intermediate, or product determines the position of the transition state along the reaction coordinate. This in turn determines the selectivity of reactions that give two or more possible products. This idea has been used, for example, to explain the effects of substituents on the rate of benzylic acid rearrangements. The type of rearrangement preferred by unsymmetrical benzils can be predicted by using the structure of the intermediate that forms upon attack of hydroxyl ion as a model of the transition state.

“It was simple-minded stuff, but it had not been stated at the time,” Hammond demurs. But the postulate's simplicity may be the secret to its success.

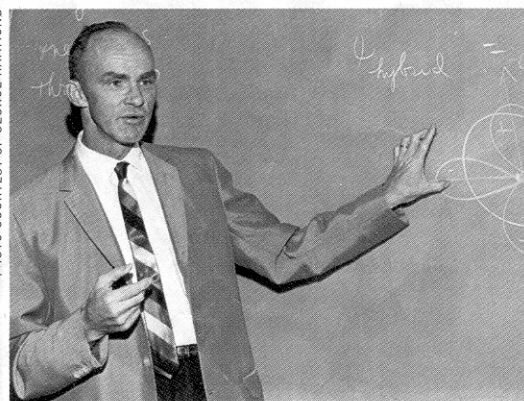
“Hammond's postulate became widely used and appreciated, not so much because it was revolutionary, but because of its clarity and generality,” says Donald G. Truhlar, a professor of chemistry at the University of Minnesota, Twin Cities. In

fact, a similar idea had been put forward by Florida State University's John E. Lefler a few years earlier [*Science*, 117, 340 (1953)]. But the qualitative nature of Hammond's version—there isn't a single mathematical equation in his 1955 *JACS* paper—gave it staying power, Truhlar says.

But Hammond's idea wasn't a “slam dunk,” notes M. Frederick Hawthorne, professor of chemistry at the University of California, Los Angeles. Although it was already entrenched in physical chem-



LOOK-ALIKE Hammond postulated that in highly exothermic reactions (left) the transition state (Ts) is structurally similar to the reactant (R), but that in highly endothermic reactions (right) the product (P) is a better model of the transition state. He cautioned against using the postulate in more thermoneutral reactions (center).



INTUITIVE Like many others, Hammond—shown here nearly a decade after his seminal paper was published—found his postulate to be a useful pedagogical tool.

and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures.” That is, along the reaction coordinate, species with similar energies also have similar structures.

Hammond's postulate built upon sem-

istry, transition-state theory was unfamiliar to many organic chemists when Hammond published his paper. It took some time to take off, Hawthorne says, but it wasn't long before the Hammond postulate became embedded in the fabric of organic chemistry.

As Hammond had suggested, chemists put it to use in explaining structure-reactivity data for a wide variety of reactions, including electrophilic aromatic substitution reactions and reactions involving highly reactive intermediates such as carbonium ions and carbanions.

In addition, a number of chemists, including Edward R. Thornton of the University of Pennsylvania and Rudolph A. Marcus of California Institute of Technology, have made key contributions to expanding the Hammond postulate. —AMANDA YARNELL

C&EN is celebrating the 125th volume of the *Journal of the American Chemical Society* by featuring selected papers from among its 125 most cited. This paper was ranked 15th.