Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

Concertedness: a Function of Dynamics or the Nature of the Potential Energy Surface?

Summary: Whether or not a given reaction is concerted depends on molecular size and reaction conditions as well as the depth of local potential energy minima between reactant and product wells; any proposed quantitative definition of concertedness must, therefore, stress maximum lifetimes of potential intermediates in relation to molecular size and reaction conditions.

Sir: The orbital symmetry approach[1] to chemical reactivity recognizes only two types of reaction channel: allowed (symmetry correlation of all bonding reactant molecular orbitals with bonding product molecular orbitals) and forbidden (symmetry correlation of at least one bonding reactant orbital with one antibonding product orbital). To fully explore the limits of this theory, and also to escape irrefutability,[2] would require a quantitative definition of concertedness.[3]

Thus, the question has been posed:[6] Should some time limit (say 10^{-12} sec) be defined as the maximum allowable lifetime for intermediates in concerted cycloreactions, or should concertedness rely on the fact that no potential energy well on the hypersurface connecting reactant and product exceeds some maximum depth (say $^1/_2 h\nu_0$)?

It is the intention here to pursue two theoretical points initially raised by Wolfgang[7,8] which lead to the conclusions that a reaction is a one-step process when (1) there are no potential energy minima between reactant and product wells, (2) there is an energy minimum on the reaction coordinate, but the reacting system contains too few atoms to exist as an intermediate complex, or (3) a potential well separates reactant and product wells but the reacting system possesses a large internal energy such that in the absence of collisional deactivation the intermediate complex is unstable and transforms directly into product.

While it is well-known that an energetically concerted reaction,[9] characterized by a potential energy surface in configuration space with no energy minima between reactant and product wells, is a one-step process, it is not generally appreciated that a potential energy hypersurface containing a distinct potential energy minimum on the way to product may correspond to either a one-step or two-step process[10] depending on the depth of the well, the density of energy states available to the intermediate, and the activation imparted to the reacting system.[11]

The actual experimental differentiation of a transition state from a true intermediate remains a fundamental problem in "reaction spectroscopy." The lifetime (τ) of a transition state is given by the reciprocal sum of all rate constants which lead to decay, one vibration leading to product and another leading to reactant, each approximately 10^{13} sec^{-1}: $\tau_{\mathrm{TS}} = 5 \times 10^{-14}$ sec.

From Rice–Ramsperger–Kassel (RRK) theory[12,13] one can obtain an estimate of the requirements for formation of an intermediate in a thermally activated reaction.[8] The rate constant, k_ϵ, for unimolecular decay of a vibrationally excited molecule of internal energy ϵ is given by eq 1, where ϵ^* is the minimum activation

$$k_\epsilon = A[(\epsilon - \epsilon^*)/\epsilon]^{s-1} \tag{1}$$

energy for spontaneous decay (see Figure 1) and s is the number of "active" vibrational modes. A more accurate RRK equation (2) only allows two-thirds of

$$k_\epsilon = A[(\epsilon - \epsilon^*)/\epsilon]^{2N-5} \tag{2}$$

the total number of vibrational modes to be active; *i.e.*, $s = {}^2/_3(3N - 6) = 2N - 4$ for a nonlinear N-atomic molecule. The lifetime follows from eq 2 with

$$\begin{aligned} \tau_\epsilon &= 1/k_\epsilon = [(\epsilon - \epsilon^*)/\epsilon]^{5-2N} \times 10^{-13}\ \text{sec} \\ \tau_\epsilon &= [1 - (\epsilon^*/\epsilon)]^{5-2N} \times 10^{-13}\ \text{sec} \end{aligned} \tag{3}$$

---

[1] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); "The Conservation of Orbital Symmetry," Academic Verlag Press, 1970.

[2] If all allowed reactions were assumed to be concerted, and similarly all forbidden reactions were nonconcerted when observed, then a failure to observe the orbital-symmetry-predicted reaction stereochemistry could be interpreted as either a violation of the theory or as a nonconcerted reaction. Hence, the theory could never be refuted, unless concertedness is placed on a quantitative basis and uncoupled from allowedness. Consideration of electronic state symmetry and configuration interaction has lead to a theoretical uncoupling of concertedness and orbital symmetry: J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

[3] A reaction is generally considered to be "concerted" if the transition state is characterized by (1) equal bond making and bond breaking for unimolecular isomerization, (2) equal bond breaking at two reaction termini in a cycloelimination, or (3) equal bond making at the reaction termini in a cycloaddition. (An analogous definition based on the synchroneity of bond cleavage and formation is also frequently employed.) Such bond breaking aided by bond making should require a lower activation energy than the corresponding dissociation–recombination process. Since the most elusive molecular property (which is even more elusive for transition states) is the distribution of electrons,[4] concertedness has defied quantification in an empirical sense.[5]

[4] *Cf.* W. H. Flygare, *Science*, **140**, 1179 (1963).

[5] *Cf.* S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 3688 (1969).

[6] Informal discussions, 14th Conference on Reaction Mechanisms, University of Vermont, Burlington, Vt., June 13–16, 1972.

[7] R. Wolfgang, *Accounts Chem. Res.*, **2**, 248 (1969).

[8] R. Wolfgang, *Accounts Chem. Res.*, **3**, 48 (1970), and references therein.

[9] J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forschung*, **15**, 281 (1970).

[10] It would not be inconsistent for such a two-step, energetically nonconcerted process simultaneously to be bondingly and orbitally concerted.[9]

[11] While this conclusion has its most direct applications to reactions in the gas phase, it surely applies whenever collisional deactivation is unable to compete with progress along the reaction coordinate.

[12] Qualitative estimates based on RRK theory have, on the whole, been fully substantiated within the refined Rice–Ramsperger–Kassel–Marcus (RRKM) theory; *cf.* H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966; G. L. Pratt, "Gas Kinetics," Wiley, New York, N. Y., 1969; and P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, New York, N. Y., 1972.

[13] Professor R. G. Bergman has pointed out that the use of exact A factors and the expanded equation given by Setser and Rabinovitch[14] leads to improved estimates of *absolute* rate constants, but the method is not so easily applied as the modified RRK approach used here since zero-point energies of the energized molecule and the activated complex are required.

[14] D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

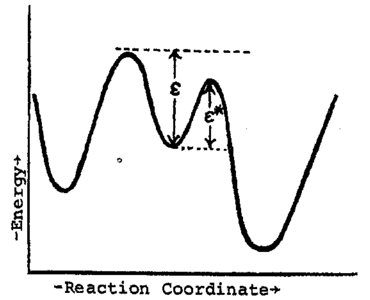

Figure 1—Energy *vs.* reaction coordinate diagram illustrating ε and ε*.

inclusion of a "normal" A factor.[8] If a true intermediate, as opposed to a transition state, must have $\tau \geqslant 10^{-12}$ sec, then eq 4 obtains. Table I lists minimum

$$\epsilon^*/\epsilon = 1 - 10^{x/(5-2N)} \quad (x \geqslant 1.0) \qquad (4)$$

TABLE I

VALUES OF ϵ^*/ϵ *vs.* N FROM EQ 4 WITH $x = 1.0$

N	3	4	5	9	14	52
ϵ^*/ϵ	0.90	0.54	0.37	0.16	0.10	0.02

values of ϵ^*/ϵ which allow an intermediate to exist with $\tau = 10^{-12}$ sec *vs.* N calculated from eq 4; Figure 2 gives the corresponding plot of ϵ^*/ϵ *vs.* N.

An interesting result is revealed by the plot in Figure 2. As the number of atoms increases, the activation energy required to contain an intermediate for 10^{-12} sec falls off rapidly for any given internal energy. For example, a 27.0-kcal mol^{-1} activation energy is required to contain a 4-atom transient with 50 kcal mol^{-1} internal energy, while a mere 5.0-kcal mol^{-1} barrier will contain a 14-atom intermediate of the same internal energy for 10^{-12} sec.

Equation 4 and the plot in Figure 2 reflect the principle that the density of vibrational states increases directly with molecular size, and it is precisely this larger density of vibrational states which permits the complex molecule to form an intermediate while experiencing only a small barrier against spontaneous decomposition.

This conclusion forces a consideration of substituent effects on molecular rearrangements: Can the replacement of small groups with large groups make some nonconcerted reaction channel competitive with an otherwise dominant concerted path? Paquette and Epstein have suggested that replacement of two hydrogens with two phenyl groups perturbs the parent bicyclo[5.2.0]-nona-2,5,8-triene system too severely to establish any mechanistic analogy.[15] This effect may contribute to the documented reactivity differences between ketene and diphenylketene,[16] 2,3,3,4-tetramethyl- and 2,4-diphenyl-3,3-dimethyltricyclo$[3.2.0.^{2,4}0^{1,5}]$hept-6-ene,[17] *meso*-3,4-dimethyl- and *meso*-3,4-diphenylhexa-1,5-diene,[18,19] and allene and phenyl-substituted allenes.[20]

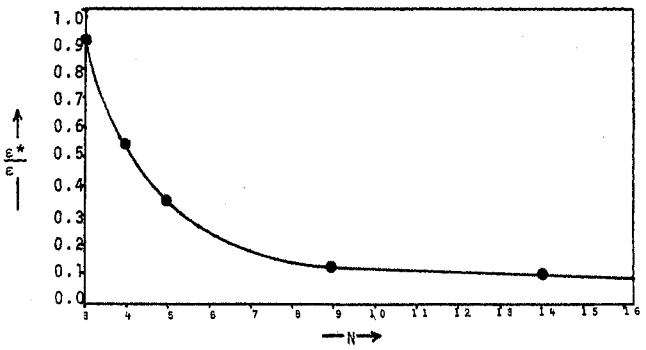

Figure 2—Plot of ϵ^*/ϵ *vs.* N from Table I.

Whether a given energized molecule may pass directly over a potential well separating it from isolable product while maintaining its internal energy above ϵ^* depends on the third parameter in eq 4, ϵ, and what opportunities for collisional deactivation may be present. Molecular beam experiments[8] on the energy dependence of bimolecular reactions have demonstrated the actual conversion of two-step, energetically nonconcerted reactions into one-step, fully concerted processes at higher internal energies.[21] Thus, even if a potential well of sufficient depth presents an opportunity for intermediate formation, it does not require that such an intermediate be formed![22,25]

In conclusion, concertedness depends not only on the nature of the potential energy surface itself, but also the motion of the system on this surface. Any empirical definition of concertedness which is adopted must focus on the dynamics of the reacting system and not simply intermediate potential well depth. Experiments aimed at distinguishing concerted from diradical or nonconcerted cycloreactions would be more meaningfully directed toward establishing maximum lifetimes of potential intermediates as a function of molecular size and reaction conditions.

Acknowledgment.—Helpful discussions with Professors John E. Baldwin and Robert G. Bergman are gratefully acknowledged.

---

(15) L. A. Paquette and M. J. Epstein, *J. Amer. Chem. Soc.*, **93**, 5936 (1971).

(16) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4868 (1970), and references cited.

(17) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970); *ibid.*, **93**, 4922, 5128 (1971).

(18) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(19) R. P. Lutz, S. Bernal, R. J. Boggio, R. O. Harris, and M. W. McNicholas, *J. Amer. Chem. Soc.*, **93**, 3985 (1971); see also M. J. S. Dewar and L. E. Wade, *ibid.*, **95**, 290 (1973).

(20) J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, **36**, 1440 (1971), and references cited.

(21) At higher ε it becomes more difficult to transfer the energy of reaction into internal vibrational modes.[8] Contrast this situation with chemical activation of stable species: B. S. Rabinovitch and M. C. Flowers, *Quart. Rev. (London)*, **18**, 122 (1964).

(22) Intermediate situations have been rationalized through a superposition of "quasiconcerted" processes[23] and as a broad, flat plateau on the potential energy surface termed a "twixtyl".[24]

(23) J. P. Freeman, D. G. Pucci, and G. Binsch, *J. Org. Chem.*, **37**, 1894 (1972).

(24) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(25) Intermediate formation is not so easily avoided at higher ε when a "spin barrier" is present; *cf.* L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO 80302

A. HARRY ANDRIST

RECEIVED OCTOBER 11, 1972

Flow Synthesis. A Substitute for the High-Dilution Steps in Cryptate Synthesis

Summary: Certain cyclization reactions, usually run under conditions of high dilution over long periods of time, give excellent yields in <1 min when the reagents are efficiently mixed in a suitable flow cell.