

References and Notes

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- This apparatus is similar to one which has been described in detail earlier. See, for example, (a) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6260 (1974), and (b) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 3214 (1977).
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- For a one-photon process, reaction 3 will not be observed for $\lambda > 400$ nm. Using laser irradiation (4545–5145 Å), we have observed a two-photon process in which $C_7H_7^+$ dissociates to $C_5H_5^+$. These results will be reported elsewhere.

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Energy Partitioning in Unimolecular Decomposition. Isotope Effects on the Kinetic Energy Release in the Loss of H_2 from $(CH_2=OH)^+$

Sir:

There now exists a very large body of data concerning the translational energies released in unimolecular decompositions of gaseous ions, much of which has been obtained from analysis of metastable peak shapes.¹ This energy originates from excess energy (i.e., internal energy in excess of the activation energy), and from the reverse activation energy. The excess energy may be partitioned statistically; however, there is conclusive evidence that the proportion of the reverse activation energy partitioned as translation varies quite considerably from reaction to reaction.^{1,2} The purpose of this paper is to show how a dynamical approach to the partition of reverse activation energy elegantly explains the large deuterium isotope effects on energy release in the elimination of H_2 from $(CH_2=OH)^+$ ³ (see Table I). It has been pointed out previously that these

Table I. Isotope Effects on Experimental and Calculated Energy Releases

	Exptl ^a	Calcd
$(CH_2=OH)^+ \rightarrow (CHO)^+ + H_2$	1	1
$(CH_2=OD)^+ \rightarrow (CHO)^+ + HD$	1.15	1.25
$(CD_2=OH)^+ \rightarrow (CDO)^+ + HD$	0.89	0.77
$(CD_2=OD)^+ \rightarrow (CDO)^+ + D_2$	1.04	0.98

^a Values taken from ref 3. Similar results were obtained in our laboratory.

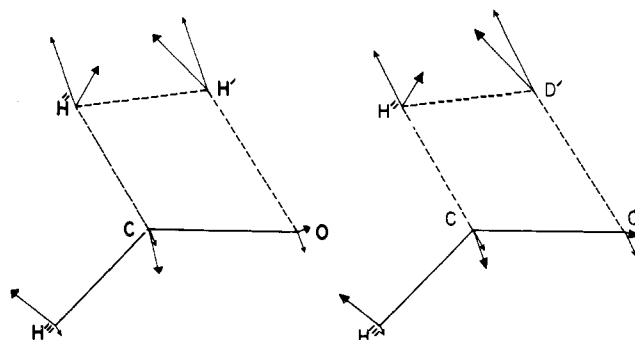


Figure 1. The compositions in terms of mass-weighted atomic displacements of the transition-state reaction coordinate (heavy arrows) and the product separation coordinate (light arrows) for (a) $(CH_2=OH)^+$ and (b) $(CH_2=OD)^+$. These displacements are proportional to the mass-weighted velocities, and to the square root of kinetic energy.

isotope effects cannot be attributed to zero point energy effects,⁴ nor are they readily explained by considering merely transition-state structure.⁵

From the point of view of reaction dynamics, two aspects of the partition of reverse activation energy can be distinguished: first, initial storage of kinetic energy in product modes determined by the local compositions of the reaction coordinate between transition state and products and, second, subsequent partial redistribution of this energy if the reaction coordinate is curved. To treat this partitioning, we consider simply the composition of the reaction coordinate at the transition state in terms of mass-weighted atomic displacements,⁶ and compare this composition with that of a translation separating the products. The more closely these two composite motions correspond to each other, the larger, we suggest, will be the proportion of reverse activation energy partitioned as translation.^{7,8} The transition-state atomic motions are normalized and expressed as a $3N$ dimensional unit vector.⁹ This unit vector is projected onto the 3 dimensional subspace of product separation coordinates, and the square of the length of the projection taken as a measure of the proportion of energy released in translation.⁹

This approach neglects redistribution of kinetic energy once it has appeared in a particular mode; however, it also underestimates the extent to which energy is initially stored in modes effecting product separation. The success of the approach depends upon the extent to which these factors compensate for each other.

The atomic motions of the transition-state reaction coordinates have been calculated for the loss of H_2 from $(CH_2=OH)^+$, HD from $(CH_2=OD)^+$, HD from $(CD_2=OH)^+$, and D_2 from $(CD_2=OD)^+$ (see Figure 1). The MINDO/3 molecular orbital method^{10,15} has been employed, and the potential energy surface has been searched to locate the saddlepoint.¹¹ The proportions of the reverse activation energy appearing as translation have been obtained using the approach discussed above, and the results satisfactorily reproduce the trend of the experimental isotope effects¹² (Table I).

Figure 1 illustrates how the significant contributions to the translational energy release arise from H' and H'' . Only these atoms show large displacements in similar directions in both the transition state and product separation. The contribution of H' is twice as large as that of H'' , again as might be evident from Figure 1, and the trend of the calculated isotope effects (Table I) reflects the effect of isotopic substitution on the contribution from the atom at the H' position. The changes in the contribution from the H'' position upon substitution in fact oppose the overall isotope effects (Table I), but these changes are masked by the much larger changes in the H' contribution.

Replacing H' by D' increases the product separation mass-weighted displacement (the velocities of D' and H'' are the same during separation, their energies in the ratio 2:1, and mass-weighted velocities (and displacements) in the ratio (2:1)^{1/2}), and the contribution of this position to the energy release is increased accordingly. Replacing H'' and H''' with deuterium decreases the product separation mass-weighted displacement of H' (H' has only 1/3 of the energy of the departing HD as opposed to 1/2 in (CH₂=OH)⁺), and the contribution of H' diminishes. Substituting for all three hydrogens has little effect on the mass-weighted displacements of the departing hydrogens, and hence there is little isotope effect.

It has been suggested that the large energy release in the loss of hydrogen from (CH₂=OH)⁺ is a consequence of the reaction following a concerted orbital symmetry-forbidden route.¹³ An earlier molecular orbital calculation⁴ on this reaction, and the later qualitative discussion,¹³ assume a symmetrical planar transition state and hence that reaction must pass over a barrier imposed by orbital symmetry. Our calculation, in which the potential surface is searched, suggests that the reaction proceeds around this particular barrier. The hydrogen atom H' on the oxygen moves a considerable distance toward the carbon before the transition state is reached. The reaction might be regarded as a 1,2 shift coupled with a 1,1 elimination.¹⁴ The energy barrier surmounted is that for the H' shift, and thereafter H₂ loss is facile. The partition of energy as translation is largely a consequence of the H' motion corresponding quite closely to a motion separating the products.

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- (6) These displacements are proportional to velocities. Using mass-weighted coordinates $q_i = x_i \sqrt{m_i}$ (see for example, J. C. D. Brand, J. C. Speakman, and J. K. Tyler, "Molecular Structure", 2nd ed, Edward Arnold, London 1975, p 129), velocity and momentum p_i become equivalent and kinetic energy is given by $\frac{1}{2} \dot{q}_i^2 = p_i^2$.
- (7) This idea, which is the essence of our approach, stems from the classic work of M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **35**, 178 (1939).
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Temperature and Substituent Dependence of Photocycloadditions Involving Exciplexes

Sir:

Temperature and substituent effects on reaction rate are ubiquitous probes of mechanism for ground-state reactions. Although a number of temperature dependences of photochemical reactions, including photocycloaddition, have previously been reported,^{1,2} we know of no series with systematic variation of substituent, in which each reaction path includes an emissive exciplex. The reactions³ of substituted 9-cyanophenanthrenes **1a-c** with anethole (**2k**) or anisylisobutylene (**2l**) provide such a series (Scheme I). We have studied four fundamental processes. Rates of cyclobutane formation and internal conversion are affected by both substituent and temperature to a markedly greater extent than are fluorescence and intersystem crossing. Our results suggest a strong similarity in the nature of the cycloaddition and internal conversion processes.

We have determined quantum yields (ϕ_i) for all four reactions of exciplexes of **1a-c** with **2k** and of **1b** with **2l**. The rate constant k_i for each process is available as $k_i = \phi_i \tau^{-1}$ if τ is known. We have measured τ by laser flash photolysis when $\tau \geq 9$ ns and have estimated it by oxygen quenching when shorter.⁴ In all cases, quantum yields were measured with [**2**] high enough to quench >95% of singlet **1**. For **1c-2k**, results as a function of [**2k**] were extrapolated to [**2k**] = ∞. The ϕ_{isc} values were taken as twice ϕ_{cis-2k} ,⁵ and k_D was computed as $\tau^{-1} - (k_F + k_R + k_{isc})$. The cumulative errors make k_D

Scheme I

