

is not significantly different from that in pure water (Table VIII). More dramatic effects are observed, however, when $8.9 \times 10^{-2} M$ water is solubilized by $2.0 \times 10^{-2} M$ DAP in benzene. In this system rate constants for the equilibrium attainment of reaction 1, k_{ψ} , do not increase linearly with increasing imidazole concentration but rather decrease logarithmically (Figure 5). At low imidazole concentration the advantageous proximity to vitamin B_{12a} is maximized. At the lowest stoichiometric imidazole concentration ($1.0 \times 10^{-5} M$) the rate constant for the anation of vitamin B_{12a} in the presence of $2.0 \times 10^{-2} M$ DAP in benzene is 353-fold faster than that in water. The 25,200-fold increase in the aquation rate is even more impressive. The more favorable destabilization of imidazole cobalamin as compared to vitamin B_{12a}, coupled with the considerably increased effective water concentration in the tight micellar cavity, is responsible for the more pronounced enhancement of k_{-1}^{app} as compared to k_1^{app} . Increasing concentrations of imidazole decrease the amounts of imidazole per micelle with resultant saturation kinetics with respect to imidazole.

Values of k_1^{app} and k_{-1}^{app} for the equilibrium formation of Bzm-Co-N₃ in the reversed micellar system are factors of 99 and 2100 times slower than those in pure water (Table IX). Alteration of the ionization equilibria, hydrogen bonding, and changes in the effective water and reagent activities is likely to be responsible for these effects.

The nature of the ligand and the size of the surfactant mantle and of solubilized water pool clearly influence anation and aquation rates of surfactant solubilized cobalamins in benzene. This type of restricted polar environment for bimolecular reactions involving relatively large substrates has pronounced effects on the reaction rates and, considering both the anation and

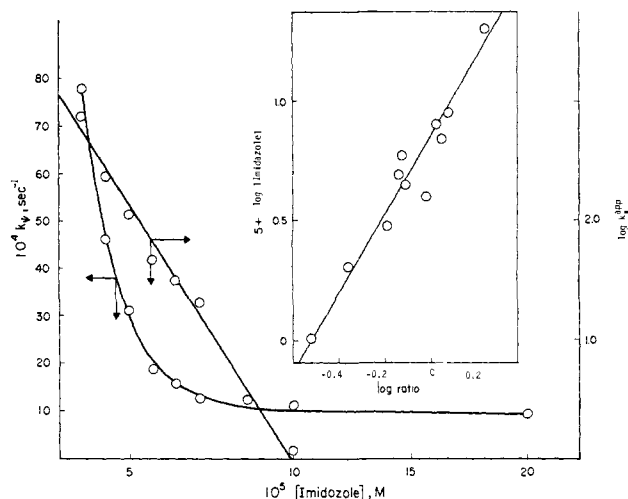


Figure 5. Plots of k_{ψ} or k_1^{app} vs. imidazole concentration for the reaction of imidazole with vitamin B_{12a} in benzene in the presence of 0.02 M DAP, containing $8.9 \times 10^{-2} M$ water. Insert shows a plot of $\log [\text{imidazole}]$ vs. $\log [\text{Bz-Co-imidazole}]/[\text{Bzm-Co-OH}_2]$ for the same system.

aquation reactions, exhibits considerable specificity. Encouraged by the versatility of our model system we are currently investigating rates and equilibrium constants for a variety of cobalamin reactions. Particularly, we hope to unravel the binding of more complex amino acids and peptides in restricted polar environments and relate the obtained information to vitamin B₁₂ dependent reactions and to membrane transport processes *in vivo*.

Acknowledgments. This work was supported by the National Science Foundation and by the Robert A. Welch Foundation.

Communications to the Editor

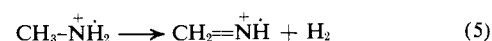
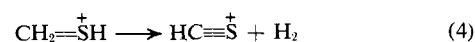
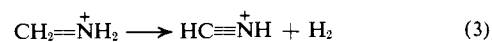
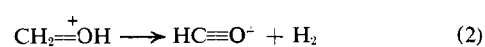
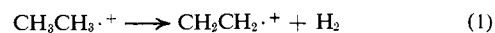
Kinetic Energy Release in Relation to Symmetry-Forbidden Reactions

Sir:

The concept of orbital symmetry conservation¹ has greatly advanced our understanding of numerous concerted reactions. It has been our aim to use this concept to develop our knowledge of the mechanisms *via* which positive ions undergo unimolecular reactions. Such unimolecular reactions are of course most conveniently examined in the mass spectrometer and, in particular, when these reactions are investigated through the observation of metastable peaks, the range of unimolecular rate constants is reasonably defined ($k = 10^4$ to 10^6 sec^{-1}) and the nonfixed energy in the transition state is relatively small.^{2,3} In the most favorable

cases, the nonfixed energy in the transition state is so small that extremely large isotope effects are observed when there is competition between C-H and C-D cleavage. For example, in metastable transitions, the molecular ion of CH₃CD₃ eliminates H in preference to D in the ratio 600:1.⁴

The reactions we have considered all correspond to loss of molecular hydrogen and are summarized in eq 1-5.



(1) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 797 (1969).

(2) D. H. Williams and I. Howe, "Principles of Organic Mass Spectrometry," McGraw-Hill, London, 1972.

(3) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions," Elsevier, Amsterdam, 1973.

(4) U. Löhle and Ch. Ottinger, *J. Chem. Phys.*, **51**, 3097 (1969).

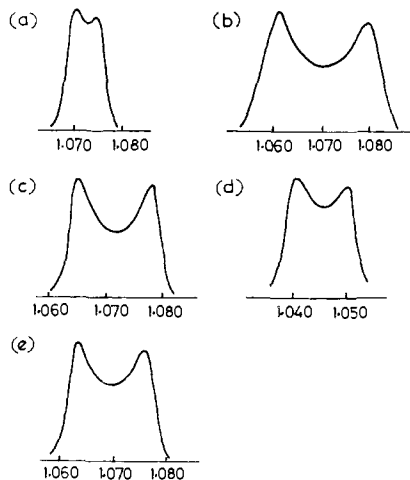


Figure 1. Metastable peaks (MS 9, first field-free region) for 1,2-elimination of molecular hydrogen from (a) ionized ethane, (b) protonated formaldehyde, (c) protonated methylene imine, (d) protonated thioformaldehyde, and (e) ionized methylamine. The peaks were recorded using the refocusing technique described by M. Barber and R. M. Elliott (12th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14 A.S.T.M., Montreal, June 1964). The horizontal coordinates in the figure are V/V_0 .

The loss of molecular hydrogen, as opposed to stepwise loss of hydrogen radicals, is established in each case through the presence of abundant metastable peaks for H_2 loss. In addition, in those cases where the heats of formation of the reactant and products are known (eq 1–3), our appearance potential measurements on metastable peaks give the activation energies as 13,⁵ 80, and 97 kcal/mol, values which are much less than the minima required to produce the product ion and two hydrogen radicals (112, 129, and 179 kcal/mol).

Prior work has established that reactions 1 and 2 proceed *via* specific 1,2-elimination since CH_3CD_3 loses only HD in metastable transitions,^{4,6} and $CD_2=O^+H$ and $CH_2=O^+D$ both lose only HD in metastable transitions.⁷ Similarly, reactions 3–5 proceed *via* 1,2-elimination since our own experiments establish that $CH_2=N^+D_2$, $CH_2=S^+D$, and $CH_3N^+D_2$ lose only HD in metastable transitions.

If these proven concerted 1,2-eliminations occur through planar transition states (*e.g.*, **1** in the case of eq 1), then the correlation diagram which is relevant to such transition states may be constructed as shown below (Scheme 1).⁸ Only reaction 1 contains the symmetry elements necessary for the construction of a formal correlation diagram, but the same principle applies to the other reactions.

It can be seen that a concerted 1,2-elimination of H_2 occurring through a planar transition state is a symmetry-forbidden reaction. Now the experimentally

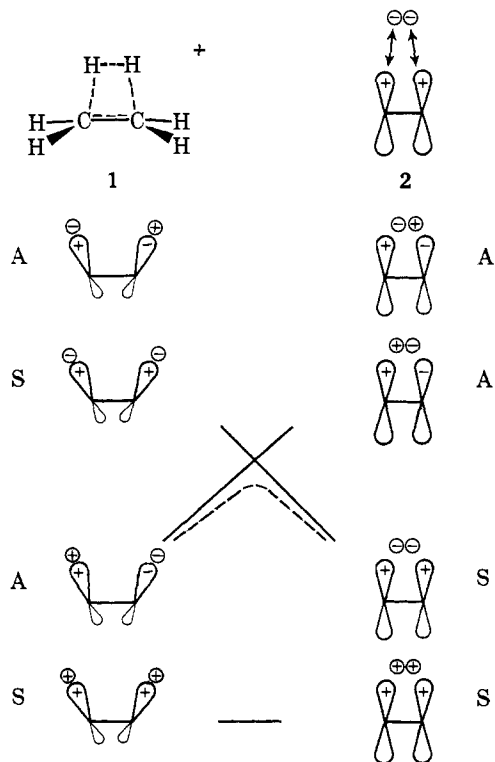
(5) This value is appreciably smaller than that (23 kcal/mol) reported by Vestal [M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, 1968, Chapter 2], perhaps (at least in part) due to the fact that our determination was carried out on a metastable peak as opposed to a daughter ion peak.

(6) C. Lifshitz and R. Sternberg, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 303 (1969).

(7) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 1 (1968).

(8) For a previous construction and analysis of the correlation diagram for reaction 2 see K. C. Smyth and T. W. Shannon, *J. Chem. Phys.*, **51**, 4633 (1969).

Scheme 1



measured activation energies for the unimolecular reactions 1–3 (*vide supra*) are insufficient to produce either the neutral hydrogen molecule or the ionic product in an excited state. As expected, the intended crossing is avoided, but the price in energy of the symmetry-imposed barrier has to be paid, although it may be reduced by configuration interaction.

The crucial relevance of the correlation diagram is evident upon closer examination. As the transition state is passed, the electronic reorganization which occurs results in a complex of hydrogen and the ionic product in which there is an occupied symmetric molecular orbital characterized by a mutual repulsion between the carbon and hydrogen nuclei (see **2**). The concerted forbidden 1,2-elimination of hydrogen will therefore occur with the release of kinetic energy.^{8,9}

The kinetic energy release in a unimolecular ionic decomposition is in fact conveniently measured from the width of "flat-topped" or "dished" metastable peaks;³ when the molecular explosion schematically illustrated in **2** occurs, discrimination against ion collection occurs in some directions, but product ions pushed along or against the direction of the beam are efficiently collected as components at higher and lower

(9) It is sometimes argued that orbital symmetry correlations cannot be applied reliably to open-shell (odd-electron) systems. It is certainly true that the stereochemical course of the cyclopropyl-allyl radical conversion cannot be so reliably inferred from orbital symmetry considerations as can the stereochemical courses of the corresponding anion and cation reactions [H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965)]. However, this situation arises since both conrotatory and disrotatory openings of the cyclopropyl radical are subject to symmetry-imposed barriers which are not very different. Longuet-Higgins and Abrahamson do not infer that their state diagrams are any less reliable in the doublet open-shell system. It is recognized that elementary molecular orbital procedure is not reliable when comparing singlet and triplet states (L. C. Allen in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn. 1970, p 227). Reactions 2–4 of course correspond to closed-shell systems of the type conventionally analyzed in thermal reactions.

mass (respectively) relative to the normal maximum of a Gaussian peak associated with a decomposition occurring with a small or negligible release of kinetic energy. The metastable peaks for H₂ loss in reactions 1–5 are reproduced in Figure 1. These peak shapes refer to data obtained for decompositions in the first field-free region of an MS 9 double focusing mass spectrometer, fitted with a variable monitor slit (set at approximately 0.020 in.). Since the energy releases computed from such data can be too low,¹⁰ the quoted kinetic energies obtained in the present work (Table I) refer to second field-free region metastables.

Table I. Kinetic Energy Release in 1,2-Elimination of Hydrogen

| Reacting ion | Product ion | K.E. release (kcal/mol) |
|---|---|-----------------------------|
| CH ₃ CH ₃ ^{·+} | CH ₂ CH ₂ ^{·+} | 4.4 (Figure 1a) |
| H ₂ C=OH ⁺ | HC≡O ⁺ | 33 ^a (Figure 1b) |
| H ₂ C=NH ₂ ⁺ | HC≡NH ⁺ | 20 (Figure 1c) |
| H ₂ C=SH ⁺ | HC≡S ⁺ | 20 (Figure 1d) |
| H ₃ C—NH ₂ ⁺ | H ₂ C=NH ⁺ | 19 (Figure 1e) |

^a Taken from ref 7.

All the 1,2-eliminations occur with release of kinetic energy, and in four cases the kinetic energy release is in the region of 1 eV or more. We infer that these eliminations proceed *via* concerted symmetry-forbidden routes; in such routes, intended crossings are foiled and as a consequence kinetic energy (which constitutes a portion of the reverse activation energy) is released.

It is noteworthy that in a recent communication on the dynamics of organic reactions, Wang and Karplus¹¹ have pointed out that trajectory calculations indicate that for the reaction H₂ + singlet CH₂, with an approach of "least motion" (C_{2v}) geometry, collisions with relative kinetic energy significantly below the calculated barrier (0.021 hartree, 13 kcal/mol) are repulsive, while those with relative kinetic energy well above the barrier height result in direct reaction. In Woodward–Hoffmann parlance,¹ a transition state of C_{2v} geometry corresponds to a concerted forbidden reaction, and in observing kinetic energy release in inferred¹² concerted forbidden dissociations, we are experimentally verifying the kinetic energy requirement for symmetry-forbidden bimolecular reactions.

(10) M. Barber, K. R. Jennings, and R. Rhodes, *Z. Naturforsch. A*, **22**, 15 (1967).

(11) I. S. Y. Wang and M. Karplus, *J. Amer. Chem. Soc.*, **95**, 8164 (1973).

(12) We use the term "inferred" since it is not possible to *prove* that the planar transition state is involved. It is conceivable, although we believe very unlikely, that the transition state could correspond to the reverse reaction in which the π-system adds as an antarafacial component to H₂. While [π_{2a} + π_{2a}] cycloadditions are well known (e.g., ref 1, pp 163–166), a [π_{2a} + σ_{2a}] process is quite a different matter, and appears geometrically most unlikely. Moreover, the symmetry-forbidden route neatly accounts for the observed kinetic energy release, which in a symmetry-allowed reaction would have to find its origin in other sources.

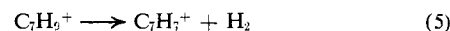
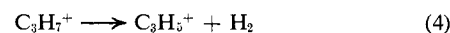
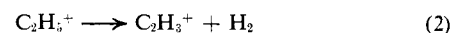
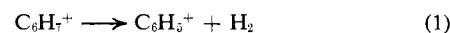
Dudley H. Williams,* Georg Hvistendahl
University Chemical Laboratory
Cambridge, England
Received March 12, 1974

Kinetic Energy Release as a Mechanistic Probe. The Role of Orbital Symmetry

Sir:

In an accompanying communication,¹ we have established that a number of concerted 1,2-eliminations of molecular hydrogen proceed with the release of kinetic energy. The release of kinetic energy is in accord with these reactions proceeding through symmetry forbidden pathways and is in contrast to the majority of unimolecular decompositions of ions which proceed without relatively large and specific releases of kinetic energy.² The experimental results suggest that concerted eliminations of H₂ which proceed without a significant release of kinetic energy are not 1,2-eliminations; the orbital symmetry arguments for (reasonably assumed) planar transition states lead one to the same conclusion.¹ We have therefore applied kinetic energy release as a mechanistic criterion in studying H₂ loss from some simple cations.

The reactions which we have studied are summarized in eq 1–5.



In four of the five cases (eq 1–4), examination of metastable transition for H₂, HD, and D₂ losses from partially deuterated precursors (C₆H₂D₅⁺,³ C₂H₂D₃⁺,³ C₂H₂D₂,⁴ C₃H₄D₃⁺³) establishes that hydrogen shifts precede decomposition and the mechanism of H₂ loss in these cases cannot therefore be studied by specific deuterium labeling. This situation is not surprising, since there is prior evidence that in numerous carbocations, H(D) shifts are fast relative to their slow (metastable) unimolecular decompositions.^{5,6} The observations are in accord with theoretical studies; for example, the barrier to 1,2-hydrogen shifts in the ethyl cation is estimated to be only 6–12 kcal/mol,⁷ which is small compared to the activation energy for H₂ loss (55 kcal/mol,⁸ 67 kcal/mol measured in the present work).

In Figure 1, we show the metastable peak shapes (first field-free region) for H₂ losses in the reactions 1–5. It is evident that reactions 1–3 occur with a small or negligible release of kinetic energy, whereas reactions 4 and 5 proceed with relatively large and specific releases of kinetic energy (8⁹ and 20¹⁰ kcal/mol, respectively,

(1) D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, **96**, 6753 (1974).

(2) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions," Elsevier, Amsterdam, 1973.

(3) G. Hvistendahl and D. H. Williams, unpublished work.

(4) I. Baumel, R. Hagemann, and R. Botter, 19th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14 A.S.T.M., Atlanta, Ga., May 1971.

(5) B. Davis, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc. B*, **81** (1970).

(6) N. A. Uccella and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 8778 (1972).

(7) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(8) M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 2.

(9) See also P. Goldberg, J. A. Hopkinson, A. Mathias, and A. E. Williams, *Org. Mass Spectrom.*, **3**, 1009 (1970).

(10) R. G. Cooks, J. H. Beynon, M. Bertrand, and M. K. Hoffmann, *Org. Mass Spectrom.*, **7**, 1303 (1973).