

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 H<sub>2</sub> 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,<sup>10</sup> 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 <sub>3</sub> CH <sub>3</sub> <sup>+</sup>	CH <sub>2</sub> CH <sub>2</sub> <sup>+</sup>	4.4 (Figure 1a)
H <sub>2</sub> C=OH <sup>+</sup>	HC≡O <sup>+</sup>	33 <sup>a</sup> (Figure 1b)
H <sub>2</sub> C=NH <sub>2</sub> <sup>+</sup>	HC≡NH <sup>+</sup>	20 (Figure 1c)
H <sub>2</sub> C=SH <sup>+</sup>	HC≡S <sup>+</sup>	20 (Figure 1d)
H <sub>3</sub> C-NH <sub>2</sub> <sup>+</sup>	H <sub>2</sub> C=NH <sup>+</sup>	19 (Figure 1e)

<sup>a</sup> 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 Karplus<sup>11</sup> have pointed out that trajectory calculations indicate that for the reaction H<sub>2</sub> + singlet CH<sub>2</sub>, with an approach of "least motion" (C<sub>2v</sub>) 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,<sup>1</sup> a transition state of C<sub>2v</sub> geometry corresponds to a concerted forbidden reaction, and in observing kinetic energy release in inferred<sup>12</sup> concerted forbidden dissociations, we are experimentally verifying the kinetic energy requirement for symmetry-forbidden bimolecular reactions.

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(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 H<sub>2</sub>. While [π<sub>2a</sub> + π<sub>2a</sub>] cycloadditions are well known (e.g., ref 1, pp 163–166), a [π<sub>2a</sub> + σ<sub>2a</sub>] 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.

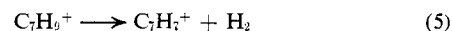
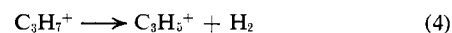
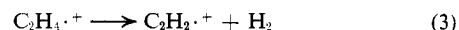
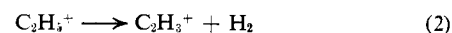
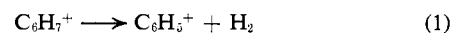
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Received March 12, 1974

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

Sir:

In an accompanying communication,<sup>1</sup> 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.<sup>2</sup> The experimental results suggest that concerted eliminations of H<sub>2</sub> 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.<sup>1</sup> We have therefore applied kinetic energy release as a mechanistic criterion in studying H<sub>2</sub> 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 H<sub>2</sub>, HD, and D<sub>2</sub> losses from partially deuterated precursors (C<sub>6</sub>H<sub>2</sub>D<sub>5</sub><sup>+</sup>,<sup>3</sup> C<sub>2</sub>H<sub>2</sub>D<sub>3</sub><sup>+</sup>,<sup>3</sup> C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>,<sup>4</sup> C<sub>3</sub>H<sub>4</sub>D<sub>3</sub><sup>+</sup><sup>3</sup>) establishes that hydrogen shifts precede decomposition and the mechanism of H<sub>2</sub> 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.<sup>5,6</sup> 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,<sup>7</sup> which is small compared to the activation energy for H<sub>2</sub> loss (55 kcal/mol,<sup>8</sup> 67 kcal/mol measured in the present work).

In Figure 1, we show the metastable peak shapes (first field-free region) for H<sub>2</sub> 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 (8<sup>9</sup> and 20<sup>10</sup> kcal/mol, respectively,

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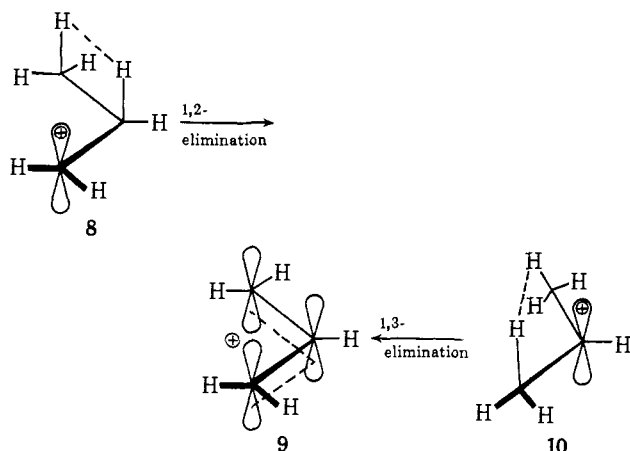
(9) See also P. Goldberg, J. A. Hopkinson, A. Mathias, and A. E. Williams, *Org. Mass Spectrom.*, **3**, 1009 (1970).

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gest the allyl ion as the ionic product. The activation energy (46 kcal/mole) given in Table I is computed relative to the 2-propyl cation ( $\Delta H_f = 192$  kcal/mol).<sup>14</sup> Since the kinetic energy release in  $H_2$  loss is 8 kcal/mol, the maximum possible energy content of the  $C_3H_5^+$  ion is 230 kcal/mol. Calculations<sup>15</sup> of the heats of formation (otherwise unavailable) of cyclopropyl (257 kcal/mol), 2-propenyl (233 kcal/mol), and 1-propenyl (249 kcal/mol) exclude all product structures except allyl (experimental  $\Delta H_f = 226$  kcal/mol<sup>16</sup>) and possibly 2-propenyl. The allyl ion is certainly the best candidate, and even this most stable structure on the  $C_3H_7^+$  manifold allows only 4 kcal/mol of internal energy of the products.

Calculations of energies of  $C_3H_7^+$  cations<sup>17</sup> indicate that the presence of 46 kcal/mol of internal energy in excess of the heat of formation of 2-propyl will allow interconversion among at least seven plausible geometries of  $C_3H_7^+$ , all of which either cannot be generated or appear unlikely to be generated, in a smooth transition *via* 1,1-addition of  $H_2$  to the allyl ion. It is therefore suggested that the forward reaction is represented *via* concerted 1,2- or 1,3-elimination from the 1-propyl or 2-propyl cation, respectively ( $8 \rightarrow 9$  or  $10 \rightarrow 9$ ).



These suggestions, based on energetic considerations, are in accord with the concepts outlined in this and the preceding communication,<sup>1</sup> since both  $8 \rightarrow 9$  and  $10 \rightarrow 9$  represent concerted symmetry-forbidden reactions which should occur with release of kinetic energy, as observed (Figure 1d).

Since reaction 5 occurs with a large release of kinetic energy (Figure 1e, 20 kcal/mol), we formulate this reaction as the symmetry-forbidden loss of  $H_2$  from a dihydrotropylium cation *via* either 1,2- or 1,3-elimination ( $11 \rightarrow 12$ , or  $13 \rightarrow 12$ ). The same flat-topped metastable peak is observed irrespective of whether the  $C_7H_9^+$  ion is generated *via* fragmentation of benzyl methyl ether,<sup>10</sup> protonation of cycloheptatriene in a chemical ionization source, or *via* protonation of toluene.<sup>18</sup>

It is striking that, in comparing the behavior of the

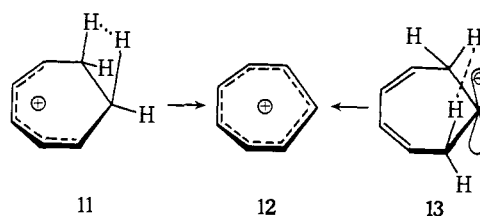
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homologs  $C_2H_3^+$  and  $C_3H_7^+$  or  $C_6H_7^+$  and  $C_7H_9^+$ , no significant kinetic energy release occurs in  $H_2$  loss where vinylum ion structures are forced upon the products, but kinetic energy release occurs where 1,2- or 1,3-elimination can give rise to  $\pi$ -delocalized cations (allyl or tropylium).

The 1,1-eliminations of hydrogen considered in this paper are "four-electron" reactions, in contrast to processes where the reverse bimolecular reaction involves the addition of molecular hydrogen to a cation in a "two-electron" reaction. Reactions of the latter type are also symmetry-allowed and accordingly may occur through the most probable channel without a large and relatively specific release of translational energy. In line with expectations, the most probable channel for the reaction  $H_3^+ \rightarrow H^+ + H_2$  results in minimum kinetic energy release and maximum vibrational excitation of  $H_2$ .<sup>19</sup> The kinetic energy released in the reaction  $CH_3^+ \rightarrow CH_3^+ + H_2$  does not appear to have been reported, but if this reaction occurs slowly enough for the observation of a metastable peak, then the peak shape is expected to indicate that this symmetry-allowed process occurs without a large release of kinetic energy.

**Acknowledgments.** We wish to thank the Science Research Council (UK) and AEI (Manchester, UK) for financial support of the work described in this and the accompanying communication.<sup>1</sup> We thank Dr. J. M. Wilson (Manchester) for the chemical ionization spectra. G. H. wishes to thank the Royal Norwegian Council for Scientific and Industrial Research and NATO for financial support.

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## Nuclear Magnetic Resonance Spectroscopy. $^{13}C$ - $^{15}N$ Coupling Constants as a Conformational Probe?<sup>1</sup>

Sir:

There have been several attempts to explain the variation in  $^{13}C$ - $^{15}N$  coupling constants with the stereochemical orientation of the carbons with respect to the nitrogen lone pairs.<sup>2,3</sup> Most of the substances in-

(1) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences.

(2) For two recent reviews on coupling constants involving  $^{14}N$  and  $^{15}N$ , see (a) R. L. Lichter in "Determination of Organic Structure by Physical Methods," Vol. 4, J. J. Zuckermann and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1972, p 195; (b) T. Axenrod in "Nitrogen NMR," M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, N. Y., 1973, p 261.

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