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 ·+ | $CH_2CH_2 \cdot +$ | 4.4 (Figure 1a) |
| H ₂ C=OH | HC≡O ⁺ | 33 ^a (Figure 1b) |
| $H_2C = NH_2$ | HC≡ŅH | 20 (Figure 1c) |
| H ₂ C=SH | HC≡Ŝ | 20 (Figure 1d) |
| $H_3C - NH_2$ | H₂C=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 H_2 + singlet CH_2 , with an approach of "least motion" $(C_{2\nu})$ 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.

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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.

$$\mathbf{C}_{6}\mathbf{H}_{7}^{+} \longrightarrow \mathbf{C}_{6}\mathbf{H}_{5}^{+} + \mathbf{H}_{2} \tag{1}$$

$$C_2H_3^+ \longrightarrow C_2H_3^+ + H_2 \tag{2}$$

$$C_{2}H_{4} + C_{2}H_{2} + H_{2}$$

$$(3)$$

$$C_3H_7' \longrightarrow C_3H_5' + H_2 \tag{4}$$

$$C_7 H_9^+ \longrightarrow C_7 H_7^+ + H_2 \tag{5}$$

In four of the five cases (eq 1-4), examination of metastable transition for H_2 , HD, and D_2 losses from partially deuterated precursors (C₆H₂D₅⁺, ³C₂H₂D₃⁺, ³ $C_2H_2D_2$, $^4C_3H_4D_3^{+3}$) 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 H_2 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,

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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 H₂. While $[\pi 2_a + \pi 2_b]$ cycloadditions are well known (e.g., ref 1, pp 163–166), a $[\pi 2_a + \sigma 2_b]$ 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.



Figure 1. Metastable peaks (MS 9 first field-free region) for loss of molecular hydrogen from (a) $C_6H_7^+$ (b) $C_2H_5^+$ (c) $C_2H_{4^{+}}^+$ (d) $C_8H_7^+$, and (e) $C_7H_9^+$. 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} .

determined by measurements carried out in the second field-free region).

We conclude that reactions 1-3 do not occur *via* concerted 1,2-elimination. Yet there is no doubt that all the reactions are concerted to a considerable degree, not only because of the intensity of the metastable peaks for one-step loss of H_2 but also because our measurements of the activation energies involved (from appearance potential measurements on the metastable peaks) establish that these activation energies fall far short of those required for loss of two hydrogen radicals (Table I).

Table I. Experimental Activation Energies (kcal/mol) for H_2 Losses in Reactions 1-5, and Total Activation Energiesfor the Hypothetical Losses of Two Hydrogen Radicals

| $E_{\rm a}$ (H ₂) | <i>E</i> _a (2 H) |
|-------------------------------|-----------------------------|
| 65 | 145 |
| 67ª | 154 |
| 56 (73) ^b | 168 |
| 46° | 138 |
| 58 | 105 |
| | |

^a Cf. 55 kcal/mol in ref 8. ^b Value in parentheses determined on the C_2H_2 · ⁺ daughter ion. ^c Cf. 47 kcal/mol in ref 8.

If the concerted loss of H_2 from the ethyl cation is not a 1,2-elimination, then the only plausible pathway seems to be a 1,1-elimination, leading to the same product as anticipated from a 1,2-elimination, namely, the vinylium ion. It is important to note that if 1,1-elimination proceeds through a linear cheletropic reaction,¹¹ it is a symmetry-allowed reaction and may in principle proceed without the release of kinetic energy (as observed, Figure 1b), although we could not of course preclude the release of kinetic energy which might originate from sources other than a symmetry-

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forbidden barrier. In a linear 1,1-elimination, the four electrons of the two σ C-H bonds involved in reaction behave as follows. The two electrons of the symmetric orbital 1 can pass into the symmetric bonding orbital of a hydrogen molecule, while the two electrons of the antisymmetric orbital 2 can pass into the π -system of the vinylium ion 3.



The ion $C_6H_7^+$ may be produced by numerous methods in the mass spectrometer (e.g., via fragmentation of benzyl alcohol¹²); the ion has also conveniently been produced in the present work via protonation of benzene in a chemical ionization source. Irrespective of its mode of product, the metastable peak for H₂ loss is narrow (Figure 1a). This reaction surely occurs because the product of H₂ loss is the aromatic phenyl cation, and it is gratifying to find that if the reacting configuration of C₆H₇+ is protonated benzene, the reaction must again be formulated as a 1,1-elimination which, in a manner exactly analogous to the loss of H_2 from $C_2H_5^+$, may occur through a linear pathway thus avoiding the necessity for kinetic energy release. A complete correlation diagram shows that the reaction is symmetry-allowed, the two electrons of the antisymmetric orbital 4 being able to pass into the π -system to complete the aromatic sextet of the phenyl cation 5.



Interestingly, the loss of H_2 from the reacting configuration of the ion derived from ionization of ethylene proceeds without a significant release of kinetic energy (Figure 1c), and we therefore propose that this reaction is a 1,1-elimination. Ionized ethylene undergoes hydrogen randomization at a rate which is fast compared with its unimolecular loss of hydrogen.⁴ The barrier to the rearrangement reaction $6 \rightarrow 7$ (which can account for

$$CH_2 = CH_2 \cdot + \underbrace{\longrightarrow}_{CH_2} CH_3 - \overset{+}{CH_3} H \xrightarrow{-H_2}_{(1,1-\text{elimination})} HC \equiv CH_2 \cdot + \underbrace{\longrightarrow}_{CH_2} HC = CH_2 \cdot + \underbrace$$

the observed randomization) is calculated to be about 18 kcal/mol,¹³ which is much less than the activation energy for H₂ loss (Table I). A probable course for the reaction is therefore 1,1-elimination from 7 to give ionized acetylene. As in the case of our formulations for eq 1 and 2, the reaction is symmetry-allowed through a linear pathway.

In contrast to the loss of H_2 from the ethyl cation, loss of H_2 from $C_3H_7^+$ occurs with kinetic energy release (Figure 1d). It is immediately striking that here the product does not have to be a vinylium ion, but *a priori* the most likely structure of the product appears to be the allyl ion. In fact, energetic considerations sug-

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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 ($\Delta H_f = 192 \text{ kcal/mol}$).¹⁴ Since the kinetic energy release in H₂ loss is 8 kcal/mol, the maximum possible energy content of the C₃H₅⁺ ion is 230 kcal/mol. Calculations¹⁵ 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 $\Delta H_f = 226 \text{ kcal/mol}^{16}$) and possibly 2propenyl. The allyl ion is certainly the best candidate, and even this most stable structure on the C₃H₇⁺ manifold allows only 4 kcal/mol of internal energy of the products.

Calculations of energies of $C_3H_7^+$ cations¹⁷ 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, ¹ 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 le, 20 kcal/mol), we formulate this reaction as the symmetry-forbidden loss of H₂ 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 C₇H₉+ ion is generated via fragmentation of benzyl methyl ether, ¹⁰ protonation of cycloheptatriene in a chemical ionization source, or via protonation of toluene.¹⁸

It is striking that, in comparing the behavior of the

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homologs $C_2H_5^+$ and $C_3H_7^+$ or $C_6H_7^+$ and $C_7H_9^+$, no significant kinetic energy release occurs in H_2 loss where vinylium ion structures are forced upon the products, but kinetic energy release occurs where 1,2- or 1,3 elimination can give rise to π -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 .¹⁹ The kinetic energy released in the reaction CH_5^+ \rightarrow CH₃⁺ + H₂ 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.

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Nuclear Magnetic Resonance Spectroscopy. ¹³C-¹⁵N Coupling Constants as a Conformational Probe?¹

Sir:

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

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