Isotope Effects as a Transition State Probe in Concerted Unimolecular Reactions of Ions

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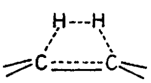
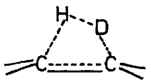
Summary Deuterium isotope effects, operating in competitive losses of H_2, HD, and D_2 from some carbocations, are used to indicate that these reactions proceed through transition states in which two C–H bonds are synchronously stretched.

The concept of orbital symmetry conservation[1] 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 observation of metastable peaks, the range of unimolecular rate constants is reasonably defined ($k = 10^4$—10^6 s^{-1}) and the non-fixed energy in the transition state is relatively small.[2,3] As a consequence of this last condition, large isotope effects are frequently observed in metastable peak abundances when X–H *vs.* X–D bond stretching is involved in attaining a transition state.[4] We now show that such isotope effects can be used to establish that the loss of molecular hydrogen in the unimolecular decomposition of some positive ions occurs through transition states in which two C–H bonds are synchronously stretched.



(1)



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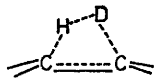


(3)

From previous considerations of isotope effects, it can be shown[5] that if, in an *inter*-molecular case, there is loss of H_2, HD, and D_2 with unimolecular rate constants k_{H_2}, k_{HD}, and k_{D_2}, then for a completely concerted reaction in which two X–H(D) bonds are synchronously stretched, equation (1) applies. Conversely, if the process is completely non-concerted,[5] then equation (2) applies.

$$[k_{HD}/k_{D_2}]^2 = k_{H_2}/k_{D_2} \qquad (1)$$

$$k_{HD} = [k_{H_2} + k_{D_2}]/2 \qquad (2)$$

We have now applied a similar analysis to cases where there is *intra*-molecular competition between H_2, HD, and D_2 loss. In the case of a symmetrical transition state [*e.g.* (**1**)], HD loss involves the stretching of only one C–D bond in the transition state, and D_2 loss involves the synchronous stretching of two C–D bonds and equation (1) still holds. Appearance potential measurements (to be reported in a full paper) establish that the reactions we consider (*vide infra*) cannot occur *via* loss of two hydrogen radicals (as indeed is also indicated by the abundant metastable peaks for H_2 loss), but in the hypothetical and limiting case, transition states might be considered in which one bond is extensively stretched and the other insignificantly so [*e.g.* (**2**) or (**3**)].

Reaction proceeding through the activated complex (**2**) would be characterised by a rate constant k_{H_2} and those proceeding through (**3**) would be characterised by a rate constant k_{D_2}. Hence, equation (2) applies.

In appropriately selected reactions, the relative abundances of the metastable peaks for loss of H_2, HD, and D_2 are in fact excellent measurements of the ratios $k_{H_2}:k_{HD}:k_{D_2}$, since we may be sure in the systems studied that the products of metastable loss of H_2, HD, and D_2 have insufficient energy to undergo significant further unimolecular decomposition.

Data for the reactions which we have studied (using, in the case of deuteriated ethylenes, data already available in the literature) are summarised in the Table.

Table

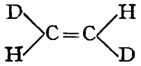
Relative areas of metastable peaks and rate constants for the loss of H_2,HD, and D_2 from selected hydrocarbon ions

Neutral precursor	Decomposing ion	$[m_{H_2}*]:[m_{HD}*]:[m_{D_2}*]$[a]	$k_{H_2}:k_{HD}:k_{D_2}$[b]
(A)	$C_2H_2D_3^+$	2·6(5) : 5·3 : 1·0	7·9 : 2·6(5) : 1·0
(B)	$C_2H_2D_2^{+\cdot}$	740 : 92 : 1·0[c]	740 : 23 : 1·0
(C)	$C_2H_2D_2^{+\cdot}$	700 : 92 : 1·0[c]	700 : 23 : 1·0
(D)	$C_3H_4D_3^+$	5·2(5) : 6·2(5) : 1·0	2·6 : 1·5(5) : 1·0
(E)	$C_6H_2D_5^+$	0·30 : 1·7 : 1·0	3·0 : 1·7 : 1·0

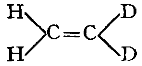
[a] Normalised to $[m_{D_2}*]$ as unity; except where otherwise indicated, these values were determined from decomposition occurring in the first field-free region of an MS-9 double focussing mass spectrometer (using the refocussing technique described by M. Barber and R. M. Elliott, 12th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14 A.S.T.M., Montreal, June, 1964), operating at 70 eV. [b] These values are obtained from the ratios of areas of metastable peaks by correction for the different statistical probabilities for H_2, HD, and D_2 losses, and then normalisation to k_{D_2} as unity. [c] Data taken from I. Baumel, R. Hagemann, and R. Botter, 19th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14 A.S.T.M., Atlanta, May, 1971.

CD_3CH_2Br

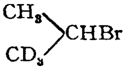
(A)



(B)



(C)



(D)

$C_6D_5CH_2OH$

(E)

In each case, the relative ratios of metastable peaks need to be corrected by a statistical factor to give the relative rate constants. The barrier to 1,2-hydrogen shifts in the ethyl cation is estimated to be only 6—12 kcal/mol[6] which is small compared to the activation energy for H_2 loss (55 kcal mol^{-1})[7] and in the absence of an isotope effect the ratios of metastable peaks would be $[m_{H_2}*]:[m_{HD}*]:[m_{D_2}*] = 0·33:2:1$. The corresponding ratios for the *trans*- and geminally-deuteriated ethylenes (Table) are 1:4:1, since the derived ions behave in the same way within experimental error, and are therefore believed to undergo 1,2-H(D) shifts at a rate which is fast compared to unimolecular decomposition. Likewise, the relevant ratios for $C_3H_4D_3^+$ and $C_6D_5H_2^+$ are statistically derived (2:4:1 and 0·1:1:1, respectively) since these ions both lose H_2, HD, and D_2, and there is prior evidence that H(D)-shifts in numerous carbonium ions are fast relative to their slow (metastable) unimolecular decompositions.[8,9]

The most striking results (Table) are those for the *trans*-[1,2-$^2H_2$]- and [1,1-$^2H_2$]-ethylenes, where the observed k_{H_2}/k_{D_2} ratios of 700—740 require a theoretical value of $k_{HD}/k_{D_2} = 26$—27 for a perfectly concerted reaction, in good agreement with the observed ratio of 23. As the isotope effect is extremely large, the observed k_{HD}/k_{D_2} ratio differs by more than an order of magnitude from that required for a non-concerted reaction. The isotope effects for the reactions of the partially deuteriated

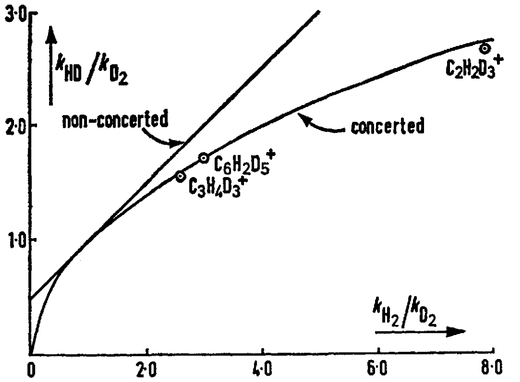


FIGURE. Plot of k_{HD}/k_{D_2} *vs.* k_{H_2}/k_{D_2} for the unimolecular metastable decomposition of some partially deuteriated hydrocarbon ions.

C_3 and C_6 cations are considerably smaller, but the data are in better agreement with the relative rate constants required for concerted reaction than with those required for a non-concerted reaction; loss of H_2 from the ethyl cation is indicated to occur with synchronous stretching of two C–H bonds (Figure). The results support the proposal[10] that orbital symmetry criteria may be usefully applied in the study of such reactions.

We thank the S.R.C. for financial support. G.H. thanks the Royal Norwegian Council for Scientific and Industrial Research and N.A.T.O. for financial support.

(*Received, 3rd September* 1974; *Com.* 1126.)

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 797.

[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,' Academic Press, New York, 1973.

[4] See, for example, U. Löhle, and Ch. Ottinger, *J. Chem. Phys.*, 1969, **51**, 3097.

[5] E. K. Thornton and E. R. Thornton in 'Isotope Effects in Chemical Reactions,' A.C.S. Monograph 167, eds. C. J. Collins, and N. S. Bowman, Van Nostrand Rheinhold Co., New York, pp. 274—275. This article develops the argument in terms of secondary isotope effects, but a similar argument can be applied to primary isotope effects. We thank Dr. I. Fleming for drawing this article to our attention.

[6] W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808.

[7] M. L. Vestal in 'Fundamental Processes in Radiation Chemistry,' ed. P. Ausloos, Wiley-Interscience, New York, 1968, ch. 2.

[8] B. Davies, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc. (B)*, 1970, 81.

[9] N. A. Uccella and D. H. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 8778.

[10] D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1974, **96**, 6753, 6755.