Experimental Evidence for the Existence of Gaseous Cyclobutyl Cation

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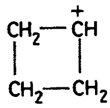
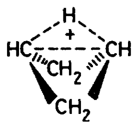
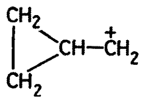
Summary It is shown from kinetic energy release measurements and collisional activation studies that Br• loss from ionised homoallyl bromide, cyclopropylmethyl bromide, and cyclobutyl bromide in the gas phase leads to formation of cyclobutyl cation.

An area of continued interest in organic chemistry is the nature of the $C_4H_7^+$ ion involved in the isomerisation of cyclopropylmethyl, cyclobutyl, and homoallyl derivatives in aprotic solvents.[1,2] Quantum mechanical calculations have been performed to estimate the relative energies of the relevant $C_4H_7^+$ ions and to attempt to elucidate the possible mechanisms whereby these ions may interconvert. *Ab initio* calculations suggest that the homoallyl (**3**) and cyclobutyl (**1**) cations collapse, essentially without activation energy, to the cyclopropylmethyl cation (**2**), which is concluded to be the most stable of these three $C_4H_7^+$ isomers.[3] In contrast, semi-empirical calculations suggest that the most stable isomer is cyclobutyl cation,[4,5] which might be regarded as a symmetrical bicyclobutonium cation (**1a**) on account of its pronounced puckered geometry. No potential energy well was found for homoallyl cation, which is expected to collapse to cyclobutyl cation with negligible activation energy. The energy barrier for rearrangement of cyclopropylmethyl cation to cyclobutyl cation was estimated to be relatively small (20[4] or 25[5] kJ mol^{-1}).

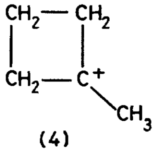

(1)


(1a)


(2)

$CH_2{=}CHCH_2\overset{+}{C}H_2$

(3)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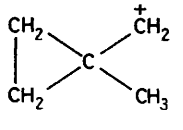
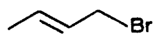
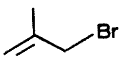

(5)

The situation is complicated in solution because of possible preferential stabilisation of one isomer of $C_4H_7^+$. However, for the homologous $C_5H_9^+$ ions, (**4**) and (**5**), it is found, from solution n.m.r. experiments, that the methylcyclobutyl cation (**4**) is more stable, by at least 10 kJ mol^{-1}, than the methylcyclopropylmethyl cation (**5**). The energy barrier for rearrangement of (**5**) to (**4**) was found to be small (at most 20 kJ mol^{-1}).[6]

A direct experimental method for determining which isomer of $C_4H_7^+$ exists in a potential energy well would clearly be useful. It has been shown that when $(R{-}X)^+$ loses X (X = Br• or CO) to form a carbonium ion R^+, exothermic isomerisation of the incipient carbonium ion may be detected by an increase in the kinetic energy release which accompanies dissociation.[7,8] This increase in kinetic energy release arises because part of the potential energy, released upon isomerisation of the incipient carbonium ion, is partitioned into the bond which breaks in the dissociation step.[9]


(A)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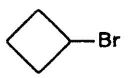
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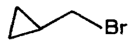
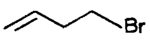

(D)


(E)

The average[10] kinetic energy release which accompanies Br• loss from the five isomers of $C_4H_7Br^{+\bullet}$ (A)–(E) is 0·4, 0·4, 0·4, 1·3, and 1·7 kJ mol^{-1}, respectively.† Loss of Br• from 1- and 2-methylallyl bromide molecular ions is evidenced by an extremely small average kinetic energy release (0·4 kJ mol^{-1} in each case). This is good evidence that these ions exist in potential energy wells in the gas phase and that there is a relatively substantial energy barrier towards their interconversion.

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† Values derived from metastable peaks arising from dissociations in the first field-free region of an AEI MS 902 double focusing mass spectrometer.

Elimination of Br· from ionised cyclobutyl bromide also gives rise to an extremely small average kinetic energy release. This indicates that cyclobutyl cation exists in a potential energy well in the gas phase. On the other hand, larger average kinetic energy releases are associated with Br· loss from the molecular ions of cyclopropylmethyl bromide and homoallyl bromide. These data reveal that cyclopropylmethyl cation and homoallyl cation can rearrange, with little activation energy, to more stable structures. The increase in the kinetic energy release is directly visible from the metastable peaks for the processes concerned which are depicted in the Figure.

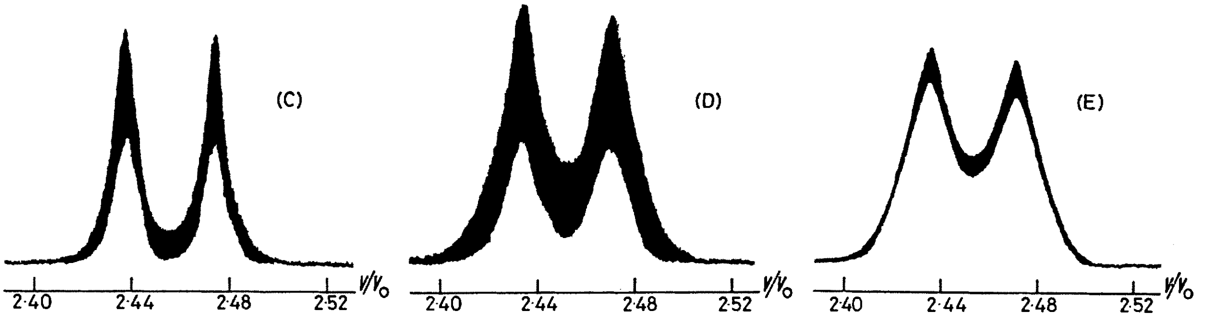

FIGURE. First field-free region metastable peaks for loss of Br· from the molecular ions of the three isomers of C_4H_7Br (C)—(E). In each case, two metastable peaks are observed, corresponding to the elimination of $^{79}Br\cdot$ and $^{81}Br\cdot$, which occur in approximately equal natural abundance. The abscissae are in units of V/V_0 where V_0 is the accelerating voltage used to transmit the main beam and V is the accelerating voltage required to transmit $C_4H_7^+$ ions formed in the first field-free region.

The structure of the $C_4H_7^+$ ions formed by Br· elimination from cyclopropylmethyl bromide and homoallyl bromide molecular ions may be investigated using collisional activation spectroscopy.[11] Relevant data are given in the Table.

TABLE. Collisional activation spectra of $C_4H_7^+$ ions formed from isomeric C_4H_7Br precursors

	Precursor				
m/e[a]	(A)	(B)	(C)	(D)	(E)
41	0·7	1·2	0·9	0·9	0·9
40	4·0	5·7	3·0	3·1	3·0
39	45	51	39	38	38
38	6·0	8·1	5·1	5·0	5·1
28	8·1	8·7	11	11	11
26	5·9	4·7	7·1	7·6	7·2
Ratio CH_3/CH_2 loss	5·7	4·8	3·3	3·4	3·3

[a] Selected values; the relative abundances are normalised to a total of 100 units over the m/e range 13—54.

The collisional activation data for the $C_4H_7^+$ ions, formed from the various precursors shown in the Table, are broadly similar. This indicates that partial interconversion of the isomeric $C_4H_7^+$ ions probably occurs before and/or after collision. Nevertheless, some diagnostic differences are observed, especially in the relative abundances of CH_3 and CH_2 losses from the $C_4H_7^+$ ions investigated. Loss of CH_2 increases in importance, relative to CH_3 loss, in progressing from ions formed from 1-methylallyl bromide to 2-methylallyl bromide to cyclobutyl bromide. The corresponding cations, if formed by simple cleavage of the C–Br bond, possess one, two, and three CH_2 groups, respectively. Thus, as the number of CH_2 groups in the initial $C_4H_7^+$ ion increases, elimination of CH_2 becomes more pronounced, relative to CH_3 loss.

The ratio of CH_3 to CH_2 losses from $C_4H_7^+$ ions formed from ionised cyclopropylmethyl bromide and ionised homoallyl bromide is in each case close to the value found when $C_4H_7^+$ is generated from ionised cyclobutyl bromide. Moreover, the complete collisional activation spectra of $C_4H_7^+$ ions derived from these three precursors are identical within experimental error. This shows that these $C_4H_7^+$ ions have the same structure, or mixture of structures. These data, together with the kinetic energy release measurements given above, indicate that cyclopropylmethyl and homoallyl cations can rearrange exothermically to cyclobutyl cation, which exists in a potential energy well in the gas phase.

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[1] H. G. Richey, Jr., 'Cyclopropylcarbonium Ions' and K. B. Wiberg, B. A. Hess, Jr.,and A. J. Ashe III, 'Cyclopropylcarbinyl and Cyclobutyl Cations,' Ch. 25 and 26, respectively, in 'Carbonium Ions,' Vol. 3, eds. G. A. Olah and P .v. R. Schleyer, Wiley, New York, 1972.
[2] H. C. Brown, 'The Nonclassical Ion Problem,' Ch. 5, Plenum Press, New York, 1977.
[3] W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, 1972, **94**, 5917; 1974, **96**, 302.
[4] J. Kollmar, *Tetrahedron Letters*, 1970, 3133.
[5] K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, 1970, **92**, 571.
[6] R. P. Kirchen and T. S. Sorensen, *J. Amer. Chem. Soc.*, 1977, **99**, 6687.
[7] D. H. Williams, B. J. Stapleton, and R. D. Bowen, *Tetrahedron Letters*, 1978, 2919.
[8] R. D. Bowen, D. H. Williams, H. Schwarz, and C. Wesdemiotis, *J. Amer. Chem. Soc.*, in the press.
[9] G. Hvistendahl and D. H. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 3097.
[10] D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *Proc. Roy. Soc.* (*A*), 1974, **341**, 135.
[11] K. Levsen and H. Schwarz, *Angew. Chem. Internat. Edn.*, 1976, **15**, 509.