Evidence for Retention of the Cyclic C_3H_5 Structure during Positive-ion Processes in the Gas Phase

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Summary The decomposition of gaseous cyclopropylmethylbromonium ions has yielded the cyclic hydrocarbons cyclopropane and methylcylclopropane, and methyl bromide.

As soon as an isolated cyclic $C_3H_5^+$ ion is formed in the gas phase, *e.g.* in a mass-spectrometer ion-source, it is converted into an allyl ion[1] *via* disrotatory ring-opening.[2,3] Although the heat of formation of the c-$C_3H_5^+$ cation has been reported,[3b,4,5] the value was regarded with caution, since it

TABLE. γ-Radiolysis of CH_3X + c-C_3H_5Br; dose 4·8 Mrad, dose rate 0·32 Mrad h^{-1}.

X	CH_3X (Torr)	c-C_3H_5Br (Torr)	O_2 (Torr)	NH_3 (Torr)	$G(+M) \times 10^2$		
					MeBr	c-C_3H_6	c-$C_3H_5CH_3$
F	720	3	14		2·29	40·50	3·30
F	720	3	15	15	0·29	6·00	0·65
Cl	720	3	15		6·22	0·85	3·34
Cl	720	3	15	15	0·08	0·03	0·22

may have referred to an excited allyl cation.[4] Until now, attempts to generate cyclopropyl ions in the gas phase and to induce their further reactions without losing the cyclic structure have failed.

We report herein new gas-phase ionic processes during which, for the first time, the cyclic C_3H_5 skeleton is retained; this has been established by analysis of the final neutral products.

Cyclopropylmethylbromonium ions (**2**), known to be stable in superacidic solutions,[6] were generated free of counterions in the gas-phase reaction of dimethylhalogenonium ions (**1**) with cyclopropyl bromide, according to equation (1) where X = F or Cl. The ions (**1**), produced by

$$\underset{(\mathbf{1})}{CH_3XCH_3^+} + c\text{-}C_3H_5Br \rightarrow \underset{(\mathbf{2})_{exc}}{(c\text{-}C_3H_5BrCH_3)^+_{exc}} + CH_3X \qquad (1)$$

the radiolysis of the corresponding methyl halides,[7,8] are known to transfer the methyl cation to substrates which are more nucleophilic than CH_3X.[7–9] The neutral decay products of $(\mathbf{2})_{exc}$ were analysed by gas chromatography with an FID detector on Porapak Q and ICO-880 columns under different conditions for products within the C_1—C_6 range. The Table gives the experimental conditions and the yields, expressed as *G* values.† The results are the mean values of several experiments and are reproducible within a standard deviation of 10%, except the lowest values which are less precise. The presence of oxygen as a thermal radical-scavenger ensured the ionic nature of these processes, which was confirmed by the 80—90% depletion of the yields when ammonia, an efficient scavenger of positive ions, was added. Only *cyclic* hydrocarbons were formed, and no sign of ring cleavage was given by the product analysis.

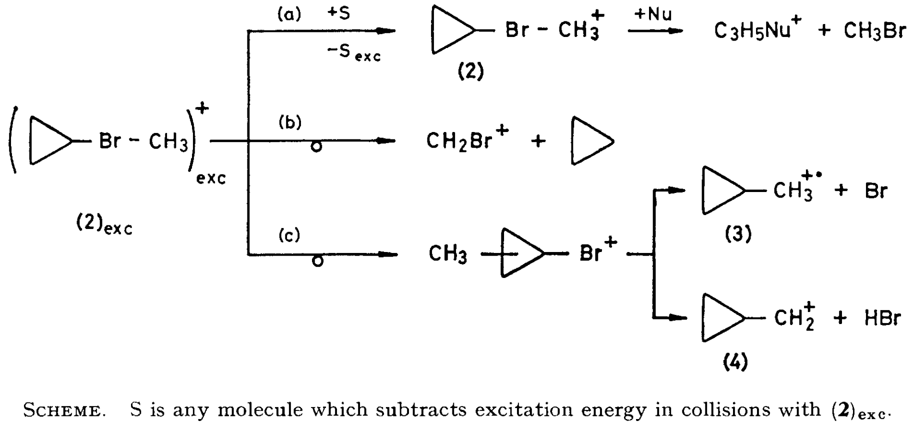
The absence of linear products rules out the occurrence of free c-$C_3H_5^{+\,1-3}$ and the processes (2) and (3). Reactions (2) and (3) would yield $G(c\text{-}C_3H_6) \leqslant G(CH_3Br)$ after the

$$(\mathbf{2}) \rightarrow c\text{-}C_3H_5^+ + CH_3Br \qquad (2)$$

$$c\text{-}C_3H_5^+ \xrightarrow[-A^+]{+AH} c\text{-}C_3H_6 \qquad (3)$$

hydride-ion abstraction from a suitable donor AH. Since $G(CH_3XCH_3^+)$ is not known, the absolute yields of the final compounds are of little significance. On the other hand the relative yields of each product in each system and the yields as a function of the halide X are the relevant factors.

The Table shows that in the CH_3F system the yield of cyclopropane and methylcyclopropane is higher than that of methyl bromide, whilst the opposite is true of the CH_3Cl system. Because of the differences between the methyl cation affinities (MCA's) of the involved alkyl halides,‡ the enthalpy of reaction (1), and therefore the excitation energy delivered by (**1**) to $(\mathbf{2})_{exc}$, depends on the difference between $MCA(CH_3X)$ and MCA(c-C_3H_5Br); the greater the difference, the larger the excitation energy acquired by $(\mathbf{2})_{exc}$. The



SCHEME. S is any molecule which subtracts excitation energy in collisions with $(\mathbf{2})_{exc}$.

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† *G* (+M) Values are the number of formed molecules (+M) per 100 eV of radiation dose, as determined by Fricke dosimetry.

‡ The methyl cation affinity (MCA) of S is defined as in J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, 1972, **94**, 2798, as $-\Delta H$ for reaction (**4**).

$$CH_3^+ + S \rightarrow CH_3S^+ \qquad (4)$$

$MCA(CH_3F) = 44$ kcal mol^{-1}, $MCA(CH_3Cl) \geqslant 51$ kcal mol^{-1} (1 cal = 4·184 J); the present understanding of the gas-phase chemistry of alkyl halides indicates that $MCA(CH_3F) < MCA(CH_3Cl) <$ MCA(c-C_3H_5Br) (*i.e.* refs. 7—9 and Beauchamp's article cited in this footnote).

most excited ions are able to undergo isomerization processes, because they can overcome the activation energy barrier. The Scheme outlines the formation of the observed products.

Since [MCA(CH_3F) – MCA(c-C_3H_5Br)] ⩽ [MCA(CH_3Cl) – MCA(c-C_3H_5Br)] the ions $(\mathbf{2})_{\mathbf{exc}}$ which were produced from $CH_3FCH_3^+$ ions possess more excitation energy than the ions $(\mathbf{2})_{\mathbf{exc}}$ which were produced from $CH_3ClCH_3^+$ ions. In the former case the more energetic rearrangement paths (b) and (c) are favoured, and in the latter case the less energetic path (a) is preferred. In path (a) the nucleophile Nu may be the walls of the irradiation Pyrex bulbs, since $C_3H_5^+$ ions were removed completely in a non-unimolecular dissociation and were not found as condensation products, *e.g.* with a radiolytic base.§

Another qualitative conclusion concerning the energetics of the processes can be made on the basis of the different yields of cyclopropane in the CH_3F and CH_3Cl systems. Since *G*(c-C_3H_6) occurs in higher yield in the CH_3F system than in the CH_3Cl system, we conclude that the isomerisation process (b) has the highest activation energy.

Finally, the c-$C_3H_5CH_3^+$ or c-$C_3H_5CH_2^+$ ions are preferred as the precursors of c-C_3H_5–CH_3, taking into account the ionization potentials of the hydrocarbons and the bromides involved in the experiments[10] and the stability of the cyclopropylmethyl cation.[11]

Further work is in progress to investigate the electrophilic cyclopropylating reactions of suitable nucleophiles Nu.

(*Received*, 3*rd March* 1981; *Com.* 241.)

§ *Note added in proof*: The glass walls of the irradiation bulbs represent the most concentrated nucleophilic base in these systems. Further work has shown that thermal c-$C_3H_5BrCH_3^+$ ions undergo hundreds of unreactive collisions with the bath molecules; therefore, at thermal kinetic energies these ions are likely to reach the glass walls and be neutralised by them.

[1] R. D. Bowen, J. Chandrasekhar, G. Frenking, P. v. R. Schleyer, H. Schwarz, C. Wesdemiotis, and D. H. Williams, *Chem. Ber.*, 1980, **113**, 1084, and references therein.
[2] R. B. Woodward and R. H. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781.
[3] (a) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 133, and preceding articles of the series; (b) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *ibid.*, 1973, **95**, 6531; (c) H. Mayr, W. Förner, and P. v. R. Schleyer, *ibid.*, 1979, **101**, 6032.
[4] C. A. McDowell, F. P. Lossing, I. H. S. Henderson, and J. B Former, *Can. J. Chem.*, 1956, **34**, 345; (b) F. P. Lossing, *ibid.*, 1971, **49**, 357.
[5] F. H. Field and J. L. Franklin, 'Electron Impact Phenomena,' Academic Press, London, 1970.
[6] G. A. Olah, G. K. Surya Prakash, and M. R. Bruce, *J. Am. Chem. Soc.*, 1979, **101**, 6463.
[7] M. Colosimo and R. Bucci, *J. Phys. Chem.*, 1979, **83**, 1952.
[8] M. Speranza and N. Pepe, *J. Chem. Soc., Perkin Trans.* 2, 1979, 1179.
[9] M. Colosimo and R. Bucci, *J. Phys. Chem.*, 1978, **82**, 2061; *ibid.*, 1980, **84**, 3326.
[10] V. I. Vedeneyev, L. V. Gurchich, V. N. Kondrat'yev, V. A. Medredev, and Ye. L. Frankevich, 'Bond Energies, Ionization Potentials, and Electron Affinities,' E. Arnold, London, 1966.
[11] F. Cacace and M. Speranza, *J. Am. Chem. Soc.*, 1979, **101**, 1587.