Gaseous 1-Methyl-1-oxoniacycloalkanes as Stable Intermediates on the $C_3H_7O^+$ and $C_4H_9O^+$ Potential Energy Surfaces

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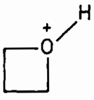
The nature and the isomeric distribution of the neutral products obtained from the gas-phase attack of CH_5^+, $C_2H_5^+$, and $CH_3FCH_3^+$ ions on cyclic $C_nH_{2n}O$ (n = 2, 3, and 4) ethers provide the first experimental evidence in favour of 1-methyl-1-oxoniacyclopropane and 1-methyl-1-oxoniacyclobutane as stable intermediates on the corresponding potential energy surface.

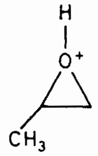
Of the possible isomeric ions of formula $C_nH_{2n+1}O^+$ ($n = 3$ or 4), several have been postulated which have a cyclic structure. The first insight into the occurrence of cyclic $C_nH_{2n+1}O^+$ ($n = 3$) intermediates in the gas phase was

Table 1. Product distribution from the attack of gaseous acids on cyclic ethers.

System composition[a]		$10^2G_{(M)}$ values of products[b]		
Gaseous acid (760 Torr)	Substrate (2—3 Torr)	Oxirane	CH_2=$CHOCH_3$	$HOCH_2CH_2OCH_3$
$C_xH_5^+(CH_4)$	Oxetane	34.9	0.9	0.8
$C_xH_5^+$ (CH_4)	2-Methyloxirane	1.8[c]	0.6[c]	1.0[c]
$CH_3FCH_3^+$ (CH_3F)	Oxirane	—	n.d.[d]	14.3

[a] O_2 (4 Torr) present in each experiment. Radiation dose: 4.8 Mrad (dose rate: 0.22 Mrad h^{-1}). [b] $G_{(M)}$ values are the number of molecules per 100 eV absorbed energy. Standard deviation of data *ca.* 10%. [c] Propionaldehyde as major product ($G_{(M)}$ value: 1.72). [d] n.d. = not detectable ($G_{(M)} < 1 \times 10^{-3}$).


(1)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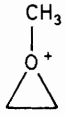
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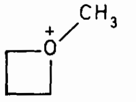
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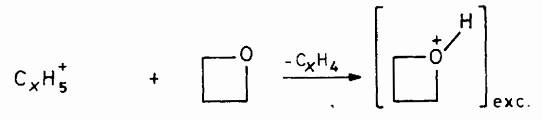
obtained from kinetic energy release experiments on suitably labelled precursors using conventional magnetic sector mass spectrometers.[1] Detailed potential energy profiles for $C_3H_7O^+$ have been constructed on these grounds, which indicate that the cyclic species (**1**) and (**2**), as well as several open-chain isomers, correspond to local energy minima. Other conceivable cyclic structures, *e.g.* 1-methyl-1-oxoniacyclopropane (**3**), were never included on the $C_3H_7O^+$ potential surface, since no direct evidence has so far been produced for the occurrence of (**3**) in the gas phase.[2] This failure is interesting in view of the fact that cyclic oxonium ions, such as (**3**) and (**4**), are often invoked in the gas phase[3] and their intermediacy is well established in solution.[4]

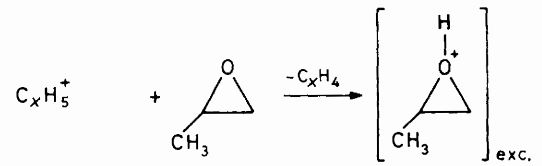
Here we report the first experimental evidence for the occurrence of the cyclic oxonium ions (**3**) and (**4**) in the gas phase, following the attack of radiolytically formed acids on suited neutral cyclic ethers. Resort to a radiolytic methodology of investigation is dictated by several considerations.[5] In the first place, the relatively high pressure (760 Torr), typical of the radiolytic experiments, permits rapid collisional quenching of all the isomeric species accessible to the exothermic ion–molecule interactions.[6] Secondly, the structural features of the isomeric $C_nH_{2n+1}O^+$ ions can be directly evaluated by actual isolation of their neutral derivatives and determination of their isomeric composition.

Gas-phase attack of $C_xH_5^+$ (x = 1, 2) and $CH_3FCH_3^+$, generated respectively by γ-radiolysis of CH_4 and CH_3F (^{60}Co source; T 37.5 °C), on oxetane, 2-methyloxirane, and oxirane afforded primarily the isomeric $C_3H_7O^+$ ions, shown in equations (1a—c).†

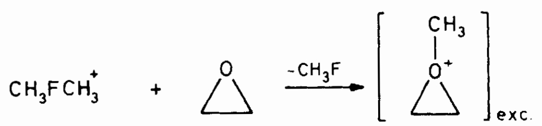
The ions, excited by the exothermicity of their formation



(1a)



(1b)



(1c)

processes,‡ may undergo extensive unimolecular isomerization before reacting with nucleophile which is present (H_2O, NH_3, *etc.*). Table 1 gives the absolute yields of the relevant products, expressed as $G_{(M)}$ values.

Isolation of substantial amounts of oxirane from reaction (1a) is consistent with an extensive isomerization of the excited species (**1**) to the tertiary oxonium ion (**3**) [reaction (2)]. Nucleophilic displacement on (**3**) by the nucleophiles present initially or formed in the irradiated mixture gives predominantly the neutral oxirane, accompanied by minor yields of 2-methoxyethanol [reactions (2a, b)].

2-Methoxyethanol is obtained in good yields from the methylation reaction (1c) as well, thus supporting the view that the cyclic oxide (**3**) is sufficiently long-lived to undergo *inter alia* ring substitution by H_2O [reaction (2b)]. An alternative mechanism would involve immediate ring-opening to the primary $^+CH_2CH_2OCH_3$ ion, which is able to isomerize to the secondary species $CH_3CH{=}\overset{+}{O}CH_3$ without activation energy,[1] before condensation with external nucleophiles. In this mechanism, no significant formation of $HOCH_2CH_2OCH_3$ would occur, contrary to experimental evidence.

Isomerization to structure (**3**) does not appear to be a route easily accessible to the excited intermediate (**2**) from reaction (1b), on account of the limited yields of the relevant products (see Table 1). Rather, almost exclusive formation of propionaldehyde from (**2**) is observed, which indicates that ring-opening isomerization is the most favoured process.

An isomerization pattern similar to reactions (2a—c) is accessible to excited *O*-protonated tetrahydrofuranium ions, when generated by $C_xH_5^+$ attack on tetrahydrofuran.

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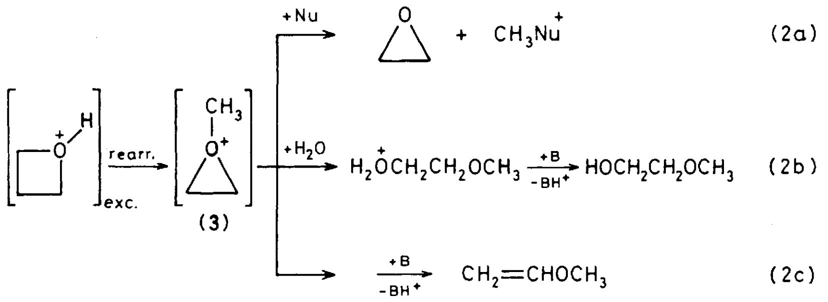
† Much evidence indicates that gas-phase electrophilic attack on ethers takes place predominantly, if not exclusively, on the oxygen atom (see *e.g.* ref. 6).

The experiments were carried out by irradiating gaseous mixtures containing CH_4 (or CH_3F) as the major component (760 Torr) and traces (2—3 Torr) of the cyclic ether, H_2O (2—3 Torr) as a nucleophile, a radical scavenger (O_2; 4 Torr), and a gaseous base (NH_3; 5 Torr), when required. The products were identified by g.l.c. by comparison of their retention volume with that of authentic samples, and their identity was confirmed by g.l.c.–mass spectrometry.

‡ $-\Delta H°$/kcal mol^{-1}; for reaction (1a), 75 (x = 1); 38 (x = 2); for (1b), 66 (x = 1); 29 (x = 2); for (1c) 30—40 (1 cal = 4.184 J).



Among other products, oxetane is formed ($G_{(M)} = 3 \times 10^{-3}$) together with higher yields of 3-methoxypropanol ($G_{(M)} = 3.2 \times 10^{-2}$), providing evidence that species (**4**) [as well as (**3**)] are legitimate intermediates on the corresponding $C_nH_{2n+1}O^+$ potential surface, with a lifetime estimated to be $>10^{-7}$ s on the basis of the experimental conditions used in the present study.

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References

1 R. D. Bowen, J. R. Kalman, and D. H. Williams, *J. Am. Chem. Soc.*, 1977, **99**, 5481.
2 K. Levsen, H. Heimbach, C. C. Van de Sande, and J. Monstrey, *Tetrahedron*, 1977, **33**, 1785.
3 J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *J. Am. Chem. Soc.*, 1973, **95**, 2184; R. D. Smith and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, 1977, **24**, 173; R. D. Smith, D. A. Herod, T. A. Elwood, and J. H. Futrell, *J. Am. Chem. Soc.*, 1977, **99**, 6042; M. Kumakura, K. Arakawa, and T. Sugiura, *Int. J. Mass Spectrom. Ion Phys.*, 1978, **26**, 303; J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, **100**, 3838.
4 J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, 1968, **90**, 1349.
5 For comprehensive reviews, see F. Cacace, in 'Kinetics of Ion-Molecule Reactions,' ed. P. Ausloos, Plenum, New York, 1979, p. 199; M. Speranza, *Gazz. Chim. Ital.*, 1983, **113**, 37.
6 R. D. Bowen and A. G. Harrison, *Org. Mass Spectrom.*, 1981, **16**, 159; *J. Chem. Soc., Perkin Trans. 2*, 1981, 1544.