

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

Giancarlo Angelini and Maurizio Speranza*

Istituto di Chimica Nucleare del C.N.R., C.P. 10, 00016 Monterotondo Stazione, Rome, Italy

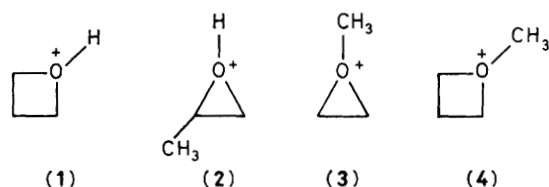
The nature and the isomeric distribution of the neutral products obtained from the gas-phase attack of CH_5^+ , $C_2H_5^+$, and $CH_3FCH_3^+$ ions on cyclic $C_nH_{2n}O$ ($n = 2, 3$, and 4) ethers provide the first experimental evidence in favour of 1-methyl-1-oxoniacyclopropane and 1-methyl-1-oxoniacyclobutane 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		$10^2 G_{(M)}$ values of products ^b		
Gaseous acid (760 Torr)	Substrate (2–3 Torr)	Oxirane	CH ₂ =CHOCH ₃	HOCH ₂ CH ₂ OCH ₃
C _x H ₅ ⁺ (CH ₄)	Oxetane	34.9	0.9	0.8
C _x H ₅ ⁺ (CH ₄)	2-Methyloxirane	1.8 ^c	0.6 ^c	1.0 ^c
CH ₃ FCH ₃ ⁺ (CH ₃ F)	Oxirane	—	n.d. ^d	14.3

^a O₂ (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 ($G_{(M)} < 1 \times 10^{-3}$).

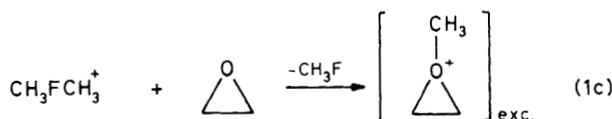
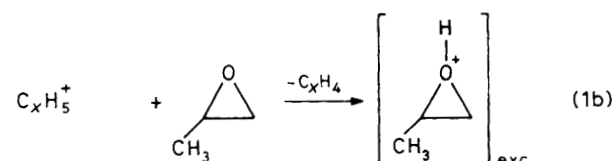
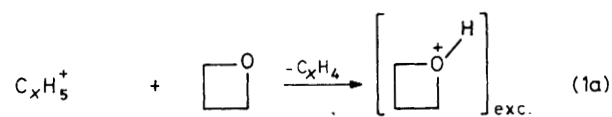


obtained from kinetic energy release experiments on suitably labelled precursors using conventional magnetic sector mass spectrometers.¹ Detailed potential energy profiles for C₃H₇O⁺ have been constructed on these grounds, which indicate that the cyclic species (1) and (2), as well as several open-chain isomers, correspond to local energy minima. Other conceivable cyclic structures, *e.g.* 1-methyl-1-oxoniacyclopropane (3), were never included on the C₃H₇O⁺ 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 phase³ 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_xH₅⁺ ($x = 1, 2$) and CH₃FCH₃⁺, generated respectively by γ -radiolysis of CH₄ and CH₃F (⁶⁰Co source; T 37.5 °C), on oxetane, 2-methyloxirane, and oxirane afforded primarily the isomeric C₃H₇O⁺ ions, shown in equations (1a–c).[†]

The ions, excited by the exothermicity of their formation



processes,[‡] may undergo extensive unimolecular isomerization before reacting with nucleophile which is present (H₂O, NH₃, *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 H₂O [reaction (2b)]. An alternative mechanism would involve immediate ring-opening to the primary ⁺CH₂CH₂OCH₃ ion, which is able to isomerize to the secondary species CH₃CH=OCH₃ without activation energy,¹ before condensation with external nucleophiles. In this mechanism, no significant formation of HOCH₂CH₂OCH₃ would occur, contrary to experimental evidence.

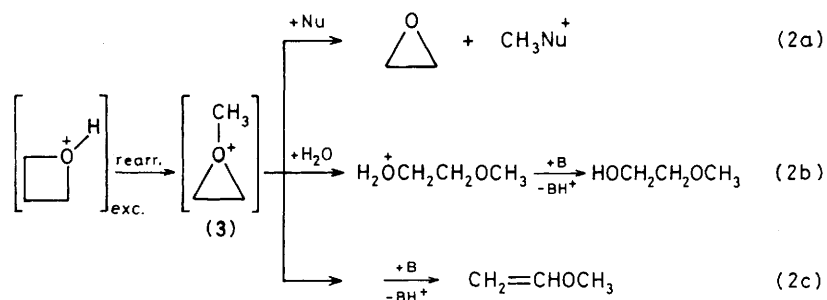
Isomerization to structure (3) does not appear to be a route easily accessible to the excited intermediate (2) from reaction (1b), on account of the limited yields of the relevant products (see Table 1). Rather, almost exclusive formation of propionaldehyde from (2) is observed, which indicates that 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_xH₅⁺ attack on tetrahydrofuran.

[†] 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 CH₄ (or CH₃F) as the major component (760 Torr) and traces (2–3 Torr) of the cyclic ether, H₂O (2–3 Torr) as a nucleophile, a radical scavenger (O₂; 4 Torr), and a gaseous base (NH₃; 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.

[‡] $-\Delta H^\circ/\text{kcal mol}^{-1}$; 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.

Received, 24th June 1983; Com. 845

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.