

## Experimental Proof of the Existence of a Fourth Stable Gas Phase $C_2H_4O^+$ Isomer: the Open Ethylene Oxide Ion

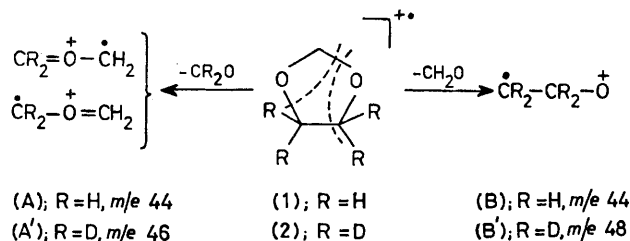
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**Summary** An ion cyclotron resonance study of the reactions of the  $C_2H_4O^+$  ion from ethylene oxide and 1,3-dioxolan and their deuteriated derivatives supports the existence of  $CH_2=O^+-CH_2$  as a stable gas phase entity in agreement with theoretical predictions.

THERE has been considerable recent interest in the study of the structures of stable isomeric gas phase cations.<sup>1</sup> In this context, the  $C_2H_4O^+$  isomers have been examined using metastable analysis,<sup>2</sup> thermochemical measurements,<sup>3</sup> collisional activation methods,<sup>4</sup> trapped ion techniques,<sup>5</sup> pulsed high pressure mass spectrometry,<sup>6</sup> and ion cyclotron resonance (i.c.r.) spectrometry.<sup>7</sup> Three distinct, non-interconvertible forms of the  $C_2H_4O^+$  ion have been proposed, corresponding to the molecular ions of acetaldehyde, ethylene oxide, and vinyl alcohol. Beauchamp<sup>7b</sup> has also postulated

the existence of an open form of the ethylene oxide ion (**A**) to account for the  $CH_2^+$  transfer reaction that occurs between ionised ethylene oxide and its neutral species. The structure (**A**) for the opened ethylene oxide ion has been challenged by Kumakura<sup>6a</sup> who, on the basis of rather outdated theoretical calculations,<sup>8</sup> has proposed that C-O bond opening of the ethylene oxide ion to give ion (**B**) would be



preferred over C-C bond cleavage. Our recent *ab initio* M.O. calculations<sup>9</sup> have indicated the unsymmetrical ion (**A**) to be stable and lower in energy than the ethylene oxide molecular ion itself while ion (**B**), if formed, would ring-close to the ethylene oxide ion.<sup>10</sup> This communication describes experimental results which fully support the existence of ion (**A**) as a stable  $C_2H_4O^+$  entity.

TABLE. Observed  $CH_2^+$  transfer reactions by  $C_2H_4O^+$  from ethylene oxide

Neutral substrate	Transfer observed	Product ion <i>m/e</i> (intensity <sup>a</sup> )
CH <sub>2</sub> O	CH <sub>2</sub> <sup>+,b</sup>	44(s)
CH <sub>3</sub> CHO	CH <sub>2</sub> <sup>+,b,c</sup>	58(m)
CH <sub>3</sub> COCH <sub>3</sub>	CH <sub>2</sub> <sup>+,b,c</sup>	72(m)
CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>2</sub> <sup>+</sup>	74(s)
CH <sub>2</sub> CH <sub>2</sub> O	CH <sub>2</sub> <sup>+,b</sup>	58(s)
	CH <sub>2</sub> <sup>+-H</sup>	57(m)
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O	CH <sub>2</sub> <sup>+,b,c</sup>	72(s)
	CH <sub>2</sub> <sup>+-H</sup>	71(m)
CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> O	CH <sub>2</sub> <sup>+,b</sup>	88(m)
	CH <sub>2</sub> <sup>+-H</sup>	87(s)
CH≡CCH <sub>2</sub> OH	CH <sub>2</sub> <sup>+-H<sup>b,c</sup></sup>	69(m)
CH≡CCH <sub>2</sub> Br	CH <sub>2</sub> <sup>+-Br<sup>c</sup></sup>	53(m)
CH≡CPh	CH <sub>2</sub> <sup>+</sup>	116(s)
	CH <sub>2</sub> <sup>+-H</sup>	115(m)
CH <sub>2</sub> =CHCH <sub>2</sub> Cl	CH <sub>2</sub> <sup>+-Cl</sup>	55(m)
CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> <sup>+-Br</sup>	55(m)
CH <sub>2</sub> =CHCH <sub>2</sub> Ph	CH <sub>2</sub> <sup>+-H</sup>	131(s)
CH <sub>3</sub> C≡N	CH <sub>2</sub> <sup>+,b,c</sup>	55(l)
CH <sub>2</sub> =CHC≡N	CH <sub>2</sub> <sup>+,b,c</sup>	67(l)
PhC≡N	CH <sub>2</sub> <sup>+</sup>	117(l)

<sup>a</sup> Intensity: s = small; m = medium; l = large. <sup>b</sup> Transfer confirmed by deuterium labelling. <sup>c</sup> Experiment also carried out with  $C_2H_4O^+$  from 1,3-dioxolan.

The Table lists a series of gas phase reactions of the  $C_2H_4O^+$  from ethylene oxide all of which involve in effect the transfer of  $CH_2^+$  from this ion to the various neutral substrates, occasionally accompanied by a subsequent hydrogen or halide radical loss. These ion-molecule processes were recorded using a Dynaspec i.c.r. spectrometer under stand-

ard drift operating conditions (20 eV, emission current 0.03  $\mu$ A, sample pressure *ca.*  $1 \times 10^{-5}$  mmHg) and confirmed by double resonance. Further confirmation of the transfer process has been obtained using [<sup>2</sup>H<sub>4</sub>]ethylene oxide and deuteriated neutral substrates. Detailed mechanisms for the reactions reported in the Table will be the subject of a forthcoming paper. It should be noted, however, that the cyano functional group (-C≡N) is the most efficient acceptor for the  $CH_2^+$  transfer from ionised ethylene oxide so far observed.

In order to substantiate that the  $CH_2^+$  transfer from ionised ethylene oxide was occurring *via* ion (**A**), we looked for an alternative source of this ion. 1,3-Dioxolan (**1**) fragments under electron impact to give a large ion at *m/e* 44 ( $C_2H_4O^+$ ) which could correspond to either ion (**A**) or (**B**). From his collisional activation studies, McLafferty<sup>4</sup> proposed that the  $C_2H_4O^+$  ion from (**1**) was a mixture of the closed ethylene oxide ion and the vinyl alcohol ion. However, measurements<sup>3</sup> of the heat of formation of this ion from (**1**) show it to be significantly lower in energy than ionised ethylene oxide but higher than the vinyl alcohol ion, in accord with our theoretical calculations<sup>9</sup> for ion (**A**).

The *m/e* 44 ion from (**1**) shows the same methylene transfer reactions as does ionised ethylene oxide (Table). In order to determine whether this transfer was occurring *via* ion (**A**) or (**B**), [4,4,5,5-<sup>2</sup>H<sub>4</sub>]-1,3-dioxolan (**2**) was prepared. The i.c.r. and mass spectra of (**2**) showed that the *m/e* 44 ion had moved exclusively to *m/e* 46 (**A'**), thus eliminating (**B**) as the reacting species. When (**2**) and acrylonitrile were examined together in the i.c.r. spectrometer, the *m/e* 46 ion (**A'**) from (**2**) transferred both  $CH_2^+$  and  $CD_2^+$  to the nitrile to give ions at *m/e* 67 and 69 in the ratio 0.7:1.0.

The foregoing results provide clear experimental evidence to support the theoretical prediction of the existence of ion (**A**) as a stable gas phase entity.

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<sup>1</sup> See, e.g., T. W. Bentley, 'Structure and Mechanism in Mass Spectrometry' in 'Mass Spectrometry,' ed. R. A. W. Johnstone, Specialist Periodical Report, The Chemical Society, London, 1977, Vol. 4, p. 36.

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<sup>10</sup> W. J. Bouma, J. K. MacLeod, and L. Radom, unpublished results.