Detection of Stable Cyclic $C_2H_5O^+$ and $C_2H_5S^+$ Ions by Collisional Activation Spectroscopy[1]

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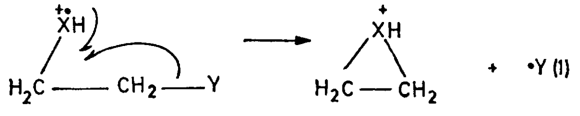
Summary Collisional activation spectra give direct evidence for the stability of cyclic $C_2H_5O^+$ and $C_2H_5S^+$ ions and their formation in a β-cleavage displacement from $Y{-}CH_2{-}CH_2{-}XH^{+\cdot}$

No direct evidence has been offered for the formation of the three-membered ring saturated ions (I) and (II) as decomposition products, although these products have been proposed for mass spectral reactions such as β-cleavage[2,3] (equation 1). Evidence for them has been sought by a variety of techniques,[4–7] which have identified the isomeric $C_2H_5O^+$ ions $CH_3CH{=}OH^+$ (III) and $CH_3{-}O{=}CH_2^+$ (IV); in several studies [4a,5,6] (I) could not be distinguished from (III), which is *ca.*26 kcal mol^{-1} more stable than (I).[4b] Beauchamp and his co-workers have reported[4b] that the long-lived $C_2H_5O^+$ ion formed by protonation of ethylene oxide can be distinguished from (III) and (IV) by reaction with PH_3 or H_2S in an ion-cyclotron resonance spectrometer. However, this reaction apparently has not been applied to the identification of (I) ions formed in dissociation reactions; its diagnostic usefulness for these is open to question because ion-molecule reactivities are affected by differences in ion energies.[8] This study employs collisional activation (CA) spectra,[1,6,9] which are not appreciably affected by ion internal energy.



(I) X = O

(II) X = S

CA spectra (Table) measured with improved instrumentation[10] clearly distinguish the $C_2H_5O^+$ ions produced by protonation of ethylene oxide, which presumably are (I),† from (III) as well as (IV). The CA spectrum of (I) is consistent with its structure; of the isomers, (I) gives the largest peak corresponding to the loss of CH_2, and the hydrogen

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† As there is no *a priori* knowledge of the CA spectrum of (I), the concurrent formation of some (III) cannot be ruled out.

TABLE. Partial CA spectra of $C_2H_5O^+$ ions

Precursor	Ion structure	Relative abundance							$\frac{[m/e\ 31]}{[m/e\ 30]}$
		m/e 24	25	26	28	30	31	32	
$CH_3OCH_2CH_2OCH_3$	(IV)	<1	<1	4	41	43	12	—	
$CH_3OCH_2CH_2CN$	(IV)	<1	2	4	39	43	12	—	
CH_3CHO^a	(III)	4	16	45	18	14	3	—	0·21 ± 0·04
$(CH_3)_2CHOH$	(III)	4	14	49	15	14	4	—	
$CH_3CH_2(CH_3)CHOH$	(III)	5	16	47	17	12	3	—	
$CH_3CHO^{b,c}$	$[^2H_1]$-(III)	4	15	45	—	—	17	3	
$(CH_3)_2CHOD^{c,d}$	$[^2H_1]$-(III)	5	15	45	—	—	16	4	
$\overline{CH_2CH_2O}^a$	(I)	4	15	42	13	11	16	—	1·7 ± 0·2
$\overline{CH_2CH_2O}^{b,c}$	$[^2H_1]$-(I)	4	15	40	—	—	9	16	
$CH_3CH_2CH_2CH_2OH$	(III)	5	16	48	17	11	3	—	0·24
$BrCH_2CH_2OH$	(I), (III)	4	16	43	16	14	6	—	0·39
$O_2NCH_2CH_2OH$	(I), (III)	5	16	42	19	13	5	—	0·31

[a] By protonation with H_2O at high pressure. [b] By deuteriation with D_2O at high pressure. [c] Based on an estimate that *m/e* 29 is *ca.* 15%. [d] From propan-2-ol by exchange with D_2O in the inlet system.

originally on oxygen is not lost in the formation of this *m/e* 31 (32 in the D-labelled analogue) peak. For the formation of (I) by displacement (equation 1), the CA spectra of the $C_2H_5O^+$ ions from n-butanol, 2-bromoethanol, and 2-nitroethanol (X = O, Y = Et, Br, or NO_2) indicate that appreciable amounts of (I) are formed with bromo or nitro, but not alkyl, as the leaving group.

For the $C_2H_5S^+$ ions, the isomers (II), $CH_3CH{=}SH^+$ (V), and $CH_3S{=}CH_2^+$ (VI) can also be characterized from their CA spectra (data not shown). The CA spectra of the $C_2H_5S^+$ ions from the n-alkyl-thiols show that a major portion of these ions have the cyclic structure (equation 1). This is consistent with the greater tendency for β-cleavage in $RCH_2CH_2SH^{+\cdot}$ than in $RCH_2CH_2OH^{+\cdot}$[2,3,7] and with the smaller bond angle for C–S–C than for C–O–C.

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[10] Experimental details are given in ref. 1 and P. P. Dymerski, R. M. Prinstein, P. F. Bente, III, and F. W. McLafferty, in preparation.