Two New Stable $[C_3H_8O]^{+\cdot}$ Isomers: the Radical Cations $[C_3H_6OH_2]^{+\cdot}$

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Two new $[C_3H_8O]^{+\cdot}$ ions have been assigned the structures $[\dot{C}H_2CH_2CH_2\overset{+}{O}H_2]$ and $[CH_3CHCH_2OH_2]^{+\cdot}$ and were characterised by their metastable ion and collisional activation mass spectra; their heats of formation were measured as 714 ± 5 and 721 ± 5 kJ mol^{-1}, respectively.

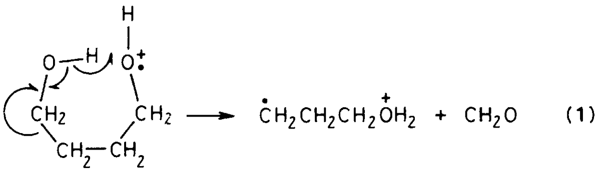
The structure-characteristic collisional activation (C.A.) mass spectra of $[CH_3CH_2CH_2OH]^{+\cdot}$, $[CH_3CH(OH)CH_3]^{+\cdot}$, and $[CH_3OCH_2CH_3]^{+\cdot}$ were described by Crow *et al.*[1] together with that of a fourth $[C_3H_8O]^{+\cdot}$ isomer for which they proposed the structure $[CH_3\overset{+}{O}(H)CH_2CH_2^{\cdot}]$. A large number of ions of this latter type, formally considered as radical-ion dipole complexes, have been shown by experiment[2] and by *ab initio* molecular orbital calculations,[3] to be stable gas phase species.

Only $[CH_3CH_2CH_2OH]^{+\cdot}$ displays an abundant loss of H_2O in its C.A. and metastable ion (M.I.) mass spectra.[1] In the

Table 1. Partial collisional activation mass spectra[a] of $[C_3H_8O]^{+\cdot}$ ions.

Precursor molecule	Relative abundance m/z 59	42	41	40	39	31	29	28	27	19
$CH_3CH_2CH_2OH$	94[b]	100[b]	7.5	1.5	7.5	83	16	5.4	14	0.1
$HOCH_2CH_2CH_2CH_2OH$	0.05	100[b]	7.8	1.6	9.5	2.2	0.8	0.8	2.5	0.3
$HOCH_2CH(CH_3)CH_2OH$	—	100[b]	14	3.5	15	0.7	0.5	0.7	4.3	1.2

[a] C.A. mass spectra measured using a VG ZAB-2F mass spectrometer, as described elsewhere (ref. 18). [b] Peaks having unimolecular contributions.

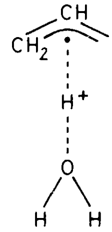


latter m/z 59 [H$^\cdot$ loss] and m/z 42 are of comparable abundance and are the only significant signals. We report here the characterisation of two more $[C_3H_8O]^{+\cdot}$ isomers which predominantly lose H_2O but which do not have the [propan-1-ol]$^{+\cdot}$ structure.

The unimolecular loss of H_2O from $[CH_3CH_2CH_2OH]^{+\cdot}$ generates an intense, simple Gaussian-type,[4] metastable peak; the kinetic energy release, $T_{0.5}$, evaluated from the peak width at half height, is 17 meV. Derrick *et al.*[5] reported that metastable $[CH_3CD_2CH_2OH]^{+\cdot}$ ions lost H_2O and HDO in a 7:1 ratio and concluded that 4- and 5-membered cyclic transition states were involved. We have found, however, that $[CH_3CH_2CD_2OH]^{+\cdot}$ ions lose solely H_2O, that $[CD_3CH_2CH_2OH]^{+\cdot}$ loses HDO together with only a trace (<2%) of H_2O, and that $[CH_3CH_2CH_2OD]^{+\cdot}$ loses only HDO. The appearance energy (A.E.) of m/z 42 from the unlabelled compound (measured using energy selected electrons[6]) was 10.56 ± 0.05 eV, which corresponds to the formation of ionised cyclopropane at its calculated threshold, 10.50 eV $\{\Delta H_f^\circ(CH_3CH_2CH_2OH) = -254.8,$[7] $\Delta H_f^\circ\,(H_2O) = -241.8,$[8] ΔH_f° $[\text{cyclo-}C_3H_6]^{+\cdot} \leqslant 999\,\text{kJ mol}^{-1}$[8]$\}$. Both the ion-source and metastably generated $[C_3H_6]^{+\cdot}$ ions have this structure as was shown by their characteristic charge-stripping mass spectra.[9]

In summary, ionised propan-1-ol generates [cyclopropane]$^{+\cdot}$ by loss of H_2O at the thermochemical threshold; the reaction is a specific 1,3-elimination process.

The $[C_3H_8O]^{+\cdot}$ ions produced by loss[10] of CH_2O from ionised butane-1,4-diol also displayed an intense metastable peak for H_2O loss[10] with the same shape as that for [propan-1-ol]$^{+\cdot}$, but, in marked contrast, only a weak signal for loss of H$^\cdot$ (7%). The $[C_3H_6D_2O]^{+\cdot}$ ion generated from $[O,O\text{-}^2H_2]$butane-1,4-diol lost *only* D_2O. The ΔH_f° for the $[C_3H_8O]^{+\cdot}$ daughter ion was measured to be 714 ± 5 kJ mol^{-1} from its A.E. = 10.70 ± 0.05 eV and ΔH_f° $[HOCH_2CH_2CH_2CH_2OH] = -426.7,$[7] ΔH_f° $[CH_2O] = -108.7,$[7] slightly below ΔH_f° for ionised [propan-1-ol], 731 kJ mol^{-1}.[8] The C.A. mass spectrum of the new ion is markedly different from that of $[CH_3CH_2CH_2OH]^{+\cdot}$, (see Table 1) having no major peaks at m/z 59 or m/z 31; indeed the C.A. mass spectrum is dominated by the group of ions m/z 42 → 37. The A.E. of the m/z 60 → m/z 42 metastable peak (= 11.1 ± 0.1 eV) was measured by a comparative method;[11] this value leads to ΔH_f° $[C_3H_6]^{+\cdot} = 995 \pm 10\,\text{kJ mol}^{-1}$, showing that [cyclopropane]$^{+\cdot}$ is the daughter ion. Thus the new ion has but one common feature with $[CH_3CH_2CH_2OH]^{+\cdot}$, the H_2O loss reaction. We propose, by analogy with the $[C_2H_6O]^{+\cdot}$ system,[12] that the structure of the ion can well be represented as $[\dot{C}H_2CH_2CH_2\overset{+}{O}H_2]$ and its formation by equation (1).[10] We further propose, because their metastable peaks are identical, that this $[C_3H_8O]^{+\cdot}$ structure is the reacting configuration for the H_2O loss from $[CH_3CH_2CH_2OH]^{+\cdot}$.



(A)

The $[C_3H_8O]^{+\cdot}$ ion generated by loss of CH_2O from ionised 2-methylpropane-1,3-diol undergoes a single metastable fragmentation, H_2O loss, and the kinetic energy released ($T_{0.5}$ = 0.6 meV) is unlike that of all other $[C_3H_8O]^{+\cdot}$ ions. The $[C_3H_6]^{+\cdot}$ daughter ions, generated metastably or in the ion source, were found from their charge stripping mass spectra, to have the $[CH_3CH{=}CH_2]^{+\cdot}$ structure. ΔH_f° for this new $[C_3H_8O]^{+\cdot}$ ion was estimated to be 721 ± 5 kJ mol^{-1} from A.E. m/z 60 = 10.86 ± 0.05 eV (energy selected electrons), ΔH_f° $[HOCH_2CH(CH_3)CH_2OH] = -436\,\text{kJ mol}^{-1}$.[13] The C.A. mass spectrum of the ion is given in Table 1. A possible structure for the ion is a water molecule σ-bonded to ionised propene *i.e.* $CH_3CH(\overset{+}{O}H_2)CH_2\dot{C}H_2$ or $CH_3\dot{C}HCH_2\overset{+}{O}H_2$, but a third possibility deserves consideration. The labelled precursor molecules $[O,O\text{-}^2H_2]$-2-methylpropane-1,3-diol and the $[1,1,3,3\text{-}^2H_4]$ analogue lose essentially only CH_2O and CD_2O respectively and thus H and D atoms have not lost their positional identity in the molecular ion prior to fragmentation. However, these two $[C_3H_6D_2O]^{+\cdot}$ ions lose H_2O and HDO *identically* (M.I. ratio 7:1, D_2O loss < 0.01); this may be interpreted as resulting from complete H,D mixing prior to fragmentation but with isotope effects governing the product distributions. (Compare the *specific* behaviours of labelled $[CH_3CH_2CH_2OH]^{+\cdot}$ and $[CH_2CH_2CH_2OH_2]^{+\cdot}$.) Furthermore, the C.A. mass spectrum of the unlabelled m/z 60 ion (see Table 1) contains relatively intense peaks at m/z 41 ($C_3H_5^+$), 27 ($C_2H_3^+$), and 19 (H_3O^+). We propose a third possible structure (A) to be a proton bound water molecule and allyl radical. Odd electron ions of this kind have been proposed elsewhere:[14] stable even electron ions, where the proton binds heteroatom sites in two small molecules have been reported.[15—17]

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