Alkane Elimination From Ionized Alkanols

John L. Holmes,[†] Peter C. Burgers and Yousuf A. Mollah

Chemistry Department, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada

The energetics, metastable characteristics and daughter ion structures for the loss of small alkane molecules from ionized 2-propanol, 2-butanol and 3-pentanol have been examined in detail. [2-Propanol]⁺⁺ ions lose CH₄ to generate the keto and enol forms of $[C_2H_4O]^{++}$ and the same daughter ions are produced by loss of C_2H_6 from [2-butanol]⁺⁺. Ionized 3-pentanol does not lose CH₄ but readily eliminates C_2H_6 to produce the enol ion $[CH_3CH=CHOH]^{++}$. The last reaction was shown to proceed by a simple 1,2 elimination mechanism in the µs time-frame; isotope effects are also discussed.

INTRODUCTION

Aliphatic alcohols are often difficult to identify from their normal mass spectra because of the weakness or absence of a molecular ion, this being particularly so for secondary and tertiary alkanols.¹ The reason for the low abundance of molecular ions is that there exist several fragmentation reactions having energy requirements close to or less than the ionisation energy (IE). For example, [2-propanol]⁺⁻ loses CH₄, appearance energy $(AE) = 10.27 \text{ eV}^2$ and CH_3 , AE = 10.26 eV, both reactions requiring little energy in excess of the IE for the molecule, 10.15 eV. *n*-Butanol, IE = $10.07 \,\mathrm{eV}^2$ eliminates H₂O with little extra energy requirement, $AE = 10.20^4 \text{ eV}$. Similarly, 2-butanol, IE = 9.88 eV,⁵ AE CH₃ loss = 10.18 eV³ and AE C_2H_5 loss = 10.22 eV.³ Thus, reactions which can formally be represented as simple bond cleavages or molecular eliminations are competing in these systems. Daughter ion structures from radical loss fragmentations are those predictable from the simple bond cleavage and these reactions proceed at or close to their calculated thermochemical threshold.³ The molecular elimination of methane from ionized 2propanol must generate [CH2=CHOH]+, calculated $AE = 9.90 \text{ eV}^6$ (calc. for $[CH_3CHO]^+ = 10.55 \text{ eV});^2$ observations on the metastable peak shapes for H' loss from $[C_2H_4O]^{+-}$ ions derived from 2-propanol have shown that both of the above $[C_2H_4O]^+$ ions are generated by molecular elimination of methane.⁷ The structure of the $[C_4H_8]^{+}$ daughter ion from *n*-butanol has not been determined. Note that at the AE (10.20 eV) the fragmenting ion is hot with respect to either [but-2-ene]⁺ or [but-1-ene]⁺, calculated AE 9.37 eV and 9.93 eV respectively.²

In this short paper we report observations on the eliminations of methane and ethane from 2-butanol and 3-pentanol with emphasis on reaction energetics, daughter ion structures and reaction mechanisms.

RESULTS AND DISCUSSION

As a preliminary experiment the AE for CH_4 loss from 2-propanol was remeasured, using energy

† Author to whom correspondence should be addressed.

selected electrons; the observed value, 10.26 eV, was in excellent agreement with the earlier photoionization result,² 10.27 eV.

2-Butanol

No fewer than four fragmentation reactions have their AE within 0.5 eV of the ionization energy of the molecule (9.88 eV). The CH₃' and C₂H₅' losses had AE 10.24 and 10.18 eV respectively, in satisfactory agreement with earlier measurements.³ Loss of CH₄ had AE = 10.22 eV and loss of C₂H₆ AE = 10.12 eV. For the former molecular elimination, both the keto and enol tautomers of propanal are possible structures on energetic grounds.

$$\begin{aligned} AE_{calc}[CH_{3}CH_{2}CHO]^{+} &= 10.24 \text{ eV}(\Delta H_{f}[CH_{3}CH_{2}CHO]^{+} \\ &= 770 \text{ kJ mol}^{-1}, \ ^{8} \quad \Delta H_{f}(CH_{4}) = -75 \text{ kJ mol}^{-1}, \ ^{2} \\ \Delta H_{f}(CH_{3}CH_{2}CH(OH)CH_{3}) = -293 \text{ kJ mol}^{-1} \ ^{9}), \\ AE_{calc}[CH_{3}CH = CHOH]^{+} = 9.15 \text{ eV} \\ (\Delta H_{f}[CH_{3}CH = CHOH]^{+} = 665 \text{ kJ mol}^{-1} \ ^{8}). \end{aligned}$$

Loss of CH_4 from this molecule only generates a very weak peak (0.8% of base peak, m/z 45) in the normal mass spectrum, however, and the question of the daughter ion structure was not pursued further. For the ethane loss

$$AE_{calc}[CH_2=CHOH]^{+}$$

= 10.01 eV ($\Delta H_f[CH_2=CHOH]^{+}$
= 757 kJ mol⁻¹, ⁹ $\Delta H_f(C_2H_6) = -85$ kJ mol⁻¹²);

ionized acetaldehyde cannot be produced at the observed AE. $(AE_{calc}[CH_3CHO]^{+-} = 10.66 \text{ eV}, \Delta H_f[CH_3CHO]^{+-} = 820 \text{ kJ mol}^{-1}^2)$. In the normal mass spectrum m/z 44 is moderately intense (~8%) and so the structure of these daughter ions was investigated. As shown elsewhere,⁷ the shape of the metastable peak for H⁻ loss from isomeric $[C_2H_4O]^{+-}$ ions is structure dependent. For $[C_2H_4O]^{+-}$ ions derived from 2-butanol, the metastable peak for H⁻ loss was composite and similar in appearance to that observed for $[C_2H_4O]^{+-}$ ions generated from 2-propanol.⁷ As was found for the latter compound, exchanging the hydroxylic hydrogen with D₂O led to a separation of the broad and narrow components; $[M-CH_4]^{+-}$ ions only

CCC-0030-493X/82/0017-0127\$02.00

lost D' and showed the characteristic broad metastable peak for ionized vinyl alcohol. [M-CH₃D]⁺⁻ ions showed the narrow metastable peak characteristic of ionized acetaldehyde. That the two $[C_2H_4O]^+$ ions were produced from $[CH_3CH_2CH(OH)CH_3]^+$ by competing unimolecular eliminations of ethane was shown by the following experiment. The shape of the composite metastable peak for H loss (from $[C_2H_4O]^{+-}$ produced from $[CH_3CH_2CH(OH)CH_3]^{+-}$ was observed as a function of ionizing electron energy. As the electron energy was reduced it was observed that the relative abundance of the narrow component increased and so the broad component (H' loss from $[CH_2=CHOH]^+$ has the higher AE. Now the latter ions are generated at the observed threshold for such $[C_2H_4O]^+$ ions, and cannot have been produced from $[2-butanol]^{+}$ by successive losses of C_2H_5 and H (or vice versa). If [CH₃CHO]⁺⁻ ions were generated by such successive fragmentations then the narrow component of the composite metastable peak should have the higher AE. This was not observed and so it is concluded that [CH₃CHO]⁺⁻ is produced by a competing molecular elimination of ethane. (Note that the calculated AE for the generation of CH₃CO via the products $[CH_3CHO]^{++} + H_2 + C_2H_4$ or $[CH_3CHO]^{++} + H^+ + C_2H_5$ lie above the AE for H⁺ atom loss from $[CH_2CHOH]^+$. This has recently been measured¹⁰ and gives an apparent $\Delta H_f[C_2H_3O]^+ \leq 774 \text{ kJ mol}^{-1}$.)

The observation that in the metastable time-frame C_2H_5D loss from $[CH_3CH_2CH(OD)CH_3]^{+\cdot}$ was much less than C_2H_6 loss (ratio 5:95), is certainly in keeping with the elimination producing $[CH_3CHO]^{+\cdot}$ having the higher AE (calculated AE difference $= \Delta H_f[CH_3CHO]^{+\cdot} - \Delta H_f[CH_2CHOH]^{+\cdot} = 0.65 \text{ eV}^9$). Note that both these elimination reactions have thresholds above the IE of 2-butanol.

3-Pentanol

The lowest energy fragmentation of ionized 3pentanol is the loss of C_2H_6 , AE = 9.84 eV, just above the IE = 9.78 eV. The reaction generates a weak Gaussian-type metastable peak $(n = 1.6, {}^{11} \langle T \rangle =$ 60 meV). The $[C_3H_6O]^{+}$ daughter ions were observed to lose essentially only a hydrogen atom in the metastable time-frame $(T_{0.5} = 170 \text{ meV})$. This metastable peak is not a Gaussian type, having very steep sides and a rounded top, n > 2.2.¹¹ The energy diagram for these reactions is shown as Fig. 1 and the data are given in the legend. Note that loss of CH₄ does not compete with C₂H₆ elimination even though the former reaction has a lower calculated thermochemical threshold (calc. AE for $[CH_3C(OH)=CHCH_3]^{+-}=$ 8.51 eV,⁸ for $[CH_2=C(OH)CH_2CH_3]^{+-}$ AE = 8.99 eV,⁸ ΔH_f (3-pentanol) = -314 kJ mol⁻¹ ⁹). Daughter ions at m/z 72 in the normal mass spectrum have an abundance <0.05% of base peak and there is no detectable metastable peak for $m/z \ 88 \rightarrow m/z \ 72$. Therefore, we conclude that this elimination must have a large critical energy.

From Fig. 1 it can be seen that in principle three daughter ions can be produced at the threshold for C_2H_6 loss, namely $[CH_3COCH_3]^{++}$,



Figure 1. Energy diagram relating to C_2H_6 loss from ionized 3-pentanol. ΔH_f neutral compounds from Ref. 9. ΔH_f [3-pentanol]⁺⁻= 628 kJ mol⁻¹ from IE=9,78 eV (this work). ΔH_f [CH₃CH=CHOH]⁺⁻= 665 kJ mol⁻¹;⁸ ΔH_f [CH₃C(CH)=CH₂]⁺⁻= 661 kJ mol⁻¹;⁸ ΔH_f [CH₃COCH₃]⁺⁻= 719 kJ mol⁻¹;² ΔH_f [CH₃CH₂CHO]⁺⁻= 770 kJ mol⁻¹;² ΔH_f [CH₂=CHCH₂OH]⁺⁻= 812 kJ mol⁻¹ from IE=9.70 eV (this work) and ΔH_f [cyclopropanol]⁺⁻= 787 kJ mol⁻¹ from IE=9.34 eV (this work), ΔH_f (cyclopropanol)=-114 kJ mol⁻¹, by additivity.¹²

 $[CH_3C(OH)=CH_2]^{+\cdot}$ and $[CH_3CH=CHOH]^{+\cdot}$. The $[C_3H_6O]^{+\cdot}$ daughter ion from ionized 3-pentanol shows only an intense metastable peak corresponding to loss of H^{\chi}. Now $[CH_3COCH_3]^{+\cdot}$ and its enol fragment largely (in the metastable time-frame) by losses of CH₃^{\chi}, CH₄ and CH₃^{\chi} respectively,¹³ with no metastable peak for loss of H^{\chi}, and so these two structures can be ruled out. Thus, ionized 3-pentanol must generate $[CH_3CH=CHOH]^{+\cdot}$ via the elimination of C_2H_6 .

At higher internal energies, e.g. ion source reactions, other daughter ion structures can be considered. [Propene oxide]⁺ and [methylvinylether]⁺ can be discarded as possible $[C_3H_6O]^+$ daughter ions because in addition to a metastable peak for loss of H', these ions show pronounced losses of CH3' and 28 u in the metastable time-frame. Ionized trimethylene oxide is also an improbable candidate; although H' atom loss provides its only significant metastable peak the kinetic energy release $T_{0.5} = 225$ meV, is significantly higher than that observed for the ions derived from 3-pentanol. The most likely structures for the $[C_3H_6O]^+$ daughter ion, $[CH_3CH_2CHO]^+$ (a) and its enol (b) cannot be differentiated by means of their metastable characteristics which are dominated by a common intense peak for H atom loss, $T_{0.5}$ values = 175 and 170 meV respectively. Accordingly, the collisional activation (CA) mass spectra of these $[C_3H_6O]^+$ structures were measured and the results are shown in Table 1. The $[C_3H_6O]^+$ daughter ions from 3pentanol have a CA mass spectrum very closely similar to that for the enol of ionized propanal and which

Table 1. Collisional activation mass spectra of [C₃H₆O]⁺⁻ ions

							m	/z of d	laught	ter ior	a,b									lon
[Compound]+-	57	56	55	53	43	42	41	40	39	38	37	31	30	29	28	27	26	25	15	structure
[CH ₃ CH ₂ CHO] ⁺⁻	(370)	4	8	2	2	8	4	2	13	6	4	7	19	100	41	48	22	4	3	а
[CH ₃ CH==CHOH] ^{++c}	(470)	9	35	6	8	10	8	10	44	16	11	44	22	100	25	43	23	4	3	b(c, d)
$[CH_{3}CH_{2}CH(OH)CH_{2}CH_{3}-C_{2}H_{6}]^{+}$	(450)	9	34	6	8	11	8	10	45	17	13	42	22	100	25	45	26	6	4	ь
⊳OH _{1+-q}	(1000)	15	29	5	9	12	6	13	44	15	11	44	(38)	100	27	50	25	6	4	b(c, d)

* Abundances relative to the base peak = 100%, ionizing energy 70 eV.

^b Values at m/z 57 have not been corrected for unimolecular contributions.

^c Generated from CH₃CH₂CH₂CH(CH₃)CHO.

^d Values at m/z 27 to 31 and 55 and 56 have been corrected for $[^{13}CC_2H_5O]^+$ contributions. Base peak in the CA mass spectrum of m/z 57 is m/z 29. This most likely corresponds to the loss of CO, calculated threshold $\Delta H_f(C_0) + \Delta H_f[C_2H_5]^+ = 802$ kJ mol⁻¹;² loss of C₂H₄, calculated threshold $\Delta H_f(C_2H_4) + \Delta H_f[HCO]^+ = 868$ kJ mol⁻¹.² Value at m/z 30 contains contribution from unimolecular decomposition.

is characteristically different from that of the ions a (see Table 1). This result is in marked contrast to the behaviour of the homologue, 2-butanol, which produced both keto and enol tautomers of $[C_2H_4O]^{+}$. It should be noted that the CA spectra of both ionized allyl alcohol $(c)^{14}$ and cyclopropanol (d) (see Table 1) are closely similar to that of b.

The simplest mechanism for $[CH_3CH=CHOH]^+$ production from $[3-pentanol]^+$ is via a 1,2elimination.



All the observations on D-labelled compounds (presented in Table 2) lend support to this mechanistic proposal. Thus 1 and 2 lose only C_2H_6 , 4 loses only C_2H_6 and $C_2H_3D_3$ and 3 mostly $C_2H_3D_3$. However, the situation is more complex for reactions of ions having internal energies greater than those corresponding to metastable fragmentations. In addition to the $[M-C_2H_3D_3]^+$ peak at m/z 59 the mass spectrum of **3** clearly also contains a peak of similar intensity at m/z 60, corresponding to the loss of C₂H₄D₂. This daughter ion displays a very intense metastable peak for the loss of H' (and D') and is unlikely to have originated via successive losses of C2H5 and H. (Note that the degree of labelling 90%, precludes their having arisen from incompletely labelled material.) Therefore we argue that this ion is the result of a molecular elimination of $C_2H_4D_2$. A metastable peak for this process is observable, but its intensity is too small to allow accurate measurement of the kinetic energy released. Because the mass spectrum of the labelled ion [CH₃CH₂CD(OH)CH₂CH₃]⁺ contains only an extremely weak peak corresponding to the loss of C₂H₅D, we conclude that we are observing specific processes, rather than randomization of the label.

It proved difficult to show how this additional process comes about because the daughter ion structures cannot be determined unequivocally (see Table 1).

In summary then, loss of C_2H_6 from ionized 3pentanol in the metastable time-frame involves a simple 1,2 elimination producing [CH₃CH=CHOH]⁺⁻. At higher internal energies other, more complex eliminations come into play.

Isotope effects

Several isotope effects may be considered (Table 2). For the asymmetrically labelled ion (5) loss of C_2H_5D is preferred over $C_2H_4D_2$, i.e. $k(H \rightarrow -CD_2CH_3)$ is smaller by a factor of ~4 than $k(D \rightarrow -CH_2CH_3)$. Similar intra-ionic isotope effects have been reported for CH_4 loss from methylpropane^{15,16} and methyl-butane;¹⁷ in these compounds the isotope effect is large in methane eliminations when H migrates to a D containing methyl group, but small or absent when a D atom is transferred to CH₃. Surprisingly, an isotope effect of similar magnitude is operating against loss of $C_2H_3D_3$ (vs C_2H_6) from 4, showing that transfer of H to a D-containing ethyl group is slower than transfer to a C_2H_5 group. We have also compared noncompetitive isotope effects by examining the relative metastable peak abundances for loss of C₂H₃D₃ from 3 and C_2H_6 from unlabelled 3-pentanol in a 1:1 mixture of the precursor molecules. Loss of C₂H₃D₃ generates the more intense metastable peak by a factor of ~ 1.7 , showing that this reaction may have the less steeply rising $\ln k$ vs E^{\neq} curve. Note that the difference in excess internal energies (E^{\neq}) corresponding to the metastable time-frames is dominated by the energy barrier for the reverse reaction (see Fig. 1) and this is the probable reason for the kinetic energy releases being the same, within experimental error $(\langle T \rangle = 60 \pm 3 \text{ meV}).$

The H and D atom losses from the labelled $[C_3H_6O]^+$ daughter ions were also examined and the

Table 2. Relative abundances (all values ± 2) of metastable peaks for the losses of ethane from labelled 3-pentanol ions

		Species lost							
Compound		C ₂ H ₆	C₂H₅D	$C_2H_4D_2$	$C_2H_3D_3$				
CH ₃ CH ₂ CH(OD)CH ₂ CH ₃	(1)	100	_	*	*				
CH ₃ CH ₂ CD(OH)CH ₂ CH ₃	(2)	100		*	*				
CH ₃ CD ₂ CH(OH)CD ₂ CH ₃ *	(3)		_	5	95				
CD ₃ CH ₂ CH(OH)CH ₂ CH ₃	(4)	74	trace		26				
CH ₃ CD ₂ CH(OH)CH ₂ CH ₃	(5)	6	76	18	*				

* No loss of C2H2D4.

Table 3.	Relative	abundances	(peal	k areas	, all	values	±1)
	of meta	stable peaks	a for	losses	of H	T' and	D.
	from	labelled	[CH ₃	СН=С	HOH	[] ^{+.}	and
	[CH2==0	HCH2OH]+	ions				

Precursor molecule	lon	H,	D.
CH ₂ CH ₂ CH(OD)CH ₂ CH ₃	[CH ₃ CH=CHOD] ⁺⁻	96	4
CH ₄ CH ₂ CD(OH)CH ₂ CH ₃	[CH ₃ CH=CDOH] ⁺⁺	92	8
CH ₃ CD ₂ CH(OH)CD ₂ CH ₃	[CH ₃ CD=CHOH]+·	91	9
CD ₃ CH ₂ CH(OH)CH ₂ CH ₃	[CD ₃ CH=CHOH] ⁺⁺	69	31
CH ₃ CD ₂ CD(OH)CD ₂ CH ₃	[CH ₃ CD=CDOH]+·	81	19
5	[CH2=CH-CD2OH]+-	82	18
	[CH ₂ =CH-CH ₂ OD] ⁺⁺	96	4

* T_{0.5} values: -H': (175±5) meV; -D': (210±5) meV.

results are shown in Table 3. It is clear that all hydrogen atoms are involved; analysis of the observations leads to O-H: α -H: β -H: γ -H = 1:2:2:6 assuming a common isotope effect $k_{\rm H}: k_{\rm D} = 2.7:1$. The Cbonded H atoms are thus lost with equal facility compatible with the complete loss of their positional identity prior to fragmentation. Participation of keto ions [CH₃CH₂CHO]⁺⁻, except as a possible reacting configuration, can be ruled out because they only lose the carbonyl bonded H-atom.

The very close similarity of the CA mass spectra of $[CH_2=CHCH_2OH]^+$, $[CH_3CH=CHOH]^+$ and $[cyclopropanol]^+$ may indicate that these structures can equilibrate prior to fragmentation. If this is so, then these CA mass spectra may represent to a large extent *a* type ions, because these have the lowest heat of formation. Note that the observed metastable losses of H' and D' from $[CH_2=CHCD_2OH]^+$ can be reproduced using the above ratios and isotope effect for the 3-pentanol daughter ions.

1. J. H. Beynon, R. A. Saunders and A. E. Williams, *The Mass Spectra of Organic Molecules*, p. 133 *et seq.* Elsevier, Amsterdam (1968).

- H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data Suppl. 1, 6 (1977).
- 3. F. P. Lossing, J. Am. Chem. Soc. 99, 7526 (1977).
- 4. F. P. Lossing, private communication.
- J. L. Holmes, M. Fingas and F. P. Lossing, Can. J. Chem. 59, 80 (1981).
- J. L. Holmes, J. K. Terlouw and F. P. Lossing, J. Phys. Chem. 80, 2860 (1976).
- J. L. Holmes and J. K. Terlouw, Can. J. Chem. 53, 2076 (1975).
- J. L. Holmes and F. P. Lossing, J. Am. Chem. Soc. 102, 1591 (1980).
- J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York (1970).
- 10. J. L. Holmes and P. C. Burgers, in preparation.
- 11. J. L. Holmes and J. K. Terlouw, Org. Mass Spectrom. 15, 383 (1980).
- S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.* 69, 279 (1969).

EXPERIMENTAL

IE and AE measurements were made using monoenergetic electrons and an apparatus described elsewhere.^{18,19} Metastable peak shapes were measured with a Kratos-AEI MS 902S mass spectrometer under conditions of good energy resolution, at selected electric sector voltages such that all the peaks were transmitted at the same acceleration voltage. To obtain accurate measurements of the relative metastable peak abundances, low energy resolution conditions were used and peak heights were recorded. Kinetic energy release values were calculated in the usual way with correction for the main beam width¹¹ (3 V at halfheight, acceleration voltage 7100 A).

CA mass spectra were recorded on a VG Micromass ZAB-2F mass spectrometer.²⁰ The 3- d_1 (95%) and 2,2,4,4- d_4 (90% d_4) labelled 3-pentanols were available from another investigation.¹⁷ 3-Pentanol-1,1,1- d_3 (90% d_3) was prepared by reduction of acetic acid-1,1,1- d_3 with LiAlH₄, followed by bromination to yield ethylbromide-2,2,2- d_3 . A Grignard reaction with propanal afforded the desired product. 3-Pentanol-2,2- d_2 (95%- d_2) was prepared similarly using CH₃COOH and LiAlD₄.

Acknowledgements

The authors wish to thank Dr F. P. Lossing for IE and AE measurements, Dr J. K. Terlouw (University of Utrecht) for the CA mass spectra and a gift of cyclopropanol, and Dr J. Krause for invaluable experimental assistance. J.H. acknowledges continuing support from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- F. W. McLafferty, D. J. McAdoo, J. S. Smith and R. Kornfeld, J. Am. Chem. Soc. **93**, 3720 (1971).
- C. C. Van de Sande and F. W. McLafferty, J. Am. Chem. Soc. 97, 4617 (1975).
- P. Wolkoff and J. L. Holmes, J. Am. Chem. Soc. 100, 7346 (1978).
- P. T. Mead, K. F. Donchi, J. C. Traeger, J. R. Christie and P. J. Derrick, J. Am. Chem. Soc. 102, 3364 (1980).
- 17. J. L. Holmes, P. C. Burgers, Y. Mollah and P. Wolkoff, J. Am. Chem. Soc. submitted for publication.
- K. Maeda, G. P. Semeluk and F. P. Lossing, Int. J. Mass Spectrom. Ion Phys. 1, 395 (1968).
- F. P. Lossing and J. C. Traeger, Int. J. Mass Spectrom. Ion Phys. 19, 9 (1976).
- 20. J. K. Terlouw, P. C. Burgers and H. Hommes, Org. Mass Spectrom. 14, 387 (1979).

Received 29 May 1981; accepted 26 October 1981 © Heyden & Son Ltd, 1982