Gas-phase, Pinacol-type Rearrangements in the Unimolecular Decomposition of Some Isomers of $C_4H_9O^+$

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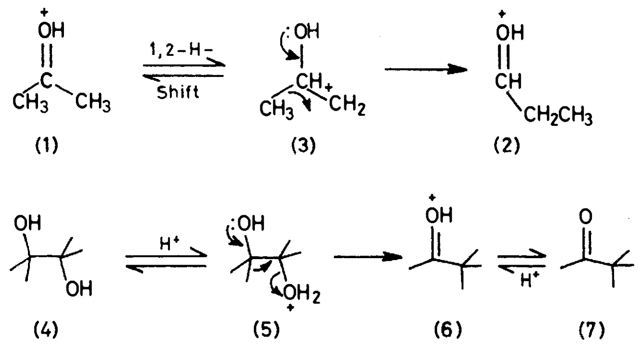
The slow unimolecular reactions undergone by three isomers of $C_4H_9O^+$ are explained in terms of a simple ' mechanistic ' approach. For two such isomers, protonated butanone and protonated isobutyraldehyde equilibration *via* a pinacol-type rearrangement precedes dissociation. The third isomer, protonated butyraldehyde, reacts differently because the energy needed to cause isomerisation of this to the other ions is greater than that needed to dissociate any of the three isomers considered. Extension of the analysis, using the potential surface approach, explains the non-occurrence of some mechanistically plausible reactions (*e.g.* C_3H_6 loss) and results of deuterium labelling studies.

In previous work,[1] we have shown that protonated acetone (1) undergoes a rate-determining isomerisation to protonated propionaldehyde (2) prior to unimolecular dissociations. A plausible mechanism for this rearrangement is shown in Scheme 1, where protonated acetone undergoes a 1,2-hydride shift to the high-energy primary cation (3); this then rearranges to protonated propionaldehyde *via* a 1,2-methyl shift.



SCHEME 1

This is analogous to the pinacol–pinacolone rearrangement depicted in (4) ⟶ (7), which is a common acid-catalysed reaction for 1,2-diols.

Using a method for estimating heats of formation for gas-phase positive ions [2] together with known heats of formation of neutral species,[3] (1) and (2),[4] $C_3H_5^+$,[5] protonated oxetan,[6] and protonated propylene oxide,† leads to a potential surface. This potential surface not only explains the unimolecular reactions undergone by (1) and (2),[1] but also provides an elegant explanation of ^{13}C and deuterium labelling studies on this ion.[7]

It is clearly of interest to extend this approach to $C_4H_9O^+$ isomers in order to observe the effect of inserting a further CH_2 group into either (1) or (2). In particular, do pinacol-type rearrangements still occur, and, if so, are these steps rate-determining?

Consideration of the three possible isomers, (8)—(10), and the plausible mechanisms (Scheme 2) whereby they may be considered to interconvert and dissociate, leads to the potential surface shown in Figure 1.

It is clear from Figure 1 and Scheme 2 that starting from (8), given sufficient energy, ions (11) and (12) may be formed by 1,2-hydride shifts. These ions may then undergo pinacol-type rearrangements to (9) and (10) respectively. The maximum internal energies available to ions generated as (8) and (9), when undergoing slow dissociations,[8-10] may be estimated as 180 and 150 kJ mol^{-1}, respectively. This follows since each of these ions undergoes a small percentage of C_2H_4 loss in metastable transitions (Table 1), and the most direct, symmetry-allowed route for this process passes through a primary carbonium ion (13) of ΔH_f *ca.* 690 kJ mol^{-1} (Figure 2). Since H_2O loss occurs from both (8) and (9), and is favoured over C_2H_4 loss (Table 1), the rate-determining step in H_2O loss is taken as corresponding

TABLE 1

Relative abundances of competing metastable transitions ($^1m^*$) for decomposition of some $C_4H_9O^+$ isomers [13]

Ion	Neutral species lost [a] H_2O	C_2H_4	CH_2O
(8)	89	3	8
(9)	90	3	7
(10)	99	1	0

[a] Abundances expressed as a percentage of the total metastable ion current ($^1m^*$) from *m/e* 73 measured using an AEI MS9 double focusing mass spectrometer.

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† Estimate based on proton affinity of ethylene oxide.[6]

[1] G. Hvistendahl, R. D. Bowen, and D. H. Williams, *J.C.S. Chem. Comm.*, 1975, 294.

[2] R. D. Bowen and D. H. Williams, *Org. Mass Spectrometry*, 1977, **12**, 475.

[3] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, ' Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington, 1969.

[4] K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, 1968, **48**, 5205.

[5] F. P. Lossing, *Canad. J. Chem.*, 1971, **49**, 357.

[6] Calculated from the proton affinity of oxetan, B. H. Solka and M. E. Russell, *J. Phys. Chem.*, 1974, **78**, 1268.

[7] G. Hvistendahl, D. H. Williams, J. R. Kalman, and R. D. Bowen, unpublished results.

[8] F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, 1968, **90**, 5915; D. H. Williams and R. G. Cooks, *Chem. Comm.*, 1968, 663.

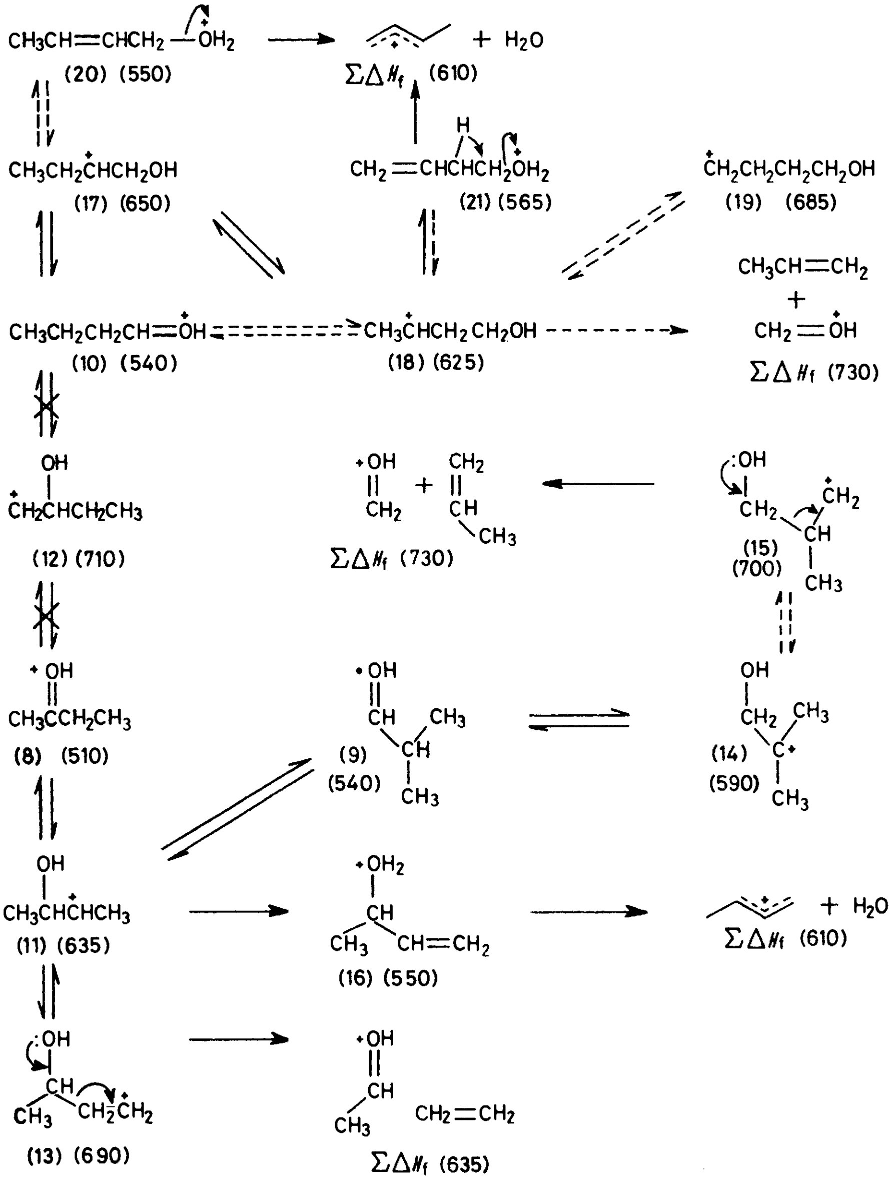
[9] J. H. Beynon, R. G. Cooks, R. M. Caprioli, and G. R. Lester, ' Metastable Ions,' Elsevier, Amsterdam, 1973.

[10] D. H. Williams and I. Howe, ' Principles of Organic Mass Spectrometry,' McGraw-Hill, New York, 1972.

to a transition state energy of *ca.* 675 kJ mol^{-1} (Figure 2).[11] The resulting surface demands that (16) cannot reversibly isomerise to (11), which is in accord with the experimental facts since (22) and (23) lose 95 and 94% HOD (respectively) in dissociations giving rise to metastable peaks.[12]

From the above arguments, and a comparison of Figures 1 and 2, it is evident that (8) and (9) should rapidly interconvert prior to dissociation, but that isomerisation of (8) or (9) to (10) is precluded. This follows since, starting from (8) or (9), dissociating ions have insufficient internal energy to reach the primary carbonium ion (12).

The equilibration of (8) and (9) prior to dissociation is in fact established by the observation[12] that they undergo the same slow dissociations (in metastable



SCHEME 2 Figures in parentheses are heats of formation (in kJ mol^{-1})

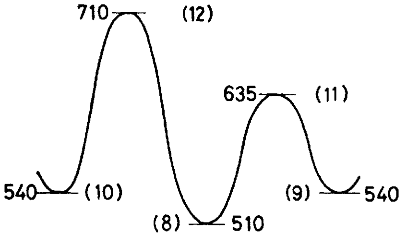


FIGURE 1 Estimated energy barriers to the unimolecular interconversion of protonated butyraldehyde, protonated butanone, and protonated isobutyraldehyde

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[11] F. P. Lossing, *Canad. J. Chem.*, 1972, **50**, 3973.

[12] T. J. Mead and D. H. Williams, *J.C.S. Perkin II*, 1972, 876.

transitions) in the same ratios[13] (Table 1). Further experimental evidence for the validity of our approach is that dissociation of (9) [or (8) after its rearrangement] to $CH_2{=}\overset{+}{O}H$ and $CH_3CH{=}CH_2$ does not occur in slow reactions (Table 1). This reaction would require two successive 1,2-hydride shifts [(9) ⟶ (14) ⟶ (15)], and then dissociation of (15) to $CH_2{=}\overset{+}{O}H$ (Figure 2). The minimum activation energy for such a reaction would be 190 kJ mol^{-1} (Figure 2) and clearly, in the slow dissociations this is not available.

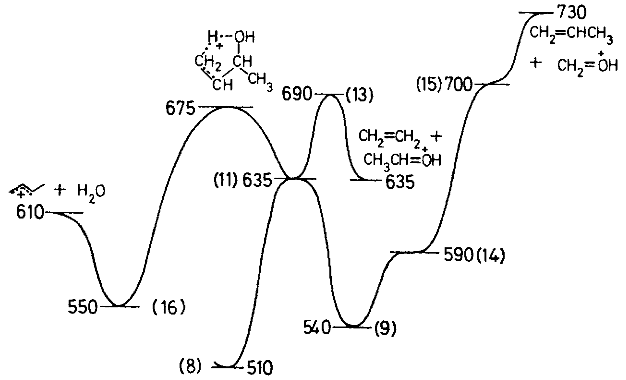
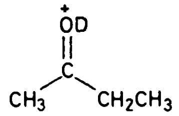
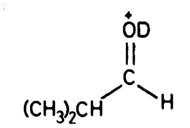


FIGURE 2 Potential energy surface for some unimolecular reactions of (8) and (9)


(22)


(23)

The lack of isomerisation of (8) or (9) to (10) is evidenced by its different behaviour in metastable transitions (Table 1); it loses almost exclusively water.

Further evidence that (10) reacts over a different surface from (8) and (9) may be deduced from deuterium labelling results[12] and the metastable peak widths for the dissociation channels. A condition for (8) and (9) to react over the same surface is that the metastable peaks for all common decay routes must be the same.[9,10] As can be seen from Table 2, this condition is satisfied; and, furthermore, the kinetic energy releases ($T_{\frac{1}{2}}$) calculated from the metastable peak widths at half-height ($W_{\frac{1}{2}}$) are different starting from (10).

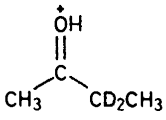
The consequences of the energy surface shown in Figure 2 for deuterium labelling data are exacting. The reversible reaction (8) ⇌ (9) equilibrates the CH_2 hydrogens of (8) with the two CH hydrogens of (9), but no others. Most ions undergoing H_2O loss will not attain the primary carbonium ion configuration (13) which may lead to C_2H_4 loss, since this process is the dissociation of higher activation energy (Table 1). Thus the surface demands that the hydrogen atoms of the H_2O should be derived almost exclusively from the OH and CH_3 groups of (8) or (9). This is in agreement with our earlier labelling studies which established that (24) loses 90% H_2O and only 10% HDO, and (25) loses 87% D_2O and only 13% HDO.[12]

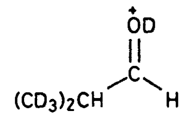
TABLE 2

Kinetic energy releases at half-height ($T_{\frac{1}{2}}$) associated with decomposition of some $C_4H_9O^+$ isomers

	$T_{\frac{1}{2}}$/kJ mol^{-1} for loss of [a]		
Ion	H_2O	C_2H_4	CH_2O
(8)	4.2	~38 [b]	7.1
(9)	4.6	[b]	7.1
(10)	0.9	[b]	

[a] Measurements performed using a reversed geometry VG Micromass ZAB 2F mass spectrometer. No correction was applied for the width of the main beam. [b] Peak too weak to permit accurate measurements.


(24)


(25)

A final point in connection with ions (8) and (9) is that appearance potential measurements should reveal that the energy needed to cause decomposition should be independent of whether the $C_4H_9O^+$ ion is generated as (8) or (9) and should be less than ΔH_f 710 kJ mol^{-1} [*i.e.* the energy needed to cause (8) ⟶ (10)]. Appearance potential measurements on metastable ions yield transition state energies of 700 kJ mol^{-1} for water loss from either (8) or (9). This is consistent with the analysis above, although in view of the inherent inaccuracies in determining appearance potentials using conventional mass spectrometers,[14,15] we wish only to emphasise the qualitative agreement.

For ions generated as (10), 99% dissociate by loss of water (Table 1). Some plausible routes for this reaction are given on the potential surface reproduced in Figure 3. The transition state energy (ΔH_f 695 kJ mol^{-1}) for the reaction (17) ⟶ (20) is estimated by analogy with that required and measured for (11) ⟶ (16) in Figure 2. Such reactions presumably have an activation energy due to the strain associated with the five-membered ring transition state.

However, the route (17) ⟶ (20) appears unlikely to be energetically accessible, since the presence of the necessary internal energies would also lead to the ready population of the primary carbonium ion (19), which could ring-close exothermically to protonated tetra-

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[13] H. M. Rosenstock, V. H. Dibeler, and F. N. Harllee, *J. Chem. Phys.*, 1964, **40**, 591.

[14] J. H. Beynon, R. G. Cooks, K. R. Jennings, and A. J. Ferrer-Correia, *Internat. J. Mass Spectroscopy Ion Phys.*, 1975, **18**, 87.

[15] H. M. Rosenstock, *Internat. J. Mass Spectroscopy Ion Phys.*, 1976, **20**, 139.

hydrofuran (ΔH_f 495 kJ mol^{-1}).[16] The occurrence of this last reaction is definitely excluded by deuterium labelling data which are presented subsequently. It appears likely that the mandatory hydrogen transfer to oxygen (before H_2O loss) could be achieved by a lower energy route now that transfer through a six-membered cyclic transition state is possible [(18) → (21)]. A case has recently been reported[17] where a proton-bridged six-membered ring is less strained than the corresponding five-membered ring by 33 kJ mol^{-1}.

Evidence for the route (10) → (18) → (21) → $C_4H_7^+$, and restrictions on the reversibility of some of these steps, are as follows. (i) The measured transition state energy (appearance potential) for the overall reaction is 625 kJ mol^{-1}. This is in qualitative agreement with the production of (18) being rate determining (Figure 3). (ii) The absence of a large barrier to (18) → (21) is supported by the very narrow metastable peak (Table 2) for the dissociation step. Thus, the excess of energy in the transition state for the dissociation step is small [*e.g.* much smaller than for H_2O loss from (8) or (9), see Table 2 and Figure 2].

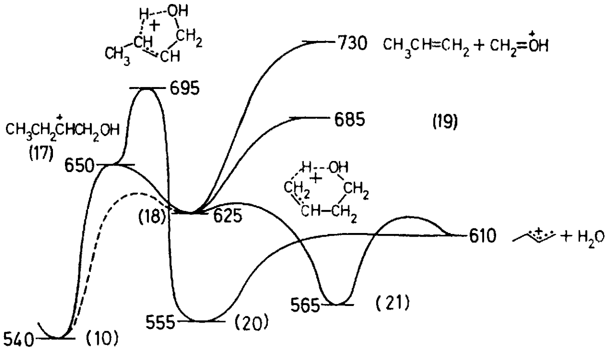

FIGURE 3 Potential energy surface for some unimolecular reactions of (10)

These first two points suggest that the intermediacy of (17) is circumvented by a direct 1,3-hydride shift [(10) → (18); dotted line in Figure 3]. (iii) The barrier to (18) → (21) must be very similar to, or less than, that to (18) → (10), since the hydrogens attached to the end two carbons of (10) do not become equivalent.[12] (iv) The surface in Figure 3 suggests that dissociation of (21) should be finely balanced with the reverse reaction (21) → (18). In the light of the above evidence [(i)—(iii)], and the well defined energy levels of (18) and the products of dissociation, this is by no means an arbitrary criterion. Notwithstanding any reversibility of (18) ⇌ (21), the hydrogen atoms of the expelled H_2O molecule should originate very largely from the original hydroxy and methyl groups of (10).

Our earlier deuterium labelling studies (summarised in Table 3) strikingly support the mechanism proposed in Figure 3.

The data from (27), (29), and (31) establish that hydrogens bonded to C-1, C-2, and C-3 are barely involved in H_2O loss. Data for (26), (28), (30), and (32) establish the involvement of the CH_3 and OH hydrogen atoms, with competing exchange between these sites. For example, some reversibility of (18) ⇌ (21) is indicated by the loss of only 0.5% D_2O from (31), but of 24% D_2O from (32).

TABLE 3

Water loss from deuterium labelled ions of structure (10) ($^1m^*$)

Ion structure	Ion no.	Percentage loss of [a] H_2O	 HOD	 D_2O
$CH_3CH_2CH_2CH{=}\overset{+}{O}D$	(26)	28	72	
$CH_3CH_2CH_2CD{=}\overset{+}{O}H$	(27)	98	2	
$CH_3CH_2CH_2CD{=}\overset{+}{O}D$	(28)	25	73	2
$CH_3CH_2CD_2CH{=}\overset{+}{O}H$	(29)	95	5	
$CH_3CH_2CD_2CH{=}\overset{+}{O}D$	(30)	26.5	72.5	1
$CH_3CD_2CH_2CH{=}\overset{+}{O}H$	(31)	92.5	7	0.5
$CD_3CD_2CH_2CH{=}\overset{+}{O}H$	(32)	9	67	24

[a] Values normalised to a total of 100 units for metastable ion current ($^1m^*$) from *m/e* 73 due to water loss. Measured on an AEI MS9 double-focusing mass spectrometer.[12]

Finally, we note that the low activation energy (*ca.* 65 kJ mol^{-1}) for H_2O loss from (10) not only precludes isomerisation to (8) and (9), but also excludes otherwise plausible reactions such as propene loss (Figure 3).

EXPERIMENTAL

The appearance potential measurements were made using an AEI MS 902 double focusing mass spectrometer on metastable peaks and analysed by the semi-log plot method. The metastable dissociations were observed by adjusting the electric sector voltage at constant accelerating voltage and magnetic field strength so as to transmit exclusively ions undergoing the reaction of interest in the first field free region. The internal calibrant used was the molecular ion of 2-chloropropane (appearance potential 10.78 eV[3]). The metastable peak widths at half-height were determined using a VG Micromass ZAB 2F mass spectrometer in which ions are transmitted by the magnetic sector before entering the electric sector.

The ions (8)—(10) were generated by ionisation and fragmentation of 2-methylbutan-2-ol, 2,4-dimethylpentan-3-ol, and heptan-4-ol, respectively.

We thank Professor J. H. Beynon for facilities at University College, Swansea (ZAB 2F mass spectrometer), Dr. J. R. Kalman for assistance in making the energy release measurements, and the S.R.C. for financial support.

[7/616 *Received, 7th April,* 1977]

[16] J. Beauchamp, personal communication.

[17] R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1973, **95**, 3504.