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Potential Energy Profiles for Unimolecular Reactions of Organic Ions: C4H9O+

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Abstract: The slow, unimolecular reactions of six isomers of C4H9O+ are discussed in terms of the potential energy profiles over which dissociation is considered to occur. Particular attention is given to the detailed mechanism whereby H2O loss may occur from the isomers considered. Intermediates, in which a carbonium ion is loosely coordinated to an aldehyde or in which an aldehyde and an olefin are coordinated to a common proton, are postulated for the rearrangement or interconversion of isomeric ions. It is shown that for some reactions of several of the isomers, the rate-determining step is isomerization to another structure of C4H9O+, the actual dissociation step being relatively fast in these cases. The reaction schemes proposed are based on mechanistic concepts and are consistent with (i) the competition observed between the various decomposition channels, (ii) the results of 2H-labeling studies, (iii) the kinetic energy release which accompanies dissociation, and (iv) approximate measurements of transition-state energies.

Introduction

In earlier work,[2-4] we have shown how the slow, unimolecular reactions of organic ions in the gas phase may be investigated conveniently by generating the ion in question in a conventional double-focusing mass spectrometer and considering the dissociations which occur in metastable transitions. In general, metastable dissociations occur with little excess energy in the transition state.[5,6] Consequently, the ability of possible decay channels to compete against one another is critically dependent on the activation energies for the processes concerned.[7] This is elegantly illustrated by the occurrence of isotope effects in the decomposition of suitably labeled ions. These isotope effects span the entire range of those encountered in solution chemistry and in some cases are spectacularly large. For instance, the metastable decompositions of all the various 2H-labeled methanes have been documented,[8] and, although

calculations indicate that the threshold for loss of D· is only 0.08 eV above that for H·, only CD4+· is observed to lose D·. Other examples of large primary deuterium isotope effects stem from studies of labeled ethane and propane;[9-11] thus, for CH3CD3+·, the ratio of H· to D· loss is ca. 600:1.[9]

A useful model for understanding the slow reactions of ions is the construction of a potential energy profile over which dissociation is considered to occur. In this approach the relative energies of reactant ions, plausible intermediates, and possible products are combined with the organic chemist's concept of mechanism so as to deduce the energetically most favorable decay route. In advantageous cases, predictions may be made concerning the dissociation of previously uninvestigated ions. These predictions may refer to the observed decomposition channels,[12] the energy needed to cause dissociation,[13] the kinetic energy released when reaction takes place,[14] the results of labeling studies,[3] or a combination of these factors. In view

Table I. Heats of Formation (kcal mol⁻¹) Determined by Photoionization, Proton Affinity, and Appearance Potential Measurements

ion	ΔH_f PI[23]	ΔH_f PA[24]	ΔH_f AP[25]
$CH_2=OH^+$	170	164	169
$CH_3CH=OH^+$	140	142	139
$CH_3CH_2CH=OH^+$	134	130	132
$(CH_3)_2C=OH^+$	128	121	120
$CH_3CH_2CH_2CH=OH^+$		123	
$(CH_3)_2CHCH=OH^+$		121	
$CH_3CH_2(CH_3)O=OH^+$		112	115
$CH_3O^+=CH_2$			158
$CH_3CH_2O^+=CH_2$			144
$CH_3CH=O^+CH_3$			133
$CH_3CH=O^+CH_2CH_3$			116[a]
$(CH_3)_2C=O^+CH_3$			114

ᵃ This value is probably substantially too low owing to the occurrence of rearrangement to a tertiary ion—see ref 25.

of the success of the method, it seems of interest to examine the behavior of several isomers of $C_4H_9O^+$ using the same approach; such an investigation is especially pertinent in view of the relatively scant attention given to $C_4H_9O^+$ [4,13,15,16] In contrast, the lower homologue, $C_3H_7O^+$, has been the subject of extensive research.[2,3,14,17-22]

Heats of Formation

A major difficulty in constructing potential energy profiles for the reactions of gas-phase ions is the lack of reliable thermochemical data for relevent species. In our earlier study of $C_3H_7O^+$,[3] we used values for the heats of formation of $CH_2=OH^+$, $CH_3CH_2CH=OH^+$, and $(CH_3)_2C=OH^+$ which had been determined by photoionization.[23] More recent data are now available from proton affinity determinations[24] and from appearance potential measurements using monoenergetic electron beams;[25] a comparison between the photoionization (PI), proton affinity (PA), and appearance potential (AP) results is given in Table I.

In this paper, for ions containing the "$=OH^+$" moiety the heats of formation derived from proton affinity measurements are used in preference to those obtained from photoionization studies. There are three reasons for this. First, the proton affinity measurements are made on an equilibrium basis. This is not the case for photoionization studies or appearance potential measurements, which correspond to vertical ionizations and may not result in the formation of the most stable geometry of the relevant ion. Second, the proton affinity values are taken from a large set of data for various neutral species, arranged in order of increasing proton affinity. The relative positions of the various neutrals in this order are accurately known. Thus, although the *absolute* values of heats of formation derived from proton affinity measurements may not be assigned to an accuracy of better than (say) ±2 kcal mol⁻¹, the *relative* values are almost certainly known to a greater degree of accuracy. In contrast, the data obtained from photoionization studies are not so readily related to one another. Third, the results of proton affinity determinations are wider in scope, data being available for all saturated carbonyl compounds up to C_4H_8O. It is therefore more consistent to use only the set of data which is sufficiently extensive to cover all the simple ions containing the "$=OH^+$" moiety (CH_3O^+, $C_2H_5O^+$, and $C_4H_9O^+$) of interest in the present context. Nevertheless, it should be noted that the data given in Table I, although obtained from different experimental measurements, are in general agreement.

In the case of ions derived from ethers, which contain the "$—O^+=$" group, the only reliable experimental values are those derived from appearance potential measurements. These values are therefore used whenever possible and when the

Scheme I

$$CH_3CH_2CH=\overset{+}{O}H \underset{shift}{\overset{1,2-H}{\rightleftharpoons}} CH_3\overset{+}{C}HCH_2OH \underset{shift}{\overset{1,2-H}{\rightleftharpoons}} \overset{+}{C}H_2CH_2CH_2OH$$
$$\quad \mathbf{3} \qquad\qquad\qquad\qquad \mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$\rightarrow CH_2=CH_2 + CH_2=\overset{+}{O}H$$

Scheme II

$$CH_3CH_2CH_2-CH_3 \qquad\qquad CH_3CH_2CH_2-OH$$
$$-30^{28} \qquad\qquad\qquad -62^{28}$$

$$\overset{+}{C}H_2CH_2CH_2-CH_3 \qquad\qquad \overset{+}{C}H_2CH_2CH_2-OH \quad (2)$$
$$201^{29} \qquad\qquad\qquad \text{estd } \Delta H_f = 201 - (-30) + (-62)$$
$$= 169$$

$$CH_3\overset{+}{C}HCH_2-CH_3 \qquad\qquad CH_3\overset{+}{C}HCH_2-OH \quad (1)$$
$$183^{29} \qquad\qquad\qquad \text{estd } \Delta H_f = 183 - (-30) + (-62)$$
$$= 151$$
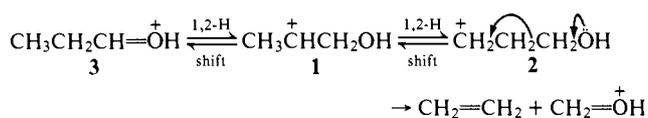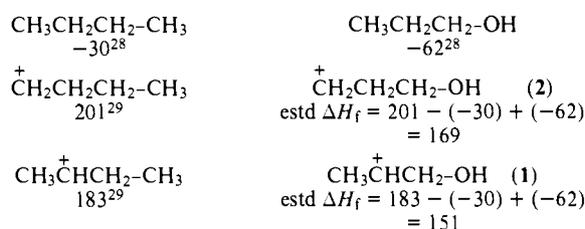
requisite data are not available (e.g., for $CH_3CH_2CH_2O^+=CH_2$), a value is estimated, using a group-equivalent approach,[26] from known[25] values for lower homologues.

The problem of obtaining heats of formation for possible intermediates involved in the decomposition of ions in the gas phase is, however, more serious. Thus, for instance, in the case of open-chain carbonium ions (e.g., **1** and **2**) there is no experimental method as yet available whereby the heats of formation of such species can be measured. These ions are likely intermediates in the dissociation of **3** via C_2H_4 loss (Scheme I).[14] In previous work,[14] we have overcome this difficulty by estimating the heats of formation of species such as **1** and **2** by means of a modified isodesmic substitution.[27] This method, which is essentially an extension of the group-equivalent approach used so successfully to estimate heats of formation for neutral species,[26] is illustrated for **1** and **2** in Scheme II; heats of formation are given in kcal mol⁻¹. Thus, the replacement of the terminal methyl group of the appropriate butyl cation by a hydroxyl group is assumed to result in the same stabilization as is observed when the corresponding change is performed on butane. This isodesmic substitution[30] does not allow for any stabilization of **1** and **2** which might occur via orbital overlap of the oxygen lone pairs with the cationic site. Equally, it does not take account of possible destabilization of **1** and **2** by inductive withdrawal of electrons by the electronegative oxygen atom. Hence, the values (151 and 169 kcal mol⁻¹, respectively) obtained for the heats of formation of **1** and **2** contain the assumption that no stabilization of **1** and **2**, relative to the appropriate butyl cations, occurs apart from that associated with the inherent difference in stability of the $-OH$ and $-CH_3$ groups themselves. Although lack of orbital overlap of the oxygen lone pairs with the cationic sites of **1** and **2** is the situation of interest, destabilization of **1** and **2** by σ withdrawal of electrons by the electronegative oxygen atom ought to occur. Calculations[30] suggest that the magnitude of this destabilization depends upon the conformation of the ion. Maximum values of ca. 10 and 3 kcal mol⁻¹, respectively, are found for the destabilizing effect of a hydroxyl group situated β and γ to the cationic site. Use of these corrections yields values for the heats of formation of **1** and **2** of 161 and 172 kcal mol⁻¹, respectively.[27] Experimental evidence that these corrections are appropriate in the systems of interest stems from our earlier work on $C_3H_7O^+$,[3,14] $C_4H_9O^+$,[4,13] and related systems.[31]

In this paper, values of 10 and 3 kcal mol⁻¹ are used for the destabilization conferred on a carbonium ion by an oxygen atom situated β or γ to the cationic site. It is recognized that these values are only approximate and are probably not accurate to better than ±5 kcal mol⁻¹. However, we feel they serve as a useful guide to the heats of formation of carbonium ions such as **1** and **2** which may be involved in the decomposition of ions in the gas phase.

In the discussion which follows, heats of formation which

are not known are estimated by using the isodesmic substitution procedure (for open-chain carbonium ions) or by estimating proton affinities (for protonated allylic alcohols) or from values known for lower homologues (for some oxonium ions).

In conclusion (concerning the heats of formation of relevant species), two important points should be kept in mind. First, for some species, no experimental method is available for the determination of the heat of formation; therefore, an estimation method must be employed. There is good experimental evidence in favor of the estimation procedure employed in this paper although it is recognized that the approach gives only approximate values. Second, using the estimation techniques outlined above, it is possible to rationalize[3,4,12-14,31] the behavior of many ions in the gas phase and, moreover, in favorable cases, to predict successfully the reactions of uninvestigated ions.[3,12,31]

Implicit in the approach is the assumption that 1,2-hydride and 1,2-methyl shifts may take place essentially without activation energy apart from that associated with the endothermicity (or exothermicity) inherent in the reaction in question. This view seems reasonable and is supported by calculations[32] and solution NMR experiments.[33] Furthermore, in some cases, the ionization of radicals is observed to be accompanied by a 1,2-hydride shift at the thermochemical threshold.[29]

Results and Discussion

A long-standing problem in organic mass spectrometry concerns the mechanism whereby "onium" ions derived from ethers (**4**, X = O), thioethers (**4**, X = S), or amines (**4**, X = NH; **5**, X = N) decompose; in particular, how does olefin elimination occur from these ions? A further point of interest is the possible rearrangement of these ions to (or their interconversion with) the isomeric "onium" ions in which the heteroatom lies at the end of a single carbon chain rather than in the middle of two carbon chains (i.e., **6**, X = O, S, NH or **7**, X = N).

$$R_1R_2C\overset{+}{=}XCR_3R_4R_5 \qquad\qquad R_1R_2C\overset{+}{=}XR_6CR_3R_4R_5$$
$$\mathbf{4} \qquad\qquad\qquad\qquad \mathbf{5}$$

$$R'R_1C\overset{+}{=}XH \qquad\qquad\qquad R'R_1C\overset{+}{=}XHR_6$$
$$\mathbf{6} \qquad\qquad\qquad\qquad\qquad \mathbf{7}$$
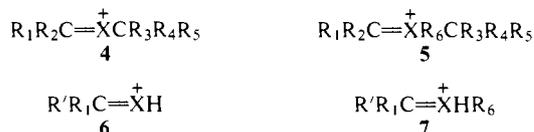
In earlier work,[34] we have proposed a mechanism whereby C_2H_4 loss may occur from ions generated as **8** (or higher homologues). This mechanism involves the formation of a complex in which C_2H_4 and $CH_2=O$ become bound to a common proton. This complex, **10**, then dissociates so that the olefin or aldehyde having the greater proton affinity (in this case $CH_2=O$) keeps the proton; Scheme III. Using this

Scheme III

$$CH\ CH_2\overset{+}{O}=CH_2 \rightleftharpoons CH_2-\overset{+}{C}H_2---O=CH_2$$
$$\mathbf{8} \qquad\qquad\qquad\qquad | \qquad\qquad$$
$$\qquad\qquad\qquad\qquad\qquad H \qquad\qquad \mathbf{9}$$

$$\Big\Updownarrow$$

$$CH_2=CH_2---CH_2-\overset{+}{O}H \rightleftharpoons \begin{matrix}CH_2\\ \vdots\ \rangle H---O=CH_2\\ CH_2\end{matrix} \overset{+}{\ } \longrightarrow \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \ +$$
$$\mathbf{11} \qquad\qquad\qquad\qquad\qquad \mathbf{10}$$

$$\Big\Updownarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \overset{+}{HO}=CH_2$$

$$\overset{+}{C}H_2CH_2CH_2OH \rightleftharpoons CH_3\overset{+}{C}HCH_2OH \rightleftharpoons CH_3CH_2CH\overset{+}{=}OH$$
$$\mathbf{2} \qquad\qquad\qquad\qquad \mathbf{1} \qquad\qquad\qquad\qquad \mathbf{3}$$

$$\Big\downarrow$$

$$CH_2=CHCH_2\overset{+}{O}H_2 \longrightarrow \ \diagup\!\!\!\!\diagdown_+ \ + \ H_2O$$
$$\mathbf{12}$$

Scheme IV

$$\overset{+}{CR_5R_6CR_3R_4CR_1R_2XH} \underset{}{\overset{?}{\rightleftharpoons}} \begin{matrix}R_6 \quad\ R_5\\ \diagdown C \diagup\\ \vdots\ \rangle\overset{+}{H}---X=CR_1R_2\\ \diagup C \diagdown\\ R_4 \quad\ R_3\end{matrix}$$
$$\mathbf{14} \qquad\qquad\qquad\qquad\qquad \mathbf{13}$$

$$\overset{?}{\rightleftharpoons} \ CHR_5R_6CR_3R_4-\overset{+}{X}=CR_1R_2$$
$$\mathbf{15}$$
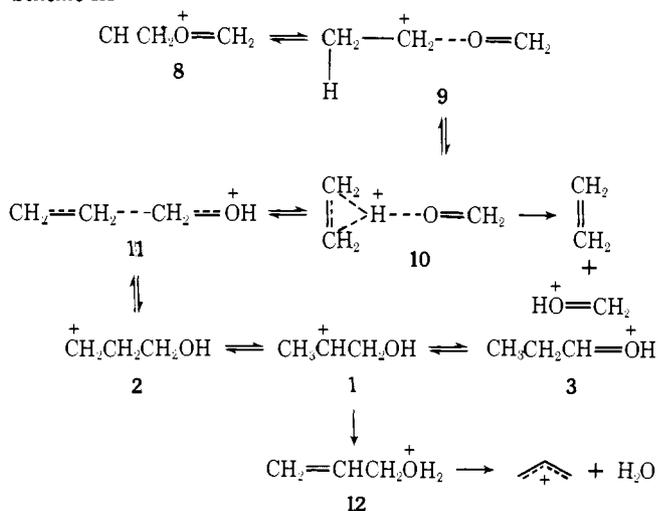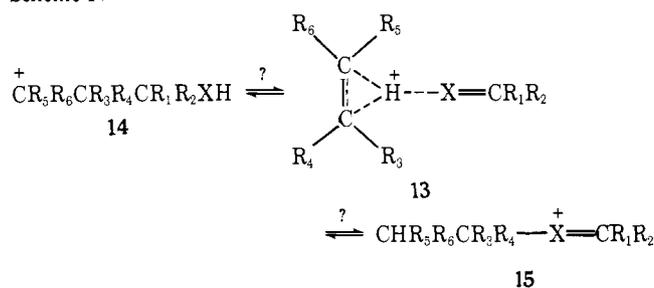
mechanism, it is possible to explain the decomposition of numerous oxonium ions of general formula $R_1R_2R_3C—O^+=CR_4R_5$ via elimination of aldehydes/ketones or olefins. In favorable cases, it is possible that the potential olefin fragment in **10** (or homologous ions) might be transferred to the carbonyl carbon atom, thus producing an open-chain carbonium ion such as **2**. Loss of H_2O may now occur by rearrangement of this carbonium ion to protonated allyl alcohol (**2** → **1** → **12**) followed by σ-bond cleavage to give allyl cation and H_2O. A stepwise route for H_2O loss from **8** seems highly plausible, direct expulsion of H_2O being inherently unlikely since it would involve the simultaneous formation of two O–H bonds and the fission of two C–O bonds. Moreover, since **3** is known to eliminate H_2O in metastable transitions,[20] probably via intermediates such as **1** and **12**, it is quite feasible that **8** may lose H_2O via similar intermediates.

It is helpful to consider the formation of **3** and **8** from the complex **10**; **10** → **2** (and hence formation of **1**) proceeds via nucleophilic addition of the incipient ethylene fragment to the carbonyl carbon atom of the potential protonated formaldehyde molecule. Clearly, if this step is energetically more favorable than dissociation (i.e., if **2** is lower in energy than the total heat of formation of C_2H_4 and $CH_2=OH^+$), it will be favored over elimination of C_2H_4; in the case in question, this situation occurs.[14,35] However, in cases where rearrangement of **10** to **2** is energetically less favorable than decomposition (i.e., if **2** were higher in energy than the products of olefin loss), dissociation would be preferred; an example of this behavior is furnished by the nitrogen analogues (NH replacing O) of **3** and **8**. Similarly, if the energy needed to cause **10** → **9** is less than that required to form products by breakup of **10**, interconversion of **8**, **9**, and **10** can occur prior to decomposition, as is found for **2**. For the nitrogen analogues of **8**, **9**, and **10**, however, **10** requires less energy to decompose via C_2H_4 loss than to attain **9** and thus return to **8**. Hence, for such nitrogen analogues, rearrangement of **8** to **10**, via **9**, is the rate-determining step in the decomposition of **8**.[35]

From this analysis, it is evident that the complex of general formula **13** is a vital connecting link between ions **14** and **15**; Scheme IV, X = O, S, NH etc. Although it would appear likely that the approach of the olefin $R_3R_4C=CR_5R_6$ to the protonated ketone (X = O) or imine (X = O) or imine (X = NH) would be exothermic when leading to the complex **13**, it is conceivable that either or both of the reactions **13** → **14** and **13** → **15** will require more energy than dissociation to products. In other words, it is probable that the complex **13** will always exist in a well on the potential energy profile; however, this well may be so shallow that one or both rearrangement processes available to **13** will be energetically less favorable than decomposition to products. For the isomers of $C_4H_9O^+$ considered in this paper, each of these two possibilities is realized.

The unimolecular decay routes for the eight possible "onium" isomers of $C_4H_9O^+$, in which the charge may be considered to reside mainly on oxygen, have already been documented.[15] The data relevant in the present context are given in Table II, from which it is evident that the dominant metastable transition is H_2O loss for every isomer apart from **21**. Analysis of the possible reactions of **21** leads to the potential
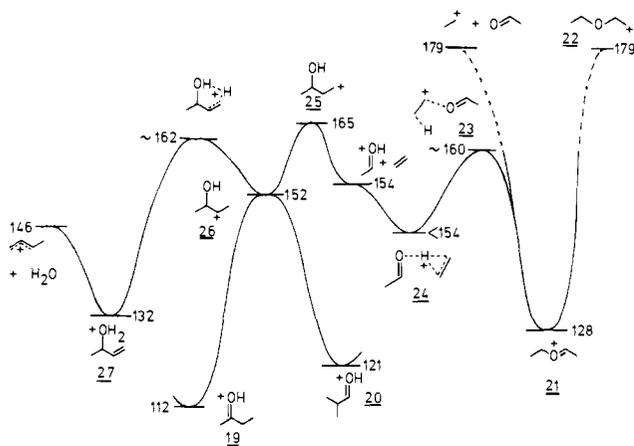
Figure 1. Potential energy profile for interconversion and dissociation of 19, 20, and 21.

Figure 2. Potential energy profile for interconversion and dissociation of 16, 17, and 20.

Table II. Slow Dissociations of Some Isomers of $C_4H_9O^+$

ion structure	neutral lost[a]		
	H_2O	C_2H_4	CH_2O
$CH_3CH_2CH_2O^+=CH_2$ (16)	80	0	20
$(CH_3)_2CHO^+=CH_2$ (17)	88	0	12
$CH_3CH_2CH_2CH=^+OH$ (18)	99	1	0
$CH_3CH_2(CH_3)C=^+OH$ (19)	89	3	8
$(CH_3)_2CHCH=^+OH$ (20)	90	3	7
$CH_3CH_2O^+=CHCH_3$ (21)	2	98	0

[a] Abundance normalized to a total metastable ion current of 100 units (1st field-free region) from m/e 73 and taken from ref 15.

energy profile of Figure 1. Heats of formation are known for neutral species,[28] $CH_3CH=OH^+$,[24] 19,[24] 20,[24] $C_2H_5^+$,[29] and $C_4H_7^+$,[36] and are estimated for open-chain carbonium ions,[27] 21,[37] and 27.[38] It is evident from Figure 1 that dissociation of the relevant complex, 24, to $CH_3CH=OH^+$ and C_2H_4 is energetically more favorable by ca. 11 kcal mol^{-1} than rearrangement to form 25. Since it is necessary for 24 to be formed en route to 19 and 20 (and hence H_2O) loss), it is clear that 24, once formed from 21, ought to dissociate via C_2H_4 loss rather than isomerize to 25 and subsequently eliminate H_2O. Thus, the observation[15] that 21 loses almost no H_2O in metastable transitions is understandable in terms of the potential energy profile of Figure 1.

In Figure 1, the rate-determining step in C_2H_4 loss from 21 is depicted as attainment of the complex 23; this view is supported by three pieces of experimental evidence. (i) The metastable peak for C_2H_4 loss is broad and Gaussian, corresponding to an average[39] kinetic energy release of 3.3 kcal mol^{-1}. This indicates that excess energy is present in the transition state for the dissociation step[22] and some of this excess energy is partitioned as translation when decomposition occurs. In contrast, for the lower homologue, 8, where rearrangement prior to C_2H_4 loss is probably not rate determining,[35] a much smaller average[39] kinetic energy release is observed (1.0 kcal mol^{-1}).[35] (ii) The results of ^2H-labeling studies[15] reveal a high specificity in the origin of the hydrogen atoms of the expeled C_2H_4; these are found to be selected only from the ethyl chain of 21. Moreover, there is a distinct preference for transfer of a β-hydrogen atom to oxygen in the course of the reaction. Thus, for example, $CH_3CD=O^+CH_2CH_3$ eliminates exclusively C_2H_4 while $CH_3CH=O^+CH_2CD_3$ eliminates 90% CH_2CD_2 and only 10% $CHDCD_2$.[15] These data suggest that 24, once formed, dissociates to $CH_3CH=OH^+$ and C_2H_4 more readily than returning to 21. However, some rearrangement of 24 to 21 must
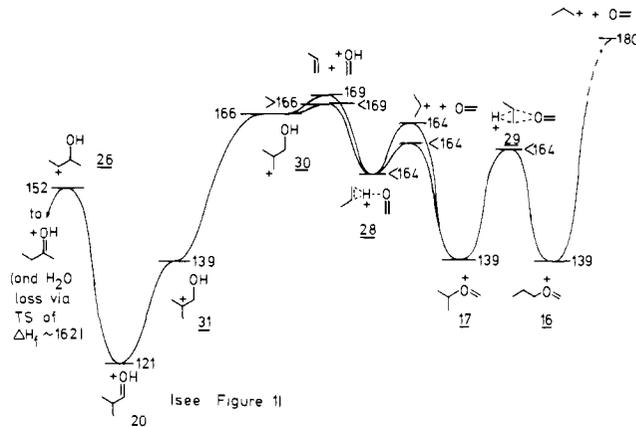
occur to account for the minor fraction (10%) of $CHDCD_2$ loss from $CH_3CH=O^+CH_2CD_3$. Therefore, it is probable that the complex 23 has a heat of formation in the region 155-160 kcal mol^{-1}. (iii) Appearance potential measurements give a value of 167 kcal mol^{-1} for the transition state energy for C_2H_4 loss from 21. Bearing in mind the inherent difficulties involved in determining appearance potentials using conventional mass spectrometers,[40,41] this approximate value is consistent with the postulated potential energy profile shown in Figure 1.

It should be noted that apart from isomerization to 24, via 23, no plausible decay routes exist for 21. Thus, elimination of CH_3CHO or rearrangement to 22 both require a total energy content of at least 179 kcal mol^{-1}.

Further support for the energy levels given in Figure 1 may be derived as follows. It is found that 19 and 20 undergo the same slow reactions in similar ratios;[15] this is strong evidence that these ions interconvert prior to decomposition.[7] In Figure 1, 19 and 20 are considered to undergo interconversion via the secondary carbonium ion, 26; water loss may occur by rearrangement of this ion to protonated but-1-en-3-ol, 27, followed by σ-bond cleavage to form 1-methylallyl cation and H_2O. Rearrangement of 26 to 27 is postulated to be the rate-determining step in H_2O loss from 19 and 20; this is consistent with the high degree of retention of the hydrogen atom originally bound to oxygen in the water molecule eliminated from the -OD analogues of 19 and 20.[15] Moreover, the transition state energy for H_2O loss from 19 and 20 must be in the region of 162 kcal mol^{-1}. This view is consistent with the fact that a minor decay channel, C_2H_4 loss, may plausibly proceed via the primary carbonium ion 25 which has an estimated heat of formation of 165 kcal mol^{-1}. Also, C_3H_6 loss which might plausibly occur, without reverse activation energy, via σ-bond cleavage of 30 (Figure 2) does not occur in slow dissociations of 19 and 20 even though the products of this reaction have a total heat of formation of only 169 kcal mol^{-1}. Hence, the population of ions with initial structures 19 and 20 which undergo decomposition in metastable transitions does not contain a significant percentage of ions with internal energies corresponding to a total energy content of 169 kcal mol^{-1}. Furthermore, only a minor fraction (3%, Table II) are able to attain a transition state having a heat of formation of approximately 165 kcal mol^{-1}; hence, it is probable that H_2O loss proceeds via a transition state with energy a few kcal mol^{-1} lower, i.e., in the region of 162 kcal mol^{-1}. This corresponds to an activation energy associated with rearrangement of 26 to 27 of ca. 10 kcal mol^{-1}. Similar results have been found in analogous systems where hydrogen transfer via a five-membered ring transition state is involved.[2,4,13,35] It is possible that this is in part a *kinetic* barrier (rather than totally an energetic barrier); i.e., 10 kcal mol^{-1} of internal energy is needed in 26
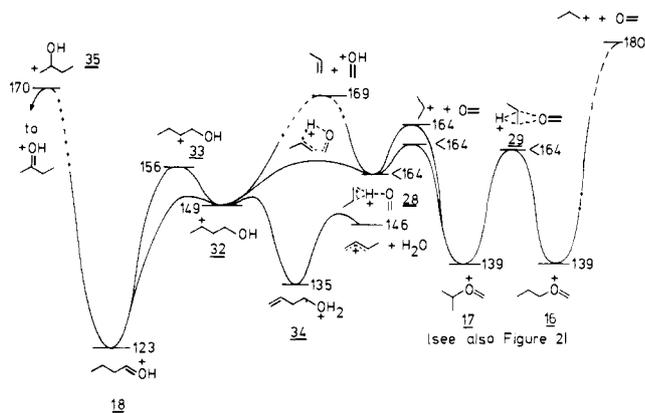
Figure 3. Potential energy profile for interconversion and dissociation of **16, 17,** and **18.**

to cause the rearrangement **26** → **27** to occur at a *rate* (log k = 4-6) appropriate to metastable transitions.

It is also possible that **19** and **20** may rearrange to a different complex, **28,** in which C_3H_6 and CH_2O share in "solvating" a common proton. This complex could also be formed from **16** and **17.** A potential energy profile for this system (Figure 2) may be constructed using thermochemical data obtained from similar sources to those utilized for Figure 1.

In Figure 2, rearrangement of **19** and **20** to the complex, **28,** is depicted as proceeding via the primary carbonium ion **30** which has an estimated heat of formation only marginally above the total heat of formation of the products of CH_2O loss. There is a considerable amount of experimental evidence in favor of the view that isomerization of **31** to **28** via **30** is the rate-determining step in CH_2O loss from **19** and **20.** First, the metastable peaks for CH_2O loss from **19** and **20** are the same shape and correspond to an average[39] kinetic energy release of 4.3 kcal mol^{-1} in each case; these values are much greater than those found to accompany CH_2O loss from **16** and **17** (0.5 kcal mol^{-1}, in each case). This result is consistent with **19** and **20** undergoing CH_2O loss through the same intermediates as **16** and **17** but with larger excess energies in the transition state for the final step.[22] Second, rearrangement of **16** and **17** to **19** and **20** is precluded because C_2H_4 loss is not observed in slow dissociations of **16** and **17.** This suggests that dissociation of the complex **28** to i-$C_3H_7^+$ and CH_2O is energetically more favorable than rearrangement to **20,** via **30.**

These arguments lead to the conclusion that CH_2O loss from **19** and **20** must proceed via a transition state having a heat of formation in excess of 164 kcal mol^{-1} (i.e., the total heat of formation of $C_3H_7^+$ and CH_2O). However, since no loss of C_3H_6 is observed in slow dissociations of **19** and **20,** an upper limit of 169 kcal mol^{-1} may be fixed for the transition state energy for CH_2O loss. Hence, CH_2O loss is expected to require some 4-7 kcal mol^{-1} more energy than H_2O loss. This is supported by two experimental facts; (i) H_2O loss is the dominant metastable decomposition of **19** and **20,** CH_2O and C_2H_4 losses being minor processes (Table II), and (ii) appearance potential measurements reveal that CH_2O (and C_2H_4) loss from **19** and **20** requires some 5 kcal mol^{-1} more energy than H_2O loss.

In contrast to the previous system, rearrangement of the complex **28** to **17** and **16** is energetically more favorable than dissociation to i-$C_3H_7^+$ and CH_2O. This follows from three pieces of experimental evidence. (i) The metastable peaks for CH_2O loss from **16** and **17** are the same shape and are narrow and Gaussian thus suggesting interconversion of **16** and **17** precedes decomposition and that there is little excess energy present in the transition state for the dissociation step. (ii) The ions **16** and **17** are observed to undergo the same reactions in similar ratios, thus indicating at least partial interconversion occurs prior to decomposition.[7] This in turn suggests that the

same intermediates must be accessible to **16** and **17** on a reversible basis. (iii) Appearance potential measurements yield an approximate transition-state energy for the reaction of 167-170 kcal mol^{-1} which is not significantly above the thermochemical threshold (164 kcal mol^{-1}) for CH_2O loss.

Two further points are noteworthy in connection with ions **16, 17, 19,** and **20.** First, loss of C_3H_6 does not occur in slow dissociations of **19** and **20** even though the products of this reaction have a total heat of formation only 3 kcal mol^{-1} above the lower limit estimated for the transition state for CH_2O loss from these ions, Figure 2. Thus, the population of ions which decompose in metastable transitions does not contain a significant number of ions with excess energies in the transition states for observed reactions greater than 5-10 kcal mol^{-1}. This in turn serves to emphasize how an examination of the reactions undergone in metastable transitions results in the selection of only those reactions which are energetically most favorable. Second, although the analysis indicates that **16** and **17** do not rearrange to **19** and **20** to a significant extent, H_2O loss is the major slow reaction (80-88%, Table II) starting from **16** and **17.** How, then, does H_2O loss occur from these ions?

The answer to this question may be deduced from a consideration of the complex **28.** In order for **28** to rearrange to **20** it must isomerize to **30;** this corresponds to anti-Markownikoff addition of C_3H_6 to $CH_2=OH^+$ (eq 1). This process leads to a primary carbonium ion, **30,** which is inaccessible at energies appropriate to metastable dissociations of **16** and **17.** However, Markownikoff addition could occur to give a secondary cation, **32,** (eq 2). Construction of a potential energy

$$\overset{\frown}{}+ CH_2\overset{\frown}{=}OH \;\xrightarrow{\times}\; \overset{CH_2OH}{\underset{+}{\overset{}{\diagup}}\diagdown} \qquad 30 \qquad (1)$$

$$\diagup\!\diagdown\!\curvearrowright CH_2\overset{\frown}{=}OH \;\longrightarrow\; \diagup\!\diagdown\overset{+}{\diagdown}CH_2OH \qquad 32 \qquad (2)$$
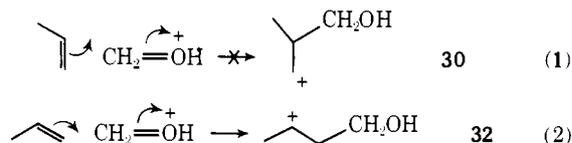
profile analogous to those examined earlier leads to the conclusion that rearrangement of **28** to **32** results in isomerization of **16** and **17** onto the same energy profile as that over which **18** reacts (Figure 3). Hydrogen transfer from the methyl group of **32** to oxygen can occur, via a six-membered ring transition state, thus resulting in protonated homoallyl alcohol, **34.** Cleavage of the C-O bond in **34,** together with an associated 1,2-hydride shift, yields 1-methylallyl cation and H_2O. It is clear from Figure 3 that this is an energetically feasible route for the decomposition of **16** and **17;** indeed, it is the most favorable decay channel.

Several pieces of experimental evidence may be cited in support of the potential energy profile shown in Figure 3. (i) Since **18** loses almost exclusively H_2O, it follows that at energies sufficient to cause this reaction, the products of CH_2O loss (i.e., an observed dissociation channel of **16** and **17**) must be energetically inaccessible. This in turn may well preclude isomerization of **18** to **16** or **17,** via **32** and **28;** this is the view given in Figure 3. (ii) Starting from **18,** the metastable peak for H_2O loss is narrow and Gaussian, corresponding to an average[39] kinetic energy release of 0.5 kcal mol^{-1}; however, starting from **16** and **17,** a much broader peak is observed (average[39] kinetic energy release 2.0 kcal mol^{-1} in each case). This is good evidence that the rate-determining step in H_2O loss from **16** and **17** is isomerization onto the same energy profile as that over which **18** dissociates; this is the situation depicted in Figure 3. Moreover, the observation that H_2O loss from **18** gives rise to a different shaped metastable peak from that observed for **16** and **17** is strong evidence that these ions are not able to interconvert with **18** prior to decomposition. (iii) The results of ^2H-labeling studies on **16** and **17** reveal that the hydrogen atoms of the expeled H_2O molecule originate exclusively from the original C_3 chain of **16** and **17.**[15] Thus, for example, $CH_3CH_2CH_2O^+{=}CD_2$ and $(CH_3)_2CHO^+{=}CD_2$

eliminate only H_2O in the water-loss reaction, while $(CD_3)_2$-CDO^+=CH_2 eliminates only D_2O. This is what would be expected if **16** and **17** were to undergo a rate-determining isomerization to **32** (via **28**) prior to H_2O loss. The first hydrogen transfer to oxygen occurs in the formation of the complex **28**; it is clear that a hydrogen atom from the original C_3 chain of **16** and **17** becomes the proton which is "solvated" by propene and formaldehyde in **28**. This hydrogen remains attached to oxygen in the rearrangement **28** → **32** and the resultant methyl group of **32** comprises only atoms from the original C_3 chain of **16** and **17** (eq 2 and Figure 3). Hence, when the second hydrogen transfer from this methyl group to oxygen occurs, it is evident that both the hydrogen atoms which become bound to oxygen in **34** (and therefore which are expelled in the H_2O molecule) originate from the C_3 chain of **16** and **17**. (iv) Approximate appearance potential measurements yield transition-state energies of 163–167 kcal mol⁻¹ for H_2O loss from **16** and **17**; the corresponding value (150 kcal mol⁻¹) for decomposition of **18** is much lower. These data are consistent with isomerization of **16** and **17** to **18** (or related ions) being the rate-determining step in H_2O loss as is represented in Figure 3.

It should be noted that C_3H_6 loss from **16, 17,** or **18** is precluded because it requires too much energy (at least 169 kcal mol⁻¹). Similarly, rearrangement of **18** to **20** and **19** via a pinacol-type isomerization is precluded by the relatively high heat of formation (170 kcal mol⁻¹) of the necessary intermediate, **35**, which is a primary carbonium ion suffering destabilization by an electron-withdrawing hydroxyl group β to the cationic site.

Finally in connection with Figure 3, it is instructive to observe that rearrangement of the complex **28** to either an open-chain carbonium ion (**32**) or **17** is energetically more favorable than CH_2O loss. This is in contrast to the situation found in Figure 1 where both analogous rearrangements of the complex **24** are less favorable than C_2H_4 loss and that in Figure 2 where one rearrangement is more favorable than CH_2O loss.

Conclusion

The concept that rearrangement of isomeric ions may occur via loosely coordinated ions is discussed for six isomers of $C_4H_9O^+$. The approach provides a self-consistent rationalization of which structures rearrange to other isomers prior to dissociation. Three general types of potential energy profiles are observed; these correspond to cases where dissociation of the loosely coordinated complex is energetically less favorable than both possible rearrangements, one possible rearrangement, and neither rearrangement, respectively. One example of each of these cases is found in the three systems discussed. In some circumstances, the rate-determining step in dissociation of an ion is isomerization to another structure; several examples of this behavior are given.

Experimental Section

All mass spectra were recorded using an AEI MS902 double-focusing mass spectrometer operating at a source pressure of ca. 10^{-6} torr with a nominal electron beam energy of 70 eV and an accelerating voltage of 8 kV. Samples were introduced using the all-glass heated-inlet system (AGHIS). Dissociations occurring in the first field-free region were observed by increasing the accelerating voltage at constant ESA voltage and magnetic field strength.[42]

The appearance potential measurements were made on ions decomposing in the first field-free region. These ions were observed by reducing the ESA voltage at constant accelerating voltage and magnetic field strength.[43] The internal calibrant employed was the molecular ion of 2-chloropropane (AP = 10.8 eV[27]) and the results were evaluated using the semilog plot method.[44]

The kinetic energy release measurements were determined using a VG Micromass ZAB 2F instrument in which ions are transmitted

by the magnetic sector before entering the ESA. No correction was applied for the width of the main beam.

All compounds were either available commercially or synthesized by unexceptional methods.

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(38) Value obtained by estimating the proton affinity of but-1-en-3-ol as 190 kcal mol⁻¹ (cf. saturated alcohols which have similar PA's[24]) and the heat of formation as −41 kcal mol⁻¹ (using a group-equivalent method[26]).
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