ucation Committee of the Gulf Oil Corporation for a grant that assisted in the construction of the tandem mass spectrometer. We also wish to thank Dr. Thomas M. Mayer for valuable comments and suggestions.

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Potential Energy Surfaces for Some $C_4H_9O^+$ Ions; Rate-Determining Isomerizations Prior to Unimolecular Decompositions

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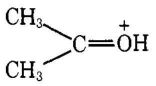
Received April 15, 1977

Abstract: A self-consistent explanation of the main reactions undergone in metastable transitions by some isomers of the $C_4H_9O^+$ ion is given in terms of the potential energy surfaces over which the reactions are considered to occur. It is shown that for some starting structures of $C_4H_9O^+$ the rate-determining step for dissociation is isomerization to another structure of $C_4H_9O^+$. The approach not only provides a simple explanation of the known chemistry, including isotopic labeling results, but also permits correct predictions to be made concerning the relative widths of the metastable peaks for the observed reactions, starting from different precursors.

In previous work,[1,2] we have shown that rate-determining isomerizations occur in the $C_3H_7O^+$ ion system prior to unimolecular decomposition. In particular, protonated acetone (**1**) was shown to undergo rate-determining rearrangement to protonated propionaldehyde (**2**), and the oxonium ion **3** to undergo rate-determining rearrangement to **4**, before dissociations (metastable transitions) occur.



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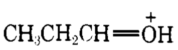
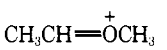


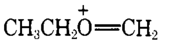
$CH_3CH_2CH{=}\overset{+}{O}H$

2



$CH_3CH{=}\overset{+}{O}CH_3$

3



$CH_3CH_2\overset{+}{O}{=}CH_2$

4

Although studies of $C_3H_7O^+$ are relatively numerous,[1-6] the higher homologue, $C_4H_9O^+$, appears to have received scant attention and it therefore seemed of interest to attempt to extend the approach used for $C_3H_7O^+$ to this ion. The metastable abundance data for the dissociation of the various ion structures possible for this ion, in which the charge may be considered as residing mainly on oxygen (i.e., the eight possible "onium" type ions) have already been documented.[7] The present work concerns four such structures, all of which may be conveniently generated in the gas phase by the fragmentation of suitable ethers, and the relevant data are summarized in Table I.

If the ions **5**–**8** are considered as higher homologues of the $C_3H_7O^+$ ions already investigated, it becomes apparent that **5** and **6** are both homologues of **4** which is known to undergo competitive loss of H_2O and C_2H_4 in metastable transitions. Further, the activation energies for these two processes are different[1] and are less than the energy (~40 kcal mol^{-1}) needed to produce $C_2H_5^+$ together with $CH_2{=}O$. In particular, loss of water from this ion, which must necessarily be a very complex reaction, dominates and requires only about 28 kcal mol^{-1} of internal energy.[1] Thus, the ions **5** and **6** would be expected to lose water with roughly the same activation energy as **4** unless another reaction can compete by virtue of possessing a similar activation energy.[8] Such a possibility could in principle arise by loss of ethylene (as occurs in the lower homolog **4**) or by loss of formaldehyde. The latter is observed to occur, with $CH_2{=}O$ loss accounting for about 15% of the metastable ion current for decomposition of **5** and **6**. The occurrence of formaldehyde loss is presumably due to the possibility of forming a secondary cation by direct bond cleavage of **6** (or bond cleavage with an associated 1,2-hydride shift in

Table I. Metastable Decompositions Undergone by Some Isomers of $C_4H_9O^+$

Ion structure		Neutral lost[a]					
		CH_4	H_2O	C_2H_4	CH_2O	CH_4O	C_3H_6
$CH_3CH_2CH_2\overset{+}{O}=CH_2$	(5)		80		20		
$(CH_3)_2CH\overset{+}{O}=CH_2$	(6)		88		12		
$CH_3CH_2CH=\overset{+}{O}CH_3$	(7)	1.5	1.5	54	8	34	1
$(CH_3)_2C=\overset{+}{O}CH_3$	(8)	3	15	14	43	17.5	7.5

[a] Abundances expressed as a percentage of the total metastable ion current (${}^1m^*$) from *m/e* 73; the values are the means of those reported in ref 7.

5) leading to the isopropyl cation plus formaldehyde. The total heat of formation of this combination is 164 kcal mol^{-1},[9,10] which is similar to the estimated transition state energy for water loss (171 kcal mol^{-1} if the activation energy for elimination of H_2O from **5** and **6** is assumed to be the same as that in **4**). Other reactions, for instance loss of ethylene or propene, might be precluded by the relatively high energy of the likely reacting configurations in the former case, or certainly by the high energy of the product combination[11] in the latter case (see Figure 1) and indeed do not occur to a significant extent. The estimated potential energy surface is depicted in Figure 1 where the activation energy for water loss is taken to be ~19 kcal mol^{-1} (see later).

Several conclusions follow from the proposed potential surface; for instance, suitably labeled forms of **5** and **6** ought to reveal that formaldehyde loss involves only the hydrogens in the terminal $-CH_2$ group since the reaction involves only the cleavage of the bond between oxygen and the C_3 chain. Deuterium labeling results[7] establish this; $CH_3CH_2CH_2{=}CD_2$ and $(CH_3)_3CH^+{=}CD_2$, for instance, lose no CH_2O or CHDO in metastable transitions, formaldehyde loss involving specifically the $O{=}CD_2$ unit. In addition, energy measurements should show that the activation energies for H_2O and CH_2O losses are roughly the same, since these reactions compete in dissociation of **5** and **6** ions of long lifetimes. Also formaldehyde loss, being a reaction which may be plausibly postulated as occurring without reverse activation energy, should be evidenced by a very narrow metastable peak. On the other hand, water loss probably proceeds *via* a suitable protonated methylallyl alcohol, the formation of which is likely to be the rate-determining step. Hence it is possible that the metastable peak for this process will be slightly wider[1,2] than that associated with formaldehyde loss. These postulates have been subjected to experimental test, the measured transition state energies, and kinetic energy releases, $T_{1/2}$ at half-height being shown in Table II.

There is good agreement between the proposed behavior of the ions and the experimental observations. The value of 0.2 kcal mol^{-1} observed for the kinetic energy release at half-height for CH_2O loss is very small; indeed, in the second field free region, this peak (at *m/e* 25.3) is scarcely wider than the low abundance main beam peaks at *m/e* 25 and 26.

A further consequence of the extension of the potential surface from **4** to **5** and **6** concerns the relative competition between loss of H_2O and CH_2O; in the case of **4**, no CH_2O loss is observed in metastable transitions, because the product ion is primary (ethyl cation) and possesses a relatively high heat of formation.[10] In progressing to **5** and **6** a new possibility occurs, namely the formation of a secondary cation; consequently CH_2O loss is able to compete with H_2O loss. Clearly, the insertion of another methyl group into the C_3 chain, yielding the ion **9**, would favor CH_2O loss still further, because this reaction can now lead to a tertiary cation. Assuming that H_2O loss can occur with an activation energy of ca. 10-20 kcal mol^{-1}, and that CH_2O loss may take place without reverse activation energy (this is plausible since the forward reaction is a simple bond-cleavage), the data of Table III are obtained.

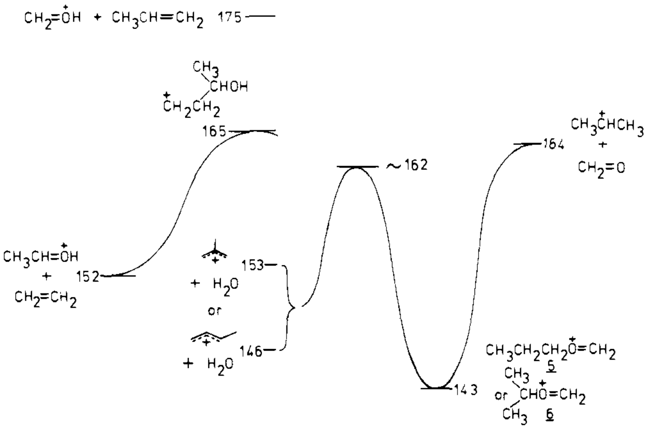


Figure 1. Some energy levels relevant to unimolecular dissociations of $CH_3CH_2CH_2O^+{=}CH_2$ (**5**) and $(CH_3)_2CHO^+{=}CH_2$ (**6**).

Table II. Transition State Energies and Kinetic Energy Releases (kcal mol^{-1}) at Half-Height Associated with Decomposition of **5** and **6**

Ion	Transition state energy for dissociation[a]		Kinetic energy release at half-height[b]	
	H_2O loss	CH_2O loss	H_2O loss	CH_2O loss
5	163	167	0.8	0.2
6	167	170	0.8	0.2

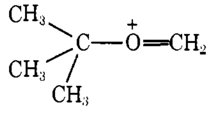
[a] Measurements made on metastable peaks (${}^1m^*$) and evaluated using the semilog plot method; see Appendix for comments on the accuracy of these values. [b] Measurements performed on a VG Micromass ZAB 2F instrument (magnetic sector preceding the electric sector).

Table III. Estimated Transition State Energies for H_2O and CH_2O Losses from Ions **4**, **5**, **6**, and **9**

Ion	ΔH_f[a] (est)[b]	Estimated transition state energy for dissociation	
		H_2O loss	CH_2O loss
4	148	176	191
5,**6**	143	162	164
9	138	148-158	139

[a] All values are in kcal mol^{-1}. [b] Estimated from ΔH_f (CH_3O^+ CH_2) = 153 kcal mol^{-1},[12] by assuming that each added methylene group lowers the heat of formation by 5 kcal mol^{-1}.

Consideration of the data of Table III reveals that for ion **9** the favored dissociation pathway should be CH_2O loss, and moreover, the elimination of CH_2O is almost thermoneutral. These factors are evidenced by two experimental observations: (i) generation of **9** via the fragmentation of suitable ethers



$(CH_3)_3C\overset{+}{O}{=}CH_2$

9, *m/e* 87

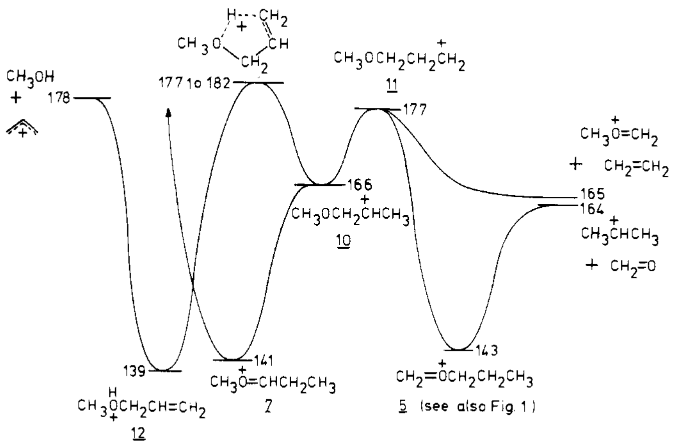
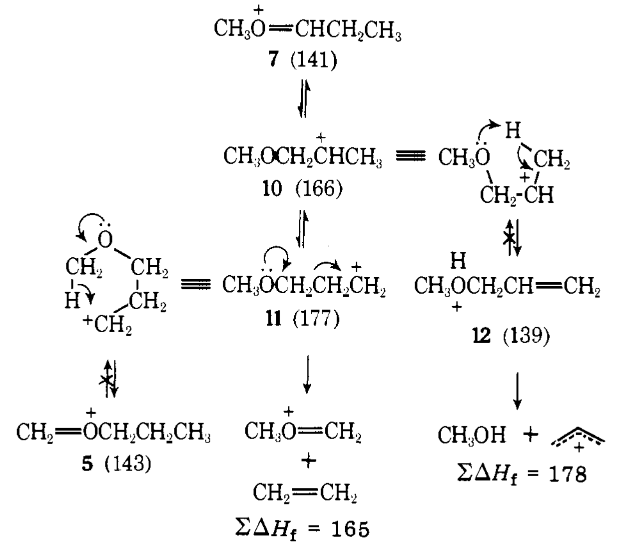


Figure 2. Proposed potential energy surface for the isomerization and dissociation of $CH_3CH_2CH{=}O^+CH_3$ (7).

yields only a small peak at *m/e* 87, thus suggesting that the ion formed by fragmentation of the molecular ion is not very stable, and (ii) CH_2O loss accounts for ~95% of the metastable ion current from *m/e* 87.

Ion 7. This ion is a higher homologue of **3**, and **3** is known to undergo rate-determining isomerization to **4** prior to unimolecular dissociations.[1] It could alternatively be considered to be a homologue of **2** in which the methyl substitution is made on oxygen rather than on carbon. It is known that the activation energy for loss of H_2O from **2** is 43 kcal mol^{-1},[2] while that needed to cause isomerization of **3** (followed by relatively fast dissociation[1]) is 63 kcal mol^{-1}.[1] Consequently, it is more reasonable to consider **7** as a higher homologue of **2** rather than **3**. On this basis, and on the basis that 1,2-hydride shifts will occur with activation energies equal to the reaction endothermicities (where such reactions are endothermic), the potential energy surface of Figure 2 is obtained (see also Scheme I). This surface also assumes that the barriers to hydride shifts via five- or six-membered ring transition states are small where such reactions are exothermic (**11** → **5**, **10** → **12**). Where heats of formation of reactants and intermediates are not directly accessible, they have been estimated by the methods outlined in the Appendix (usually based on isodesmic substitution[13]).

Scheme I



If the potential energy surface shown in Figure 2 does indeed represent approximately the true surface, then several consequences follow.

Table IV. Transition State Energies and Kinetic Energy Releases at Half-Height for Decomposition of Ion 7

Neutral lost	E_{TS}, kcal mol^{-1} [a]	$T_{1/2}$, kcal mol^{-1} [b]
H_2O	192	1.4
C_2H_4	189	1.4
CH_2O	191	2.0
CH_3OH	190	1.4
C_3H_6	*c*	2.6

[a] See Appendix for discussion of the accuracy of these values. [b] Measurements performed on the VG Micromass ZAB 2F instrument. [c] Too weak to measure accurately.

(i) The lowest energy pathway for decomposition of **7** is C_2H_4 loss via ion **11**; moreover, this ion approximates to the transition state for CH_2H_4 loss and consequently the reaction is expected to occur with the release of energy in passing from **11** to products.

(ii) Assuming that the configuration **11** is accessible from **7** via **10** on a reversible basis and that the rearrangement **11** → **5** is essentially irreversible (as it should be, see Figure 2), it follows that ethylene loss from partially deuterated analogues of **7** should involve only the atoms in the C_3 chain. Moreover, the decomposition of labeled ions should be explicable in terms of statistical selection of the necessary atoms from the C_3 chain together with a possible isotope effect.

(iii) CH_3OH loss should specifically involve the OCH_3 entity in labeled ions and, since the rate-determining step in the elimination of CH_3OH is probably isomerization to the protonated methyl allyl ether (**12**), the metastable peak for this process should be broadened owing to the presence of excess energy in the reacting configuration above that needed to promote dissociation.

(iv) Loss of CH_2O and H_2O may occur via isomerization of **7** to **5**, which is produced with considerably more energy than that needed for dissociation. In such circumstances, energy ceases to be the dominant parameter,[1] and "entropy" effects become important. The outcome of this is that dissociations requiring little rearrangement are greatly favored over those needing complex rearrangement. Hence, ions dissociating from **7** via rate-determining isomerization to **5** should show a preference for CH_2O loss over H_2O loss compared to ions dissociating directly from **5**. In addition to this trend, the metastable peaks for the processes starting from **7** should be broadened relative to those starting from **5** because a certain percentage of the excess energy present in rearranged ions of structure **5** will be partitioned as kinetic energy accompanying the dissociation.[1,14]

(v) Loss of CH_2O from deuterated analogues of **7** should show that the eliminated neutral contains two hydrogens from the OCH_3 entity.

(vi) The activation energies for decompositions of ions initially generated as **7** should reflect the energy needed to form **11** rather than the sums of the heats of formation of the requisite products. This condition may not apply to loss of CH_3OH, which probably proceeds via rearrangement of **10** to protonated methyl allyl ether; nevertheless the criterion for competition between decomposition channels[8] demands that the activation energy for this process be similar.

Experimentally, the following observations are made.

(i) C_2H_4 loss accounts for over 50% of the metastable ion current from **7**, and the metastable peak for this process, although not flat-topped (thus indicating the release of a relatively specific quantity of translational energy[15]), is broad. Using the relation between the kinetic energy release computed from the metastable peak width at half height ($T_{1/2}$, see Table IV) and the average kinetic energy release, T_{av}, namely $T_{av} = 2.69T_{1/2}$,[16] a value of 3.8 kcal mol^{-1} is obtained for T_{av}. This

Table V. Decomposition of Labeled Ions of Structure 7 via Loss of Ethylene

Ion structure	Neutral lost (A)[a]			Neutral lost (B)[a]		
	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2H_4	C_2H_3D	$C_2H_2D_2$[b]
$CH_3CH_2CD{=}O^+CH_3$	33	67	–	30	70	0
$CH_3CD_2CH{=}O^+CH_3$	7	53	40	5	53	42
$CH_3CH_2CH{=}O^+CD_3$	100	0	0	100	0	0

[a] Values normalized to a total metastable ion current of 100 due to loss of ethylene; (A), calculated ratios; (B), observed ratios. [b] A correction is applied to these figures to compensate for the component (ca. 12%) due to loss of CH_2O.

is in marked contrast to the corresponding value (0.8 kcal mol^{-1} [2]) associated with the dissociation of the lower homologue **2** via C_2H_4 loss from $C^+H_2CH_2CH_2OH$ (as expected, since this disssociation step is in contrast endothermic).

(ii) C_2H_4 loss involves specifically the hydrogen atoms in the C_3 chain. This is especially clear for $CH_3CH_2CH{=}O^+CD_3$, in which ethylene loss is due solely to C_2H_4, no significant loss of deuterated ethylene being observed in metastable transitions.[7] Assuming that the four hydrogens needed for ethylene elimination are selected at random from the C_3 chain and that no isotope effects are in operation leads to the predicted decomposition ratios for the specifically labeled ions shown in column A of Table V. The observed ratios[7] are given in column B. The data of Table V are in excellent agreement with the conclusions drawn from the potential surface.

(iii) Loss of methanol from labeled forms of **7** reveals that the OCH_3 unit is specifically involved; thus, for example, $CH_3CH_2CH{=}O^+CD_3$ loses only CD_3OH in metastable transitions.[7] Furthermore, there is a distinct preference[7] for selection of H rather than D from the C_3 chain in completing the $CH_3OH(D)$ neutral. This is possible evidence for an isotope effect in the transfer of the hydrogen from carbon to oxygen, which would be consistent with the postulate that this is the rate-determining step in elimination of methanol (see Figure 2 and Scheme I). The alternative explanation, that the hydrogens in the methyl group of the C_3 chain are specifically involved, is possible, but this postulate requires that equilibration of **7**, **10**, and **11**, leading eventually to hydrogen "scrambling"[17] in the C_3 chain, is slow compared to isomerization of **10** to **12**. In view of the apparently statistical selection of hydrogens from the C_3 chain in the ethylene loss reaction (see above), the latter explanation seems less likely. It should also be noted that, although there are no valid comparison processes, loss of methanol occurs with the release of a relatively large amount of kinetic energy (T_{av} = 3.8 kcal mol^{-1}), the metastable peak for this process being relatively broad.

(iv) Loss of CH_2O is indeed favored over H_2O loss starting from **7** (see Table I); whereas for **5**, H_2O loss is dominant, it is a very minor reaction for **7**, occurring to the extent of only ca 1%. This is strong evidence in favor of the postulate that H_2O and CH_2O losses occur only after **7** has undergone rate-determining isomerization to **5**. In addition, the metastable peaks for these reactions starting from **7** are considerably broadened relative to those starting from **5**. The change in the value of $T_{1/2}$ in the case of CH_2O elimination is particularly large, being an order of magnitude (see Tables II and IV).

(v) Loss of CH_2O from **7** does involve specifically the OCH_3 entity, one of these hydrogens being retained in the fragment ion. Thus, for instance, $CH_3CH_2CH{=}O^+CD_3$ eliminates only CD_2O in the formaldehyde loss transition.[7]

(vi) As may be seen from Table IV, the observed transition state energies for dissociations of **7** are all the same within experimental error (see Appendix for discussion of the accuracy of these values). Furthermore, these values are 10–15 kcal mol^{-1} higher than those measured for the decompositions of **5** or **6**.

In view of the agreement between the consequences of the potential surface depicted in Figure 2 and the observed behavior of **7**, it is very probable that the formulation of the dissociation of **7** over this surface is correct.

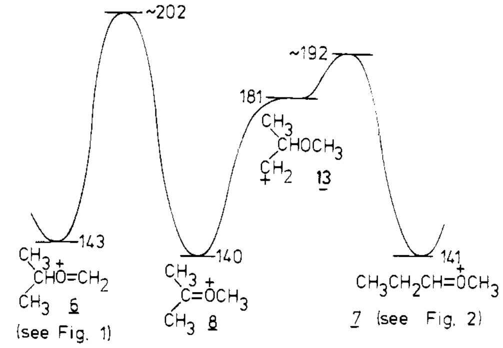
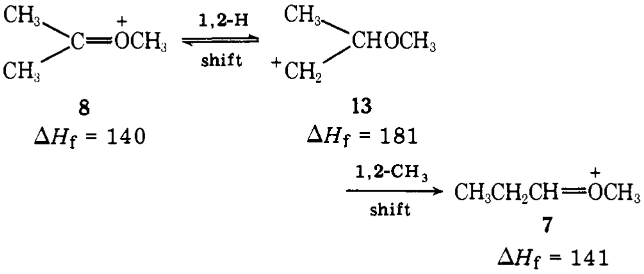


Figure 3. Pathways for rate-determining isomerization of $(CH_3)_2C{=}O^+CH_3$ (**8**).

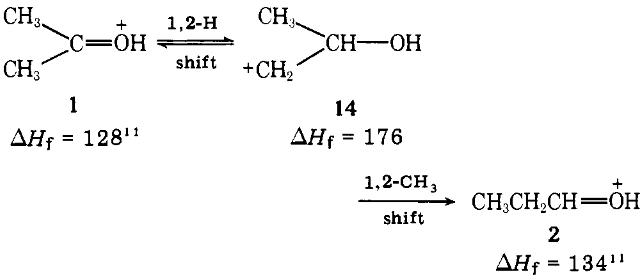
Ion 8. This ion could be considered as a homologue of either **1** or **3**, both of which are known to undergo rate-determining isomerization prior to unimolecular dissociations.[1,2] Consideration of the possible hydrogen rearrangements in **8** leads to the conclusions summarized in Scheme II and Figure 3. The heats of formation of the relevant species are estimated by use of the methods outlined in the Appendix and are given in kcal mol^{-1}.

Scheme II



It is evident from Scheme II that formation of **13** followed by a 1,2-methyl shift can lead to isomerization of **8** to **7**. This is exactly analogous to the behavior of **1** which is believed to undergo a rate-determining rearrangement to **2** via **14** (see Scheme III).[2] The measured activation energy for this rearrangement is some 10 kcal mol^{-1} higher than the estimated heat of formation of **14**.[2] Hence, a reasonable value for the transition state energy for rearrangement of **8** to **7** via **13** is ca. 190–195 kcal mol^{-1}.

Scheme III



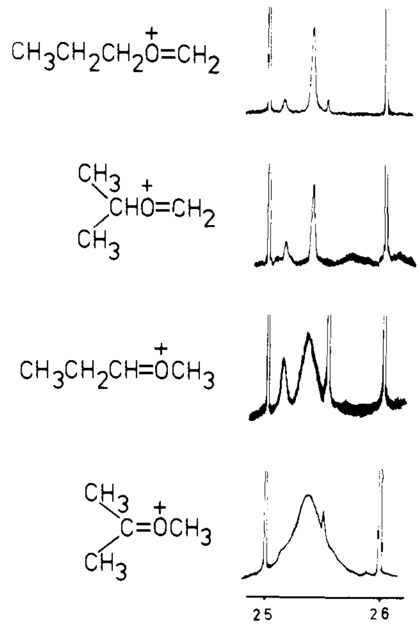
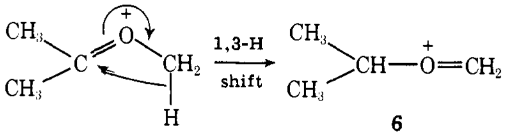


Figure 4. Metastable peaks (i.e., energy release profiles) at *m/e* 25.3 for CH_2O loss commencing from the ions shown; data recorded on an AEI MS 902 mass spectrometer operating at an accelerating voltage of 8 kV and an electron beam energy of 70 eV.

Alternatively, if **8** is considered as a homologue of **3** it would be expected to undergo a rate-determining isomerization to **6** via a symmetry-forbidden[18] 1,3-hydride shift (Scheme IV).[19]

Scheme IV



8

ΔH_f = 140

6

ΔH_f = 143

In the case of the lower homologue **3**, the activation energy for this process is measured as 63 kcal mol^{-1},[1] which leads to a transition state energy for rearrangement of **8** to **6** of ca. 202 kcal mol^{-1} (Figure 3).

Apart from these two isomerization pathways, no plausible reactions of **8** exist which might be expected to compete at energies appropriate to metastable transitions. It is reasonable to infer from this analysis that **8** will undergo rate-determining isomerization to *either* **6** or **7** *or* possibly *both*. Whichever of these possibilities is true, several general predictions concerning the decompositions of ion **8** should hold.

(i) The metastable peak widths for decomposition of ions generated as **8** should be greater than the corresponding values starting from **5**, **6**, or **7**.

(ii) The measured transition state energies should reflect the barrier(s) to isomerization rather than the sums of the heats of formation of the requisite products. A further point in this connection is that if the barrier to isomerization is relatively high, the ions formed by rearrangement of **8** may possess sufficient internal energies to undergo new dissociations in metastable transitions, these reactions being precluded for energetic reasons if the ions are generated directly.

(iii) Following rate-determining isomerization there should be a general preference for dissociations which do not involve further extensive rearrangement; thus water loss, for instance, is expected to be a minor reaction.

(iv) A specificity is expected in the decompositions of deuterated analogues of **8**. For instance, CH_2O and CH_3OH losses should involve specifically the original OCH_3 entity in **8**, while C_2H_4 loss should involve only the components of the C_3 chain. Experimentally, the following observations were made.

Table VI. Transition State Energies and Kinetic Energy Releases at Half-Height for Decomposition of Ion **8**[a]

Neutral lost	E_{TS}, kcal mol^{-1} [a]	$T_{1/2}$, kcal mol^{-1} [a&b]
CH_4	204	4.4
H_2O	204	1.7
C_2H_4	205	2.6
CH_2O	203	3.7
CH_4O	204	2.0
C_3H_4	*c*	3.0
C_3H_6	*c*	3.3

[a] The superscripts *a*, *b*, and *c* have the same significance as in Table IV.

(i) In all five cases where measurements could be made, the metastable peak widths at half-height are greater starting from **8** than from **7** (Tables IV and VI). In particular, that for loss of CH_2O is almost twice as broad as the corresponding peak for decomposition of **7**, which as noted above, is no less than ten times as broad as the peak for CH_2O loss from **5** and **6**.

In every reaction for which comparisons are possible, the peak widths at half-height are greater for decomposition of ions generated as **8** than the corresponding widths for *any* of the ions **5**, **6**, or **7**. The dramatic increases in the energies released in CH_2O loss on passing from **5** and **6** to **7** and **8**, as directly observable in the normal mass spectrum, are illustrated in Figure 4.

(ii) The measured activation energies for reaction of **8** are (a) the same within experimental error, and (b) greater than those for the analogous dissociations starting from any of the other ions considered. Furthermore, the reaction for loss of 40 mass units (presumably C_3H_4) which occurs *only* for ions originally generated as **8**, leads to products whose total heat of formation is at least 179 kcal mol^{-1} (i.e., $CH_3O^+H_2$, ΔH_f = 135[20] plus $CH_3C{\equiv}CH$, ΔH_f = 44[9] kcal mol^{-1}). Although this is a minor reaction (so minor that it was not detected in a previous study of $C_4H_9O^+$ [7]), its occurrence indicates that dissociation of **8** proceeds via intermediates with relatively high heats of formation.

(iii) The reactions undergone by **8** do show a general preference for those which can occur without considerable rearrangement after the postulated isomerization of **8**. Thus water loss is a relatively minor reaction (Table I), although, interestingly, it occurs to a greater extent than for **7**. This effect is not currently understood. Loss of CH_2O, which should be highly favored by "entropy" factors, is the major dissociation of **8**, occurring to the extent of almost 50%.

(iv) The expected specificity for loss of CH_2O and CH_4O is observed; thus $(CH_3)C{=}O^+CD_3$ loses only methanol CD_3OH and formaldehyde CD_2O;[7] loss of ethylene is observed to be almost exclusively C_2H_4, as expected if the components of the expelled neutral are selected from the C_3 chain.

There can be little doubt, on the basis of the evidence that we have presented, that $(CH_3)_2C{=}O^+CH_3$ undergoes rate-determining isomerization(s) prior to unimolecular decomposition. The occurrence of slow isomerizations in the field-free regions of mass spectrometers, followed by relatively fast dissociations of the product ions (which contain excess energy), provides a convenient experimental method for determining the barriers to unimolecular isomerizations. Moreover, such rate-determining isomerizations, being followed by dissociation in the field-free region of species with relatively large amounts of excess energy, are probably a major cause of broad metastable peaks. We refer here to those metastable peaks which correspond to the release of a wide range of energies, rather than those which are "flat-topped "or" dished" and correspond to a relatively specific release of kinetic energy (often characterizing the release of potential energy in the actual dissociation step).

Conclusions

Compelling evidence is presented which shows that rate-determining isomerizations precede dissociations for some isomers of $C_4H_9O^+$. In particular, ion **7** is shown to rearrange to **5**, and **8** to either **7** or **6** (or both). The intriguing possibility exists that in order for **8** to react it must undergo a rate-determining isomerization to **7** followed by a further rearrangement to **5**, the latter rearrangement being itself rate-determining for the dissociation of **7**. Construction of suitable potential energy surfaces for the ions permits much of the detailed chemistry, including labelling results, of the various isomers to be understood. In addition, qualitative predictions concerning the transition state energies and average kinetic energy releases for the various isomers can be made.

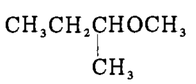
Experimental Section

The AP measurements were made using an AEI MS902 mass spectrometer, metastable dissociations being observed in the first field-free region by altering the electric sector voltage at constant accelerating voltage and magnetic field strength.[25] The internal calibrant used was the molecular ion of isopropyl chloride (AP = 10.78 eV[9]).

The ions **5**, **6**, **7**, and **8** were generated by ionization and fragmentation of the following ethers.

$$CH_3CH_2CH_2OCH_2CH_2CH_3 \xrightarrow[-\cdot CH_2CH_3]{-e} \underset{\mathbf{5}}{CH_3CH_2CH_2O^+{=}CH_2}$$

$$(CH_3)_2CHOCH_2CH_2CH_3 \xrightarrow[-\cdot CH_2CH_3]{-e} \underset{\mathbf{6}}{(CH_3)_2CHO^+{=}CH_2}$$



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_3 \xrightarrow[-\cdot CH_3]{-e} \underset{\mathbf{7}}{CH_3CH_2CH{=}O^+CH_3}$$

$$(CH_3)_3COCH_3 \xrightarrow[-\cdot CH_3]{-e} \underset{\mathbf{8}}{(CH_3)_2C{=}O^+CH_3}$$

The metastable peak widths at half height were determined using a reverse Nier-Johnson geometry (VG Micromass ZAB 2F) mass spectrometer. Our thanks are due to Dr. J. R. Kalman and Dr. R. P. Morgan for assistance in performing these measurements and to Professor J. H. Beynon and the Science Research Council (U.K.) for making the instrument available for our measurements.

Acknowledgment. We thank the SRC and Shell Research (U.K.) for financial support.

Appendix

Heats of Formation Sources and Appearance Potential Measurements. (i) **Appearance Potential Measurements.** These were made on metastable peaks and analyzed by the semilog plot method. It is acknowledged that there are systematic errors inherent in the determination of APs using this technique.[21,22] When considering the usefulness of these values two points should be kept in mind. (a) Although systematic errors occur, these may tend to cancel out (kinetic shift leading to a positive systematic error, and the normalization procedure to a negative systematic error). Certainly, negative systematic errors are not so large in the present work as to lead to negative reverse activation energies or other spurious conclusions. Furthermore, the reaction of interest is unambiguously measured; this is in contrast to determinations on daughter ions, where very small quantities of impurities can lead to spurious results. (b) The arguments presented in favor of the rate-determining isomerizations do not depend on the accuracy of the AP's. Even without the transition state energies the case would be strong. Nevertheless, the evidence derived from the AP's is relevant insofar as the transition state energies derived are consistent with the postulated potential surfaces.

(ii) **Heats of Formation.** In view of the unavailability of values for the open chain isomers discussed (e.g., **10**) these values are estimated using a method based on the isodesmic substitution[13] approach. Thus for **10**, the heats of formation of *n*-butane,[9] 2-butyl cation,[10] and *n*-propylmethyl ether[9] are known or readily estimated. Assuming that the replacement of the methyl group in 2-butyl cation by a methoxy radical produces no change in the heat of formation apart from that associated with the *inherent* stability of the two radicals results in a value of 156 kcal mol^{-1} for $\Delta H_f(\mathbf{10})$. A correction for the destabilizing effect of the electronegative oxygen atom in the methoxy group of 10 or 3 kcal mol^{-1} is made, depending on whether the oxygen is β or γ to the positive charge; this leads to a corrected value of 166 kcal mol^{-1} for $\Delta H_f(\mathbf{10})$. These values are consistent with calculations on similar systems.[13]

$CH_3CH_2C^+HCH_3$	$CH_3OCH_2C^+HCH_3$
$\Delta H_f = 183$	**10**, $\Delta H_f = 183 - (-30) + (-57)$ $= 156$
$CH_3CH_2CH_2CH_3$	$CH_3OCH_2CH_2CH_3$
$\Delta H_f = -30$	$\Delta H_f = -57$

Other cases where recourse has been made to estimation techniques are protonated allyl alcohols or ethers (here the proton affinities may be plausibly inferred from the corresponding saturated alcohols or ethers) and the oxonium ions **5–8**. In the latter case, a method similar to that used for the $C_nH_{2n+1}{}^+$ ions[23] is employed, using as a reference point $\Delta H_f(CH_3O^+{=}CH_2) = 153$.[12] Insertion of further methylene groups into this ion is assumed to affect the stability as follows. (a) Insertion into the saturated side chain produces only "spectator" stabilization (i.e., ΔH_f is reduced by 5 kcal mol^{-1}). This is analogous to the methods used to estimate heats of formation of neutrals.[24] (b) Insertion into the side chain which carries the positive charge is assumed to lower ΔH_f by 8 kcal mol^{-1} for the first insertion (primary cation stabilized by π-donation from oxygen, to the corresponding secondary cation) but by only 5 kcal mol^{-1} ("spectator" stabilization) for all subsequent insertions. Thus to obtain $\Delta H_f(\mathbf{8})$, an addition of -13 kcal mol^{-1} to $\Delta H_f(CH_2O^+CH_3) = 153$ kcal mol^{-1} is necessary, yielding $\Delta H_{f_{est}} = 140$ kcal mol^{-1}. It should be noted that the values obtained in this way are in qualitative agreement with previously reported values, where available.

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Excited-State Solvation vs. Ground-State Solvation in the n → π* Solvent Blue Shift of Ketones and Azo Compounds[1]

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Received July 14, 1976

Abstract: The enthalpies of transfer from one solvent to another of the n → π* Franck-Condon excited states of some ketones and azo compounds were determined by combining calorimetric and spectroscopic data. It was found that the enthalpy of transfer of the ground state and of the excited state into the blue shifted solvent could be either exothermic or endothermic. Examples of all three possible combinations were found and are described. The total solvation energy of the acetone n → π* excited state in six solvents is reported.

The blue shift of n → π* transitions on going to more polar solvents is one of the oldest and most reliable rules in the electronic spectroscopy or organic compounds.[2] It has been utilized to distinguish n → π* transitions.[3] One explanation of this phenomenon has been that the blue shift is caused by stabilization of the polar ground state in the more polar solvent. In those cases where the more polar solvent is a hydrogen bond donor, the formation of a hydrogen bond with the n-electrons is then considered to lower the energy of the n-orbital by an amount equal to the blue shift relative to a nonhydrogen bonding solvent.[4] On the other hand, part of the blue shift could arise from the destabilization of the Franck-Condon excited state in the hydrogen bonding solvent.[6]

These two possible effects can be distinguished and their relative importance evaluated by comparing the enthalpy of transfer from one solvent to another of the ground state, $\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$ with the energy of transfer of the Franck-Condon excited state, $\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, and seeing the extent to which the solvent blue shift, $\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, is influenced by changes in the solvation of the ground state and changes in the solvation of the excited state.

Results and Discussion

The enthalpy of solvent transfer of a compound, $\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, is obtained by measuring its heat of solution, ΔH_{S} in the two solvents of interest

$$\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \Delta H_{\text{S2}} - \Delta H_{\text{S1}}$$

With the solvent blue shift $\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, defined in the usual way as the difference in the excitation energies, $\Delta E^{\text{n}\rightarrow\pi^*}$, in the two solvents

$$\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 2}} - \Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}}$$

the energy of transfer of the Franch-Condon excited state, $\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$ is then readily calculated by eq 1.

$$\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} + \delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}} \quad (1)$$

Ketones. The blue shift of acetone and benzophenone on going from a nonpolar to a hydrogen bonding solvent (Table I and Figure 1) is evidently a cooperative effect. Comparable contributions to the blue shift are made by an *exothermic enthalpy of transfer into the protic solvent of the ground state and an endothermic enthalpy of transfer into the protic solvent of the excited state.* The former effect, attributable to the lowering of the n-orbital energy by hydrogen bonding, accounts for only half or less of the observed effect. The rest is attributable to Franck-Condon orientation strain,[5a] i.e., the fact that the carbonyl group dipole finds itself in a solvation shell which was optimal for the ground state, but is not optimal for the substantially diminished excited state carbonyl dipole.

The blue shifts of ketones on going from a dipolar aprotic to a polar protic solvent (Table I and Figure 2) present a very different picture. Enthalpies of transfer of both *ground states and excited states are endothermic into the protic ("blue") solvent.* The net interaction[6] between the carbonyl dipole and the solvent being less in the protic than in the dipolar aprotic solvent, the ground state contribution alone would predict a red shift of the n → π* transition on going to the protic solvent. The observed blue shift is caused by the fact that the orientation strain in the Franck-Condon excited state is evidently greater in the hydrogen bonding solvents than it is in the dipolar aprotic solvents. A possible way of accounting for this might be found in the difference in the nature of the solvent-solute dipole-dipole interactions present in the two kinds of solvents. The most plausible dipole-dipole alignment existing between a carbonyl solute and a dipolar aprotic solvent (a carbonyl or cyano compound) would include the side-by-side head-to-tail arrangement shown in Figure 3, left. On the other hand, the lowest energy interaction between a carbonyl group and a hydrogen bond donor is the linear head-to-tail arrangement (Figure 3, right).[7] Decrease of the solute dipole moment on going to the n → π* excited state would lead to a greater loss of electrostatic and polarization interaction energy in the linear case than in the side-by-side case. This would lead to a greater Franck-Condon orientation strain in the protic solvent than