Unimolecular Reactions of Isolated Organic Ions. The Importance of Ion–Dipole Interactions

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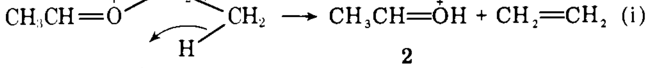
Abstract: Possible mechanisms are discussed for the decomposition of "onium" ions of general formula $R_1CH{=}X^+CR_2R_3CHR_4R_5$ (R = H or alkyl; X = O, S, NH, or NCH_3). For olefin elimination, to form $R_1CH{=}X^+H$ and $R_2R_3C{=}CR_4R_5$, a simple concerted, "four-center" process can account for a considerable proportion of ^{2}H-labeling results. However, such a mechanism would be symmetry forbidden and may be excluded on orbital symmetry and energetic grounds. A highly nonsynchronous mechanism is proposed, involving the formation of a loose complex of the carbonyl component, $R_1CH{=}X$, and the carbonium ion, $R_2R_3C^+CHR_4R_5$. Extensive stabilization of this intermediate is possible, by ion–dipole attraction; subsequent rearrangement can lead to a second complex, in which the carbonyl component and the incipient olefin are coordinated to a common proton. Isomerization of the nascent olefin fragment may take place, in the second complex, by protonation followed by deprotonation at a different site. Finally, the second complex breaks down, with elimination of an olefin or carbonyl component, the incipient fragment with the greater proton affinity remaining bound to the common proton.

Introduction

The slow, unimolecular reactions of organic ions in the gas phase may be studied conveniently using conventional magnetic-sector mass spectrometers.[2,3] The ion of interest is generated by ionization and fragmentation of suitable precursors; the decompositions of the ion may then be investigated by examining the metastable peaks which appear in the mass spectrum. These metastable peaks are produced by the eventual dissociation of ions that have survived for some 10^8 molecular vibrations. Consequently, there is sufficient time for essentially all energetically accessible reacting configurations to be attained. As a result, the ability of possible decay channels to compete against one another is largely determined by the relative activation energies for the requisite processes.[4] Therefore, careful observation of these metastable peaks may be used to discover and characterize the lowest activation energy decompositions of the ion of interest. Reference to primary deuterium isotope effects in representative cases[5,6] reveals that pathways with higher activation energies usually compete poorly, or are not observed. There are exceptions to this general rule, especially when H· or H_2 losses are involved;[7,8] however, these exceptions appear to be uncommon. Equally, the intervention of isolated electronic states is known,[9] but such interference is rare and need not be invoked in normal circumstances.

The shapes of metastable peaks contain useful information concerning the mechanism(s) whereby ions decompose.[10] In particular, it has been demonstrated that the dissociation of ions via concerted, symmetry-forbidden routes gives rise to a relatively large and specific kinetic energy release.[11,12] This shows that, when such reactions occur, a considerable proportion of the associated reverse activation energy is released as translational energy of the products.

The oxonium ion, **1**, loses predominantly C_2H_4 in reactions which produce metastable peaks;[13] the reaction may be rationalized by eq i. Suppose that this reaction were to occur in

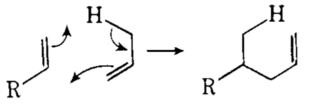


$$CH_3CH{=}\overset{+}{O}CH_2CH_2H \longrightarrow CH_3CH{=}\overset{+}{O}H + CH_2{=}CH_2 \quad (i)$$

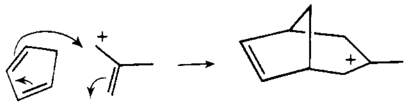
1 **2**

a concerted manner, as shown; it would be symmetry forbidden[14] and kinetic-energy release accompanying the dissociation would be expected. However, **1** loses C_2H_4 without the release of a large and relatively specific amount of kinetic energy. Instead, a range of kinetic-energy release occurs; the average[15] value, computed from the metastable peak width at half-height, is 3.5 kcal mol^{-1}. Furthermore, the observed reverse activation energy, based on appearance-potential measurements, is only 15 kcal mol^{-1}. Consideration of eq i reveals that the reverse reaction corresponds to addition of the π system of C_2H_4 across the O–H σ bond in protonated acetaldehyde, **2**. This is a [2 + 2] symmetry-forbidden process, with poor orbital overlap in the transition state. Therefore, it is difficult to understand why there is neither a large and specific kinetic energy release associated with the forward reaction nor a large, symmetry-imposed barrier to both forward and reverse reactions.

The orbital symmetry arguments are not invalidated either by the absence of appropriate molecular symmetry or by the presence of a charge in the species of interest. Thus, the occurrences of the "ene" reaction (eq ii) and the addition of allyl



(ii)



(iii)

cations to dienes (e.g., eq iii) are consistent with orbital symmetry considerations.[14] The importance of orbital symmetry in influencing the decomposition of isolated organic ions has been discussed previously.[11,12]

Nevertheless, the overall effect of the dissociation, as regards the origin of the hydrogen atom transferred to the protonated acetaldehyde fragment, is adequately represented by eq i. Thus, for example, **3** and **4** lose specifically C_2H_4 in metastable transitions; **5** eliminates mainly $C_2H_2D_2$ (83%) together with some C_2H_3D (17%); **6** loses mainly $C_2H_2D_2$ (90%) with some C_2HD_3 (10%).[13] The olefin component is selected exclusively from the intact ethyl group of **1**, with hydrogen transfer occurring to oxygen from predominantly the β-carbon atom, as required by eq i. However, either a small amount of exchange occurs between the hydrogen atoms bound to the α- and β-carbon atoms, or some transfer of an α-hydrogen atom takes place, via a different route.

$CH_3CD{=}\overset{+}{O}CH_2CH_3$ **3** $CD_3CH{=}\overset{+}{O}CH_2CH_3$ **4**

$CH_3CH{=}\overset{+}{O}CD_2CH_3$ **5** $CH_3CH{=}\overset{+}{O}CH_2CD_3$ **6**

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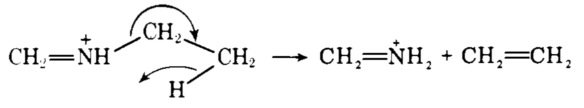
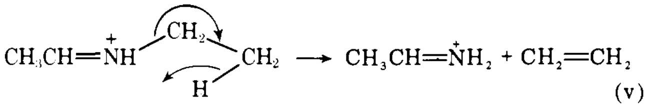
Precisely similar behavior is encountered in the decomposition of the nitrogen analogues 7[16,17] and **8**. Both these ions eliminate exclusively C_2H_4 in metastable transitions, eq iv and v, respectively. In the case of **7** the forward activation energy



$$CH_2{=}\overset{+}{N}HCH_2CH_2H \rightarrow CH_2{=}\overset{+}{N}H_2 + CH_2{=}CH_2 \quad \text{(iv)}$$

7



$$CH_3CH{=}\overset{+}{N}HCH_2CH_2H \rightarrow CH_3CH{=}\overset{+}{N}H_2 + CH_2{=}CH_2 \quad \text{(v)}$$

8

is larger (70[17] kcal mol^{-1}), but the associated kinetic energy, released upon C_2H_4 loss, is relatively small (average value = 4.3 kcal mol^{-1}) and is not specific. The results of ^{2}H-labeling studies establish that eq iv proceeds with transfer of a β-hydrogen atom to nitrogen. Thus, for instance, **9** and **10** eliminate exclusively C_2H_4, whereas an approximately 1:1 mixture of **10** and **11** loses 55% C_2H_4 (from **10**), 45% $C_2H_2D_2$ (from **11**), but no C_2H_3D.[16] Similarly, ^{2}H-labeling studies on **8** establish

$CH_2{=}\overset{+}{N}DCH_2CH_3$ **9**

$CD_2{=}\overset{+}{N}HCH_2CH_3$ **10**

$CH_2{=}\overset{+}{N}HCD_2CH_3$ **11**

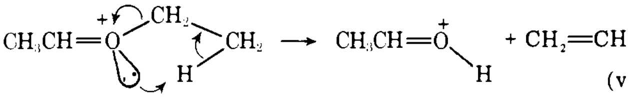
that a hydrogen atom is transferred from the ethyl group to nitrogen, with a preponderance of β-hydrogen transfer. Ion **12** eliminates exclusively C_2H_4, while **13** loses mainly $C_2H_2D_2$

$CH_3CH{=}\overset{+}{N}DCH_2CH_3$ **12**

$CH_3CH{=}\overset{+}{N}HCH_2CD_3$ **13**

(88%) with a minor fraction of C_2HD_3 (12%). Moreover, only a relatively small and nonspecific kinetic-energy release (1.2 kcal mol^{-1}) accompanies C_2H_4 loss from **8**.

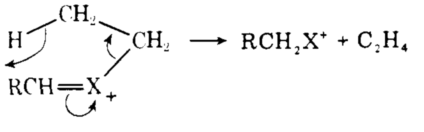
The parallel behavior of these oxonium and analogous immonium ions excludes a general explanation of this type of reaction, which involves participation of the oxygen lone pair, in the olefin elimination from oxonium ions such as **1**, eq vi. For



$$CH_3CH{=}\overset{+}{O}CH_2CH_2H \rightarrow CH_3CH{=}\overset{+}{O}H + CH_2{=}CH_2 \quad \text{(vi)}$$

oxonium ions, this mechanism could in principle avoid the symmetry-imposed barrier; however, in the nitrogen analogues, **7** and **8**, no such lone pair is available. Olefin elimination appears to be a general process for onium ions containing oxygen, nitrogen, or sulfur; hence participation of oxygen (or sulfur) lone pairs, as depicted in eq vi, cannot be an adequate general explanation.

Finally, a five-membered-ring transition state, resulting in hydrogen transfer to carbon, eq vii, can also be ruled out. In

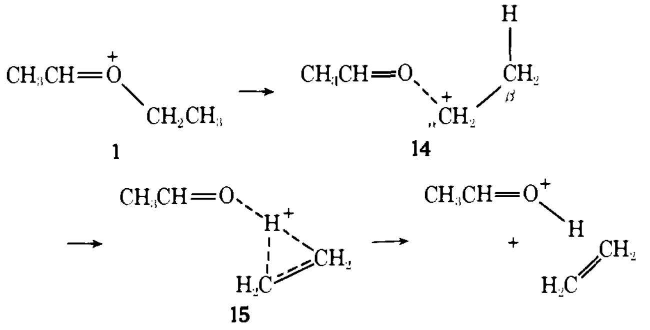


$$RCH{=}\overset{+}{X}CH_2CH_2H \rightarrow RCH_2X^+ + C_2H_4 \quad \text{(vii)}$$

X = O, NH, S
R = H or alkyl

the case of the oxonium ion **1** (X = O; R = CH_3), the ionic product would be $CH_3CH_2O^+$, which is known to undergo facile 1,1 elimination of H_2, yielding $CH_3C^+{=}O$.[18] In contrast, the ionic product of C_2H_4 loss from **1** possesses a high energy barrier toward decomposition. This product ion only decomposes further when C_2H_4 loss occurs as a high-energy reaction in the ion source. Moreover, even then, the observed dissociations are loss of CH_4 and C_2H_2 in a ratio characteristic[19] of protonated acetaldehyde, **2**. In addition, the total heat of formation of the products ($CH_3CH_2O^+$ and C_2H_4) which would be formed via eq vii is estimated to be 200 kcal mol^{-1}.[18] In fact, the measured transition-state energy for C_2H_4 loss from **1** is much lower (167 kcal mol^{-1}),[20] thus excluding eq vii. Similar arguments lead to the conclusion that **7** produces $CH_2{=}NH_2^+$, rather than CH_3NH^+, and that **8** yields $CH_3CH{=}NH_2^+$, rather than $CH_3CH_2NH^+$, at threshold.

Scheme I



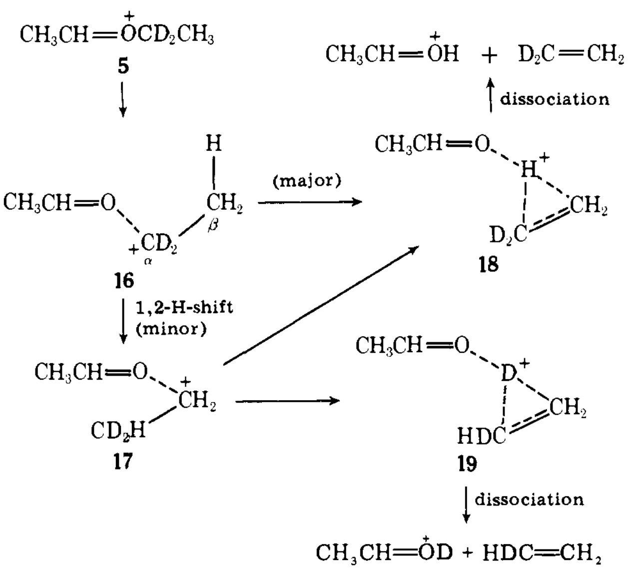
In summary, eq i, iv, and v seem to represent these reactions adequately, at least at a naive level of sophistication; however, orbital-symmetry and energetic considerations lead to the plausible hypothesis that the reactions must be highly nonconcerted. Hence, a more precise description of the dissociation formulated as eq i is possibly that given in Scheme I. First, the C-O σ bond in **1** is stretched, thus producing a loose complex, **14**, of acetaldehyde and the ethyl cation. Second, a slight reorganization of **14** leads to another complex, **15**, in which a β-hydrogen atom becomes a proton coordinated to acetaldehyde and ethylene. Finally, the latter complex breaks down, with the incipient carbonyl component or olefin having the greater proton affinity retaining the proton.[21] In this example, acetaldehyde has a greater proton affinity (185[22] kcal mol^{-1}) than ethylene (160[23] kcal mol^{-1}); consequently, ethylene is lost. The intermediates involved in Scheme I are quite plausible. The complex **14** is stabilized, relative to the separated cation and aldehyde, by an ion-dipole attraction. In representative oxonium ions, experimental evidence shows that the stabilization may amount to approximately 15-25 kcal mol^{-1}, depending upon the dipole moment[24] of the aldehyde or ketone.[25] The second complex, **15**, may be considered to be a protonated aldehyde (or ketone, for homologues of **15**) in which the proton bound to oxygen is "solvated" by the π electrons of ethylene. Such a complex would be expected to be stablized, relative to the isolated protonated aldehyde and olefin, possibly by several kcal mol^{-1}. Thus, for example, the π coordination of ethylene to Li^+ releases ca. 20 kcal mol^{-1}.[26]

The mechanism depicted in Scheme I obviates the difficulty in understanding the reverse reaction. In the concerted process, eq i, C_2H_4 would initially have to add across an O-H σ bond. However, in Scheme I, the first interaction in the reverse reaction is the coordination of the π electrons of ethylene to the proton attached to oxygen in protonated acetaldehyde. This interaction, leading to the complex **15**, ought to be exothermic. Consequently, bad orbital interactions are circumvented, and the absence of a large and relatively specific kinetic energy release in the forward reaction is explained.

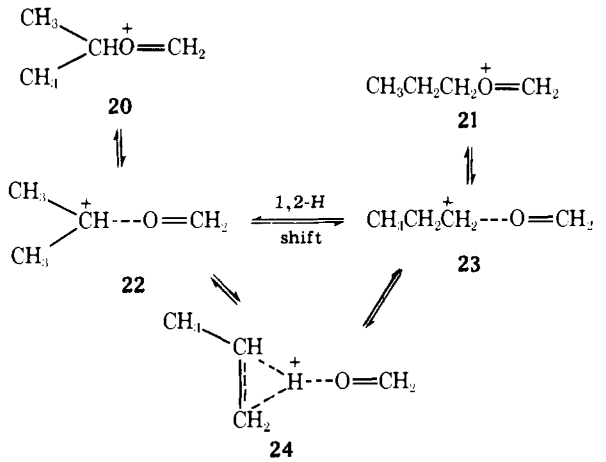
Further experimental evidence in favor of the mechanism depicted in Scheme I may be cited as follows.

(i) The intermediacy of a complex such as **15**, in which a carbonyl compound and an olefin share in "solvating" a common proton, is supported by the observed decomposition channels for numerous onium ions. On the assumption that the incipient carbonyl compound or olefin with the greater proton affinity retains the proton, the losses of aldehydes or olefins

Scheme II



Scheme III

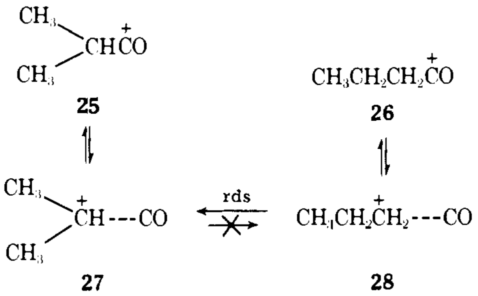


from a large range of oxonium ions may be either rationalized or predicted correctly.[21] In addition, the observation that the nitrogen analogues eliminate almost exclusively the olefin component may be understood in terms of the relatively high proton affinities of imines, compared to olefins.[17] This in turn reflects the greater basicity of nitrogen bases in comparison with oxygen bases.

(ii) Poor competition of a 1,2-hydride shift (**16** → **17**) in the incipient ethyl cation of **16**, with dissociation (**16** → **18** → products), accounts for the limited exchange between the α- and β-hydrogen atoms of **5**. This in turn explains the small percentage of apparent α-hydrogen transfer from carbon to oxygen,[13] Scheme II. Similar arguments can be employed for **6** and the nitrogen analogue, **13**.

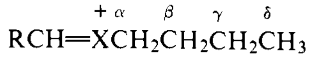
(iii) In higher homologues of **1**, where the nascent carbonium ion is composed of three or more carbon atoms, interconversion of isomeric side chains may occur via complexes analogous to **14** and **15**. For instance, the similar behavior of **20** and **21**, which lose H_2O and CH_2O in almost the same ratios (7:1 and 5:1, respectively), may be understood in this way, Scheme III. Starting from **21**, stretching of the C–O σ bond leads to **23**, which is a loose complex of the *n*-propyl cation and formaldehyde. An exothermic 1,2-hydride shift in **23** results in the formation of **22**, which is a loose complex of the isopropyl cation and formaldehyde. In this case, the ion-dipole interaction is sufficiently strong to prevent dissociation of **22**, even though the rearrangement **23** → **22** would be expected to release some 18 kcal mol^{-1} of potential energy. Consequently, **20** and **21** may interconvert, via **22** and **23**, at energies below that needed to promote dissociation.[20,25] The complex **24** may also be accessible to **20** and **21**, via reorganization of **22**, or **23**, or both. It may be noted, in passing, that **20** and **21** eliminate CH_2O rather than C_3H_6 in slow reactions; this is expected from the model because the proton affinity of propene (179[23] kcal mol^{-1}) is greater than that (175[22] kcal mol^{-1}) of formaldehyde.

Scheme IV



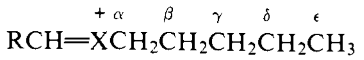
(iv) In some instances the rearrangement of incipient carbonium ions, to give more stable isomers, is the rate-determining step in dissociation of the ion in question. Particularly pertinent examples of this situation are to be found when the initial bond stretching produces an incipient cation, together with a netural molecule having only a small dipole moment. Thus, in the ions **25** and **26**, where carbon monoxide is substituted for formaldehyde in **20** and **21**, respectively, rate-determining rearrangement of **26** → **25** takes place,[27] Scheme IV. Clearly, the ion-dipole interactions are of fundamental importance in rearrangements of this general nature. Formaldehyde has a relatively large permanent electric dipole moment (μ = 2.3 D[24]); hence, significant stabilization of complexes such as **22** and **23** can occur. In contrast, carbon monoxide has an almost negligible dipole moment (μ = 0.1 D[24]); consequently, almost no stabilization of the analogous complexes **27** and **28** is possible.

(v) Previous studies have been made on oxygen,[28,29] nitrogen,[30] and sulfur[31] onium ions of general formulas **29** and **30**.



$$\mathrm{RCH{=}\overset{+}{X}\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3}$$

29



$$\mathrm{RCH{=}\overset{+}{X}\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_2\overset{\epsilon}{C}H_3}$$

30

R = alkyl; X = O, NCH_3, or S

These ions are known to undergo loss of C_4H_8 and C_5H_{11}, respectively, in the ion source (i.e., in relatively fast dissociations, which can take place with larger excess energy in the transition state). The extent to which the hydrogen atoms, bound initially to the α, β, γ, δ (and ε) carbon atoms, are transferred to the heteroatom, when C_4H_8 (or C_5H_{10}) loss occurs, is known from ^2H-labeling studies; these data are summarized in Table I. Apparently, the hydrogen atoms in every position in the butyl (or pentyl) side chain participate to some extent in the transfer of hydrogen from carbon to the heteroatom. This effect was explained originally as involving competing mechanisms through transition states of various ring sizes.[28,30,31] However, the apparent multiple origin of the transferred hydrogen atom persists even in metastable transitions.[29] This implies that all the proposed reactions, occurring through different transition states (three- to seven-membered rings), have nearly identical activation energies. In slow reactions of a representative oxonium ion, **31** (**29**, R = CH_3; X = O), the hydrogen transferred originates mainly from the β- and γ-carbon atoms.[29] Moreover, the metastable peaks for these two processes are identical

Table I. Origin of the Hydrogen Atom Transferred to the Heteroatom When C_4H_8 (or C_5H_{10}) Is Eliminated from Various Onium Ions of Structure **29** (or **30**)

	original hydrogen atom site	heteroatom (X)		
		S	O	NCH_3
C_4H_8 loss (**29**)	α	15	16	10-26
	β	31	35	21-25
	γ	36	40	23
	δ	15	29	17
C_5H_{10} loss (**30**)	α	10	10	14-18
	β	25	26	22-26
	γ	28	25	19
	δ	28	29	20
	ϵ	6	1-10	6

in shape.[29] This seems inconsistent with two distinct mechanisms, involving four- and five-membered-ring transition states. Rather, the result suggests strongly that only one mechanism is operating for hydrogen transfer to oxygen, but that this transfer process occurs after hydrogen migrations have occurred between the carbon atoms of the butyl or pentyl chains.

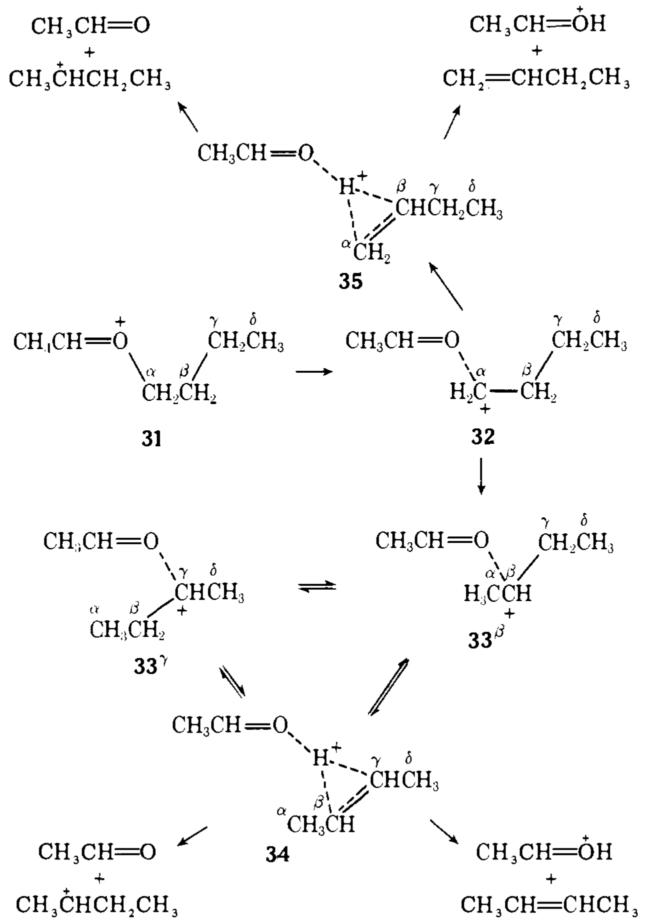
$$CH_3CH{=}\overset{+}{O}CH_2CH_2CH_2CH_3$$

31

Even more compelling evidence is available from a study of the origin of the hydrogen transferred in **31** as a function of ion lifetime. Longer ion lifetimes correspond to lower average internal energies and smaller excess energies in the transition states for decomposition. In fast reactions, elimination of C_4H_8 from **31** involves hydrogen transfer, to an important extent, from each of the α-, β-, γ-, and δ-carbon atoms (16, 29, 40, and 15%, respectively, in source reactions at 70 eV).[29] However, in the decomposition of longer lived metastable ions, the transferred hydrogen atom originates approximately equally, and almost exclusively, from the β- and γ-carbon atoms (5, 46, 45, and 4%, respectively, in the second field-free region).[29] This result can be accommodated by the nonconcerted mechanism, involving complexes, in this case, of acetaldehyde and the butyl cation. As the initial complex, **32**, of acetaldehyde and the *n*-butyl cation develops, rearrangement of the incipient carbonium ion can occur, via a 1,2-hydride shift, to give another complex, **33**$^\beta$, of the *sec*-butyl cation and acetaldehyde. This complex may then undergo a degenerate rearrangement, via a 1,2-hydride shift in the incipient *sec*-butyl cation, to yield **33**$^\gamma$. Rapid equilibration of **33**$^\beta$ and **33**$^\gamma$ would render equivalent all three hydrogen atoms attached to the β- or γ-carbon atoms. A slight reorganization in either **33**$^\beta$ or **33**$^\gamma$ results in formation of the aldehyde-olefin complex **34**; dissociation of this complex may now occur to produce protonated acetaldehyde and 2-butene. Alternatively, reorganization of the complex **32** may take place to give an aldehyde-olefin complex **35**; decomposition of this species can lead to loss of 1-butene and the formation of protonated acetaldehyde.

The route for 2-butene loss from **31**, via **32**, **33**, and **34**, permits the original two γ-hydrogen atoms and one of the β-hydrogen atoms of **31** to become equivalent, prior to any one of these hydrogen atoms being transferred to oxygen. The other β-hydrogen atom is removed because it is specifically transferred to the α-carbon atom in the 1,2-hydride shift, leading from **32** to **33**$^\beta$. Consequently, if this mechanism operated exclusively, a ratio of 1:2 would be expected for the relative abundance of β- and γ-hydrogen transfer to oxygen. The observed ratio is close to 1:1. However, the expected preference for γ-hydrogen transfer could be offset if a fraction of the complex **32** rearranged to **35**. In this case, a different aldehyde-olefin complex is formed, and a β-hydrogen atom is now transferred specifically to oxygen. In order to account for the experimental 1:1 ratio for β- and γ-hydrogen transfer to oxygen, one-quarter of ions **32** must isomerize to **35** and three-quarters to **33**.

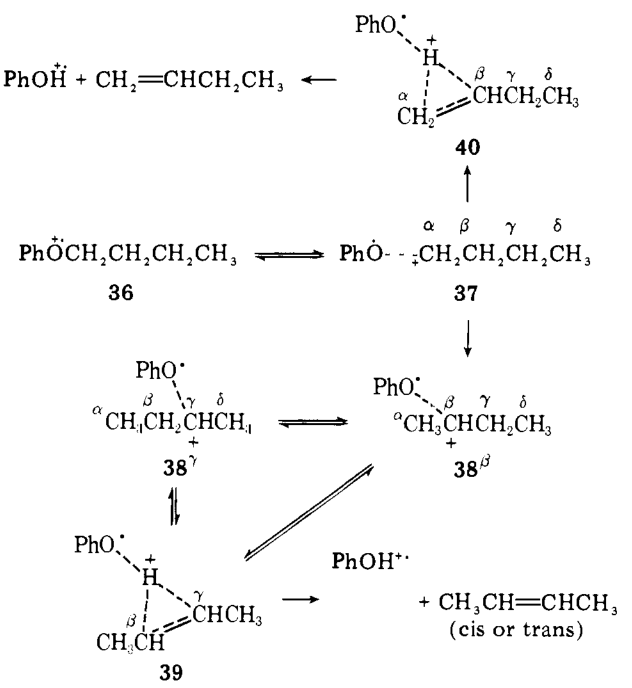
Scheme V



While the mechanisms depicted in Scheme V may appear somewhat complicated, there is no doubt that much of the ^2H-labeling data may be understood in these terms. For example, the degenerate rearrangement **33**$^\beta$ $\rightleftharpoons$ **33**$^\gamma$ occurs because the two isomeric ions contain an incipient *sec*-butyl cation. Further 1,2-hydride shifts, leading to extensive interchange of the α- and δ-hydrogen atoms with the β- and γ-hydrogen atoms, are improbable. This is because such rearrangements lead to systems containing incipient *n*-butyl cations; this is energetically unfavorable. Therefore, in a general case, the hydrogen atom transferred to oxygen ought to originate mainly from the nonterminal carbon atoms in the alkyl side chain. This is clearly the case, even for relatively fast dissociations, Table I.

It is significant that the detailed mechanism given in Scheme V requires that both 1-butene and 2-butene (but no 2-methylpropene) be eliminated from **31**. Loss of isomeric butenes occurs from the molecular ions of ionized phenyl *n*-butyl ether (**36**).[32] This reaction may well be related and could be formulated as shown in Scheme VI; these mechanisms are analogous to those suggested in Scheme V. Experimentally, loss of 1-butene, *trans*-2-butene, and *cis*-2-butene is observed in the ratio 2:1:1.[32] In this elegant work, the isomeric butenes were identified, following electron impact induced decomposition of **36**, using a flow reactor.[32] This is strong evidence that competition between **37** → **38**$^\beta$ and **37** → **40** can occur at energies appropriate to the decomposition of **36**. The fact that no 2-methylpropene is lost from **36** shows that the incipient *n*-butyl or *sec*-butyl cations in **37** and **38** do not rearrange to branched isomers. This would be expected since *sec*-butyl cation exists in a potential-energy well[33] and is stable on the microsecond time scale.[34]

Scheme VI



The similar behavior of **36** and **31**, referred to above, is evidence in favor of the proposed mechanisms in Scheme V. In particular, the observation of elimination of isomeric butenes from **36** supports the hypothesis that more than one isomer of butene is lost from **31**. Moreover, the apparent general operation of this type of mechanism suggests that ion-dipole interactions are most important in the unimolecular reactions of organic ions. These ion-dipole interactions have already been invoked in the decomposition of relatively large molecules, for example, some steroid derivatives.[35]

Further evidence in support of the general mechanism may be derived from a number of sources, including analysis of the dissociations observed for homologous oxonium[36,37] and immonium ions.[38]

Conclusion

Intermediates involving the coordination of a carbonyl molecule to an incipient carbonium ion are shown to be of importance in the unimolecular reactions of various onium ions. These intermediates are extensively stabilized by ion-dipole interactions. Rearrangement of the incipient carbonium ion may occur, to give thermodynamically more stable isomers. Alternatively, isomerization may take place to yield other complexes, in which an olefin and the carbonyl compound are both bound to a common proton. These complexes may break down, with the elimination of the olefin or the carbonyl compound.

Experimental Section

The ethers and amines required were synthesized by conventional methods. All mass spectra were obtained using an AEI MS902 double-focusing mass spectrometer, operating at a source pressure of $\sim 10^{-6}$ Torr, with an ionizing electron beam energy of nominally 70 eV. Compounds were admitted into the source through the all glass heated inlet system (AGHIS).

The relative abundances of competing decay routes were determined by the areas of the corresponding metastable peaks. Average kinetic energy release values were computed from the width at half-height of these peaks; no correction was applied for the width of the main beam. In all cases where comparisons were to be made between isomeric ions produced from different precursors, the measurements were made consecutively, under identical operating conditions.

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References and Notes

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