Energy Barrier to Symmetry-Forbidden 1,3-Hydrogen Shifts in Simple Oxonium Ions. Metastable Peaks from Fast Dissociations

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Abstract: Previous work has established that a similar channeling ratio between two or more competitive decomposition pathways, as measured by metastable peak abundance ratios, is a useful criterion for structural identity of ions from which the dissociations occur. It is now shown that $CH_3CH{=}O^+CH_3$ (**2**) and $CH_3CH_2O^+{=}CH_2$ (**1**) both decompose via **1**, but that the barrier to the isomerization **2** → **1** is high (58 kcal mol^{-1}) and rate determining. Under these circumstances, **1** is produced with internal energy considerably in excess of that necessary to promote its unimolecular decomposition (23 kcal mol^{-1}). Hence, ions generated as **2** undergo a "metastable isomerization" followed by fast unimolecular dissociation ($k > 10^6$ sec^{-1}) in a field-free region. The isomerization **2** → **1** is most simply formulated as a symmetry-forbidden 1,3-hydrogen shift, although it is also possible to achieve the same result via successive 1,2- and 1,4-hydrogen shifts. Symmetry-forbidden 1,3-hydrogen shifts occur prior to unimolecular decomposition of $CH_2{=}O^+{-}CH_3$ via loss of methane, which requires 83 kcal mol^{-1}. It is concluded that the barrier to a symmetry-forbidden 1,3-hydrogen shift in this type of oxonium ion lies in the range 58–83 kcal mol^{-1}. Measurements of the metastable peak width for the decomposition of **1**, formed from **2**, show that the portion of the excess energy present in the reaction coordinate at the instant of decomposition is comparable to that calculated on a classical basis (which assumes that the excess energy may be statistically distributed into the reaction coordinate).

The mass spectrum of an organic compound potentially contains a wealth of information of interest to the organic chemist in terms of the unimolecular reactions undergone by cations and cation radicals in the absence of solvent. Yet it has often proved difficult to extract this information in an unambiguous manner. A classical method for obtaining information about the structure of decomposing ions originates in the work of Rosenstock et al.[1] These authors compared the behavior of hexyl ions ($C_6H_{13}^+$) prepared by electron-impact ionization and decomposition of a variety of normal alkanes, *n*-hexyl bromide, and di-*n*-hexyl ether. In slow reactions (metastable transitions), allowing of the order of 10^8 vibrations before decomposition, the $C_6H_{13}^+$ ions react via the following pathways:

$$C_6H_{13}^+ \longrightarrow C_4H_9^+ + C_2H_4$$
$$C_6H_{13}^+ \longrightarrow C_3H_7^+ + C_3H_6$$

Appearance-potential measurements indicate that the energy requirements of the two reaction channels are within 5–7 kcal mol^{-1} of each other, and this suggests that the reactions are in competition. The competition between the two channels (as measured by the abundance ratio of the metastable transitions) is a constant indicating that the ions are decomposing from the same structure, or structures, in all cases. Moreover, this experiment establishes that the different methods of preparation of the $C_6H_{13}^+$ ions are unimportant, despite the fact that these different methods will presumably lead to somewhat different internal-energy distributions of the $C_6H_{13}^+$ ions. This factor appears to be unimportant because the rate constant for reaction rises very rapidly with energy just above the threshold for reaction (Figure 1a); consequently, the range of rate constants weighted in metastable transitions ($k = 10^4$–10^6 sec^{-1}) corresponds to a relatively narrow range of energies (ΔE) just in excess of the activation energy. In the hypothetical case where this band of energies is infinitely narrow, the energy distribution of the ions becomes irrelevant; it appears that normally the range of energies weighted in metastable transitions is sufficiently narrow to make variations in the internal-energy distributions unimportant.[2]

The same ratio of competing metastable transitions is observed even if the $C_6H_{13}^+$ ions are produced from secondary or tertiary bromides,[3] indicating that the same decomposing ions are produced from ions which are initially produced as secondary and tertiary cations. Evidently, the energy required for isomerization between the various cations is less than that required for unimolecular decomposition of $C_6H_{13}^+$, and so decomposition occurs from a common state, or states, although the criterion of competing metastable transitions does not in itself determine the structure of the decomposing ion (Figure 1b).

The criterion of competing metastable transitions has been usefully applied in many studies, one of the most notable and earliest establishing that $C_2H_5O^+$ ions generated from $HOCH_2CH_2Y$ and $CH_3CH(OH)Y$ decompose over the same potential surfaces by competitive loss of CH_4 and C_2H_2, whereas those from CH_3OCH_2Y decompose over a different potential surface by essentially exclusive loss of CH_4.[4] The criterion is clearly a useful one and, where isomerization to and decomposition from a common intermediate is indicated, appearance-potential measurements for the fragmentation can give upper limits for the isomerization energy, which may be useful in comparison with theoretical calculations. Our present study is concerned with application of this approach to the isomeric oxonium ions **1** and **2**

$$CH_3-CH_2-\overset{+}{O}{=}CH_2 \qquad CH_3-CH{=}\overset{+}{O}-CH_3$$

1 **2**

(generated, for example, via methyl radical loss from ionized diethyl ether and methyl isopropyl ether, respectively), which leads us to the conclusion that metastable peaks can sometimes arise from fast decompositions ($k \gg 10^6$ sec^{-1}), even in the absence of collision activation.

Discussion

Comparisons of the unimolecular chemistry of isomeric $C_3H_7O^+$ ions (e.g., **1** and **2**) are numerous.[2,5-8]

There is clear evidence that, as expected, the oxonium ions **1** and **2** do correspond to stable species formed in potential wells since their "mass spectra" produced by collision-induced decomposition (which will include a weighting of both "fast" and "slow" processes) are quite different;[8] since the oxonium ions behave differently after lifetimes of

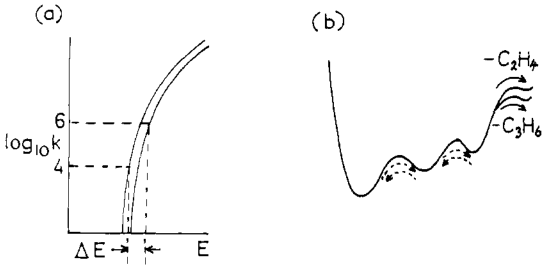


Figure 1. Schematic illustrations of (a) k vs. E curves for competing reactions, indicating relatively narrow energy range (ΔE) giving rise to metastable transitions; and (b) potential surfaces for isomerization (··→) and decomposition (→) of $C_6H_{13}^+$ ions. In the schematic illustration, the number of potential barriers to isomerization is arbitrarily chosen, as is the loss of C_3H_6 and C_2H_4 from the same, and highest energy minimum.

Table I. Relative Abundance (%) of Metastable Transitions for Decomposition of Ions Generated as 1 and 2[a]

Ion	Field-free region	$[m^*_{H_2O}]$	$[m^*_{C_2H_4}]$	$[m^*_{CH_2O}]$
1	1st[b]	70	30	0
1	2nd	95	5	0
2	1st[b]	1.4	77	22
2	2nd	1.7	86	12

[a] Relative intensities refer to relative metastable peak areas. [b] Determined by the refocusing technique in which the accelerating voltage is increased at constant electrostatic analyzer voltage.

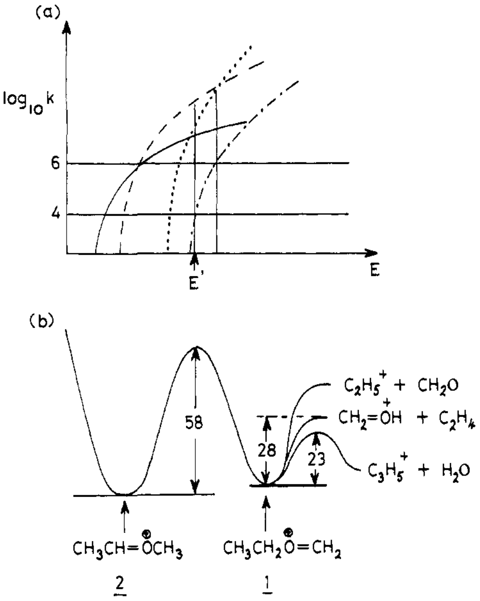


Figure 2. Schematic illustrations of (a) k vs. E curves for the rate-limiting step prior to H_2O loss from **1** (—), rate-limiting step prior to C_2H_4 loss from **1** (- - -), direct CH_2O loss from **1** (· · ·), and the isomerization **2** → **1** (·· ··); and (b) potential surfaces for isomerization of **2** → **1** and unimolecular decomposition of **1**; the reaction **1** → $C_3H_5^+$ (and perhaps **1** → $CH_2{=}O^+H$) involves more than one step, but the barriers shown are the rate-determining ones. Activation energies are given in kcal mol^{-1} and are estimated to be accurate within ±3 kcal mol^{-1}.

the order of microseconds, they must be a potential barrier to their interconversion.

Tsang and Harrison[5] have determined the metastable abundance ratios for decomposition of ions generated as **1** and **2**, for example, via fragmentation of diethyl ether and methyl isopropyl ether, respectively. Ions initially generated as **1** competitively lose H_2O and C_2H_4 in metastable transitions, while those initially generated as **2** competitively lose H_2O, C_2H_4, and CH_2O. The metastable abundance ratios observed in our work are recorded in Table I and are in qualitative agreement with those of Tsang and Harrison.[5]

It is apparent from Table I that the "branching ratios" into the three possible reaction channels are very different depending on whether the initially generated ion is **1** or **2**, and in particular **1** does not lose formaldehyde in metastable transitions. On the basis of this evidence, Tsang and Harrison were inclined toward the conclusion that **1** and **2** "do not fragment through an intermediate which is common to both". However, they noted that the evidence is "not overwhelming and, indeed, this example serves to illustrate some of the difficulties one can expect to encounter in using metastable characteristics to arrive at conclusions concerning ion structures and fragmentation mechanisms".[5] Our present conclusions underscore the cautionary note of these authors since we now present a case that **2** does rearrange to **1** prior to unimolecular decomposition in normal metastable transitions, albeit that our case rests on factors which have not hitherto been considered.

Both **1** and **2** must rearrange extensively before decomposition to $C_3H_5^+ + H_2O$, but it is clear that at least one step en route to $C_3H_5^+$ has a highly ordered transition state since the overall rate of formation of $C_3H_5^+$ is relatively slow. Thus, 95% of ions proceeding from **1** lose H_2O after a lifetime of about 10 μsec (Table I, second field-free region), whereas only 70% lose H_2O after a lifetime of about 5 μsec. It is clear that the energy requirement for eventual loss of H_2O from **1** is less than that of any other fragmentation route, but the rate of increase of k with E is slow for the rate-limiting step (Figure 2a). By the same criteria, the route leading to ethylene loss from ions generated as **1** has a higher energy requirement (poor competition with H_2O loss at long ion lifetimes) and less stringent geometrical requirement [better competition with H_2O loss in the first field-free region (Table I)], as summarized by the relevant k vs. E curves shown in Figure 2a. In addition, although ion **1** could directly lose CH_2O in a one-step process given sufficient energy, it does not do so in metastable transitions. However, if **1** is energized by a collision gas in a field-free region (this work, and see also ref 8), then loss of CH_2O does occur. Hence, **1** does not lose CH_2O in normal unimolecular metastable decompositions since the activation energy for this reaction is relatively high, and ions with the energy required for $k = 10^4$–10^6 sec^{-1} for this reaction undergo ethylene loss and [probably to a lesser extent (vide infra)] water loss in the source (Figure 2a).

The above conclusions with regard to energetics are established by direct measurement or calculation of the energies involved in these reactions. Appearance-potential measurements establish that the activation energy of the rate-limiting step for loss of H_2O from $H_2C{=}O^+CH_2CH_3$ (**1**) is 23 ± 3 kcal mol^{-1} and for C_2H_4 loss is 28 ± 3 kcal mol^{-1} (average of nine determinations in both cases). The activation energy for CH_2O loss from **1** is calculated as 40 kcal mol^{-1} on the basis of the known heats of formation of $C_2H_5^+$ and CH_2O[9] and the assumption that the dissociation does not involve a reverse activation energy (it seems reasonable that the addition of formaldehyde to ethyl cation will occur with a zero or small activation energy).

It is most striking that, given the qualitative relative positioning of the k vs. E curves dictated for **1** by the metastable peak intensities (Table I) and the activation energies in question, then **2** behaves in its metastable decompositions exactly as anticipated for ion **1** generated in a field-free region with a relatively high internal energy. For example, ion

Table II. Relative Abundance of Metastable Transitions (First Field-Free Region) for Ethylene Losses from Ions Generated as 3 and 5

Fragment lost	3_{obsd}	3_{calcd}[a]	5_{obsd}	5_{calcd}[a]
C_2H_4	16	14	16	3
C_2H_3D	56	57	80	34
$C_2H_2D_2$	28	29	3	51
C_2HD_3			1	12

[a] Calculated on the basis that H and D may eventually participate equivalently in ethylene loss.

Table III. Activation Energies and Thermochemical Data

Ion	ΔH_f, kcal/mol^{-1} [g]	Activation energies[a] for metastable decompositions of 1 and 2, kcal mol^{-1}		
		$-C_2H_4$	$-H_2O$	$-CH_2O$
$CH_3CH_2\overset{+}{O}{=}CH_2$ (1)	153 ± 3[b]	28 ± 3	23 ± 3	40[c]
$CH_3CH{=}\overset{+}{O}{-}CH_3$ (2)	150 ± 3[b]	58 ± 3	58 ± 3	62 ± 3
$CH_2{=}\overset{+}{O}H$	170[d]			
$CH_2{=}CH{-}\overset{+}{C}H_2$	226[e]			
$C_2H_5^+$	219[f]			

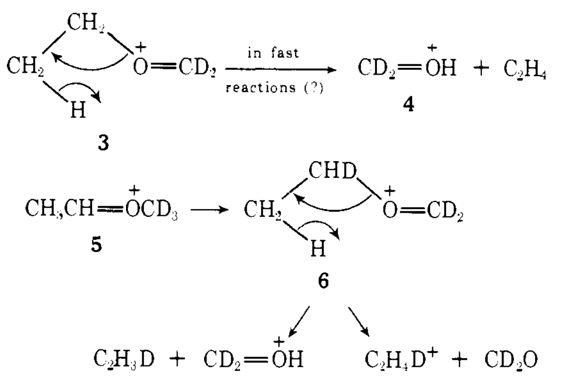
[a] All experimental values represent an average of nine determinations. [b] These values are slightly higher than those reported earlier.[5] [c] Calculated from the heats of formation of the ions and neutrals in question, assuming no reverse activation energy (see text). [d] M. Haney and J. L. Franklin, *Trans. Faraday Soc.*, 65, 1794 (1969). [e] F. P. Lossing, *Can. J. Chem.*, 50, 3973 (1972). [f] Reference 9. [g] For further comment on footnotes *b–f* see Appendix.

1 of internal energy ≫ E^1 (Figure 2a) would undergo mainly loss of C_2H_4 and CH_2O (the latter process, being a single-bond cleavage, having a high frequency factor),[5] with H_2O loss competing only poorly, as observed (Table I). We therefore propose that **2** (which cannot *directly* lose CH_2O, C_2H_4, or H_2O) undergoes a rate-determining slow isomerization to **1** over a high potential barrier (Figure 2b). The resulting high internal energy of **1** as a product of isomerization will result in fast loss of H_2O, C_2H_4, and CH_2O in a field-free region.

If the above suggestions are correct, then three consequences which can be subject to experimental test follow.

(i) The collision-induced decomposition (which weights some high-energy processes)[10,11] of ions generated as **1** should show a discrimination relative to the normal metastable spectrum against water loss in comparison to loss of C_2H_4; this spectrum should also show the anticipated loss of CH_2O. In accord with this prediction, the observed ratios for H_2O, C_2H_4, and CH_2O losses in the collision-induced spectrum of ions generated as **1** are 28:62:10 (cf. 30:60:10 in the work of McLafferty and Sakai).[8]

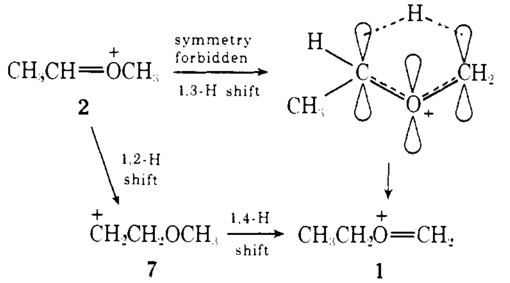
(ii) Deuterium-labeling experiments establish that **1** undergoes further, perhaps reversible or degenerate, intramolecular rearrangement prior to C_2H_4 loss. For example, the H and D atoms of **3** eventually participate in an equivalent manner in the loss of ethylenes and deuterated ethylenes in the first or second field-free region (Table II). Since **3** could in principle lose C_2H_4 without further isomerization (**3** → **4**), such a direct process [which would be expected to preempt the (low frequency factor) rearrangement of **3** uncovered by deuterium labeling] might be preferred in a high energy form of **3**. Indeed, when **6** is produced via isomerization of **5**, the resulting ion undergoes loss of d_1-ethylene with no less than 80% specificity (Table II). Furthermore, ions generated as **5** undergo specific loss (>90%) of CD_2O.



(iii) If the potential surfaces are related as shown in Figure 2b, then the activation energies for H_2O, C_2H_4, and CH_2O loss from **2** should be the same and will be a measure of the activation energy for the isomerization **2** → **1**. In fact the measured activation energies for H_2O, C_2H_4, and CH_2O loss from **2** are 58 ± 3, 58 ± 3, and 62 ± 3 kcal mol^{-1}; these values and other relevant activation energies and thermochemical data are summarized in Table III.

The appearance-potential measurements, made on first field-free region metastable peaks, give values for the barrier to isomerization of **2** → **1** which are the same within experimental error.

The barrier to the isomerization **2** → **1** is relatively high (58 kcal mol^{-1}), and since the energy barriers to unimolecular decomposition of **1** lie in the range 23-40 kcal mol^{-1}, the isomerization reaction should be effectively irreversible; this view is supported experimentally by the highly specific loss (>90%) of CD_2O from **5** via **6**. Although the isomerization can be formulated as a two-step process **2** → **7** → **1**, it is most simply formulated as a symmetry-forbidden 1,3-hydrogen shift.[12] If such a symmetry-forbidden process is operative, the symmetry-imposed barrier is unlikely to be less than 15 kcal mol^{-1},[13,14] and may be appreciably larger.[14]



In independent experiments, we have shown that the ion $CD_3O^+{=}CH_2$ loses CD_3H and CD_2H_2 in the ratio 43:57 in transitions occurring in the first field-free region. The expected statistical ratio, neglecting isotope effects, is 40:60. These results indicate that H and D can pass through equivalent states in the precursor oxonium ion. Yet $CH_3O^+{=}CH_2$ does not pass onto the same potential surfaces as $CH_3CH{=}O^+H$ or $\dot{C}H_2CH_2\dot{O}H^+$,[4] thus rendering the intermediacy of $\dot{C}H_2{-}^+OH{-}\dot{C}H_2$ unlikely in the rearrangement process. Hence the experimentally proved isomerization of $CD_3O^+{=}CH_2$ appears likely to occur via a symmetry-forbidden 1,3-hydrogen shift. The heat of formation of $CH_3O^+{=}CH_2$ has previously been determined from measurements on $CH_3O^+{=}CH_2$ daughter ions,[15,16] but these values (170,[15] 171[16] kcal mol^{-1}) are certainly too high since, for example, the loss of a methyl radical from methyl ethyl ether in fast reactions in the source has been shown to involve excess energy.[16] Our own measurements for these fast source reactions involving excess energy also

Table IV. Average Kinetic Energy (kcal mol^{-1}) Released in the First Field-Free Region in the Loss of H_2O and C_2H_4 from Ions Generated as 1 and 2

Ion generated	$-H_2O$	$-C_2H_4$
1	1.0	0.4
2	1.6	1.3
Δ[a]	0.6	0.9
Calcd[b]	1.3	1.1

[a] This parameter represents the difference in average kinetic-energy release according to whether the inital ion structure is 1 or 2. [b] Values calculated from eq 1.

give a high value of 179 kcal mol^{-1}. Haney and Franklin[16] have made a correction for the excess energy involved and obtain 141 kcal mol^{-1} for ΔH_f ($CH_3O^+{=}CH_2$).[17] A third derivative method has also been employed and gives a value of 153 kcal mol^{-1}.[18] In the light of these earlier observations, we have determined the appearance potential of $CH_3O^+{=}CH_2$ from dimethyl ether in metastable transitions (first field-free region) and obtain a value of ΔH_f ($CH_3O^+{=}CH_2$) = 144 kcal mol^{-1}, in reasonable accord with Haney and Franklin's corrected value.[16] Our value does not have to be corrected for kinetic-energy release since the shape of the first field-free region metastable peak indicates that there is no significant kinetic-energy release in the slow reaction. Using this value, the measured activation energy for CH_4 loss from $CH_3O^+{=}CH_2$ in first field-free region metastable transitions is 83 kcal mol^{-1}, establishing the energy requirement of the 1,3-hydrogen shift as $\lesssim$83 kcal mol^{-1}. Thus it appears that the activation energy for the symmetry-forbidden 1,3-hydrogen rearrangement in this type of oxonium ion lies in the range 58-83 kcal mol^{-1}.

In relatively recent work,[19] it has been established that careful measurements of metastable peak shapes can be used to characterize the potential surface over which an ion is decomposing. The observation that, even when no specific release of kinetic energy occurs in a dissociation, the sides of metastable peaks are less steeply sloping than those of normal peaks indicates that a small range of kinetic energies is released upon dissociation.[20,21] The metastable peak shape can be an excellent criterion to provide information on ion structure and reaction mechanism,[19] but it is clearly of interest to find if the metastable peak width is a sensitive or insensitive function of the excess energy present in the ion when the metastable transition occurs. In the case of gaussian-shaped metastable peaks, the average kinetic-energy release is a measure of the probability that the excess energy present in the transition state will fluctuate into the reaction coordinate. The classical calculation for the fluctuation of excess energy into the reaction coordinate gives, for a conventional one-dimensional reaction coordinate:

$$T = \epsilon_{\text{excess}}/N \tag{1}$$

where T is the average kinetic-energy release, and N is the total number of vibrational degrees of freedom in the decomposing ion.[22] The $C_3H_7O^+$ ions examined in this study provide an excellent opportunity to test the validity of the simple classical equation; as a result of the rate-determining isomerization, the additional excess energies involved in metastable loss of H_2O and C_2H_4 from **1** are 35 and 30 kcal mol^{-1}, respectively (Figure 2b). The average kinetic energies released in the first field-free region in the loss of H_2O and C_2H_4 from ions generated as **1** and **2** are given in Table IV. Following the conclusion of Terwilliger et al.,[23] the average kinetic-energy release is taken as 2.5 times the kinetic-energy release calculated from the peak width at half-height of the gaussian metastable peaks.[24]

The agreement between the observed fraction of the excess energy appearing as kinetic energy and the calculated value (Table IV) is relatively good considering the simplicity of the model used to derive eq 1. It is noteworthy that, in the present work, the fraction of the excess energy appearing as kinetic energy is somewhat less than the classical value, whereas Haney and Franklin (using an analysis of peak shapes in a time-of-flight mass spectrometer) obtained values somewhat greater than the classical values.[25] The method of calculating the kinetic-energy release, which has been employed in the present work,[23] gives results in good agreement with those from the deflection method where comparison is possible.[26]

One of the main conclusions arising from the present work is that the criterion of competing metastable transitions cannot be used as a criterion for ion structure in those cases where a rate-determining isomerization is involved. Under these circumstances, it is noteworthy that the total abundance of metastable peaks will be influenced primarily according to the weighting of internal energies appropriate to the occurrence of the isomerization with $k = 10^4$-10^6 sec^{-1} (which will in turn be dependent on the frequency factor for the isomerization[27,28]), whereas the shapes of the metastable peaks will still be dependent on the characteristics of the dissociation step.[19] In addition, these circumstances allow the determination of the activation energy for rearrangement processes which do not result in direct dissociation.

Experimental Section

The mass spectra were recorded on an AEI MS 9 mass spectrometer. Simple modification to the defocusing unit of the instrument was made allowing the ESA potential to be lowered using the decade box while keeping the acceleration potential at 8 kV. The ionization efficiency (IE) curves of the metastable peaks from the first field-free region[29] could then be recorded at the highest possible sensitivity and at constant (8 kV) acceleration potential. The IE curves were essentially parallel and were interpreted by the semilog plot method.[30] Argon served as the reference gas. During the recording of the IE curves, the repeller was kept at cage potential. The metastable peak intensities in the first field-free region were recorded using the voltage scan technique.[31]

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Appendix. Sources and Accuracy of ΔH_f Values

Since the accuracy of the calculated activation energies depends, among other factors, on the accuracy of the heats of formation of the cations and neutrals used in the calculations, the sources and probable accuracy of the heat of formation data used are given in detail below. The heats of formation of cations are usually determined by mass spectrometric methods, and the reliability of such methods depends on the specific method used. Photoionization has been considered to give the most precise results since ionization potentials determined by this method are close to the adiabatic ionization potentials determined spectroscopically. On the other hand, data from conventional electron-impact sources are generally higher by 0.1-0.7 eV in most cases.[32] However, recent electron-impact measurements either by the Retarding Potential Difference (RPD) method or by the use of energy-resolved electron beams have proved to give results comparable in accuracy to results obtainable by photoionization.[32]

The heat of formation of the allyl cation has recently been determined, using an energy-resolved electron beam,

Table V

Compd	ΔH_f, kcal mol^{-1}	Ref
CH_3	34.0 ± 1	42
CH_3OCH_3	−44.0 ± 0.1	43
$(CH_3CH_2)_2O$	−60.3 ± 0.2	44
$CH_3CH(OCH_3)_2$	−93.15 ± 0.2	45

from the appearance potential of the $C_3H_5^+$ fragment ion from a number of simple hydrocarbon precursors. An average value of 226 kcal mol^{-1} was found with an uncertainty of 1-2 kcal mol^{-1} (Table III, footnote *e*). Combined with the ionization potential of the allyl radical (8.07 ± 0.03 eV),[32] a heat of formation of the allyl radical of 40 kcal mol^{-1} was calculated.[32] This compares well with 41.7 ± 1 kcal mol^{-1} determined by kinetic methods.[33,34]

Ionization potentials of the ethyl radical measured by the RPD technique (8.34 eV)[35] or by using an energy-resolved electron beam (8.38 ± 0.05 eV)[36] are close to the photoionization value of 8.4 eV.[37] It was pointed out, that, because of low ionization probability, the adiabatic transition was not accessible by photoionization and ordinary electron impact.[37] The results are probably best considered as an upper limit of the adiabatic ionization potential.[36] Combining the average of the above values with the heat of formation of the ethyl radical (25.7 ± 1 kcal mol^{-1}),[38] a heat of formation of 219 kcal mol^{-1} for the ethyl cation is obtained.

The heat of formation of protonated formaldehyde has been determined from the appearance potential of $CH_2{=}O^+H$ from methanol using photoionization.[39] The recorded value (170 ± 1 kcal mol^{-1})[39] compares well with a similar determination (170 ± 5 kcal mol^{-1})[40] using the RPD technique and correcting for the excess energy involved in the process.

The heat of formation of $CH_3CH{=}O^+CH_3$ has previously been determined by measuring the appearance potential (10.63 ± 0.04 eV)[41] for loss of OCH_3 from $CH_3CH(OCH_3)_2$ by the RPD technique. However, there is some uncertainty concerning the heat of formation of the methoxy radical; a value of 2 ± 2 kcal mol^{-1} has been determined by kinetic methods,[42] but −3 ± 3 kcal mol^{-1} was found using mass spectrometric methods (RPD).[40] We have used the average value (−0.5 kcal mol^{-1}) in this work which combined with the above appearance potential gives $\Delta H_f(CH_3CH{=}O^+CH_3) = 151$ kcal mol^{-1}. $\Delta H_f(CH_3CH_2O^+{=}CH_2)$ has recently been determined as 150 ± 2 kcal mol^{-1} using a conventional electron-impact source.[5] No photoionization measurements or electron-impact measurements using monoenergetic electrons are available for this ion. We therefore independently determined the heats of formation of the above isomeric $C_3H_7O^+$ ions from the appearance potentials for the loss of CH_3 and OCH_3 radicals from $(C_2H_5)_2O$ and $CH_3CH(OCH_3)_2$, respectively. The metastable peaks for these transitions were of very low abundance, and the measurements were therefore made on the daughter ions. The heats of formation of $CH_3CH{=}O^+CH_3$ and $CH_3CH_2O^+{=}CH_2$ determined in this manner were 150 and 153 kcal mol^{-1}, in good accord with the published values.

The heats of formation of the neutrals not discussed above were selected from a recent compilation[9] or from the references cited in Table V.

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