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Heats of Formation of Some Isomeric $[C_nH_{2n+1}O]^+$ Ions. Substitutional Effects on Ion Stability

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Abstract: Heats of formation for a number of isomeric ions of formula $[CH_3O]^+$, $[C_2H_5O]^+$, $[C_3H_7O]^+$, $[C_4H_9O]^+$, and $[C_5H_9O]^+$ have been measured by monoenergetic electron impact. The stabilization brought about by substituting methyl groups on the C and O atoms in these ionic species is compared with that found in their alkyl ion counterparts. The question of the localization of charge in such species is discussed.

In recent papers of this series[1,2] the heats of formation of a variety of isomeric hydrocarbon positive ions have been reported. In these experiments free radicals of known structure, generated by flash thermolysis at pressures of around 10^{-3} Torr, were bombarded by a monochromatic electron beam. With sufficient experimental sensitivity and appropriate calibration of the energy scale[3] the ionization onset is generally found to be lower than the vertical ionization potential and may approximate to the adiabatic ionization potential. Provided that radicals of the desired structure can be produced by thermolysis and that the heats of formation of the neutral radicals are known or can be estimated sufficiently closely, this method can yield heats of formation of different isomeric ions of the same composition. This is particularly valuable in the situation, frequent for the less stable isomers of hydrocarbon ions, where dissociative ionization thresholds (appearance potentials) correspond to rearrangements to one of the more stable isomers and not to the ion expected on the basis of simple bond rupture.[1,4]

Attempts in this laboratory to obtain ionic heats of formation for isomers of oxygen-containing carbocations (oxycarbonium ions) by this method have been frustrated by the difficulties of producing the corresponding oxygenated free radicals in sufficient yields by flash thermolysis. Only two of these radicals, CH_3OCH_2 and CH_3CHOCH_3, have been produced so far in acceptable yields. It is therefore necessary at present to rely on dissociative ionization thresholds. The lower reliability of such measurements, resulting from the possibility of ionic rearrangements, is perhaps less serious for these ions than for hydrocarbon ions. There is considerable evidence that at low energy contents oxycarbonium ions rearrange much less freely than do hydrocarbon ions. McLafferty and Sakai[5] have concluded that the evidence from metastable ion spectra[6] and particularly from collisional activation spectra[5] shows that the four structures of formula $[C_3H_7O]^+$ discussed in the present work are stable ion structures. Ion cyclotron[7] and collisional activation[8] studies have identified the two $[C_2H_5O]^+$ structures discussed below as stable species, noninterconverting at low energy contents. By careful choice of dissociation processes, that is, by selecting a parent molecule from which the desired ion can be made by the minimum-energy, single-bond rupture process, the possibility of rearrangements has been minimized in the present work. The choice of such processes is also desirable for minimizing uncertainties resulting from the kinetic shift and reverse activation energies.[9]

A number of earlier studies of the energetics of $[CH_3O]^+$, $[C_2H_5O]^+$, $[C_3H_7O]^+$, and $[C_4H_9O]^+$ ions have been published. The most recent data are those of Haney and Franklin[10] using RPD electron impact, and of Refaey and Chupka[11] and of Botter, Pechine, and Rosenstock[12] using photon impact. Earlier results, using conventional ion sources, are reported in the NBS compilation.[13] The emphasis in the present work is directed toward obtaining a consistent scheme for the heats of formation of isomeric oxycarbonium ions rather than toward interpreting the dissociation mechanisms of their precursors.

Some of the ions investigated here, those containing -OH groups, are identical with the structures formed by proton transfer to aldehydes and ketones; for these, ionic heats of formation are in some cases available from gas-phase ionic equilibria. As will be seen below, the results of this investigation are in satisfactory agreement with current data of this origin. For the ions containing C-O-C linkages, however, such data are not available.

Experimental Section

Ionization efficiency and appearance potential curves were obtained as described previously, using an electrostatic electron monochromator coupled to a quadrupole mass filter.[14] The initial portions of the curves

Table I. Appearance Potentials and ΔH_f for $[CH_3O]^+$ Ions

Process	AP, V EM	AP, V Other	$\Delta H_f(R^+)$, kcal/mol
$CH_3OH \rightarrow {}^+CH_2OH + H$	11.69	11.67 PI[a]	169
$CH_3CH_2OH \rightarrow {}^+CH_2OH + CH_3$	11.30	11.25 PI[a]	169
$CH_3OCH_3 \rightarrow (CH_3O)^+ + CH_3$	⩽11.8	11.95 RPD[b] 13.35 PI[c]	⩽195
$CH_3OC_2H_5 \rightarrow (CH_3O)^+ + C_2H_5$[d]	⩽11.7	12.50 RPD[b]	⩽192

[a] Reference 11. [b] Reference 10. [c] Reference 12. [d] If the neutral product is taken as $H + C_2H_4$, the $\Delta H_f(CH_3O)^+$ calculated is impossibly low (i.e., 153 kcal/mol).

Table II. Appearance Potentials and ΔH_f for $[C_2H_5O]^+$ Ions

Process	AP, V EM	AP, V PI	$\Delta H_f(R^+)$, kcal/mol
$C_2H_5OC_2H_5 \rightarrow CH_3CH_2O^+ + C_2H_5$	11.85		187 (?)
$CH_3OCH_3 \rightarrow CH_3O^+CH_2 + H$	10.99	11.23[b]	157
$CH_3OCH_2CH_3 \rightarrow CH_3O^+CH_2 + CH_3$	10.47		156
$CH_3OCH_2CH_2OH \rightarrow CH_3O^+CH_2 + CH_2OH$	10.36		157
$(CH_3OCH_2)_2 \rightarrow CH_3O^+CH_2 + CH_3O\dot{C}H_2$	10.27		156
$IP(CH_3OCH_2 \text{ radical}) = 6.94$ V $\Delta H_f(CH_3OCH_2 \text{ radical}) = -2.1 \pm 2$ kcal/mol			158
$CH_3CH_2OH \rightarrow CH_3{}^+CHOH + H$	10.67	10.78[a,c]	139
$(CH_3)_2CHOH \rightarrow CH_3{}^+CHOH + CH_3$	10.26	10.40[a]	139
$CH_3CH(OH)CH_2OH \rightarrow CH_3{}^+CHOH + CH_2OH$	10.25		138
$CH_3CH(OH)C_2H_5 \rightarrow CH_3{}^+CHOH + C_2H_5$	10.22		140

[a] Reference 11. [b] Reference 29. [c] 10.75 in ref 29.

were scanned repeatedly over a 0.8-V range, and analyzed using a minicomputer data system.[1] The electron beam current was of the order of 2×10^{-8} A with an energy dispersion (FWHM) of about 0.07 V.

The CH_3OCH_2 and $CH_3\dot{C}HOCH_3$ radicals were produced by low-pressure flash thermolysis of $CH_3OCH_2CH_2ONO$ and $CH_3OCH(CH_3)CH_2ONO$, respectively, according to the overall reaction

$$RCH_2ONO \rightarrow R + CH_2O + NO$$

Samples of methyl ethyl, methyl isopropyl, methyl *tert*-butyl, ethyl isopropyl, and ethyl *tert*-butyl ethers, and of 2 methoxy-1-propanol, were prepared and purified by Dr. L. C. Leitch. Other compounds used were commercial samples of high purity.

Results and Discussion

$[CH_3O]^+$ Ions. $^+CH_2OH$. Attempts to prepare ch$_2$OH radicals by flash pyrolysis of various precursors were unsuccessful, leading in all cases to dissociation of the radical to formaldehyde. Consequently no direct measurement of the ionization potential could be made. The production of $^+CH_2OH$ as a fragment ion by H loss from methanol and CH_3 loss from ethanol appears, however, to be quite unambiguous. The isotope-labeling evidence, discussed by Harrison et al.,[15] clearly rules out the CH_3O^+ structure. The appearance potentials found in the present work for $^+CH_2OH$ fragment ion (see Table I) are in satisfactory agreement with the photoionization results of Refaey and Chupka,[11] leading to $\Delta H_f(^+CH_2OH) = 169$ kcal/mol. This value is about 3 kcal/mol higher than a value obtained from ionic equilibrium studies, as discussed below.

CH_3O^+. The evidence for the formation of methoxy ion as a fragment ion is inconclusive. The reported appearance potentials for *m/e* 31 from ethers and esters correspond to ΔH_f values closer to 200 kcal/mol than to the 169 kcal/mol corresponding to $^+CH_2OH$, and in some cases at least, the fragmentation is accompanied by release of relatively large amounts of excitational energy.[10] The two simplest fragmentations which might produce CH_3O^+ are CH_3 loss from dimethyl ether, and C_2H_5 loss (or C_2H_4 + H loss) from methyl ethyl ether. The appearance potentials found in the present work (see Table I) are lower than those reported in RPD studies.[10] The onsets for the *m/e* 31 ion in these two molecules were extremely "tailed" and the derived heats of formation are only upper limits. A recent photoionization study[12] reports a much higher appearance potential, 13.35 V, for the *m/e* 31 peak from dimethyl ether. Since several independent measurements of this appearance potential by electron impact gave values in the range 11.95–12.5 V[13] it seems unlikely that the low EI values are caused by an impurity. A more probable, and more interesting, explanation would be that the EI values refer to an excited state of $CH_3OCH_3{}^+$ whose formation is optically forbidden.[12] Assuming that the threshold of ≤11.8 V in Table I does correspond to onset of CH_3O^+ production, one would obtain $\Delta H_f(CH_3O^+) \leq 195$ kcal/mol. Similarly, the appearance potential curve for *m/e* 31 ion from methyl ethyl ether was extremely "tailed". Assuming that this ion arises from the parent molecule in two steps, H loss to $C_3H_7O^+$ followed by C_2H_4 loss, a heat of formation of ≤153 kcal/mol would be obtained. This is much lower than $\Delta H_f(^+CH_2OH) = 169$ kcal/mol, and it must be concluded that at the threshold the reaction proceeds in one step by loss of neutral C_2H_5. On this basis, $\Delta H_f(CH_3O^+)$ would be ≤192 kcal/mol. Although a value of this magnitude is not entirely inconsistent with a value of ~198 kcal/mol from the gas-phase equilibrium[16]

$$HCO^+ + H_2 \rightleftharpoons H_3CO^+$$

it should be emphasized that the AP data for this ion in Table I do not yield a reliable estimate for $\Delta H_f(CH_3O^+)$.

$[C_2H_5O]^+$ Ions. $CH_3O^+CH_2$. The heat of formation of this isomer can be obtained from the ionization potential of the CH_3OCH_2 radical measured in this work, 6.94 V, together with the heat of formation of the neutral radical, −2.1 ± 2 kcal/mol, given by Golden and Benson.[17] The resulting $\Delta H_f(CH_3O^+CH_2) = 158$ kcal/mol is in excellent agreement with values obtained by fragmentation of four derivatives (see Table II). The clear distinction in heat of formation between the $CH_3O^+CH_2$ and $CH_3{}^+CHOH$ ions (see below) is in agreement with the findings from ion cyclotron resonance studies by Beauchamp and Dunbar[7] and from collisional activation spectra by McLafferty et al.[8] that these two structures are stable and noninterconverting at low energy contents. A similar conclusion was reached by Harrison and co-workers[15,18] on the basis of appearance potentials and isotopic labeling experiments.

It is of interest to note the nearly 3-V reduction in ionization potential between $\dot{C}H_3$ radical (9.84 V)[13] and $CH_3O\dot{C}H_2$ radical (6.94 V) brought about by substituting the strongly electron-donating CH_3O group for a H atom. By comparison with *tert*-butyl radical (IP = 6.93 V)[19] it is seen that one CH_3O group is as effective in this respect as three CH_3 groups.

$CH_3{}^+CHOH$. The appearance potentials (see Table II) obtained from four parent molecules, which can dissociate to $CH_3{}^+CHOH$ by simple bond rupture, give $\Delta H_f(CH_3{}^+CHOH) = 139$ kcal/mol. The agreement with the photoionization result of Refaey and Chupka,[11] 140 kcal/mol, is satisfactory. Recent measurements of proton transfer to

Table III. Appearance Potentials and ΔH_f for $[C_3H_7O]^+$ Ions

Process	AP, V EM	AP, V PI	$\Delta H_f(R^+)$, kcal/mol
$CH_3CH_2OCH_2CH_3 \rightarrow CH_3CH_2O^+CH_2 + CH_3$	10.26		142
$CH_3CH_2OCH_2CH_2OH \rightarrow CH_3CH_2O^+CH_2 + CH_2OH$	10.26		147
$CH_3CH_2OCH_3 \rightarrow CH_3{}^+CHOCH_3 + H$	10.32		134
$(CH_3)_2CHOCH_3 \rightarrow CH_3{}^+CHOCH_3 + CH_3$	9.82		132
$CH_3OCH(CH_3)CH_2OH \rightarrow CH_3{}^+CHOCH_3 + CH_2OH$	9.68		133
IP($CH_3\dot{C}HOCH_3$ radical) ≤ 6.50 V ΔH_f($CH_3\dot{C}HOCH_3$ radical) ~ -13.8 kcal/mol			<136
$CH_3CH_2CH_2OH \rightarrow CH_3CH_2{}^+CHOH + H$		10.72[a]	134
$CH_3CH_2CH(CH_3)OH \rightarrow CH_3CH_2{}^+CHOH + CH_3$	10.18		131
$(CH_3)_2CHOH \rightarrow (CH_3)_2{}^+COH + H$ (Note: IP(2-propanol) = 10.2 V)	<10.48		<124
$(CH_3)_3COH \rightarrow (CH_3)_2{}^+COH + CH_3$	9.86	9.87[b]	119
$C_2H_5C(CH_3)_2OH \rightarrow (CH_3)_2{}^+COH + C_2H_5$	9.80		121

[a] Reference 11. [b] Reference 28.

acetaldehyde give $\Delta H_f(CH_3{}^+CHOH) = 141$ kcal/mol.[20] This ion is clearly the most stable form of $[C_2H_5O]^+$.

$CH_3CH_2O^+$. The evidence for a separate existence of the ethoxy ion, like that of the methoxy ion, is not strong. Ion cyclotron resonance[7] and collisional activation[8] studies do not indicate a reaction intermediate corresponding to this structure. The appearance potential for $[C_2H_5O]^+$ from diethyl ether (Table II) could correspond either to $\Delta H_f[C_2H_5O]^+ = 187$ kcal/mol, assuming the neutral product to be C_2H_5, or to 148 kcal/mol, assuming $C_2H_4 + H$ to be the neutral products. The second assumption could correspond to $CH_3{}^+CHOH$ formation with ~8 kcal/mol of excitational energy. Consequently no reliable value for the $CH_3CH_2O^+$ structure can be obtained from this appearance potential. It is possible that this ion does not have a energy minimum on the $[C_2H_5O]^+$ energy surface which is separate from that of $CH_3{}^+CHOH$.

$CH_2CH_2O^+H$. This cyclic isomer has been proposed as an intermediate on the basis of metastable peak characteristics[21] and isotope labeling studies.[22] Its heat of formation, based on the proton affinity of ethylene oxide, is 170 kcal/mol.[7] It can be seen from Table II that none of the compounds investigated gave a fragment ion corresponding to this energy.

$[C_3H_7O]^+$ Ions. $CH_3CH_2O^+CH_2$. This ion is a homologue of $CH_3O^+CH_2$, and according to its collisional activation spectrum[5] it also does not interconvert to other $[C_3H_7O]^+$ isomers at low energy contents. Based on the two single-bond fission process in Table III, its heat of formation is 144 ± 3 kcal/mol.

$CH_3{}^+CHOCH_3$. This structure is the only one of the C_3H_7O isomers for which the neutral radical could be prepared in reasonable yield by flash thermolysis of the appropriate nitrite. The ionization efficiency curve, however, rose only gradually from the noise background, so that a firm value for the ionization potential could not be obtained. The estimate of ≤6.50 V for the ionization potential is an upper limit. The heat of formation of the CH_3CHOCH_3 radical can be estimated from $D(H\text{-}CH_2OCH_3) = 94$ kcal/mol[17] and the assumption that the difference between the strength of this primary bond and the secondary bond $H\text{-}CH(CH_3)OCH_3$ is, as in alkanes, 3 kcal/mol.[23] This gives $\Delta H_f(CH_3\dot{C}HOCH_3) = -12.8$ kcal/mol. From IP $\leq$ 6.50 V one then obtains $\Delta H_f(CH_3{}^+CHOCH_3) \leq 137$ kcal/mol. The three single-bond fission processes in Table III yield a heat of formation for this ion of 133 ± 1 kcal/mol. In view of the uncertainty in the above estimates, the lower value is more reliable. This ion can be regarded as a protonated methyl vinyl ether, but no PA value for this ether has been reported.

$CH_3CH_2{}^+CHOH$. This isomer is a protonated propionaldehyde homologue of $CH_3{}^+CHOH$, which according to its collisional activation spectrum does not interconvert to other $[C_2H_5O]^+$ isomers at low energy contents. Assuming this $[C_3H_7O]^+$ species to be similarly stable, the two appearance potentials in Table III give a heat of formation of 132 ± 2 kcal/mol for this ion. This is indistinguishable from that obtained for the preceding isomer. Recent proton transfer measurements for propionaldehyde give $\Delta H_f = 132.7$ kcal/mol[20] in excellent agreement.

$(CH_3)_2{}^+COH$. As would be expected on structural grounds, this isomer is the most stable form of $[C_3H_7O]^+$. From the appearance potentials in Table III, its heat of formation is 120 kcal/mol. The most recent proton affinity measurements for acetone[20,25] are in nearly perfect agreement at a PA of 192.8 and 193.9 kcal/mol. From $\Delta H_f(H^+) = 366$ kcal/mol and $\Delta H_f(CH_3COCH_3) = -51.90$ kcal/mol,[26] this result gives $\Delta H_f((CH_3)_2{}^+COH) = 120.2$ kcal/mol, in good agreement with the present result. It should be noted that the appearance potential curve for H loss from 2-propanol showed considerable "tailing", and only an upper limit was obtained for the appearance potential. Taking $\Delta H_f((CH_3)_2{}^+COH) = 120$ kcal/mol, the calculated AP for H loss is 10.28 V. This is only marginally greater than the ionization potential of the parent molecule, 10.22 V,[11] and the dissociation would be expected to have a low cross section at the threshold.

Table IV. Appearance Potentials and ΔH_f for $[C_4H_9O]^+$ and $[C_5H_{11}O]^+$ Ions

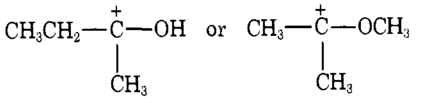
Process	AP, V EM	AP, V PI	$\Delta H_f(R^+)$, kcal/mol
$[C_4H_9O]^+$			
$(CH_3)_2CHOCH_2CH_3 \rightarrow CH_3{}^+CHOCH_2CH_3 + CH_3$	9.50		116[a]
$CH_3CH_2C(CH_3)_2OH \rightarrow CH_3CH_2{}^+C(CH_3)OH + CH_3$	9.89		115
$(CH_3)_3COCH_3 \rightarrow (CH_3)_2{}^+COCH_3 + CH_3$	9.46		114
$[C_5H_{11}O]^+$			
$(CH_3)_3COC_2H_5 \rightarrow (CH_3)_2{}^+COC_2H_5 + CH_3$	9.24		104

[a] This ion has probably rearranged to a tertiary ion.

$[C_4H_9O]^+$ and $[C_5H_{11}O]^+$ Ions. A few measurements were made for C_4 and C_5 oxycarbonium ions. These results are given in Table IV. The $[C_4H_9O]^+$ fragment from ethyl isopropyl ether, if formed by the rupture of the weakest bond (a secondary C-C bond), would correspond to the fragmentation

$$(CH_3)_2CHOCH_2CH_3 \rightarrow CH_3{}^+CHOCH_2CH_3 + CH_3 + e$$

However, the $\Delta H_f[C_4H_9O]^+$ derived, 116 kcal/mol, is clearly too low to correspond to a secondary ion. This value can probably be attributed to a rearranged ion with a tertiary structure, either



$$CH_3CH_2-\overset{+}{\underset{CH_3}{C}}-OH \quad \text{or} \quad CH_3-\overset{+}{\underset{CH_3}{C}}-OCH_3$$

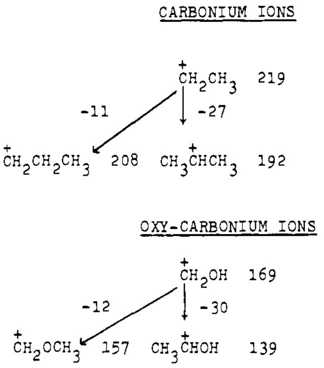
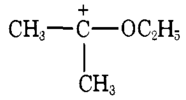


Figure 1. The stabilizing effect of substituting CH_3 for H in carbonium and oxycarbonium ions. Note that the effect of substituting CH_3 for the hydroxyl H in CH_2OH ion is similar to that for substitution on the "uncharged" atom in the $^+CH_2CH_3$ ion. Substitution on the C atom in $^+CH_2OH$ ion has a much greater stabilizing effect, comparable to substitution on the "charged" C atom in $^+CH_2CH_3$ ion. Numbers are ΔH_f (ion) in kcal/mol.

On the basis of structure, these two ions should be the most stable $[C_4H_9O]^+$ isomers. By analogy with the corresponding C_3 ions $CH_3{}^+CHOCH_3$ and $CH_3CH_2{}^+CHOH$, which were found to have the same heat of formation (see above), one would expect these two C_4 structures to be close in energy.

The only measurement for $[C_5H_{11}O]^+$ ions is the AP for loss of CH_3 from ethyl *tert*-butyl ether, presumably to give the stable tertiary ion



$$CH_3\text{—}\overset{+}{\underset{\displaystyle CH_3}{C}}\text{—}OC_2H_5$$

Comparison with Recent Proton Affinity Data. The ionic heats of formation obtained in this work, calculated as proton affinities (PA) of carbonyl compounds (where applicable) from the relationship

$$PA = \Delta H_f(R_1R_2CO) + \Delta H_f(H^+) - \Delta H_f(R_1R_2{}^+COH)$$

are summarized in Table V. For comparison, recent PA data obtained from equilibrium studies of proton transfer reactions, either by high-pressure mass spectrometry[20] or ion cyclotron resonance,[7,24,25] are also given. The agreement is generally quite satisfactory. Surprisingly, the worst discrepancy is for the smallest ion. The most recent value for the PA of formaldehyde is 174.6 kcal/mol.[25] Taking $\Delta H_f(H_2CO) = -25.95$ kcal/mol,[26,27] $\Delta H_f(^+CH_2OH) = 165.4$ kcal/mol, nearly 4 kcal/mol lower than the electron and photon impact result. The impact results give the PA of formaldehyde as 171 kcal/mol, barely larger than that of H_2O, for which recent values are 168.9[20] and 170.3 kcal/mol.[25] In view of the multiple cross checks in the ionic equilibria data[25] it would seem possible that the impact value for $\Delta H_f(^+CH_2OH)$ may be 2-4 kcal/mol too high because of excess energy or reverse activation energy in the dissociation.

Table V. Comparison of Proton Affinities for Aldehydes and Ketones

		PA, kcal/mol	
Molecule	EM[a]	Yamdagni-Kebarle[b]	Wolf et al.[c]
CH_2O	171		174.6
CH_3CHO	187	185.4	185
CH_3CH_2CHO	189	187.9	188
CH_3COCH_3	194	194.6	193.9
$C_2H_5COCH_3$	194		197

[a] This work. [b] Reference 20. [c] Reference 25.

Correlation of Heats of Formation and the Question of Localization of Charge. To illustrate the delocalization of charge resulting from the presence of electron-donating groups OR, ions such as $[CH_2OH]^+$ and $[CH_3OCH_2]^+$ can be written as the hybrid structures

$$^+CH_2OH \leftrightharpoons CH_2{=}^+OH$$

and

$$^+CH_2OCH_3 \leftrightharpoons CH_2{=}^+OCH_3$$

The current convention among organic mass spectrometrists is to represent these ions and their analogues by the formulas on the right-hand side of these equations. However, the effect of CH_3 substitution on the ionic heats of formation suggests that the charge resides mainly on the C atom, as in the left-hand side of the equations. In the scheme shown in Figure 1 the effect of substituting CH_3 for H in $[CH_2OH]^+$ ion is compared to substitution of CH_3 for H on the "charged" and "uncharged" C atoms in ethyl ion (19). Substitution on the "uncharged" atom leads to a primary propyl ion, accompanied by a lowering in ΔH_f of 11 kcal/mol, compared to a lowering of 27 kcal/mol for substitution on the "charged" C atom, leading to secondary propyl ion. Note that substitution of CH_3 for H on the O atom in $[CH_2OH]^+$ to give $^+CH_2OCH_3$ ion

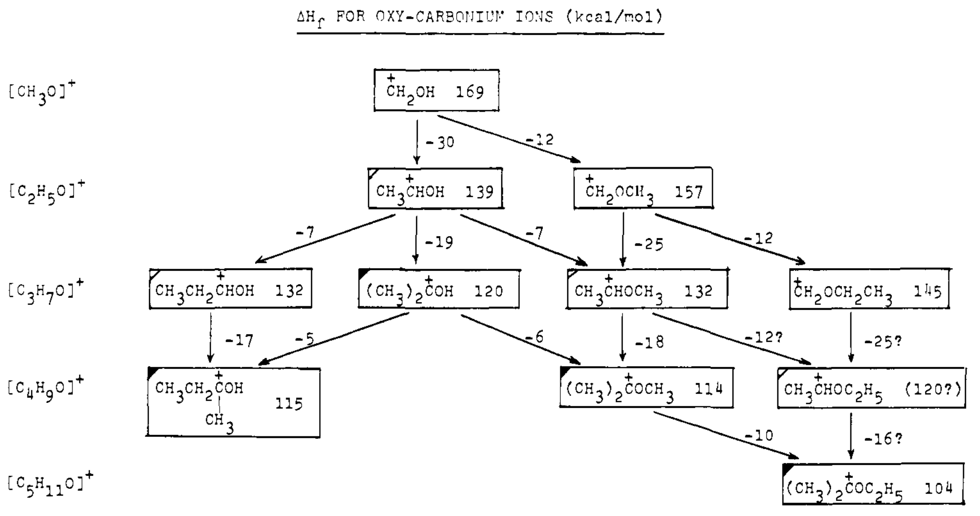


Figure 2. Schematic illustration of the relationships in heats of formation of oxycarbonium ions (ΔH_f (ion) in kcal/mol). Secondary and tertiary ions are identified by corner markings. Vertical arrows correspond to CH_3 substitution on charged atoms, slant arrows correspond to CH_3 substitution on uncharged atoms.

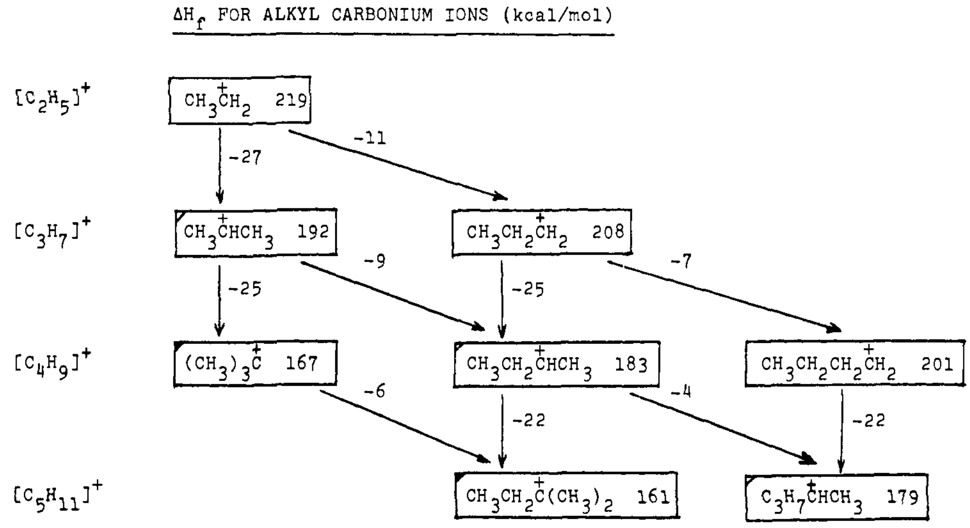


Figure 3. Schematic illustration of the relationships in heats of formation of alkyl carbonium ions for comparison with Figure 2 (ΔH_f (ion) in kcal/mol). Arrows and other symbols have the same meaning as in Figure 2.

causes a reduction of 12 kcal/mol, analogous to substitution on the "uncharged" C atom. Substitution on the C atom in $[CH_2OH]^+$, however, causes a reduction of 30 kcal/mol in ΔH_f, analogous to substitution on a "charged" atom. If the analogy is valid, it suggests that in $[CH_2OH]^+$ ion most of the charge residues on the C atom. Consistent with this view one should write $^+CH_2OH$ and $^+CH_2OCH_3$ as primary ions, CH_3C^+HOH as a secondary ion, and $(CH_3)_2C^+OH$ as a tertiary ion. This relationship is not apparent when these ions are written $CH_2{=}^+OH$, $CH_3CH{=}^+OH$, and $(CH_3)_2C{=}^+OH$.

A correlation scheme for the heats of formation obtained in this work is given in Figure 2. In this figure vertical arrows correspond to CH_3 substitution on a charged atom, and slant arrows correspond to substitution on an uncharged atom. For ease of comparison, a similar schematic for C_2–C_5 alkyl carbonium ions[2] is given in Figure 3. The similarity is immediately obvious, but there are two minor differences. The successive decreases in ΔH_f along the sequence primary → secondary → tertiary are more rapidly attenuated in the oxycarbonium series. Secondly, the decreases between OCH_3 and OCH_2CH_3 derivatives are nearly double those between CH_3 and CH_2CH_3 derivatives. The ΔH_f $(CH_3{}^+CHOC_2H_5)$ given in Figure 2 has been estimated from its neighbors in the schematic, and is not the experimental value from Table IV. As noted above, a heat of formation of 116 kcal/mol is more appropriate to a tertiary ion.

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