(14) Barton, T. J.; Kline, E. A.; Garvey, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 3078.
(15) Norsoph, E. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 994.
(16) Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536.
(17) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1971**, *29*, 389.
(18) Peterson, D. J. *J. Organomet. Chem.* **1967**, *9*, 373.
(19) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.
(20) Seyferth, D.; Flood, T. C. *J. Organomet. Chem.* **1971**, *29*, C25.
(21) Gröbel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.
(22) Schmidbauer, H. *Chem. Ber.* **1964**, *97*, 270.
(23) Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, *6*, 1026.
(24) Our final amounts of these compounds were submitted in Nov 1978 to the Midwest Center for Mass Spectrometry, Lincoln, Nebr., for exact mass measurement.
(25) Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* **1955**, *77*, 907.
(26) Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, *9*, 1563.
(27) Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, *4*, 768.
(28) Lappert, M. F.; Lorbeth, J.; Poland, J. S. *J. Chem. Soc. A* **1970**, 2954.
(29) Krommes, P.; Lorbeth, J. *J. Organomet. Chem.* **1977**, *127*, 19.

Gas-Phase Heats of Formation of Keto and Enol Ions of Carbonyl Compounds

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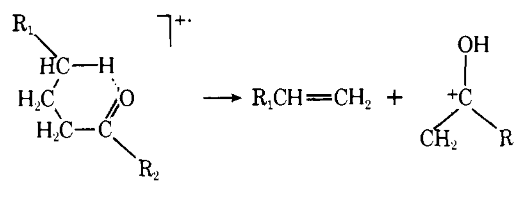
Abstract: The gas-phase heats of formation of 13 enol positive ions of aliphatic aldehydes, ketones, acids, and esters have been measured and are compared with those of the corresponding keto ions. The enolic ions are all much more stable thermodynamically, by amounts ranging from 14 to 31 kcal mol^{-1}. This is in marked contrast to the neutral tautomers, in which the keto forms are generally the more stable. Enol ions have often been postulated as product structures in ionic fragmentations, but quantitative thermochemical data for such ions have not been available.

Introduction

In recent papers we have reported measurements of the gas-phase heats of formation of the enol ions of methyl acetate[2a] and of acetic acid.[2b] These measurements, made by impact of energy-selected electrons, showed that the enol forms of ionized methyl acetate and acetic acid, formed by dissociative ionization of appropriate precursor molecules, are more stable by 24 and 22 kcal mol^{-1}, respectively, than the corresponding carbonyl forms of the ions.

This is consistent with an earlier study[3] which showed that the molecular ion of vinyl alcohol, produced by dissociative ionization processes, is more stable than the tautomeric acetaldehyde ion by 15 kcal mol^{-1}. For the neutral enol and keto forms of C_2H_4O, the thermodynamic stabilities are in the reverse order by 12–13 kcal mol^{-1}.[3,4] According to energies calculated by ab initio MO theory there is an activation energy barrier of some 85 kcal mol^{-1} for the isomerization vinyl alcohol → acetaldehyde. Although it is found experimentally that enols are thermodynamically less stable than their carbonyl forms,[5] enol intermediates have been detected by NMR.[6] Vinyl alcohol has recently been prepared in the gas phase[7] by thermolysis of ethylene glycol at 1000 °C; it had a half-life in Pyrex of ca. 30 min. As pointed out by Radom et al.,[4] this observation is hard to reconcile with the large energy barrier calculated for unimolecular isomerization to acetaldehyde, and so the short half-life may be attributed to intermolecular and/or heterogeneous reactions. Whatever the explanation, it is noteworthy that, in spite of their unfavorable thermodynamic stability, the proposed participation by enol forms in oxidation-reduction[8] and in photochemical reactions (the Norrish type II reaction) is not uncommon.

The condition for participation of enolic molecular ions in ionic reactions is, as a consequence of their relative stability, much more favorable than for their neutral counterparts. The well-known McLafferty rearrangement[9,10] which plays an important role in the mass spectra of aldehydes, ketones, acids, and esters has as its motive force this favorable stability. Because this enhanced stabilization may well be a general phenomenon, we have undertaken an extended study of the thermochemistry of $C_nH_{2n}O^{+\cdot}$ and $C_nH_{2n}O_2^{+\cdot}$ ions, comparing the heats of formation of product ions of these formulas with those of their ionized isomeric carbonyl compounds. The existing quantitative data for such comparisons are fragmentary, and in many cases too inaccurate to be useful. We have measured the appearance energies of $C_2H_4O_2^{+\cdot}$, $C_3H_6O^{+\cdot}$, $C_4H_8O^{+\cdot}$, $C_3H_6O_2^{+\cdot}$, and $C_4H_8O_2^{+\cdot}$ ions formed in the fragmentation of aldehydes, ketones, esters, and acids (in whose mass spectra these ions are major or prominent peaks) by elimination of a neutral olefin via a six-centered activated complex, e.g.



In addition, we have measured the ionization energies of a number of carbonyl compounds for which data are conflicting or nonexistent.

Experimental Section

Appearance energies (AE) were measured by impact of an energy-resolved electron beam from an electrostatic electron monochromator,[11] together with a quadrupole mass spectrometer and minicomputer data system.[12] All the compounds were of research grade, carefully purified where necessary by GLC. In this work, the purity was of particular importance, since appearance energies for $C_nH_{2n}O^{+\cdot}$ and $C_nH_{2n}O_2^{+\cdot}$ product ions were in some cases quite close to the ionization energies of possible isomeric impurities.

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Table I. Heats of Formation of $C_3H_6O^{+\cdot}$ Ions

compd	ΔH_f, kcal mol^{-1}	neutral fragment	appearance energy [$C_3H_6O^{+\cdot}$], eV	$\Delta H_f[C_3H_6O^{+\cdot}]$, kcal mol^{-1}
$CH_3CO(CH_2)_2CH_3$	−61.92[a]	C_2H_4	10.08	158
$CH_3CO(CH_2)_3CH_3$	−66.87[a]	C_3H_6	10.04	160
$CH_3COCH_2CH(CH_3)_2$	−68.6[b]	C_3H_6	9.98	157
	enol ion of acetone (**1**)			av 158
	keto (molecular) ion of acetone			172[c]
$CH_3(CH_2)_3CHO$	−54.45[d]	C_2H_4	9.82	160
$CH_3(CH_2)_4CHO$	−59.5[b]	C_3H_6	9.72	160
$CH_3(CH_2)_2CH(CH_3)CHO$	−61.5[b]	C_3H_6	9.80	160
c-C_5H_9OH	−59.97[a]	C_2H_4	9.98	158
	enol ion of propanal (**2**)			av 159
	keto (molecular) ion of propanal			184[c]

[a] Reference 13. [b] Calculated by additivity.[17] [c] Reference 14. [d] Reference 15.

Table II. Heats of Formation of $C_4H_8O^{+\cdot}$ Ions

compd	ΔH_f, kcal mol^{-1}	neutral fragment	appearance energy, eV	$\Delta H_f[C_4H_8O^{+\cdot}]$, kcal mol^{-1}
$(CH_3CH_2)_2CHCHO$	−61.5[a]	C_2H_4	9.68	149
$CH_3CH(CH_3)CH(C_2H_5)CHO$	−68.5[a]	C_3H_6	9.68	150
	enol ion of butanal (**3**)			av 150
	keto (molecular) ion of butanal			177[b]
$CH_3CH_2C(CH_3)_2CHO$	−63.2[a]	C_2H_4	9.58	145
	enol ion of 2-methylpropanal (**4**)			145
	keto (molecular) ion of 2-methylpropanal			172[b]
$CH_3COCH(CH_3)CH_2CH_3$	−68.6[a]	C_2H_4	9.52	138
$CH_3COCH(CH_3)(CH_2)_2CH_3$	−73.4[a]	C_3H_6	9.41	139
	enol ion (2-en-2-ol) ion of 2-butanone (**5**)			av 139
	keto (molecular) ion of 2-butanone			162[b]
$CH_3CH_2COCH_2CH_2CH_3$	−66.51[c]	C_2H_4	9.89	149
$CH_3CH_2CO(CH_2)_3CH_3$	−71.4[a]	C_3H_6	9.82	150
	enol (1-en-2-ol) ion of 2-butanone (**6**)			av 150

[a] Calculated by additivity.[17] [b] Reference 14. [c] Reference 13.

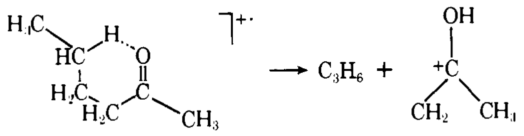
Table III. Heats of Formation of $C_2H_4O_2^{+\cdot}$

compd	ΔH_f, kcal mol^{-1}	neutral fragment	appearance energy, eV	$\Delta H_f[C_2H_4O_2^{+\cdot}]$, kcal mol^{-1}
$CH_3CH_2CH_2COOH$	−112.8[a]	C_2H_4	10.60	119
$CH_3(CH_2)_3COOH$	−117.2[b]	C_3H_6	10.56	121
$CH_3(CH_2)_4COOH$	−122.7[b]	1-C_4H_8[c]	10.52	120
$CH_3(CH_2)_5COOH$	−127.7[b]	1-C_5H_{10}[c]	10.54	121
	enol ion of acetic acid (**7**)			av 120
acetic acid	−103.3[a]		10.70[d]	143
			10.63[e]	142
			10.66[f]	142
	keto (molecular) ion of acetic acid			av 142

[a] Calculated (see Appendix). [b] Reference 13. [c] The formation of this isomer is assumed. [d] Sweigert, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972,** *94,* 5592. [e] Benoit, F. M.; Harrison, A. G. *Ibid.* **1977,** *99,* 3980. [f] This work.

Results and Discussion

$C_3H_6O^{+\cdot}$ Ions (*m/z* 58). The *m/z* 58 peak, which after *m/z* 43 is the most abundant peak in the mass spectra of 2-hexanone and 4-methyl-2-hexanone, is generated via a rearrangement in which a neutral propene molecule is eliminated:



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The appearance energies, given in Table I, for the *m/z* 58 peak derived from these compounds and 2-pentanone, lead to $\Delta H_f(C_3H_6O^{+\cdot})$ = 159 kcal mol^{-1}, with an uncertainty of ±2 kcal mol^{-1}. The product ion **1** must have the enol configuration because its formation takes place at an energy 14 kcal mol^{-1} below the thermochemical threshold for formation of the acetone molecular ion (see Table I). This stabilization energy is comparable with that found (15 kcal mol^{-1}) for the analogous vinyl alcohol-acetaldehyde tautomeric $C_2H_4O^{+\cdot}$ ions.[3]

The $C_3H_6O^{+\cdot}$ ion formed from the appropriate dissociative ionization of C_5 and C_6 aldehydes and cyclopentanol is produced at an energy 25 kcal mol^{-1} below the threshold for the formally expected [propanal]$^{+\cdot}$ ion. Although the derived heat of formation, $\Delta H_f(C_3H_6O^{+\cdot})$ = 159 kcal mol^{-1}, is almost the same as that found for **1**, this ion can with confidence be assigned the structure of the [propanal]$^{+\cdot}$ enol **2**. This ion is

Table IV. Heats of Formation of $C_3H_6O_2^{+\cdot}$

compd	ΔH_f, kcal mol^{-1}	neutral fragment	appearance energy, eV	$\Delta H_f[C_3H_6O_2^{+\cdot}]$, kcal mol^{-1}
$CH_3CH_2CH(CH_3)COOH$	-119.8^a	C_2H_4	10.27	105
$CH_3CH(CH_3)CH(CH_3)COOH$	-126.6^a	C_3H_6	10.20	104
	enol ion of propanoic acid (**8**)			av 105
propanoic acid	-108.4^b		10.24^c	128
			10.51^d	134
			10.41^e	132
	keto (molecular) ion of propanoic acid			av 131
$CH_3CH_2CH_2COOCH_3$	-107.8^a	C_2H_4	10.18	114
$CH_3(CH_2)_3COOCH_3$	-112.7^b	C_3H_6	10.06	114
$(CH_3)_2CHCH_2COOCH_3$	-114.8^a	C_3H_6	10.16	115
	enol ion of methyl acetate (**9**)			av 114
	keto (molecular) ion of methyl acetate			139^c

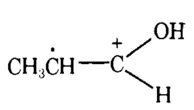
[a] Calculated (see Appendix). [b] Reference 13. [c] Reference 14. [d] Benoit, F. M.; Harrison, A. G. *J. Am. Chem. Soc.* **1977,** *99*, 3980. [e] This work.

Table V. Heat of Formation of $C_4H_8O_2^{+\cdot}$ Ions

compd	ΔH_f, kcal mol^{-1}	neutral fragment	appearance energy, eV	$\Delta H_f[C_4H_8O_2^{+\cdot}]$, kcal mol^{-1}
$(CH_3CH_2)_2CHCOOH$	-124.5^a	C_2H_4	10.14	97
	enol ion of butanoic acid (**10**)			97
butanoic acid	-112.8^a		10.16^b	121
			10.24^c	123
	keto (molecular) ion of butanoic acid			av 122
$CH_3CH_2C(CH_3)_2COOH$	-126.3^a	C_2H_4	10.02	92
$CH_3CH_2CH_2C(CH_3)_2COOH$	-131.3^a	C_3H_6	9.96	93
	enol ion of 2-methylpropanoic acid (**11**)			av 92
2-methylpropanoic acid	-114.7^a		10.02^b	117
			10.12^c	119
	keto (molecular) ion of 2-methylpropanoic acid			av 118
$CH_3CH_2CH(CH_3)COOCH_3$	-114.7^a	C_2H_4	9.81	99
	enol ion of methyl propanoate (**12**)			99
methyl propanoate	-103.3^a		10.15	131
	keto (molecular) ion of methyl propanoate			131
$CH_3CH_2CH_2COOC_2H_5$	-115.8^a	C_2H_4	10.06	104
$CH_3(CH_2)_4COOC_2H_5$	-125.7^a	$1\text{-}C_4H_8$	9.96	104
	enol ion of ethyl acetate (**13**)			av 104
ethyl acetate	-106.3^d		10.20^e	129
			10.24^f	130
			10.16^c	128
	keto (molecular) ion of ethyl acetate			av 129

[a] Calculated (see Appendix). [b] Reference 14. [c] This work. [d] Reference 13. [e] Goldenfeld, I. V.; Korostyshevsky, I. Z.; Mischanchuk, B. G. *Int. J. Mass Spectrom. Ion Phys.* **1974,** *13*, 297. [f] Sweigert, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972,** *94*, 5592.

therefore more stable than its keto isomer by 25 kcal mol^{-1} (see Table I).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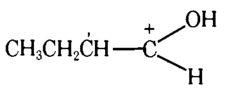
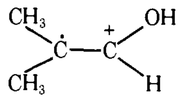
It is instructive to consider these two isomeric enol ions as derivatives of the vinyl alcohol molecular ion in which CH_3 has replaced H on the α and β carbons on either side of the "double" bond. In an earlier paper[16] it was proposed that the stabilization effects of CH_3 substitution provided a measure of the charge distribution in oxycarbonium ions. The only slightly greater stabilization brought about by α substitution compared with β substitution leads us to suggest that the charge is almost equally distributed between the two carbons in $[CH_2{=}CHOH]^{+\cdot}$. By comparison, substitution of CH_3 for the hydroxyl H atom to give ionized methyl vinyl ether has a much smaller stabilizing effect. The IE of methyl vinyl ether, 8.93 eV,[14] together with ΔH_f(neutral methyl vinyl ether) = −26.7 kcal mol^{-1} calculated by group equivalents,[17] gives $\Delta H_f(CH_3OCH{=}CH_2)^{+\cdot}$ = 179 kcal mol^{-1}. This represents a stabilization of only 2 kcal mol^{-1} relative to the vinyl alcohol ion (181 kcal mol^{-1}).[3] If this criterion is valid[16,18] it must be concluded that the amount of charge on the O atom in vinyl alcohol ion is much less than that on either of the two carbon atoms.

$C_4H_8O^{+\cdot}$ Ions (m/z 72). Four enol ions of formula $C_4H_8O^{+\cdot}$ can be identified in Table II (**3–6**). Ions **3** and **4** are formed by C_2H_4 loss from the 2-ethyl- and 2,2-dimethylbutanols and are both 27–28 kcal mol^{-1} more stable than the corresponding keto


3
enol ion of butanal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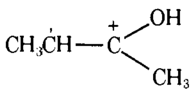
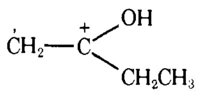
enol ion of 2-methylpropanal


5 (2-buten-2-ol)
enol ions of 2-butanone


6 (1-buten-2-ol)

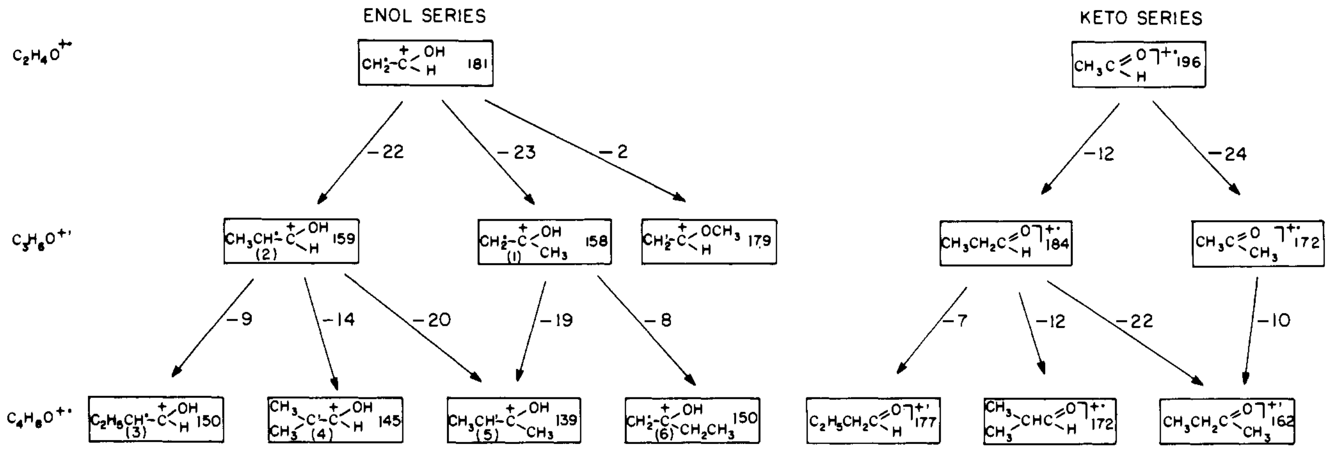
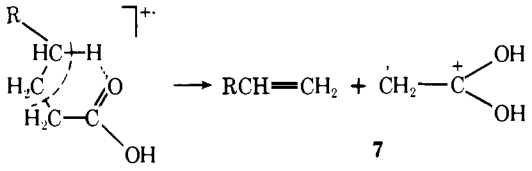


Figure 1. Schematic illustration of the relationships in ionic heats of formation resulting from CH_3 substitution for H in enol and keto ions of formula $C_nH_{2n}O^{+\cdot}$ Enol and keto isomers are in corresponding boxes (ΔH_f(ion) in kcal mol^{-1})

forms. As expected the branched enol ion **4** is the more stable, being doubly substituted by CH_3 on the β carbon.

The molecular ion of 2-butanone possesses two enolic forms, ions **5** and **6**, which are formed well below the thermochemical threshold for the keto ion, as shown in Table II: 23 kcal mol^{-1} in the case of **5** and 12 kcal mol^{-1} in the case of **6**. The most stable of these four isomeric enol ions is **5**, which is substituted on both the α and β C atoms of vinyl alcohol. The greater stability of **5** over **4** is consistent with the conclusion reached above, namely, that the charge density on the α carbon in vinyl alcohol is slightly greater than on the β carbon. However, enol ions **3** and **6**, formed by ethyl substitution on the α and β carbons of vinyl alcohol ion, do not reinforce this conclusion, being the same within the experimental accuracy.

$C_2H_4O_2^{+\cdot}$ Ions (*m/z* 60). In the mass spectra of C_4-C_7 *n*-alkanoic acids, the largest peak by far is *m/z* 60. This also arises from a McLafferty rearrangement,[19] generating the enol ion.



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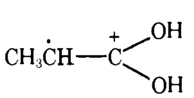
The latter produces characteristic metastable peaks[2,20,21] for its loss of OH· and H_2O. As reported earlier[2b] (and presented again in Table III) the appearance energies for *m/z* 60 from the four alkanoic acids show that the enol ion **7** is produced at an energy 22 kcal mol^{-1} below the thermochemical threshold for acetic acid molecular ion. The energy releases for these rearrangement processes, measured from the half-height widths of the metastable peaks for olefin loss, are only a few millielectronvolts, giving no evidence for a reverse activation energy.[2b] We conclude therefore that the heat of formation of the enol ion of acetic acid **7** is close to 120 kcal mol^{-1}. The consequences of this large stabilization of the enol ion for the ionic dissociations of alkanoic acids have been discussed[2b] and will not be repeated here.

$C_3H_6O_2^{+\cdot}$ Ions (*m/z* 74). ΔH_f values for two enol product ions of this formula, **8** and **9**, produced by dissociation reactions



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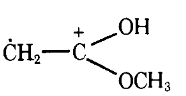

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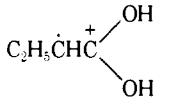
analogous to the foregoing, are presented in Table IV. The branched butanoic acids give as an abundant ion the enol ion of propanoic acid (**8**), and the methyl esters of C_4 and C_5 alkanoic acids give the enol ion of methyl acetate (**9**).

Both of these product ions appear 25-26 kcal mol^{-1} below the thermochemical thresholds for the corresponding ketonic species, propanoic acid and methyl acetate molecular ions. The results in Table IV show that **8**, which may be regarded as an enol ion of acetic acid, **7**, substituted on the β carbon, is 9 kcal mol^{-1} more stabilized than **9**, which is ion **7** substituted by CH_3 on the O atom.

$C_4H_8O_2^{+\cdot}$ Ions (*m/z* 88). Four enol ions of this formula can be identified in Table V; their derived heats of formation are given, together with the heats of formation of the corresponding keto ions. Similarly to the enol ions discussed above, their stabilization energies relative to the keto ions are in the range 25-32 kcal mol^{-1}. As expected, the enol ion of isobutanoic acid is the most stable, being doubly substituted on the β carbon.



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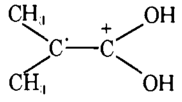

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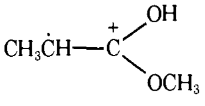

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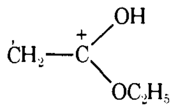

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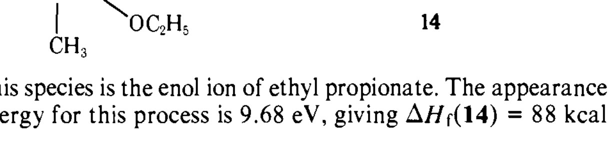
The effect of CH_3 substitution on the β carbon is further illustrated by reference to the heats of formation of the pairs of enol ions **7** and **8** and **9** and **12**. Ion **8** is derived from ion **7** by substitution on the β carbon, resulting in a 15 kcal mol^{-1} decrease in ΔH_f. Similarly, ion **12** is derived from ion **9** by the same substitution giving an identical decrease in ΔH_f. By contrast, substituting CH_3 on the methoxy group in **9** to give **13** brings about an appreciably smaller decrease, 10 kcal mol^{-1}, while substitution on the γ carbon in **8**, giving ion **10**, brings about a decrease of 8 kcal mol^{-1}. Evidently the amount of charge on carbon atoms remote from the double bond decreases rapidly with distance.

$C_5H_{10}O_2^{+\cdot}$ Ions (*m/z* 102). Only one enol product ion of this formula was investigated. The parent ion of the ethyl ester of 2-methylbutanoic acid loses neutral C_2H_4, giving the abundant ion $C_5H_{10}O_2^{+\cdot}$.



14

This species is the enol ion of ethyl propionate. The appearance energy for this process is 9.68 eV, giving ΔH_f(**14**) = 88 kcal

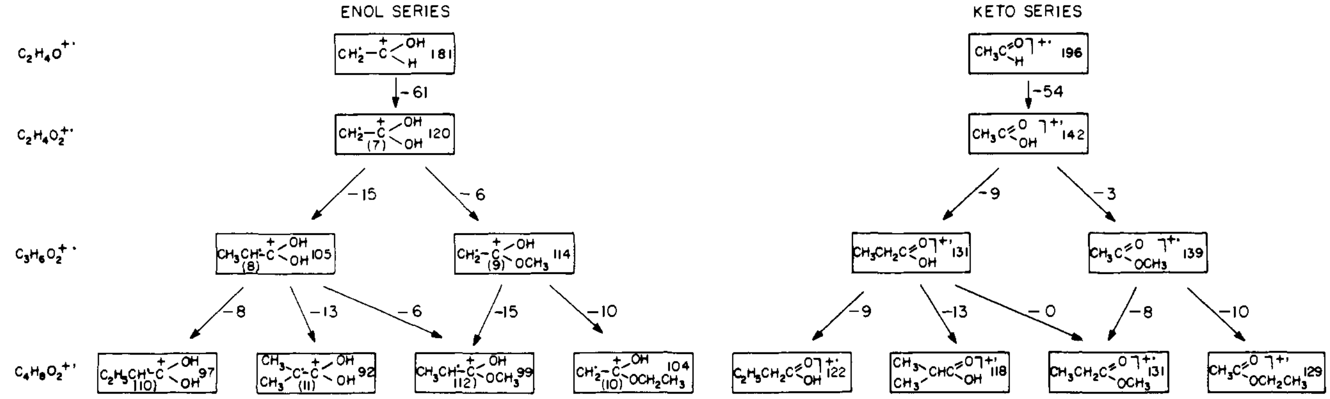


Figure 2. Schematic illustration of the relationships in ionic heats of formation resulting from CH_3 substitution for H in enol and keto ions of formula $C_nH_{2n}O_2^{+\cdot}$. Enol and keto isomers are in corresponding boxes (ΔH_f(ion) in kcal mol^{-1}).

mol^{-1}. For comparison, the heat of formation of the keto ion of ethyl propionate is 119 kcal mol^{-1}, based on the ionization energy 10.00 eV, measured in this work, and the calculated ΔH_f(neutral) = -111.3 kcal mol^{-1}. The substitution of CH_3 on the methoxy-group carbon atom in ion **12** resulted in a decrease in ΔH_f of 11 kcal mol^{-1}, similar to a 10-kcal decrease for the same substitution in ion **9**.

Conclusions

The present results show that enol positive ions as a class are much more thermodynamically stable than the corresponding keto forms. The stabilization ranges from 14 to 31 kcal mol^{-1}, depending on the species. This is in marked contrast to the neutral tautomeric pairs, in which the keto forms are generally the more stable. The thermochemical relationships in the enol and keto series of ions are shown in schematic form in Figures 1 and 2. It was proposed earlier[16] that the changes in ionic heats of formation resulting from CH_3 substitution on C and O atoms are a measure of the charge distribution on these atoms. This effect is clearly illustrated in the figures.

The present results deal only with threshold energetics, and throw no light on the ratio of the two forms generated at energies above the threshold for keto ion formation. From earlier work it appears that the two forms may interconvert freely at internal energies below the dissociation threshold, for example, in methyl acetate ion and its enol ion.[2a] For others, such as acetic acid,[2b] some interconversion can take place but it is slow compared to fragmentation. In the case of the ionized vinyl alcohol and acetaldehyde, these species were unable to interconvert up to at least the energy corresponding to their fragmentation by H-atom loss.[22] Further experiments on these and related matters are in progress and will be reported in future publications.

Appendix. Heats of Formation of Neutral Molecules

For many of the compounds listed in the tables reliable ΔH_f(neutral molecule) values were obtainable from standard reference works.[13-15] However, for acids and esters such data were far from satisfactory and so for consistent values the following methods were used.

Acids. Reference 13 contained "selected values" only for acetic acid (-103.3 kcal mol^{-1}), pentanoic acid (-117.2 kcal mol^{-1}), hexanoic acid (-122.7 kcal mol^{-1}), heptanoic acid (-127.7 kcal mol^{-1}), and octanoic acid (-132.7 kcal mol^{-1}). All these values could be reproduced to within 0.2 kcal mol^{-1} by the use of additivity rules[17] plus a correction term of +1 kcal mol^{-1}. All ΔH_f(acid) values used in this work were calculated by this method ($\Delta H_f(\text{acid})_{\text{calcd}}$).

Esters. Reference 13 contained only one "selected value" for a methyl ester, methyl pentanoate (-112.7 kcal mol^{-1}). Other data from ref 13 indicate that ΔH_f(Me ester) = $\Delta H_f(\text{acid})_{\text{calcd}}$ + (5.0 ± 0.8) kcal mol^{-1}. Accordingly, ΔH_f(Me esters) were obtained from the corresponding $\Delta H_f(\text{acid})_{\text{calcd}}$ by *adding* 5 kcal to the value derived from additivity rules. Similarly, the few values for ΔH_f(Et esters) were satisfactorily reproduced by use of the formula ΔH_f(Et ester) = $\Delta H_f(\text{acid})_{\text{calcd}} - 3$ kcal mol^{-1}.

References and Notes

(1) (a) University of Ottawa. (b) National Research Council.
(2) (a) Holmes, J. L.; Lossing, F. P. *Org. Mass. Spectrom.* **1979**, *14*, 512. (b) *J. Am. Chem. Soc.*, in press.
(3) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.
(4) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443. Bouma, W. J.; Radom, L. *Aust. J. Chem.* **1978**, *31*, 1167.
(5) Le Noble, W. J. "Highlights of Organic Chemistry"; Marcel Dekker: New York, 1974; p. 418.
(6) Schmidt, E. A.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1972**, *94*, 7382. Hoffmann, H. M. R.; Schmidt, E. A. *Ibid.* **1972**, *94*, 1373.
(7) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.
(8) Walling, C.; El-Taliawi, G. *J.Am. Chem. Soc.* **1973**, *95*, 848.
(9) McLafferty, F. W. *Anal. Chem.* **1959**, *31*, 82.
(10) McLafferty, F. W. In "Mass Spectrometry of Organic Ions", McLafferty, F. W., Ed.; Academic Press: New York, 1963.
(11) Maeda, K.; Semeluk, G. P.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 395.
(12) Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9.
(13) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press; New York, 1970.
(14) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*.
(15) Stull, D. R.; Westrum. E. F.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.
(16) Lossing, F. P. *J. Am. Chem. Soc.* **1977**, *99*, 7526.
(17) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions", *Natl. Stand. Ref. Data Ser., Nat. Bur. Stand.* **1970**, *No. 21*.
(18) Vajda, J. H.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 293.
(19) Fairweather, R. B.; McLafferty, F. W. *Org. Mass Spectrom.* **1969**, *2*, 755. Smith, J.S.; McLafferty, F. W. *Ibid.* **1971**, *5*, 483.
(20) Levsen, K.; Schwarz, H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1231.
(21) Schwarz, H.; Williams, D. H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1978**, *100*, 7052.
(22) Holmes, J. L.; Terlouw, J. K. *Can. J. Chem.* **1975**, *53*, 2076.