Energetics and structural effects in the fragmentation of protonated esters in the gas phase

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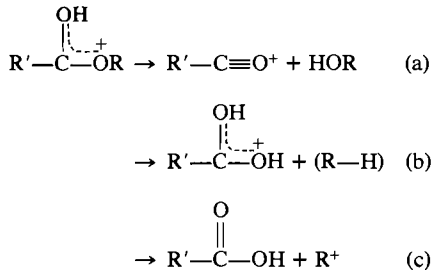
A series of formate (methyl through butyl) and acetate (methyl through pentyl) esters have been protonated in the gas phase by the Brønsted acids H_3^+, N_2H^+, CO_2H^+, N_2OH^+, and HCO^+. Carbonyl oxygen protonation is 87–97 kcal mol^{-1} exothermic for H_3^+ and 47–57 kcal mol^{-1} exothermic for the weakest acid HCO^+, permitting a study of the effect of protonation exothermicity on the decomposition modes of the protonated esters. With the exception of protonated methyl formate, three decomposition modes, (a) to (c) are observed.



Reaction (a) is unimportant for formates; for acetates it is the sole decomposition channel for the methyl ester, but is less important for higher acetates. The dependence of the relative importance of this reaction mode on the protonation exothermicity indicates an activation energy considerably in excess of ΔH^0, presumably because the reaction involves a symmetry-forbidden 1,3-H shift for the carbonyl protonated ester. For the higher acetates where the difference in the proton affinities of the carbonyl and ether oxygens is less, acyl ion formation results, in part, from protonation at the ether oxygen. For protonated methyl formate the major fragmentation reaction yields $CH_3OH_2^+ + CO$; this reaction also appears to have an activation energy considerably in excess of the ΔH_0. For the remaining esters either reaction (b) or (c) is the major decomposition mode. The competition between these two channels depends strongly on the protonation exothermicity and the relative activation energies. From the reaction competition we conclude that 1,2-H shifts occur in the case of primary alkyl esters yielding more stable secondary or tertiary alkyl ions. This rearrangement appears to occur after the excess energy has been partitioned between the alkyl ion and the neutral acid since the extent of further fragmentation of the alkyl ion reflects the original structure of the alkyl group.

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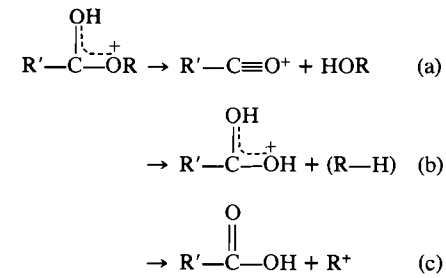
Les acides de Brønsted H_3^+, N_2H^+, CO_2H^+, N_2OH^+ et HCO^+ ont servi à l'étude de la protonation en phase gazeuse des deux séries d'esters: formiates (de méthyle à butyle) et acétates (de méthyle à pentyle). L'exothermicité de la réaction de protonation du groupement carbonyle varie de 87–97 kcal mol^{-1} pour H_3^+ à 47–57 kcal mol^{-1} pour l'acide le plus faible, HCO^+, ce qui permet d'étudier l'effet de la chaleur de la réaction de protonation sur les modes de décomposition des esters protonés. Sauf dans le cas du formiate de méthyle protoné, on observe trois modes de décomposition, (a) à (c).



Alors qu'elle n'intervient guère dans le cas des formiates, la réaction (a) est l'unique voie de décomposition de l'acétate de méthyle et perd ensuite de l'importance pour les acétates supérieurs. La dépendance de l'importance relative de ce mode de réaction vis-à-vis l'exothermicité de la protonation indique une énergie d'activation excédant considérablement ΔH^0, probablement en raison du transfert d'H-1,3 symétriquement interdit impliqué dans la réaction de l'ester protoné. La différence des affinités protoniques des oxygènes du carbonyle et de l'éther étant moindres pour les acétates supérieurs, la formation de l'ion acylium provient en partie de la

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protonation de l'oxygène de l'éther. Dans le cas du formiate de méthyle protoné, la principale réaction de fragmentation produit $CH_3OH_2^+ + CO$; cette réaction semble elle aussi avoir une énergie d'activation beaucoup plus grande que le ΔH^0. Le principal mode de décomposition des autres esters est l'une des deux dernières réactions (b) ou (c). La compétition entre ces deux voies est fortement influencée par l'exothermicité de la protonation et les énergies d'activation relatives. Cette compétition permet de voir que les transferts d'hydrogène-1,2 se produisent dans le cas des esters d'alkyle primaire pour conduire aux ions alkyles secondaires ou tertiaires plus stables. Ce réarrangement s'effectue apparemment après répartition de l'excès d'énergie entre l'ion alkyle et l'acide neutre puisque le degré de fragmentation ultérieure de l'ion alkyle reflète la structure originale du groupement alkyle.

Introduction

Since the original survey (1) of the chemical ionization (CI) mass spectra of esters, there have been numerous investigations (2–7) designed to elucidate details of the dissociation reactions occurring following proton transfer to esters in the gas phase. It has been established clearly that there are three main fragmentation modes, reactions [1] to [3].

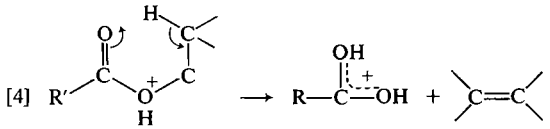
[1] $R'CO_2R \cdot H^+ \rightarrow R'C{\equiv}O^+ + ROH$

[2] $\rightarrow R'CO_2H + R^+$

[3] $\rightarrow R'CO_2H_2^+ + (R{-}H)$

Reaction [1], involving formation of the acylium ion by acyl carbon–oxygen bond cleavage, and reaction [2], involving formation of the alkyl carbonium ion by alkyl carbon–oxygen bond cleavage, are analogous to the $A_{Ac}I$ and $A_{Al}I$ mechanisms for fragmentation of esters in concentrated acid solutions (8). Reaction [3] has no direct solution analogue.

The factors which determine the competition between these three channels in the gas phase have not been established clearly. In general, reaction [1] appears to be of lesser importance in the gas phase than in solution, possibly (6, 7) because it requires formation of the energetically less favourable ether oxygen-protonated ester. Alternatively, it has been suggested (7) that the ether oxygen-protonated species may fragment in the gas phase preferentially to form the protonated acid (reaction [3]) through formation of a six-membered cyclic transition state (reaction [4]).

[4] 

However, for propyl esters at least, it has been shown (6) that the hydrogen transferred from the alkyl group is not specifically the β-hydrogen as required by the proposed mechanism.

From a detailed study of the H_2 and CH_4 CI mass spectra of a series of formate esters, Harrison and Tsang (5) concluded that the relative importance of the fragmentation reactions of protonated formates was not determined by the relative enthalpies of decomposition of ground state $HCO_2R \cdot H^+$ but rather was determined by the relative fragmentation rate coefficients averaged over the appropriate internal energy distribution of the excited $HCO_2R \cdot H^+$ ions formed in the protonation reaction.

In electron impact studies a valuable approach in elucidating the factors controlling the competition between decomposition channels has been that of varying the average internal energy of the fragmenting species (9–11); it appeared that a similar approach should prove equally fruitful in chemical ionization systems. Recent work in this laboratory (12, 13) has shown that the protonation exothermicity and, thus, the average internal energy of the protonated species, can be varied over a significant and useful range by using the family of protonating agents XH^+, where X = H_2 (101), N_2 (117), CO_2 (129), N_2O (137), and CO (141); the numbers in brackets give the proton affinities of X in kcal mol^{-1} (14) and show that the protonation exothermicity can be varied by ~40 kcal mol^{-1}. The present work reports a detailed study of the effect of reaction exothermicity on the CI mass spectra of formate and acetate esters using this family of protonating agents. A similar study of a few selected esters using the flowing afterglow method has been reported recently (7).

Experimental

The chemical ionization mass spectra were obtained using a DuPont 21-490 mass spectrometer equipped with a high pressure chemical ionization source. The source temperature was ~60°C and the ionizing electron energy 70 eV, with the repellers at cage potential. The liquid samples were introduced through a heated inlet system held below 100°C. Reagent gas pressures were not measured directly but were estimated to be 0.2–0.3 Torr. The mass resolution of the instrument is sufficient to resolve the $C_2H_3O^+$–$C_3H_7^+$ doublet at m/z 43.

The H_3^+ reactant ion (X = H_2) was produced in pure H_2. As described elsewhere (12, 13) the N_2H^+, CO_2H^+, N_2OH^+, and HCO^+ reactant ions were prepared by electron impact ionization of the appropriate gas X (~10%) in H_2. Except for the N_2O/H_2 mixture the relevant XH^+ ion was the only significant ion in the reagent gas mass spectrum; in the N_2O/H_2 system ~10–15% of the total ionization was found as NO^+. As is evident from the results presented in the following section the NO^+ ion reacts with the esters primarily by addition to give the $M \cdot NO^+$ complex.

Reagent gases were of highest possible purity (Matheson and Co.) while the esters were either commercial samples of high purity or were prepared by standard procedures. Ethyl-d_5 formate was obtained from Merck, Sharp, and Dohme, Montreal.

Results and Discussion

Some general observations are in order to set the stage for the discussion of the chemical ionization results. The proton affinities reported (15) for formate and acetate esters range from 188 kcal mol^{-1} for methyl formate to 198 kcal mol^{-1} for *n*-propyl acetate; both refer to protonation at the carbonyl oxygen, the proton affinity of the ether oxygen being 11 to 22 kcal mol^{-1} lower depending on the ester (16). Thus carbonyl oxygen protonation of the esters by ground state H_3^+ is 87 to 97 kcal mol^{-1} exothermic, while protonation by ground state HCO^+ is 47 to 57 kcal mol^{-1} exothermic. In addition it is likely that the reagent ions in our system are not completely thermalized, making the protonation exothermicity even larger. The fraction of this reaction exothermicity which remains with the protonated molecule is not known, although arguments have been presented (12) from a detailed study of the protonation of C_3H_6O isomers, that, on average, a large fraction, approaching unity, of the exothermicity is retained by the product ions.

As discussed previously (12), the fragmentation of these excited ions (reaction [5]) is in competition with collisional stabilization (reaction [6]). At the

$$[5] \quad RH^{+*} \xrightarrow{k_5} \text{Fragments}$$

$$[6] \quad RH^{+*} \xrightarrow{k_6[M]} RH^+$$

total pressures applicable in the present study, and assuming that a single collision with M is sufficient to stabilize RH^{+*} to below the decomposition threshold, $k_6[M] \simeq 1 \times 10^7 s^{-1}$. Thus the fragmentation reactions observed as reaction [5] correspond to those with rate coefficients, k_5, equal to or greater than $\sim 10^7 s^{-1}$. This is significantly higher than the threshold rate coefficients observed in electron impact mass spectrometry, particularly those observed as metastable ions ($k \simeq 10^4$–$10^6 s^{-1}$). This has important implications for the fragmentation reactions observed in chemical ionization mass spectrometry compared to those observed in electron impact mass spectrometry. The rate coefficient for the unimolecular decomposition of a gas-phase ion can be expressed in its simplest form (9–11) as

$$[7] \quad k(E) = \nu\left(\frac{E - \varepsilon_0}{E}\right)^S$$

where ν is an energy independent term or frequency factor, E is the internal energy, S is the effective number of oscillators, and ε_0 is the activation energy (referred to the ground state of the ion) for the reaction. It is well established (9–11) in electron impact studies that, at low internal energies, the relative rates of competing fragmentation reactions are determined largely by the relative activation energies, while at high internal energies the relative rates are strongly influenced by the energy independent term or frequency factor. In general, simple bond cleavage reactions have high frequency factors compared to those reactions which involve molecular rearrangement. Consequently, rearrangement fragmentation reactions cannot compete effectively with simple bond cleavage reactions at high internal energies and, normally, are observed following electron impact ionization because they have lower activation energies and, therefore, are dominant at lower internal energies. Similar considerations should apply in chemical ionization systems. Because, as discussed above, the average internal energy of fragmenting ions in CI systems is higher than in electron impact systems (especially for EI metastable ion studies), simple bond cleavage reactions should be favoured over rearrangement reactions. Further, as the average internal energy is increased by increasing the protonation exothermicity, the simple bond cleavage reactions should become increasingly favoured. These effects are observed in the results presented below.

The discussion which follows relies heavily on thermochemical arguments. The heats of formation of the carbonyl protonated esters and acids were derived from the reported proton affinities (15) or proton affinities estimated from these data, while the heats of formation of the ether oxygen-protonated species were derived from the estimates (16) of the proton affinities of these species. The heats of formation of alkyl ions were taken from the work of Lossing and Maccoll (17) or estimated from these data by the method outlined by Bowen and Williams (18). The remaining thermochemical data were taken from standard sources (19, 20). The data used are summarized in the Appendix.

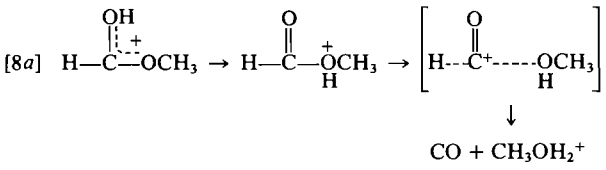
Chemical Ionization Mass Spectra of Formate Esters

The chemical ionization mass spectra of the formate esters studied are summarized in Table 1. The H_2 CI mass spectra are in satisfactory agreement with those reported earlier (5).

The major fragmentation reaction of protonated methyl formate involves formation of protonated methanol (reaction [8]), a reaction which has a ΔH^0

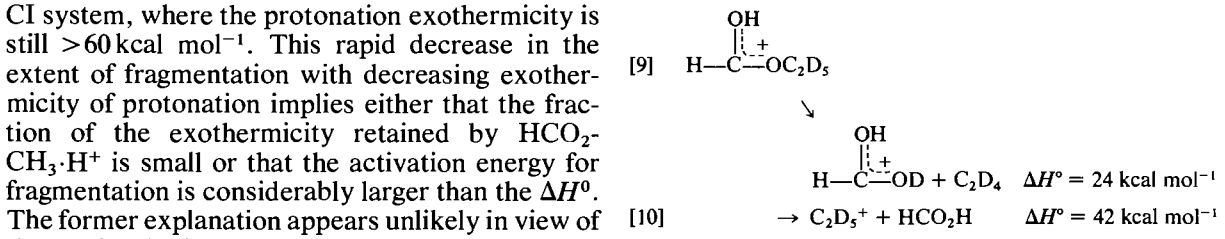
$$[8] \quad \begin{matrix} & & OH \\ & & | \\ H- & C & -OCH_3 \end{matrix} \rightarrow CO + CH_3OH_2^+ \quad \Delta H^\circ = 15 \text{ kcal mol}^{-1}$$

of 15 kcal mol^{-1} for the carbonyl protonated ester but would be ~5 kcal mol^{-1} exothermic for the ester protonated at the ether oxygen. Despite these low ΔH^0 values, the extent of fragmentation decreases rapidly with decreasing protonation exothermicity, with the $CH_3OH_2^+$ ion signal representing less than 20% of the total ionization in the N_2/H_2 CI system and less than 10% in the CO_2/H_2 CI system, where the protonation exothermicity is still >60 kcal mol^{-1}. This rapid decrease in the extent of fragmentation with decreasing exothermicity of protonation implies either that the fraction of the exothermicity retained by HCO_2-$CH_3 \cdot H^+$ is small or that the activation energy for fragmentation is considerably larger than the ΔH^0. The former explanation appears unlikely in view of the results obtained for the remaining esters and for other compounds (12, 13) and we conclude that the latter explanation holds. The overall reaction forming $CH_3OH_2^+$ probably is best represented by [8*a*] involving hydrogen migration from the carbonyl to the ether oxygen followed by bond cleavage accompanied by synchronous or near-synchronous proton transfer from the carbon to the developing methanol molecule (7, 21).



The initial step in this reaction has a ΔH^0 of 20 kcal mol^{-1} but probably has a considerably higher activation energy since the H transfer reaction is a [1,3]-symmetry-forbidden shift and such migrations have been shown to have an activation energy considerably in excess of the ΔH^0 (22). The ether oxygen-protonated form of the ester should have a much lower activation energy for fragmentation and it is possible that the small extent of fragmentation observed with weaker protonating agents represents fragmentation of this species.

In the CI of ethyl-d_5 formate, formation of $C_2D_5OH_2^+$ (*m*/*z* 52) is only a minor process even though this is the thermochemically favoured mode of fragmentation ($\Delta H^0 \simeq 12$ kcal mol^{-1}); this supports the contention that the activation energy for this rearrangement is considerably higher than the ΔH^0. As observed previously (15), the major fragmentation reaction is [9] to form HCO_2HD^+; this fragmentation channel remains important (forming the base peak) even following protonation by HCO^+. The alternative fragmentation [10], forming $C_2D_5^+$ by simple bond fission, has a much higher ΔH_0 (and presumably, activation energy) and consequently competes ineffectively with the rearrangement reaction of lower activation energy. However, it should be noted that the simple bond fission reaction becomes more important at higher average internal energies (cf. H_2 CI), where the relative rates are more strongly influenced by frequency factors.



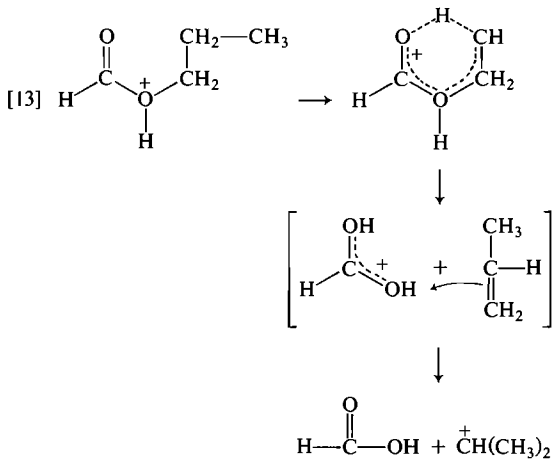
The CI mass spectra of both *n*-propyl and *i*-propyl formate are dominated, for all protonating agents, by the $C_3H_7^+$ alkyl ion, with $HCO_2H_2^+$ being only 10–20% of the alkyl ion intensity. For *i*-propyl formate the ΔH^0's, and, presumably, the activation energies, of the two reaction channels [11] and [12] are very similar consequently, it is not

surprising that the simple bond cleavage reaction [12] should dominate. The relative importance of the rearrangement reaction [11] increases slightly as the average internal energy is decreased by using weaker protonating agents. For protonated *n*-propyl formate, cleavage to form the *n*-propyl cation has a ΔH^0 of ~38 kcal mol^{-1}, considerably higher than that for formation of $HCO_2H_2^+$ ($\Delta H^0 \simeq$ 28 kcal mol^{-1}) yet $C_3H_7^+$ is the dominant fragment ion. It is probable that the bond fission is accompanied by a [1,2]-H shift to form the *i*-$C_3H_7^+$ ion. As Hopkinson *et al.* (7) have noted, *ab initio* MO calculations (23, 24) have shown that *n*-$C_3H_7^+$ collapses into *i*-$C_3H_7^+$ without an energy barrier. The alternative mechanism proposed by Hopkinson *et al.* (7) (reaction [13]), involving hydrogen transfer to the carbonyl oxygen followed by proton transfer from protonated formic acid to propene as the products separate, appears unlikely. First, it involves the thermochemically disfavoured ether

TABLE 1. Chemical ionization mass spectra of formate esters[a]

m/z	Ion	H_2 CI	N_2/H_2 CI	CO_2/H_2 CI	N_2O/H_2 CI	CO/H_2 CI
Methyl formate						
90	$HCO_2CH_3 \cdot NO^+$				4	
61	$HCO_2CH_3 \cdot H^+$	21	100	100	100	100
33	$CH_3OH_2^+$	100	27	10	3	12
31	CH_2OH^+	8	3	2	1	5
15	CH_3^+	6	—	—	—	—
Ethyl-d_5-formate						
109	$HCO_2C_2D_5 \cdot NO^+$				26	
80	$HCO_2C_2D_5 \cdot H^+$	15	25	48	97	71
52	$C_2D_5OH_2^+$	4	1	2	3	4
48	HCO_2HD^+	100	100	100	100	100
34	$C_2D_5^+$	22	11	4	6	7
n-Propyl formate						
118	$HCO_2C_3H_7 \cdot NO^+$				16	
89	$HCO_2C_3H_7 \cdot H^+$	5	15	37	44	27
59	C_3H_7O	8	3	2	6	2
47	$HCO_2H_2^+$	13	12	15	16	18
43	$C_3H_7^+$	100	100	100	100	100
41	$C_3H_5^+$	8	5	2	2	2
31	CH_2OH^+	9	6	3	6	3
i-Propyl formate						
118	$HCO_2C_3H_7 \cdot NO^+$				12	
89	$HCO_2C_3H_7 \cdot H^+$	6	16	47	45	37
59	$C_3H_7O^+$	6	3	2	8	2
47	$HCO_2H_2^+$	11	14	16	16	21
45	CH_3CHOH^+	12	11	R[b]	R[b]	17
43	$C_3H_7^+$	100	100	100	100	100
41	$C_3H_5^+$	5	3	2	2	2
n-Butyl formate						
132	$HCO_2C_4H_9 \cdot NO^+$				15	
103	$HCO_2C_4H_9 \cdot H^+$	9	12	17	25	16
57	$C_4H_9^+$	100	100	100	100	100
55	$C_4H_7^+$	14	4	1	2	1
47	$HCO_2H_2^+$	4	4	7	7	7
41	$C_3H_5^+$	21	7	3	3	3
i-Butyl formate						
132	$HCO_2C_4H_9 \cdot NO^+$				9	
103	$HCO_2C_4H_9 \cdot H^+$	6	8	12	16	8
73	$C_4H_9O^+$	8	3	1	3	1
59	$C_3H_7O^+$, $HCO_2CH_2^+$	6	4	3	1	1
57	$C_4H_9^+$	100	100	100	100	100
55	$C_4H_7^+$	5	1	—	—	—
47	$HCO_2H_2^+$	3	3	5	5	8
41	$C_3H_5^+$	12	5	3	3	1
sec-Butyl formate						
132	$HCO_2C_4H_9 \cdot NO^+$				16	
103	$HCO_2C_4H_9 \cdot H^+$	8	22	29	20	25
73	$C_4H_9O^+$	9	3	1	2	3
59	$C_3H_7O^+$, $HCO_2CH_2^+$	6	3	3	2	2
57	$C_4H_9^+$	100	100	100	100	100
55	$C_4H_7^+$	3	3	1	2	2
47	$HCO_2H_2^+$	3	3	7	10	8
45	$C_2H_5O^+$	6	4	R[b]	R[b]	6
41	$C_3H_5^+$	8	3	3	3	2

[a]Intensities as % of base peak arising from additive.
[b]R indicates fragment ion obscured by reagent ion peak.



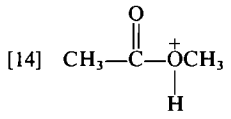
oxygen-protonated species. More importantly, it would suggest that with deuterated reagent gases, which form $HCO_2C_3H_7{\cdot}D^+$ originally, the isopropyl cation produced should contain significant deuterium; earlier studies (5) of the D_2 CI mass spectra of formates show that there is practically no deuterium incorporation in the $C_3H_7^+$ product from either *n*-propyl or *i*-propyl formate. Finally, reaction [13] is a rearrangement at least as complex as that resulting in formation of $HCO_2H_2^+$ and consequently one would not anticipate the observed increase in importance of $HCO_2H_2^+$ formation with decreasing internal energy in such a situation.

The butyl formates examined all show extensive fragmentation, with $C_4H_9^+$ the dominant fragment ion with all reagent gases. For protonated *sec*-butyl formate, formation of *s*-$C_4H_9^+$ (ΔH^0 = 24 kcal mol^{-1}) is favoured over formation of $HCO_2H_2^+$ (ΔH^0 = 26 kcal mol^{-1}); consequently, dominant fragmentation by simple bond cleavage is to be expected. However, for the *n*-butyl formate and *i*-butyl formate, formation of the primary butyl cations ($\Delta H^0 \simeq$ 40 kcal mol^{-1}) is thermochemically unfavourable compared to formation of $HCO_2H_2^+$ (ΔH^0 = 25 kcal mol^{-1}). It appears that in these two cases fragmentation must be accompanied by [1,2]-H shifts to form the more stable *sec*-butyl and *tert*-butyl structures respectively.

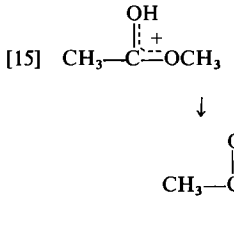
Chemical Ionization Mass Spectra of Acetates

The chemical ionization mass spectra of the methyl through butyl acetates are presented in Table 2, while the CI mass spectra of some isomeric pentyl acetates are presented in Table 3.

The only significant fragmentation channel for protonated methyl acetate involves methanol elimination to form the acetyl ion (*m*/*z* 43). The intensity of this fragment drops off markedly with decreasing protonation exothermicity, accounting for only ~20% of the total ionization in the CO_2/H_2 CI system. Pescheck and Butrill (3) have proposed that this fragment arises as a result of protonation at the ether oxygen followed by simple bond cleavage (reaction [14]), the analogue of the $A_{Ac}l$ solution

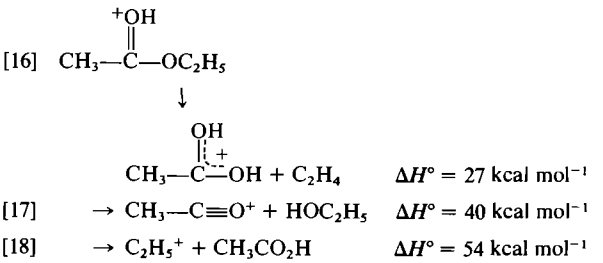


reaction. This simple bond cleavage reaction should not have an activation energy significantly greater than the endothermicity; consequently, assuming this mechanism, it is surprising that the acetyl ion is not more abundant in the CO_2/H_2 CI system where the protonation exothermicity to form the ether oxygen-protonated species is 53 kcal mol^{-1}. A likely explanation is that the major part of the acetyl ion arises by the route



This route, involving initial formation of the thermodynamically favoured carbonyl protonated species, requires a symmetry-forbidden [1,3]-H shift prior to fragmentation. The activation energy barrier for this step is undoubtedly much higher than the ΔH^0 of ~15 kcal mol^{-1} or the overall ΔH^0 of ~37 kcal mol^{-1}; such a high activation energy barrier would explain the strong dependence of the extent of fragmentation on the protonation exothermicity. The persistent $CH_3{-}C{\equiv}O^+$ ion signal with the weaker protonating agents may represent a contribution from reaction [14].

In the CI mass spectra of ethyl acetate the dominant fragmentation reaction involves formation of protonated acetic acid (reaction [16]), with minor formation of the acetyl ion (reaction [17]); formation of $C_2H_5^+$, the product of the $A_{Al}l$ fragmentation (reaction [18]), is observed with very low abundance in the H_2 CI spectrum



[16] $CH_3—C(^+OH)—OC_2H_5$

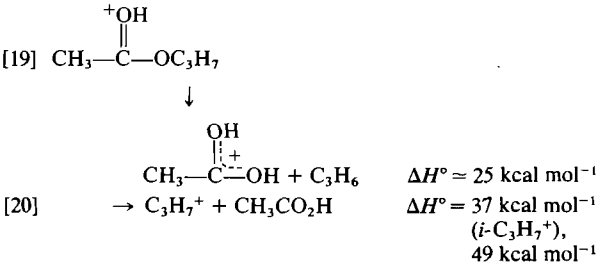
$\rightarrow CH_3—C(OH)^+—OH + C_2H_4$ $\Delta H° = 27$ kcal mol^{-1}

[17] $\rightarrow CH_3—C\equiv O^+ + HOC_2H_5$ $\Delta H° = 40$ kcal mol^{-1}

[18] $\rightarrow C_2H_5^+ + CH_3CO_2H$ $\Delta H° = 54$ kcal mol^{-1}

The relative fragment ion abundances are in agreement with the relative reaction endothermicities. The acetyl ion may arise, in part, by formation of the ether oxygen-protonated species and simple bond cleavage; this fragmentation reaction would have a ΔH^0 of ~22 kcal mol^{-1} and, if it were a major route, should be more competitive with that leading to formation of protonated acetic acid. Thus it appears likely that the major route to acetyl ion formation is by fragmentation of the carbonyl protonated species, as discussed in detail for protonated methyl acetate.

Three fragmentation modes, reactions [19] to [21], are observed for protonated *i*-propyl acetate and protonated *n*-propyl acetate. Reaction [19],



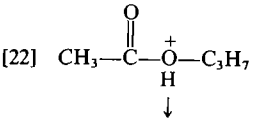
[19] $CH_3—C(^+OH)—OC_3H_7$

$\rightarrow CH_3—C(OH)^+—OH + C_3H_6$ $\Delta H° \simeq 25$ kcal mol^{-1}

[20] $\rightarrow C_3H_7^+ + CH_3CO_2H$ $\Delta H° = 37$ kcal mol^{-1} (i-$C_3H_7^+$), 49 kcal mol^{-1} (n-$C_3H_7^+$)

[21] $\rightarrow CH_3—C\equiv O^+ + C_3H_7OH$ $\Delta H° \simeq 40$ kcal mol^{-1}

forming protonated acetic acid, has a considerably lower ΔH^0 and, presumably, activation energy, than the other fragmentation reactions and the protonated acetic acid ion froms the base peak in all CI mass spectra. The $C_3H_7^+$ and $CH_3—C\equiv O^+$ fragment ions are of approximately equal intensity in all CI spectra and decrease in abundance relative to the rearrangement product $CH_3CO_2H_2^+$ with decreasing protonation exothermicity. Reaction [21], as written, involves a symmetry-forbidden [1,3]-shift and, as discussed above, the activation energy should be considerably higher than the ΔH^0 and one would not anticipate that this reaction should be competitive with the other two reactions. However, the ether oxygen proton affinity of *n*-propyl acetate is only ~12 kcal mol^{-1} less than the carbonyl oxygen proton affinity (16) and it may be that an appreciable fraction of the $CH_3—C\equiv O^+$ ion signals arises by the fragmentation

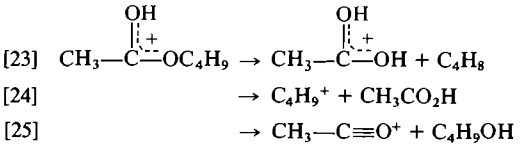


[22] $CH_3—C(=O)—O^+(H)—C_3H_7$

$\rightarrow CH_3—C\equiv O^+ + C_3H_7OH$ $\Delta H° = 28$ kcal mol^{-1}

which would not be expected to have an activation energy significantly greater than the ΔH^0. The formation of $C_3H_7^+$ in the CI mass spectra of *n*-propyl acetate has a ΔH^0 of ~49 kcal mol^{-1} (assuming n-$C_3H_7^+$ formation) and should not be competitive with the alternative fragmentations. It is probable that, here also, rearrangement to the *i*-propyl structure occurs. In addition, formation of alkyl ions by the $A_{Al}1$ mechanism from the ether oxygen-protonated species is possible and would have $\Delta H°$'s ~12 kcal mol^{-1} lower than those quoted for reaction [20].

The CI mass spectra of the four butyl acetates show an interesting dependence of the relative importance of the three fragmentation reactions [23] to [25] on the identity of the butyl group.



[23] $CH_3—C(OH)^+—OC_4H_9 \rightarrow CH_3—C(OH)^+—OH + C_4H_8$

[24] $\rightarrow C_4H_9^+ + CH_3CO_2H$

[25] $\rightarrow CH_3—C\equiv O^+ + C_4H_9OH$

For *tert*-butyl acetate, formation of t-$C_4H_9^+$ is favoured thermochemically ($\Delta H^0 \simeq 21$ kcal mol^{-1}) over formation of protonated acetic acid ($\Delta H^0 \simeq 29$ kcal mol^{-1}) or formation of $CH_3—C\equiv O^+$ ($\Delta H^0 \simeq 40$ kcal mol^{-1}) and $C_4H_9^+$ is the dominant fragment ion in all CI mass spectra. For protonated *sec*-butyl acetate, fragmentation to form s-$C_4H_9^+$ has a ΔH^0 (~33 kcal mol^{-1}) higher than that for formation of protonated acetic acid ($\Delta H^0 \simeq 25$ kcal mol^{-1}); as a consequence, $CH_3CO_2H_2^+$ is the base peak in all CI mass spectra. The $C_4H_9^+$ ion is of appreciable intensity and increases in relative abundance with increasing protonation exothermicity, as expected for a simple bond cleavage reaction compared to a rearrangement fragmentation.

For both the *n*-butyl and *i*-butyl acetate systems fragmentation of the protonated ester to form the primary *n*-butyl or *i*-butyl cations would be much less favourable thermochemically ($\Delta H^0 \simeq 47$ kcal mol^{-1}) than formation of protonated acetic acid ($\Delta H^0 \simeq 25$ kcal mol^{-1}); nevertheless, $C_4H_9^+$ is the base peak in all CI mass spectra of *i*-butyl acetate

TABLE 2. Chemical ionization mass spectra of methyl through butyl acetates[a]

m/z	Ion	H_2 CI	N_2/H_2 CI	CO_2/H_2 CI	N_2O/H_2 CI	CO/H_2 CI
Methyl acetate						
104	$CH_3CO_2CH_3 \cdot NO^+$				16	
75	$CH_3CO_2CH_3 \cdot H^+$	31	100	100	100	100
59	$CO_2CH_3^+$	4	4	1	1	1
43	$CH_3C{\equiv}O^+$	100	91	27	22	16
15	CH_3^+	1	1	—	—	—
Ethyl acetate						
118	$CH_3CO_2C_2H_5 \cdot NO^+$				31	
89	$CH_3CO_2C_2H_5 \cdot H^+$	45	60	64	100	100
61	$CH_3CO_2H_2^+$	100	100	100	76	70
43	$CH_3C{\equiv}O^+$	31	17	12	10	9
n-Propyl acetate						
132	$CH_3CO_2C_3H_7 \cdot NO^+$				34	
103	$CH_3CO_2C_3H_7 \cdot H^+$	44	68	45	79	52
61	$CH_3CO_2H_2^+$	100	100	100	100	100
43	$C_3H_7^+$	84	55	39	32	30
43	$CH_3C{\equiv}O^+$	82	56	39	32	30
41	$C_3H_5^+$	6	—	—	—	—
i-Propyl acetate						
132	$CH_3CO_2C_3H_7 \cdot NO^+$				19	
103	$CH_3CO_2C_3H_7 \cdot H^+$	30	48	34	46	65
61	$CH_3CO_2H_2^+$	100	100	100	100	100
43	$C_3H_7^+$	43	27	19	12	16
43	$CH_3C{\equiv}O^+$	43	27	19	12	16
41	$C_3H_5^+$	3	2	—	—	—
n-Butyl acetate						
146	$CH_3CO_2C_4H_9 \cdot NO^+$				36	
117	$CH_3CO_2C_4H_9 \cdot H^+$	42	66	41	62	35
115	$C_6H_{11}O_2^+$	6	3	1	5	—
73	$C_3H_5O_2^+$	6	5	4	2	4
61	$CH_3CO_2H_2^+$	100	100	100	100	100
57	$C_4H_9^+$	76	55	31	21	20
55	$C_4H_7^+$	15	5	2	1	2
43	$CH_3C{\equiv}O^+$	42	21	12	10	11
41	$C_3H_5^+$	9	2	—	—	—
i-Butyl acetate						
146	$CH_3CO_2C_4H_9 \cdot NO^+$				54	
117	$CH_3CO_2C_4H_9 \cdot H^+$	38	54	37	86	87
115	$C_6H_{11}O_2^+$	8	3	1	6	3
73	$C_3H_5O_2^+$	3	—	5	3	6
61	$CH_3CO_2H_2^+$	57	73	89	86	67
57	$C_4H_9^+$	100	100	100	100	100
55	$C_4H_7^+$	4	5	—	—	—
43	$CH_3{-}C{\equiv}O^+$	46	27	24	14	40
41	$C_3H_5^+$	6	5	—	—	—
sec-Butyl acetate						
146	$CH_3CO_2C_4H_9 \cdot NO^+$				19	
117	$CH_3CO_2C_4H_9 \cdot H^+$	35	47	26	49	40
115	$C_6H_{11}O_2^+$	3	—	2	5	—
87	$C_4H_7O_2^+$	5	2	5	3	8
73	$C_3H_5O_2^+$	14	2	4	2	5
61	$CH_3CO_2H_2^+$	100	100	100	100	100
57	$C_4H_9^+$	62	40	22	13	13
55	$C_4H_7^+$	2	2	—	—	—
43	$CH_3C{\equiv}O^+$	32	16	13	6	38
41	$C_3H_5^+$	5	2	—	—	—

TABLE 2. (*Concluded*)

m/z	Ion	H_2 CI	N_2/H_2 CI	CO_2/H_2 CI	N_2O/H_2 CI	CO/H_2 CI
tert-Butyl acetate						
146	$CH_3CO_2C_4H_9 \cdot NO^+$				10	
117	$CH_3CO_2C_4H_9 \cdot H^+$	6	29	18	37	30
101	$CH_3CO_2C(CH_3)_2^+$	3	3	4	2	7
61	$CH_3CO_2H_2^+$	4	5	9	8	4
57	$C_4H_9^+$	100	100	100	100	100
55	$C_4H_7^+$	1	2	—	—	—
43	$CH_3—C\equiv O^+$	15	8	6	4	14
41	C_3H_5	3	2	—	—	—

[a]Intensities expressed as % of base peak.

and is of appreciable abundance in the CI mass spectra of *n*-butyl acetate. It appears likely that there is significant rearrangement to the *tert*-butyl and *sec*-butyl structures, respectively, during fragmentation of these protonated esters. These rearrangements can occur by relatively simple [1,2]-H shifts in the developing cation. For all the butyl acetates there is significant formation of the $CH_3—C\equiv O^+$ ion; this may represent fragmentation of the ether oxygen protonated species. The proton affinity difference between the carbonyl oxygen and the ether oxygen of esters decreases as the size of the ester increases (16) and one might expect more protonation at the ether oxygen as a result.

The CI mass spectra of the six pentyl acetates examined are summarized in Table 3. The usual fragmentation reactions, [26] to [28], are observed.

[26] $CH_3—\overset{OH}{\overset{\|}{C}}—OC_5H_{11} \rightarrow CH_3—\overset{OH}{\overset{\|}{C}}—OH + C_5H_{10}$

[27] $\rightarrow C_5H_{11}^+ + CH_3CO_2H$

[28] $\rightarrow CH_3—C\equiv O^+ + C_5H_{11}OH$

In addition, in several cases extensive fragmentation of $C_5H_{11}^+$ is observed by the reaction channels, [29, [30], and [31], established previously (13).

[29] $C_5H_{11}^+ \rightarrow C_5H_9^+ + H_2$

[30] $\rightarrow C_4H_7^+ + CH_2$

[31] $\rightarrow C_3H_7^+ + C_2H_4$

The fragmentation of $C_5H_{11}^+$ ions produced by dissociative proton transfer to isomeric pentyl alcohols has been studied in detail (13). It was observed that the extent of fragmentation was greatest for $C_5H_{11}^+$ ions derived from primary alcohols, less for $C_5H_{11}^+$ derived from secondary alcohols, and very slight for the $C_5H_{11}^+$ ion derived from *tert*-pentanol. As expected, the extent of fragmentation decreased as the protonation exothermicity decreased. These results were interpreted as indicating that there was negligible rearrangement to more stable alkyl structures prior to achievement of the critical reacting configuration which determined the energy partitioning between R^+ and H_2O in the decomposition of ROH_2^+. In terms of the extent of further fragmentation of the $C_5H_{11}^+$ ions the present results for protonated pentyl acetates are in essential agreement with the results for the protonated pentyl alcohols. However, in terms of the competition between reactions [26] and [27] there is substantial evidence for alkyl ion rearrangement. This is illustrated most clearly in terms of the relative intensities for the $CH_3CO_2H_2^+$ and $C_5H_{11}^+$ ions observed in the CO_2/H_2 CI spectra summarized in Table 4, along with the ΔH^0 for formation of these ions from the ground state protonated ester. The ΔH^0 values for $C_5H_{11}^+$ formation have been calculated assuming an alkyl ion structure identical to the neutral alkyl moiety. For 2-pentyl acetate and 3-pentyl acetate the ΔH^0 for formation of $C_5H_{11}^+$ is slightly larger than that for formation of $CH_3CO_2H_2^+$ and we observe that the alkyl ion intensity is lower than that of the protonated acetic acid ion. For the secondary acetate, 3-methyl-2-pentyl acetate, the ΔH^0 values are very similar, yet the $C_5H_{11}^+$ ion is the dominant ion in the mass spectra. This strongly indicates a [1,2]-H shift to yield the more stable *tert*-pentyl ion. Collin and Herman (25) have reported an activation energy of $\sim$2 kcal mol^{-1} for this isomerization from studies of the protonation of 3-methyl-1-pentene in radiolysis experiments. Indeed, their results for the extent of fragmentation of $C_5H_{11}^+$ as a function of protonation exothermicity are in agreement with the present data. For the primary acetates the ΔH^0's for formation of the respective primary alkyl ions are much larger than the ΔH^0 for formation of $CH_3CO_2H_2^+$, yet the alkyl ion intensities are as great as, or greater than, the $CH_3CO_2H_2^+$ ion intensities. Clearly this unexpected result can only be accommodated by assum-

TABLE 3. Chemical ionization mass spectra of pentyl acetates[a]

m/z	Ion	H_2 CI	N_2/H_2 CI	CO_2/H_2 CI	N_2O/H_2 CI	CO/H_2 CI
n-Pentyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				23	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	34	58	72	21	29
129	$C_7H_{13}O_2^+$	4	2	—	4	—
71	$C_5H_{11}^+$	51	65	71	45	43
69	$C_5H_9^+$	37	23	7	4	6
61	$CH_3CO_2H_2^+$	86	100	100	100	100
55	$C_4H_7^+$	15	19	10	4	2
43	$C_3H_7^+$	100	85	18	9	16
43	$CH_3—C\equiv O^+$	66	35	20	17	21
3-Methyl-1-butyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				17	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	40	68	56	13	37
129	$C_7H_{13}O_2^+$	4	2	1	4	—
71	$C_5H_{11}^+$	100	100	100	100	100
69	$C_5H_9^+$	35	9	4	2	2
61	$CH_3CO_2H_2^+$	56	35	42	57	47
55	$C_4H_7^+$	19	12	7	4	2
43	$C_3H_7^+$	97	50	12	9	16
43	$CH_3—C\equiv O^+$	62	30	15	12	22
2-Methyl-1-butyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				36	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	39	6	77	87	48
129	$C_7H_{13}O_2^+$	4	—	2	8	2
71	$C_5H_{11}^+$	100	100	100	100	100
69	$C_5H_9^+$	35	9	3	3	2
61	$CH_3CO_2H_2^+$	62	62	51	52	26
55	$C_4H_7^+$	19	15	5	3	2
43	$C_3H_7^+$	96	71	15	13	11
43	$CH_3—C\equiv O^+$	50	31	12	8	12
3-Pentyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				11	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	30	34	39	39	51
129	$C_7H_{13}O_2^+$	—	—	—	4	—
101	$C_5H_9O_2^+$	13	10	8	3	5
87	$C_4H_7O_2^+$	30	7	3	11	5
71	$C_5H_{11}^+$	81	90	74	58	68
69	$C_5H_9^+$	13	7	3	5	3
61	$CH_3CO_2H_2^+$	100	100	100	100	100
55	$C_4H_7^+$	11	10	3	—	3
45	$C_2H_5O^+$	6	4	R[b]	R[b]	—
43	$C_3H_7^+$	80	62	13	8	15
43	$CH_3C\equiv O^+$	72	40	20	15	28
2-Pentyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				14	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	41	15	65	33	42
129	$C_7H_{13}O_2^+$	3	—	—	6	—
87	$C_4H_7O_2^+$	36	15	12	7	5
71	$C_5H_{11}^+$	84	85	76	44	62
69	$C_5H_9^+$	18	9	3	5	2
61	$CH_3CO_2H_2^+$	100	100	100	100	100
55	$C_4H_7^+$	8	9	3	2	2
45	$C_2H_5O^+$	9	6	R[b]	R[b]	—
43	$C_3H_7^+$	70	58	11	7	15
43	$CH_3C\equiv O^+$	52	25	18	14	27
3-Methyl-2-butyl acetate						
160	$CH_3CO_2C_5H_{11}\cdot NO^+$				19	
131	$CH_3CO_2C_5H_{11}\cdot H^+$	14	11	27	51	43
87	$C_4H_7O_2^+$	16	3	5	2	4

TABLE 3. (*Concluded*)

m/z	Ion	H_2 CI	N_2/H_2 CI	CO_2/H_2 CI	N_2O/H_2 CI	CO/H_2 CI
71	$C_5H_{11}^+$	100	100	100	100	100
69	$C_5H_9^+$	4	2	2	—	—
61	$CH_3CO_2H_2^+$	6	6	8	7	7
55	$C_4H_7^+$	4	2	—	—	—
43	$C_3H_7^+$	33	19	10	7	11
43	$CH_3—C\equiv O^+$	30	20	12	8	14

[a]Intensities as % of base peak.
[b]R denotes ion signal obscured by reagent ion signal.

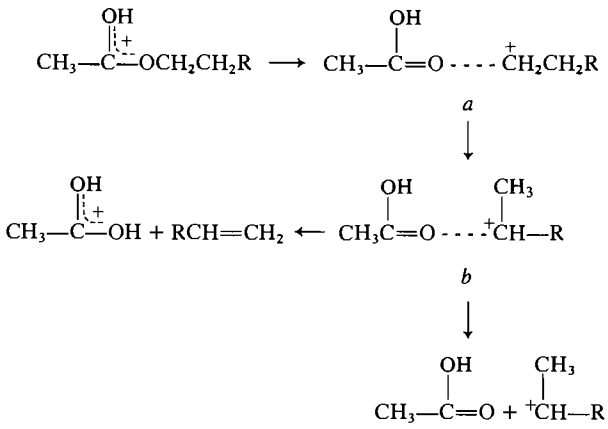
TABLE 4. Relative $C_5H_{11}^+$ and $CH_3CO_2H_2^+$ intensities in CO_2/H_2 CI of pentyl acetates

R of $ROCOCH_3$	$C_5H_{11}^+$	ΔH^{0a}	$CH_3CO_2H_2^+$	ΔH^{0a}
$CH_3CH_2CH_2CH_2CH_2—$	45	45	100	27
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2CH_2—$	100	47	57	26
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—$	100	45	52	26
$CH_3CH_2—\underset{\displaystyle \vert}{CH}—CH_2—CH_3$	48	34	100	26
$CH_3CH_2CH_2\underset{\displaystyle \vert}{CH}—CH_3$	44	34	100	26
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—\underset{\displaystyle \vert}{CH}—CH_3$	100	29	7	26

[a]ΔH^0 (kcal mol^{-1}) for formation of fragment ion from carbonyl protonated ester.

ing that rearrangement to a more stable secondary or tertiary alkyl ion occurs during fragmentation. The extent of formation of $CH_3—C\equiv O^+$ is higher than one would anticipate for fragmentation of the carbonyl protonated species and formation of this fragment may represent an increased importance of protonation at the ether oxygen.

Thus, we are left with the apparent paradox that the energy partitioning between neutral and ionic fragments, as reflected in the extent of further fragmentation of the alkyl ions, supports a reaction model in which no significant rearrangement in the alkyl moiety occurs, while the competition between fragmentation channels indicates that rearrangement has occurred in the alkyl moiety. A possible resolution of this paradox is given by the detailed reaction model proposed in Scheme 1 for a primary alkyl acetate. As the alkyl carbon–oxygen bond lengthens, a critical state (or transition state) *a* is reached corresponding to an unrearranged alkyl ion bonded to neutral acetic acid largely by ion–dipole interactions (21). The partitioning of the excess energy between the neutral acetic acid and alkyl ion appears to be determined at this stage. A simple [1,2]-H shift in the alkyl ion leads to the secondary ion interacting with acetic acid by ion–dipole forces; this structure *b*, which will be more stable than *a*, may then undergo simple fission of the weak bond to acetic acid yielding the alkyl ion or may transfer a proton to acetic acid yielding the protonated acid and an appropriate olefin. Isotopic labelling studies (6) in *n*-propyl acetate show that the H transferred from the propyl group does not originate from a specific position of the alkyl group but may come from any position. It is possible that this proton shift may go through the intermediacy of *c*, a proton solvated by both the olefin and acetic acid (21), which might be considered as an alterna-



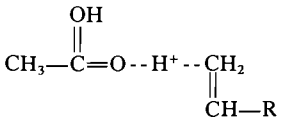
SCHEME 1

TABLE 5. Thermochemistry of carboxylic acids and protonated carboxylic acids[a]

R—COOR'	ΔH_f (RCOOR')[b]	PA[c] C=O	OR'[d]	OH | + ΔH^0_f(R—C⁺—OR')	O || + ΔH^0_f(R—C—OHR')
HCOOH	−90.6	178	152	97	123
$HCOOCH_3$	−83.7	188	167	94	115
$HCOOC_2H_5$	−88.7	191	168	86	109
HCOO*n*-C_3H_7	−95	192	171	79	100
HCOO*i*-C_3H_7	−99	192	171	75	96
HCOO*n*-C_4H_9	−100	191	171	75	95
HCOO*i*-C_4H_9	−102	192	171	72	93
HCOO*s*-C_4H_9	−104	192	171	70	91
HCOO*t*-C_4H_9	−109	192	171	65	86
CH_3COOH	−103.3	189	161	74	102
CH_3COOCH_3	−97.9	195	180	73	88
$CH_3COOC_2H_5$	−105.9	198	180	62	80
CH_3COO*n*-C_3H_7	−111	199	187	56	68
CH_3COO*i*-C_3H_7	−115	199	183	52	68
CH_3COO*n*-C_4H_9	−116	199	183	51	67
CH_3COO*i*-C_4H_9	−118	199	183	49	65
CH_3COO*s*-C_4H_9	−120	199	183	47	63
CH_3COO*t*-C_4H_9	−124	199	183	43	59

[a]All data in kcal mol^{-1}.
[b]Taken from refs. 19 and 20 or estimated by group equivalent methods (27).
[c]Taken from ref. 15 or, for higher members, estimated.
[d]Taken from estimates given in ref. 16 or estimated from that data.

tive structure to *b*; in principle *c* could fragment to either the protonated acid or the appropriate stable alkyl ion. However, if such were the case, the rate constant expressions for formation of both the alkyl ion and protonated acetic acid should have similar frequency factors. As discussed above, the internal energy dependence of the relative fragment ion yields suggests that the reaction forming protonated acetic acid has a lower frequency



c

factor, indicating a more complex rearrangement. This is most readily interpreted on the basis that the alkyl ion originates by simple dissociation of the loosely-bound complex *b* of Scheme 1.

Acknowledgements

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Appendix

The thermochemical data relevant to the heats of formation of protonated carboxylic acids and esters are summarized in Table 5. In view of the estimates made the uncertainty is probably at least ± 3 kcal mol^{-1} in the heats of formation.

Other relevant ion heats of formation (all in kcal mol^{-1}) are: $C_2H_5^+$, 219; n-$C_3H_7^+$, 208; i-$C_3H_7^+$, 192; n-$C_4H_9^+$, 201; i-$C_4H_9^+$, 199; s-$C_4H_9^+$, 183; t-$C_4H_9^+$, 167; all from ref. 17. A value of ΔH^0_f (CH_3—$C{\equiv}O^+$) = 158 kcal mol^{-1} was used (26). ΔH_{0f} ($CH_3OH_2^+$) = 136 kcal mol^{-1} was derived from the reported proton affinity of 182 kcal mol^{-1} (15).

Neutral heats of formation, from refs. 19 and 20, all in kcal mol^{-1}, are: CH_3OH, −48.1; C_2H_5OH, −56.1; n-C_3H_7OH, −61.2; i-C_3H_7OH, −65.1; n-C_4H_9OH, −65.8; i-C_4H_9OH, −67.8; s-C_4H_9OH, −70.0; t-C_4H_9OH, −74.7; C_2H_4, 12.5; C_3H_6, 5.0; 1-C_4H_8, −0.2; 2-C_4H_8, −1.9; i-C_4H_8, −4.3.