Chemical Ionization Mass Spectrometry. II. Esters

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Abstract: Chemical ionization spectra are reported and discussed for ten alkyl and six other propionate esters and five other esters using methane as the reactant gas. These spectra are well explained in terms of predominant attack at the carboxyl group by CH_5^+, $C_2H_5^+$, and $C_3H_5^+$. Proton transfer occurs giving $(MW + 1)^+$ ions, some of which dissociate to give $RCO_2H_2^+$, RCO^+, and alkyl ions, R'^+, from the alcohol chain. Collision-stabilized addition of $C_2H_5^+$ and $C_3H_5^+$ occurs with some of the esters as well as displacement reactions in which $C_2H_5^+$ and $C_3H_5^+$ are added to the molecule and an olefin is expelled. For some compounds, the protonated alcohols are produced. Plausible mechanisms are offered for several of the decomposition processes. The temperature dependence of certain spectra has been studied, and the relative concentration of $(MW + 1)^+$ ions increases with decreasing temperature. Spontaneous or collision-induced decompositions were observed which give rise to diffuse peaks in the spectra, some of which have been assigned.

In a previous publication[1] we gave a general introduction to a new technique for the production of mass spectra, chemical ionization mass spectrometry, and we presented and discussed spectra for several types of compounds obtained with methane as the reactant gas. The purpose of this paper is to give more careful consideration to the spectra and reactions of several compounds of the same type in order to develop the detailed understanding necessary for the prediction of spectra. In addition, these spectra will show the usefulness of this method for qualitative analysis and determination of structure.

Although the method has been discussed in detail previously, it is worthwhile to review it briefly here. Within the source of the mass spectrometer there is a high pressure of methane (1 torr) and a low pressure of an additive (approximately 10^{-3} torr). Under these conditions the primary ionization by the electron beam will be predominantly of methane. The major ions of methane produced by electron impact, CH_4^+, CH_3^+, and CH_2^+, react rapidly with the very large excess of methane to give CH_5^+, $C_2H_5^+$, and $C_3H_5^+$. These three ions, which comprise approximately 95% of the total ionization of methane at 1 torr, react only very slowly with methane, but they will react rapidly with most other compounds. Consequently, the reactions of these ions with the additives will produce ions from the additive which form characteristic mass spectra.

Product ions from reactions with methane and impurities present in methane interfere with the additive ion spectra at certain masses. These interferences are particularly bad for ions of m/e 17 (CH_5^+), 29 ($C_2H_5^+$), and 41 ($C_3H_5^+$), so the spectra are generally reported for ions of m/e greater than 43. However, we do not believe that significant amounts of additive ionization are thus omitted.

The compounds to be considered in this paper are primarily aliphatic propionates, but several other esters are also included. In this series of compounds it is possible to maintain the same center for attack, the ester group, and systematically vary the molecular structure by changing either end of the molecule. The dominant ions from these compounds are in a convenient region of the spectrum, and the vapor pressures are such that the compounds are easily handled as liquids.

Apparatus. The instrument has been described in the previous paper.[1] The conditions for the present experiments are as follows: $P(CH_4) = 1.00 \pm 0.02$ torr; source temperature = 237 ± 5°; sample reservoir temperature = 240 ± 5°; sample size = 1.8 μl of liquid; pressure of methane within the additive reservoir = 4.4 torr; electron energy = 210 v; repeller = 2.0 v, 5 v/cm; ion accelerating voltage = 3000 v; and the monitored unresolved ion current was maintained constant at $1.50 \pm 0.1 \times 10^{-12}$ amp. The emitted and collected electron currents are not constant, probably because surface potentials within the source may vary with the state of cleanliness within the source so that the fraction of the ions expelled from the source for a given electron current is not always the same. All of these parameters will affect the ionization due to the additive, and as we will discuss later, the source temperature has a marked effect on the ionic distribution of the additive spectra.

At this point it seems worthwhile to point out that the mass resolution of the instrument does not deteriorate markedly with increasing pressure. For butyl propionate it was possible to observe two well-separated peaks (less than 10% valley) at m/e 57, $C_4H_9^+$ and $C_2H_5CO^+$: $\Delta M_{\text{exptl}} = 0.036$; $\Delta M_{\text{theo}} = 0.0364$; $M/\Delta M = 1600$. The conditions used in these experiments are not those which will give the best resolution with this instrument, since that may be improved by using smaller slits. However, the resolution at a source pressure of 1 torr is essentially the same as that which can be achieved at 10^{-5} torr with the present instrument geometry.

The esters which were used in these experiments were obtained from Eastman Chemical or K & K Laboratories. The purities, presumably high, are not known.

The same volumes of liquid were introduced into the reservoir at temperatures high enough to volatilize all of the sample. We feel that we have no special problems in handling these compounds although problems have been observed with materials of lower vapor pressure. An additional pressure of methane was always present in this reservoir to carry the additive into the source. The procedures for obtaining the

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[1] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

Table I. Chemical Ionization for Propionate Esters

Propionate, X	Σ_{add}	$\left[\frac{MW(X)}{MW(MeOPr)}\right]^a$	$\Sigma_{add}(MW)^{1/2}$
Methyl	8558 ± 16	1.00	8.56×10^3
Ethyl	7238 ± 37	1.16	9.05×10^3
n-Propyl	6413 ± 148	1.32	9.75×10^3
Isopropyl	6271 ± 78	1.32	9.55×10^3
n-Butyl	4693 ± 34	1.48	8.45×10^3
Isobutyl	5775 ± 552	1.48	10.35×10^3
n-Pentyl	5048 ± 305	1.64	10.58×10^3
	4034 ± 144	1.64	8.47×10^3
Isopentyl	4550 ± 585	1.64	9.55×10^3
	4176 ± 93	1.64	8.77×10^3
Cyclohexyl	5006 ± 204	1.77	11.8×10^3
	4570 ± 17	1.77	10.8×10^3
n-Heptyl	3597	1.95	9.80×10^3

[a] MW = molecular weight.

hole leak and a long section of glass tubing. Because there is the additional pressure of 4.4 torr within the additive reservoir and also a pressure of 1-2 torr of CH_4 within the line leading to the source, it is not possible to determine the different rates of flow for these esters from the reservoir into the source. However, a variation of approximately $MW^{-1/2}$ (MW = molecular weight) would be reasonable. Consequently, we expect $\Sigma_{add}(MW)^{1/2}$ to be constant for the alkyl esters. The values, relative to methyl propionate, are shown in the last column of Table I. The average deviations are those for duplicate sample introductions done immediately in succession. The duplicate numbers for some of the compounds are obtained from experiments several days apart and give more realistic information about the reliability of the data.

Table II. Chemical Ionization Spectra of Propionate Esters (CH_4 Reactant) % of Additive Ionization

	$ROCOC_2H_5$ R =	(MW + 1)$^+$	(MW)$^+$	(MW − 1)$^+$	57 $C_2H_5CO^+$	75 C_2H_5-CO_2-H_2^+	103 C_2H_5-COHO $C_2H_5^+$	115 C_2H_5-CO-HO-$C_3H_5^+$	(MW + C_2H_5)$^+$	(MW + C_3H_5)$^+$	R^+	$(R-H)^+$	$(R-H_2)^+$	RO^+	ROH^+	ROH_2^+	Σ^a
1	Methyl	79	1.0	0.1	10.1	0.0	0.1	0.03	1.7	1.4	...	...	...	<0.1	<0.03	0.9	98
2	Ethyl	48	1.0	0.1	9.0	32	(MW + 1)$^+$	0.04	2.6	2.0	...	<0.1	<0.1	1.1	<0.02	0.3	99
3	*n*-Propyl	17.4	0.1	1.6[b]	8.8	54	8.5	1.6[c]	0.05	1.2	1.6	<0.1	Low	0.9	<0.03	0.05	97
4	Isopropyl	5.8	0.3	2.6[b]	4.3	71	7.6	2.6[c]	<0.05	<0.05	2.5	<0.1	Low	0.7	<0.03	<0.03	97
5	*n*-Butyl	7.9	0.05	0.5	16.8[d]	55	8.0	2.3	<0.05	<0.05	16.8[e]	1.0	1.9	0.8	<0.05	(75)$^+$	97
6	Isobutyl	3.0	0.04	0.5	43[d]	35	6.9	2.6	<0.05	<0.05	43[e]	1.2	0.5	1.0	<0.04	(75)$^+$	96
7	*n*-Pentyl	4.8	0.03	0.3	9.4	47	6.8	1.9	<0.05	0.3	13.9	1.3	5.4	1.0	<0.02	0.3[f]	96
8	Isopentyl	5.6	<0.05	0.2	7.2	7.5	5.4	1.5	0.03	0.4	56	2.2	4.3	0.5	<0.02	0.2[f]	95
9	*n*-Heptyl	5.0	0.06	0.6	15.9	39	9.0	3.1[g]	0.1	0.5	4.0	1.5	8.8	3.1[b]	<0.05	0.6	90
10	*n*-Octyl	7.9	0.08	1.2	7.9	25	10.2	2.4	1.0	1.0	5.8	1.9	12.3	1.0	<0.09	0.1	81
11	Vinyl	11.3	0.2	0.03	71	0.06	0.06	0.04	1.3	0.1	...	...	...	<0.1	<0.05	12.3	99
12	Allyl	15.9	0.2	0.05	57[h]	0.3	0.07	(MW + 1)$^+$	0.5	0.7	15.0	<0.1	<0.1	57[e]	<0.1	0.2	94
13	Cyclohexyl	1.7	0.05	0.5	3.0	42	4.9	1.8	<0.04	<0.04	19.6	1.9	8.5	3.9	<0.04	0.04	90
14	Phenyl	27.9	0.6	0.05	4.4	0.2	<0.05	<0.05	1.8	0.2	<0.05	<0.05	<0.05	0.2	2.4	40	84
15	Benzyl	0.7	0.05	0.05	<0.1	0.05	0.05	0.05	1.4	0.1	78	<0.05	<0.05	2.7	1.9	<0.1	90
16	Tetrahydrofurfuryl	18.0	0.1	1.7	<0.1	0.04	2.0	0.1	0.6	0.7	60	0.7	0.6	0.1	<0.05	0.1	90

[a] Includes ^{13}C isotopes. [b] Also 115. [c] Also (MW − 1)$^+$. [d] Also $C_4H_9^+$. [e] Also $C_2H_5CO^+$. [f] Also $C_2H_5COHOCH_3^+$. [g] Also RO^+. [h] Also $C_3H_5O^+$.

spectra for this series of compounds were kept as nearly the same as possible for all of these experiments.

Results and Discussion

If one compares the additive ionization for this series of compounds, one can obtain information on the relative rates of reaction of these compounds with the ions from methane, CH_5^+, $C_2H_5^+$, and $C_3H_5^+$, as a function of molecular structure. If the attack is predominantly at the electronegative, nucleophilic ester group, then one may expect that the rates of reaction of these ions with a series of esters will be approximately constant.

The total additive ionization, Σ_{add}, for a series of propionate esters decreases with increasing molecular weight as shown in Table I. However, this comparison is on the basis of equal volumes of liquid added to the reservoir rather than equal gaseous concentrations within the source. Since the densities of these esters are constant,[2] the number of moles introduced varies inversely with the molecular weight. The additive flows from the reservoir into the source through a pin-

To a first approximation the additive ionization is independent of the molecular weight or molecular structure. A more detailed study of a few compounds indicates that there may be a variation, but it is not a large one. Within the precision of the present set of data, the rates of reaction of these compounds with CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ are constant—most probably to within ±25%. This observation is consistent with the postulate that the attack is predominantly at the ester group in these molecules.

In Table II are listed the major ions in the spectra of ten alkyl and six other propionates which have been assigned according to what we believe are their structures. With these assignments we can account for the overwhelming majority of the additive ionization. The last column in Table II shows the sum of the percentages of all of the ions in this tabulation.

Alkyl Propionates. Let us first consider the alkyl propionates, 1–10. The ions in the spectra of these compounds can be interpreted on the basis of attack of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ at the carboxyl group. The reaction of CH_5^+ is proton transfer.

$$CH_5^+ + C_2H_5COOR \longrightarrow C_2H_5COHOR^+ + CH_4 \qquad (1)$$

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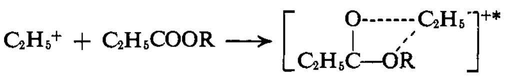
[2] J. H. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. I, Elsevier Publishing Co., New York, N. Y., 1950.

Since (MW + 1)$^+$ ions are observed for all of these compounds, the ions are stable; but the variation in relative abundance in Table II indicates that some of the ions formed in (1) must dissociate to give fragment ions. Both simple and dissociation proton-transfer reactions have been reported previously for CH_5^+.[1,3,4] $C_2H_5^+$ may react with these compounds by proton transfer

$$C_2H_5^+ + C_2H_5COOR \longrightarrow C_2H_5COHOR^+ + C_2H_4 \quad (2)$$

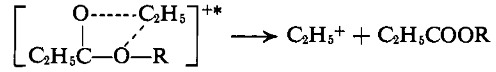
as has been shown previously for water.[4] As is the case for the ions formed from reaction of CH_5^+ in (1), the protonated molecule ion may also dissociate to lower molecular weight fragment ions, although the (MW + 1)$^+$ ions formed in (2) have a lower energy than those formed in (1). However, the presence of ions with m/e = MW + 29 and the even larger abundance of ions of m/e 103 suggest that we consider the reaction in somewhat more detail.

The incoming ethyl group may attack the carboxyl group at either oxygen atom and form a complex intermediate of moderate stability



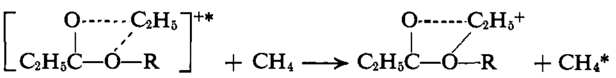
$$C_2H_5^+ + C_2H_5COOR \longrightarrow \left[\begin{matrix} O\cdots\cdots C_2H_5 \\ | \\ C_2H_5C{-}OR \end{matrix}\right]^{+*} \quad (3)$$

For the present we cannot distinguish between the two positions and the dotted lines are used to indicate attack at either oxygen atom. This intermediate complex ion may react in five ways. It may reversibly dissociate into the reactants, which produces no change.



$$\left[\begin{matrix} O\cdots\cdots C_2H_5 \\ | \\ C_2H_5C{-}O{-}R \end{matrix}\right]^{+*} \longrightarrow C_2H_5^+ + C_2H_5COOR \quad (4)$$

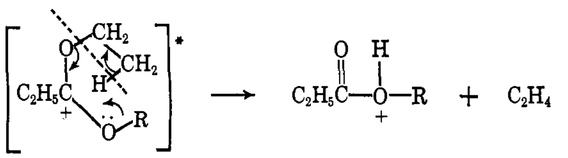
It may also collide with a molecule and be stabilized by loss of energy to form the (MW + C_2H_5)$^+$ ions which are observed.



$$\left[\begin{matrix} O\cdots\cdots C_2H_5 \\ | \\ C_2H_5C{-}O{-}R \end{matrix}\right]^{+*} + CH_4 \longrightarrow \begin{matrix} O\cdots\cdots C_2H_5^+ \\ | \\ C_2H_5C{-}O{-}R \end{matrix} + CH_4^* \quad (5)$$

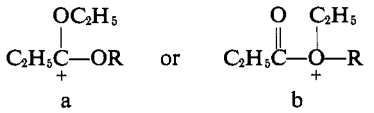
The relative abundances of these (MW + C_2H_5)$^+$ ions are sensitive functions of the source temperature, and a previous set of experiments on this series of compounds at lower temperatures showed consistently larger concentrations of (MW + C_2H_5)$^+$ ions than are indicated in Table II. The methane pressure is sufficiently high that the reactions of this sort may well be expected to occur. However, we have not made the detailed studies on these mixtures necessary to establish the pressure dependence of the (MW + C_2H_5)$^+$ ions.

The intermediate complex may dissociate by transferring a proton from the ethyl group to a carboxyl oxygen—the proton-transfer reaction (2).


(6)

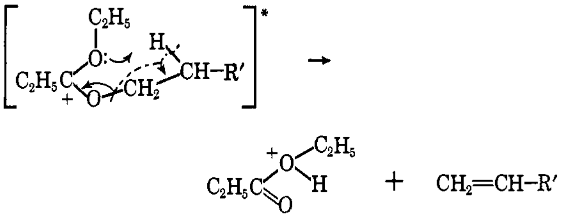
The detailed cyclic intermediate shown in (6) is admittedly speculative, but it provides a convenient picture for the formation of $CH_2{=}CH_2$ rather than the higher energy CH_3CH which would be formed if proton transfer occurred from the other carbon atom. An exactly equivalent mechanism can be written for the complex in which the ethyl group is attached to the ether oxygen.

For the fourth reaction of the intermediate formed in (3), let us consider that no matter which oxygen atom is attacked by the ethyl ion, there are two essentially equivalent O–R bonds, either



$$\underset{a}{\overset{OC_2H_5}{\underset{+}{C_2H_5C}}{-}OR} \quad \text{or} \quad \underset{b}{\overset{O}{\underset{+}{C_2H_5C}}{-}\overset{C_2H_5}{\underset{+}{O}}{-}R} \quad (7)$$

If the complex may dissociate by elimination of C_2H_4 to give the protonated molecule ion, then we must expect dissociation by elimination of the appropriate olefin from R to give protonated ethyl propionate, m/e 103, by an analogous mechanism.

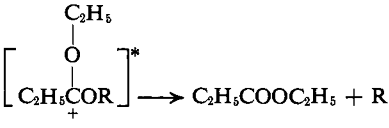

(8)

Appreciable amounts of ions of m/e 103 are formed from all of the alkyl esters by this exchange reaction, and to a first approximation the relative abundance of $C_2H_5COHOC_2H_5^+$ is independent of the number of carbon atoms in the alkyl chain, 7.8 ± 1.1% (except for methyl). Small concentrations of ions of m/e 115 and smaller concentrations of ions of m/e = (MW + 41)$^+$ are also observed for these alkyl propionates. The existence of these ions indicates that a set of reactions analogous to (6) and (8) is occurring with $C_3H_5^+$.

Ethyl and allyl exchange does not occur for methyl propionate. The nonoccurrence of this reaction is not surprising since the product which would be produced is CH_2. Approximate calculations from estimates of heats of formation indicate that ethyl and allyl exchange are endothermic for methyl propionate.[5]

Obviously, ethyl exchange cannot be observed for ethyl propionate in these experiments and no experiments with deuterium-labeled compounds have yet been done. The failure to observe allyl exchange with ethyl propionate is somewhat surprising. The energetics should be about the same for ethyl and propyl propionates since the additional $-CH_2-$ group decreases the heats of formation by about 6 kcal/mole for both the esters[6] and olefins.

It is also possible that the alkyl ions may be formed from a decomposition of the ethyl addition complex ion.



$$\left[\begin{matrix} C_2H_5 \\ | \\ O \\ | \\ \underset{+}{C_2H_5C}OR \end{matrix}\right]^{*} \longrightarrow C_2H_5COOC_2H_5 + R^+ \quad (9)$$

This reaction is exothermic for any secondary alkyl

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[3] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).

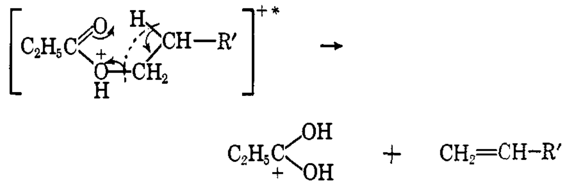
[4] M. S. B. Munson and F. H. Field, *ibid.*, **87**, 4242 (1965).

[5] Unless otherwise specified, ionic heats of formation are taken from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Table 45, and heats of formation of neutral molecules, from conventional sources.

[6] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

ion and exothermic or thermoneutral for primary alkyl ions except methyl.

Let us now consider the protonated molecule ions formed in reaction 1 or 2. An appreciable fraction of these ions must dissociate to give the resulting fragment ions. It is convenient to consider some of these decompositions as resulting from an intermediate with the proton bound to the ether oxygen in the carboxyl group; however, others which will be discussed later are best considered as resulting from an intermediate with the proton bound to the carbonyl oxygen. We consider protonation at each oxygen to be likely. A proton may be transferred through a cyclic intermediate from a carbon β to the carboxyl group to the carbonyl oxygen to form protonated propionic acid and an olefin.



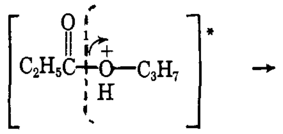
This reaction may be considered as a displacement reaction of a proton, formally equivalent to (8). This decomposition path is probably endothermal for methyl esters since the neutral product is CH_2, but it is exothermal for the other esters. Examples are given for *n*-propyl propionate, but the relative energetics should be reliable for the higher alkyl esters as well. Thus

$$CH_5^+ + C_2H_5COOC_3H_7 \longrightarrow [C_2H_5COHOC_3H_7^+]^* + CH_4 \quad \Delta H_f^{(*)} \cong 130 \text{ kcal/mole} \quad (11)$$

$$[C_2H_5COHOC_3H_7^+]^* \longrightarrow C_2H_5CO_2H_2^+ + C_3H_6 \quad \Delta H_{11} \cong -40 \text{ kcal/mole} \quad (12)$$

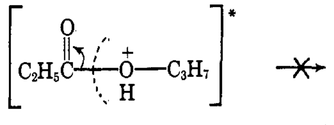
if one takes $\Delta H_f(C_2H_5CO_2H_2^+)$ = 65–70 kcal/mole[7] and $\Delta H_f(CH_5^+)$ = 229 kcal/mole.[3]

Simple heterolytic fission of the bond between the carbonyl group and the ether oxygen will give the propionoxy ion.



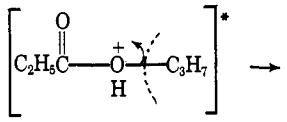
$$C_2H_5CO^+ + C_3H_7OH \quad \Delta H \cong -40 \text{ kcal/mole} \quad (13)$$

This reaction is exothermic if $\Delta H_f(C_2H_5CO^+)$ = 152–161 kcal/mole.[8] Fission of this bond to give the alcohol ion and the propionoxy radical does not occur to any appreciable extent, and approximate calculations indicate that the reaction is endothermic.



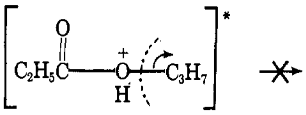
$$C_2H_5CO + C_3H_7OH^+ \quad \Delta H \cong 30 \text{ kcal/mole} \quad (14)$$

If the alkyl–oxygen bond breaks then the *n*-alkyl ion and propionic acid will be produced.



$$C_2H_5COOH + n\text{-}C_3H_7^+ \quad \Delta H \cong -30 \text{ kcal/mole} \quad (15)$$

This value is obtained using $\Delta H_f(n\text{-}C_3H_7^+)$ = 214 kcal/mole.[9] Fission of this bond to give the propionic acid ion according to (16) is endothermic and $C_2H_5COOH^+$ is not observed as a product ion.



$$C_2H_5COOH^+ + n\text{-}C_3H_7 \quad \Delta H = 16 \text{ kcal/mole} \quad (16)$$

The alkenyl ions, $C_nH_{2n-1}^+$ or $(R-H_2)^+$, may be formed by hydrogen elimination from the alkyl ions, $C_nH_{2n+1}^+$ as may also be the case in the spectra of alcohols.[1] This type of reaction is exothermic if one assumes that the alkenyl ions have allylic structures.

$$n\text{-}C_6H_{13}^+ \longrightarrow C_6H_{11}^+ + H_2 \quad \Delta H_{16} = -14 \text{ kcal/mole} \quad (17)$$

There is no readily available explanation for the formation of the olefin ions, but they are generally of rather small (<2%) abundance.

On the basis of the previous discussion we expect the spectra of the alkyl propionates to be very similar. There are, however, occasional values which are out of line with expectations. Thus, the much larger relative abundance of the $(MW + 1)^+$ ions for methyl propionate is simply the result of the fact that two of the major decomposition paths are endothermic. The larger relative abundance of *m/e* 57 for the butyl propionates is the result of the fact that $C_2H_5CO^+$ and $C_4H_9^+$ have the same mass and $C_4H_9^+$ is the expected alkyl ion for these esters. The much larger contribution of R^+ for isobutyl and isopentyl propionates is perhaps the result of steric hindrance of reaction 10 by the methyl groups β and γ to the carboxyl group so that the molecule dissociates by C–O fission instead. Several other variations exist, but we have no explanation.

Since the ionization potentials of the esters are all likely to be approximately 10 v,[10] it is gratifying that virtually no ions corresponding to $(MW)^+$ were observed. Hydride abstraction reactions have been reported with hydrocarbons,[1] and it is of interest to note that there is a small concentration of ions corresponding to $(MW - 1)^+$ in these spectra. The relative abundance of these ions increases with increasing number of carbon atoms in the molecules.

The other ions (not listed in Table II) which are formed in the spectrum of octyl propionate are $C_7H_{13}^+$ (*m/e* 97), 3.0%; $C_6H_{11}^+$ (*m/e* 83), 1.3%; $C_5H_{11}^+$ (*m/e* 71), 6.8%; $C_5H_9^+$ (*m/e* 69), 2.1%. The alkenyl ions may presumably result from the decomposition of $C_8H_{17}^+$. However, since we have shown that hydrocarbons will produce characteristic spectra,[11] it is possible

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[7] (a) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964); (b) E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962).

[8] R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

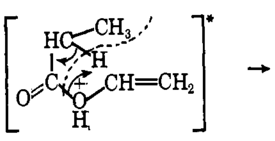
[9] C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 3464 (1964).

[10] K. Watanabe, T. Nakayama, and J. Mottl, Final Report on Ionization Potential of Molecules by a Photoionization Method, Army Project No. 5B99-01-004, Dec 1959.

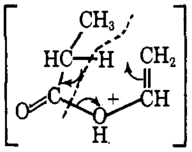
that these ions may result from attack of CH_5^+ or $C_2H_5^+$ on the carbon chain. We expect that the relative concentration of these hydrocarbon ions will increase with increasing numbers of carbon atoms in the molecules. The spectra indicate that most of the attack occurs at the carboxyl, but alkyl attack increases as the size of the radical increases.

Vinyl Propionate. Let us briefly consider each of the other propionate esters in Table II. For vinyl propionate the reactions previously discussed account for essentially all of the total ionization. Small amounts of $C_2H_3^+$ could be missed because this ion reacts with CH_4, but the formation of this ion is likely to be highly endothermic. The failure to observe $C_2H_5COHOC_2H_5^+$ (*m/e* 103) and $C_2H_5OHOC_3H_5^+$ (*m/e* 115), formed by ethyl and allyl ion displacements analogous to (8), and $C_2H_5CO_2H_2^+$ from the decomposition of the $(MW + 1)^+$ ions in a manner analogous to (10) is undoubtedly the result of the fact that the high heat of formation of acetylene makes the reactions endothermic.

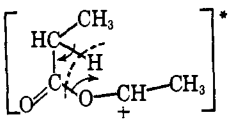
The ion of *m/e* 45, listed as ROH_2^+ in Table II, is the second most abundant ion in the spectrum. Three plausible mechanisms exist for the formation of an ion with this value of *m/e*.



$$CH_3CH{=}C{=}O + CH_2{=}CH{-}\overset{+}{O}H_2 \quad (18)$$



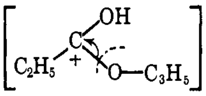
$$\rightarrow CH_3CH{=}C{=}O + CH_3\overset{+}{C}HOH \quad (19)$$



$$\rightarrow CH_3CHCO + CH_3\overset{+}{C}HOH \quad (20)$$

We have no basis for choosing between these three.

Allyl Propionate. For allyl propionate, the mechanisms previously described for the alkyl esters will explain all of the product ions. The reactions analogous to (10) and (8) leading to the formation of $C_2H_5CO_2H_2^+$ and $C_2H_5COHOC_2H_5^+$ do not occur, probably because they are endothermic. The larger relative abundance of ions of *m/e* 57 is perhaps due to the formation of $C_3H_5O^+$ as well as $C_2H_5CO^+$. The formation of $C_3H_5O^+$ can most easily be explained as the result of decomposition of a complex in which the protonation occurs at the carbonyl oxygen rather than the ether oxygen in the ester. There is no ready explanation for

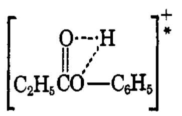


$$\rightarrow C_2H_5COH + C_3H_5O^+ \quad (21)$$

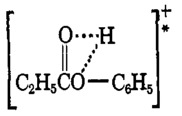
the failure to observe larger amounts of "ROH_2^+" ions produced by mechanisms analogous to those suggested for vinyl alcohol (eq 18–20).

Cyclohexyl Propionate. There is nothing unexpected in the spectrum of cyclohexyl propionate. The other major ions which are not included in Table II are hydrocarbon ions: $C_4H_7^+$ (*m/e* 55), 2.6%; $C_5H_9^+$ (*m/e* 69), 2.0%.

Phenyl Propionate. The greater abundance of $(MW + 1)^+$ ions for phenyl propionate compared with alkyl esters of similar molecular weight may be simply the result of the fact that decomposition of the intermediate by two of the usual modes is endothermic because of the high heats of formation of the phenyl ion and benzyne. $C_6H_5^+$ and $C_2H_5CO_2H_2^+$ are not observed as product ions in this spectrum.



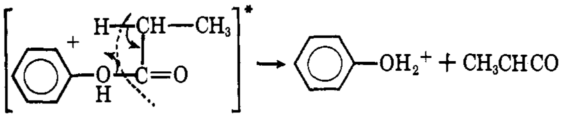
$$\not\rightarrow C_6H_5^+ + C_2H_5COOH \quad (22)$$



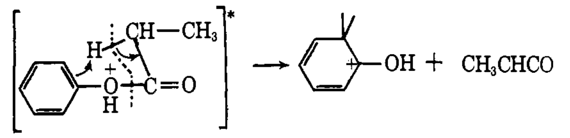
$$\not\rightarrow C_2H_5CO_2H_2^+ + C_6H_4 \quad (23)$$

The proton affinity of benzene is about 150 kcal/mole.[12] This value is sufficiently lower than the proton affinity of propionic acid to suggest that the attack is predominantly at the carboxyl group rather than the aromatic ring. However, proton-transfer reactions to aromatic hydrocarbons to give $(MW + 1)^+$ ions have been observed,[13] so that it is possible that protonation may occur to some extent on the aromatic ring.

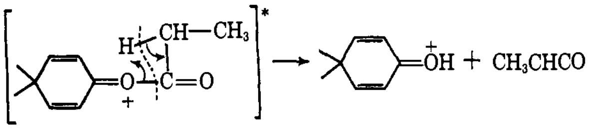
The major difference between this spectrum and those of the alkyl propionates is the very large abundance of protonated phenol, *m/e* 95. Mechanisms for the formation of this ion may readily be written analogous to eq 18–20 for vinyl propionate. Reaction 24 is perhaps



(24)



(25)



(26)

the most likely. The formation of this ion in such a large concentration must mean that the reaction is energetically favored although the heat of reaction cannot be calculated.

There are two other ions which constitute the major portion of the remainder of the ionization: *m/e* 123, perhaps $C_6H_5OHC_2H_5^+$ (8.3%) and *m/e* 135, perhaps $C_6H_5OHC_3H_5^+$ (3.3%). These ions may be considered as being formed from decompositions of the ethyl addition complex ions formed in (3) or the allyl analogs. The reactions are very similar to eq 24–26 and

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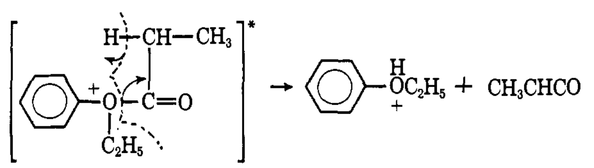
(11) See ref 1; also, F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, American Chemical Society, Washington, D. C., to be published.

(12) J. L. Franklin, F. W. Lampe, and H. E. Lumpkin, *J. Am. Chem. Soc.*, 81, 3152 (1959).

(13) F. H. Field and M. S. B. Munson, work to be reported subsequently.

are most easily considered as the result of addition to the ether oxygen.



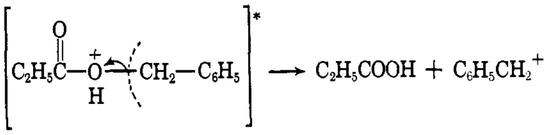
(27)

Similar reactions may be written analogous to (25) and (26). The same explanation will hold for allyl ion attack.

This is another displacement reaction very similar to that shown in (8), and the occurrence of this ion in the spectrum suggest that reactions (6) and (8) might also result from attack at the ether oxygen.

Benzyl Propionate. The spectrum of benzyl propionate bears no obvious relationship to the spectra of the other propionate esters. Practically all of the ionization is in the form of ions containing only the benzyl group, and essentially none of the ionization is represented by ions characteristic of the ester of carboxyl group. There is only a very small ionic concentration at *m/e* = MW + 1.

These observations may still be rationalized on the basis of attack at the carboxyl group but it is necessary to assume that the stability of the benzyl ion, $C_7H_7^+$, *m/e* 91, is sufficiently great that the decomposition reaction forms this ion predominantly, that is, decomposition of the protonated intermediate complex ion occurs by fission of the benzyl–oxygen bond.



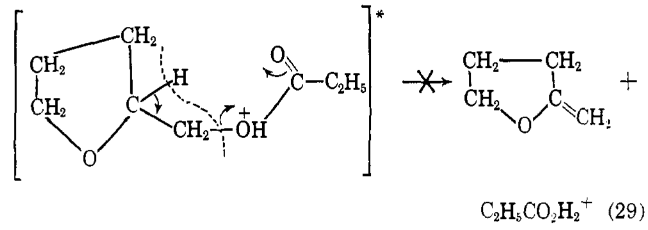
$$C_2H_5COOH + C_6H_5CH_2^+ \quad (28)$$

In the light of the experiments with phenyl propionate, we would not expect to observe $C_2H_5CO_2H_2^+$, $C_2H_5COHOC_2H_5^+$, or $C_2H_5COHOC_3H_5^+$ because of the high energy of formation of the radicals which would be produced by proton transfer from the ring to an oxygen.

The other two ions observed in the spectrum are *m/e* 119, perhaps $C_9H_{11}^+$ (5.2%) and *m/e* 131 (1.4%). The structure and origin of these two ions are not known.

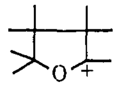
Tetrahydrofurfuryl Propionate. There are three oxygen atoms as probable centers for attack in tetrahydrofurfuryl propionate, a situation which complicates the reactions somewhat. Proton addition to the tetrahydrofurfuryl group is probably the cause of the higher concentration of (MW + 1)$^+$ ions in the spectrum of this compound than in the spectra of the alkyl propionates of similar molecular weights or numbers of carbon atoms.

Failure to observe $C_2H_5CO_2H_2^+$ probably results from the high heats of formation of the possible radical decomposition products and/or steric hindrance of the removal of the only hydrogen which can give an olefin (eq 29).



(29)

The other ions not included in Table II are *m/e* 71 (2.4%)



and *m/e* 67, $C_5H_7^+$ (1%).

Table III shows the major ions for five other esters. These will be discussed briefly according to the mechanisms presented for the propionate esters.

Propyl Acetate. All of the ions in the spectrum of this compound are explained completely in terms of the previously discussed mechanisms. This compound can be distinguished easily from the isomeric ethyl propionate by the RCO^+ and $RCO_2H_2^+$ ions: CH_3CO^+, *m/e* 43, and $CH_3CO_2H_2^+$, *m/e* 61, for propyl acetate and $C_2H_5CO^+$, *m/e* 57, and $C_2H_5CO_2H_2^+$, *m/e* 75, for ethyl propionate. The total additive ionizations for these two compounds are equal within experimental error.

Butyl Butanoate. The majority of the ionization of this compound can readily be explained according to the previous mechanisms, as indicated in Table III. As was the case for the two isomers just mentioned, butyl butanoate may be distinguished readily from its isomer pentyl propionate by the RCO^+ and $RCO_2H_2^+$ as well as R'^+ ions present in both spectra. In a comparison between butyl butanoate and pentyl propionate, we also note a higher (MW − 1)$^+$ concentration of butyl butanoate, although both have the same number of carbon atoms. The (MW − 1)$^+$ ions account for only 1.5% of the additive ionization, however.

$C_4H_9OH_2^+$ is 5% of the additive ionization for this compound. This value is higher than the ones observed for the other alkyl esters. Since this ion has an *m/e* value of 75, it is possible that we had a propionate impurity in this sample.

There are several other ions which are observed in this spectrum by processes which are not readily identifiable: *m/e* 87, perhaps $C_3H_7COO^+$, 5.7% (it is not apparent why this ion should be observed only for this compound and not for the other alkyl esters); *m/e* 103, perhaps $C_3H_7COHOCH_3^+$, 4.9% (this ion could be protonated methyl butanoate formed from a displacement reaction of CH_5^+)

$$CH_5^+ + C_3H_7COOC_4H_9 \longrightarrow C_3H_7COHOCH_3^+ + C_4H_{10} \quad (30)$$

and small amounts of what might be analogous reactions have been observed for other esters, but never as high as 5% of the additive ionization. Small relative concentrations have been observed at *m/e* 115 (0.9%), 131 (1.5%), and 159 (1.2%), which cannot be explained.

While it is not a satisfying explanation it must be considered that impurities may be the source of many of the ions of small concentration in all of these compounds.

Methyl Octanoate. This compound may be considered typical for methyl esters of higher molecular weight acids. The spectrum is very similar to the spectrum of methyl propionate: a large concentration

Table III. Chemical Ionization Spectra of Esters (CH_4 Reactant) % of Additive Ionization

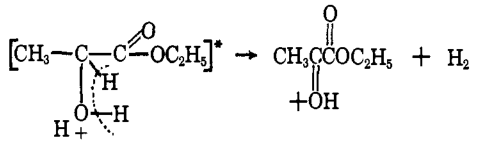
Compound RCOOR′	(MW + 1)$^+$	MW$^+$	(MW − 1)$^+$	RCO$^+$	RCO_2-H_2^+	RCOHO-$C_2H_5^+$	RCO-HO-$C_3H_5^+$	(MW + C_2H_5)$^+$	(MW + C_3-H_5)$^+$	R′$^+$	(R′− H)$^+$	(R′− H_2)$^+$	R′O$^+$	R′-OH$^+$	R′-OH_2^+	Σ[a]
n-Propyl acetate	15.6	0.1	2.2[b]	3.2[c]	64	9.2	2.2[d]	<0.02	0.9	3.2[e]	<0.1	<0.1	0.1	<0.02	$RCO_2H_2^+$	98
n-Butyl butanoate	7.4	0.1	1.5	8.4	36	5.7	1.1	<0.05	0.7	6.7	0.9	1.2	0.6	<0.06	5.0	79
Methyl octanoate	50	0.8	8.7	5.6	<0.05	0.1	0.1	6.0	1.4	...	...	...	<0.1	<0.05	3.1	82
Ethyl α-hydroxy-propionate	15.7	0.2	4.5	7.1[f]	16.6	(MW + 1)$^+$	<0.05	0.3	0.2	...	...	...	12.9[g]	<0.05	22.2	82
Ethyl[h] β-chloro-propionate	12.5	0.2	<0.05	2.3	13.3	(MW + 1)$^+$	<0.05	0.3	0.6	...	...	...	0.8	<0.05	0.3	31

[a] Includes ^{13}C isotope. [b] Also $RCOHOC_3H_5^+$. [c] Also R′$^+$. [d] Also (MW − 1)$^+$. [e] Also RCO$^+$. [f] Also $C_2H_3CO_2H_2^+$. [g] Also CH_3-$CHOH^+$. [h] $^{35}Cl + ^{37}Cl$.

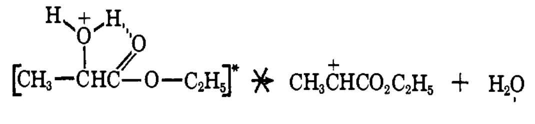
of ions at m/e = (MW + 1)$^+$ and a moderate concentration for RCO$^+$ and virtually no ionization for m/e = $RCO_2H_2^+$, $RCOHOC_2H_5^+$, or $RCOHOC_3H_5^+$. For some unknown reason ionic concentrations at m/e = (MW − 1)$^+$ and (MW + C_2H_5)$^+$ are much higher than we would expect from the previous data.

The other ions in the spectrum are m/e 125 (5.0%), 115 (0.9%), 111 (2.0%), 97 (1.2%), 83 (1.5%), and 74 (2.0%). The only two of these ions for which a ready explanation exists are those at m/e 97 and 83, perhaps $C_7H_{13}^+$ and $C_6H_{11}^+$ caused by attack on the carbon chain and carbon–carbon bond fission. The relative abundance of these hydrocarbon ions should increase with increasing number of carbon atoms in the chain.

Ethyl α-Hydropropionate. The presence of an additional oxygen atom in this molecule increases the complexity of the spectrum. We certainly expect some protonation at each of the three oxygen atoms. There is a greater abundance of (MW − 1)$^+$ ions in this spectrum than in the spectra of the other esters (except the anomalous methyl octanoate). In the spectra of alcohols there are moderate concentrations of (MW − 1)$^+$ ions, perhaps formed by elimination of H_2 from adjacent C and O atoms of the protonated alcohol,[14] so that these ions may result from attack at the hydroxyl group.

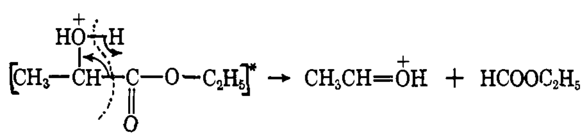

(31)

There is virtually no ionization at m/e 101 so that the loss of water from this intermediate ion does not occur.

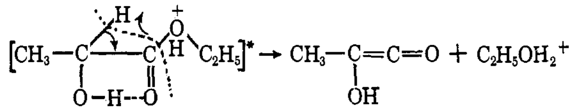

(32)

The nonoccurrence of this reaction is perhaps the result of internal hydrogen bonding as indicated by the dotted line for the intermediate shown in (32). If such internal hydrogen bonding exists, it should be manifest in increased stabilities of (MW + 1)$^+$ ions for 1,2- and 1,3-dihydroxy and dialkoxy compounds.

The concentration of the "RO$^+$" ions is larger for this compound than for the others, and a likely explanation for the enhancement of this ion also involves the decomposition of the molecule protonated at the hydroxyl group.


(33)

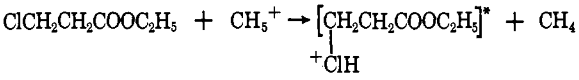
The enhanced concentration of ROH_2^+ is perhaps the result of the greater lability of the α hydrogen and the stability and favorable configuration brought about by internal hydrogen bonding in this protonated intermediate when compared with alkyl esters. The mechanism is the same as that suggested for the formation of ROH_2^+ in (18). The other ions in the spectrum


(34)

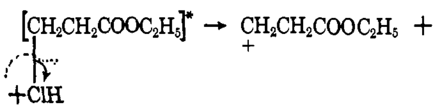
are m/e 43 (4.4%), 63 (2.9%), 75 (1.1%), 85 (2.2%), and 89 (1.5%).

Ethyl β-Chloropropionate. The tabulation of ions in this spectrum is for the sum of ^{35}Cl and ^{37}Cl isotopes. The processes which have been discussed previously will explain the ions listed in Table III. The spectrum is, however, profoundly altered by the presence of the Cl atom in the molecule, but the effects are readily explained.

The most abundant of the ions not listed in this table is m/e 101 (33.4%). This ion may be C_2H_4-$COOC_2H_5^+$ formed by proton transfer to the Cl atom followed by elimination of HCl.



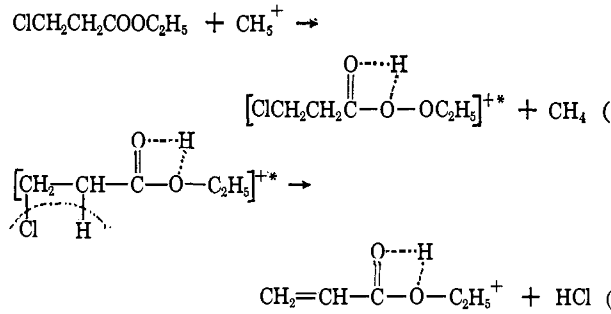
$$ClCH_2CH_2COOC_2H_5 + CH_5^+ \rightarrow [\underset{+ClH}{C}H_2CH_2COOC_2H_5]^* + CH_4 \qquad (35)$$



$$[\underset{+ClH}{C}H_2CH_2COOC_2H_5]^* \rightarrow \underset{+}{C}H_2CH_2COOC_2H_5 + HCl \qquad (36)$$

Alternatively, it may be $C_2H_3COHOC_2H_5^+$ formed by proton transfer to the carboxyl followed by elimination of HCl.

[14] Reference 1 and additional work to be reported subsequently.



$$ClCH_2CH_2COOC_2H_5 + CH_5^+ \rightarrow [ClCH_2CH_2\overset{\overset{O\cdots H}{\|}}{C}-O-OC_2H_5]^{+*} + CH_4 \quad (37)$$

$$[CH_2-CH-\overset{\overset{O\cdots H}{\|}}{C}-O-C_2H_5]^{+*} \rightarrow CH_2{=}CH-\overset{\overset{O\cdots H}{\|}}{C}-O-C_2H_5^+ + HCl \quad (38)$$

Of course, it is possible that both mechanisms operate simultaneously. These processes could be distinguished by using CD_4, but these experiments have not yet been done.

The next most abundant ion in the spectrum is *m/e* 73 (22.5%). This ion may be $C_2H_3CO_2H_2^+$ formed either by decomposition of the $C_2H_3COHOC_2H_5^+$ formed in (38) by the usual elimination of ethylene, (10), or by elimination of HCl from $ClC_2H_4CO_2H_2^+$ in a manner analogous to (38). It may also be $C_2H_4CO_2H^+$ formed by ethylene elimination from $C_2H_4CO_2C_2H_5^+$.

$C_2H_3CO^+$ is present as 4.1% of the additive ionization and its formation may be explained in an analogous manner: either by decomposition of $C_2H_3COHOC_2H_5^+$ as in (13) or by elimination of HCl from $ClC_2H_4CO^+$. The only other ion of consequence is *m/e* 129 (1.3%).

Temperature Dependence of Spectra. As we mentioned previously there is a dependence of these spectra upon temperature. The relative abundance of the $(MW + C_2H_5)^+$ and $(MW + C_3H_5)^+$ ions increases by a factor of two for some compounds on decreasing the temperature of the source from 240 to 140°. Figure 1 shows the variation with temperature of the major ions from ethyl β-chloropropionate. The additive ionization shows no systematic variation with temperature so that there is no marked temperature effect on the over-all rate of reaction. There is, however, a very marked effect on the decomposition pattern of the intermediate complex. Systematic studies were made on five compounds over this temperature range, which is as wide as can be covered with the present instrument. For all of these compounds there is a marked increase in the higher molecular weight ions with a decrease in temperature. This phenomenon is illustrated in Figure 1 by the increase in relative concentration of the $(MW + 1)^+$ ions from approximately 10% at 240° to 20% at 130°.

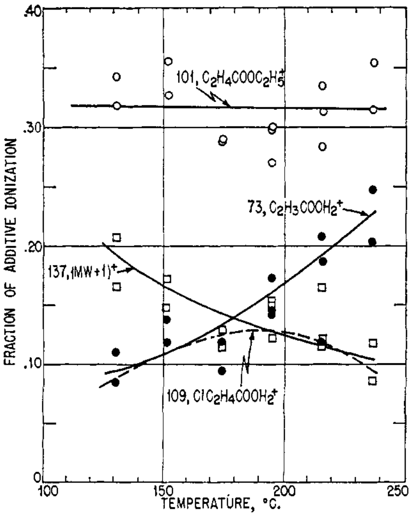


Figure 1. Temperature dependence of the major ions of ethyl β-chloropropionate. Data points omitted for $ClC_2H_4COOH_2^+$ (dashed curve) for purposes of clarity.

The apparent maximum in the relative concentration of $ClC_2H_4CO_2H_2^+$ and the invariance of $C_2H_4COOC_2H_5^+$ may be the result of compensating effects. As previously suggested, the $(MW + 1)^+$ ions may decompose by two paths.

$$\begin{tikzcd} & C_2H_4COOC_2H_5^+ \\ (MW+1)^+ \arrow[ur] \arrow[dr] & & (39) \\ & ClC_2H_4CO_2H_2^+ \end{tikzcd}$$

Since the relative concentration of $(MW + 1)^+$ ions increases with a decrease in temperature, the formation of these two ions must be decreased by a decrease in temperature. Since the formation of *m/e* 73 is drastically reduced by decreasing the temperature, we can expect that reactions 40 and 41 will also be decreased by a decrease in temperature. Thus the concentrations of $ClC_2H_4CO_2H_2^+$ and $C_2H_4COOC_2H_5^+$ may not vary strongly with temperature over this range.

$$C_2H_4CO_2C_2H_5^+ \longrightarrow C_2H_4CO_2H^+ \quad (40)$$

$$ClC_2H_4CO_2H_2^+ \longrightarrow C_2H_3CO_2H_2^+ \quad (41)$$

This variation in spectral pattern with source temperature is reminiscent of the temperature dependence of the abundance of molecule ions of hydrocarbons in electron impact spectra. This effect may be explained by the "quasi-equilibrium" theory in terms of the distribution of energy among the excited vibrational states.[15] In the present experiments it is also possible that some of the fragment ions may be produced by collisions within the source and this process might also produce a temperature coefficient.

Whatever the cause of this phenomenon, it is apparent that the analytical usefulness of this process will be greater at the lower temperatures since the dissociation processes are less extensive.

Metastable or Collision-Induced Dissociations. There is one other phenomenon about these spectra worthy of mention. For most of the compounds there are low concentrations (<0.1%) of broad peaks in the spectra. These peaks frequently occur at nonintegral masses and generally may be easily distinguished from the normal ions by their shape. These peaks may be the result of collision-induced dissociations of the ions.

Several diffuse peaks are present in methane alone at this pressure of 1 torr and some of these have been interpreted as collision-induced dissociations of the methane product ions.[16]

We have not undertaken the pressure studies to determine whether the diffuse peaks from the additives are spontaneous or collision-induced, but it seems reasonable that these peaks are partly, if not wholly, collision-induced because of the high pressures. Nevertheless, these processes may provide useful information

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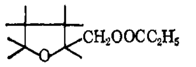
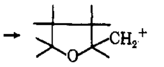
Table IV. Dissociation Processes in Esters

Compound	m^* Exptl	m^* Calcd	Reaction
$CH_3OOCC_2H_5$	36.5	36.5	$(MW + 1)^+ \longrightarrow C_2H_5CO^+$
$C_2H_5OOCC_2H_5$	54.5	54.5	$(MW + 1)^+ \longrightarrow C_2H_5CO_2H_2^+$
$n\text{-}C_3H_7OOCC_2H_5$	48	48.1	$(MW + 1)^+ \longrightarrow C_2H_5CO_2H_2^+$
	54.5	54.5	$(C_2H_5COHOC_2H_5)^+ \longrightarrow C_2H_5CO_2H_2^+$
$i\text{-}C_3H_7OOCC_2H_5$	48	48.1	$(MW + 1)^+ \longrightarrow C_2H_5CO_2H_2^+$
	54.5	54.5	$(C_2H_5COHOC_2H_5)^+ \longrightarrow C_2H_5CO_2H_2^+$
$n\text{-}C_4H_9OOCC_2H_5$	54.5	54.5	$(C_2H_5COHOC_2H_5)^+ \longrightarrow C_2H_5CO_2H_2^+$
$i\text{-}C_4H_9OOCC_2H_5$	54.5	54.5	$(C_2H_5COHOC_2H_5)^+ \longrightarrow C_2H_5CO_2H_2^+$
$n\text{-}C_5H_{11}OOCC_2H_5$	54.5	54.5	$(C_2H_5COHOC_2H_5)^+ \longrightarrow C_2H_5CO_2H_2^+$
$C_6H_5OOCC_2H_5$	59.7	59.8	$(MW + 1)^+ \longrightarrow C_6H_5OH_2^+$
$C_2H_3OOCC_2H_5$	32	32.2	$(MW + 1)^+ \longrightarrow C_2H_5CO^+$
	45.5	45.4	$(MW + 1)^+ \rightarrow$ 
$C_2H_5OOCC_2H_4Cl$	86.5	86.7	${}^{35}ClC_2H_4COHOC_2H_5^+ \longrightarrow {}^{35}ClC_2H_4CO_2H_2^+$
	88.5	88.6	${}^{37}ClC_2H_4COHOC_2H_5^+ \longrightarrow {}^{37}ClC_2H_4CO_2H_2^+$
	52.5	52.8	$C_2H_4COOC_2H_5^+ \longrightarrow C_2H_4CO_2H^+$

about the reactions which are occurring. Table IV shows a tabulation of the diffuse peaks which have been observed. These have been assigned to a transition according to the usual formula for decomposition of an ion after electrostatic acceleration but prior to entrance into the magnetic field: $m^* = (m_f)^2/m_i$, in which m^* is the mass at which the diffuse peak occurs and m_f and m_i are the final and initial ionic masses.[17]

The diffuse peaks which are observed are generally those involving the dissociation of an abundant ion to give another abundant ion, and the initial ion is frequently the $(MW + 1)^+$ ion. Even if these diffuse peaks are produced wholly by collision-induced reactions, these reactions reflect the spontaneous decompositions as well. Since the diffuse peaks are small, it is not always possible to observe them if there is a large normal mass nearby. The failure to observe many of these diffuse peaks for different compounds is undoubtedly the result of this interference.

Comparison with Electron-Impact Spectra. The electron-impact spectra of many aliphatic esters have been determined and extensively studed.[18-27] The electron-impact spectra for the lower molecular weight esters are simple and readily interpretatable in terms of their molecular structure. However, as the molecular weight of the esters increases, the electron-impact spectra become more complicated and less useful for the identification of the compounds. For a given acid group, the abundance of the molecule ions is a sharply decreasing function of the alcohol chain length and is essentially zero for the alkyl groups larger than butyl;[23] but the chemical ionization spectra has about 5% of $(MW + 1)^+$ ions even for octyl propionate. Molecular ions are formed from all of the methyl esters,[23,27] but the relative abundances are much lower than the 50% of additive ionization in the chemical ionization mass spectrum of methyl octanoate, of the order of 0.1% of the ionization for methyl hexanoate.[23]

There are many complicated rearrangement ions formed in these spectra and deuterium-labeled compounds have been used to study the rearrangement processes.[7b,18-22,24,26] Several of these rearrangements have been interpreted in terms of cyclic intermediates[28] very similar to those suggested in this paper for ethyl and allyl displacements and formation of $RCO_2H_2^+$ from the protonated complex. The hydrogen is transferred from carbons 1, 2, 3, and even 4 atoms removed from the carbonyl group, but there are preferential positions.[7b,28] Since the chemical ionization reactions are somewhat gentler or lower energy than many of the electron-impact processes, it is possible that the hydrogens may be removed from only the carbon two atoms removed from the carbonyl group since this is the only process which will give an olefin without a more complicated rearrangement. Studies of labeled compounds are planned for future experiments.

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