

# Ion Cyclotron Resonance Studies of the Chemical Ionization of Esters

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**Abstract:** Deuterium labeling combined with several types of ion cyclotron resonance (icr) studies are used to determine the mechanisms of formation of the principal fragment ions in the methane chemical ionization (CI) of esters. In contrast to the behavior observed in solution, esters appear to protonate at the ether oxygen in the gas phase. The relative intensities of the fragment ions in the CI spectra of esters are determined by the relative activation energies for their formation from the protonated ester. It is thus possible to detect rearrangements of the protonated esters to more stable structures occurring before or during the fragmentation.

Chemical ionization mass spectrometry is rapidly becoming established as a valuable analytical tool.<sup>1</sup> Compared with conventional mass spectrometry, the number of fragment ions is greatly reduced and almost all compounds produce peaks of good intensity from which the molecular weight can be determined.<sup>1</sup> The usefulness of chemical ionization techniques will undoubtedly increase as more information becomes available on the energetics and mechanisms of the reactions between the chemical ionization reagent ions and the sample molecules. We have therefore used a variety of ion cyclotron resonance (icr) techniques together with extensive deuterium labeling to elucidate the mechanisms of the reactions producing the methane chemical ionization spectra of esters.

The conditions in the icr cell are somewhat different from those existing in the high-pressure mass spectrometer used by Munson and Field<sup>2</sup> in their study of the chemical ionization of esters. Using the analysis developed by Sroka, Chang, and Meisels,<sup>3</sup> we estimate that under the conditions of Munson and Field<sup>2</sup> (ion path length = 0.4 cm, repeller field = 5 V/cm,  $T = 513^\circ\text{K}$ , and pressure = 1.0 Torr) the reagent ions experience approximately 800 collisions within the ion source during their 32  $\mu\text{sec}$  residence time. In the present icr experiments, a  $\text{CH}_3^+$  ion undergoes an average of 22 collisions during the 3.8 msec spent in the cell with a methane pressure of  $8 \times 10^{-5}$  Torr. While these different experimental conditions produce little difference in the spectra of pure methane, the longer time between collisions leads to significant differences in the distributions of ions produced by the reactions of methane ions with esters.

## Experimental Section

The basic icr spectrometer used is a commercial instrument very similar to those which are extensively described elsewhere.<sup>4</sup> Pressures were measured with a Varian Milli-Torr ion gauge connected

through large bore tubing directly to the cell enclosure as described previously.<sup>5</sup> Unless otherwise noted, the methane pressure was  $8 \times 10^{-5}$  Torr, the highest pressure which did not produce excessive broadening of the icr peaks.

The ion ejection experiments used the method developed by Beauchamp and Armstrong.<sup>6</sup> A radiofrequency electric field applied across the trapping plates of the icr cell will increase the amplitude of the natural oscillatory motion of ions in the trapping potential well. Since the frequency,  $\omega_T$ , of this motion is<sup>6</sup>

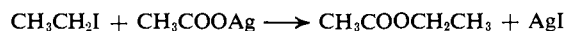
$$\omega_T = (4qV_T/md^2)^{1/2}$$

the mass of the ions ejected is determined by the frequency of the applied field. The resolution of this ejection experiment is only  $m/\Delta m = 5$  in our flat cell, so both  $\text{CH}_3^+$  and  $\text{CH}_4^+$  are ejected simultaneously. By modulating the amplitude of the trapping plate rf voltage, one modulates the  $\text{CH}_3^+$  and  $\text{CH}_4^+$  ion current through the cell without affecting other ions at higher mass. Thus the phase-detected signal from the marginal oscillator yields a spectrum of the ions resulting only from methane ion reactions.<sup>6</sup> Other ions, such as those formed directly by electron impact on the esters, do not appear in the ion ejection spectrum.

In all experiments, the cell temperature was  $300^\circ\text{K}$  and the electron energy was 23 eV unless otherwise noted. Typical cell voltages were trapping = 0.4 V, source drift = 0.18 V/cm, and analyzer drift = 0.13 V/cm.

All ion intensities reported are the icr peak height divided by the ion mass. This is an exact correction for primary ions at low pressure and approximately correct for all others.<sup>4b</sup>

Several deuterated ethyl acetates were prepared by the reaction<sup>7</sup>



Both  $\text{CD}_3\text{CH}_2\text{I}$  and  $\text{CD}_3\text{COOD}$  were obtained from Stohler Isotope Chemicals.  $\text{CD}_3\text{COOAg}$  was prepared by neutralizing the  $\text{CD}_3\text{COOD}$  with aqueous ammonia to pH 8, then precipitating with a 1.5-fold excess of  $\text{AgNO}_3$  dissolved in a small amount of water. The  $\text{CD}_3\text{COOAg}$  precipitate was filtered, washed once with cold water, and dried in a vacuum desiccator. The ethyl acetates were prepared by placing 0.01 mol of  $\text{CD}_3\text{COOAg}$  or  $\text{CH}_3\text{COOAg}$  (obtained from Baker Chemical Company, and used as obtained) in a vial with 0.01 mol of  $\text{CH}_3\text{CH}_2\text{I}$  (from Aldrich Chemical Co., purified by distillation) or  $\text{CD}_3\text{CH}_2\text{I}$  (used as obtained). The vial was sealed and suspended in a flask of refluxing ethanol to maintain the temperature at  $78.5^\circ$  overnight. This mixture was then totally distilled and analyzed by nmr to determine the amount of unconverted ethyl iodide. The distillate was then combined with triple the amount of silver acetate needed to complete the conversion, and the above procedure was repeated until all the ethyl iodide had been converted to ethyl acetate. Nmr showed no measurable contaminants in the resulting acetate.  $\text{CD}_3\text{COOCH}_2\text{CH}_3$  and  $\text{CH}_3\text{COOCH}_2\text{CD}_3$  were prepared by this method. The  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$  was a Baker analytical reagent, vacuum distilled once. The  $\text{CD}_3\text{COOCD}_2\text{CD}_3$  was obtained from Baker and used as obtained.

(5) S. E. Buttrill, Jr., *J. Chem. Phys.*, **58**, 656 (1973).

(6) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

(7) B. Nolin, *Can. J. Chem.*, **31**, 1257 (1954).

(1) (a) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968); (b) F. H. Field in "Ion Molecule Reactions," J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, pp 261-313; (c) M. S. B. Munson, *Anal. Chem.*, **43**, 28A (1971).

(2) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 4337 (1966).

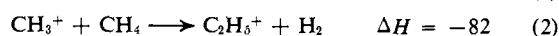
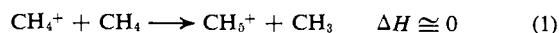
(3) G. Sroka, C. Chang, and G. G. Meisels, *J. Amer. Chem. Soc.*, **94**, 1052 (1972).

(4) (a) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (b) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); (c) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 126 (1970).

Methane was obtained from Matheson and methane- $d_4$  from Stohler Isotope Chemicals. Both were used as obtained. The other esters were obtained from various sources and vacuum distilled at least once prior to use.

### Methane

The major reactions in methane are<sup>1a,8</sup>

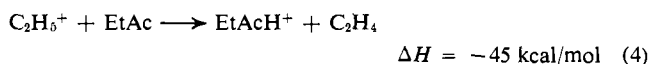
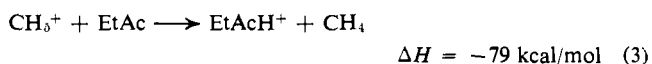


where the enthalpy changes are given in kilocalories per mole.<sup>9</sup> At 23 eV only very small amounts of  $\text{C}_2\text{H}_3^+$  are observed in the icr experiments although they are present to a small extent in conventional chemical ionization (CI) spectra obtained at 210 eV.<sup>1</sup> Since we are interested in the mechanisms of the formation of the major ions in the CI spectra of esters, the reduced abundance of these minor high-energy<sup>10</sup> ions is an advantage.

It is important to identify the possible sources and magnitudes of any excess internal energy in the  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  reagent ions. The methane ion may contain up to 36 kcal/mol of internal energy without fragmenting to  $\text{CH}_3^+ + \text{H}$ . Since the probability of forming ground state  $\text{CH}_4^+$  is low,<sup>11</sup> the average  $\text{CH}_4^+$  energy is probably near 25 kcal/mol, and the 30% of  $\text{CH}_5^+$  ions formed by a hydrogen abstraction mechanism<sup>12</sup> can be expected to retain this excess energy. On the basis of simple statistical arguments,<sup>13</sup> most of the 82 kcal/mol exothermicity of reaction 2 is expected to be retained in the  $\text{C}_2\text{H}_5^+$  product ion. Thus while the proton affinity of  $\text{C}_2\text{H}_4$  is 33 kcal/mol greater than that of  $\text{CH}_4$ , the difference is almost exactly compensated for by the much larger excitation energy of the  $\text{C}_2\text{H}_5^+$  ion. As a result, one expects that the amount of excitation energy deposited in an ester molecule by protonation from either of these two reagent ions will be about the same.

### Ethyl Acetate

Proton transfer to ethyl acetate is exothermic<sup>9,14</sup> for both  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  ions.



The two predominant modes of fragmentation of the protonated ethyl acetate are shown in Scheme I. Protonated ethyl acetate ions with at least 33 kcal/mol of excess internal energy can decompose into protonated acetic acid and ethylene while those with 42 kcal/mol or more excitation can fragment into acyl cation and ethanol. Table I shows the chemical ionization

(8) F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966).

(9) (a) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **54**, 4256 (1971); (b) J. G. Dillard, K. Droxl, J. L. Franklin, F. H. Field, J. T. Herron, and H. H. Rosenstock, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

(10) (a) S. Wexler and N. Jesse, *J. Amer. Chem. Soc.*, **84**, 3425 (1962); (b) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

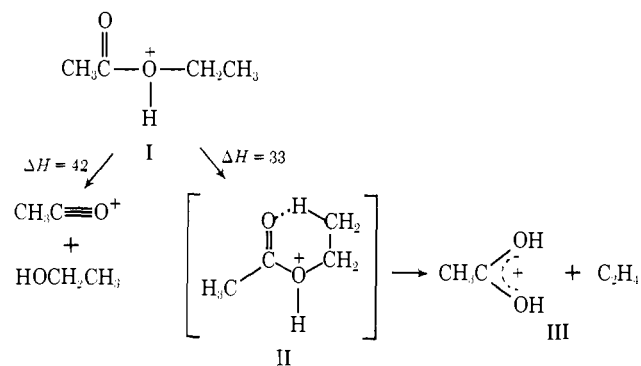
(11) B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, **53**, 768 (1970); see also ref 9a.

(12) W. T. Huntress, *J. Chem. Phys.*, **56**, 5111 (1972); see also ref 8.

(13) M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, pp 59-118.

(14) J. Long and B. Munson, *J. Amer. Chem. Soc.*, **95**, 2427 (1973).

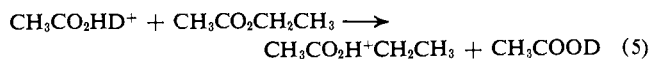
### Scheme I



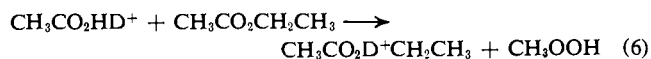
products in various deuterium labeled ethyl acetates. These data were obtained using the electron beam modulation technique of McIver.<sup>4e</sup> Similar experiments using the trapping plate ejection method<sup>6</sup> to exclude contributions from electron impact on the ester were identical within experimental error except that the signal-to-noise ratio was approximately five times smaller. The numbers in Table I are  $(I_{m_i}/\sum I_{m_i})100\%$  where only ions originating from the esters are included in the sum. These results are therefore directly comparable to Munson and Field's data which were reported as per cent of additive ionization.<sup>2</sup>

The results in Table I are in all respects consistent with the mechanism shown in Scheme I. Thus the acyl cation,  $\text{CX}_3\text{CO}^+$ , always retains the hydrogens or deuteriums originally in the acetate part of the ester. The ion corresponding to protonated acetic acid always contains the acetate hydrogens (deuteriums) plus one hydrogen (deuterium) from the methane plus one from the  $\beta$  position on the ethyl group.

The largest peak in the spectrum of ethyl acetate and methane corresponds to protonated ethyl acetate ( $M + 1$ )<sup>+</sup> formed by reactions 3 and 4. In mixtures of various ethyl acetates with  $\text{CD}_4$ , this peak shifts to ( $M + 2$ )<sup>+</sup> as expected. However, close examination of Table I shows that whenever both hydrogen and deuterium are present in the ethyl acetate-methane combination, both ( $M + 1$ )<sup>+</sup> and ( $M + 2$ )<sup>+</sup> ions are formed. This observation indicates that additional ion-molecule reactions are occurring after the initial proton (deuteron) transfer to the ethyl acetate. The variation with ethyl acetate pressure of the spectrum of  $\text{CD}_4$  and unlabeled ethyl acetate was examined in order to determine the importance of these secondary reactions. The results shown in Figure 1 were obtained using trapping plate ejection of the  $\text{CD}_3^+$  and  $\text{CD}_4^+$  ions, so ions formed from the ester by electron impact do not contribute to the observed ion intensities. The increase of the ( $M + H$ )<sup>+</sup> intensity with increasing ester pressure and the corresponding decrease in  $\text{CH}_3\text{CO}_2\text{HD}^+$  intensity are caused by the reaction



which is confirmed by conventional double resonance<sup>15</sup> experiments. Reaction 6 in which a deuteron is trans-



ferred to the ester was also detected by double reso-

(15) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

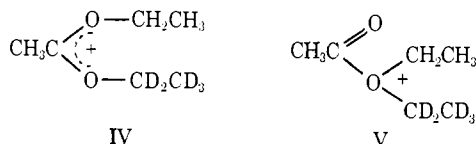
Table I. Ester Ion Intensities in Mixtures of Various Deuterium Labeled Ethyl Acetates and Methane,<sup>a</sup> X = H and D

System	<i>m/e</i> and %													
	CX <sub>3</sub> CO <sup>+</sup>		CX <sub>3</sub> CX <sub>2</sub> O <sup>+</sup>		CX <sub>3</sub> CO <sub>2</sub> X <sub>2</sub> <sup>+</sup>				C <sub>4</sub> X <sub>6</sub> O <sup>+</sup>		CX <sub>3</sub> CO <sub>2</sub> CX <sub>2</sub> CX <sub>3</sub> X <sup>+</sup>			
CH <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	43	8.2	45	1.2	61	27.9			70	1.8	89	58.6	90	2.2 <sup>d</sup>
CH <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub>	43	9.9	48	1.3	61	4.5	63	1.6 <sup>d</sup>	71	0.5	89	0.6	92	35.6
					62	29.5			72	1.1	90	1.5 <sup>f</sup>	93	8.7
									73	0.7	91	1.5		
CH <sub>4</sub> + CD <sub>3</sub> CO <sub>2</sub> CD <sub>2</sub> CD <sub>3</sub>	43	0.5			61	0.4	65	25.0	75	0.6 <sup>e</sup>	92	1.3	96	3.6 <sup>e</sup>
	45	0.5	50	0.9	62	0.7	66	2.1	76	1.7	93	1.3 <sup>f</sup>	97	28.4
	46	9.0			64	2.2					94	0.4	98	15.0
CH <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> + CD <sub>3</sub> CO <sub>2</sub> CD <sub>2</sub> CD <sub>3</sub> <sup>b</sup>	43	5.8	45	1.1	61	21.0	65	17.1	70	1.0	89	17.6	96	1.8 <sup>e</sup>
	46	4.9	50	1.0	62	1.2	66	1.5	73	0.3	90	4.3	97	14.6
					64	1.7 <sup>e</sup>			75	0.5	93	0.7 <sup>f</sup>	98	3.3
									76	1.1				
CD <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> + CD <sub>3</sub> CO <sub>2</sub> CD <sub>2</sub> CD <sub>3</sub> <sup>b</sup>	43	5.3	45	1.3	61	1.4	65	1.8 <sup>e</sup>	70	1.1	89	5.5	94	0.8 <sup>f</sup>
	44	0.7	50	1.0	62	17.6	66	15.7	76	1.1	90	13.3	96	0.7 <sup>e</sup>
	46	6.0 <sup>c</sup>			63	0.9	67	0.4 <sup>d</sup>			91	0.9	97	4.7
											92	0.3	98	10.7
													99	0.7 <sup>d</sup>
CD <sub>4</sub> + CD <sub>3</sub> CO <sub>2</sub> CD <sub>2</sub> CD <sub>3</sub>	46	10.2 <sup>c</sup>	50	1.3	65	3.3 <sup>e</sup>	67	1.0	76	2.3	96	1.4 <sup>e</sup>	98	38.1
					66	29.2					97	7.1	99	1.9 <sup>d</sup>
CD <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	43	8.3	45	1.0	61	2.8	63	0.7	70	2.0	89	25.7	92	0.3
	44	0.4			62	29.1					90	23.5	94	1.0 <sup>f</sup>
											91	1.2 <sup>d</sup>	95	0.3
CD <sub>4</sub> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub>	43	7.4	48	1.0	61	0.4	63	28.7	71	0.5	90	1.0	93	28.8
	44	0.6			62	6.9	64	0.9 <sup>d</sup>	72	1.1	91	1.0	94	1.8 <sup>d</sup>
									73	0.7	92	11.1	95	1.3 <sup>f</sup>
CD <sub>4</sub> + CD <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	43	0.8	45	1.4	64	4.1	66	1.1 <sup>d</sup>	72	0.4	91	1.5	94	1.5 <sup>d</sup>
	46	8.4 <sup>c</sup>			65	24.0			73	1.2	92	18.8	96	0.6
											93	24.3	97	0.9 <sup>f</sup>

<sup>a</sup> Ester pressure =  $5 \times 10^{-6}$  Torr; methane pressure =  $8 \times 10^{-5}$  Torr. Drift voltages were 0.17 V/cm in the source and 0.13 V/cm in the analyzer. Trapping = 0.38 V, spectra taken using electron beam modulation. <sup>b</sup> Equal parts of CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CD<sub>3</sub>CO<sub>2</sub>CD<sub>2</sub>CD<sub>3</sub> were used at a total pressure of  $5 \times 10^{-6}$  Torr. <sup>c</sup> Corrected for C<sub>3</sub>D<sub>5</sub><sup>+</sup>. The correction is approximately 1.0%. <sup>d</sup> These peaks are primarily due to <sup>13</sup>C. <sup>e</sup> Primarily due to isotopic impurity of the ethyl acetate-d<sub>3</sub> which contained about 13% of the d<sub>1</sub> material. <sup>f</sup> These peaks are formed by the fragmentation of a (M + C<sub>2</sub>X<sub>5</sub>)<sup>+</sup> complex.

nance, although from Figure 1 there is obviously a large isotope effect favoring proton over deuteron transfer. If the protonated acetic acid ion actually has structure III, then the proton (deuteron) originating from methane and the proton (deuteron) originating from the ethyl group of the ester should be chemically equivalent. Several other systems were examined and they confirmed this hypothesis. In particular, in a mixture to CH<sub>4</sub> and CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CD<sub>3</sub>, reactions analogous of (5) and (6) are observed with a similar isotope effect. Because of the possibility of additional reactions and the unexplained dependence of *m/e* 90 on pressure in Figure 1, we cannot at this time give an accurate value for the isotope effect for this proton transfer reaction; however, we have established  $k_H/k_D \geq 2$ .

Small amounts of isotopically exchanged protonated molecular ions are formed by a reaction of C<sub>2</sub>H<sub>5</sub><sup>+</sup> or C<sub>2</sub>D<sub>5</sub><sup>+</sup> ions with ethyl acetate. For C<sub>2</sub>D<sub>5</sub><sup>+</sup> reacting with unlabeled ethyl acetate, the reaction complex can have either structure IV or V. The two structures are



indistinguishable in these experiments since the two ethyl groups are chemically equivalent in both. Structure IV can decompose in two ways, one of which is shown in reaction 7. The pathway shown results in the

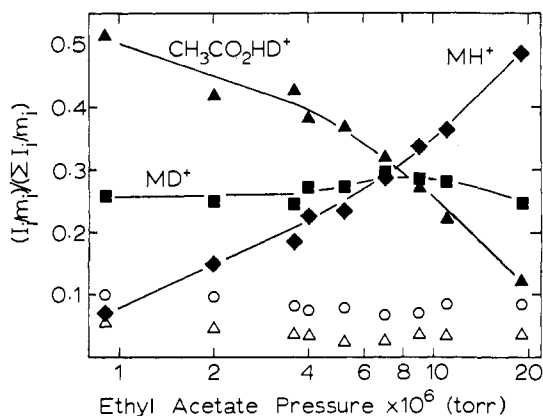
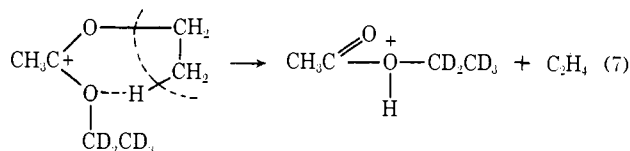
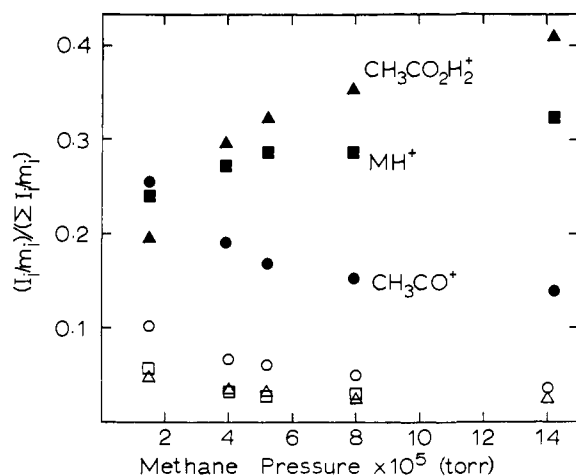


Figure 1. Variation with ester pressure of the ionic methane-d<sub>1</sub> chemical ionization spectrum of ethyl acetate. The CD<sub>4</sub> pressure was held constant at  $8 \times 10^{-5}$  Torr. As the ester pressure increases, the *m/e* 62 (▲) signal decreases while the protonated ester *m/e* 89 (◆) increases as a result of reaction 5. The fraction of *m/e* 90 (■) rises slowly with pressure initially as expected from reaction 6 but decreases at the highest pressure. Other ions shown are *m/e* 43 (○) and *m/e* 61 (△), both of which decrease with increasing ester pressure.



incorporation of all five deuteriums into the (M + 1)<sup>+</sup>



**Figure 2.** Variation with methane pressure of the methane chemical ionization spectrum of ethyl acetate. At low methane pressure corresponding to larger amounts of energy being deposited in the protonated ester ion, the acyl cation is the major fragment. At higher methane pressures the methane reagent ions are collisionally deactivated, less energy is transferred into the protonated ester ion, and  $m/e$  61 (protonated acetic acid) is the major fragment. The unfragmented protonated ester also increases with increasing pressure. Minor ions which are not labeled are  $m/e$  70 (O),  $m/e$  45 ( $\Delta$ ), and  $m/e$  88 ( $\square$ ).

ion whereas the other equivalent pathway would leave only one. Similar reactions can be written for structure V. This mechanism was postulated by Munson and Field and is proven by these deuterium labeling results. The ions produced by this pathway are noted in Table I. The small intensities of all of these ions show that while the reaction occurs it is not the major mode of proton transfer from ethyl cations to ethyl acetate. Even assuming that the other small peaks in the ( $M + 1$ )<sup>+</sup> region in Table I arise from this pathway with some additional intramolecular hydrogen rearrangement, we estimate that no more than 10% of the  $C_2H_5^+$  ions react in this way. The dominant reaction is a direct proton transfer.

Two other minor ions in the chemical ionization spectra of the ethyl acetates in Table I are somewhat puzzling. All of the hydrogens (deuteriums) in the  $CH_3CH_2O^+$  ion clearly originate in the ethyl group of the labeled ethyl acetates, yet a direct fragmentation of protonated ethyl acetate to give the ethoxy cation is endothermic by at least 117 kcal/mol ( $\Delta H_f(CH_3CH_2O^+) = 211$  kcal/mol<sup>16</sup>). This suggests that there must be considerable rearrangement prior to fragmentation so that the product ion has a more stable structure. If the  $C_2H_5O^+$  ion has the protonated acetaldehyde structure, the reaction endothermicity may be as low as 49 kcal/mol. The other ion is  $C_4H_6O^+$  corresponding to loss of  $H_2O$  from the ethyl acetate. All six hydrogens originate in the ester, but little more can be said about the mechanism of formation of this ion.

In solution, esters are protonated on the keto oxygen,<sup>17</sup> but in view of the large effect of the solvation energy on solution ion stability,<sup>18</sup> it is of interest to try

(16) J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968).

(17) G. Fraenkel, *J. Chem. Phys.*, **34**, 1466 (1961); G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 3591 (1967); G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

(18) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).

to determine the site at which esters are protonated in the gas phase. Scheme I shows the ester protonated on the ether oxygen (structure I). In the unimolecular fragmentation of I, formation of the acyl cation has a high-frequency factor and a high-activation energy while formation of protonated acetic acid III has a low-frequency factor and a low-activation energy. Thus for low average excitation energies (in the protonated ester), III is favored because of its lower activation energy, while at higher energies, acyl cation is favored because of its larger frequency factor.

The average amount of excitation energy in the  $C_2H_5^+$  ions formed by reaction 2 can be varied by changing the methane pressure. Higher methane pressures increase the average number of collisions which the  $C_2H_5^+$  ions suffer before reacting with the ester. Since these non-reactive collisions can remove some of the excess energy in the ethyl ions, they serve to decrease the amount of energy deposited in the protonated ester. Figure 2 shows the variation with methane pressure of the relative intensities of the ester ions resulting from proton transfer from  $CH_5^+$  and  $C_2H_5^+$ . These data were obtained at 23 eV and an ethyl acetate pressure of  $4.6 \times 10^{-6}$  Torr using trapping plate ejection of  $CH_3^+$  and  $CH_4^+$  as before. As the methane pressure is lowered and the excitation of the protonated ethyl acetate is increased, the relative intensity of the acyl cation increases until it becomes the largest peak in the spectrum. There is a corresponding decrease in the intensity of III and a smaller decrease in the intensity of the protonated ester. This is exactly the behavior expected if Scheme I is correct. On the other hand, if the ester is keto protonated, then formation of both III and the acyl cation requires formation of a four-membered ring, and both should have about the same low frequency factor, causing III to dominate at all energies. Since this is not observed, we conclude that esters in the gas phase are probably protonated on the ether oxygen. See Discussion.

### Other Esters

Table II shows the methane chemical ionization spectra of ten esters obtained in the icr spectrometer under conditions very similar to those for Table I. All of the spectra were recorded under identical conditions. The slight differences in the intensities of the ethyl acetate ions in Table I and Table II illustrate the reproducibility of the spectra from week to week.

In general, the major ions in these other esters are those expected on the basis of the mechanisms discussed above for the chemical ionization of ethyl acetate. All of the esters in Table II show a large ( $M + 1$ )<sup>+</sup> peak. All except methyl acetate have a large peak corresponding to the protonated carboxylic acid analogous to the  $CH_3CO_2H_2^+$  peak in ethyl acetate. Formation of this ion in methyl esters is very endothermic because the neutral fragment would be  $CH_2$ . The  $RCO^+$  ion is observed for all esters except the formates where it is obscured by the  $C_2H_5^+$  ion from methane. Experiments with  $CD_4$  and several formates showed that the  $HCO^+$  peak was less than 2% of the total ester ionization.

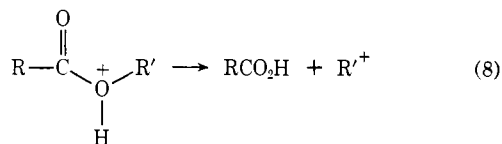
Table II shows several types of ions which are not analogous to those seen in ethyl acetate. By far the largest of these in the  $R^+$  ion formed when the pro-

**Table II.** Chemical Ionization Spectra of Esters Obtained in an Icr Spectrometer<sup>a</sup> (% of Ester Ionization)

Compd RCOOR'	(M + 1) <sup>+</sup>	M <sup>+</sup>	(M - 1) <sup>+</sup>	RCO <sup>+</sup>	RCO <sub>2</sub> H <sub>2</sub> <sup>+</sup>	RCO <sub>2</sub> <sup>+</sup> C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	R' <sup>+</sup>	(R' - 1) <sup>+</sup>	R'O <sup>+</sup>	R'OH <sub>2</sub> <sup>+</sup>
Isopropyl formate	49.0		0.7	<i>b</i>	6.2	5.8	25.6	1.7		
<i>sec</i> -Butyl formate	32.5			<i>b</i>	2.4	5.8	40.6	2.9	1.4	<i>c</i>
Methyl acetate	71.6	2.1		20.6	1.2					
Ethyl acetate	57.8			8.1	27.5	<i>d</i>	<i>b</i>		1.2	
<i>n</i> -Propyl acetate	32.9 (15.6) <sup>f</sup>	(0.1)	1.2 (2.2)	10.2 (3.2)	40.7 (64)	4.3 (9.2)	<i>e</i>	0.8 (<0.1)	0.8 (0.1)	<i>g</i>
<i>n</i> -Butyl acetate	26.7		0.4	6.9	31.6	5.1	8.2	4.4	1.0	1.4
Isobutyl acetate	32.3		0.4	6.4	14.0	3.5	28.6	3.8	1.0	1.0
Ethyl propionate	40.4 (48)	1.3 (1.0)		11.0 (9.0)	27.7 (32)	<i>d</i>	<i>b</i>		1.2 (1.1)	2.2 (0.3)
<i>n</i> -Propyl propionate	43.0 (17.4)		1.2 (1.6)	14.5 (8.8)	28.5 (54)	2.8 (8.5)	3.1 (1.6)	1.2 (<0.1)	(0.9)	(0.05)
Ethyl butyrate	48.8	1.1		9.5	24.0	<i>d</i>	<i>b</i>		(1.4)	

<sup>a</sup> The ester pressure was  $5 \times 10^{-6}$  Torr; methane pressure was  $8 \times 10^{-6}$  Torr. Source drift field = 0.18 V/cm; analyzer drift field = 0.10 V/cm. Trapping potential = 0.35 V. Electron energy 23 eV. Spectra were taken using electron beam modulation. <sup>b</sup> Obscured by C<sub>2</sub>H<sub>5</sub><sup>+</sup> from methane. <sup>c</sup> Same mass as RCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub><sup>+</sup>. <sup>d</sup> Same mass as (M + 1)<sup>+</sup>. <sup>e</sup> Same mass as RCO<sup>+</sup>. <sup>f</sup> Values in parentheses are from ref 2. <sup>g</sup> Same mass as RCO<sub>2</sub>H<sub>2</sub><sup>+</sup>.

tonated ester fragments to produce a neutral carboxylic acid and an alkyl cation as shown in reaction 8. This



peak is particularly large in the formates and isobutyl acetate.

A close examination of the spectra in Table II shows that while RCO<sup>+</sup>, RCO<sub>2</sub>H<sub>2</sub><sup>+</sup>, and R'<sup>+</sup> ions are the principal fragments produced, there is a wide variation in the relative intensities of these peaks. As discussed above, and noted by Munson and Field,<sup>2</sup> some of this variation is obviously caused by the extreme endothermicity of particular fragmentations in specific esters. In order to establish the importance of the thermochemistry in determining the chemical ionization spectrum of an ester, the activation energies<sup>19</sup> and intensities for these three principal fragment ions are compared in Table III. For nine of the ten spectra, the largest fragment ion is the one formed by the lowest energy process. In isobutyl acetate, the one exception, the largest fragment peak is R'<sup>+</sup>, which for formation of isobutyl cation has an activation energy of 58 kcal/mol. Thus from Table III, R<sup>+</sup> should be the smallest fragment peak. However, if the *sec*-butyl group rearranges *via* a 1,2-hydrogen shift to a *tert*-butyl group either before or during the fragmentation, then the activation energy for R<sup>+</sup> formation is only 26 kcal/mol, and R<sup>+</sup> is expected to be the largest fragment ion.

### Discussion

Knowing that the relative intensities of ester CI fragment ions are determined by the thermochemistry of the fragmentation allows us to obtain thermochemical, and therefore structural, information about the fragment ions. Thus, the fact that the R'<sup>+</sup> peak in *n*-butyl

(19) Enthalpy changes are computed from data in ref 4b, 9, and 14.

**Table III.** Activation Energies (kcal/mol) and Intensities as Per Cent of Ester Ionization for the Principal Fragment Ions in the CI Spectra of Some Esters

Ester RCOOR'	Fragment		
	RCO <sup>+</sup> ΔH %	RCO <sub>2</sub> H <sub>2</sub> <sup>+</sup> ΔH %	R' <sup>+</sup> ΔH %
Isopropyl formate	59 <i>a</i>	30 6.2	30 25.6
<i>sec</i> -Butyl formate	59 <i>a</i>	28 2.4	26 40.6
Methyl acetate	39 20.6	104 1.2	92 0.0
Ethyl acetate	42 8.1	33 27.5	62 0 <sup>b</sup>
<i>n</i> -Propyl acetate	44 10.2	34 40.7	59 <i>c</i>
<i>n</i> -Butyl acetate	45 6.9	35 31.6	58 8.2
Isobutyl acetate	46 6.4	33 14.0	58 <sup>d</sup> 28.6
Ethyl propionate	43 11.0	35 27.7	66 <i>e</i>
<i>n</i> -Propyl propionate	44 14.5	35 28.5	62 3.1
Ethyl butyrate	41 9.5	33 24.0	66 <i>e</i>

<sup>a</sup> Obscured by C<sub>2</sub>H<sub>5</sub><sup>+</sup> in CH<sub>4</sub>. A small peak at *m/e* 29 is observed using CD<sub>4</sub>, but it may be entirely due to background and C<sub>2</sub>D<sub>2</sub>H<sup>+</sup> from isotopic impurity of the methane-*d*<sub>4</sub>. In any event, this peak is less than 2% of ester ionization. <sup>b</sup> Same as *a*, but upper limit is 1%. <sup>c</sup> Same mass as RCO<sup>+</sup>. <sup>d</sup> This activation energy is for formation of the isobutyl cation. If the alkyl group rearranges so that *tert*-butyl cation is formed, the activation energy is 26 kcal/mol. <sup>e</sup> Obscured by C<sub>2</sub>H<sub>5</sub><sup>+</sup>.

acetate is relatively small shows that the *n*-butyl group does not rearrange to a *tert*-butyl structure prior to or during the fragmentation. Similar conclusions can be drawn from Munson and Field's<sup>2</sup> spectra of *n*-butyl and isobutyl propionate and *n*-pentyl and isopentyl propionate. Rearrangement to the more stable tertiary carbonium ion occurs when only hydrogen migration is required but does not occur when rearrangement of the carbon skeleton is necessary.

The fact that the relative activation energies determine the distribution of fragment ions provides additional indirect support for our mechanism of ester chemical ionization since it indicates that all of the fragments result from the decomposition of a single intermediate. In other words, the fragment ions are the products of competing unimolecular reactions of the protonated ester. In the two formate esters where the activation energies for  $\text{RCO}_2\text{H}_2^+$  and  $\text{R}'^+$  are approximately equal, the formation of  $\text{R}'^+$  is favored indicating that this fragmentation has a higher frequency factor than formation of  $\text{RCO}_2\text{H}_2^+$ . This fact is also consistent with Scheme I and reaction 8. It should be noted, however, that neither these results nor our mechanisms preclude the formation of *some* keto-protonated ester.<sup>20</sup> The difference in the proton affinity of the keto and ether oxygen should not be more than a few kilocalories per mole, and the average of the internal energies of the fragmenting protonated esters is obviously much greater than this. Thus the keto-protonated form is certainly accessible and in fact provides the most straightforward explanation for the small  $\text{R}'\text{O}^+$  peaks in Table II.

It is instructive to compare the CI spectra of esters obtained in the icr spectrometer with those of Munson and Field obtained under conventional CI conditions. There are two principal differences in the two experiments: (a) in the conventional CI mass spectrometer, the time between collisions is about  $4 \times 10^{-8}$  sec whereas in these icr experiments it is about  $2 \times 10^{-4}$  sec, (b) in Munson and Field's experiments<sup>2</sup> the ratio of methane to ester was about 1000 compared to about 16 in the icr experiments. The effect of (b) is to increase the size of the  $(\text{M} + 1)^+$  at the expense of  $\text{RCO}_2\text{H}_2^+$  as a result of reactions such as 5 and 6; this is a chemical complication rather than a fundamentally different result. However, the result of (a) is that no collision stabilized ions such as  $(\text{M} + \text{C}_2\text{H}_5)^+$  are observed in the

(20) In this and earlier discussion we refer only to those protonated ester ions which decompose. Our experiments say nothing about the structure of ions which do not fragment.

icr experiments. Table II includes three compounds also studied by Munson and Field<sup>2</sup> and their results are shown in parentheses below ours. In view of the differences between the experiments, the agreement is excellent. The larger  $\text{RCO}_2\text{C}_2\text{H}_6^+$  peaks reported by Munson and Field probably result from the greatly increased probability that a  $(\text{M} + \text{C}_2\text{H}_5)^{+*}$  complex will be partially deexcited by collision prior to decomposition thus reducing the rate of dissociation back to  $\text{M} + \text{C}_2\text{H}_5^+$  compared to the rate of rearrangement to  $\text{RCO}_2\text{-C}_2\text{H}_6^+$ . One consequence of the different time scales of the two experiments is that *any fragment ion which appears in a conventional CI spectrum will also appear in the icr spectrum of the same system.*<sup>21</sup> Thus icr techniques should be generally useful in elucidating the mechanisms leading to the formation of chemical ionization fragment ions.

The primary purpose of these experiments was to increase our understanding of the fundamental properties and processes important in producing chemical ionization spectra. They also point out, however, one area in which information is almost totally lacking: the exact distribution of energies transferred to the protonated molecule. As an extreme example, in *n*-propyl propionate some of the protonated ester ions do not fragment at all, and on the long time scale of the icr experiments, this fact implies that these ions contain less than 35 kcal/mol (Table III) of excitation. On the other hand, at least 3.1% of the  $(\text{M} + \text{H})^{+*}$  ions contain more than 62 kcal/mol since they fragment into propyl cations. These observations suggest that studies of the fragmentation of protonated molecules, such as esters, which have a number of fragmentation pathways with different activation energies may provide quantitative data on the distribution of reaction exothermicity in proton transfer reactions.

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(21) Note, however, that the converse is not true. An ion which fragments in the icr experiment could well be collisionally stabilized in a conventional CI experiment.