For the trifluoroacetolysis of all tosylates except *exo*-norbornyl, Peterson's method[37] for spectrophotometric assay of quenched aliquots was used. Initial substrate concentrations were *ca.* 0.050 *M* in carefully distilled trifluoroacetic acid containing 0.060 *M* sodium trifluoroacetate and 1.0 wt % trifluoroacetic anhydride. *exo*-Norbornyl tosylate reacted too swiftly to allow sampling procedures. A new technique was thus developed[12] for continuous photometric observation of the reaction following rapid reactant introduction in a closed thermostated cell; it was applied to this reaction at 22.6, 20.2, and 12.9°. A fourth rate constant was measured at 5.6° as follows. Fifteen samples of *ca.* 13 mg (0.05 mmol) of pulverized tosylate were accurately weighed in 25-ml volumetric flasks. In a cold room, each flask was suspended in turn in a large ambient water bath (5.6°), and after several minutes for temperature equilibration 1.0 ml of trifluoroacetolysis medium (see above, this paragraph), prethermostated in the same bath, was added quickly by syringe. The flask was shaken briskly for 3 sec

to dissolve the reactant uniformly, and after a programmed interval the reaction was quenched by rapid, turbulent addition of 20 ml of −70° 95% ethanol from a syringe. Points were thus distributed over 2 half-lives (after preliminary runs established the approximate rate). From Dry Ice storage, each flask in turn was warmed to 25° with gentle agitation in a thermostated water bath, filled to the mark with 95% ethanol, and mixed well. Without delay, a sample was transferred to an optical cell and its absorbance in the region of 273 nm measured with a Cary 15 spectrophotometer. After normalization of initial concentrations, the data were treated as in the aliquot procedure[37] to obtain the rate constant.

(37) (a) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965); see also (b) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

Ion–Molecule Reactions of Acids and Esters with Alcohols. Gas Phase Analogs of Acidic Esterification Processes

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Abstract: The main ion–molecule reactions that formic acid, acetic acid, propionic acid, and their esters undergo with the lower alcohols have been investigated by ion cyclotron resonance at low electron energies and pressures up to 5×10^{-5} Torr. Formation of protonated ester has been observed to occur readily at 10^{-5} Torr by the reaction of protonated acetic acid, or propionic acid, and the neutral alcohol. Formic acid yields a protonated ester only with the protonated propanols and butanols suggesting a different mechanism. Esters are shown to react only with protonated propanols and butanols to yield ions of the type $(RCO_2R'R'')^+$, when the proton affinity of the alcohol is higher than that of the ester. The mechanism of this reaction is compared with chemical ionization studies which show such ions to be intermediates in the gas phase transesterification induced by carbonium ions.

The elucidation of reaction pathways for the esterification of organic acids and hydrolysis of esters constitutes a classical chapter of mechanistic organic chemistry which dates back to the beginning of the century.[1] A multiplicity of mechanisms has been recognized for these reactions according to their class (basic or acidic), the site of cleavage, and the molecularity of the rate-determining step.[2]

The fact that esterification and hydrolysis involve the participation of ionic species suggests that these reactions may be in principle sensitive to solvent participation, or solvation effects. Such effects can be eliminated, and the intrinsic reactive features of these processes unraveled by techniques like ion cyclotron resonance, when applied to the gas phase analogs of these reactions.[3,4] Preliminary observations using icr techniques on the analog of the base-promoted transesterification have already been reported, and similarities drawn between gas phase and solution mechanisms.[5,6]

The present paper describes the gaseous ion–molecule reactions originating when formic acid, acetic acid, and their esters are allowed to react with the lower aliphatic alcohols in the cell of an ion cyclotron resonance spectrometer. Such reactions can be viewed as gas phase analogs of the acid-promoted esterification. Two distinct pathways are encountered for these reactions which depend on the relative gas phase basicities of the reactant species, and the type of alcohol used in the reactions. The results are also used to compare the gas phase behavior with the mechanisms usually found in solution.

Experimental Section

Spectra were taken in a Varian V-5900 ICR-9 spectrometer provided with a dual inlet system and a cell of $1.27 \times 2.54 \times 12.7$ cm³. Ionization was achieved with 15 eV electrons, using low emission currents (in general less than 0.2 μA). Double resonance experiments were carried out with low irradiating fields (about 10 mV/cm), and usually in the pulsed mode. Pressures were read directly from the ion pump control. The systems reported in the

(1) B. Holmberg, *Ber.*, **45**, 2997 (1912).
(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 752–782.
(3) J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971).
(4) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(5) P. W. Tiedemann, Abstracts, 23rd Meeting of the SBPC, Curitiba, Brazil, July 1971, Paper C-67.
(6) L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Amer. Chem. Soc.*, **95**, 1057 (1973).
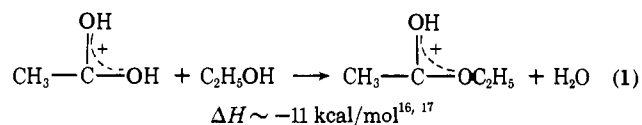
present work were investigated in the pressure range of 10^{-7}–5 × 10^{-5} Torr.

Formic acid, acetic acid, propionic acid, all of the alcohols, and most of the esters were obtained from commercial sources. Their purity was established by low pressure icr. Methyl formate-d_3, n-propyl formate, and isopropyl formate-d_6 were prepared as described elsewhere,[6] and ethyl trifluoroacetate was synthesized from trifluoroacetic acid and ethanol. The following deuterated compounds were also used in this study: acetic acid-d_4 (Stohler), methanol-d_4 (Merck), and methyl acetate-d_6 (Merck). Formic acid was repeatedly distilled until reproducible icr spectra could be obtained and free of high mass peaks.

Results

The interpretation of the main gas phase ion–molecule reactions that take place between organic acids and alcohols, and esters and alcohols, is considerably simplified by the extensive knowledge of the individual gas phase ion chemistry of methanol,[7–9] ethanol,[7,8] 2-propanol,[10,11] 2-butanol,[12] and tert-butyl alcohol.[13] Likewise, the gas phase ionic condensation–elimination reactions in acetic acid, propanoic acid, and their esters have been briefly described by us,[14] and relative proton affinities have been established for alcohols, acids, and esters.[15]

The icr spectra of gaseous mixtures of separately introduced acetic acid and methanol, or ethanol, at 2 × 10^{-5} Torr reveal the rapid formation of an ion with mass to charge ratio corresponding to the protonated ester. Similar behavior is observed with propanoic acid in mixtures with methanol, or ethanol. Such reactions can be viewed as analogous to the acid-catalyzed process in solution, i.e., eq 1.

$$CH_3-\overset{\overset{\displaystyle OH}{\|\,+}}{C}=OH + C_2H_5OH \longrightarrow CH_3-\overset{\overset{\displaystyle OH}{\|\,+}}{C}=OC_2H_5 + H_2O \quad (1)$$

$$\Delta H \sim -11 \text{ kcal/mol}^{16,\,17}$$

The formation of the protonated ester in these reactions, independently of the actual site of protonation, is actually achieved not only by the reaction of the protonated acid with ethanol, but also by the direct reaction of protonated ethanol with acetic acid. This observation is based on double resonance experiments of the product ion which show roughly equal contribution from $C_2H_5OH_2^+$ and $CH_3COOH_2^+$. Since acetic acid has a higher proton affinity than ethanol,[15] the formation of protonated ester by $C_2H_5OH_2^+$ is apparently

(7) K. R. Ryan, L. W. Sieck, and J. H. Futrell, J. Chem. Phys., 41, 111 (1964).

(8) L. W. Sieck, F. P. Abramson, and J. H. Futrell, J. Chem. Phys., 45, 2859 (1966).

(9) J. M. S. Henis, J. Amer. Chem. Soc., 90, 844 (1968).

(10) J. L. Beauchamp and R. C. Dunbar, J. Amer. Chem. Soc., 92, 1477 (1970).

(11) T. A. Lehman, T. A. Elwood, J. T. Bursey, M. M. Bursey, and J. L. Beauchamp, J. Amer. Chem. Soc., 93, 2108 (1971).

(12) J. L. Beauchamp and M. C. Caserio, J. Amer. Chem. Soc., 94, 2368 (1972).

(13) J. L. Beauchamp, J. Amer. Chem. Soc., 91, 5925 (1969).

(14) P. W. Tiedemann and J. M. Riveros, J. Amer. Chem. Soc., 95, 3140 (1973).

(15) (a) P. W. Tiedemann, P. C. Isolani, and J. M. Riveros, J. Chem. Soc., Faraday Trans. 2, 1023 (1973); (b) J. Long and B. Munson, J. Amer. Chem. Soc., 95, 2427 (1973).

(16) Differences in proton affinities between the ester and the acid were estimated from the difference in ionization potentials, and assuming the hydrogen affinities to be approximately constant (see ref 15). For ionization potentials, see D. A. Sweigart and D. W. Turner, J. Amer. Chem. Soc., 94, 5592 (1972).

(17) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field: "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

competitive with proton transfer. The reactions with methanol and ethanol are favored by the use of an excess of the alcohol, presumably because of the effectiveness of the alcohol ionic fragments in promoting protonation of the neutral species. A rough guidance of the ease of formation of the protonated ester by reaction 1 is illustrated in Table I, where the relative

Table I. Relative Intensities of Ionic Species Involved in the Esterification Process for Various Compositions and Pressures[a,b]

RCOOH	R″OH	P_{RCOOH}, Torr × 10^5	$P_{R″OH}$, Torr × 10^5	I_{RCOOH}^+	$I_{R″OH_2}^+$
CH_3COOH	CH_3OH	1.0	1.0	3.3	1.0
		0.5	2.5	0.55	0.17
CH_3COOH	C_2H_5OH	1.0	1.0	2.6	0.62
		0.3	2.7	0.38	0.27
C_2H_5COOH	CH_3OH	1.2	0.4	8.1	3.6
		0.5	1.5	3.5	5.8
		0.5	2.0	2.8	5.8
C_2H_5COOH	C_2H_5OH	1.2	0.4	4.5	1.2
		0.7	2.1	1.6	1.3
HCOOH	$(CH_3)_2CHOH$	2.0	2.0	1.1	2.1

[a] Relative intensity of the product ion, $(RCOOR')H^+$, is taken as 1 for all cases. [b] Residence time in the cell ca. 2 × 10^{-3} sec.

intensity of the product ion is compared with that of the protonated alcohol and acid at various pressures, and at various compositions of the mixtures.

Experiments were carried out to measure relative rates of esterification reactions in acetic acid with methanol and ethanol. The comparison was made by maintaining the pressure of perdeuterated acetic acid constant,[18] while the partial pressure of a methanol–ethanol mixture was increased stepwise, and the intensity of the two products was recorded in the pressure range of 1 × 10^{-5}–5 × 10^{-5} Torr. The relative intensities of the two protonated esters remained constant indicating that the two reactions proceed at similar rates.

Acetic acid was also investigated in the presence of higher alcohols up to 1-pentanol. The formation of protonated esters becomes less important with alcohols above 2-propanol, and the overall spectra become complicated due to the extensive reactions of the alcohols themselves.

Formic acid represents a significantly different case. Thus, in the presence of methanol, or ethanol, the only process which is observed under our conditions is the proton transfer (eq 2), corresponding to the fact that

$$HCOOH_2^+ + CH_3OH \longrightarrow HCOOH + CH_3OH_2^+ \quad (2)$$

$$\Delta H = -1 \text{ kcal/mol}^{19}$$

the alcohols have a higher proton affinity than formic acid. Formation of the protonated ester cannot be detected with CH_3OH and C_2H_5OH. However, protonated 2-propanol reacts with formic acid (as well as protonated formic acid with 2-propanol) to yield an ion of m/e 89, presumably corresponding to protonated isopropyl formate. The ease of formation of the product ion is illustrated in Table I. This esterification

(18) The use of CD_3COOD was necessary to separate the peak of the protonated methyl acetate from the protonated diethyl ether (m/e 75), a product of ion–molecule reactions in ethanol.

(19) S. L. Chong and J. L. Franklin, J. Amer. Chem. Soc., 94, 6347 (1972).
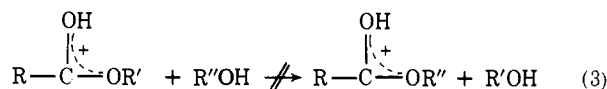
Table II. Relative Intensities of Ionic Species Involved in the Reaction of Esters with Higher Alcohols for Various Compositions and Pressures[a,b]

RCOOR'	R''OH	$P_{RCOOR'}$, Torr × 10⁵	$P_{R''OH}$, Torr × 10⁵	$I_{RCOOR'H^+}$	$I_{R''OH_2^+}$
HCOOC₂H₅	(CH₃)₂CHOH	0.9	0.9	2.1	0.48
HCOOC₂H₅	CH₃CH₂CH₂OH	0.5	0.5	6.8	1.5
		0.5	2.3	1.6	1.2
HCOOCH₂CH₂CH₃	(CH₃)₂CHOH	0.6	0.6	6.4	1.6
		2.0	2.0	2.4	0.57
HCOOCH₂CH₂CH₃	CH₃CH₂CH₂OH	0.5	0.5	16.5	4.3
		2.0	2.0	4.6	1.0
HCOOCH(CH₃)₂	(CH₃)₂CHOH	1.0	1.0	6.7	0.58
ClCOOC₂H₅	(CH₃)₂CHOH	0.5	2.0	7.3	3.5
		2.0	2.0	1.9	2.4
CF₃COOC₂H₅	(CH₃)₂CHOH	1.0	1.0	2.5	0.66
		2.0	2.0	1.2	0.63

[a] Relative intensity of the product ion, $(RCO_2R'R'')^+$, is taken as 1 for all cases. [b] Residence time in the cell $ca.$ 2 × 10⁻³ sec.

is also observed with 2-butanol and *tert*-butyl alcohol although to a lesser extent. This drastic change in behavior takes place even though the proton affinity of these alcohols is even higher than that of methanol or ethanol.

Transesterification or alcoholysis reactions like the one depicted in process 3 are not observed in the gas phase under the conditions present in an ion cyclotron resonance spectrometer at pressures below 5 × 10⁻⁵ Torr. This result is based on a number of experiments

$$R-\overset{\overset{\displaystyle OH}{|}}{C}\!\!\overset{+}{=}OR' + R''OH \nrightarrow R-\overset{\overset{\displaystyle OH}{|}}{C}\!\!\overset{+}{=}OR'' + R'OH \quad (3)$$

involving methyl formate, ethyl formate, *n*-propyl formate, isopropyl formate, ethyl chloroformate, methyl acetate, ethyl acetate, and ethyl trifluoroacetate with methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, and *tert*-butyl alcohol. Reaction 3 was actually probed for several cases in both the exothermic and endothermic directions. For the case of acetates, with $R' = CH_3$ and $R'' = C_2H_5$, the ΔH of the forward reaction is approximately -2 kcal/mol.[16,17] Transesterification reactions have been observed in chemical ionization studies of esters as a result of direct attack of a carbonium ion onto the esters, and breakage of the original alkyl-oxygen bond.[20,21]

The failure to detect alcoholysis in our systems is compensated by the observation of a water displacement ion–molecule reaction that most of the above esters (protonated or neutral) undergo with the propanols and butanols, but not with methanol, or ethanol. This reaction was first detected with deuterated methyl formate.[22] The structure of the product ion is pre-

$$\overset{\overset{\displaystyle O}{||}}{H-C}\!-OCD_3 + (CH_3)_2CHOH_2^+ \longrightarrow$$

$$HCO_2CD_3C_3H_7^+ + H_2O \quad (4)$$
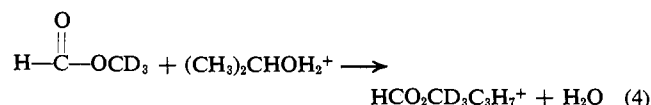
sumably of an acetal type, although an oxonium ion structure cannot be ruled out on the basis of our experiments (see Discussion and ref 20). The importance of this reaction for several esters is illustrated in Table II

(20) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 4357 (1966).

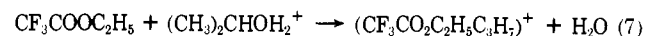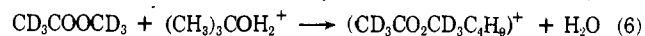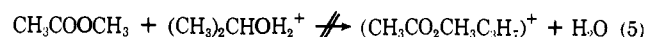(21) W. A. Laurie and F. H. Field, *J. Amer. Chem. Soc.*, **94**, 2913 (1972).

(22) The use of deuterated methyl formate was necessary to shift the product ion of reaction 4 away from m/e 103, which is due to the formation of protonated diisopropyl ether (ref 10).
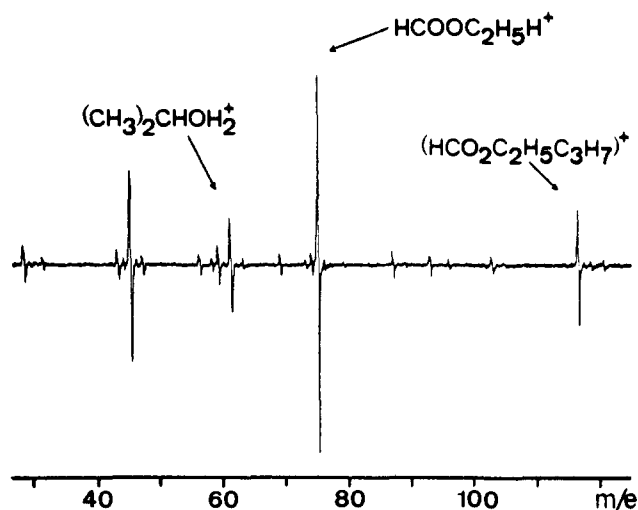
Figure 1. Single resonance spectrum of an equimolar mixture of ethyl formate and 2-propanol at 1.0 × 10⁻⁵ Torr and 15 eV electron energy. The small peaks present in the spectrum can be explained by the individual ion chemistry of the ester and of the alcohol (see ref 10).

and in Figure 1. Double resonance signals indicate that either the protonated ester or the protonated alcohol is capable of initiating reaction 4. The water displacement reaction is also observed for ethyl chloroformate, isopropyl formate, *n*-propyl formate, methyl acetate (see below), and ethyl trifluoroacetate. As previously indicated, protonated isopropyl formate and methanol do not yield the product ion of reaction 4.
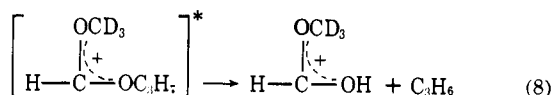
Relative proton affinities of the alcohol and ester are apparently important in the mechanism of reaction 4. Whereas reaction 5 is not observed, reactions 6 and 7 are detected readily. The relative basicities of the
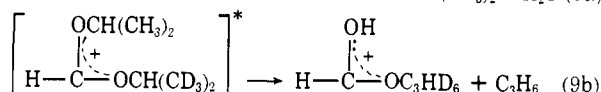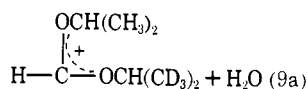
$$CH_3COOCH_3 + (CH_3)_2CHOH_2^+ \nrightarrow (CH_3CO_2CH_3C_3H_7)^+ + H_2O \quad (5)$$

$$CD_3COOCD_3 + (CH_3)_3COH_2^+ \longrightarrow (CD_3CO_2CD_3C_4H_9)^+ + H_2O \quad (6)$$

$$CF_3COOC_2H_5 + (CH_3)_2CHOH_2^+ \longrightarrow (CF_3CO_2C_2H_5C_3H_7)^+ + H_2O \quad (7)$$
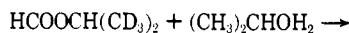
neutrals were tested by double resonance techniques and pressure studies.[15,23]

A final point of interest in these reactions is the fact that the product ions generated by the prototype reaction 4 can further decompose according to reaction 8.

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

$$\left[\begin{array}{c} OCD_3 \\ \| + \\ H-C\overset{\cdot\cdot}{-}OC_3H_7 \end{array}\right]^* \longrightarrow \begin{array}{c} OCD_3 \\ \| + \\ H-C\overset{\cdot\cdot}{-}OH \end{array} + C_3H_6 \qquad (8)$$

It is not clear from our limited pressure studies whether or not these reactions occur spontaneously. However, double resonance experiments performed on these systems show that reaction 8 becomes favorable with an increase in translational energy of the reactant ion. The species which decompose always do so by expulsion of an olefinic residue derived from the original alcohol. A clear example of this behavior was observed in the sequence of reactions 9a and 9b. The fact that the

$$HCOOCH(CD_3)_2 + (CH_3)_2CHOH_2 \longrightarrow$$

$$\begin{array}{c} OCH(CH_3)_2 \\ \| + \\ H-C\overset{\cdot\cdot}{-}OCH(CD_3)_2 + H_2O \quad (9a) \end{array}$$

$$\left[\begin{array}{c} OCH(CH_3)_2 \\ \| + \\ H-C\overset{\cdot\cdot}{-}OCH(CD_3)_2 \end{array}\right]^* \longrightarrow \begin{array}{c} OH \\ \| + \\ H-C\overset{\cdot\cdot}{-}OC_3HD_6 + C_3H_6 \quad (9b) \end{array}$$

product ion of 9b corresponds to expulsion of C_3H_6, even when $(HCO_2C_3H_7C_3HD_6)^+$ is continuously irradiated with a second rf field, suggests that: (1) no hydrogen and deuterium scrambling takes place in the $(HCO_2C_3H_7CHD_6)^+$ ion, and alkyl groups apparently retain their identity; and (2) complete vibrational equilibration is not achieved under our conditions so as to make the two alkyl groups equivalent. It is important to emphasize that in a vibrationally stabilized species, either an acetal type ion or an oxonium ion would yield equivalent alkyl groups.

The formation of product ions like those of reactions 4, 6, and 7 and the decomposition *via* reactions 8 and 9b are completely analogous to species formed in methane chemical ionization of esters, where the attack is done by a carbonium ion.[20] Transesterification was observed by Munson and Field as a result of a decomposition process like (9b) with olefinic elimination of the alkyl group originally bound to the ester.
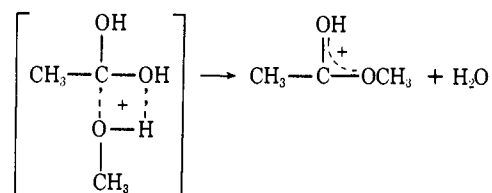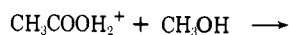
Discussion

Ion–molecule esterification reactions in acetic acid and propionic acid with methanol and ethanol are seen to occur in the gas phase when the reaction is exothermic and the proton affinity of the acid is higher than that of the alcohol. This pattern parallels the simple considerations set forth for nucleophilic displacement reactions in the gas phase involving protonated substrates.[24–26] Although the latter observations were based on reactions taking place at coordinately saturated carbon centers, the rules are apparently identical in the present case where nucleophilic attack by the alcohol on the protonated acid is followed by elimination of water. The initial position of the labile proton (on the acid or on the alcohol) probably does not affect the mechanism, as rapid proton transfer very likely occurs in the collision complex. That the rules advanced by Beauchamp and coworkers[24–26] are applicable for our reactions involving an attack at a carbo-

$$CH_3COOH_2^+ + CH_3OH \longrightarrow$$

$$\left[\begin{array}{c} OH \\ | \\ CH_3-C-OH \\ | + | \\ O-H \\ | \\ CH_3 \end{array}\right] \longrightarrow \begin{array}{c} OH \\ \| + \\ CH_3-C\overset{\cdot\cdot}{-}OCH_3 \end{array} + H_2O$$

nium ion center is exemplified by the failure to observe esterification in formic acid with methanol and ethanol. In these cases, the nucleophile, *i.e.*, the alcohol, has a higher proton affinity than the acid, although the overall reaction is exothermic. Reactions like (1) apparently follow a similar mechanism to esterification in acidic solution by primary alcohols.[2] However, the actual site of cleavage in the gas phase cannot be established with certainty on the basis of the present data.

The dramatic change in the behavior of formic acid with protonated 2-propanol, 2-butanol, *tert*-butyl alcohol, and to a lesser extent 1-propanol suggests a significant change in the mechanism of the reaction which presumably should also account for the reaction of some esters with these same alcohols. A nucleophilic attack by the 2-propanol species (protonated or neutral) could almost be ruled out on the basis that such a process is not observed for the lower alcohols, even though this alcohol should be a better nucleophile. Thus, the actual structure of the alcohol would seem to be an important consideration in this mechanism.

The fact that products like those observed in reactions 4, 6, and 7 have been identified in chemical ionization studies[20] as a result of carbonium ion attack $(C_2H_5^+$ and $C_3H_5^+)$ has an interesting implication for the present cases. If such products are in fact characteristic of carbonium ion attack, reaction 4 could be interpreted as undergoing a pathway like the one indicated in (10).

$$HCOOCD_3 + (CH_3)_2CHOH_2^+ \longrightarrow$$

$$\left[\begin{array}{c} OCD_3 \\ | \\ H-C=O\cdots CH(CH_3)_2 \\ | + | \\ H-O-H \end{array}\right] \longrightarrow \text{product ion} + H_2O \quad (10)$$

Although such an intermediate is admittedly speculative in nature, the ease with which protonated secondary and tertiary alcohols eliminate H_2O to yield a carbonium ion as opposed to primary alcohols[10,12,27] suggests that such a process may be important as a driving force in the reaction. The fact that 2-butanol and *tert*-butyl alcohol (protonated or neutral) also react with esters and with formic acid is consistent with these ideas.

Other important aspects of the reactions of the higher alcohols with esters and formic acid are the relative proton affinities (PA) of the reacting species.[28] Unlike the reactions of acetic acid and propionic acid with methanol and ethanol, reactions 4, 6, and 7 occur when the proton affinity of the alcohol is higher than that of the ester. This is clearly illustrated by the fact that reaction 5 is not observed in our experiments (PA of $CH_3COOCH_3 >$ PA of $(CH_3)_2CHOH)$. Thus, there are two essential components for these reactions: the

(24) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

(25) D. Holtz and J. L. Beauchamp, *Nature (London), Phys. Sci.*, **231**, 204 (1971).
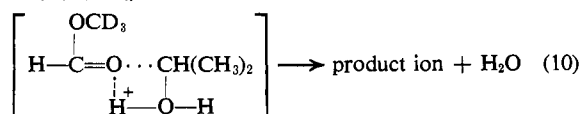
(26) M. S. Foster and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 2425 (1972).

(27) The formation of carbonium ions from protonated methanol or ethanol is not observed at all in an ICR spectrometer.

(28) The reaction of acetic acid with 2-propanol and the different butanols may also fall in this category. However, as reactions are already observed with methanol and ethanol, it is difficult to establish convincingly a change in mechanism from our data.

nature of the alcohol and the relative proton affinities. A further example of these requirements is illustrated by the failure to observe reaction 11, although ethanol has a higher proton affinity than ethyl chloroformate.

$$ClCOOC_2H_5 + C_2H_5OH_2^+ \not\rightarrow ClC(OC_2H_5)_2^+ + H_2O \qquad (11)$$
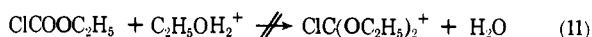
In short, this mechanism can be visualized under the rules established for nucleophilic displacement if attack by an oxygen of the ester is assumed to take place on the hydroxylic carbon of the alcohol.

No definite conclusions can be reached on the structure of the ions $(HCO_2RC_3H_7)^+$, as either an oxonium type structure I or an acetal (II) has been postulated as possible.[20] Qualitative considerations in terms of
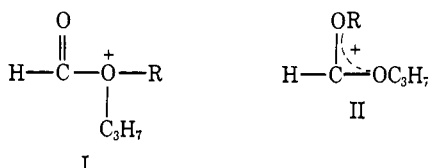
delocalization would perhaps favor structure II, a species which is usually identified in the mass spectra of orthoformates.[29] Thermochemical values obtained from appearance potentials for the simplest ion of this type, namely $HC(OCH_3)_2^+$,[30] can be used to establish that the exothermicity of reaction 4 is below 10 kcal/mol. The species I or II can be regarded as the intermediate for gas phase transesterification as demonstrated by Munson and Field[20] under conditions where

vibrational equilibration has been established for the alkyl groups. It is interesting to note that transesterification for reaction 4 would be unlikely, as decomposition of even the completely equilibrated system would result in the expulsion of CD_2 as the neutral fragment.

A meaningful comparison between reactions 4, 6, and 7 and solution studies cannot be established because of the uncertainties in our proposed mechanism. However, it is well known that esterification and hydrolysis involving tertiary alkyl groups in solution proceed *via* carbonium ion intermediates.[2]

Other systems can be studied which are directly related to this particular chapter of organic chemistry, and which can be explained by a variety of mechanisms. Thus, protonated methanol reacts with CH_3COCl to yield protonated methyl acetate in the gas phase, and protonated methylamine reacts with acetic acid to yield a protonated amide.[31]

The relationship between gas phase ion chemistry and solution processes is once again heavily stressed in our present results because of the importance in establishing a correct correlation between structure and intrinsic reactivity for even the most common reactions in chemistry.

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Stable Carbocations. CXLV.[1] The 2,3-Dimethyl-2-norbornyl Cation and Its Rearrangement to the 1,2-Dimethyl-2-norbornyl Cation

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Abstract: Under stable ion conditions the 2-methyl-*exo*-3-methyl-2-norbornyl cation (1) was obtained from several dimethyl-substituted norbornyl precursors at low temperature. Ion 1 is characterized as a rapidly equilibrating carbenium ion by ^1H and ^{13}C nmr spectroscopy. When 1 was allowed to warm to $-60°$, it slowly rearranged into the more stable 1,2-dimethyl-2-norbornyl cation 2. The structure of ion 1 and its rearrangement reaction are discussed.

Addition of hydrogen halides,[2] acetic acid,[3] trifluoroacetic acid,[4] and mercuric acetate[5] to *gem*-dimethylnorbornenyl derivatives under electrophilic conditions has been reported to give exclusively the exo products *via* nonclassical ions.[2-7] Substantial an-

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