Acid catalysis in the gas phase: dissociative proton transfer to formate and acetate esters

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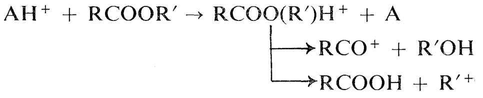
Received March 16, 1979

A. C. Hopkinson, G. I. Mackay, and D. K. Bohme. Can. J. Chem. 57, 2996 (1979).

The flowing afterglow and selected ion flow tube techniques are employed in gas-phase measurements of the intrinsic kinetics of protonation of methyl formate, *n*-propyl formate, ethyl acetate, and *n*-propyl acetate and subsequent fragmentation according to



$$\begin{array}{l}\mathrm{AH^+ + RCOOR' \rightarrow RCOO(R')H^+ + A}\\ \qquad\qquad\qquad\qquad\mathrm{\rightarrow RCO^+ + R'OH}\\ \qquad\qquad\qquad\qquad\mathrm{\rightarrow RCOOH + R'^+}\end{array}$$

with R = H and CH_3, R′ = CH_3, C_2H_5, and $(CH_2)_2CH_3$, and A = H_2, CH_4, CO, and H_2O. Protonation by the acids, AH^+, with relative strengths spanning a range of 65 kcal mol^{-1}, is observed to proceed extremely rapidly with rate constants at 299 ± 2 K encompassing values of 2.9 to 8.5×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. Fragmentation is observed for $HCOOCH_3$ only with the strongest acid, H_3^+, to produce $CH_3OH_2^+$. For $HCOO(CH_2)_2CH_3$, fragmentation is observed to produce $C_3H_7^+$ with H_3O^+, and also $HCOOH_2^+$ with H_3^+. Little fragmentation of $CH_3COOC_2H_5$ occurs with H_3O^+ but with H_3^+ the major product is $CH_3COOH_2^+$ with smaller amounts of CH_3CO^+ and $C_2H_5^+$. Proton transfer from H_3O^+ to $CH_3COO(CH_2)_2CH_3$ results in considerable dissociation to form $CH_3COOH_2^+$. The fragmentation of these esters is discussed in terms of known reaction energetics and in terms of mechanisms for unimolecular acyl–oxygen, $A_{Ac}1$, and alkyl–oxygen, $A_{Al}1$, fission often invoked for analogous reactions in solution as well as modifications of these mechanisms which have been proposed in the context of recent gas-phase measurements.

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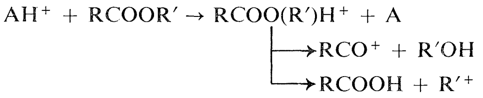
On a utilisé les techniques de la lueur d'écoulement et du tube à écoulement d'ions pour mesurer en phase gazeuse, la cinétique intrinsèque de la protonation des formates de méthyle et de *n*-propyle des acétates d'éthyle et de *n*-propyle suivi d'une fragmentation se produisant d'après le schéma suivant:



$$\begin{array}{l}\mathrm{AH^+ + RCOOR' \rightarrow RCOO(R')H^+ + A}\\ \qquad\qquad\qquad\qquad\mathrm{\rightarrow RCO^+ + R'OH}\\ \qquad\qquad\qquad\qquad\mathrm{\rightarrow RCOOH + R'^+}\end{array}$$

dans lequel R = H et CH_3, R′ = CH_3, C_2H_5 et $(CH_2)_2CH_3$, et A = H_2, CH_4, CO et H_2O. On a observé que la protonation par les acides AH^+ ayant une force relative s'étendant sur une échelle de 65 kcal mol^{-1} est extrêmement rapide avec une constante de vitesse à 299 ± 2 K qui englobe des valeurs allant de 2.9 à 8.5×10^{-9} cm^3 $molécule^{-1}$ s^{-1}. On observe la fragmentation du CH_3COOH qu'en présence de l'acide le plus fort, H_3^+, et il se produit des $CH_3OH_2^+$. La fragmentation $CH_3(CH_2)_2COOH$ produit du $C_3H_7^+$ lors de la protonation par H_3O^+ et également du $HCOOH_2$ lors de la protonation par H_3^+. Il ne se produit que peu de fragmentation du $CH_3COOC_2H_5$ si on utilise H_3O^+ toutefois avec H_3^+ le produit principal est $CH_3COOH_2^+$ avec des quantités plus faibles de CH_3CO^+ et de $C_2H_5^+$. Le transfert de proton de H_3O^+ à $CH_3(CH_2)_2COOH$ conduit à une dissociation considérable provoquant la formation de $CH_3COOH_2^+$. On discute de la fragmentation de ces esters en termes des énergies connues des réactions et en termes des mécanismes unimoléculaires de fission oxygène–acyle, $A_{Ac}1$, et oxygène–alkyle $A_{Al}1$ auxquels on fait souvent appel pour les réactions analogues en solutions ainsi qu'à des modifications de mécanismes qui ont été proposés dans le contexte de mesures récentes en phase gazeuse.

[Traduit par le journal]

Introduction

We have recently initiated an experimental program designed to explore, in a systematic manner, the kinetics of the gas-phase fragmentation of protonated molecules, BH^+, which have been activated by proton-transfer reactions of the type

$$[1] \quad AH^+ + B \rightarrow [BH^+]^* + A$$

The flowing afterglow technique employed in these investigations allows the deliberate alteration of the identity of AH^+ and thus the overall exothermicity of this process (1). The ensuing fragmentation

$$[1a] \quad [BH^+]^* \rightarrow \text{products}$$

may thus be followed as a function of the degree of chemical activation of BH^+, at least to the extent to

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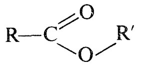
which changes in overall exothermicity alter the excess energy deposited in this ion.[1] In an earlier study (3*a*) we reported the intrinsic kinetics of the protonation of formic and acetic acid and the ensuing formation of acylium ions according to dissociative proton transfer of the type

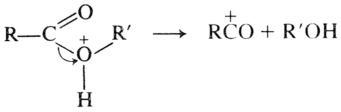
[2] $AH^+ + RCOOH \rightarrow [RCOOH_2{}^+]^* + A$

[2*a*] $\hookrightarrow RCO^+ + H_2O$

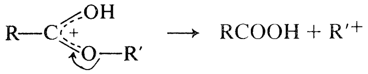
with $R = H$, CH_3, and acids AH^+ whose relative strengths spanned a range of 65 kcal mol^{-1}. These carboxylic acids are members of a larger group of molecules of the type

[3] 

which, when protonated, may undergo heterolysis in one of two ways commonly invoked to explain their cleavage in concentrated acid solutions (4–6): unimolecular acyl–oxygen fission, $A_{Ac}1$, according to

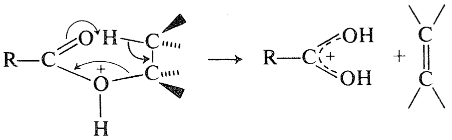
[4] 

or unimolecular alkyl–oxygen fission, $A_{Al}1$, according to

[5] 

The preferred route of cleavage in solution appears to be sensitive to the nature of R′. In concentrated acid solution the esters of secondary and tertiary alcohols hydrolyse by the $A_{Al}1$ mechanism producing a carboxylic acid and a secondary or tertiary carbonium ion. Esters of primary alcohols would produce the much less stable primary carbonium ions by this mechanism, and consequently cleave by the $A_{Ac}1$ mechanism, except when the carbonium ion is stabilized by an adjacent electron-donating group (e.g. phenyl or methoxy).

The products of both A1 mechanisms have been observed in the gas phase (7, 8). The $A_{Al}1$ mechanism, although the less common in solution reactions, appears to predominate in the gas phase. Two possible explanations of this change in behaviour are (*i*) the $A_{Ac}1$ mechanism requires the energetically less accessible ether-protonated ester as an intermediate (9, 10) and thus, in the absence of solvent, is difficult to obtain or (*ii*) that in the gas phase the internally assisted $A_{Al}1$ mechanism,

[6] 

employing a six membered cyclic transition state (reaction [6]) established experimentally (7) by use of deuterium on the β-carbon of the ether group, does not require formation of the unstable primary carbonium ion.

The previous gas phase studies (7, 8) have employed protonated hydrocarbons as the acid ($CH_5{}^+$, $C_2H_5{}^+$, t-$C_4H_9{}^+$) to initiate the dissociative proton transfer of esters. Here we have used the acids $AH^+ = H_3{}^+, CH_5{}^+, HCO^+$, and H_3O^+ which have exothermicities varying over a much wider range (65 kcal mol^{-1}) and we have studied, under the more controlled conditions of the flowing afterglow apparatus, the dissociation mechanisms ([7*a*] and [7*b*])

[7] $AH^+ + RCOOR' \rightarrow [RCOOR'H^+]^* + A$

[7*a*] $\hookrightarrow RCOOH + R'^+$

[7*b*] $\hookrightarrow R\overset{+}{C}O + R'OH$

of some formate and acetate esters as a function of the excess energy provided in the proton transfer reaction.

Experimental

The majority of the measurements were carried out in a hydrogen buffer using a conventional flowing plasma mass-spectrometer (flowing afterglow) system which has been described previously (1). A few of the measurements were carried out in a helium buffer with the apparatus in the Selected Ion Flow Tube (SIFT) configuration modelled after the original design reported by Adams and Smith (11). In this configuration a differentially pumped quadrupole mass filter was interposed between the ion production and reaction regions. Ions were extracted from the ion production region through a 1 mm diameter orifice into the quadrupole mass filter which communicated with the flow tube through a 5 mm diameter gas entrainment orifice. The ions were injected into the flow tube at ca. 40 eV and allowed to thermalize by collision at 299 ± 2 K before they entered the reaction region 106 cm further downstream. This procedure eliminated ion types other than the reagent ion and the neutral reagent and buffer gas molecules from the reaction region.

The ions were produced in hydrogen carrier gas in the usual manner according to reactions of the type

[8] $H_3{}^+ + X \rightarrow XH^+ + H_2$

with $k = (2.4 \pm 0.5), (2.0 \pm 0.4)$, and $(4.3 \pm 1.1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for $X = CH_4$, CO, and H_2O, respectively (unpublished results from this laboratory, refs. 13, 14). We have shown elsewhere that the protonation of CO accomplished in this manner establishes the HCO^+ and not the COH^+ isomer (13).

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[1] For a flowing afterglow study of the fragmentation of $CH_3NO_2H^+$, see ref. 2.

TABLE 1. Rate constants for proton transfer to methyl- and *n*-propyl formate and ethyl and *n*-propyl acetate at 299 ± 2 K

Reaction	k^a	k_{ADO}^b	ΔH_{298}^{0c}
$H_3O^+ + HCOOCH_3 \to HCOO(CH_3)H^+ + H_2O$	3.3±0.8 (3)	2.27	−22±5
$HCO^+ + HCOOCH_3 \to HCOO(CH_3)H^+ + CO$	2.9±0.7 (8)	1.95	−45±3
$CH_5^+ + HCOOCH_3 \to HCOO(CH_3)H^+ + CH_4$	4.1±1.0 (2)	2.37	−57±3
$H_3^+ + HCOOCH_3 \to HCOO(CH_3)H^+ + H_2$	7.3±2.2 (3)	5.11	−87±3
$\hookrightarrow CH_3OH_2^+ + CO$			+15±5
$H_3O^+ + HCOO(CH_2)_2CH_3 \to HCOO((CH_2)_2CH_3)H^+ + H_2O$	4.6±1.4 (2)	2.48	−26±5
$\hookrightarrow i\text{-}C_3H_7^+ + HCOOH$			+20±5
$H_3^+ + HCOO(CH_2)_2CH_3 \to HCOO((CH_2)_2CH_3)H^+ + H_2$	8.5±2.6 (2)	5.77	−91±3
$\to i\text{-}C_3H_7^+ + HCOOH$			+20±5
$\hookrightarrow HCOOH_2^+ + C_3H_6$			+22±6
$H_3O^+ + CH_3COOC_2H_5 \to CH_3COO(C_2H_5)H^+ + H_2O$	2.8±0.7 (3)	2.62	−29±4
$\hookrightarrow CH_3COOH_2^+ + C_2H_4$			+23±4
$H_3^+ + CH_3COOC_2H_5 \to CH_3COO(C_2H_5)H^+ + H_2$	5.7±1.4 (4)	6.09	−94±3
$\to CH_3COOH_2^+ + C_2H_4$			+23±4
$\to CH_3CO^+ + C_2H_5OH$			+44±2
$\hookrightarrow C_2H_5^+ + CH_3COOH$			+52±5
$H_3O^+ + CH_3COO(CH_2)_2CH_3 \to CH_3COO((CH_2)_2CH_3)H^+ + H_2O$	3.8±1.0 (3)	2.85	−32±4
$\hookrightarrow CH_3COOH_2^+ + C_3H_6$			+25±4

[a] The measured reaction rate constant, k, is given in units of 10^{-9} cm^3 molecule^{-1} s^{-1} along with its estimated accuracy and the number of measurements which is given in parentheses.

[b] The collision rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1} calculated using the average-dipole-orientation theory (the $\overline{\cos\theta}$ model) (ref. 16). Permanent dipole moments were taken from ref. 12*a*. Mean polarizabilities of 5.90 Å^3 for $HCOOCH_3$, 8.50 Å^3 for $HCOO(CH_2)_2CH_3$ and $CH_3COOC_2H_5$, and 11.7 Å^3 for $CH_3COO(CH_2)_2CH_3$ were calculated from bond and group polarizabilities taken from ref. 12*b*.

[c] Standard enthalpy change in kcal mol^{-1}, PA(H_2, CH_4, CO, H_2O) = 101 ± 1, 131.5 ± 2.2, 143 ± 1, and 166.4 ± 2.4 kcal mol^{-1}, respectively (ref. 13). PA($HCOOCH_3$, $HCOO(CH_2)_2CH_3$, $CH_3COOC_2H_5$, $CH_3COO(CH_2)_2CH_3$) = 187.8 ± 2, 191.6 ± 2, 195.4 ± 2, and 198 ± 2 kcal mol^{-1} taken from ref. 18*a*. Auxiliary thermodynamic data were taken from ref. 18*b*.

The formates were added into the reaction region as vapors diluted to ca. 10% in helium. The determination of their flows required separate viscosity measurements (15). Reagent and product ions were monitored as a function of addition of the vapor in the range from 5×10^{-5} to 5×10^{-3} mTorr, at total gas pressures, P, between 0.196 and 0.50 Torr, average gas velocities, $\bar{v}$, in the range 7.6 to 8.6×10^3 cm s^{-1}, effective reaction lengths, L, of 48, 59, and 85 cm, and a gas temperature, T, of 299 ± 2 K. Rate constants were determined in the usual manner (1). Branching ratios were obtained by computer fitting and inspection of observed variation in the reactant and product ion signals. This analysis (15) required a knowledge of the mass discrimination, m, between the various ion signals. When a reaction resulted in more than one product ion, m had to be inferred from complementary studies performed under similar experimental conditions. The majority of the uncertainty in the branching ratios (±20%) arose from the error associated with this method of determining the mass discrimination.

The gases used were hydrogen (Linde, Very Dry Grade, 99.95% H_2), methane (Matheson, Ultra High Purity, 99.9% CH_4), helium (Linde, Prepurified Grade, 99.995% He), and carbon monoxide (Matheson, C.P. Grade, 99.5% CO). The vapors were derived from methyl formate and methyl acetate (both from BDH Chemicals), and *n*-propyl formate and *n*-propyl acetate (both from Chem. Service Media). The purities of the esters were checked by conventional gas chromatograph – mass spectrometer assays and, when necessary, redistilled before use.

Results and Discussion

Kinetics of Proton Transfer and Product Distributions

The rate constants measured in this study are listed in Table 1. All of these reactions were observed to be rapid with the rate constant, k, spanning a range in values from 2.8 to 8.5×10^{-9} cm^3 molecule^{-1} s^{-1}. As has been our previous experience with other similar systems, these values are systematically higher by ~50% than the values of the collision rate constants derived from the average-dipole-orientation theory (16) (these are included in Table 1). The implications of such deviations have been discussed elsewhere (16, 17).

For the reactions of H_3O^+, HCO^+, and CH_5^+ with methyl formate only one product ion (m/e = 61) was observed. This ion was identified as protonated methyl formate. There was no measurable evidence for subsequent dissociation. In contrast, the reaction of H_3^+ with methyl formate was observed to produce predominantly (>90%) $CH_3OH_2^+$ which reacted further by proton transfer to establish $HCOO(CH_3)H^+$ according to the reaction

$$[9] \quad CH_3OH_2^+ + HCOOCH_3 \rightarrow HCOO(CH_3)H^+ + CH_3OH$$

Figures 1 and 2 provide an indication of the results obtained with *n*-propyl formate. H_3O^+ reacted to produce considerable (~50%) amounts of $C_3H_7^+$ and a small amount (~5%) of $HCOOH_2^+$. Both product ions reacted further with *n*-propyl formate by proton transfer to produce $HCOO((CH_2)_2CH_3)H^+$ in addition to that amount which is produced directly by protonation with H_3O^+. Figure 2 shows that both dissociative channels increased in importance with H_3^+ as the reactant ion, the $C_3H_7^+$ and $HCOOH_2^+$ ions being produced approximately in the ratio of 9:1. The $HCOO((CH_2)_2CH_3)H^+$ appeared to be produced in this case entirely by secondary proton transfer reactions with the weaker second-generation acids $C_3H_7^+$ and $HCOOH_2^+$. The subsequent reaction of $HCOO((CH_2)_2CH_3)H^+$ is presumably due to 3-body association with *n*-propyl acetate. The product ion of this association reaction was outside the detection range of the mass spectrometer used in this study.

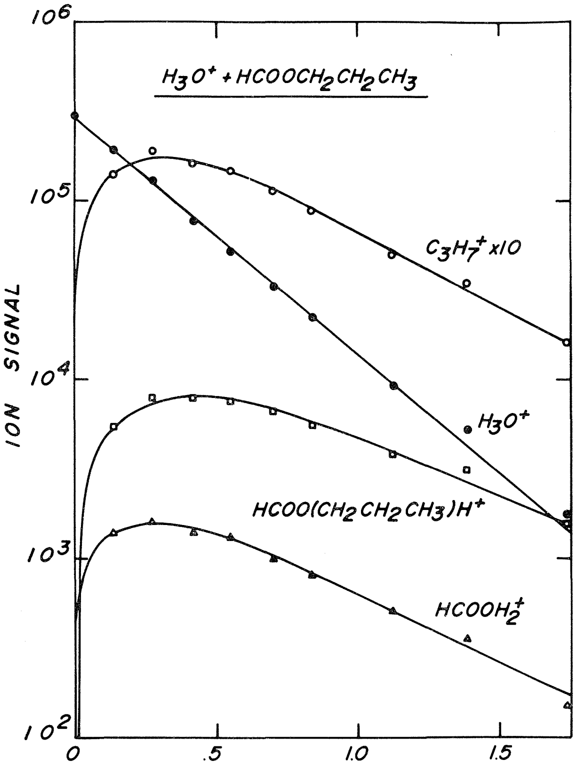


FIG. 1. The variation in major positive ions observed upon the addition of *n*-propyl formate vapour into a flowing H_2O–H_2 plasma in which H_3O^+ is initially the dominant ion. The decay of H_3O^+ provides a rate constant of 4.2×10^{-9} cm^3 molecule^{-1} s^{-1}. $T = 297$ K, $P = 0.363$ Torr, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}, and $L = 45.9$ cm.

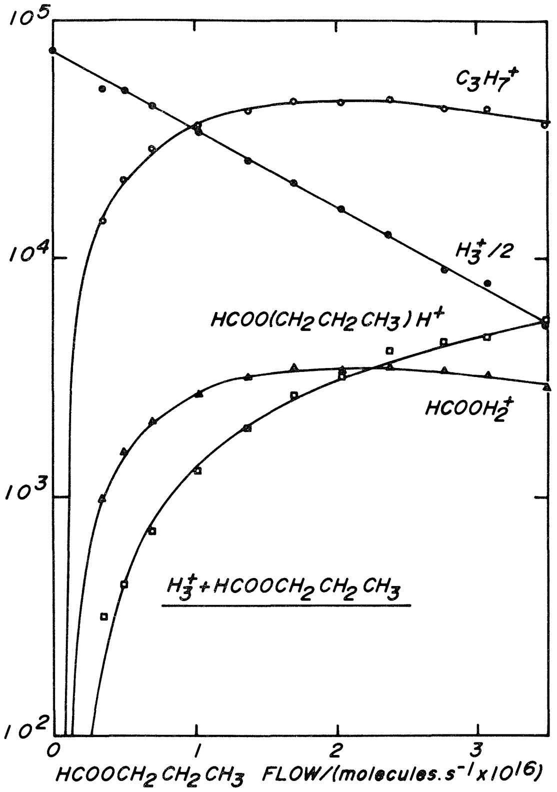


FIG. 2. The variation in major positive ions observed upon the addition of *n*-propyl formate vapour into a flowing H_2 plasma in which H_3^+ is initially the dominant ion. The decay of H_3^+ provides a rate constant of 8.5×10^{-9} cm^3 molecule^{-1} s^{-1}. $T = 299$ K, $P = 0.296$ Torr, $\bar{v} = 8.5 \times 10^3$ cm s^{-1}, and $L = 58.9$ cm.

H_3O^+ was observed to react with ethyl acetate to produce primarily (>90%) an ion ($m/e = 89$) corresponding to protonated ethyl acetate. A concomitant but much smaller (<10%) increase was observed in the signal of an ion at $m/e = 61$, presumably $CH_3COOH_2^+$, which was suggestive of a small dissociative proton transfer channel. In contrast, the results shown in Fig. 3 indicate that dissociative proton transfer predominates in the reaction of H_3^+ with ethyl acetate. $CH_3COOH_2^+$ has become the dominant product (~75%) and two additional products at $m/e = 29$ and 43, identified as $C_2H_5^+$ (~5%) and CH_3CO^+ (~20%), were observed. The shape of the $CH_3COO(C_2H_5)H^+$ signal variation is

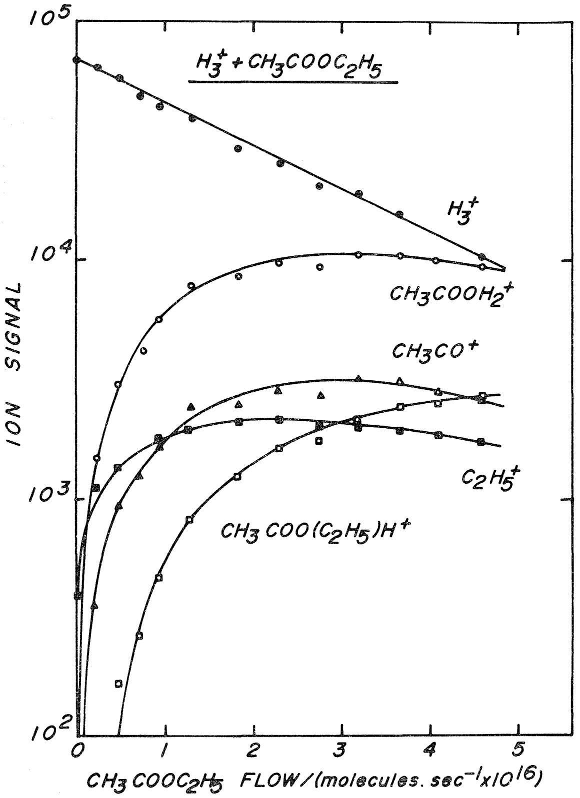


FIG. 3. The variation in the major positive ions observed upon the addition of ethyl acetate vapour into a flowing H_2 plasma in which H_3^+ is initially the dominant ion. The decay of H_3^+ provides a rate constant of 5.0×10^{-9} cm^3 molecule^{-1} s^{-1}. $T = 296$ K, $P = 0.508$ Torr, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $L = 46.9$ cm.

indicative of a secondary product arising entirely from proton transfer reactions with the second-generation acids $CH_3COOH_2^+$, $C_2H_5^+$, and CH_3CO^+.

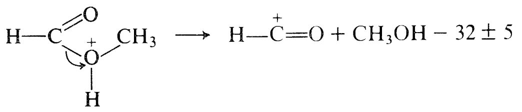
Finally, H_3O^+ was observed to react with n-propyl acetate to form ions corresponding to $CH_3COOH_2^+$ and $CH_3COO((CH_2)_2CH_3)H^+$ in approximately equal amounts. Both ions reacted further, presumably by proton transfer and 3-body association, respectively.

Energetics and Mechanism of Dissociative Proton Transfer

Available thermochemical information enabled us to calculate the relative energies of most of the possible dissociation products of the two protonated formate esters and some of these are shown in Fig. 4. Many combinations of ions and molecules fall within the reaction exothermicities available from the protonation of the esters, particularly by H_3^+, but, in order to simplify the diagram, only products not requiring extensive skeletal rearrangements have been included. For example, the dissociation of $HCOO(CH_3)H^+$ into $CH_3CO^+ + H_2O$, which is only 7 ± 3 kcal mol^{-1} endothermic, has been excluded from Fig. 4.

Methyl Formate

The known energetics indicate that if the majority of the reaction exothermicity from the initial protonation reaction is deposited in $HCOO(CH_3)H^+$ then, in the absence of any barrier to reaction, dissociation of this ion into $CH_3OH_2^+$ and CO should be energetically favorable regardless of which acid (H_3^+, CH_5^+, HCO^+, or H_3O^+) performed the initial protonation.[2] Other plausible reaction products would become accessible with the acids CH_5^+, viz. $HCO^+ + CH_3OH$, and H_3^+, viz. $HCO^+ + CH_3OH$ and $CH_3^+ + HCOOH$. Experimentally, however, only H_3^+ produced measurable dissociation and even with this acid only the most stable products, $CH_3OH_2^+ + CO$, were formed. The absence of $HCO^+ + CH_3OH$ in the dissociation by CH_5^+ and particularly H_3^+ is somewhat surprising, as these species are expected to be formed initially by the $A_{Ac}1$ fission of the C—O bond of the methoxy-protonated tautomer.

[10]


Also, the work of Pesheck and Buttrill (7) has established that protonated methyl acetate dissociates by the $A_{Ac}1$ mechanism to form the acetyl ion and methanol. Furthermore, previous observations made in this laboratory under similar operating conditions indicated that in the dissociative proton transfer reaction of H_3^+ with HCOOH both $HCO^+ + H_2O$, and $H_3O^+ + CO$ were produced with the former, the *less* stable, predominating by a factor of approximately two (3*a*). In this case the production of $H_3O^+ + CO$ from $HCOOH_2^+$ which is analogous to the production of $CH_3OH_2^+ + CO$ from $HCOO(CH_3)H^+$, was viewed to proceed by $A_{Ac}1$ cleavage accompanied by synchronous or near-synchronous transfer of a proton from the carbon atom to the developing water molecule (3*a*).[3] The

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[2] At the pressures employed in these measurements collisional stabilization of the excited product ions formed by the initial protonation reaction may be important. The influence of the H_2 or He bath pressure on the observed product spectrum was not investigated systematically in this study.

[3] Sequential proton (deuteron) transfer within a reaction intermediate also has been invoked recently to account for gas-phase observations of hydrogen–deuterium exchange reactions involving hydrogen-containing anions and weak acids such as H_2O (3*b*, 3*c*).

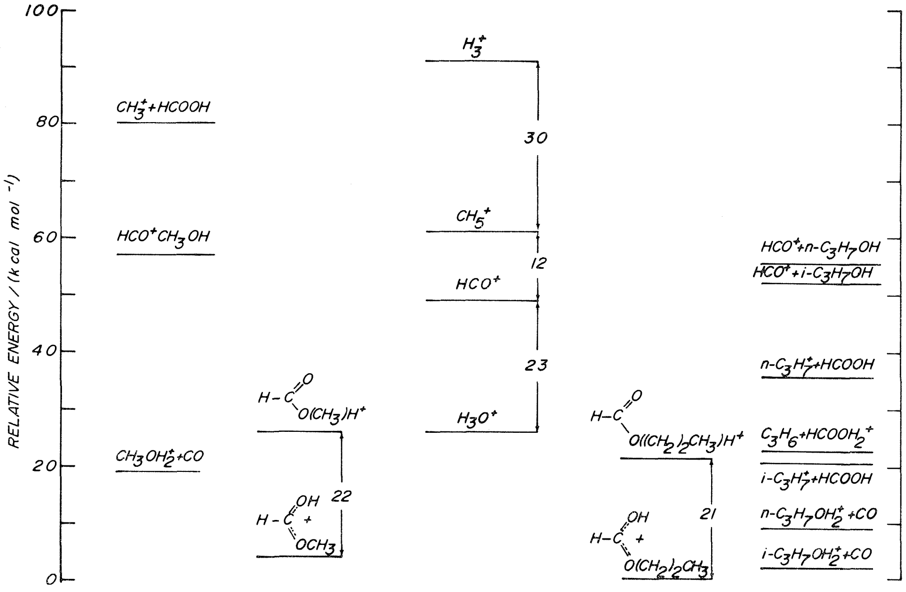
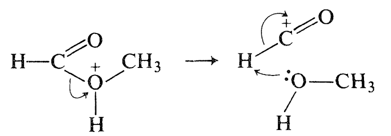


FIG. 4. Relative energies of the acids H_3^+, CH_5^+, HCO^+, and H_3O^+, the two-tautomers of protonated methyl- and *n*-propyl formate, and possible dissociation products of the protonated formates.

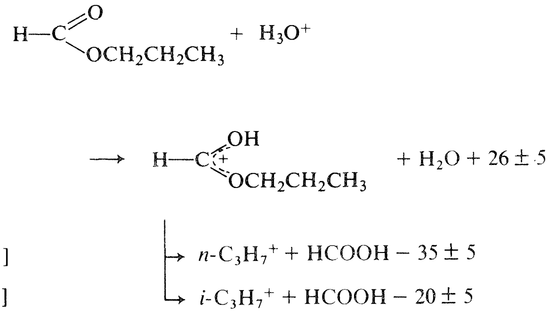
analogous route in the decomposition of HCOO(CH_3)H^+ would involve proton transfer to the developing methanol molecule according to

[11] 

The failure to observe production of any HCO^+ in this case, then, would imply that this intramolecular proton transfer is essentially quantitative. Methanol has a much higher proton affinity than carbon monoxide ($\Delta PA = 38 \pm 4$ kcal mol^{-1}) (13) and we have previously observed rapid proton transfer from HCO^+ to CH_3OH initially at infinite separation (13). The difference in proton affinity between water and carbon monoxide which is relevant in the analogous decomposition of $HCOOH_2^+$ is considerably smaller ($\Delta PA = 23 \pm 3$ kcal mol^{-1}) (13) while proton transfer between the products of the $A_{Ac}1$ fission in protonated methyl acetate, viz. $CH_3CO^+ + CH_3OH$, is actually *endothermic* by 13 ± 4 kcal mol^{-1} for ground states at infinite separation. Although the extent of intramolecular transfer which proceeds according to this model is likely to be sensitive to the total excess energy deposited by the initial protonation reaction which is expected to be different in each of the three protonated species, the trend in dissociation with ΔPA which has been identified for these three species appears to be consistent with this intramolecular proton transfer mechanism invoked originally for this dissociation of $HCOOH_2^+$. The same overall result can be viewed to be achieved by a 1,2-hydride shift from the carbon to the positive oxygen atom with concomitant cleavage of the C—O bond. Such shifts are invoked in many acid-catalysed reactions in solution (19).

n-*Propyl Formate*

In contrast with methyl formate, *n*-propyl formate underwent extensive dissociation, even when the weakest acid, H_3O^+, was used as the protonating agent. If the dissociation is to be exothermic in the latter case, the product, $C_3H_7^+$, must be the isopropyl cation and not the expected *n*-propyl cation:

[12] 

$$H\text{—}C(=O)OCH_2CH_2CH_3 + H_3O^+ \longrightarrow H\text{—}C^+(OH)OCH_2CH_2CH_3 + H_2O + 26 \pm 5$$

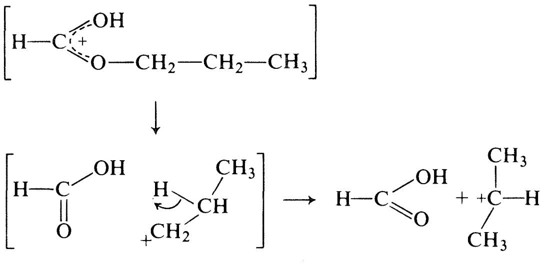
[12*a*] $\rightarrow n\text{-}C_3H_7^+ + HCOOH - 35 \pm 5$

[12*b*] $\rightarrow i\text{-}C_3H_7^+ + HCOOH - 20 \pm 5$

Even with the isopropyl cation as the product, most of the exothermicity of the initial protonation reaction must be incorporated into HCOO((CH_2)$_2$$CH_3$)$H^+$ and the barrier to dissociation must be very low in order to explain the observations.

The $A_{Al}1$ cleavage would result in the *n*-propyl cation and formic acid and if this mechanism is operative it is necessary to postulate that cleavage of the C—O bond is accompanied by a 1,2-hydride shift in the propyl fragment to achieve the more stable isopropyl cation:

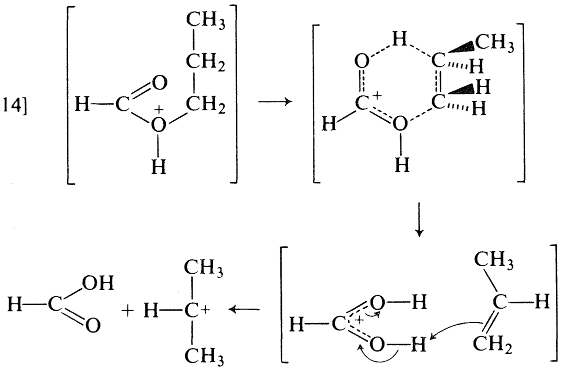
[13]



Ab initio molecular orbital calculations have established that n-$C_3H_7^+$ collapses into i-$C_3H_7^+$ without a barrier (20, 21). Such a mechanism has been invoked by Pesheck and Buttrill (7) to account for what appeared to be an abnormally large production of $C_4H_{10}^+$ from protonated isobutyl acetate. In this case the *s*-butyl group is conceived to rearrange via a 1,2-hydride shift to the more stable *tert*-butyl group.

A modification of this mechanism, again involving fission of the alkyl–oxygen bond but with concomitant migration of a β-hydrogen of the alkyl group to the carbonyl oxygen has been indicated in the dissociation of protonated ethyl acetate (9). The mechanism requires protonation of the energetically less favourable alkoxy oxygen, which is accessible even in protonation by H_3O^+, and proceeds via a 6-membered cyclic transition state:

[14]



According to this scheme the initial products from protonated *n*-propyl formate are protonated formic acid and propene but proton transfer may again be postulated to occur during the fragmentation to form the isopropyl cation. Propene actually has a slightly higher proton affinity than formic acid ($\Delta PA = 2$ kcal mol^{-1}) (3*a*). Our experimental observations of the dissociative proton transfer with H_3^+ indicated the production of appreciable amounts (~10%) of $HCOOH_2^+$ and this may well be attributed to this internally assisted $A_{Al}1$ mechanism initiated by protonation of the alkoxy oxygen. Protonation at this position by H_3O^+ would require the deposition of at least 80% of the reaction exothermicity as internal energy of the ion so that production of $HCOOH_2^+$ and $C_3H_7^+$ via this mechanism is somewhat less plausible in this case. Production of $C_3H_7^+$ at low reaction exothermicities for the initial protonation may well proceed preferentially by the $A_{Al}1$ cleavage initiated by protonation at the carbonyl oxygen and accompanied by a 1,2-hydride shift. Some support for this viewpoint is provided by recent observations which we have made of the generation of $C_3H_7^+$ from *n*-propanol at exothermicities considerably lower than required for formation of $CH_3CH_2CH_2^+$:

[15] $CH_3CH_2CH_2OH + H_3O^+$

$$\rightarrow CH_3CH_2CH_2OH_2^+ + H_2O + 23 \pm 4$$

[15*a*] $\rightarrow n\text{-}C_3H_7^+ + H_2O - 33 \pm 4$

[15*b*] $\rightarrow i\text{-}C_3H_7^+ + H_2O - 17 \pm 4$

In this decomposition internal assistance by a carbonyl group of the type suggested for $HCOO(CH_2)_2CH_3$ is not available so that C—O cleavage accompanied by a synchronous 1,2-hydride shift is definitely the preferred mechanism in this reaction. This suggests in turn that $C_3H_7^+$ may also not be formed via the 6-membered cyclic transition state in its generation from $HCOO(CH_2)_2CH_3$, at least not at low reaction exothermicities.

Ethyl Acetate

Protonated formic acid does not cleave readily by the $A_{Ac}1$ mechanism to form the acylium ion HCO^+ and it seemed probable that this mechanism should be more competitive with esters of larger carboxylic acids. In fact methyl acetate has been found to react with CH_5^+ mainly by proton transfer but with formation of about 20% CH_3CO^+ and no $CH_3COOH_2^+$ (7), indicating that the cleavage of this ester occurs only by the $A_{Ac}1$ mechanism. Ethyl acetate might therefore be expected to form both the acetyl ion, CH_3CO^+, via the $A_{Ac}1$ mechanism and also $CH_3COOH_2^+$ by the internally assisted $A_{Al}1$ mechanism. Experimentally we found that H_3O^+ simply transferred a proton to ethyl acetate and the product of the $A_{Al}1$ mechanism, although slightly exothermic assuming all the reaction exothermicity to be in the protonated ester, occurred only to a small amount (<10%). In the reaction with H_3^+ (Fig. 3), there is sufficient energy to produce dissociation into $CH_3COOH_2^+$ and $C_2H_5^+$, the products of the internally assisted and unassisted $A_{Al}1$ mechanisms, and also the acetyl ion, the product of the $A_{Ac}1$ mechanism. All three products were observed experimentally, with the relative concentrations in the same order as expected from the exothermicities. The CH_3CO^+ could possibly be generated by secondary dissociation of $CH_3COOH_2^+$ as a result of the excess energy in this ion. However, this interpretation is not substantiated by the results of the reaction of CH_5^+ with ethyl acetate (7) where the ratio of $CH_3COOH_2^+$ to CH_3CO^+ ($\sim 3.5:1$) is approximately the same as with the much stronger acid H_3^+. If the $CH_3COOH_2^+$ were the major primary source of CH_3CO^+ then the amount of dissociation might be expected to be much larger in the reaction initiated by the highly exothermic proton transfer from H_3^+ than in the dissociation initiated by the much weaker acid CH_5^+.

In summary, then, it appears that the dissociation of ethyl acetate, when protonation is accompanied by large exothermicities, can be induced to dissociate by both $A_{Al}1$ and $A_{Ac}1$ mechanisms with the relative frequencies being approximately 4:1.

n-*Propyl Acetate*

Dissociation of *n*-propyl acetate was induced by even the weakest acid, H_3O^+. However, $CH_3COOH_2^+$ was the only dissociation product, in contrast with dissociation of *n*-propyl formate, where $C_3H_7^+$ was the only major product.

$$[16] \quad H_3O^+ + CH_3COO(CH_2)_2CH_3 \rightarrow CH_3COO((CH_2)_2CH_3)H^+ + H_2O + 32 \pm 4$$

$$[16a] \quad \longrightarrow CH_3COOH_2^+ + C_3H_6 - 25 \pm 4$$

$$[16b] \quad \longrightarrow i\text{-}C_3H_7^+ + CH_3COOH - 32 \pm 4$$

$$[16c] \quad \longrightarrow n\text{-}C_3H_7^+ + CH_3COOH - 48 \pm 4$$

$$[16d] \quad \longrightarrow CH_3CO^+ + n\text{-}C_3H_6OH - 44 \pm 5$$

Acetic acid has a larger proton affinity than propene ($\Delta PA = 7\ \mathrm{kcal\ mol^{-1}}$) and formation of $CH_3COOH_2^+$ is the only dissociative channel requiring less energy than the maximum available from the initial proton transfer between *n*-propyl acetate and H_3O^+. The observed product suggests that only the $A_{Al}1$ mechanism is operative.

The stronger acid, CH_5^+, also yields predominantly the protonated carboxylic acid with *n*-propyl acetate and *n*-propyl propionate but small amounts of further decomposition products were observed for each ester ($\sim 10\%$ of $m/e = 43$, CH_3CO^+ and/or $C_3H_7^+$, for *n*-propyl acetate (7), and 8.8% of $C_7H_5CO^+$ and 1.6% of $C_3H_7^+$ for *n*-propyl propionate (8*b*)). It is not possible to deduce whether the $A_{Ac}1$ mechanism is operative for these two esters, but clearly it is at most a minor pathway for both esters.

Conclusions

Our results, combined with the results of icr and mass spectrometer studies on larger esters, permit certain generalisations about the mechanism of cleavage of esters in the gas phase. For methyl esters the $A_{Ac}1$ mechanism is the only one followed and even this requires high energy to achieve cleavage. For esters containing larger alkyl groups as the ether substituent the $A_{Al}1$ mechanism is dominant and even when the reaction exothermicity is increased and the $A_{Ac}1$ mechanism has become operative for the ethyl and *n*-propyl esters examined here, it never becomes the dominant channel. This behaviour is in marked contrast with the reactions in solution where the $A_{Ac}1$ mechanism is the most common. One possible explanation for this change in behaviour is that the $A_{Ac}1$ mechanism requires protonation on the energetically less accessible ether oxygen and this is more easily achieved in solution where the solvent can assist in accommodating some of the positive charge. In the gas phase the charge on the ether protonated ester is formally localised on the ether oxygen but the hydrogen atoms of the ester group carry considerable positive charge and this can be partly delocalised by forming a hydrogen bond between a hydrogen atom on the β-carbon and the carbonyl oxygen. This "internally solvated" structure then provides the 6-membered ring arrangement which is necessary for the internally assisted $A_{Al}1$ mechanism. Alternatively the normal product of $A_{Al}1$ fission, R^+, may be formed directly from the carbonyl protonated ester, or indirectly by the internally assisted mechanism followed by proton transfer, if this channel is energetically the more favourable.

Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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