The Gas Phase Reaction of F^- and OH^- with Alkyl Formates

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Received July 7, 1975

Abstract: The ion-molecule reactions of fluoride and hydroxide ions with alkyl formates have been studied by ion cyclotron resonance spectroscopy. Two reactions are observed to take place: (1) indirect gas phase ion solvation, $ROHF^-$ and $(ROHOH)^-$; and (2) formation of $HCOO^-$. Absolute and relative rate constants have been obtained for esters up to the different butyl groups, as well as for $DCOOC_2H_5$ and $HCOOC_2D_5$. The formation of $HCOO^-$ is shown to be enhanced by the presence of β hydrogens for the fluoride reactions. This fact is interpreted in terms of an intermediate which is capable of assuming a six-membered ring configuration. The suggested neutrals from this mechanism, C_2H_4 and HF, are consistent with neutral analysis. A general discussion is presented for the overall mechanism of these systems.

A large volume of chemical research has been accumulated over the last decades regarding the reactivity of nucleophiles toward esters. The mechanistic details of classical examples like ester hydrolysis are by now well understood and appear profusely illustrated in elementary textbooks. However, and in spite of the impressive amount of data available, the extent to which the intrinsic features of the reagents dictate the outcome of the reaction may still be considered a complex question.

The role of the solvent in a chemical reaction can be eliminated in some instances by recreating the solution process in the gas phase through an ion-molecule reaction. In a recent example relevant to the gas phase ion chemistry of esters, we showed that alcohols attack a protonated acid as a nucleophile when its proton affinity is lower than that of the acid.[1,2] Esters in turn can also act as gas phase nucleophiles toward protonated alcohols when the proton affinity of the latter allows it.

The reaction of negatively charged nucleophiles with esters of formic acid has also been studied in our laboratories by ion cyclotron resonance techniques.[3,4] In this respect, it has been shown that reaction 1 is the most common reactive channel for several negative ions.

$$X^- + HCOOCH_3 \rightarrow CH_3OHX^- + CO \qquad (1)$$
$$X^- = RO^- \ (R = \text{alkyl}),\ C_2H^-,\ F^-,\ OH^-$$

The observation of associated ions has enabled the determination of the solvating ability of neutrals in the gas phase.[3,5,6]

The present paper deals with the details of the reaction of F^- and OH^- with alkyl formates in the gas phase. These two nucleophiles are unique in the sense that they can generate $HCOO^-$ competitively with reaction 1. The mechanistic implications of the reactions of F^- and OH^- are particularly interesting because the product distribution is significantly dependent on the alkyl group of the ester.

The results included in this paper are potentially of theoretical interest because these systems are in principle amenable to quantum mechanical calculations. Thus, reports have already appeared on the minimum energy path of a nucleophile, H^-, approaching a model carbonyl system, H_2CO.[7] Our observations suggest that our reactions exhibit a much more complex potential energy surface than that suspected on the basis of solution results.

Experimental Section

The ICR spectrometer used in this investigation is similar to that described previously.[2] Modifications introduced in the emission current circuitry improved the regulation capabilities of the original Varian version.[6] A two-pulse method developed to work with a conventional ICR cell allowed the measurement of residence times of the ions as a function of electric and magnetic fields.[8]

Hydroxide ions were generated from H_2O by electron impact at 7.6 eV (uncorrected electron energy). Fluoride ions were obtained from SO_2F_2 (Matheson) at a nominal electron energy of 4.2 eV.

The esters of formic acid were prepared in most cases by esterification followed by distillation of the product. Ethyl formate-d_5, $HCOOC_2D_5$, was prepared from 98% C_2D_5OD (Merck). The small percentage of undeuterated species is well below the reproducibility of our rate constants. Ethyl formate-d_1, $DCOOC_2H_5$, was prepared by an adaptation of the method outlined by Stevens and Van Es.[9] The starting material, DCO_2Na, was kindly provided by Dr. Luciano de Amaral from this Institute. The purity of the esters was assessed by low-pressure ICR spectroscopy. Esters were used after these spectra agreed with conventional mass spectra.

Kinetic experiments were carried out in a flat drift cell of three regions. Pressures were read from an ion gauge located above the cell, and with the Vac-Ion throttled to about one quarter of its pumping capacity. The ion gauge was calibrated against an MKS Baratron Model 90 capacitance manometer. Readings and calibration of the ion gauge were obtained at 2000 G. Experiments designed to measure the rate constants of the fluoride ion were carried out at an SO_2F_2 pressure of 1.5 to 2.0×10^{-6} Torr. This was necessary because $ROHF^-$ ions formed by reactions similar to (1) react rapidly with SO_2F_2 to yield $SO_2F_3^-$. At these pressures of SO_2F_2, the amount of $SO_2F_3^-$ was always negligible. Other ionic species obtained from SO_2F_2 (F_2^-, SO_2F^-, and $SO_2F_2^-$) proved to be unreactive toward the esters. In the hydroxide ion experiments, the pressure of water was kept around 5×10^{-5} Torr.

The rate constants were calculated using the procedure recently outlined by Bowers.[10] The reproducibility of these constants is on the order of 10%, but the combined errors in the determination of residence times and absolute pressures make these constants probably no better than 20% accurate.

The relative rate constants shown in Tables I and II ($k_{\mathrm{I}}/k_{\mathrm{II}}$) were initially obtained in a series of experiments in which the pressure was monitored only by the Vac-Ion current. The use of an ion gauge at a later date did not affect the values in any noticeable way. Therefore, the possibility of pyrolysis of the esters on the ion gauge filament to yield HCOOH which would undergo proton transfer with F^-, or OH^-, and result in a different source of $HCOO^-$ was regarded as minimal. This conclusion is reinforced by the fact that no $HCOO^-$ was observed for the systems of ref 3 and 4 in the presence of an ion gauge.

Results

1. Fluoride Ion Reactions. The reaction of F^- with $HCOOCH_3$ proceeds almost exclusively according to (2). Nevertheless, the formation of $HCOO^-$ through reaction 3 is also detected, although the rate constant is considerably slower for this case (Table I).

Table I. Rate Constants for the Reactions (I) $F^- + HCOOR \rightarrow ROHF^- + CO$ (k_I) and (II) $F^- + HCOOR \rightarrow HCOO^- +$ Neutral (k_{II}) (See Text)[a]

	$10^{10}k_I$	$10^{10}k_{II}$	k_I/k_{II}[b]
$HCOOCH_3$	7.2	0.8	9.0
$HCOOC_2H_5$	2.7	2.7	1.0
$HCOOC_2D_5$	2.6	1.7	1.6
$DCOOC_2H_5$	2.9	2.9	1.0
$HCOOCH_2CH_2CH_3$	2.8	1.5	1.8
$HCOOCH(CH_3)_2$	2.5	2.8	0.90

	k_I/k_{II}		k_I/k_{II}
$HCOOCH_2CH_2CH_2CH_3$	1.9	$HCOOCH(CH_3)(C_2H_5)$	2.0
$HCOOCH_2CH(CH_3)_2$	9.5	$HCOOC(CH_3)_3$	0.52

[a] Absolute rate constants are given in $cm^3/(molecule\ s)$. [b] Relative rate constants are reproducible to within 5%.

$$F^- + HCOOCH_3 \rightarrow CH_3OHF^- + CO \qquad \Delta H_2 = -15\ kcal/mol^{4,11} \quad (2)$$

$$F^- + HCOOCH_3 \rightarrow HCOO^- + CH_3F \qquad \Delta H_3 = -26\ kcal/mol^{12} \quad (3)$$

While the absolute rate constants were not determined for $HCOOCD_3$, the relative rates showed no appreciable difference.

The fact that alkyl formates other than $HCOOCH_3$ experience a sizable acceleration for the $HCOO^-$ reaction motivated a closer analysis of the ethyl formate reaction.

$$F^- + HCOOC_2H_5 \rightarrow C_2H_5OHF^- + CO \qquad \Delta H_4 \simeq -18\ kcal/mol^{13} \quad (4)$$

The second reaction offers two possibilities with respect to neutral products.

$$F^- + HCOOC_2H_5 \rightarrow HCOO^- + C_2H_5F \qquad \Delta H_5 = -25\ kcal/mol^{12} \quad (5)$$

$$F^- + HCOOC_2H_5 \rightarrow HCOO^- + C_2H_4 + HF \qquad \Delta H_6 = -18\ kcal/mol^{12} \quad (6)$$

Several attempts were made to identify the neutral products by using the procedure outlined by Brauman[14] in a normal drift cell. Because of background interfering mass peaks in the mass spectra of the accumulated reaction products with $HCOOC_2H_5$ and $HCOOC_2D_5$, the experiments are not completely clear-cut cases. However, the data are consistent with reaction 6 and not with (5).

Absolute and relative rate constants of the fluoride reactions with alkyl formates are tabulated in Table I. For the higher alkyl formates, the equivalent reactions to (5) and (6) are obviously possible.

2. Hydroxide Ion Reactions. The reaction of OH^- with $HCOOCH_3$ gives rise to three products.

$$OH^- + HCOOCH_3 \rightarrow HCOO^- + CH_3OH \qquad \Delta H_7 = -45\ kcal/mol^{12,15} \quad (7)$$

$$OH^- + HCOOCH_3 \rightarrow (HOHOCH_3)^- + CO \qquad \Delta H_8 \simeq -15\ kcal/mol^4 \quad (8)$$

The third ionic product is CH_3O^- for which two pathways are possible: either displacement as in (9), or decomposition of excited $(HOHOCH_3)^-$ ions in (10).

$$OH^- + HCOOCH_3 \rightarrow HCOOH + CH_3O^- \qquad \Delta H_9 = -13\ kcal/mol^{16} \quad (9)$$

Table II. Rate Constants for the Reactions (I) $OH^- + HCOOR \rightarrow CO + (HOHOR)^-$ and $CO + H_2O + RO^-$ (k_I) and (II) $OH^- + HCOOR \rightarrow HCOO^- +$ Neutral (k_{II})[a]

	$10^{10}k_I$	$10^{10}k_{II}$	k_I/k_{II}[b]
$HCOOCH_3$	6.7	8.4	0.80
$HCOOC_2D_5$	2.2	9.0	0.25

	k_I/k_{II}		k_I/k_{II}
$HCOOCH_2CH_2CH_3$	0.31	$HCOOCH_2CH(CH_3)_2$	0.51
$HCOOCH(CH_3)_2$	0.28	$HCOOCH(CH_3)(C_2H_5)$	0.37
$HCOOCH_2CH_2CH_2CH_3$	0.37	$HCOOC(CH_3)_3$	0.31

[a] Absolute rate constants are given in $cm^3/(molecule\ s)$. [b] Relative constants are reproducible within 5%.

$$OH^- + HCOOCH_3 \rightarrow H_2O + CO + CH_3O^- \qquad \Delta H_{10} = -4\ kcal/mol \quad (10)$$

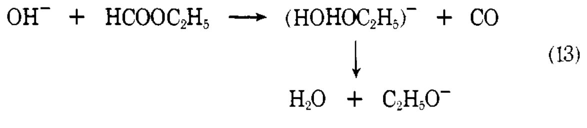
Double resonance experiments carried out at low levels of translational energy excitation reveal that the ionic concentration of CH_3O^- *increases* when either OH^- or $(HOHOCH_3)^-$ are accelerated. Pressure studies show that the relative amounts of $(HOHOCH_3)^-$ and CH_3O^- do not remain constant, but that the ion current ratio $N_{HCOO^-}/(N_{CH_3O^-} + N_{(HOHOCH_3)^-})$ is essentially independent of pressure.[17] These observations were taken as evidence for reaction 10 being the preferred mechanism for the formation of CH_3O^-. Rate constants tabulated in Table II have been obtained assuming that both $(HOHOCH_3)^-$ and CH_3O^- arise from the same process. A similar assumption has been made for the other cases.

By analogy to the reactions of F^-, higher alkyl formates offer again two sets of possible neutrals upon formation of $HCOO^-$.

$$OH^- + HCOOC_2H_5 \rightarrow HCOO^- + C_2H_5OH \qquad \Delta H_{11} = -48\ kcal/mol \quad (11)$$

$$OH^- + HCOOC_2H_5 \rightarrow HCOO^- + C_2H_4 + H_2O \qquad \Delta H_{12} = -37\ kcal/mol \quad (12)$$

No attempts were made to identify the neutral products in this case. The competing reaction responsible for the formation of $(HOHOC_2H_5)^-$, and presumably $C_2H_5O^-$, could only be measured quantitatively by using $HCOOC_2D_5$ in order to separate the mass peaks due to $HCOO^-$ and $C_2D_5O^-$.

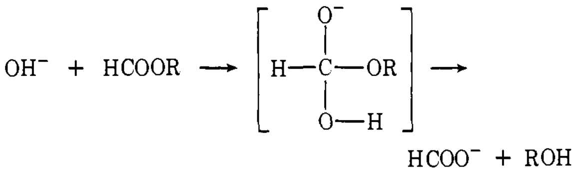


$$\begin{array}{l} OH^- + HCOOC_2H_5 \longrightarrow (HOHOC_2H_5)^- + CO \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad H_2O + C_2H_5O^- \end{array} \quad (13)$$

Relative rate constants for the reactions of OH^- and a few absolute ones are listed in Table II. Absolute rate constants were not determined for the propyl formates because of significant decrease in sensitivity in the spectra arising from recording of the spectra at a lower marginal oscillator frequency (153.5 kHz) than that used for reactions 7-13 (307 kHz).

Discussion

The observation that $HCOO^-$ constitutes the major product of the gas phase reaction of OH^- with alkyl formates can be understood in terms similar to those used in solution chemistry. A carbonyl center represents a good nucleophile acceptor and it can generate a tetrahedral intermediate by addition of the nucleophile. While no such intermediate has been detected in our work, its existence has been claimed in negative ion-molecule reactions of perfluoroacetic anhydride.[18] This line of reasoning results in an intermediate which besides encountering a large exothermicity for product formation requires only a facile internal proton transfer to eliminate the alcohol molecule.

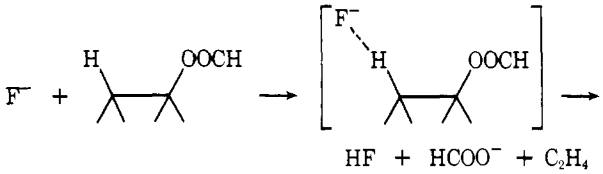


(14)

This mechanism is entirely similar to the solution process. It also provides a good understanding of why the displacement reaction 9 would not compete effectively with (7) as the proton will stay with the least acidic moiety. This intermediate, however, offers no obvious clue as to the efficiency of reaction 8.

The effectiveness of F^- to promote the formation of $HCOO^-$ constitutes a more subtle problem. It is particularly remarkable in view of the failure to observe this product when nucleophiles like RO^-, RS^- (R = alkyl), SH^-, or NH_2^- are allowed to react in the gas phase with alkyl formates.[6] While reaction 3 makes up only 10% of the reactive collisions, a tetrahedral intermediate like (14) would be faced with a rather awkward CH_3F elimination. Thus, reaction 3 may actually be an S_N2 type process for which the activation energy is not negligible but less than for other nucleophiles.[19] However, the most important aspect of the fluoride ion reactions is the large acceleration observed in other alkyl formates. The several-fold increase in the rate constant k_{II} (Table I) for ethyl formate does not fit the pattern of S_N2 type reactions for which it is unrealistic to expect such drastic changes.[20]

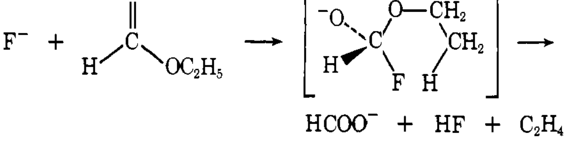
A different approach can be used to account explicitly for reaction 6 on the basis of the gas phase induced elimination mechanism advanced by Beauchamp.[21] In this interpretation, the reaction would proceed as outlined in (15). This



(15)

pathway would predict correctly the neutrals which were shown to be the most likely from our experiments. However, given the exothermicity of reaction 6 and the results of ref 21, the expected ionic product would be $(HCOOHF)^-$. This species should have a sizable bonding energy.[22] This mechanism would also fail to explain why stronger bases like alkoxide ions are unable to promote this elimination process. Thus, this explanation would appear doubtful.

A more likely mechanism for reaction 6 can be illustrated by (16) which assumes again the formation of a tetrahedral

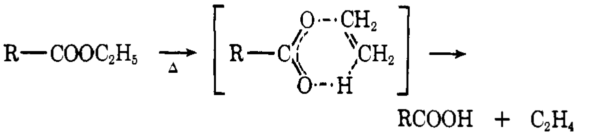


(16)

intermediate by addition of the nucleophile onto the carbonyl.[23] This kind of intermediate is attractive because it is able to provide a straightforward answer to the variation of the rate constants with alkyl groups. Any increase in the number of hydrogens at the β position results in an increase of statistical possibilities for HF elimination. This is in clear agreement with the decrease in the rate constant k_{II} in going from ethyl to *n*-propyl, and the increase in going from *n*-propyl to isopropyl formate. The butyl formates provide a beautiful example of the importance of the β hydrogens, and the relative rate constants (k_{II}/k_I) are seen to follow the order: *tert*-butyl > *sec*-butyl, *n*-butyl > isobutyl. These features make the scheme shown in (16) a reasonable choice for these reactions.

The variation in the relative rate constants of OH^- with alkyl formates is less pronounced than for F^-. Undoubtedly, the pathway described in (14) is likely to be the most important for $HCOO^-$ formation in the case of OH^-. However, our results point out some possible contribution from the mechanism proposed in (16), with OH^- instead of F^-, leading to the neutral products of reaction 12. Experiments with oxygen-18 enriched OH^- should be able to detect this process.

The kinetic enhancement of the $HCOO^-$ reaction by β hydrogens (at least for the F^- reactions) finds its analogies in other ester reactions. Ester pyrolysis is a unimolecular process which gives rise to olefin elimination. A six-member cyclic transition state has been successful in explaining the trend of the rate constants as a function of alkyl groups, and in particular of β hydrogens (reaction 17).[24] Further com-



(17)

parisons can be made between our system and reaction 17 on the basis of isotope effects. The rate constants of $HCOOC_2H_5$ and $HCOOC_2D_5$ with fluoride ions (reaction 5 or 6) yields $k_H/k_D = 1.6$. This value is very close to the ratio of 1.8 observed for the thermal rate constants of these two compounds.[25] Care must be of course exercised in this comparison as the isotope effect will be a sensitive function of the bond making and breaking processes. For the case of OH^-, the isotope effect is more difficult to establish because $HCOOC_2H_5$ yields two products of the same mass, $HCOO^-$ and $C_2H_5O^-$. Presumably, this effect could be helpful in determining the extent of the participation of pathway 16 for the OH^- reactions.

While our considerations above have been focused on the $HCOO^-$ reactions, the overall mechanism of our systems must also explain the formation of $ROHX^-$ ions present in all cases. The energetics of the ion solvation induced reaction have been discussed at length in a previous paper for several nucleophiles.[4] It was concluded from these arguments that these systems behaved as if the reaction proceeds through attack at the formyl hydrogen. Thus, only gas phase bases stronger than PH_2^- were observed to give rise to $ROHX^-$. The data in Tables I and II reveal that the solvation induced reaction is characterized by similar rate constants for OH^- and F^- with methyl formate. This rate constant decreases drastically on going to ethyl formate in both cases but no appreciable change is observed with the higher alkyl formates, at least in the case of the fluoride ion. Finally, differences in the rate of reaction of $HCOOC_2H_5$ and $DCOOC_2H_5$ with F^- are practically within the experimental error.

The facts summarized above make a tetrahedral intermediate as in (14) or (16) difficult to accommodate reaction 1. A slow displacement of RO^- from the tetrahedral intermediate followed by expulsion of $ROHX^-$ while satisfactory in terms of lack of isotope effect at the formyl hydrogen is inconsistent with the anion dependence of this reaction, and the inability to see appreciable contribution from reaction 9.[26]

Our explanation for the $ROHX^-$ reactions is based on our previous results[4] and a qualitative description of the potential energy surface. A local minimum in the approach of an X^- ion to the neutral could be represented by a loose hydrogen bonded association ($X^- \cdots HCOOR$). This species could then evolve either into the $ROHF^- + CO$ products, or into the tetrahedral intermediate, for which changes are needed in the molecular geometry of the neutral. The example referred to in our introduction[7] illustrates in this respect the complexity of the potential energy as a nucleophile approaches a simple carbonyl system.

It is clear from the above arguments that our understanding of these systems is still precarious at the molecular level. It is also evident that the gas phase reaction brings out details on the mechanistic side which are quite unsuspected from the results in solution. Further studies on other carbonyl systems[27] reveal that the general discussion presented here is a good starting point for understanding nucleophilic processes in esters.

This study draws attention to the importance in many cases of determining the neutrals produced in an ion-molecule reaction. Although our experience in trying to distinguish reactions 5 and 6 has not been completely successful, the overall evidence seems to favor reaction 6. It is finally interesting to point out that given the quoted exothermicity of the reaction (18 kcal/mol) and the postulated intermediate, it is not improbable that some of the HF eliminated in reaction 6 may be vibrationally excited ($\nu_{HF} = 4138.5$ cm^{-1}).[28] Investigation of vibrational chemiluminescence in ion-molecule reactions of the type described here would represent indeed an exciting possibility.

Acknowledgment. This work has been made possible by the support of Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brasil and the Fundação de Amparo à Pesquisa do Estado de São Paulo (J.F.G.F.). We are indebted to Geraldo Ayrosa for technical assistance, and to Professor Keith Wellman for many helpful discussions.

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