A Comprehensive View of the Gas-phase Reaction of Fluoride Ions and Acetic Acid Derivatives

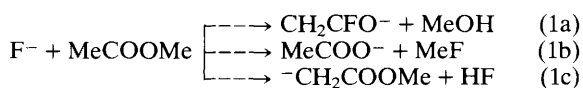## Jose M. Riveros

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The gas-phase reaction of F⁻ with several acetic acid derivatives (MeCOX) is shown to proceed primarily by proton abstraction in the collision complex, rather than nucleophilic displacement, leading to the facile formation of FHX⁻ or CH_2CFO^-.

It is a well established fact that the gas-phase reaction of anionic nucleophiles with the simplest esters proceeds by a variety of competitive mechanisms ($B_{AC}2$, S_N2, elimination, proton transfer).[1,2] The preferred pathway is dependent on the nature of the anion and the substrate, a fact which has precluded a unified view of these gas-phase ion–molecule reactions that properly takes into account the dynamic and energetic parameters.

This communication reports new observations on the gas-phase reaction of F⁻ with acetic acid derivatives which help to establish the variety of reaction products that originate from initial proton abstraction in the collision complex. Earlier studies by ion cyclotron resonance techniques[3] and negative ion chemical ionization[4] shows that three major pathways are observed with methyl acetate.

$$F^- + MeCOOMe \begin{cases} \longrightarrow CH_2CFO^- + MeOH & (1a) \\ \longrightarrow MeCOO^- + MeF & (1b) \\ \longrightarrow {}^-CH_2COOMe + HF & (1c) \end{cases}$$
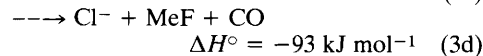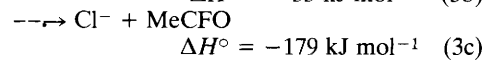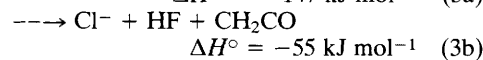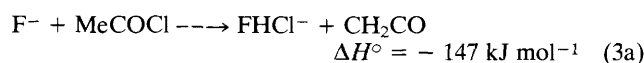
However, we find a significantly different reactivity pattern when the simple methoxy group is replaced by a group X, for which the corresponding gas-phase acid HX is stronger than HF. Fluoride ions generated from SO_2F_2 in an ion cyclotron resonance spectrometer,[3] at pressures of the order of 1.3×10^{-5} mbar (1 bar = 10^5 Pa), react rapidly with corresponding partial pressures of the MeCXO substrates according to reaction (2).

$$F^- + MeCOX \begin{cases} \longrightarrow FHX^- + CH_2CO & (2a) \\ \longrightarrow X^- + (C_2H_3CFO) & (2b) \end{cases}$$
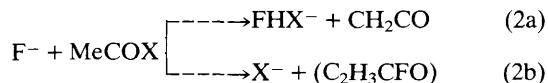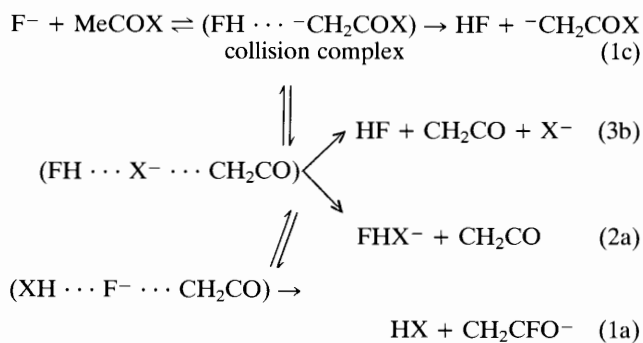
X = Cl, SEt, F, OC(O)Me, p-YC₆H₄O (Y = H, Me, F, Cl)

Although the formation of FHCl⁻ in reaction (2a) with MeCOCl has been observed before,[5] no particular significance was attached to the observation. Likewise, an associated ion has been suggested as a minor product in the gas-phase reaction of OH⁻ with phenyl acetate.[6]

The product distribution in these reactions cannot establish unequivocally the mechanism responsible for reaction (2b), and thus the nature of the neutral product. For example, Cl⁻ can originate from the dissociation of the FHX⁻ moiety, or by displacement at the carbonyl centre ($B_{AC}2$ type) or at the alkyl group (S_N2) in the case of acetyl chloride.[7]

$$F^- + MeCOCl \longrightarrow FHCl^- + CH_2CO$$
$$\Delta H^\circ = -147 \text{ kJ mol}^{-1} \quad (3a)$$
$$\longrightarrow Cl^- + HF + CH_2CO$$
$$\Delta H^\circ = -55 \text{ kJ mol}^{-1} \quad (3b)$$
$$\longrightarrow Cl^- + MeCFO$$
$$\Delta H^\circ = -179 \text{ kJ mol}^{-1} \quad (3c)$$
$$\longrightarrow Cl^- + MeF + CO$$
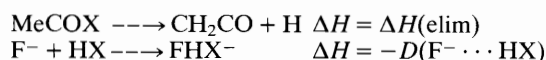$$\Delta H^\circ = -93 \text{ kJ mol}^{-1} \quad (3d)$$

For phenyl acetate, the formation of PhO⁻ is unlikely to proceed *via* the associated anion as this process is endothermic. Yet, there is a noticeable trend favouring the formation of X⁻ as a function of the increasing stability of the areneO⁻ species. This is clearly illustrated for X = p-MeC₆H₄O where the product ratio, (FHX)⁻:X⁻ is 3.8 while for X = p-ClC₆H₄O this ratio drops to 0.7.

The occurrence of reaction (2a) can be rationalised by thermochemical arguments similar to those used for the 'Riveros reaction' in alkyl formates.[8] Fluoride ions undergo reaction (2a) provided that the F⁻ ··· HX binding energy is large enough to overcome the energy required to break up

$$F^- + MeCOX \rightleftharpoons (FH \cdots {}^-CH_2COX) \rightarrow HF + {}^-CH_2COX$$

collision complex   (1c)

$$(FH \cdots X^- \cdots CH_2CO) \Big\langle \begin{array}{l} \nearrow HF + CH_2CO + X^- \quad (3b) \\ \\ \searrow FHX^- + CH_2CO \quad (2a) \end{array}$$

$$(XH \cdots F^- \cdots CH_2CO) \rightarrow$$

$$HX + CH_2CFO^- \quad (1a)$$

Scheme 1

the acetyl substrate into ketene and HX, *i.e.*, $\Delta H_{2a} < 0$ if $D(F^- \cdots HX) > \Delta H$ (elim).

$$MeCOX \dashrightarrow CH_2CO + H \quad \Delta H = \Delta H(\text{elim})$$
$$F^- + HX \dashrightarrow FHX^- \qquad \Delta H = -D(F^- \cdots HX)$$

Fluoride affinities in the gas-phase[9,10] range from 125—146 kJ mol⁻¹ for alcohols, to 173 kJ mol⁻¹ for phenols and 250 kJ mol⁻¹ for HCl. This explains why reaction (2a) is unlikely to occur in simple alkyl acetates where ΔH(elim) is of the order 165 kJ mol⁻¹. On the other hand, ΔH(elim) for the MeCOX systems above decreases to values below 125 kJ mol⁻¹ while the $D(F^- \cdots HX)$ becomes very large. This same argument, independent of any kinetic considerations, would predict the failure of Cl⁻ to undergo reaction (2a) as there is a significant decrease in binding energy for the same substrate in going from F⁻ to Cl⁻, *i.e.*, $D(Cl^- \cdots HCl) = 96.5$ kJ mol⁻¹.[11]

The observation that reactions (1a), (1c), (2a), and in some cases (2b), are the main reaction channels suggests that proton abstraction in the collision complex by F⁻ is the dominant mechanism. Scheme 1 outlines a typical multiple minima energy surface[12] that can account, in a unified way, for the main reactions of the systems previously discussed[3] and those presented here.

In Scheme 1, partition into different products is determined by the energetic factors responsible for the relative exothermicity of each channel. However, products originating from this type of mechanism are more favourable than those formed *via* an S_N2 [(1b) or (3d)] or $B_{AC}2$ (3c) owing to the much larger entropies of activation required for the collision complexes to undergo the latter reactions. Scheme 1 predicts correctly the main products of reaction (1) where channels (2a) and (3b) are endothermic. Our proposal further argues that reaction (2a)

will be favoured over CH_2CFO^- in the MeCOX substrates by the stronger fluoride binding energy of HX over ketene. Our general approach neglects, at this preliminary stage, factors which may be important if stereochemical differences need to be taken into consideration as proposed for elimination type reactions in ethers.[13]

The present model provides further support to the general idea that ionic gas-phase reactions mediated through the initial strong association between an anion and a hydrogen bonding substrate are more facile than those which require more constrained transition states for their collision complexes.

Discussion of the relative contributions of $B_{AC}2$ and S_N2 to the mechanisms of these reactions will be presented elsewhere based on kinetic isotope effects and product distribution.

References

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