Fragmentation Reactions of Some Aliphatic Esters in the NCI(F⁻) and NCI(NH₂⁻) Mass Spectra

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The NCI(F⁻) and NCI(NH₂⁻) mass spectra of a series of aliphatic acetates and of methyl and ethyl trimethylacetate have been obtained. The formation of fluoroenolate ions CH_2COF^- and of carboxamide anions $RCONH^-$ (R = CH_3, $(CH_3)_3C$), respectively, is observed besides formation of [M − H]⁻ ions and carboxylate ions $RCOO^-$ (R = CH_3, $(CH_3)_3C$). The relative intensities of the different anions depend on the structure of the ester molecules and on the primary reactant anions. Usually, the NCI(NH₂⁻) spectra of the acetates are dominated by [M − H]⁻ ions ([M − D]⁻ ions in the case of trideuteroacetates) fragmenting unimolecularly by elimination of an alcohol. The carboxylate ions are important fragments, too, but carboxamide ions are only observed with large intensities in the NCI(NH₂⁻) spectra of the trimethylacetates. The NCI(F⁻) spectra show much larger intensities of carboxylate ions and fluoroenolate ions. The mechanisms of the fragmentation reactions are discussed. The results indicate that most or even all of the fragment ions in the NCI(F⁻) mass spectra of aliphatic esters are formed by addition–elimination reactions via a tetrahedral intermediate, while competition between direct proton abstraction and addition–elimination reactions occurs in the NCI(NH₂⁻) mass spectra because of the higher basicity of NH_2^- resulting in an early transition state for direct proton abstraction.

INTRODUCTION

In the course of a study of intramolecular reactions of organic anions in the gas phase[1] we became interested in the reactions of F⁻ and OH⁻ with aliphatic esters under the conditions of Negative Chemical Ionization (NCI) mass spectrometry. The gas phase reactions of anions with organic molecules have been studied by the ICR and flowing afterglow techniques.[2,3] The reactions of carbonyl compounds are of special interest. By analogy with reactions in the condensed phase an anion may react with these compounds as a base by proton abstraction and as a nucleophile by substitution at the carbonyl group either by a direct displacement reaction or via an addition–elimination pathway. Both types of reactions have been observed by ICR[4] and, obviously, the products of ion/molecule reactions between anions and carbonyl compounds arise from a competition between base-catalysed elimination and nucleophilic substitution, which are fundamental elementary processes of organic chemistry.

The NCI mass spectra of some aliphatic esters[5] and acyl chlorides[6] using OH⁻ as reactant ion also indicate fragment ion formation by a competition between these reaction channels. Hence, it is expected that the types and the intensities of fragment ions in the NCI mass spectra will depend both on the nature of the reactant ions and on the structure of the ester molecules. As will be shown below, the NCI mass spectra of certain aliphatic esters show large differences by using F⁻ and NH₂⁻, respectively, as reactant

ions, reflecting the different thermochemistry and probably also the different mechanisms of the reactions of these anions with ester molecules.

RESULTS AND DISCUSSION

The structures of the aliphatic esters **1–9** investigated by NCI mass spectrometry are shown below. Their NCI mass spectra obtained with CF_4 and NH_3, respectively, as reactant gas are shown in Figs 1 and 2. The reproducibility of these NCI spectra is good and the
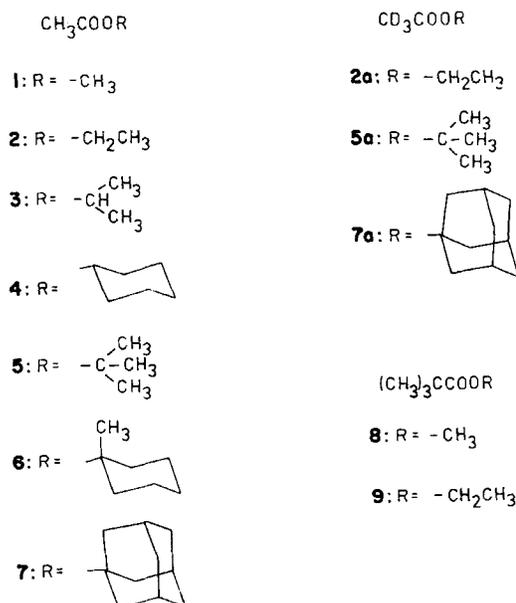
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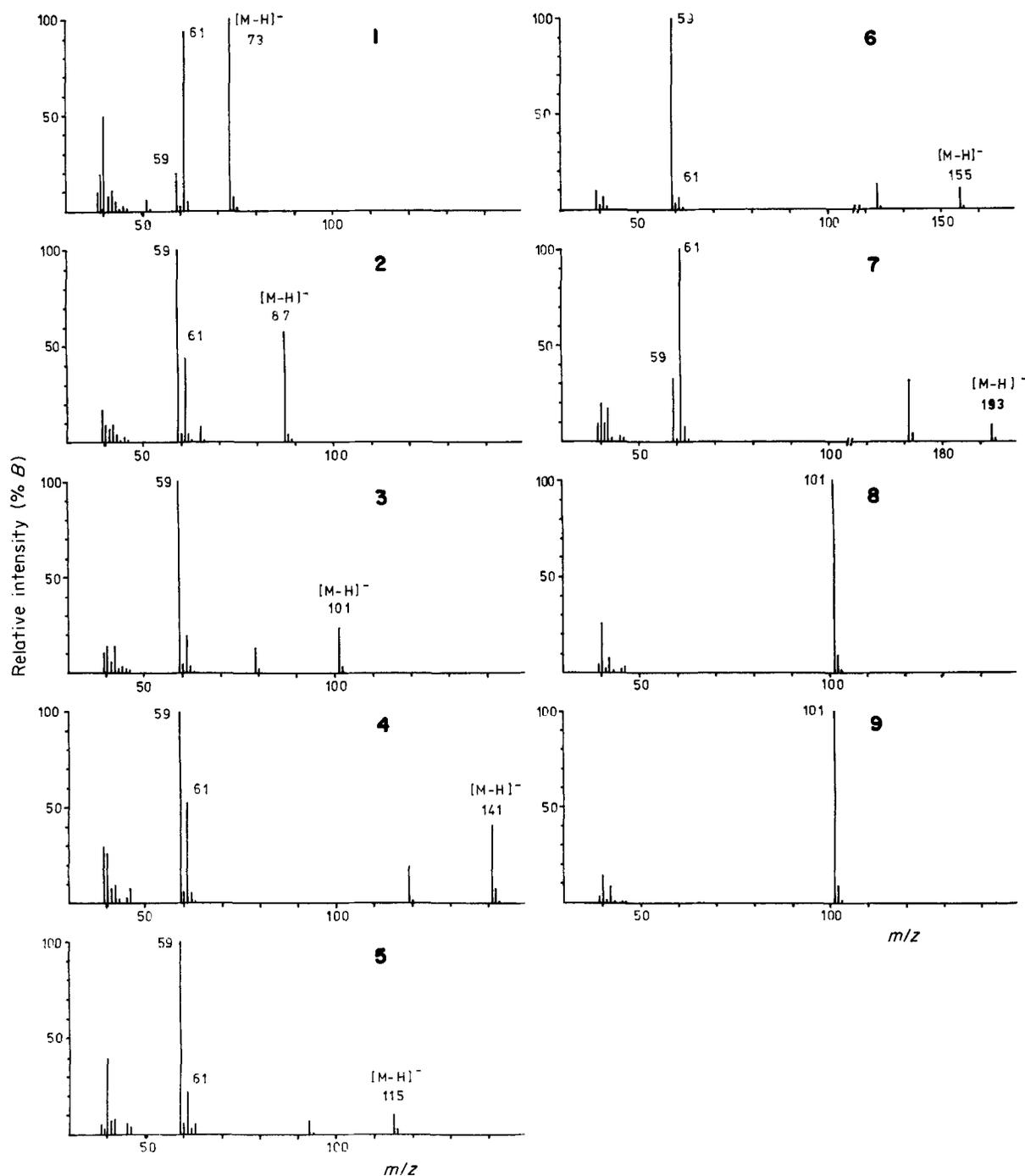
Figure 1. NCI(F⁻) mass spectra of the acetates 1–7 and the trimethylacetates 8 and 9.

differences observed between the NCI (F⁻) and NCI(NH₂⁻) spectra and the intensity variations of corresponding fragment ions in the NCI spectra of the different esters are far outside the limits of experimental error.

A common feature of the NCI mass spectra of these aliphatic esters with OH⁻ as reactant ion[5] and F⁻ or NH₂⁻ is the formation of [M−H]⁻ ions and of carboxylate ions RCOO⁻. In addition, an ion C_2HO^-, m/z 41, is observed with especially large intensities in the spectra of the acetates of tertiary alcohols.

The NCI (F⁻) mass spectra of the acetates 1–7 show two types of fragment ions into which the reactant ion F⁻ has been incorporated. These are the ions

$C_2H_2OF^-$, m/z 61, and the solvated ions R'OH·F⁻. Both types of ions are not observed in the mass spectra of the trimethylacetates 8 and 9. In the NCI (NH₂⁻) mass spectra carboxamide anions RCONH⁻ (R = CH₃, m/z 58; R = (CH₃)₃C, m/z 100) are observed, which again must be formed by an incorporation of the reactant ion NH₂⁻. However, this time the intensity of RONH⁻ ions is quite small in the case of the acetates 1–7 and large in the case of the trimethylacetates 8 and 9.

The formation of [M−H]⁻ ions in the NCI mass spectra of the acetates 1–7 is easy to explain by proton abstraction from the CH₃CO group as suggested earlier by Smit and Field.[5] The gas phase acidity of 1 is
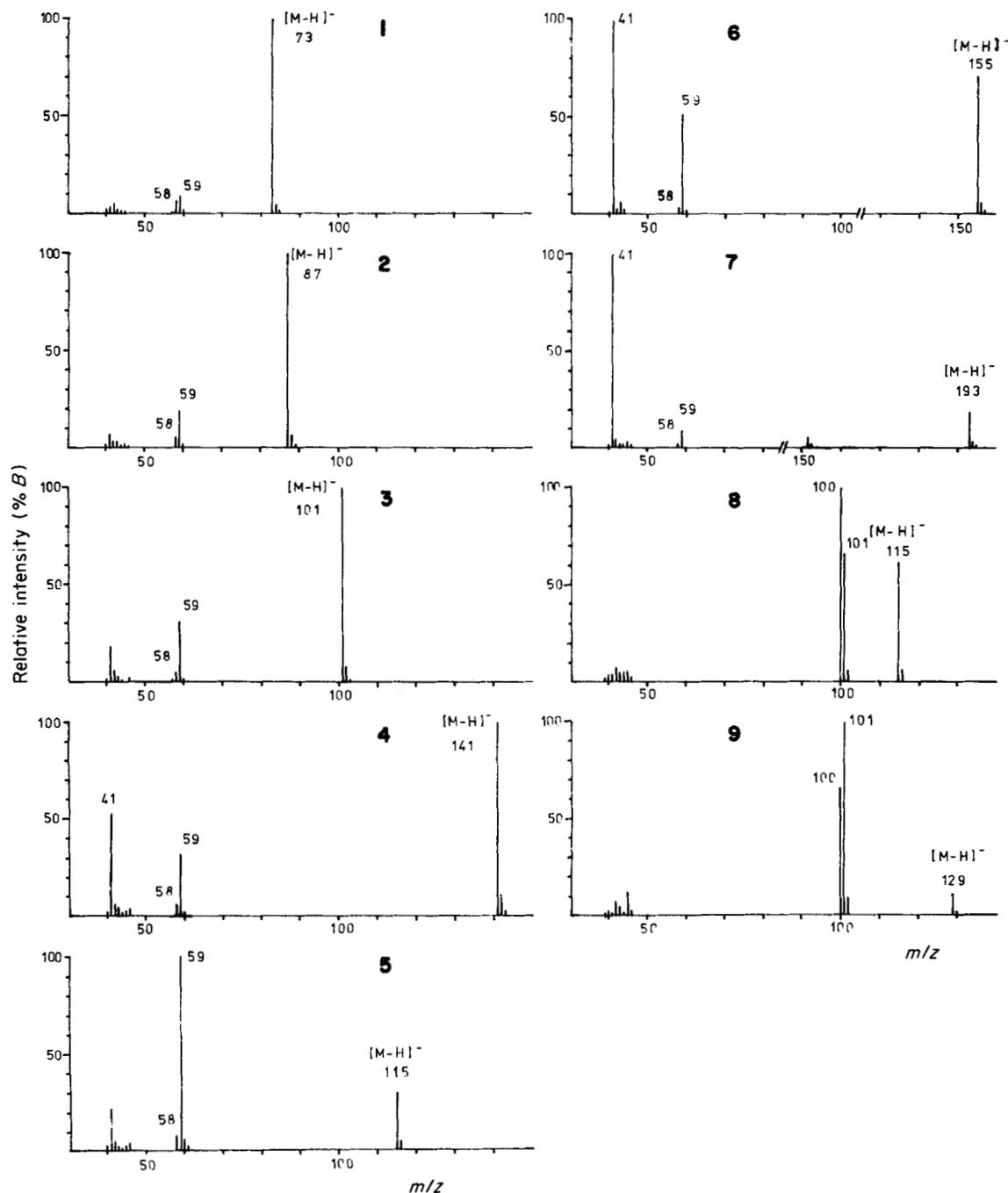
Figure 2. NCI(NH$_2^-$) mass spectra of the acetates **1-5** and **7** and the trimethylacetates **8** and **9**.

known,[7] and by a calculation using the relevant thermochemical data[7,8] reactions (1a) and (1b) are slightly and strongly exothermic, respectively.

$$CH_3COOCH_3 + F^-$$
$$\rightarrow \bar{C}H_2COOCH_3 + HF \qquad \Delta H_R = -4 \text{ kJ mol}^{-1}$$
$$(1a)$$

$$CH_3COOCH_3 + NH_2^-$$
$$\rightarrow \bar{C}H_2COOCH_3 + NH_3 \qquad \Delta H_R = -136 \text{ kJ mol}^{-1}$$
$$(1b)$$
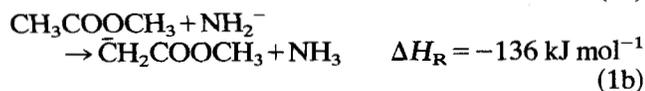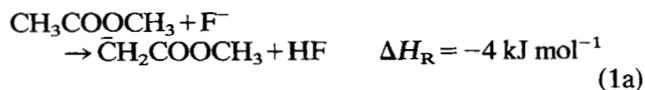
The NCI mass spectra of the trideuteroacetates **2a**, **5a** and **7a**, obtained by reaction with F$^-$ and NH$_2^-$, contain only [M−D]$^-$ ions as expected from reactions (1a) and (1b). Formation of [M−H]$^-$ ions by proton

abstraction from an acidic position α to the ester carbonyl group also explains why these ions are absent in the NCI(F$^-$) mass spectra of the trimethylacetates **8** and **9**.

However, [M−H]$^-$ ions are observed in the corresponding NCI(NH$_2^-$) mass spectra, indicating a proton abstraction from other positions of the ester molecules by the strong base NH$_2^-$. The shift to [M−D]$^-$ ions in the NCI(NH$_2^-$) mass spectrum of the trideuteromethyl ester of **8** proves a proton abstraction from the α-position to the other oxygen of the ester group.

In both series of NCI spectra the relative amount of the total ion current carried by the [M−H]$^-$ ions decreases with increasing size of the alkoxy group of

1-7. The same behaviour has been observed in the NCI(OH⁻) mass spectra of acetates.[5] One possible explanation of this effect is increasing decomposition of the [M−H]⁻ ions by ketene elimination and alkoxide ion formation[5] with increasing size and stability of the alkoxide ion (reactions (2a) and (2b)).

$$CH_3COOR + F^- \rightarrow CH_2{=}C{=}O + HF + {^-}OR \quad (2a)$$
$$CH_3COOR + NH_2^- \rightarrow CH_2{=}C{=}O + NH_3 + {^-}OR \quad (2b)$$
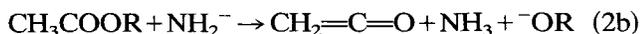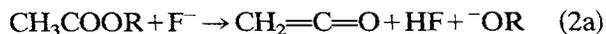
Both reactions are endothermic, however, and no ⁻OR ions are observed in the NCI spectra.[9] The NCI(F⁻) mass spectra show small peaks due to the solvated ions R′OHF⁻ which may arise from a reaction similar to (2a), since these ions are known to be very stable.[10] However, the intensity of the R′OHF⁻ ions shows no systematic increase with decreasing intensity of the [M−H]⁻ ions. The only fragment ion with an inverse intensity relationship to that of the [M−H]⁻ ion is the acetate ion CH₃COO⁻, m/z 59. Hence, it appears possible that the [M−H]⁻ ions decompose by reaction (3). With $\Delta H_f(\bar{C}H_2COOC_2H_5) = -427$ kJ mol⁻¹ [11], $\Delta H_f(CH_3COO^-) = -512$ kJ mol⁻¹ [7] and $\Delta H_f(C_2H_4) = +52$ kJ mol⁻¹ [8] reaction (3) is exothermic by

$$(3)$$
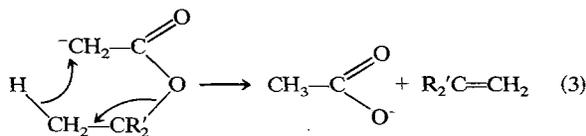
−33 kJ mol⁻¹ for ethyl acetate (2) and should be somewhat more exothermic for the larger esters. Furthermore, Hunt et al.[12] have shown recently by Collision Induced Dissociation (CID) mass spectra that the [M−H]⁻ of ketones fragment in an analogous reaction via alkene elimination. In the case of the trideuteroacetates 2a, 5a and 7a, fragmentation of the [M−D]⁻ ions via reaction (3) should give rise to dideuteroacetate ions, m/z 61. In the NCI mass spectra of 2a, 5a and 7a most of the intensity at m/z 59 in the unlabelled esters is shifted to m/z 62 but small peaks at m/z 61 and m/z 60 are also observed. It is not possible to exclude that the corresponding ions CHD₂COO⁻ and CH₂DCOO⁻ arise from a H/D exchange of the ester molecule in the NCI plasma prior to fragmentation, however. Additional information has been obtained from the fragmentations of metastable [M−H]⁻ ions in the NCI(F⁻) and NCI(NH₂⁻) mass spectra of 2 and 5 and [M−D]⁻ ions of their deuterated derivatives 2a and 5a. The only unimolecular reaction of metastable [M−H]⁻ ions of 2 and 5 observed in the second field free region of a VG ZAB 2F mass spectrometer by MIKE spectrometry is the formation of the ions m/z 41, which are completely shifted to m/z 42 in the MIKE spectra of the labelled compounds. This indicates fragmentation via reaction (4) by elimination of alcohol instead of alkene elimina-

$$(4)$$
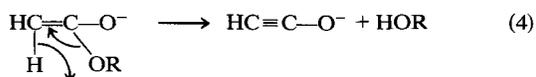
tion (reaction 3). $\Delta H_f(HC{\equiv}C{-}O^-)$ and, hence, the thermochemistry of reaction (4) is not known. How-

ever, RC≡C—O⁻ ions have also been observed in the NCI(OH⁻) mass spectra of simple aliphatic acyl chlorides, where they are formed with high intensities by HCl elimination from the corresponding [M−H]⁻ ions.[6]

The CID MIKE spectra of the [M−H]⁻ ions of 2 and 5 show additional peaks at m/z 45 and 73, respectively, which are not shifted in the spectra of the deuterated analogues 2a and 5a and, hence, correspond to the alkoxide ions C₂H₅O⁻ and (CH₃)₃CO⁻. Another broad signal is centred at m/z 58 and appears at m/z 60 in the spectra of the deuterated derivatives. This latter ion corresponds to the radical anion ĊH₂CO₂⁻, which has not been observed before. However, the acetate ion CH₃COO⁻, m/z 59, is formed neither by an unimolecular reaction nor by a collisionally activated decomposition from metastable [M−H]⁻ ions. Obviously, this fragmentation pathway is not favoured by the [M−H]⁻ ions of aliphatic esters and cannot explain the systematic decrease of the [M−H]⁻ intensity with the size of the alkoxy group. It is more likely that this effect is due to a competition between proton abstraction from the ester molecule and other ion/molecule reactions of the reactant anions.

The carboxylate ions CH₃COO⁻, m/z 59, and (CH₃)₃CCOO⁻, m/z 101, respectively, may arise from the esters 1-9 by a S_N2 reaction involving nucleophilic attack of the reactant anion at the α-carbon atom of the ester alkoxy group (reaction (5)) or by a concerted E2 mechanism with proton abstraction from the β-carbon atom of the alkoxy group by the anion (reaction (6)). Using the relevant thermochemical data[7,8]

$$F{-}C_2H_5 + CH_3COO^- \qquad \Delta H_R = -77 \text{ kJ mol}^{-1} \quad (5a)$$

$$H_2N{-}C_2H_5 + CH_3COO^- \qquad \Delta H_R = -222 \text{ kJ mol}^{-1} \quad (5b)$$

$$HF + CH_2{=}CH_2 + CH_3COO^- \qquad \Delta H_R = -37 \text{ kJ mol}^{-1} \quad (6a)$$

$$NH_3 + CH_2{=}CH_2 + CH_3COO^- \qquad \Delta H_R = -169 \text{ kJ mol}^{-1} \quad (6b)$$
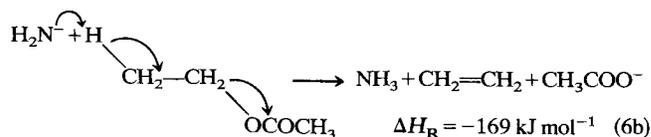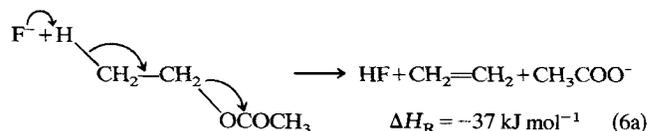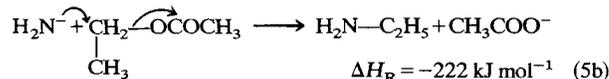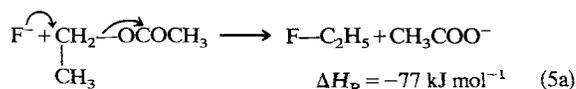
both reactions are exothermic for ester 2, especially for the NH₂⁻ reactant ion. A change in the alkoxy group will influence the heats of formation of the neutral ester and of the neutral products of reactions (5) and (6) similarly; hence, the exothermicity of these reactions will not be altered much for the other esters. Reaction (5) is more exothermic than reaction (6), and direct nucleophilic displacement reactions have been observed in the gas phase[4,13,14] including trifluoroacetates as substrates.[4a] However, the variation of the CH₃COO⁻ intensity in the NCI mass spectra with the structure of the alkoxy groups in 1-7 does not follow an S_N2 order. The dramatic increase of the CH₃COO⁻ intensity between the NCI(F⁻) mass spectra of the

$$F^- + \overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}OC_2H_5 \longrightarrow F\text{—}\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}OC_2H_5 \longrightarrow \begin{array}{l} CH_3COO^- + CH_2\text{=}CH_2 + HF \\ CH_3COO^- + C_2H_5F \\ CH_2COF^- + C_2H_5OH \end{array}$$ (7a)

$$H_2N^- + \overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}OC_2H_5 \longrightarrow H_2N\text{—}\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}OC_2H_5 \longrightarrow \begin{array}{l} CH_3COO^- + CH_2\text{=}CH_2 + NH_3 \\ CH_3COO^- + C_2H_5NH_2 \\ CH_3CONH^- + C_2H_5OH \end{array}$$ (7b)
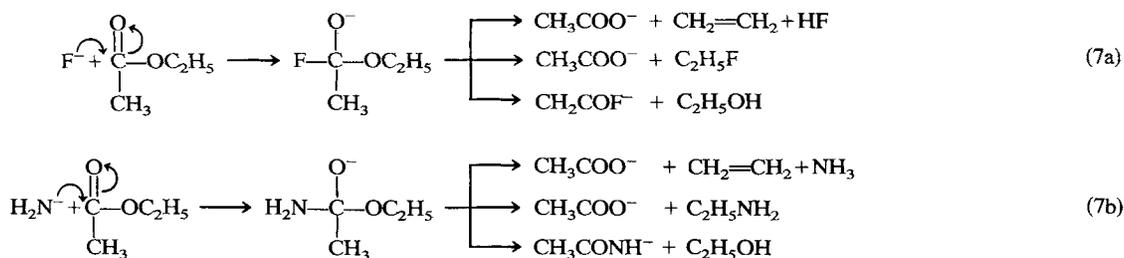
methyl ester **1** and ethyl ester **2** is of special interest. Riveros et al.[10] have observed a similar effect of the alkoxy groups on the rates of the formation of HCOO⁻ ions in an ICR study of the reactions of F⁻ and OH⁻ with alkyl formates. This proves clearly, that the formation of carboxylate ions from ethyl and higher alkyl esters occurs by an elimination mechanism under ICR conditions. The smooth trend in the relative amounts of CH₃COO⁻ ions formed in the NCI(F⁻) and NCI(NH₂⁻) mass spectra of the alkyl acetates **1–7** (Figs 1 and 2) with the number of hydrogen atoms at the β-position of the alkoxy group shows that the same mechanism also predominates for the generation of acetates ions under NCI conditions. The CH₃COO⁻ ions are also observed in the NCI mass spectra of methyl acetate (**1**) and 1-adamantyl acetate (**7**), though in smaller amounts, and the (CH₃)₃CCOO⁻ ions are the only fragment ions observed in the NCI(F⁻) mass spectrum of methyl trimethylacetate (**8**). With methyl esters the carboxylate ions cannot arise from an E2 reaction and in the case of the adamantyl ester **7** this reaction is very unlikely because a highly strained anti-Bredt olefin has to be formed. Hence, there must be a second mechanism giving rise to the carboxylate ions. Riveros et al.[10,18] have suggested that this is the S_N2 reaction (5a, b). However, a S_N2 reaction with backside attack of the nucleophile at the α-carbon atom of the ester alkoxy group is not possible in the 1-adamantyl ester **7** for steric reasons. In view of the similar amounts of CH₃COO⁻ ions formed in the NCI(F⁻) mass spectra of the methyl ester **1** and the 1-adamantyl ester **7**, it is doubtful whether a S_N2 displacement reaction occurs at all. Furthermore, the S_N2 displacement reaction is usually associated with an activation energy[14] and this is the reason why the S_N2 reaction (5) cannot compete effectively with the E2 reaction (6) in spite of its greater exothermicity. The S_N2 reaction (5b) of the NH₂⁻ is very exothermic, and one expects larger reaction efficiencies for NH₂⁻ than for F⁻. However, the relative intensity of CH₃COO⁻ ions in the NCI (NH₂⁻) mass spectrum of methyl acetate (**1**) is very small.

It can be argued that the CH₃COO⁻ ion intensity is suppressed by competition of a proton abstraction by the strong base NH₂⁻. Indeed, the intensity of the (CH₃)CCOO⁻ ions, m/z 101, in the NCI(NH₂⁻) mass spectrum of methyl trimethylacetate (**8**) (Fig. 2) with no acidic hydrogen atoms is much higher, but the base peak of the spectrum is given by the amide anions (CH₃)₃CCONH⁻, m/z 100. These latter ions and also the fluoroenolate ions CH₂COF⁻, m/z 61, in the NCI(F⁻) mass spectra of the acetates **1–7**, must be

formed by an addition of the reactant anion to the ester carbonyl group. This shows that reaction (7) involving a tetrahedral intermediate makes an important contribution to the fragmentation of ester molecules under NCI conditions and may also give rise to carboxylate ions by an addition–elimination mechanism. Although tetrahedral intermediates are not usually detected in the ion/molecule reaction of carbonyl compounds in the gas phase, their important role in these reactions is concluded from kinetic experiments.[2]

A MINDO/3 calculation of the heats of formation of the tetrahedral addition complexes and the other species of reactions (7a) and (7b) have been performed to get some insight into the corresponding reaction energies. The results are given in Table 1 and are compared with experimental values where possible. A schematic diagram of the reaction energies (relative to

Table 1. Heats of formation (KJ mol⁻¹) used for calculation of reaction energies

	MINDO/3	Exptl	Reference
CH₃COOC₂H₅	−448	−443	8
ĊH₂COOC₂H₅	−431	−429	11
CH₃—Ċ(O⁻)(OC₂H₅)(F)	−853 −870	−836	4b
CH₃—Ċ(O⁻)(OC₂H₅)(NH₂)	−525 −527		
CH₂=C(O⁻)(F)	−481	<−464	18
CH₂=C(O⁻)(NH₂)	−212		
CH₃—C(=O)(NH⁻)	−235		
CH₃—C(=O)(O⁻)(O⁻)	−512		7
F⁻	−251		7
NH₂⁻	+106		7
HF	−271		8
NH₃	−46		8
CH₂=CH₂	+52		8
C₂H₅F	−259		8
C₂H₅NH₂	−47		8
C₂H₅OH	−235		8
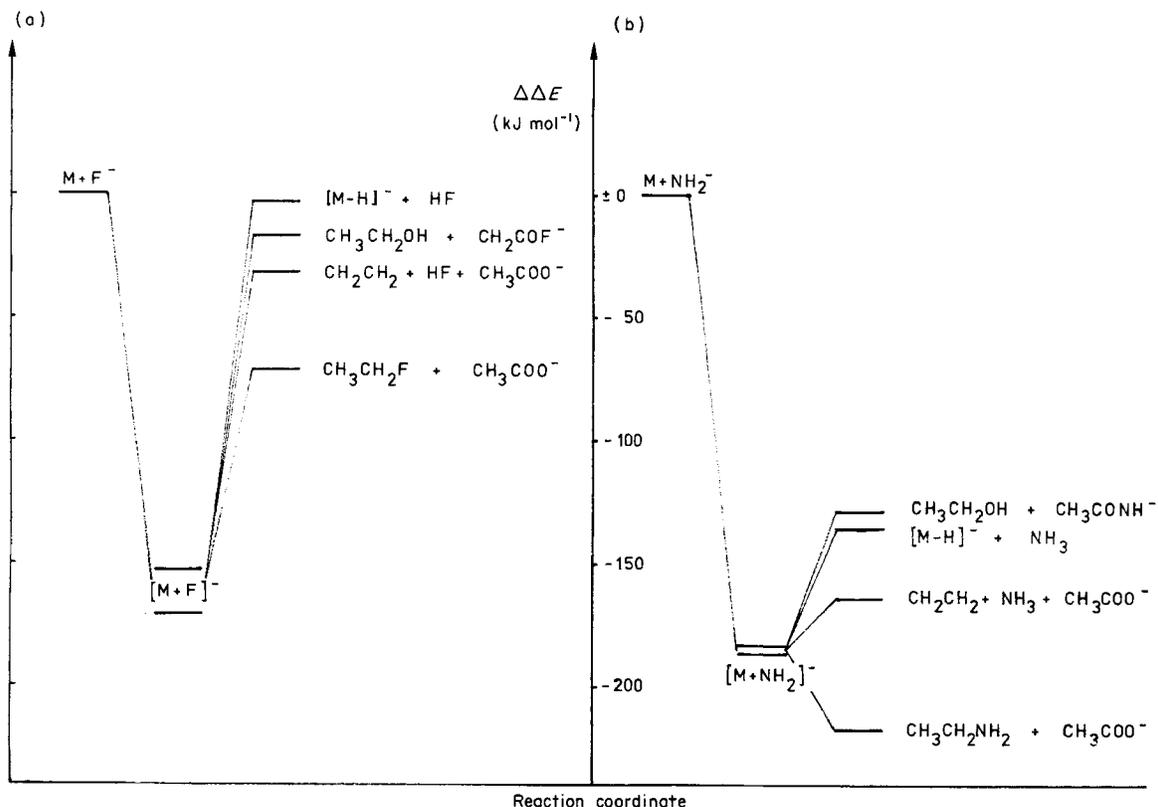
Figure 3. Schematic reaction energy diagram of reactions (7a) and (7b) calculated by MINDO/3.

the neutral ester molecule and F^- and NH_2^-, respectively), is shown in Fig. 3. Note that not only the formation of $[M-H]^-$ ions is much more exothermic for NH_2^- than for F^-, but all the other reactions as well. By contrast, the formation of the tetrahedral intermediate is exothermic in both systems with approximately the same reaction energy. The fully optimized geometry of both intermediates is shown in Fig. 4. Note that the structure of these addition complexes around the carbon atom of the original carbonyl group corresponds to a rather distorted tet-

rahedron. There are two reactive conformations possible for each of these intermediates. In the case of the NH_2^- adduct the energies of both conformations are very similar and no rotational barrier has been calculated. In the case of the F^- adduct the conformation leading to the cis β-alkene elimination is more stable as suggested by Riveros.[18] Of special interest for the discussion below are the very short distances between the fluorine atom and one of the active hydrogen atoms in each of the conformations of the F^- adduct.

The products and thermochemistry of CH_3COO^-
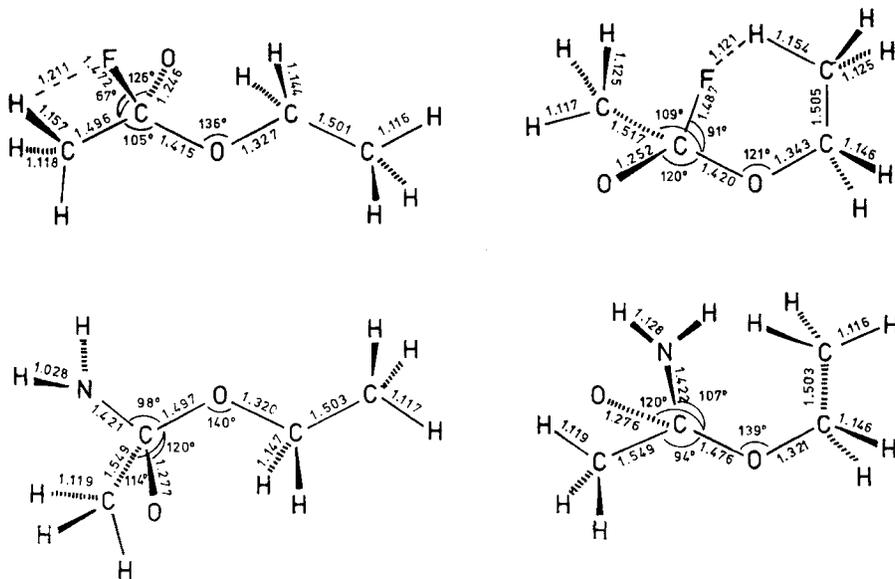
Figure 4. Geometries of the stable conformations of the tetrahedral addition complexes of reactions (7a) and (7b) calculated by MINDO/3.

formation by reaction (7) are the same as for reactions (5) and (6), but the mechanisms, and hence the activation energies, are different. Riveros et al.[10] have suggested from their ICR study of the reactions of OH⁻ and F⁻ with alkyl formates that the HCOO⁻ ions in this system arise by an attack of the fluorine atom in the corresponding tetrahedral intermediate on a hydrogen atom at the β-carbon atom of the ester alkoxy group with elimination of an alkene and HF or attack on the β-carbon atom with concomitant H⁻ shift to the α-carbon atom and elimination of the alkyl fluoride. Both mechanisms are impossible for the methyl ester 1 and the 1-adamantyl ester 7. Hence, the CH₃COO⁻ ions in the NCI mass spectra of 1 and 7 are either formed by a rather unusual cis 1,2-elimination of alkyl fluoride and alkylamine, respectively, from the tetrahedral intermediate, or the tetrahedral intermediate rearranges into a 'loose' complex of unknown structure which allows a combination of the fluorine atom or NH₂ group with the α-carbon atom of the original ester alkoxy group. Both reactions will have probably large activation energies and compete poorly with other fragmentation pathways of the tetrahedral intermediate. In the intermediates formed by the acetates and F⁻ (reaction (7a)) competing reactions are, besides cis β-elimination of alkene, transfer of a hydrogen atom from the acetyl group to the ester alkoxy group and subsequent elimination of an alcohol molecule, generating the fluoroenolate ion CH₂COF⁻, m/z 61. It can be seen clearly in Fig. 1 that these latter reactions predominate in the NCI(F⁻) mass spectra if the cis β-alkene elimination is not possible. This is plausible because one expects a smaller activation energy for hydrogen transfer and subsequent elimination than for a cis 1,2-elimination of an alkyl fluoride. If no hydrogen atoms in the position α to the carbonyl group are available for the transfer reaction in the tetrahedral intermediate, i.e. in the intermediate formed by methyl trimethylacetate (8), alkyl fluoride elimination appears to be the source of the carboxylate ions.

The intermediate formed by addition of NH₂⁻ to the ester carbonyl group (reaction (7b)) decomposes by the same pathways. However, the NCI(NH₂⁻) mass spectra of the trideuteroacetates 2a, 5a and 7a show that one of the hydrogen atoms of the NH₂ group is transferred during the elimination of the alcohol. Hence, alcohol elimination is still possible in the intermediate formed by the trimethylacetates 8 and 9 and, indeed, their NCI(NH₂⁻) mass spectra contain large peaks of the amide anion (see Fig. 2). Thus, the relative intensities of the amide anion and the trimethylacetate ion at m/z 100 and 101, respectively, in the spectrum of 8 reflect the relative rates of alcohol elimination and alkyl amine elimination from the tetrahedral intermediate, and the increase of the relative intensity of the trimethylacetate ions in the spectrum of 9 is due to the opening of a third reaction channel for the intermediate of this compound i.e. cis β-elimination of an alkene. Thus, the rates of the fragmentations of the tetrahedral intermediate from these esters and NH₂⁻ appear to be similar within a factor of 2. The reaction energy diagram (Fig. 3) shows that cis 1,2-elimination of an alkylamine from the tetrahedral

intermediate is exothermic, in contrast to the F⁻ system, and this may indicate a reduced activation energy of the amine elimination and explain the competition with the other fragmentations.

The intensity of the [M−H]⁻ ions is much larger in the NCI(NH₂⁻) mass spectra of the acetates than in the corresponding NCI(F⁻) spectra. As can be seen from the reaction energy diagram in Fig. 3 not only the proton abstraction from the acetate group by a NH₂⁻ ion is much more exothermic than deprotonation by a F⁻ ion (reaction (1)), but also the other fragmentations via a tetrahedral intermediate (reaction (7)). Hence, one would expect a similar competition between these reactions in both the NCI(NH₂⁻) and the NCI(F⁻) mass spectra. Two explanations can be given why this is not observed.

Firstly, the [M−H]⁻ ions are assumed to arise not from a direct proton abstraction from the ester molecule but via a tetrahedral intermediate by elimination of HF and NH₃, respectively. The MINDO/3 calculation of the reaction energies (Fig. 3) indicates that HF elimination from the addition complex is less exothermic than the other fragmentations of reaction (7a), while in reaction (7b) elimination of NH₃ from the tetrahedral intermediate is more exothermic than elimination of an alcohol molecule. Hence, in the NCI(F⁻) mass spectra of the acetates the formation of [M−H]⁻ ions by elimination of HF from the intermediates is less favoured than the elimination of an alcohol with formation of the fluoroenolate ion CH₂COF⁻ and the cis β-elimination of an alkene with formation of the acetate ion CH₃COO⁻. By contrast, in the NCI(NH₂⁻) mass spectra the formation of the [M−H]⁻ ion by elimination of NH₃ competes successfully with alcohol elimination and concomitant amide anion formation. This would explain why the intensity of the amide anion in the NCI(NH₂⁻) spectra of the acetates is always low and only the CH₃COO⁻ ion intensity increases.

The second explanation relies not only on the different thermochemistry of the reactions of the F⁻ and NH₂⁻ ions with ester molecules, but on a related different dynamic behaviour of these ion/molecule reactions. An ab initio study of nucleophilic addition to a carbonyl group has shown[15] that the nucleophile approaches the carbonyl group from the backside—as expected by ion/dipole interactions—and the carbonyl carbon atom becomes tetrahedrally coordinated after the nucleophile has reached a bonding distance. Assuming the same direction of approach for F⁻ and NH₂⁻, respectively, to the carbonyl group of the acetate molecules the nucleophile (or base) will come close to the hydrogen atoms at the α-carbon atom of the acetyl group, i.e. at least during the early stages the reaction coordinates of proton abstraction and of formation of the tetrahedral complex are identical. However, according to the Hammond postulate[16] the transition state for the very exothermic proton abstraction by NH₂⁻ will be 'early' on the reaction coordinate, but not for proton abstraction by F⁻, while rehybridization of the carbonyl function to the tetrahedral intermediate will be 'late' in both cases. A similar picture of these reactions follows from the valence bond description of Pross and Shaik for base-

catalysed eliminations and nucleophilic substitutions.[17] Following these arguments, all reactions of F^- with ester molecules including the formation of $[M-H]^-$ ions will be governed by the formation and fragmentation of the tetrahedral intermediate, while the proton abstraction by NH_2^- will occur independently before the tetrahedral addition complex is formed. This difference of the reaction mechanism and the dynamic behaviour of the system is reflected in the much higher intensities of the $[M-H]^-$ ions in the $NCI(NH_2^-)$ mass spectra.

EXPERIMENTAL

The NCI mass spectra were recorded with a VG ZAB-2F double focusing instrument with reversed geometry and a combined EI/CI source. The following conditions were used: electron energy, 50 eV; emission current, 0.2–0.5 mA (optimized for sample ion intensity); accelerating voltage, 6 kV; source temperature, c. 200 °C. The pressure at the ion gauge head below the source was $1-5 \times 10^{-5}$ Torr corresponding to a source pressure of c. 0.1–0.5 Torr and was optimized for sample ion intensity. The plasma gases used were commercial grade (tetrafluormethane Matheson, 99.7%; ammonia Matheson, 99.5%) and were used without further purification. The ion source was thoroughly flushed with the plasma gas and the desired primary plasma ions (NH_2^- or F^-) corresponded to more than 90% of the total plasma ion itensity. Furthermore, NH_2^- and F^- ions, respectively, was the only ions of which the intensity was reduced by sample introduction proving these ions to be the only reactive ones. Sample introduction was achieved via the septum inlet system at a temperature of 200 °C.

The acetates 1–3 and 5 were commercially available and purified by distillation. The acetates 4, 7, 2a and 7a and the trimethylacetates 8 and 9 were synthesized from the corresponding alcohols via standard methods.[19] The tertiary acetates 6 and 5a were synthesized with $ZnCl_2$ catalysis.[20]

The calculations were carried out by the standard MINDO/3 procedure together with the associated DFP geometry program.[21]

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