# Reactivity of mono-halogen carbene radical anions (CHX⁻·; X = F, Cl and Br) and the corresponding carbanions (CH₂X⁻; X = Cl and Br) in the gas phase

## Monique Born, Steen Ingemann and Nico M. M. Nibbering *

*Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

The gas-phase reactions of mono-halogen substituted carbene radical anions, CHX⁻· (X = F, Cl and Br) and the corresponding carbanions, CH₂X⁻ (X = Cl and Br) with halomethanes and organic esters have been examined with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The chlorine and bromine containing (radical) anions react by $S_N2$ substitution with the parent chloro- and bromo-methanes, whereas an $S_N2$ and/or a $B_{AC}2$ reaction occurs with the methyl ester of trifluoroacetic acid and dimethyl carbonate. The main features of the results are: (*i*) the $S_N2$ substitution of a given carbene radical anion with CH₃Cl or CH₃Br is less efficient than this reaction of the corresponding carbanion, (*ii*) the radical anions react less efficiently with dimethyl carbonate than the carbanions, (*iii*) the $S_N2$ substitution is less important for the radical anions than for the carbanions in the reactions with the two carbonyl compounds, (*iv*) for both types of ions, the $B_{AC}2$ pathway becomes relatively more important as the halogen atom is changed from chlorine to bromine. These findings are discussed in terms of the thermodynamics of the overall processes in combination with considerations of the potential energy surfaces which can describe these gas-phase processes.

## Introduction

The chemistry of (radical) ions is an important and established field of research as reflected in the relatively large number of condensed-phase reactions, which are known to involve such ionic species as intermediates.[1-7] Reactions of (radical) ions in the condensed phase are influenced inevitably by solvent molecules and/or counter ions whose presence often hampers experimental studies aimed at obtaining insight into the intrinsic stability and reactivity of the species of interest. A more direct approach to experimental studies of the intrinsic properties and reactivity of organic (radical) ions involves examination of the kinetics and thermodynamics of ion/molecule reactions in the gas phase.[8,9] In this respect, relatively little is known about the bimolecular chemistry of radical anions in the gas phase irrespective of the fact that these ions have been studied extensively in the condensed phase.[1,2] A major part of the reported studies concerned with organic radical anions in the gas phase is focussed on the determination of the electron affinities of the corresponding neutral species and/or the kinetic aspects of electron transfer reactions.[10-18] In addition, proton transfer reactions involving radical anions in the gas phase have been studied in a number of instances and these studies have resulted in the determination of the gas-phase acidities of various radicals,[15,19-25] such as the phenyl radical[22,23] and mono-halogen substituted methyl radicals.[25] In contrast with the number of reports concerned with the thermodynamic properties, relatively few studies have addressed the reactivity of organic radical anions in typical nucleophilic processes in the gas phase.[26-30] In particular, attack on a carbonyl group by carbene type species, such as the C₅H₄⁻· carbene radical anion derived from cyclopentadiene,[27] and the diphenylcarbene ion (C₆H₅)₂C⁻·, has been examined and, in addition, a study has been concerned with the interplay between 1,2- and 1,4- additions in reactions of the phenylnitrene radical anion, C₆H₅N⁻·, with α,β-unsaturated esters.[28]

The majority of the published studies concerned with radical anions in the gas phase are focussed entirely on the characterization of the reactions of these ions and do not include an examination of the reactivity of the corresponding anions. Experimental studies concerned with a comparison of the reactions of radical anions and the corresponding anions may be of particular importance in view of the discussion concerned with the reactivity of radical cations and cations towards nucleophiles. Based on the curve-crossing model[31,32] it has been proposed that radical cations should react less efficiently with neutral nucleophiles than cations.[33] This argument was based on the notion that in reactions of radical cations, the product configuration is doubly excited with respect to the reactants, while in reactions of cations with nucleophiles the electronic configuration describing the products is singly excited. This suggestion has been disputed on the basis of results for reactions occurring in the gas phase as well as in the condensed phase, which reveal that radical cations often react readily with nucleophiles.[34,35] Notwithstanding this discussion, it is an open question whether or not radical anions react less efficiently in the gas phase than the corresponding anions. The present study was initiated with the purpose of performing a more systematic investigation focussed on the possible reactivity difference between a given radical anion, A⁻·, and the corresponding anion, HA⁻, in gas-phase ion/molecule reactions. As model systems, the mono-halogen substituted carbene radical anions (CHX⁻·, X = F, Cl and Br) and the related halogen-substituted methyl anions (CH₂X⁻, X = Cl and Br) were selected since their thermodynamic properties have been determined.[25,36] As substrates, the halomethanes CH₃Cl and CH₃Br were chosen together with the carbonyl compounds, CF₃CO₂CH₃ and CH₃OCO₂CH₃. The former substrates were selected since the carbene radical anions as well as the halogen-substituted anions are likely to react with these species only by an $S_N2$ substitution, whereas the esters were chosen with the purpose of determining the possible interplay between $S_N2$ and $B_{AC}2$ reactions.

## Experimental

The experiments were performed with a Fourier transform ion cyclotron resonance (FT-ICR) instrument designed and

constructed at the University of Amsterdam.[37-39] In a typical experiment, the primary negative ions, $O^{-\cdot}$ and $NH_2^-$, were generated by dissociative attachment of electrons to $N_2O$ (electron energy: 1.2–1.5 eV) and $NH_3$ (electron energy: 5 eV), respectively. The duration of the electron beam pulse was normally 150 ms and the trapping of the ions was achieved by applying a voltage of $\approx -1$ V to the appropriate plates of the cubic inch cell located in a magnetic field of 1.23 T. Subsequently and during the electron beam pulse, the $O^{-\cdot}$ ions were allowed to react with one of the halogen-substituted methanes to generate the $CHX^{-\cdot}$ ions, whereas the $CH_2X^-$ anions were formed with the use of $NH_2^-$ as the Brønsted base. The $CHX^{-\cdot}$ and $CH_2X^-$ ions were isolated by ejecting all other ions from the cell by radio frequency (RF) pulses chosen such that off-resonance excitation of the remaining ions was minimized.[40] The reactions of the (radical) anions with the selected substrates were then followed as a function of time by varying the delay between the selection of the ions of interest and the start of the excitation pulse. The relative abundances of the ions were determined with an accuracy of about 2% following procedures described previously.[25,38] The formation of primary negative ions from the halomethanes or the methyl ester of trifluoroacetic acid during the period in which the (radical) anions were allowed to react with the given substrate was prevented by continuous ejection of the low-energy electrons from the FT-ICR cell.[41]

The total pressure in the cell was in most experiments in the range $5 \times 10^{-5}$ to $10^{-4}$ Pa as measured with an uncalibrated ionization gauge placed in a side arm of the main vacuum system. The ratio of the partial pressures of $N_2O$ and the halogen-substituted methane was typically 1:1. The partial pressure of an additional halogen-substituted methane was similar to the pressure of the other neutral compounds in the cell, whereas the pressure of the methyl ester of trifluoroacetic acid was lower than of the other species in most experiments. With dimethyl carbonate, a series of experiments was performed with a different partial pressure of this substrate (ranging from $1 \times 10^{-5}$ to $6 \times 10^{-5}$ Pa). The temperature of the trapping plate situated opposite the filament side was roughly 330 K, whereas the inlet systems, leak valves and the vacuum vessel of the instrument were at room temperature.

## Materials
Most of the chemicals used in this study were commercially available and used without further purification. The $CD_3OCO_2CD_3$ compound (>99% $D_3$) was prepared by reacting dry silver carbonate with $CD_3I$ in a sealed tube which was heated to 60 °C in a rocking furnace for about 60 h.[42] Subsequently, the crude product was distilled prior to use and the identity of the sample was ascertained with the use of mass spectrometry.

## Results
The present experimental approach to the study of the reactivity of the $CHX^{-\cdot}$ (X = F, Cl and Br) radical anions and the related carbanions ($CH_2X^-$, X = Cl and Br) involves the determination of the product ion distributions and the kinetic aspects of their reactions with the halomethanes, $CH_3Cl$ and $CH_3Br$, and the carbonyl containing compounds, $CF_3CO_2CH_3$ and $CH_3OCO_2CH_3$. A complication in these experiments arises from the fact that not only is the substrate present in the cell of the FT-ICR instrument, but also the parent compound of the (radical) anions. In addition, nitrous oxide is present in the cell in the experiments with the carbene radical anions since these ions are generated by a formal $H_2^{+\cdot}$ abstraction in the reaction of the $O^{-\cdot}$ ion (see the Experimental) with the parent halomethane as indicated in eqn. (1) and detailed elsewhere.[25] In the
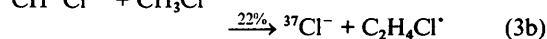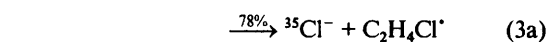
$$O^{-\cdot} + CH_3X \longrightarrow CHX^{-\cdot} + H_2O \qquad (1)$$

experiments with the $CH_2Cl^-$ and $CH_2Br^-$ carbanions, nitrous oxide is replaced by ammonia since the $NH_2^-$ ion reacts efficiently with the chloro- and bromo-methanes by proton abstraction as shown in eqn. (2). The presence of various

$$NH_2^- + CH_3X \longrightarrow CH_2X^- + NH_3 \qquad (2)$$
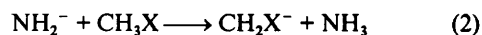
neutral species in the FT-ICR cell requires, of course, that the possible reactions of the different (radical) anions with these neutral species are characterized prior to the examination of the reactions with one of the selected substrates.

### Reactions with halomethanes
These experiments were focussed on the reactions of the $CHCl^{-\cdot}$ and $CH_2Cl^-$ ions with $CH_3Br$ as the substrate in combination with the reactions of the comparable bromine-containing (radical) anions with $CH_3Cl$. With respect to the carbene radical anions, a previous study from our group indicated that these ions are unreactive toward nitrous oxide, whereas they react slowly with their parent halomethane.[25] In these reactions, halide ions are formed that originate in part from the parent halomethane and in part from the reactant radical anion. This is observed when for example, the $CH^{35}Cl^{-\cdot}$ ion is selected and allowed to react with the parent halomethane, $CH_3Cl$. In this reaction slightly more of the $^{35}Cl^-$ ions relative to the $^{37}Cl^-$ ions is generated [eqn. (3)] than expected

$$CH^{35}Cl^{-\cdot} + CH_3Cl \quad \xrightarrow{78\%} \quad ^{35}Cl^- + C_2H_4Cl^{\cdot} \qquad (3a)$$
$$\xrightarrow{22\%} \quad ^{37}Cl^- + C_2H_4Cl^{\cdot} \qquad (3b)$$

for the sole occurrence of a direct substitution reaction, which would yield the isotopic chloride ions in their natural abundance ratio (75% $^{35}Cl^-$ and 25% $^{37}Cl^-$).

Fortunately, the same ratio between the isotopic chloride ions as given in eqn. (3) is obtained if the $CH^{35}Cl^{-\cdot}$ ion is allowed to react with $CH_3Cl$ in the presence of $CH_3Br$. This finding indicates that no chloride ions are formed in the reaction with the latter substrate, or stated otherwise, the $CHCl^{-\cdot}$ ions react with $CH_3Br$ to afford only bromide ions as shown in eqn. (4). Similar

$$CHCl^{-\cdot} + CH_3Br \longrightarrow CH_3\dot{C}HCl + Br^- \qquad (4)$$
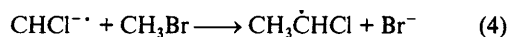
experiments with the $CH^{79}Br^{-\cdot}$ ion show that this ion reacts with the parent halomethane to afford the $^{79}Br^-$ and $^{81}Br^-$ ions in an abundance ratio of 53:47. This ratio indicates that the $^{79}Br^-$ ions arises to a minor extent from the reactant radical anion since a direct substitution process is expected to yield the isotopic bromide ions in an essentially 1:1 abundance ratio. The relative abundances of the isotopic bromide ions are observed to be independent of the additional presence of $CH_3Cl$ in the FT-ICR cell, that is the $CHBr^{-\cdot}$ ion reacts with $CH_3Cl$ to afford exclusively chloride ions.

A comparable complication arises for the $CH_2X^-$ (X = Cl and Br) carbanions which also react with the parent halomethanes to afford $X^-$ ions arising in part from the reactant ion. In addition, the $CH_2X^-$ ions react with the ammonia molecules present in the FT-ICR cell with formation of $X^-$ ions as detailed in previous reports from our group.[36,43] Similarly to the experiments with the carbene radical anions, the relative abundances of the isotopic chloride or bromide ions formed in the reactions with ammonia and the parent halomethanes were determined prior to the addition of the second halomethane. As observed for the carbene radical anions, no change in the relative abundances of the isotopic halide ions was observed in the presence of the second halomethane. In other words, the reaction of the $CH_2Cl^-$ ion with $CH_3Br$ is concluded to lead only to $Br^-$ ions and likewise, the reaction of the $CH_2Br^-$ ion with $CH_3Cl$ yields only $Cl^-$ ions as shown in eqn. (5).
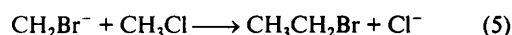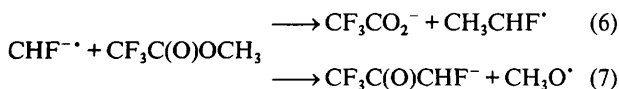
$$CH_2Br^- + CH_3Cl \longrightarrow CH_3CH_2Br + Cl^- \qquad (5)$$

**Table 1** Normalized and corrected distributions of the abundances of the product ions formed in the reactions of the radical anions CHX⁻• (X = F, Cl and Br) and anions CH₂X⁻ (X = Cl and Br) with CF₃CO₂CH₃, CH₃OCO₂CH₃ and CD₃OCO₂CD₃[a]

| Substrate | Product ions[b] | CHF⁻• | CHCl⁻• | CHBr⁻• | CH₂Cl⁻ | CH₂Br⁻ |
|---|---|---|---|---|---|---|
| CF₃CO₂CH₃ | X⁻ | — | 15 | 30 | 15 | 40 |
| | CF₃⁻[c] | 5 | — | — | 5 | 5 |
| | CF₃C(O)CHX⁻ | 10 | 30 | 40 | | |
| | CF₃CO₂⁻ | 85 | 55 | 30 | 80 | 55 |
| CH₃OCO₂CH₃ | X⁻ | — | 40 | 75 | 25 | 80 |
| | C₂HXO⁻• | 35 | 60 | 25 | | |
| | CH₃OC(O)CX⁻• | 5 | — | — | | |
| | CH₃OC(O)CHX⁻ | | | | 50 | 10 |
| | CH₃OCO₂⁻ | 60 | — | — | 25 | 10 |
| CD₃OCO₂CD₃ | X⁻ | — | 35 | 100 | 30 | 80 |
| | C₂DXO⁻• | 25 | 30 | | | |
| | CD₃OC(O)CX⁻• | 25 | 30 | traces | | |
| | CD₃OC(O)CHX⁻ | | | | 50 | 10 |
| | CD₃OCO₂⁻ | 50 | 5 | — | 20 | 10 |

[a] See the text; the normalized product ion distributions are reproducible to within 5%. [b] Assumed structures of the product ions. [c] The generation of the CF₃⁻ ions can be ascribed to dissociation of some of the CF₃CO₂⁻ ions formed in the $S_N2$ substitution. The formation of CF₃⁻ as the final product ion of the $S_N2$ pathway is estimated to be exothermic for all reactant ions.

## Reactions with carbonyl compounds

In the experiments concerned with the distribution of the product ions formed in the reactions with the esters, nitrous oxide or ammonia is also present in the cell together with the appropriate parent halomethane. In the experiments with the CHF⁻• ion, the additional presence of $N_2O$ and CH₃F in the FT-ICR cell appeared not to be a complication since no disturbing reactions occur between the CHF⁻• ion and these neutral species. In the reactions of CHF⁻• with the methyl ester of trifluoroacetic acid, CF₃CO₂⁻ and CF₃C(O)CHF⁻ ions [eqns. (6) and (7)] are formed together with minor amounts of CF₃⁻ ions (Table 1).

$$CHF^{-\bullet} + CF_3C(O)OCH_3 \longrightarrow CF_3CO_2^- + CH_3CHF^{\bullet} \quad (6)$$

$$\longrightarrow CF_3C(O)CHF^- + CH_3O^{\bullet} \quad (7)$$

Likewise, in the reaction of CHCl⁻• with the methyl ester of trifluoroacetic acid, CF₃CO₂⁻ and CF₃C(O)CHCl⁻ ions are formed (Table 1). However, if the CH³⁵Cl⁻• ion is allowed to react with this ester in the presence of chloromethane, the ³⁵Cl⁻ and ³⁷Cl⁻ ions are formed in an abundance ratio of 90:10 (ratio between the partial pressures of the ester and chloromethane: 1:1; see also the Experimental). This abundance ratio between the isotopic chloride ions is significantly different from that obtained for the reaction between the CH³⁵Cl⁻• ion and chloromethane [see eqn. (3)] in the sense that a higher relative yield of the ³⁵Cl⁻ ion is obtained with CF₃CO₂CH₃ present in the system. In other words, the ³⁵Cl⁻ ions are formed in part as a result of the reaction of the CH³⁵Cl⁻• ion with the ester [eqn. (8); see also the Discussion].

$$CH^{35}Cl^{-\bullet} + CF_3C(O)OCH_3 \longrightarrow$$
$$^{35}Cl^- + \text{neutral products} \quad (8)$$
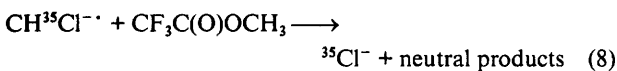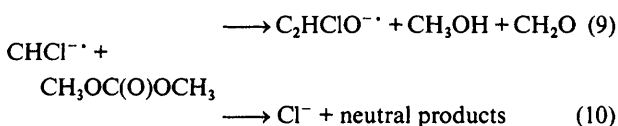
The relative contribution to the total abundance of the ³⁵Cl⁻ ions from the reaction with the ester can now be estimated relatively easily since the ³⁷Cl⁻ ions are formed only in the reaction with CH₃Cl whereas the ³⁵Cl⁻ ions arise in the reactions with both substrates. This estimate involves multiplication of the normalized abundance of the ³⁷Cl⁻ ions formed in the experiments with both substrates present in the FT-ICR cell with the ratio between the normalized abundances of the isotopic chloride ions formed in the independent experiments with CH₃Cl as the sole substrate [(78/22) × 10 ≈ 35; see also eqn. (3)]. Corrected for the contribution from the reaction with CH₃Cl, this leads to the result that about 60% {[(90 − 35)/90] × 100} of

the total amount of the ³⁵Cl⁻ ions are formed in the reaction with the methyl ester of trifluoroacetic acid. In combination with the relative yields of the other product ions formed in the reaction of the CHCl⁻• ion with the ester, it is finally estimated that this carbene radical anion reacts with CF₃CO₂CH₃ to afford 15% Cl⁻ ions, 30% CF₃C(O)CHCl⁻ ions and 55% of the CF₃CO₂⁻ ions as indicated in Table 1.

Similarly, the CHBr⁻• ion reacts with the methyl ester of trifluoroacetic acid to form not only CF₃C(O)CHBr⁻ and CF₃CO₂⁻, but also bromide ions as shown in Table 1. The formation of bromide ions in this system is revealed also by the determination of the relative yields of the isotopic bromide ions formed in experiments in which the CH⁷⁹Br⁻• ion is selected and allowed to react with the various neutral species present in the cell. If the partial pressures of the ester and CH₃Br are equal (see the Experimental), the ⁷⁹Br⁻ and ⁸¹Br⁻ ions are formed in an abundance ratio of 75:25, whereas the reaction with CH₃Br alone yields these ions in a ratio of 53:47 (*vide supra*). Following the same procedure as outlined for the CH³⁵Cl⁻• ion, 62% of the total yield of the ⁷⁹Br⁻ ions is estimated to arise from the reaction with the ester, thus leading to the relative yields of the various product ions given in Table 1.

For the carbanions, it is observed that the CH₂Cl⁻ ion reacts with the methyl ester of trifluoroacetic acid to yield CF₃CO₂⁻ and Cl⁻ ions. In the experiments with the CH₂Br⁻ ion, CF₃CO₂⁻ is also the major ionic product even though the tendency to form halide ions is more pronounced in this system than if CH₂Cl⁻ is the reactant species. The relative yields of the halide ions generated in the reactions of these anions with the ester and given in Table 1 were determined as described for the carbene radical anions.

With dimethyl carbonate as the substrate, CHF⁻• reacts to afford CH₃OCO₂⁻ ions together with two radical anions, CH₃OC(O)CF⁻• and C₂HFO⁻•. In the reaction between CHCl⁻• and dimethyl carbonate, C₂HClO⁻• and Cl⁻ ions are generated [eqns. (9) and (10)] in relative yields, which were

$$CHCl^{-\bullet} + CH_3OC(O)OCH_3 \longrightarrow C_2HClO^{-\bullet} + CH_3OH + CH_2O \quad (9)$$

$$\longrightarrow Cl^- + \text{neutral products} \quad (10)$$

determined by the same procedure as outlined for the experiments with CF₃CO₂CH₃ as the substrate. Likewise, the CHBr⁻• ion reacts with dimethyl carbonate to afford significant amounts of bromide ions in addition to a C₂HBrO⁻• ion (Table 1).

A marked influence on the product ion distributions is observed upon the introduction of deuterium atoms into dimethyl carbonate, that is in the reactions of the CHF⁻˙ ion with $CD_3OC(O)OCD_3$, the $CD_3OC(O)CF^{-\cdot}$ and $C_2DFO^{-\cdot}$ ions are formed in an abundance ratio of 25:25, whereas in the reaction of this particular carbene radical anion with the unlabelled carbonate the ratio between these product ions is 5:35 (Table 1). An even more drastic influence on the product ion distributions is observed if CHCl⁻˙ or CHBr⁻˙ is the reactant ion. In particular, in the reaction of the CHCl⁻˙ radical anion with the labelled dimethyl carbonate the relative abundances of the $CD_3OC(O)CCl^{-\cdot}$ and the $C_2DClO^{-\cdot}$ ions are essentially the same, whereas only the latter ion is formed in the reaction with the unlabelled substrate. In addition, minor amounts of $CD_3OCO_2^-$ ions are generated in the reaction with the labelled dimethyl carbonate. For the CHBr⁻˙ ion, the introduction of deuterium atoms into the substrate results in the almost exclusive formation of Br⁻, in contrast with the reaction with the unlabelled dimethyl carbonate, which leads to 25% of the $C_2HBrO^{-\cdot}$ radical anion in addition to the bromide ions.

The $CH_2Cl^-$ ion also reacts with dimethyl carbonate to afford chloride ions together with $CH_3OCO_2^-$ and $CH_3OC(O)CHCl^-$ ions (Table 1) and a similar reactivity pattern is observed for the $CH_2Br^-$ carbanion. However, the product ion abundances of the reactions of the two carbanions with dimethyl carbonate appear to be unaffected by the introduction of deuterium atoms, in contrast with the behaviour observed for the corresponding radical anions (*vide supra*).

A few experiments were performed with the iodine-containing ions, CHI⁻˙ and $CH_2I^-$. These ions react mainly or almost exclusively with dimethyl carbonate to afford I⁻ and only traces of other ionic species were observed, in particular at relatively high pressures of the substrate ($\approx 10^{-4}$ Pa). For this reason, the iodine-containing (radical) anions were not examined further.

### Reaction efficiencies

The reactions occurring under the experimental conditions typical of the FT-ICR method are described by pseudo-first-order kinetics since the number of ions is about a factor of $10^4$ lower than the number of neutral species. In general, the second-order rate constant for a given ion/molecule reaction in the gas phase is obtained by first determining the slope of the linear plot of the natural logarithm of the normalized abundance of the reactant ion as a function of time. Subsequently, this slope is divided by the particle density (expressed as number of molecules $\times$ cm⁻³) of the substrate present in the instrument. For the systems examined in this study, the occurrence of the reactions of the (radical) anions with neutral species present in the FT-ICR cell other than the selected substrate poses limits to the experiments pertaining to the reactivity of the ions of interest. The overall kinetics of the different reactions, however, is still pseudo-first-order. This allows the pseudo-first-order rate constant for the reaction between a (radical) anion and a given substrate to be obtained as the difference between the total rate constant and the rate constant of the reaction with the parent halomethane as determined in an independent experiment.

The experimental determination of the rate constants in Table 2 is exemplified by the results shown in Fig. 1 for the reaction between CHCl⁻˙ and $CH_3Cl$ and the combined reactions of this radical anion with $CH_3Cl$ and with $CH_3Br$. The difference between the slopes of the two regression lines in Fig. 1 leads then to the pseudo-first-order rate constant for the reaction of CHCl⁻˙ with $CH_3Br$. Subsequently, the second-order rate constant can be obtained if the particle density of $CH_3Br$ in the FT-ICR cell can be estimated. This estimation requires knowledge of the temperature of the reactant chemical system and the true pressure of the substrate. Normally, the temperature of the reactant chemical system is assumed to be 298 K irrespective of the fact that the pressure in the instrument is too low for a true thermodynamic temperature to be assigned to the system. With respect to the pressure of the substrate, the ionization gauge readings (see the Experimental) of $CH_3Br$ and $CH_3Cl$ have been corrected following the procedure described in a recent report.[44]

The final values for the rate constants of the reactions of the CHCl⁻˙ ion with $CH_3Br$ and the CHBr⁻˙ ion with $CH_3Cl$ are given in Table 2 together with the values for the reactions of the $CH_2Cl^-$ and $CH_2Br^-$ carbanions. Table 2 also lists the reaction efficiencies of these processes as given by the ratio between the experimental rate constant and the collision rate constant estimated by means of the average dipole orientation theory.[45-47] In addition, the efficiencies of the processes are given relative to the efficiency of the reaction between the CHBr⁻˙ ion and $CH_3Cl$.

For the methyl ester of trifluoroacetic acid, a number of kinetic experiments—performed as described for the reactions with the halomethanes—revealed that both the radical anions and the carbanions react readily with this substrate. These experiments lead also to the pseudo-first-order rate constants for the reactions with the methyl ester of trifluoroacetic acid which can be used to estimate the relative efficiencies. This estimation of the relative efficiencies is based on the fact that the relative collision rates between the different ions with the ester depend only on the reduced mass of the system.[45] With this correction,
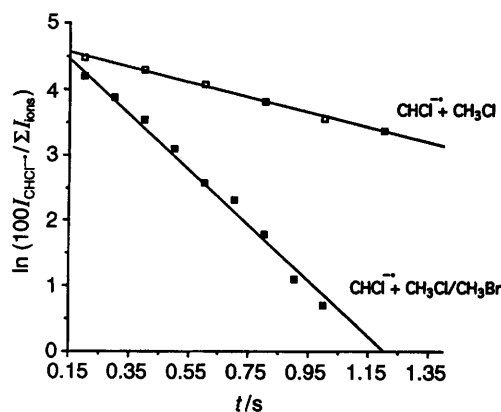


Fig. 1 Natural logarithm of the normalized abundance of the reactant CHCl⁻˙ ion as a function of reaction time for (*i*) the reaction with the parent compound, $CH_3Cl$ and (*ii*) the reactions with $CH_3Cl$ and $CH_3Br$ (see also the text)

**Table 2** Second-order rate constants and (relative) efficiencies for the reactions of CHX⁻˙ and $CH_2X^-$ ions, respectively, with the halomethanes, $CH_3Cl$ and $CH_3Br$ (see the text)

| Ion | Substrate | Rate constant $k/10^{-10}$ cm³ molecule⁻¹ s⁻¹ | Efficiency[a] | Relative efficiency |
|---|---|---|---|---|
| CHBr⁻˙ | $CH_3Cl$ | 0.8 | 0.05 | 1 |
| $CH_2Br^-$ | $CH_3Cl$ | 1.1 | 0.1 | 2 |
| CHCl⁻˙ | $CH_3Br$ | 3.9 | 0.25 | 5 |
| $CH_2Cl^-$ | $CH_3Br$ | 6.5 | 0.4 | 8 |

[a] The efficiency of a given reaction was determined as the ratio between the experimental rate constant and the collision rate constant calculated by the average dipole orientation theory, ADO (see also the text and refs. 45–47).

**Table 3** Relative importances (%) of the $S_N2$ and $B_{AC}2$ pathways in the reactions of the (radical) anions with the methyl ester of trifluoroacetic acid and dimethyl carbonate

| Ions (A⁻˙/HA⁻) | $E_{ea}$ (A/HA˙)[a] | $CF_3CO_2CH_3$ | | Relative efficiency[b] | $CH_3OCO_2CH_3$ | | Relative efficiency[b] | $CD_3OCO_2CD_3$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | $S_N2$ | $B_{AC}2$ | | $S_N2$ | $B_{AC}2$ | | $S_N2$ | $B_{AC}2$ |
| CHF⁻˙ | 52 | 90 | 10 | 1 | 60 | 40 | 5 | 50 | 50 |
| CHCl⁻˙ | 117 | 50 | 50 | 1 | — | 100 | 2 | 10 | 90 |
| CHBr⁻˙ | 140 | 30 | 70 | 1 | — | 100 | 1 | — | 100 |
| $CH_2Cl^-$ | 77 | 80 | 20 | 1 | 25 | 75 | 8 | 20 | 80 |
| $CH_2Br^-$ | 96 | 60 | 40 | 1 | 10 | 90 | 4 | 10 | 90 |

[a] Values in kJ mol⁻¹. The $E_{ea}$ values are taken from refs. 25 and 66. [b] The relative efficiencies were obtained as outlined in the text.
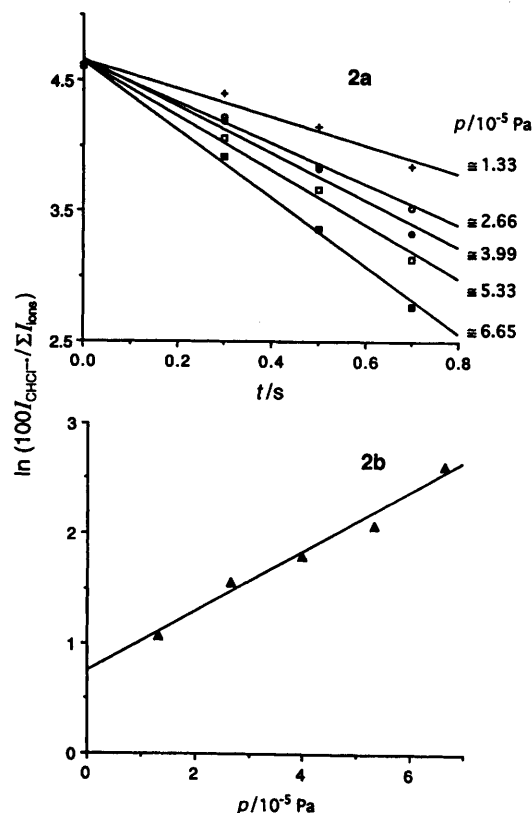


**Fig. 2** (*a*) Natural logarithm of the normalized abundance of the reactant CHCl⁻˙ ion as a function of time at five different pressures of dimethyl carbonate in the FT-ICR cell; (*b*) the slopes of the linear regression lines shown in Fig. 2(*a*) as a function of the pressure of dimethyl carbonate (see also the text)

all reactions with the trifluoroacetic acid methyl ester turned out to proceed with equal efficiency indicating that these processes may be collision-controlled under the present experimental conditions in line with other observations that show that this ester often reacts exceedingly fast with negative ions in the gas phase.[48]

The reactions of the various (radical) anions with dimethyl carbonate proved to be relatively slow. In order to obtain the relative efficiencies of the reactions with dimethyl carbonate unperturbed by other processes, it was decided to determine the time dependence of the natural logarithm of the normalized abundance of a given reactant ion at different pressures of this substrate. This is illustrated in Fig. 2(*a*) for a series of independent experiments concerning the reactions between the CHCl⁻˙ radical anion and the carbonate. At each pressure, the slope of the regression line represents the observed sum of the pseudo-first-order rate constants for the various reactions. The slopes of the linear regression lines were plotted as a function of the pressures of the substrate as shown in Fig. 2(*b*). The linear dependence of these slopes on the pressure of
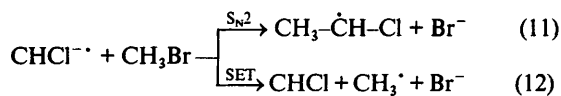
dimethyl carbonate leads to the second-order rate constant uncorrected for the difference between the pressure as measured by the ionization gauge (see the Experimental) and the true pressure of the carbonate. A correction of the ionization gauge readings of the pressure of the dimethyl carbonate was not attempted owing to the absence of a suitable correction procedure which would require known values for the rate constants of a number of ion/molecule reactions with this substrate. The relative efficiencies of the reactions of the (radical) anions, however, can be obtained relatively easily by correction of the kinetic results for the differences in the reduced mass of the reactant systems (*vide supra*). The final relative efficiencies given in Table 3 show that the reactivity of the radical anions towards dimethyl carbonate decreases in the series CHF⁻˙, CHCl⁻˙ and CHBr⁻˙. Similarly, the $CH_2Cl^-$ reacts faster with dimethyl carbonate than the bromine-containing carbanion, $CH_2Br^-$. In addition, a given radical anion is observed to react a factor of four times slower than the related halogen-containing carbanion.

## Discussion

The main emphasis in the present study is a comparison of the reactivity of the mono-halogen substituted carbene radical anions and the related carbanions. With respect to the reactions with the halomethanes, these appear relatively simple in the sense that the CHCl⁻˙ and $CH_2Cl^-$ ions react with $CH_3Br$ to yield Br⁻ as the sole ionic product. Similarly, in the reactions of CHBr⁻˙ or $CH_2Br^-$ with $CH_3Cl$ only Cl⁻ ions arise. In contrast, the experiments with the reactions of the different (radical) anions with $CF_3CO_2CH_3$ and $CH_3OCO_2CH_3$ reveal a somewhat more complex chemistry involving the formation of carboxylate anions, $CF_3CO_2^-$ and $CH_3OCO_2^-$, respectively, as well as a number of other product ions including halide ions originating from the reactant (radical) anions. Some of the other product ions are inclined to involve initial attack on the carbonyl group as exemplified by the $CF_3C(O)CHX^-$ ions generated in the reactions of the CHX⁻˙ ion with the methyl ester of trifluoroacetic acid or the $CH_3OC(O)CHX^-$ ions formed in the reactions of the $CH_2X^-$ ions with dimethyl carbonate. The assignment of a mechanism to the pathway that leads to the formation of halide ions in the reactions with the esters is obviously less straightforward. However, the halide ions are formed in significant yields in most of the reactant systems indicating that the processes leading to these product ions cannot be neglected in the ensuing discussion of the reactivity of (radical) anions toward the esters.

### $S_N2$ substitution and/or electron transfer

With respect to the formation of halide ions in the reactions with halomethanes and the carboxylate anions in the reactions with the carbonyl compounds, these ions may arise, in principle, by an $S_N2$ substitution and/or by a dissociative single electron transfer (SET)[1,5-7] process as exemplified in eqns. (11) and (12) for the reaction of the CHCl⁻˙ ion with $CH_3Br$.

$$CHCl^{-\cdot} + CH_3Br \begin{cases} \xrightarrow{S_N2} CH_3-\dot{C}H-Cl + Br^- & (11) \\ \xrightarrow{SET} CHCl + CH_3^{\cdot} + Br^- & (12) \end{cases}$$

Both processes lead to $Br^-$ ions but different neutral products. The latter products are not detected with the present experimental method, which precludes a direct distinction between the possible pathways leading to the halide ions in the reactions with halomethanes. In keeping with the fact that only exoergic or thermoneutral reactions normally occur under the present experimental conditions, thermodynamic considerations of the overall processes may be used to assign possible mechanisms for the formation of the halide ions. For example, the $S_N2$ reaction between $CHCl^{-\cdot}$ and $CH_3Br$ is estimated to be exothermic by 294 kJ $mol^{-1}$, whereas the SET process is endothermic by 91 kJ $mol^{-1}$ (Table 4).[25,49–51] The entropy change in the former process is considered to be relatively small, whereas the latter reaction is associated with a favourable change in entropy caused mainly by the transformation of two reactants into one ionic product and two neutral species [eqn. (12)]. This entropy change is estimated to be $\approx 105$ J $K^{-1}$ $mol^{-1}$.[49,51] With an assumed temperature of 298 K of the reactant chemical system, the change in the Gibbs energy for the dissociative electron transfer process becomes roughly 60 kJ $mol^{-1}$. The occurrence of electron transfer can thus be excluded for the $CHCl^{-\cdot}/CH_3Br$ system. Likewise, the $S_N2$ process is estimated to be strongly exothermic for reactions of the other (radical) anions with the halomethanes, whereas the SET process is energetically disfavoured (Table 4). In conclusion, the substitution reaction is considered to be responsible for the formation of halide ions in the reactions of the (radical) anions with chloro- and bromo-methane.

Similarly, the (radical) anions can react with the methyl ester of trifluoroacetic acid by an $S_N2$ substitution and/or a dissociative electron transfer. Both processes lead to the same ionic product, $CF_3CO_2^-$, but different neutral products. With respect to the $S_N2$ substitution, this process is estimated to be strongly exothermic for all reactant ions (Table 4; see also the Appendix). For $CHF^{-\cdot}$, dissociative electron transfer is associated with a negligible reaction enthalpy, whereas electron transfer from the other (radical) anions to the methyl ester of trifluoroacetic acid is estimated to be endothermic. The electron transfer pathway is also favoured for these systems by a change in entropy, which causes this pathway to be energetically feasible for the $CHF^{-\cdot}$ and $CH_2Cl^-$ ions as shown in Table 4. Taken together, the thermodynamic considerations for the formation of the $CF_3CO_2^-$ ions in the reactions with $CF_3CO_2CH_3$ indicate that this product ion is formed by an $S_N2$ substitution if $CHCl^{-\cdot}$, $CHBr^{-\cdot}$ or $CH_2Br^-$ is the reactant ion, whereas electron transfer may play a role in the reactions of the $CHF^{-\cdot}$ and $CH_2Cl^-$ ions.

**Table 4** Thermodynamics of the $S_N2$ substitutions and dissociative single electron transfer (SET) reactions of the (radical) anions with $CH_3Cl$, $CH_3Br$ and $CF_3CO_2CH_3$ (all values in kJ $mol^{-1}$)[a,b]

| Substrate | Ion | $\Delta H_r^\circ(S_N2)$ | $\Delta H_r^\circ(SET)$ | $\Delta G_r^\circ(SET)$[c] |
|---|---|---|---|---|
| $CH_3Cl$ | $CHBr^{-\cdot}$ | $-264$ | 144 | 112 |
| | $CH_2Br^-$ | $-282$ | 99 | 67 |
| $CH_3Br$ | $CHCl^{-\cdot}$ | $-294$ | 91 | 59 |
| | $CH_2Cl^-$ | $-332$ | 49 | 17 |
| $CF_3CO_2CH_3$ | $CHF^{-\cdot}$ | $-317$ | 2 | $-32$ |
| | $CHCl^{-\cdot}$ | $-317$ | 67 | 33 |
| | $CHBr^{-\cdot}$ | $-317$ | 90 | 56 |
| | $CH_2Cl^-$ | $-356$ | 25 | $-9$ |
| | $CH_2Br^-$ | $-336$ | 45 | 11 |

[a] Estimated with the use of data given in refs. 25, 49–51. [b] Temperature assumed to be 298 K. [c] The $T\Delta S_r^\circ$ term is estimated to be about 32 kJ $mol^{-1}$ for the reactions with the halomethanes and about 34 kJ $mol^{-1}$ for the reactions with the methyl ester of trifluoroacetic acid.

For the formation of the $CH_3OCO_2^-$ ions in the reactions with dimethyl carbonate, the absence of a reliable enthalpy of formation for this ion hampers thermodynamic considerations with respect to the occurrence of an $S_N2$ substitution and/or a dissociative electron transfer reaction. However, in analogy with the reactions of the various ions with the methyl ester of trifluoroacetic acid, it might be expected that the $S_N2$ process is energetically favoured and that electron transfer leading to $CH_3OCO_2^-$ is possible only for the $CHF^{-\cdot}$ and $CH_2Cl^-$ ions.

### $B_{AC}2$ reaction and halide ion formation

The occurrence of attack on the carbonyl group in the methyl ester of trifluoroacetic acid by the carbene radical anions is revealed by the formation of $CF_3C(O)CHX^-$ ions (X = F, Cl and Br; Table 1). For $CHF^{-\cdot}$, this pathway is of minor importance as compared with the reaction yielding the $CF_3CO_2^-$ ions. In contrast, the chlorine- and bromine-containing radical anions react to afford relatively abundant $CF_3C(O)CHX^-$ ions. The pathway leading to these product ions is indicated in Scheme 1 as involving the formation of a tetrahedral inter-
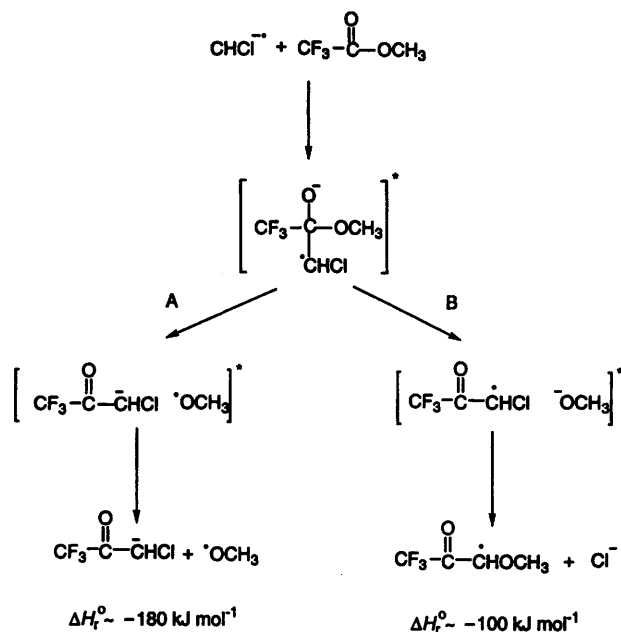


**Scheme 1** Proposed mechanism for attack on the carbonyl group of the methyl ester of trifluoroacetic acid by the $CHCl^{-\cdot}$ radical anion. The tetrahedral intermediate is indicated to dissociate either by a homolytic cleavage (pathway A) or a heterolytic cleavage (pathway B). The ion–neutral complex formed in pathway A dissociates directly to the observed product ion and a methoxyl radical, whereas the complex formed in pathway B is suggested to react further with formation of $Cl^-$ as the final product ion. The enthalpy changes given in the scheme refer to the overall processes.

mediate which reacts to form a complex of the $CF_3C(O)CHX^-$ ion and a $CH_3O^{\cdot}$ radical prior to dissociation. The overall process is estimated to be exothermic by about 180 kJ $mol^{-1}$ for the $CHCl^{-\cdot}$ ion as the reactant species (see Scheme 1; see also the Appendix) and a similar exothermicity is obtained for the $CHBr^{-\cdot}$ ion.

In addition, the chlorine- and the bromine-containing radical anions react with the methyl ester of trifluoroacetic acid to form relatively abundant halide ions (see Table 1 and Results). These halide ions can, in principle, arise by a number of pathways including an initial $S_N2$ substitution with formation of a complex composed of a $CF_3CO_2^-$ ion and a halogen-containing neutral species as indicated in Scheme 2 for the $CHCl^{-\cdot}$ ion. The complex thus formed may react further either by a substitution process (pathway A) or by an elimination-type reaction (pathway B) with the formation of free halide ions.
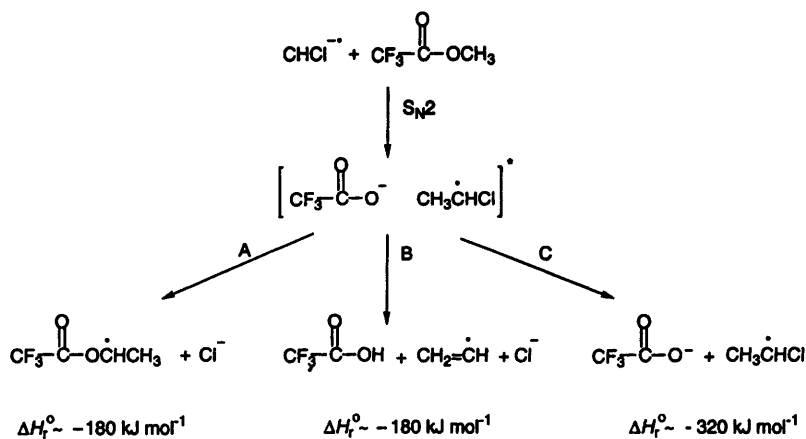
**Scheme 2** Proposed pathways leading to the $Cl^-$ and $CF_3CO_2^-$ ions in the reactions of the $CHCl^{-\bullet}$ radical anion with the methyl ester of trifluoroacetic acid. The initial step is suggested to be an $S_N2$ substitution with formation of an ion–neutral complex. This complex may react further with formation of $Cl^-$ ions by undergoing an $S_N2$ substitution (pathway A) or an elimination process (pathway B), whereas the $CF_3CO_2^-$ ions arise by a simple dissociation of the complex (pathway C). The enthalpy changes given in the scheme refer to the overall processes.

Both of the overall processes are estimated to be exothermic (Scheme 2) and a similar situation holds for the comparable overall reactions of the $CHBr^{-\bullet}$ radical anion.

Notwithstanding that the overall processes shown in Scheme 2 are estimated to be exothermic, the formation of halide ions by such pathways is unlikely. The main reason for this is that the direct $S_N2$ process leading to the $CF_3CO_2^-$ ion is exothermic by more than 300 kJ mol$^{-1}$ for all reactant (radical) anions (Table 4). This indicates that the assumed $[CF_3CO_2^- \ CH_3\dot{C}HCl]^*$ complex (pathway C in Scheme 2) is generated with a considerable amount of internal energy. At relatively large internal energies, such a complex is likely to undergo direct dissociation into free components instead of reacting further by an additional $S_N2$ and/or elimination-type process. This is in line with the expectation that both of these secondary reactions are likely to be associated with an energy barrier and with the reported decrease in the rate of a number of simple exothermic substitution processes in the gas phase as the internal energy of the reactant system is increased.[52] This implies that the halide ions are formed by a route that is distinct from the pathways shown in Scheme 2. A possible route may involve initial carbonyl group attack and formation of a $[CF_3C(O)\dot{C}HCl \ CH_3O^-]^*$ complex (pathway B in Scheme 1). Direct dissociation of this complex to free $CH_3O^-$ ions is not observed in agreement with the fact that this process is endothermic with $\approx 100$ kJ mol$^{-1}$ (see the Appendix). Instead, the complex may react by a substitution-type process with the formation of a $CF_3C(O)\dot{C}HOCH_3$ radical and $Cl^-$ ions. Overall, this process is estimated to be exothermic by $\approx 100$ kJ mol$^{-1}$.

In the reactions of the $CH_2Cl^-$ and $CH_2Br^-$ ions with the methyl ester of trifluoroacetic acid no direct evidence for the occurrence of attack on the carbonyl group is obtained; that is, formation of a $CF_3C(O)CHX^-$ ion is not observed in these systems (Table 1). However, abundant halide ions are formed in the reactions of the carbanions with this substrate. In line with the suggestions put forward for the carbene radical anions, it is proposed that the carbanions react by a pathway involving initial attack on the carbonyl group followed by formation of a $[CF_3C(O)CH_2X \ CH_3O^-]^*$ complex which reacts by a substitution process prior to dissociation into free halide ions.

A similar complication arises for the reactions of the (radical) anions with the substrate dimethyl carbonate in the sense that relatively abundant halide ions are formed except in the reactions of the $CHF^{-\bullet}$ species. That attack on the carbonyl group in this substrate by the radical anions occurs is indicated by the formation of the $CH_3OC(O)CX^{-\bullet}$ and $C_2HXO^{-\bullet}$ ions (Table 1). The mechanism of the reactions leading to these ions is shown in Scheme 3 for deuterium-labelled dimethyl carbonate as involving initial formation of a tetrahedral intermediate, which dissociates to form a complex comprising a radical
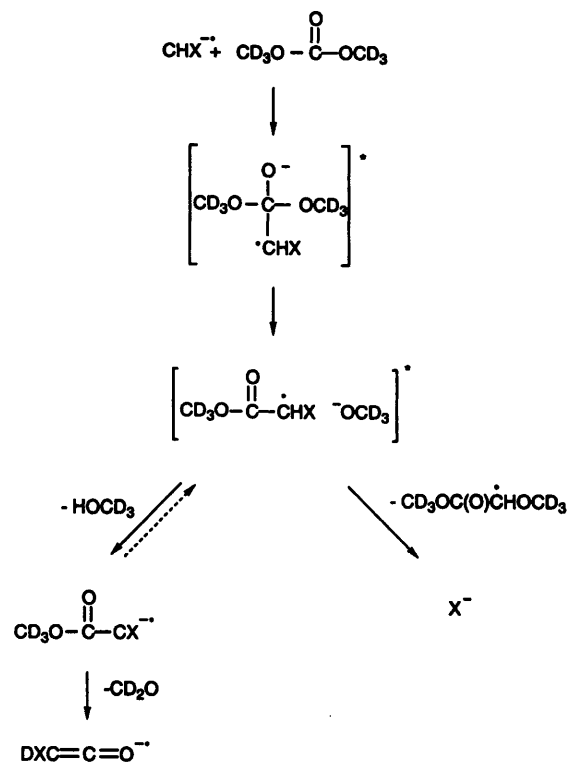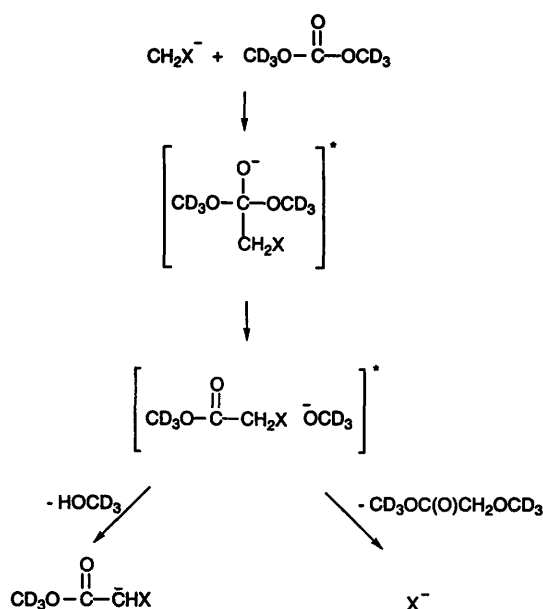


**Scheme 3** Proposed mechanism for the formation of the $CD_3OC(O)CX^{-\bullet}$, $C_2DXO^{-\bullet}$ and $X^-$ ($X = Cl$ and Br) ions in the reactions of $CHX^{-\bullet}$ radical anions with deuterium-labelled dimethyl carbonate. The $C_2DXO^{-\bullet}$ ions are assumed to have the structure of the molecular radical anion of a mono-halogen substituted ketene.

species and a methoxy anion. Subsequent proton transfer within the complex precedes the elimination of methanol with formation of the $CH_3OC(O)CX^{-\bullet}$ ion, which can then eliminate formaldehyde. This mechanistic proposal is supported by the finding that the $CDBr^{-\bullet}$ ion reacts to form only unlabelled product ions; that is, only $C_2HBrO^{-\bullet}$ ions are formed in addition to bromide anions. In agreement with this, the reactions of the unlabelled radical anions, $CHF^{-\bullet}$ and $CHCl^{-\bullet}$, with the labelled dimethyl carbonate lead to product ions which contain only deuterium atoms. Moreover, the yield of the $CD_3OC(O)CX^{-\bullet}$ ions is drastically increased relative to the $C_2DXO^{-\bullet}$ ions, compared with the relative yield of the $CH_3OC(O)CX^{-\bullet}$ ions formed in the reactions with unlabelled dimethyl carbonate (see Table 1 and Results). This increase in the relative yield of the $CD_3OC(O)CX^{-\bullet}$ ion suggests that the

final step in the sequence leading to the $C_2HXO^{-\cdot}$ ions is associated with a significant isotope effect (Scheme 3).

For the $CHBr^{-\cdot}$ radical anion, the introduction of deuterium atoms at the methyl groups in the carbonate causes $Br^-$ to be the sole product ion. The absence of formation of the $C_2DBrO^{-\cdot}$ ions in this system may be seen as a result of the proton-transfer step in the $[CD_3OC(O)CHBr^{\cdot}\ ^-OCD_3]^*$ species lead to a complex of $CD_3OC(O)CBr^{-\cdot}$ and $CH_3OH$. Instead of reacting further as implied in Scheme 3, the suggested isotope effect on the loss of formaldehyde causes this latter complex to undergo proton transfer and thus return to the $[CD_3OC(O)CHBr^{\cdot}\ ^-OCD_3]^*$ complex which then reacts further to form the bromide ions. This proposal is also in keeping with the suggestion that halide ions are formed as a result of an initial attack on the carbonyl group by the reactant carbene radical anion (*vide supra*).

Attack on the carbonyl group in dimethyl carbonate by one of the halogen-substituted carbanions is revealed by the formation of $CH_3OC(O)CHX^-$ (Scheme 4). Further fragmentation

**Scheme 4** Proposed mechanism for the formation of the $CD_3OC(O)$-$CHX^-$ and $X^-$ (X = Cl and Br) ions in the reactions of $CH_2X^-$ carbanions with deuterium-labelled dimethyl carbonate

of these ions is not observed and, in addition, the relative yields of these products are unaffected by the introduction of deuterium atoms at the methyl groups of the substrate. Nevertheless, the halide ions formed in these systems can be considered to arise as a result of a subsequent reaction within the complex formed after initial attack on the carbonyl group. The possible formation of halide ions in the subsequent reaction shown in Scheme 4 is supported by independent experiments in which the $CH_3O^-$ ion was allowed to react with the methyl ester of bromoacetic acid. The experiments revealed the occurrence of a facile proton transfer with formation of $CH_3OC(O)CHBr^-$ as well as the generation of abundant $Br^-$ ions, presumably by a substitution process.

### Reactivity trends
The kinetic experiments concerned with the reactivity of the different ions toward chloro- and bromo-methane demonstrate that a given carbene radical anion reacts less efficiently with these substrates than does the corresponding carbanion (Table 2). The formation of halide ions in these reactant systems can be ascribed entirely to the occurrence of an $S_N2$ substitution (*vide supra*). For both types of reactant ion, $S_N2$ substitution is strongly exothermic indicating that the difference in reactivity is related to the relative heights of the energy barriers associated
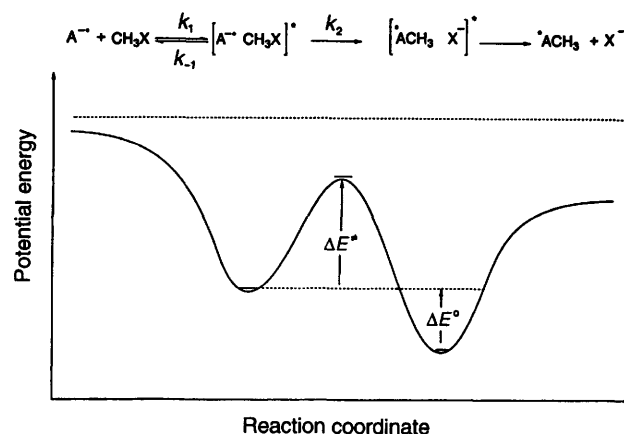
**Fig. 3** Double-minimum potential energy surface for the $S_N2$ substitution between a radical anion and a mono-halogen substituted methane in the gas phase (see the text). The dotted line represents the fixed energy level of the system given as the sum of the potential energy and the internal energy of the reactant system.
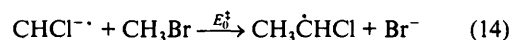
with these processes. The potential energy surface of $S_N2$ substitutions occurring in the gas phase has been the subject of numerous experimental[53-58] and theoretical[59-61] studies. Based on these studies it is accepted generally that this process is described by a double-minimum potential energy surface as illustrated in Fig. 3 for the reaction between a radical anion and a halomethane. The two minima on the potential energy surface correspond to ion/molecule complexes, whereas the local maximum in energy separating these two complexes represents the transition state for the actual substitution step. According to this model, the efficiency of the overall reaction is determined mainly by the competition between the step corresponding to crossing the central energy barrier and redissociation of the first-formed ion/molecule complex into the separated reactant species (see Fig. 3). With respect to the reactions of the $CHCl^{-\cdot}$ and $CH_2Cl^-$ ions with $CH_3Br$, respectively, the rate constant for the redissociation of the first-formed ion/molecule complex is likely to be similar in the two instances. This suggests that the difference in efficiency between the $S_N2$ substitutions of these species is a result of a larger energy barrier for the reaction of the $CHCl^{-\cdot}$ radical anion than for the reaction of the $CH_2Cl^-$ carbanion with $CH_3Br$.
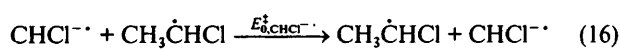
A number of studies concerned with $S_N2$ substitutions in the gas phase have analysed the energetic aspects of this process in terms of the Marcus theory developed originally for electron transfer processes in the condensed phase.[1,62-64] For gas-phase $S_N2$ reactions,[55,65] the Marcus equation can be written as shown in eqn. (13) in which $\Delta E^{\ddagger}$ is the height of the local barrier for the

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}\left[1 + \frac{\Delta E^{\circ}}{4\Delta E_0^{\ddagger}}\right]^2 \qquad (13)$$

substitution step (see Fig. 3), $\Delta E^{\circ}$ the energy difference between the two ion/molecule complexes and $\Delta E_0^{\ddagger}$ the barrier height for the hypothetical situation in which the change in energy is zero for the transformation of the reactant ion/molecule complex into the product complex.

A central aspect of the application of the Marcus theory to gas-phase $S_N2$ substitutions is the assumption that the height of the intrinsic barrier for a given substitution process is given as the average of the intrinsic barriers for the two identity reactions. For example, the intrinsic barrier for the reaction of the $CHCl^{-\cdot}$ ion with $CH_3Br$, can be written as the average of the barriers for the reaction of $Br^-$ with $CH_3Br$ and of the hypothetical identity reaction of $CHCl^{-\cdot}$ with $CH_3\overset{\cdot}{C}HCl$ [eqns. (14)–(17)].

$$CHCl^{-\cdot} + CH_3Br \xrightarrow{E_0^{\ddagger}} CH_3\overset{\cdot}{C}HCl + Br^- \qquad (14)$$

$$Br^- + CH_3Br \xrightarrow{E^{\ddagger}_{0,Br^-}} CH_3Br + Br^- \qquad (15)$$

$$CHCl^{-\bullet} + CH_3\dot{C}HCl \xrightarrow{E^{\ddagger}_{0,CHCl^-}} CH_3\dot{C}HCl + CHCl^{-\bullet} \qquad (16)$$

$$E^{\ddagger}_0 = \tfrac{1}{2}[E^{\ddagger}_{0,Br^-} + E^{\ddagger}_{0,CHCl^-}] \qquad (17)$$

In view of the fact that the substrate is the same in the reactions of the CHCl$^{-\bullet}$ and CH$_2$Cl$^-$ ions, the difference in reactivity of these ions can be ascribed to a larger intrinsic barrier for the identity reaction of the radical anion than for the carbanion. The barrier height for a series of identity reactions involving anions as nucleophiles has been indicated experimentally to correlate linearly with the methyl cation affinity (MCA) of the reactant ion,[53] whereas recent theoretical results do not seem to substantiate such a correlation.[58] Nevertheless, we note that the MCA of the CHCl$^{-\bullet}$ species (MCA $\approx$ 1210 kJ mol$^{-1}$) is about 40 kJ mol$^{-1}$ lower than the value for the CH$_2$Cl$^-$ ion (MCA $\approx$ 1250 kJ mol$^{-1}$).[49,51] Even though the lower MCA of the radical anion than of the carbanion is in line with the efficiencies in Table 2, it is uncertain whether the relatively minor difference in MCA of the two reactant species can give rise to a difference of a factor of 2 in the efficiency of the overall reaction with CH$_3$Br. Furthermore, it should be emphasized that the electronic coupling between the reactant species in the transition state may be different for the odd-electron ion, CHCl$^{-\bullet}$, and the even-electron species, CH$_2$Cl$^-$. It should also be mentioned that the reactivity trends in S$_N$2 substitutions have been discussed on the basis of a configuration mixing model,[31,61] which describes these reactions as involving a so-called single electron shift. In terms of this model, the energy barrier for S$_N$2 substitutions involving negatively charged nucleophiles is suggested to correlate with the difference in electron affinity between the neutral species corresponding to a reactant ion and the substrate. For the present reactions, this implies that the reactivity difference between, for example, the CHCl$^{-\bullet}$ and CH$_2$Cl$^-$ ions is determined in part by the difference in electron affinity between the CHCl carbene and the CH$_2$Cl$^\bullet$ radical. As reported, the electron affinity of CHCl is about 40 kJ mol$^{-1}$ [$E_{ea}$(CHCl) = 117 kJ mol$^{-1}$][66] higher than of the CH$_2$Cl$^\bullet$ radical [$E_{ea}$(CH$_2$Cl$^\bullet$) = 77 kJ mol$^{-1}$].[25] This difference in electron affinity is thus in line with the obtained reactivity difference between these ions towards bromomethane. It should be re-emphasized, however, that the precise nature of the transition states for the reactions of the CHCl$^{-\bullet}$ and CH$_2$Cl$^-$ ions with CH$_3$Br remains to be elucidated.

In the reactions of the various ions with the methyl ester of trifluoroacetic acid and dimethyl carbonate, the S$_N$2 substitution is observed to compete with the B$_{AC}$2 process (*vide supra*). The determination of the relative importances of these two processes is based upon the assumption that the halide ions formed in the reactions with the esters arise only as a result of attack on the carbonyl group. The values listed in Table 3 for the reactions of the carbene radical anions with the methyl ester of trifluoroacetic acid reveal that the S$_N$2 substitution becomes less important relative to the B$_{AC}$2 process in the series, CHF$^{-\bullet}$, CHCl$^{-\bullet}$ and CHBr$^{-\bullet}$. The same trend in the relative importances of the two processes is observed for the reaction of the two carbanions with the trifluoromethyl-containing substrate. This decrease in the relative extent of S$_N$2 substitution with increasing size of the halogen atom of the reactant ions is also observed for dimethyl carbonate as the substrate (Table 3).

Nucleophilic attack on a carbonyl group in the gas phase has been the subject of a number of studies.[67–73] This process has been proposed to involve the formation of a tetrahedral structure as a stable intermediate as indicated by the potential energy surface shown in Fig. 4. For the present systems, the details of the surfaces describing attack on the carbonyl group are unknown and—in addition—the multistep character of the pathways leading to the final product ions succeeding the attack on the carbonyl group in dimethyl carbonate suggests an even
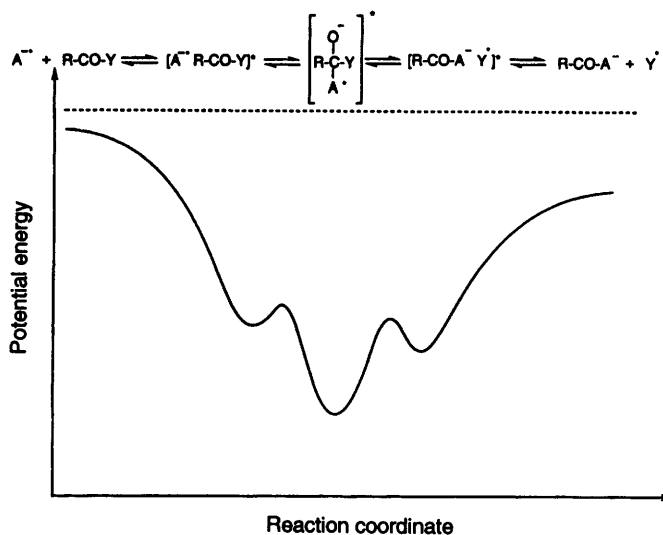


**Fig. 4** Proposed potential energy surface for the B$_{AC}$2 reaction of a radical anion with a carbonyl compound in the gas phase (see the text)

more complex surface than the one shown in Fig. 4. Irrespective of the relatively complex nature of the process involving initial attack on the carbonyl group, it may be assumed that the efficiency of the overall process is determined by the step leading to the tetrahedral structure. This implies that the heights of the local energy barriers for the S$_N$2 substitution and the attack on the carbonyl group determine the observed relative importances of these two processes. In view of the suggestions advanced for the S$_N$2 reactions, it could then be envisaged that the energy barrier for attack on the carbonyl group is determined also in part by the difference in electron affinity between the neutral species corresponding to the reactant ion and the substrate. With respect to the two carbonyl-group-containing compounds, the electron affinities of these species are unknown, whereas the values in Table 3 reveal that the electron affinity increases in the series CHF, CHCl and CHBr, and a similar situation holds for the halomethyl radicals. With respect to the experimental results, these reveal that the relative importance of the B$_{AC}$2 pathway increases as the halogen atom becomes larger (Table 3). In conclusion, this finding can be seen as a result of the height of the energy barrier towards attack on the carbonyl group being less strongly dependent on the electron affinity of the reactant ion than the barrier height for the S$_N$2 reaction.

Even though the radical anions CHCl$^{-\bullet}$ and CHBr$^{-\bullet}$ react relatively more by the B$_{AC}$2 pathway than the corresponding carbanions with the methyl ester of trifluoroacetic acid, the variation in the relative importance of the two pathways does not influence the efficiency of the overall process (Table 3). The results for this substrate do not allow, therefore, a conclusion to be reached whether the radical anions react intrinsically more readily by attack on a carbonyl group than the carbanions. For dimethyl carbonate, the B$_{AC}$2 process dominates for both types of reactant ions and is likely to be the only process occurring in the reactions of the CHCl$^{-\bullet}$ and CHBr$^{-\bullet}$ ions with the unlabelled dimethyl carbonate. Concomitant with the change in favour of the B$_{AC}$2 process, the efficiency of the overall process decreases and, in addition, it is observed that the efficiency of the overall reaction of the CHCl$^{-\bullet}$ and CHBr$^{-\bullet}$ radical anions with dimethyl carbonate is a factor of four lower than that of the reactions of the corresponding carbanions. If the minor extent of the S$_N$2 substitution is disregarded for the carbanions, the relative efficiencies suggest that the carbene radical anions react less readily by the B$_{AC}$2 pathway than the carbanions with this substrate. This reactivity difference is in line with the higher electron affinity of a given halogen-substituted carbene than the corresponding halomethyl radical. However, the relatively limited results obtained in the present

study do not allow a more detailed discussion of the intrinsic reactivity of a simple radical anion towards a carbonyl group in a given substrate.

## Conclusions

The present results reveal that the mono-halogen substituted carbene radical anions as well as the corresponding carbanions react with the simple halomethanes, $CH_3Cl$ and $CH_3Br$, only by $S_N2$ substitution, whereas a $B_{AC}2$ process competes efficiently with the $S_N2$ pathway in the reactions with $CF_3CO_2CH_3$ and $CH_3OCO_2CH_3$. With chloro- or bromo-methane as the substrate, the $S_N2$ process is a factor of two less efficient for the radical anions than for the corresponding carbanions. This difference in reactivity is concluded to be a result of a larger kinetic barrier for the $S_N2$ substitution of the radical anions than of the carbanions in view of the fact that all these processes are strongly exothermic. The reactions of the various (radical) anions with the methyl ester of trifluoroacetic acid are equally fast and are suggested to proceed at the collision rate. Nevertheless, the $B_{AC}2$ pathway appears to play a more dominant role in the reactions of the radical anions than in the reactions of the corresponding carbanions with this substrate. In addition, the $B_{AC}2$ pathway is relatively more important for the bromine-containing (radical) anions than for the chlorine-substituted species. A similar finding is obtained for dimethyl carbonate even though attack on the carbonyl group is more favoured in the reactions with this species than if the methyl ester of trifluoroacetic acid is the substrate. In particular, the two carbene radical anions, $CHCl^{-\cdot}$ and $CHBr^{-\cdot}$, react exclusively by the $B_{AC}2$ pathway with this substrate, whereas the corresponding carbanions react to a minor extent by the $S_N2$ pathway. The overall reactions of the radical anions are about a factor of four less efficient than the reactions of the corresponding carbanions with dimethyl carbonate. In other words, the $B_{AC}2$ reaction of the radical anions is suggested to be associated with a larger kinetic barrier than this reaction of the carbanions with dimethyl carbonate. The combined results may indicate that mono-halogen substituted carbene radical anions tend to react less efficiently than the corresponding carbanions in typical nucleophilic processes in the gas phase. The results of the present study are relatively limited, however, and it should be re-emphasized that the precise nature of the transition state involved in the crucial steps of these gas-phase reactions is still unknown, in particular with respect to the electronic coupling between the various reactant (radical) anions and the selected substrates.

## Acknowledgements

## Appendix

Most of the enthalpy changes given in the text have been taken from refs. 25, 49–51 or estimated with the use of data given in these references. The enthalpy of formation of $CF_3CO_2CH_3$ has been estimated to be $\Delta H_f^\circ = -1008$ kJ mol$^{-1}$ upon the assumption that the difference in enthalpy of formation between $CH_3CO_2H$ ($\Delta H_f^\circ = -432$ kJ mol$^{-1}$) and $CH_3CO_2CH_3$ ($\Delta_f^\circ = -410$ kJ mol$^{-1}$) is the same as the difference in enthalpy of formation between the $CF_3CO_2H$ ($\Delta_f^\circ = -1030$ kJ mol$^{-1}$) and the methyl ester of this acid. The enthalpy change for the reaction between $CHCl^{-\cdot}$ and the $CF_3CO_2CH_3$ ester leading to $CF_3C(O)CHCl^-$ and $CH_3O^\cdot$ (see Scheme 1) was obtained upon the assumption that this enthalpy change is roughly the same as that for the corresponding reaction between the $CH_2^{-\cdot}$ radical anion and $CF_3CO_2CH_3$ ($\Delta H_r^\circ = -180$ kJ mol$^{-1}$). This assumption is based

upon the expectation that the difference in enthalpy of formation between the $CH_2^{-\cdot}$ and $CHCl^{-\cdot}$ ions is roughly the same as the difference in enthalpy of formation between the $CF_3C(O)CH_2^-$ and $CF_3C(O)CHCl^-$ ions. Such a suggestion is in line with the finding that the difference in enthalpy of formation between a given $CHX^{-\cdot}$ radical anion and the corresponding carbanion, $CH_2X^-$, is the same for the four different halogen atoms (see ref. 25). The enthalpy change for the reaction between the $CHCl^{-\cdot}$ and the $CF_3CO_2CH_3$ ester leading to $Cl^-$ ion and $CF_3C(O)\dot{C}HOCH_3$ (see Scheme 1) has been estimated with the use of an enthalpy of formation of the latter species of $-680$ kJ mol$^{-1}$. This value was obtained from an estimated $\Delta H_f^\circ$ of $-960$ kJ mol$^{-1}$ for $CF_3C(O)CH_2OCH_3$ and upon the assumption that the bond dissociation energy ($E_d$) of the C–H bonds of the methylene group connected to the carbonyl function and the ether oxygen atom is the same as the C–H $E_d$ of dimethyl ether; that is, 390 kJ mol$^{-1}$. The enthalpy change for the reaction of the $CHCl^{-\cdot}$ ion with $CF_3CO_2CH_3$ yielding $Cl^-$ and $CF_3C(O)O\dot{C}HCH_3$ was estimated with an enthalpy of formation of the radical species of this radical of $-180$ kJ mol$^{-1}$. This value was obtained with the use of an assumed $E_d$ of 390 kJ mol$^{-1}$ of the C–H bonds of the methylene group of the ester $CF_3CO_2CH_2CH_3$.

## References

1 L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, Berlin, 1987.
2 R. A. Rossi and R. H. Rossi, *Aromatic Substitution by the S_{RN}1 Mechanism*, ACS Monograph 178, American Chemical Society, Washington DC, 1983.
3 J. F. Bunnett, *Acc. Chem. Res.*, 1987, **11**, 413.
4 J. K. Kochi, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1227.
5 E. C. Ashby, *Acc. Chem. Res.*, 1988, **21**, 414.
6 J.-M. Savéant, *Acc. Chem. Res.*, 1993, **26**, 455.
7 H. Lund, K. Daasbjerg, T. Lund and S. U. Pedersen, *Acc. Chem. Res.*, 1995, **28**, 313.
8 J. M. Riveros, S. M. José and K. Takashima, *Adv. Phys. Org. Chem.*, 1985, **21**, 197.
9 N. M. M. Nibbering, *Adv. Phys. Org. Chem.*, 1988, **24**, 1.
10 A. Kasdan, E. Herbst and W. C. Lineberger, *Chem. Phys. Lett.*, 1975, **31**, 78.
11 P. Kebarle and S. Chowdhury, *Chem. Rev.*, 1987, **87**, 513.
12 J. E. Bartmess, *Mass Spectrom. Rev.*, 1989, **8**, 297.
13 A. A. Christodoulides, D. L. McCorkle and L. G. Christophorou in *Electron-Molecule Interactions and their Applications*, ed. L. G. Christophorou, Academic Press, New York, 1984, vol. 2, ch. 6.
14 D. G. Leopold, A. M. S. Miller and W. C. Miller, *J. Am. Chem. Soc.*, 1986, **108**, 1379.
15 S. Ingemann, R. H. Fokkens and N. M. M. Nibbering, *J. Org. Chem.*, 1991, **56**, 607.
16 M. K. Gilles, K. M. Ervin, J. Ho and W. C. Lineberger, *J. Phys. Chem.*, 1992, **96**, 1130.
17 W. B. Knighton and E. P. Grimsrud, *J. Am. Chem. Soc.*, 1992, **114**, 2336.
18 L. Crocker, T. Wang and P. Kebarle, *J. Am. Chem. Soc.*, 1993, **115**, 7818.
19 R. N. McDonald, A. K. Chowdhury and D. W. Setser, *J. Am. Chem. Soc.*, 1981, **103**, 6599.
20 R. N. McDonald, A. K. Chowdhury and W. D. McGhee, *J. Am. Chem. Soc.*, 1984, **106**, 4112.
21 Y. Guo and J. J. Grabowski, *Int. J. Mass Spectrom. Ion Processes*, 1990, **97**, 253.
22 H. E. K. Matimba, A. M. Crabbendam, S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Chem. Commun.*, 1991, **9**, 644.
23 Y. Guo and J. J. Grabowski, *J. Am. Chem. Soc.*, 1991, **113**, 5923.
24 H. E. K. Matimba, A. M. Crabbendam, S. Ingemann and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, 1992, **114**, 85.
25 M. Born, S. Ingemann and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1994, **116**, 7210.
26 R. N. McDonald, *Tetrahedron*, 1989, **45**, 3993.
27 R. N. McDonald, A. K. Chowdhury and D. W. Setser, *J. Am. Chem. Soc.*, 1981, **102**, 6491.
28 R. N. McDonald and A. K. Chowdhury, *J. Phys. Chem.*, 1982, **86**, 36419.
29 R. N. McDonald and W. Y. Gung, *J. Am. Chem. Soc.*, 1987, **109**, 7328.

30 M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.*, 1981, **103**, 676.

31 S. S. Shaik and A. Pross, *J. Am. Chem. Soc.*, 1982, **104**, 2708.

32 S. S. Shaik and A. Pross, *J. Am. Chem. Soc.*, 1989, **111**, 4306.

33 A. Pross, *J. Am. Chem. Soc.*, 1986, **108**, 3537.

34 T. Drewello, W. P. M. Maas, N. M. M. Nibbering, T. Weiske and H. Schwarz, *J. Am. Chem. Soc.*, 1987, **109**, 4810.

35 V. D. Parker, K. L. Handoo and B. Ritstoën, *J. Am. Chem. Soc.*, 1991, **113**, 6218.

36 S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 1985, 837.

37 N. M. M. Nibbering, *Rapid Commun. Mass Spectrom.*, 1993, **7**, 747.

38 L. J. de Koning, C. W. F. Kort, F. A. Pinkse and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, 1989, **95**, 71 and references cited therein.

39 R. A. L. Peerboom, S. Ingemann, N. M. M. Nibbering and J. F. Liebman, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1825 and references cited therein.

40 A. J. R. Heck, L. J. de Koning, F. A. Pinkse and N. M. M. Nibbering, *Rapid Commun. Mass Spectrom.*, 1991, **5**, 406.

41 J. C. Kleingeld and N. M. M. Nibbering, *Lect. Notes Chem.*, 1982, **31**, 209.

42 R. Renaud and L. C. Leitch, *Can. J. Chem.*, 1956, **34**, 181.

43 F. M. Bickelhaupt, L. J. de Koning, N. M. M. Nibbering and E. J. Baerends, *J. Phys. Org. Chem.*, 1992, **5**, 179.

44 P. O. Staneke, G. Groothuis, S. Ingemann and N. M. M. Nibbering, *J. Phys. Org. Chem.*, 1996, **9**, 471.

45 T. Su and M. T. Bowers, in *Gas Phase Ion Chemistry*, ed. M. T. Bowers, Academic Press, New York, 1979, vol. 1, ch. 3.

46 T. Su and M. T. Bowers, *J. Chem. Phys.*, 1973, **58**, 3027.

47 T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 1973, **12**, 347.

48 Y. Ikezoe, S. Matsuoka, M. Takebe and A. Viggiano, *Gas-Phase Ion–Molecule Reaction Rate Constants Through 1986*, Maruzen, Tokyo, 1987.

49 S. W. Benson, *Methods for the Estimation of Thermochemical Data and Rate Parameters*, Wiley, New York, 1976.

50 J. D. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: *Organic and Organometallic Compounds*, University of Sussex, 1977.

51 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl. 1.

52 T. F. Magnera and P. Kebarle in *Ionic Processes in the Gas Phase*, ed. M. A. Almoster Ferreira, NATO ASI Series, vol. 118, Reidel, Dordrecht, The Netherlands, 1984.

53 M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.*, 1983, **105**, 2672.

54 G. Caldwell, T. F. Magnera and P. Kebarle, *J. Am. Chem. Soc.*, 1984, **106**, 959.

55 J. A. Dodd and J. I. Brauman, *J. Am. Chem. Soc.*, 1986, **90**, 3559.

56 S. T. Graul and M. T. Bowers, *J. Am. Chem. Soc.*, 1991, **113**, 9696.

57 B. D. Wladkowski, J. L. Wilbur and J. I. Brauman, *J. Am. Chem. Soc.*, 1994, **116**, 2471.

58 M. N. Glukhovtsev, A. Pross and L. Radom, *J. Am. Chem. Soc.*, 1995, **117**, 2024.

59 W. L. Hase, *Science*, 1994, **266**, 998.

60 M. N. Glukhovtsev, A. Pross and L. Radom, *J. Am. Chem. Soc.*, 1995, **117**, 2024, and references therein.

61 S. S. Shaik, H. B. Schlegel and S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry, The $S_N2$ Mechanism*, Wiley, New York, 1992.

62 R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.

63 N. Sutin in *Inorganic Reactions and Methods*, ed. J. J. Zuckerman, VCH, Deerfield Beach, Florida, 1986, vol. 15, ch. 12.3.2.1.

64 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.

65 J. A. Dodd and J. I. Brauman, *J. Phys. Chem.*, 1986, **90**, 3559.

66 M. K. Giles, K. M. Erwin, J. Ho and W. C. Lineberger, *J. Phys. Chem.*, 1992, **96**, 1130.

67 H. van der Wel and N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 491.

68 S. Baer, E. A. Brinkman and J. I. Brauman, *J. Am. Chem. Soc.*, 1991, **113**, 805.

69 S. Yamabe, T. Minato and Y. Kawabata, *Can. J. Chem.*, 1984, **62**, 235.

70 O. I. Asubiojo and J. I. Brauman, *J. Am. Chem. Soc.*, 1979, **101**, 3715.

71 M. J. S. Dewar and D. M. Storch, *J. Chem. Soc., Chem. Commun.*, 1985, 94.

72 J. F. Blake and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1987, **109**, 3856.

73 P. O. Staneke, S. Ingemann and N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas*, 1996, **115**, 179.