

# COMPETING ELECTRON TRANSFER, PROTON ABSTRACTION AND NUCLEOPHILIC SUBSTITUTIONS IN GAS-PHASE REACTIONS OF (RADICAL) ANIONS WITH CHLORO- AND BROMOMETHANES

P. O. STANEKE, G. GROOTHUIS, S. INGEMANN AND N. M. M. NIBBERING\*

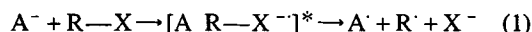
*Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

The product ion distributions and rates of the gas-phase reactions of two series of (radical) anions with chloro- and bromomethanes ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CBr}_4$ ) were determined with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The first series consists of anions ( $\text{HO}^-$ ,  $\text{CH}_3\text{O}^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{C}_3\text{H}_7\text{O}^-$  and  $\text{CH}_3\text{S}^-$ ), for which the corresponding neutral radicals have a relatively high electron affinity ( $EA > 150 \text{ kJ mol}^{-1}$ ). The second series consists of (radical) anions ( $\text{CH}_2\text{S}^-$ ,  $\text{CH}_2=\text{CHCH}_2^-$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2^-$ ,  $\text{C}_4\text{H}_4^-$  and  $\text{C}_6\text{H}_5^-$ ), for which the corresponding neutral species have a relatively low electron affinity ( $EA < 100 \text{ kJ mol}^{-1}$ ). These (radical) anions react mainly with the halomethanes to afford (i) halide ions, (ii) halomethyl anions with the same number of halogen atoms as in the parent halomethane and (iii) halomethyl anions with one halogen atom less than the parent substrate. The last process involves nucleophilic attack on a halogen atom and is particularly important in the reactions with substrates containing three or four halogen atoms. The halide ions may arise by a number of different pathways, such as  $\text{S}_{\text{N}}2$  substitution,  $\alpha$ -elimination, halogen attack followed by dissociation of the thus formed halomethyl anion and overall dissociative electron transfer. The  $\text{S}_{\text{N}}2$  process is held responsible for the formation of halide ions in the reactions with monohalomethanes, whereas  $\alpha$ -elimination is likely to be of importance only for the reactions with trichloro- and tribromomethanes. Attack on a halogen atom followed by dissociation of the ion generated initially is likely to be important if  $\text{CCl}_4$  or  $\text{CBr}_4$  is the substrate. Electron transfer is only a dominant pathway in the reactions of the  $\text{CH}_2\text{S}^-$  ion with the halomethanes. The occurrence of electron transfer in the reactions of this ion with  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and  $\text{CHBr}_3$  is evidenced by the formation of minor amounts of stable halomethane radical anions in addition to the generation of  $\text{CH}_2\text{S}^-$  or  $\text{CH}_2\text{S}^-$  ions and abundant halide ions. The interplay between the various possible reactions is discussed on the basis of thermodynamic considerations and the rates of the overall processes.

## INTRODUCTION

The transfer of a single electron has become recognized as a central step in many organic reactions described commonly as two electron centered processes.<sup>1</sup> In particular, the role of single electron transfer (SET) in organic processes has been studied extensively since the pioneering work of Kornblum, Russell and Bunnett concerning nucleophilic aromatic substitutions proceeding by a pathway which is now known as the  $\text{S}_{\text{RN}}1$  mechanism.<sup>2-7</sup> The experimental results of a large number of studies concerned with electron transfer reactions in organic systems provide evidence that SET can merge and compete with processes such as the  $\text{S}_{\text{N}}2$  substitution in the reactions of anions ( $\text{A}^-$ ) or radical anions with haloalkanes ( $\text{RX}$ ).<sup>1,8-18</sup> The electron

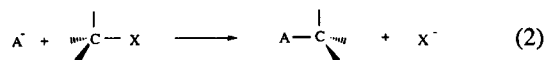
transfer process leads initially to a molecular radical anion of the haloalkane as indicated in equation (1). For most haloalkanes, the molecular radical anion is not observed as a stable species and dissociation into an alkyl radical and a halide ion is normally considered to occur concomitantly with or essentially synchronous with electron transfer.



In the condensed phase, the products corresponding to the overall substitution process arise mostly by subsequent bond formation between the  $\text{A}^-$  ion and the  $\text{R} \cdot$  radical followed by oxidation to a neutral species or by coupling between the  $\text{R} \cdot$  and  $\text{A} \cdot$  radicals. In the well known  $\text{S}_{\text{N}}2$  reaction, the product of substitution,  $\text{RA}$ , arises directly by nucleophilic attack from the backside of the carbon-halogen bond leading to cleavage of this bond with the formation of a halide ion and inversion of

\* Author for correspondence.

the configuration of the carbon atom:<sup>19,20</sup>



From a theoretical point of view, these two processes have been related to each other on the basis of a configuration mixing model, which describes the pathways as involving a so-called single electron shift.<sup>10,21-24</sup> Within the terminology of the Marcus theory for electron transfer reactions,<sup>25</sup> electron transfer to form a radical anion of the substrate which is stable within the time-scale of a given experiment has been referred to as an outer-sphere process, whereas electron transfer occurring concomitantly with bond formation and bond cleavage has been described as an inner-sphere process.<sup>15,26</sup> Experimentally, the Marcus theory has often been applied in the analysis of kinetic data with the purpose of determining whether a given chemical system reacts by a SET process or an  $S_N2$  substitution.<sup>1,11,13-18</sup> This distinction has been accomplished also on the basis of the detection of products of radical processes such as cyclization of an R' radical containing a remote double bond.<sup>18,27</sup> In addition, the degree of inversion of configuration in reactions with stereochemically pure substrates has been utilized as a measure of the extent to which  $S_N2$  substitution competes with a SET process, since the latter is expected to lead to a racemic mixture of the final products.<sup>1,11,12</sup>

Almost all of the studies concerned with the interplay between SET and  $S_N2$  processes have been focused on reactions occurring in the condensed phase. Under these conditions, the competition between the different processes can be influenced by solvation phenomena and thus only limited insight may be obtained into the molecular properties which determine the extent to which SET occurs for a given chemical system. Obviously, the effects of solvation can be avoided by performing ion-molecule reactions in the gas phase as has been documented extensively in the last few decades for a variety of organic and inorganic systems.<sup>28-30</sup> However, only a limited number of these studies have addressed the extent to which SET competes with polar processes in typical organic ion-molecule reactions in the gas phase. Pertinent examples of gas-phase studies involving positive ions include the nitration of aromatic species,<sup>31,32</sup> acylation of heteroaromatic compounds with acylium ions<sup>33,34</sup> and the competition between  $E2$ ,  $S_N2$  and SET in the reactions of the methyldiethyloxonium ion with amines.<sup>35</sup> With respect to reactions of negative ions, the interplay between electron transfer and substitution processes has been discussed for the reactions of a limited number of (radical) anions with some halomethanes. In particular, electron transfer has been observed from the  $O_2^{\cdot -}$  ion to halomethanes such as  $CF_2Cl_2$  and  $CFCl_3$ ,<sup>36-38</sup> and also from the radical

anions of substituted nitrobenzenes and azulene to the halomethanes  $CHCl_3$ ,  $CCl_4$ ,  $CH_2Br_2$ ,  $CH_3I$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CF_2Br_2$  and  $CCl_3Br$ .<sup>39</sup> Furthermore, the azobenzene radical anion is reported to react only with the chloro- and bromomethanes with more than a single halogen atom in the gas phase if dissociative electron transfer with formation of free halide ions is exoergic.<sup>40</sup> Recently, we observed that the thioformaldehyde radical anion,  $CH_2S^{\cdot -}$ , reacts with  $CXCl_3$  ( $X=H, F$  and  $Cl$ ) halomethanes to afford minor amounts of stable radical anions of these species.<sup>41</sup> In addition, we have reported that the  $CH_2S^{\cdot -}$  ion reacts efficiently by electron transfer with various completely halogen-substituted fluorochloro- and fluorobromomethanes in the gas phase and also with some esters of trifluoroacetic acid.<sup>42,43</sup>

The radical anions of azobenzene and substituted nitrobenzenes are relatively large species with delocalized charge and radical centers. For such radical anions, the  $S_N2$  pathway may be associated with a substantial kinetic barrier causing these species to react with halomethanes preferentially by the SET pathway. Likewise, the thioformaldehyde radical anion is a weak nucleophile in the gas phase and reacts mostly, if not exclusively, as an electron donor.<sup>41-43</sup> However, a systematic study concerned with the interplay between SET and nucleophilic processes in the gas-phase reactions of various anions and radical anions with halomethanes has not been performed. To this end, we decided to react a variety of (radical) anions with the complete series of chloro- and bromomethanes in the gas phase.

A disadvantage of studying reactions of (radical) anions with halomethanes in the gas phase is that only halide ions may be detected, irrespective of whether the reaction proceeds by the SET or, for example, the  $S_N2$  pathway. However, under normal operating conditions only overall thermoneutral or exoergic processes are observed with the most common mass spectrometric instrumentation applied for studies of ion-molecule reactions in the gas phase. Thermodynamic considerations of the overall reactions may thus allow the formation of halide ions to be assigned, for example, to an  $S_N2$  process if dissociative electron transfer is endoergic. Of course, both processes can be thermoneutral or exoergic for ion-molecule systems, indicating that thermodynamic considerations do not necessarily permit this distinction to be achieved. In these situations, a possible approach involves the determination of the rates of the overall reactions. As indicated by a number of studies, a SET reaction may be a relatively fast process in the gas phase even if only slightly exoergic,<sup>44</sup> whereas, for example, an  $S_N2$  substitution is often a slow process notwithstanding that the overall process is strongly exoergic.<sup>45-49</sup> In order to examine whether this conjecture applies to the interplay between SET and nucleophilic substitutions in the reactions of (radical)

anions with halomethanes, we decided to determine the rates and the product ion distributions of the reactions of two series of ions with the various chloro- and bromomethanes. The first series consists of anions ( $\text{HO}^-$ ,  $\text{CH}_3\text{O}^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{C}_3\text{H}_7\text{O}^-$  and  $\text{CH}_3\text{S}^-$ ) for which the corresponding neutral species have a relatively high electron affinity ( $EA > 150 \text{ kJ mol}^{-1}$ ).<sup>50</sup> SET for these ions is expected to be prohibited by the endoergicity of this process, whereas  $S_N2$  substitution is estimated to be exoergic. The second series consists of (radical) anions ( $\text{CH}_2\text{S}^-$ ,  $\text{CH}_2\text{CHCH}_2^-$ ,  $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2^-$ ,  $\text{C}_6\text{H}_4^-$  and  $\text{C}_6\text{H}_5^-$ ) for which the corresponding neutral species have a relatively low electron affinity ( $EA \leq 100 \text{ kJ mol}^{-1}$ ).<sup>50</sup> For these ions, both pathways are expected to be thermodynamically feasible for most of the chloro- and bromomethanes included in the present study.

## EXPERIMENTAL

The experiments were performed with use of a Fourier transform ion cyclotron resonance (FT-ICR)<sup>51</sup> instrument designed and constructed at the University of Amsterdam.<sup>52</sup> The experimental procedure for studying ion-molecule reactions with this instrument has been described in previous papers from our group.<sup>53,54</sup> The primary negative ions  $\text{O}^-$ ,  $\text{NH}_2^-$  and  $\text{HO}^-$  were generated by dissociative electron attachment to  $\text{N}_2\text{O}$  (electron energy 1.2–1.5 eV),  $\text{NH}_3$  (5 eV) and  $\text{H}_2\text{O}$  (6 eV; electron capture leads to  $\text{H}^-$  ions which react with  $\text{H}_2\text{O}$  to afford  $\text{HO}^-$ ), respectively. The radical anion of 1,2-dehydrobenzene,  $\text{C}_6\text{H}_4^-$ , and the thioformaldehyde radical anion,  $\text{CH}_2\text{S}^-$ , were generated by a formal  $1,2\text{-H}_2^+$  abstraction in the reactions of  $\text{O}^-$  with benzene<sup>55,56</sup> and methanethiol,<sup>57</sup> respectively. The  $\text{CH}_2=\text{CHCH}_2^-$  and  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2^-$  ions were generated by first forming  $\text{HO}^-$  in the reactions of the  $\text{O}^-$  ion with propene and 2-methylpropene, respectively, and then allowing the  $\text{HO}^-$  ions to abstract a proton from one of the alkenes. The  $\text{CH}_3\text{S}^-$  ions were generated by proton transfer from the methanethiol to  $\text{O}^-$  or  $\text{HO}^-$ , whereas  $\text{C}_6\text{H}_5^-$  was formed by proton abstraction from benzene by the  $\text{NH}_2^-$  ion. The  $\text{RO}^-$  ions ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_2$ ) were generated by proton abstraction from the corresponding alcohols with the use of  $\text{HO}^-$  as the Brønsted base. The ions of interest were reacted selectively with a given halomethane by ejecting all other ions from the FT-ICR cell as described in detail elsewhere.<sup>58,59</sup> Abundant halide ions were formed by dissociative capture of low energy electrons to the halomethanes containing three or four halogen atoms. The occurrence of this process during the period in which a given ion was allowed to react with a halomethane was suppressed by ejecting the low energy electrons from the FT-ICR cell as described previously.<sup>60</sup> A complete inhibition of the capture of low-energy electrons was achieved in most instances

with the exception of some of the experiments with  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CBr}_4$ . For these substrates, ejection of the primary reactant ion followed by a time-delay of 1–2 s proved that dissociative capture of residual electrons trapped in the FT-ICR cell may have contributed to the formation of 10–20% of the  $\text{Br}^-$  ions generated under normal operating conditions.

In the experiments concerned with the reactions of the  $\text{O}^-$  ion with the halomethanes, the pressure of  $\text{N}_2\text{O}$  was  $3 \times 10^{-6}$  Pa, whereas a given halomethane was present at an indicated pressure of  $3 \times 10^{-5}$ – $4 \times 10^{-5}$  Pa. A low partial pressure of  $\text{N}_2\text{O}$  was chosen in order to minimize the occurrence of the reaction of the  $\text{O}^-$  ion with nitrous oxide, which yields  $\text{NO}^-$  ions.<sup>61,62</sup> With nitrous oxide present at a low partial pressure,  $\text{NO}^-$  ions were not observed, indicating that the reaction with  $\text{N}_2\text{O}$  could not compete with the reaction of  $\text{O}^-$  with a halomethane under the chosen experimental conditions. The details of the reactions of the  $\text{O}^-$  ion with various halomethanes are given elsewhere.<sup>63</sup>

In most of the experiments, the total pressure was normally around  $10^{-4}$  Pa and the ratio between the partial pressures of the precursor of the primary negative ions, the parent compound of the reactant ion of interest and the halomethane was approximately 1:1:1. The pressures were measured with an uncalibrated ionization gauge placed in a side-arm of the main pumping line (see Results). The temperature of the trapping plate situated opposite the filament side was measured to be 330 K. The inlet systems, the leak valves and the vacuum vessel of the instrument were at room temperature.

*Materials.* All the chemicals used were commercially available and used without further purification, with the exception of tribromomethane, which was purified by distillation.

## RESULTS

### Reactions with chloromethanes

The product ions formed in the reactions of the  $\text{RO}^-$  ( $\text{R} = \text{H}$ ,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{CH}_3\text{CH}_2\text{CH}_2$ ) and  $\text{CH}_3\text{S}^-$  ions with the chloromethanes are given in Table 1, which lists the initial normalized abundances of the product ions as obtained by following the abundances as a function of time and subsequently extrapolating to zero reaction time as described previously.<sup>64</sup> In addition, Table 1 lists the normalized abundances of the product ions present in the cell after 90% of the selected anions have reacted with a given substrate.

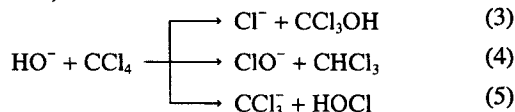
The ions given in Table 1 react with  $\text{CH}_3\text{Cl}$  to form only  $\text{Cl}^-$  ions, in agreement with a number of other studies.<sup>45–49</sup> With  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  as the substrates, the dominant reaction is proton transfer with formation of  $\text{CHCl}_2^-$  and  $\text{CCl}_3^-$  ions, respectively. With  $\text{CCl}_4$  as

Table 1. Normalized abundances of the product ions formed in the reactions of the RO<sup>-</sup> and CH<sub>3</sub>S<sup>-</sup> ions with chloromethanes<sup>a</sup>

Compound	Product ion	HO <sup>-</sup>		CH <sub>3</sub> O <sup>-</sup>		C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>		C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>		CH <sub>3</sub> S <sup>-</sup>	
		Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion
CH <sub>3</sub> Cl	Cl <sup>-</sup>	100	100	100	100	100	100	100	100	100	100
CH <sub>2</sub> Cl <sub>2</sub>	Cl <sup>-</sup>		5	10	10	5	10	5	15	No reaction	
	CHCl <sub>2</sub> <sup>-</sup>	100	95	90	90	95	90	95	85		
CHCl <sub>3</sub>	Cl <sup>-</sup>									100	15
	CCl <sub>3</sub> <sup>-</sup>	100	100	100	100	100	100	100	100	100	85
CCl <sub>4</sub>	Cl <sup>-</sup>	40				5	10	10	20	35	45
	CCl <sub>3</sub> <sup>-</sup>	40		100	100	95	90	90	80	65	55
	OCl <sup>-</sup>	20									

<sup>a</sup>The initial product ion abundances are determined by following them as a function of reaction time and subsequently extrapolating to zero time. The values at 90% conversion represent the normalized abundances of the product ions present in the FT-ICR cell after 90% of the RO<sup>-</sup> or CH<sub>3</sub>S<sup>-</sup> ions have reacted with a given substrate; see also text.

the substrate, a more diverse chemistry is observed. For example, the HO<sup>-</sup> ion reacts with CCl<sub>4</sub> to afford not only Cl<sup>-</sup> but also CCl<sub>3</sub><sup>-</sup> and ClO<sup>-</sup> ions as indicated in equations (3)–(5), which also show the elemental compositions of the expected neutral products (see also Discussion).



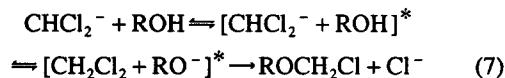
In the reaction of CH<sub>3</sub>O<sup>-</sup> with CCl<sub>4</sub>, only CCl<sub>3</sub><sup>-</sup> ions are generated. Similarly, the CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup> ions react with CCl<sub>4</sub> to afford mainly CCl<sub>3</sub><sup>-</sup>, whereas significant amounts of Cl<sup>-</sup> are generated in addition to the CCl<sub>3</sub><sup>-</sup> species if CH<sub>3</sub>S<sup>-</sup> is the reactant ion (see Table 1).

In several of these systems, the time dependence of the abundance of the Cl<sup>-</sup> ions indicates that secondary reactions either contribute to the formation of these ions or are the only source of the Cl<sup>-</sup> ions present after 90% of the reactant ions have reacted to afford products. For example, the slight increase in the relative abundance of Cl<sup>-</sup> ions in the experiments with CH<sub>2</sub>Cl<sub>2</sub> (Table 1) may be a result of a reaction between the CHCl<sub>2</sub><sup>-</sup> ion and the parent chloromethane as shown in equation (6).



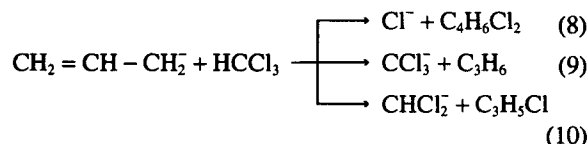
The Cl<sup>-</sup> ions may also be generated in secondary reactions of the CHCl<sub>2</sub><sup>-</sup> ion with the neutral alcohol of the RO<sup>-</sup> ions as illustrated in equation (7). In this equation, initial proton transfer to CHCl<sub>2</sub><sup>-</sup> from the ROH species is indicated to lead to a complex of a RO<sup>-</sup> ion and a CH<sub>2</sub>Cl<sub>2</sub> molecule, which can react subsequently to afford Cl<sup>-</sup> ions. A similar reactivity pattern

has been observed in a number of other gas-phase ion–molecule systems as discussed in detail in reports published previously.<sup>65,66</sup>



The ions listed in Table 2 display only to some extent a similar reactivity pattern to that observed for the reactions of the HO<sup>-</sup>, RO<sup>-</sup> and CH<sub>3</sub>S<sup>-</sup> ions with the chloromethanes. As expected, the two allylic anions, CH<sub>2</sub>=CHCH<sub>2</sub><sup>-</sup> and CH<sub>2</sub>=C(CH<sub>3</sub>)CH<sub>2</sub><sup>-</sup>, react with CH<sub>3</sub>Cl to form only Cl<sup>-</sup> ions (Table 2). Similarly, the phenyl anion and the *o*-benzyne radical anion react with CH<sub>3</sub>Cl to afford Cl<sup>-</sup> ions, whereas the thioformaldehyde radical anion shows no reactivity towards this substrate. The CH<sub>2</sub>S<sup>-</sup> ion is also unreactive towards CH<sub>2</sub>Cl<sub>2</sub>, whereas proton transfer with formation of CHCl<sub>2</sub><sup>-</sup> occurs readily in the reactions of the other ions in Table 2 with CH<sub>2</sub>Cl<sub>2</sub>.

A distinct reactivity pattern is observed for the reactions with CHCl<sub>3</sub>. For example, the two allylic anions and the phenyl anion react to form Cl<sup>-</sup>, CCl<sub>3</sub><sup>-</sup> and CHCl<sub>2</sub><sup>-</sup> ions as shown in equations (8)–(10) for CH<sub>2</sub>=CHCH<sub>2</sub><sup>-</sup>. Subsequently, the CHCl<sub>2</sub><sup>-</sup> product ions react with CHCl<sub>3</sub> by proton transfer, in agreement with the fact that CHCl<sub>3</sub> is more acidic than CH<sub>2</sub>Cl<sub>2</sub> in the gas phase.



Interestingly, the *o*-benzyne radical anion reacts with CHCl<sub>3</sub> to generate minor amounts of C<sub>6</sub>H<sub>4</sub>Cl<sup>-</sup> ions

Table 2. Normalized abundances of the product ions formed in the reactions of selected (radical) anions with chloromethanes<sup>a</sup>

Compound	Product ion	CH <sub>2</sub> CHCH <sub>2</sub> <sup>-</sup>		CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> <sup>-</sup>		CH <sub>2</sub> S <sup>-</sup>		C <sub>6</sub> H <sub>4</sub> <sup>-</sup>		C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	
		Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion
CH <sub>3</sub> Cl	Cl <sup>-</sup>	100	100	100	100	No reaction		100	100	100	100
CH <sub>2</sub> Cl <sub>2</sub>	Cl <sup>-</sup>	20	20	10	20	No reaction		30	25		
	CHCl <sub>2</sub> <sup>-</sup>	80	80	90	80			70	75	100	100
CHCl <sub>3</sub>	Cl <sup>-</sup>	25	30	10	10	70	65	30	30	40	35
	CCl <sub>3</sub> <sup>-</sup>	45	50	55	60			60	60	35	55
	CHCl <sub>2</sub> <sup>-</sup>	30	20	35	30			5	5	25	10
	Other					30 <sup>b</sup>	35 <sup>c</sup>	5 <sup>d</sup>	5 <sup>d</sup>		
CCl <sub>4</sub>	Cl <sup>-</sup>	80	80	50	50	90	90	75	75	60	60
	CCl <sub>3</sub> <sup>-</sup>	20	20	50	50			25	25	40	40
	Other					10 <sup>e</sup>	10 <sup>f</sup>				

<sup>a</sup>The initial product ion abundances are determined by following them as a function of reaction time and subsequently extrapolating to zero time. The values at 90% conversion represent the normalized abundances of the product ions present in the FT-ICR cell after 90% of a given (radical) anion has reacted with the substrate; see also text.

<sup>b</sup>The residual 30% corresponds to 10% CHCl<sub>3</sub><sup>-</sup> and 20% CH<sub>2</sub>SHCl<sup>-</sup>.

<sup>c</sup>The remaining 35% consists of 30% CHCl<sub>4</sub><sup>-</sup> and 5% CH<sub>3</sub>SHCl<sup>-</sup>.

<sup>d</sup>C<sub>6</sub>H<sub>4</sub>Cl<sup>-</sup> ions are formed; see text.

<sup>e</sup>The 10% consists of 8% CH<sub>2</sub>SHCl<sup>-</sup> and 2% CCl<sub>4</sub><sup>-</sup>.

<sup>f</sup>The 10% corresponds to 9% CH<sub>3</sub>SHCl<sup>-</sup> and 1% CCl<sub>3</sub><sup>-</sup> ions.

[equation (11)] and CHCl<sub>2</sub><sup>-</sup> ions, as indicated in Figure 1, which shows the time evolution of the relative abundance of the different product ions and the reactant ion.



The CH<sub>2</sub>S<sup>-</sup> ion reacts uniquely with CHCl<sub>3</sub> to yield Cl<sup>-</sup> ions and minor amounts of the molecular radical anion of CHCl<sub>3</sub> and CH<sub>2</sub>SHCl<sup>-</sup> ions as detailed elsewhere

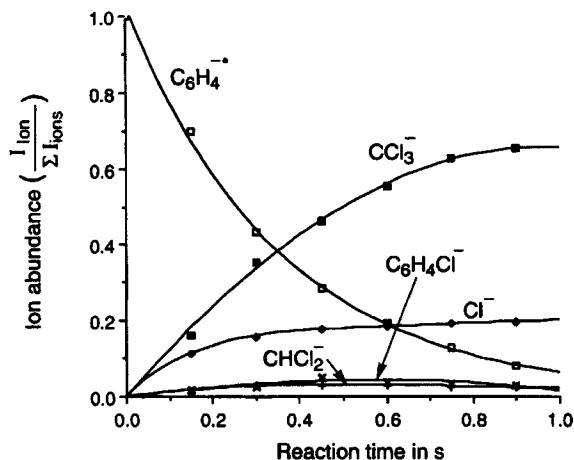


Figure 1. Normalized abundances of the ions present in the C<sub>6</sub>H<sub>4</sub><sup>-</sup>-CHCl<sub>3</sub> system as a function of reaction time (see also text)

(Table 2).<sup>41</sup> Minor amounts of the molecular radical anion are also generated in the reactions of the CH<sub>2</sub>S<sup>-</sup> ion with CCl<sub>4</sub> together with Cl<sup>-</sup> as the main product ion. With CH<sub>2</sub>S<sup>-</sup> as the reactant species, no CCl<sub>3</sub><sup>-</sup> ions are formed in the reactions with CCl<sub>4</sub>. In contrast, the other ions listed in Table 2 react with this substrate to generate considerable amounts of CCl<sub>3</sub><sup>-</sup> in addition to Cl<sup>-</sup> ions.

### Reactions with bromomethanes

The product ions formed in the reactions of the RO<sup>-</sup> (R = H, CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), CH<sub>2</sub>=C(CH<sub>3</sub>)CH<sub>2</sub><sup>-</sup>, CH<sub>2</sub>S<sup>-</sup> and C<sub>6</sub>H<sub>4</sub><sup>-</sup> ions with the bromomethanes are collected in Table 3, which lists the initial ion distributions and the relative yields of the product ions present in the cell after 90% conversion into products.

With CH<sub>3</sub>Br as the substrate, only Br<sup>-</sup> ions are formed, whereas proton abstraction with formation of CHBr<sub>2</sub><sup>-</sup> competes with Br<sup>-</sup> generation in the reactions with CH<sub>2</sub>Br<sub>2</sub>. The slight increase in the relative abundance of the Br<sup>-</sup> ions with increasing reaction time may be a result of a slow secondary reaction of CHBr<sub>2</sub><sup>-</sup> with the neutral species in the cell and/or inefficient ejection of low energy electrons trapped in the FT-ICR cell (see Experimental).

Proton abstraction is the only pathway open in the reaction of HO<sup>-</sup> with CHBr<sub>3</sub> and dominates for the two alkoxide ions, CH<sub>3</sub>O<sup>-</sup> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup>. In addition, the latter two ions react with this substrate to form

Table 3. Normalized abundances of the product ions formed in the reactions of the selected (radical) anions with bromomethanes<sup>a</sup>

Compound	Product ion	HO <sup>-</sup>		CH <sub>3</sub> O <sup>-</sup>		C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>		CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> <sup>-</sup>		CH <sub>2</sub> S <sup>-</sup>		C <sub>6</sub> H <sub>4</sub> <sup>-</sup>	
		Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion	Initial	At 90% conversion
CH <sub>3</sub> Br	Br <sup>-</sup>	100	100	100	100	100	100	100	100	100	100	100	100
CH <sub>2</sub> Br <sub>2</sub>	Br <sup>-</sup>	5	15	5	10		10	75	70	90	85	40	40
	CHBr <sub>2</sub> <sup>-</sup>	95	85	95	90	100	90	25	30			60	60
	Other									10 <sup>b</sup>	15 <sup>c</sup>		
CHBr <sub>3</sub>	Br <sup>-</sup>			5	5		5	100	100	90	95	100	100
	CHBr <sub>2</sub> <sup>-</sup>				15	10	5	5					
	CBr <sub>3</sub> <sup>-</sup>	100	100	80	85	90	90						
	Other									10 <sup>d</sup>	5 <sup>e</sup>		
CBr <sub>4</sub>	Br <sup>-</sup>		5	5	5			100	100	100	100		
	CBr <sub>3</sub> <sup>-</sup>	100	95	95	95	100	100						

<sup>a</sup>The initial product ion abundances are determined by following them as a function of reaction time and subsequently extrapolating to zero time. The values at 90% conversion represent the normalized abundances of the product ions present in the FT-ICR cell after 90% of the (radical) anions have reacted with the given substrate. The slight increase in the relative abundance of the Br ions in some of the systems may be attributed to an inefficient ejection of low-energy electrons from the cell and/or secondary reactions between the primary product ions and the neutral species present in the FT-ICR cell; see also text.

<sup>b</sup>Ion corresponds to CH<sub>2</sub>SBr<sup>-</sup>.

<sup>c</sup>The remaining 15% consists of 10% CH<sub>2</sub>Br<sub>2</sub><sup>-</sup> and 5% CH<sub>2</sub>SBr<sup>-</sup>.

<sup>d</sup>The 10% consists of 5% CH<sub>2</sub>SBr<sup>-</sup> and 5% CHBr<sub>3</sub><sup>-</sup>.

<sup>e</sup>The 5% corresponds to 2% CH<sub>2</sub>SBr<sup>-</sup>, 2% CHBr<sub>4</sub><sup>-</sup> and 1% CHBr<sub>3</sub><sup>-</sup>.

minor amounts of CHBr<sub>2</sub><sup>-</sup> ions:



Only Br<sup>-</sup> ions are formed in the reactions of the CH<sub>2</sub>=C(CH<sub>3</sub>)CH<sub>2</sub><sup>-</sup> ion and the *o*-benzyne radical anion with CHBr<sub>3</sub>. A distinct reactivity pattern is again observed for the CH<sub>2</sub>S<sup>-</sup> radical anion, which reacts with CHBr<sub>3</sub> to form minor amounts of CHBr<sub>3</sub><sup>-</sup> and CH<sub>2</sub>SBr<sup>-</sup> ions in addition to Br<sup>-</sup> [equations (13)–(15) and Table 3].



With CBr<sub>4</sub> as the substrate, the hydroxy and alkoxy anions react predominantly or exclusively to afford CBr<sub>3</sub><sup>-</sup> ions. These ions are not generated in the reactions of the CH<sub>2</sub>=C(CH<sub>3</sub>)CH<sub>2</sub><sup>-</sup> and CH<sub>2</sub>S<sup>-</sup> ions, which lead only to Br<sup>-</sup> (Table 3).

### Determination of reaction rates

The overall rate constants for the reactions of the (radical) anions and the chloromethanes are given in Table 4 and the values for the reactions with some of these reactant ions and the bromomethanes are collected in Table 5. In addition to the rate constants, we have listed the efficiencies of the processes estimated as the ratio between the corrected overall experimental rate constants and the collision rate constants calculated on

the basis of the average dipole orientation (ADO) theory (see below).<sup>67</sup>

All the reactions occur with pseudo-first order kinetics since the number of ions is roughly a factor of 10<sup>4</sup> lower than that of the neutral reactants in the FT-ICR instrument. The second-order rate constants are thus derived as the ratio between the slope of linear plots of the natural logarithm of the normalized abundances of the reactant ions as a function of reaction time and the pressure of a given halomethane. Examples of the kinetic plots are given in Figure 2, which shows the time dependence of the natural logarithm of the normalized abundances of the *o*-benzyne radical anion with the full series of chloromethanes. The linear regression correlation coefficients for these results are >0.990. Similarly, the other rate constants given in Tables 4 and 5 are based on plots with linear regression coefficients of >0.990.

The major uncertainties in the conversion of the slopes of the regression lines into second-order rate constants are related to establishing the temperature of the chemical system and the determination of the pressure of a given halomethane in the cell of the instrument. Normally, the pressure in an FT-ICR instrument is too low for assigning a true thermodynamic temperature to the reactant chemical system. It should be emphasized, however, that the observed linear dependence of the natural logarithm of the normalized abundances of the reactant ions indicates that the distribution of the translational and internal energy of the reactant species is similar and relatively

Table 4. Rate constants ( $k$ ) and efficiencies (Eff.) of the reactions of the selected (radical) anions with chloromethanes<sup>a</sup>

Reactant ion, A <sup>-</sup>	$EA(A)^b$ (kJ mol <sup>-1</sup> )	$\Delta H_{acid}^o(AH)^b$ (kJ mol <sup>-1</sup> )	CH <sub>3</sub> Cl		CH <sub>2</sub> Cl <sub>2</sub>		CHCl <sub>3</sub>		CCl <sub>4</sub>	
			$k$	Eff.	$k$	Eff.	$k$	Eff.	$k$	Eff.
HO <sup>-</sup>	176	1635	1.8	0.70	2.1	0.86	2.6	1.1	0.22	0.11
CH <sub>3</sub> O <sup>-</sup>	156	1592	1.3	0.63	1.4	0.69	2.4	1.3	1.3	0.87
C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>	168	1579	1.0	0.52	1.3	0.75	—	—	1.1	0.82
C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>	172	1573	0.73	0.42	0.94	0.59	—	—	0.64	0.54
CH <sub>3</sub> S <sup>-</sup>	183	1493	0.11	0.05	No reaction		Equilibrium <sup>c</sup>		1.2	0.95
CH <sub>2</sub> S <sup>-</sup>	45	1434 <sup>d</sup>	No reaction		No reaction		0.83	0.54	1.9	1.4
CH <sub>2</sub> CHCH <sub>2</sub> <sup>-</sup>	35	1635	0.31	0.16	0.56	0.31	1.1	0.66	1.9	1.3
CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> <sup>-</sup>	35	1633	0.40	0.23	1.2	0.73	1.6	1.1	2.1	1.7
C <sub>6</sub> H <sub>4</sub> <sup>-</sup>	54	1592	0.04	0.03	0.68	0.46	0.96	0.50	1.2	1.1
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	100	1677	0.56	0.33	0.96	0.66	1.1	0.84	1.5	1.4

<sup>a</sup>Bimolecular rate constants in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The efficiency of a given reaction is obtained as the ratio between the experimental rate constant and the collision rate constant calculated from the average dipole orientation (ADO) theory; see text and Ref. 67.

<sup>b</sup>The values are from Ref. 50.

<sup>c</sup>The gas-phase acidity of CHCl<sub>3</sub> is close to the value for CH<sub>3</sub>SH, see Ref. 50.

Table 5. Rate constants ( $k$ ) and efficiencies (Eff.) of the reactions of selected (radical) anions with bromomethanes<sup>a</sup>

Reactant ion	CH <sub>3</sub> Br		CH <sub>2</sub> Br <sub>2</sub>		CHBr <sub>3</sub>		CBr <sub>4</sub>	
	$k$	Eff.	$k$	Eff.	$k$	Eff.	$k$	Eff.
HO <sup>-</sup>	2.3	0.93	2.8	1.1	2.8	1.2	1.1	0.55
CH <sub>3</sub> O <sup>-</sup>	1.4	0.72	2.2	1.1	2.0	1.1	1.6	1.0
C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>	1.9	1.2	1.9	1.3	1.5	1.1	0.52	1.1
CH <sub>2</sub> S <sup>-</sup>	0.6	0.34	1.3	0.8	1.4	1.0	2.0	1.5
CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> <sup>-</sup>	1.7	1.1	2.1	1.4	1.9	1.4	1.3	1.1
C <sub>6</sub> H <sub>4</sub> <sup>-</sup>	0.50	0.35	1.0	0.75	1.2	1.0		

<sup>a</sup>Bimolecular rate constants in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The efficiency of a given reaction is obtained as the ratio of the experimental rate constant to the collision rate constant calculated from the average dipole orientation (ADO) theory; see text and Ref. 67.

narrow. In other words, this may imply that an assumed temperature may be assigned to the reactant chemical system. With respect to the instrument used in the present study, the inlet lines and the main vacuum system are kept at room temperature, suggesting that the chemical system can be assumed to have a temperature of 298 K (see also Discussion).

A considerable uncertainty is associated with the determination of the pressures of the various halomethanes. The low pressures in the instrument necessitate the use of an ionization gauge whose sensitivity is dependent on the nature of the chemical species. The correction of an ionization gauge pressure reading is often achieved by first determining the rate constant for the reaction between the CH<sub>4</sub><sup>+</sup> radical cation and CH<sub>4</sub> with the given instrument and then comparing the result with the average value of the reported rate constants for this process (1.13 × 10<sup>-9</sup> cm<sup>3</sup>

molecule<sup>-1</sup> s<sup>-1</sup>).<sup>46,68</sup> Subsequently, the correction factor needed for other compounds may be estimated with the method based on an indicated linear dependence of the response of an ionization gauge with the polarizability of the neutral species in question.<sup>69</sup> Following this procedure yielded reasonable rate constants for the reaction of the various ions with chloromethane (see below), whereas the values for the rate constants of the reactions with tetrachloromethane and tetrabromomethane obtained by this method were considered to be unrealistic, that is, a factor of 2 or more greater than the  $k_{ADO}$  rate constant. We decided, therefore, to perform the correction of the ionization gauge readings for the pressures of the different halomethanes by examination of the kinetics of reactions with known rate constants and/or reactions which are indicated or highly likely to proceed with the collision rate.

For the correction of the indicated pressure of chlor-

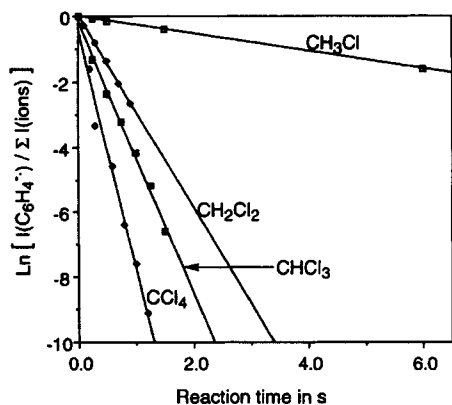


Figure 2. Variation in the natural logarithm of the normalized abundance of the *o*-benzyne radical anions in the reactions with  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  (see text). The results have been corrected for the difference in the ionization gauge pressure readings of the different chloromethanes. The corrected pressures were  $p(\text{CH}_3\text{Cl}) = 1.6 \times 10^{-5}$  Pa,  $p(\text{CH}_2\text{Cl}_2) = 1.6 \times 10^{-5}$  Pa,  $p(\text{CHCl}_3) = 1.4 \times 10^{-5}$  Pa and  $p(\text{CCl}_4) = 1.0 \times 10^{-5}$  Pa (see text for details)

omethane, the reaction with  $\text{HO}^-$  was chosen as a reference since the rate constants for this process obtained with different experimental methods are in reasonable agreement with each other (average value  $1.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>45-48</sup> Based on this approach, we obtain a rate constant for the reaction of  $\text{CH}_3\text{O}^-$  with chloromethane which is in agreement with the values reported in other studies, that is,  $1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>45-48</sup> Similarly, we obtained the same value for the rate constant for the reaction of the  $\text{CH}_3\text{S}^-$  ion with  $\text{CH}_3\text{Cl}$  ( $0.11 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) as reported previously.<sup>47</sup>

For the two substrates  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , a recent study indicated that the  $\text{O}^{\cdot-}$  ion reacts with these substrates with rate constants which are close or equal to the collision rate constant as determined by the ADO theory.<sup>38</sup> The rate constants given in Table 4 for the reactions of the various ions with these two substrates are therefore based on the assumption that the  $\text{O}^{\cdot-}$  ion reacts with the ADO collision rate constant also under the present experimental conditions. With this procedure for correcting the pressure readings of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , we obtain for the proton transfer reactions of the  $\text{HO}^-$  ion with  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  (see Table 1) efficiencies of 0.9–1.1. This lends credibility to the procedure for correcting the pressure readings of these substrates, since exothermic proton abstractions in the gas phase involving small and charge-localized anions often proceed with an efficiency close to unity.<sup>70</sup>

The value in Table 4 for the rate constant of the

reaction of the *o*-benzyne radical anion with  $\text{CH}_2\text{Cl}_2$  is lower than the value obtained with the flowing afterglow (FA) method ( $1.01 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>56</sup> A possible reason for this may be sought in the difference in the pressures used in the FA and the FT-ICR methods. In the former method, the reactions are performed in a flow of helium at a pressure of *ca* 70 Pa, whereas the pressure in an FT-ICR instrument is normally  $10^{-4}$  Pa or lower. The much higher pressure in the FA method may lead to collisions between the intermediate short-lived complexes formed by the approach of the reactants to each other and as a result the internal energy of these complexes may be lowered. For the overall process, this implies that the observed rate constant increases in line with the fact that rates of gas-phase ion–molecule reactions often display a negative temperature dependence.<sup>71</sup>

With  $\text{CCl}_4$  as the substrate, a recent study indicates that the reaction with  $\text{O}^{\cdot-}$  proceeds at room temperature with a rate constant ( $1.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) which is about 10% lower than the ADO collision rate constant.<sup>38</sup> Irrespective of whether the correction of the ionization gauge reading for the pressure of  $\text{CCl}_4$  is based on the reported rate constant or the assumption that this reaction proceeds with the ADO collision rate constant under our experimental conditions, we obtain for the reactions of the second series of (radical) anions efficiencies ranging from 1.1 to 1.7. These efficiencies could suggest that the reported rate constant for the  $\text{O}^{\cdot-}$  reaction with  $\text{CCl}_4$  is in error, thus leading to an inaccurate pressure correction. If an average value for the rate constant of the reaction of  $\text{O}^{\cdot-}$  with  $\text{CCl}_4$  (*ca*  $1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is used for the pressure corrections, the efficiencies are decreased to *ca* 80% of the values given in Table 4, that is, for the second series of ions, we obtain efficiencies ranging from 0.9 to 1.3. However, the ADO theory is known to underestimate the collision rate constants and efficiencies larger than unity have been reported for gas-phase ion–molecule reactions, such as exothermic electron transfer reactions involving ionized noble gas atoms and organic molecules and also for exothermic proton transfer reactions.<sup>44,70</sup> For the present systems, the efficiencies for the reactions of the second series of (radical) anions with  $\text{CCl}_4$  should only be taken as an indication that these processes are essentially collision controlled.

The rate constants for the reactions with the bromomethanes are also based on the assumption that the reaction of the  $\text{O}^{\cdot-}$  ion with these substrates proceeds with the rate constant  $k_{\text{ADO}}$ . With this assumption, we obtain a value for the reaction of the  $\text{HO}^-$  ion with  $\text{CH}_3\text{Br}$  which is close to a recent value ( $2.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>47</sup> For the remaining bromomethanes, no rate constants have been published for the reactant ions given in Table 5, thus preventing an evaluation of the obtained results. We note, however, that the results in Table 5 are in keeping with the fact



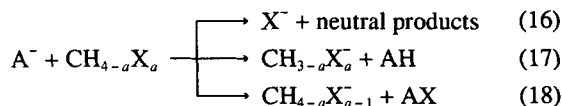
that the strongly exothermic proton abstractions from the  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  species with, for example, the  $\text{HO}^-$  ion proceed essentially with the collision rates.

In conclusion, it can be mentioned that the rate constants given in Tables 4 and 5 are reproducible to within ca 20% over an extended period of time if the procedure outlined for the corrections of the pressure readings is followed repeatedly. The absolute error on the values for the rate constants for the reactions with the various halomethanes is unknown, however, irrespective of the fact that we obtained reasonable agreement with literature values and the expected behavior for strongly exothermic proton transfer reactions (see above).

## DISCUSSION

### Reaction pathways and thermodynamics

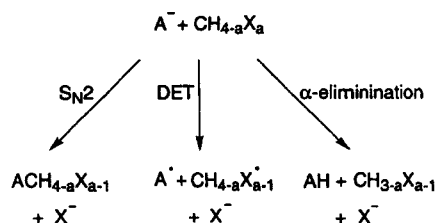
The combined results reveal that the various (radical) anions react mainly with the chloro- and bromomethanes ( $\text{CH}_{4-a}\text{X}_a$ ) with the formation of halide ions,  $\text{X}^-$  [equation (16)], and halomethyl anions containing either the same number of halogen atoms as in the parent compound [ $\text{CH}_{3-a}\text{X}_{a-1}$ , equation (17)] and/or one halogen atom less [ $\text{CH}_{4-a}\text{X}_{a-1}$ , equation (18)].



The halomethyl anions  $\text{CH}_{3-a}\text{X}_{a-1}$  are evidently a result of proton abstraction, whereas the ions  $\text{CH}_{4-a}\text{X}_{a-1}$  in a formal sense arise by transfer of a halogen cation from the substrate molecule to the reactant ion (see below). For a few of the reactant systems other ionic products are generated. In particular, stable radical anions of  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and  $\text{CHBr}_3$  are formed in low yields together with  $\text{CH}_2\text{SCl}^-$  or  $\text{CH}_2\text{SBr}^-$  ions if  $\text{CH}_2\text{S}^-$  is the reactant ion. In addition, minor amounts of  $\text{C}_6\text{H}_4\text{Cl}^-$  ions are generated in the reaction of  $\text{C}_6\text{H}_4^-$  with  $\text{CHCl}_3$  [Table 2 and equation (11)].

Irrespective of the apparent simplicity of some of the product ion distributions, various reaction types may play a role in the ion-molecule chemistry of the halomethanes. This holds in particular for the formation of halide ions which may arise as a result of a number of pathways, including  $\text{S}_{\text{N}}2$  substitution,  $\alpha$ -elimination and/or dissociative electron transfer (see Scheme 1).

The various processes leading to halide ions yield, of course, different neutral species and their occurrence in the reactions of a particular (radical) anion with a halomethane could in principle be ascertained by an analysis of the neutral products. Notwithstanding that the neutral products of gas-phase ion-molecule reac-



Scheme 1. Summary of the possible pathways leading to halide ions in the reactions of the anions (or radical anions) with the halomethanes  $\text{CH}_{4-a}\text{X}_a$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ;  $a = 1-4$ ; see also text).

tions have been characterized in a few instances with the use of specialized and dedicated instrumentation,<sup>72,73</sup> the most commonly applied methods do not allow for a direct identification of the neutral species generated in the reactions. This holds also for the FT-ICR method applied in the present study, thus implying that the role of the various pathways leading to the halide ions in the reactions with the halomethane can be assessed only indirectly.

A possible procedure for obtaining insight into the role of the different pathways in Scheme 1 is to rely on thermodynamic considerations in keeping with the fact that only overall exoergic or thermoneutral reactions occur under normal operating conditions of an FT-ICR instrument. In other words, if an overall process is estimated to be exoergic or thermoneutral, its occurrence cannot be excluded. A weak aspect of this approach is, of course, that an exoergic process may be prevented by an insurmountable kinetic barrier. Furthermore, the application of thermodynamic considerations in determining the role of different pathways leading to the same ionic product necessitates the assignment of a temperature to the reactant chemical system. In this respect, the low-pressure conditions in the present series of experiments cause the reactant species to be isolated species and as a result hamper the assignment of a true thermodynamic temperature to the reactant system. Nevertheless, the criterion of exoergicity with respect to the spontaneous occurrence of a reaction is commonly observed to be valid and in support of the assignment of a temperature to the reactant system, it should be noted that thermodynamic results obtained with low pressure methods, such as FT-ICR, mostly agree with the results obtained with the use of the high pressure methods flowing afterglow (FA) and high pressure mass spectrometry (HPMS).<sup>74,75</sup> For the present series of results, it can be assumed for simplicity that the temperature of the chemical system is 298 K (see also the sections Determination of reaction rates and Experimental). This allows the use of thermodynamic arguments in the assignments of the pathways which may play a role in the reactions of the various (radical) anions with the

halomethanes, in particular with respect to the formation of the halide ions.

The reaction enthalpies which could be estimated for the  $S_N2$  substitutions, proton abstractions and the reaction involving formal transfer of a halide cation are given in Table 6 for the chloromethanes and in Table 7 for the bromomethanes. For these pathways, the overall reactions are likely to be associated with a relatively

small entropy change and accordingly the occurrence of these processes may, in a thermodynamic sense, be discussed on the basis of the reaction enthalpy. Also included in Tables 6 and 7 are the reaction enthalpies of the  $\alpha$ -elimination and halide cation transfer followed by dissociation of the initially formed product ion into a halide ion and a carbene. For these pathways, a significant increase in entropy change is expected for the

Table 6. Reaction enthalpies (in  $\text{kJ mol}^{-1}$  and at 298 K) for the different possible pathways between the two series of reactant ions and the chloromethanes (see also text)

Reactant ion	$\text{CH}_3\text{Cl}$				$\text{CH}_2\text{Cl}_2$				$\text{CHCl}_3$				$\text{CCl}_4$	
	$S_N2$	PT <sup>a</sup>	$\alpha$ -El <sup>b</sup>	Cl-at <sup>c</sup>	PT	$\alpha$ -El	Cl-at	Carb <sup>d</sup>	PT	$\alpha$ -El	Cl-at	Carb	Cl-at	Carb
$\text{HO}^-$	-210	22	140	266	-68	81	186	304	-141	-9	91	240	1	133
$\text{CH}_3\text{O}^-$	-190	65	182		-25	123			-98	33				
$\text{C}_2\text{H}_5\text{O}^-$	-175	78	196		-12	137			-85	47				
$\text{C}_3\text{H}_7\text{O}^-$	-171	84	202		-6	143			-79	53				
$\text{CH}_3\text{S}^-$	-123	164	282		74	223			1	133				
$\text{CH}_3\text{S}^{\cdot-}$	-66 <sup>e</sup>	223 <sup>f</sup>	341 <sup>f</sup>		113 <sup>f</sup>	282 <sup>f</sup>			60 <sup>f</sup>	192 <sup>f</sup>				
$\text{C}_3\text{H}_5^-$	-270	22	140	90	-68	81	10	128	-141	-9	-85	64	-175	-43
$\text{C}_4\text{H}_7^-$	-267	24	142	93	-66	83	13	131	-139	-7	-82	67	-172	-40
$\text{C}_6\text{H}_4^{\cdot-}$	-239	65	188		-25	129			-98	39				
$\text{C}_6\text{H}_5^-$	-324	-20	99	46	-110	40	-34	84	-183	-47	-129	20	-219	-87

<sup>a</sup> Proton transfer.

<sup>b</sup>  $\alpha$ -Elimination.

<sup>c</sup> Attack on a chlorine atom.

<sup>d</sup> Chlorine atom attack followed by dissociation of the product ion into a carbene molecule and a chloride ion.

<sup>e</sup> Refers to the formation of a  $\text{CH}_3\text{SCH}_2\cdot$  radical.

<sup>f</sup> Refers to the formation of a  $\cdot\text{CH}_2\text{SH}$  radical.

Table 7. Reaction enthalpies (in  $\text{kJ mol}^{-1}$  and at 298 K) for the different possible pathways between the two series of reactant ions and the bromomethanes (see also text)

Reactant ion	$\text{CH}_3\text{Br}$				$\text{CH}_2\text{Br}_2^a$			$\text{CHBr}_3$		$\text{CBr}_4$
	$S_N2$	Pt <sup>b</sup>	$\alpha$ -El <sup>c</sup>	Br-at <sup>d</sup>	$\alpha$ -El	Br-at	Carb <sup>e</sup>	PT <sup>f</sup>	Carb	Br-at <sup>f</sup>
$\text{HO}^-$	-240	8	110	235	55	133	235	<-89	194	<14
$\text{CH}_3\text{O}^-$	-220	51	152		97			<-46		
$\text{C}_2\text{H}_5\text{O}^-$	-205	64	166		111			<-33		
$\text{C}_3\text{H}_7\text{O}^-$	-201	70	172		117			<-27		
$\text{CH}_3\text{S}^-$	-153	150	252		197			<53		
$\text{CH}_3\text{S}^{\cdot-}$	-110 <sup>g</sup>	209 <sup>h</sup>	311 <sup>h</sup>		256 <sup>h</sup>			<112 <sup>h</sup>		
$\text{C}_3\text{H}_5^-$	-300	8	110	100	55	-2	100	<-89	59	<-121
$\text{C}_4\text{H}_7^-$	-297	10	112	95	57	-7	95	<-87	54	<-126
$\text{C}_6\text{H}_4^{\cdot-}$	-269	51	158		103			<-46		
$\text{C}_6\text{H}_5^-$	-354	-34	69	52	14	-50	52	<-131	11	<-169

<sup>a</sup> The reaction enthalpy of proton abstraction has not been given since a reliable value has not been reported for the gas-phase acidity of this bromomethane.

<sup>b</sup> Proton transfer.

<sup>c</sup>  $\alpha$ -Elimination.

<sup>d</sup> Attack on a bromine atom.

<sup>e</sup> Bromine atom attack followed by dissociation of the product ion into a carbene molecule and a bromide ion.

<sup>f</sup> The given reaction enthalpies refer to formation of  $\text{CBr}_3^-$  ions. The heat of formation of this ion as given in Ref. 50 is likely to be in error since the quoted value for the gas-phase acidity of the  $\text{CHBr}_3$  compound given in this reference is probably too high.

<sup>g</sup> Refers to the formation of a  $\text{CH}_3\text{SCH}_2\cdot$  radical.

<sup>h</sup> Refers to the formation of a  $\cdot\text{CH}_2\text{SH}$  radical.

overall processes owing mainly to the transformation of two reactant species into three distinct products. The Gibbs energies for these reactions are not listed in the tables, however, since the necessary data are not available for all chemical species involved in the reactions. With respect to the overall dissociative electron transfer, the reaction Gibbs energies could be estimated, however, and are collected in Table 8.<sup>50,76-78</sup>

In the reactions with  $\text{CH}_3\text{Cl}$ , the formation of  $\text{Cl}^-$  ions can be ascribed to an exothermic  $S_{\text{N}}2$  substitution, in agreement with various other studies.<sup>45,48</sup> The  $S_{\text{N}}2$  pathway may also be important for the formation of  $\text{Cl}^-$  ions in the reactions with the chloromethanes containing more than a single chlorine atom. The enthalpy changes for the  $S_{\text{N}}2$  reactions in these systems are not given in Table 6 since only limited heat of formation data are available for the expected neutral chlorine-containing products of these processes. For the allyl anion as the reactant ion, however, the  $S_{\text{N}}2$  substitution with the  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  is estimated to be exothermic by 283, 285 and 300  $\text{kJ mol}^{-1}$ , respectively.<sup>50</sup> Similarly, we expect that an  $S_{\text{N}}2$  process is exothermic for the other reactant ions and the chloromethanes with more than a single chlorine atom. From studies of reactions in the condensed phase it is known, however, that the rate of the  $S_{\text{N}}2$  process with a halomethane decreases as the number of halogen atoms is increased.<sup>19,79</sup> For the present systems, the  $S_{\text{N}}2$  substitution may be expected, therefore, to decrease in importance as the number of chlorine atoms is increased in the halomethane, even though energetically favourable. Similar considerations apply to the bromomethanes, notwithstanding that the occurrence of dissociative electron transfer in addition to the  $S_{\text{N}}2$  substitution cannot be excluded for the reactions of the  $\text{CH}_2\text{S}^-$ ,  $\text{CH}_2=\text{CHCH}_2^-$ ,

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2^-$  and  $\text{C}_6\text{H}_4^-$  ions with  $\text{CH}_3\text{Br}$  (see below).

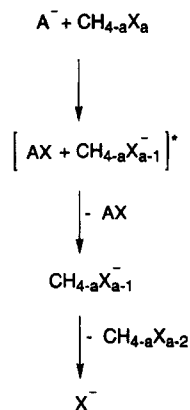
With respect to the formation of halide ions by  $\alpha$ -elimination, this requires that the proton abstraction involved is sufficiently exothermic for the product ion to dissociate into a carbene molecule and a halide ion. For the mono- and dihalogen-substituted methanes,  $\alpha$ -elimination is estimated to be significantly endothermic, as can be seen in Tables 6 and 7. Even though the overall process is inclined to be associated with a favorable change in entropy, this change may not be sufficiently large to cause the reaction to be exoergic for most of the reactant systems. For example, the enthalpy change for  $\alpha$ -elimination in the reaction of the  $\text{HO}^-$  ion with  $\text{CH}_3\text{Cl}$  is estimated to be 140  $\text{kJ mol}^{-1}$  (Table 6). With an estimated entropy change for this process of *ca.* 133  $\text{JK}^{-1}\text{mol}^{-1}$ , a reaction Gibbs energy of *ca.* 100  $\text{kJ mol}^{-1}$  is obtained for the overall process if the temperature is assumed to be 298 K. For trichloromethane, the  $\alpha$ -elimination pathway is endothermic for most of the (radical) anions but becomes energetically possible for  $\text{HO}^-$ , the two allylic anions as well as for the  $\text{C}_6\text{H}_5^-$  ion (see Table 6).<sup>77,80</sup> For tribromomethane,  $\alpha$ -elimination may be energetically possible for more reactant ions even though the absence of a heat of formation of the dibromocarbene prevents a determination of the enthalpy changes associated with this process for the various reactant ions.

In addition to substitution and  $\alpha$ -elimination, the halide ions may arise by dissociation of an initially formed halomethyl anion containing one halogen atom less than the parent compound. The reaction sequence indicated in Scheme 2 involves an initial nucleophilic attack on a halogen atom followed by dissociation of the generated  $\text{CH}_4-\alpha\text{X}_{\alpha-1}^-$  ion into a carbene and an  $\text{X}^-$  ion.

Table 8. Reaction Gibbs energies (in  $\text{kJ mol}^{-1}$  and at 298 K) for dissociative electron transfer between the two series of reactant ions and the bromo- and chloromethanes (see also text)

$T\Delta S_7^{\circ a}$	$\text{CH}_3\text{Cl}$ 34	$\text{CH}_2\text{Cl}_2$ 35	$\text{CHCl}_3$ 38	$\text{CCl}_4$ 42	$\text{CH}_3\text{Br}$ 34	$\text{CH}_2\text{Br}_2$ 36	$\text{CHBr}_3$ 40	$\text{CBr}_4$ 44
$\text{HO}^-$	143	130	109	78	113	97	85	40
$\text{CH}_3\text{O}^-$	122	109	88	57	92	76	64	19
$\text{C}_2\text{H}_5\text{O}^-$	137	124	103	72	107	91	79	34
$\text{C}_3\text{H}_7\text{O}^-$	138	125	104	73	108	92	80	35
$\text{CH}_3\text{S}^-$	152	139	118	87	122	106	94	49
$\text{CH}_2\text{S}^-$	16	3	-18	-49	-14	-30	-42	-87
$\text{C}_3\text{H}_5^-$	5	-8	-29	-60	-25	-41	-53	-99
$\text{C}_4\text{H}_7^-$	2	-11	-32	-63	-28	-44	-56	-101
$\text{C}_6\text{H}_4^-$	21	8	-13	-44	-9	-25	-37	-82
$\text{C}_6\text{H}_5^-$	67	54	33	2	37	21	9	-36

<sup>a</sup>The  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$  values used in the estimation of the Gibbs energy changes are based on data given in Refs. 50, 77, 78 and 80. The  $T\Delta S_7^\circ$  value for the reactions with a given halomethane represents the average of the estimates for the individual reactions. The variation in the individual  $T\Delta S_7^\circ$  values for the various reactions with a given halomethane is only a few  $\text{kJ mol}^{-1}$ .



Scheme 2. Formation of halide ions by initial halogen atom attack in the reactions of the anions (or radical anions) with the halomethanes  $CH_{4-a}X_a$  ( $X = Cl$  and  $Br$ ;  $a = 1-4$ ; see also text)

Direct nucleophilic attack on a halogen atom in organic molecules has been described for reactions occurring in the condensed phase<sup>1,81</sup> and more recently for the reactions of negative ions with fluorochloro- and fluorobromomethanes in the gas phase.<sup>42</sup> Based on the results for the condensed-phase reactions, it has been suggested that this process is less important for chlorine than for bromine containing species and that it becomes more facile as the number of halogen atoms is increased in the substrate.<sup>81</sup> For the present systems, halogen attack is not observed in the reactions with chloro- and dichloromethane, whereas  $CHCl_2^-$  ions are formed in the reactions of most of the second series of ions with trichloromethane (Table 2), in spite of the fact that proton transfer is significantly exothermic (Table 6). With  $CCl_4$  as the substrate, attack on a chlorine atom is particularly important for the first series of ions, as indicated by the pronounced formation of  $CCl_3^-$  ions in these systems (Table 1).

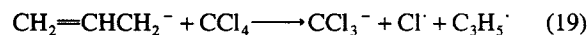
The overall formation of  $Cl^-$  ions by chlorine atom attack followed by dissociation of a  $CHCl_2^-$  ion is estimated to be endothermic for the reactions of the two allylic anions and the  $C_6H_5^-$  ion with trichloromethane (Table 6). As mentioned for  $\alpha$ -elimination, such a process is associated with a favorable change in entropy and it cannot be concluded *a priori* whether  $Cl^-$  ions may arise by this pathway in the reactions of, for example, the  $C_6H_5^-$  ion with  $CHCl_3$ . For  $CCl_4$ , formation of  $Cl^-$  by halogen atom attack followed by dissociation of the  $CCl_3^-$  ions is overall exothermic for both the allylic anions and the  $C_6H_5^-$  ion and may thus contribute to the formation of the observed  $Cl^-$  ions.

In the reactions with the bromomethanes, halogen attack is observed as a minor channel in the reactions of the two alkoxy anions with  $CHBr_3$ , notwithstanding that proton transfer is expected to be significantly exother-

mic (see Tables 3 and 7). With  $CBr_4$ , the  $HO^-$  ion and the alkoxy anions react to afford exclusively or predominantly  $CBr_3^-$  ions by bromine atom attack, whereas the 2-methylallyl anion and the  $CH_2S^-$  radical anion react with this substrate to form only  $Br^-$  ions. The extent to which these  $Br^-$  ions arise by initial attack on a bromine atom in  $CBr_4$  followed by dissociation of the  $CBr_3^-$  ion is uncertain. Furthermore, the absence of a heat of formation of the  $CBr_2$  carbene hampers the determination of the exothermicity of the overall process involving  $Br^-$  formation by this pathway.

In addition to  $S_N2$  substitution,  $\alpha$ -elimination and halogen atom attack, dissociative electron transfer may lead, in principle, to halide ions in the reactions of the various (radical) anions with the halomethanes. Dissociative electron transfer is endoergic, however, for the first series of ions and all the substrates studied but is, as expected, exoergic for the second series of ions (with the exception of the  $C_6H_5^-$  species) and  $CHCl_3$ ,  $CCl_4$  and all the bromomethanes (Table 8). In addition, dissociative electron transfer is estimated to be associated with a negative Gibbs energy if one of the two allylic anions is the reactant ionic species and  $CH_2Cl_2$  the substrate, whereas this reaction with the  $CH_2S^-$  ion is estimated to be slightly endoergic (Table 8).

The dissociative electron transfer to the halomethanes could also be suggested to yield the halomethyl anions,  $CH_{4-a}X_{a-1}^-$ . However, this process is significantly endothermic for the halomethanes examined in this study, as exemplified by an enthalpy change of  $126 \text{ kJ mol}^{-1}$  for this reaction of the allyl anion with tetrachloromethane:



A unfavourable enthalpy change for electron transfer leading to the  $CCl_3^-$  ion is also directly indicated by the much larger electron affinity of, for example, the chlorine atom ( $EA = 350 \text{ kJ mol}^{-1}$ ) than of the  $CCl_3^-$  radical ( $EA = 211 \text{ kJ mol}^{-1}$ ).<sup>50</sup>

Even though an exoergic or thermoneutral nature of the overall reaction is a requirement for its occurrence under the present experimental conditions, it is not a sufficient criterion. For example, dissociative electron transfer from  $CH_2S^-$  to  $CH_2Cl_2$  is essentially thermoneutral but only slightly exoergic with  $CHCl_3$  as the substrate (Table 8). Nevertheless, the  $CH_2S^-$  ion displays no reactivity towards  $CH_2Cl_2$  but reacts readily with  $CHCl_3$  to afford  $Cl^-$  and  $CH_2S^-$  ions in addition to minor amounts of the radical anion of  $CHCl_3$  (Table 2).<sup>41</sup> The formation of a stable radical anion of  $CHCl_3$  and also of the halomethanes,  $CCl_4$  and  $CHBr_3$ , provides direct evidence for the occurrence of electron transfer from the  $CH_2S^-$  ion. In addition, the formation of the  $CH_2S^-$  ion and also the  $CH_2SBr^-$  ion in the reactions with  $CH_2Br_2$  and  $CHBr_3$  is taken as an indication of the occurrence of electron transfer followed by

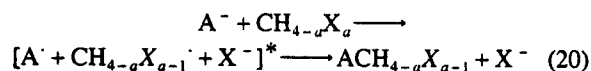
halide ion transfer in the thus formed complex of a halomethane radical anion and a thioformaldehyde molecule, as depicted in Scheme 3.

For the other ions of the second series, stable radical anions are not formed in the reactions with any of the halomethanes. Dissociative electron transfer may, of course, still be important and its occurrence in other systems is indicated in part by the additional formation of  $C_6H_4Cl^-$  ions in the reactions of the  $C_6H_4^{\cdot-}$  radical anion with  $CHCl_3$  [Table 2 and equation (11)]. In conclusion, overall dissociative electron transfer leading to halide ions is thus considered a likely pathway if this process is exoergic even though other processes, such as  $\alpha$ -elimination or halogen atom attack followed by dissociation of halogen-containing methyl anions, are indicated also to contribute to the generation of the halide ions, in particular for the substrates containing three or four halogen atoms.

#### Aspects of electron transfer to halomethanes in the gas phase

Dissociative electron transfer is indicated in Scheme 1 to lead directly to a halide ion, a methyl radical and an  $A^\cdot$  radical for an even-electron reactant ion. If the electron transfer process involves the initial formation of a complex of an  $A^\cdot$  radical and a radical anion of the halomethane followed by dissociation of the latter species, this may result in a complex containing two radicals in addition to the halide ion. If this complex is sufficiently long lived, coupling may occur prior to dissociation and thus lead to the same neutral species as indicated in Scheme 1 for the  $S_N2$  pathway. Whether the pathway shown in equation (20) can play a role, how-

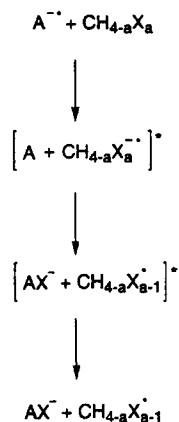
ever, is uncertain.



The involvement of intermediate complexes with a certain lifetime is implied, however, by the formation of  $CH_2S^-$  and  $C_6H_4Cl^-$  (see Scheme 3) if the  $CH_2S^{\cdot-}$  and  $C_6H_4^{\cdot-}$  radical anions, respectively, act as electron donors. For these reactant ions, the implied tertiary complex contains, of course, the neutral molecule corresponding to the reactant ion, a halomethyl radical and halide ion instead of two radicals which may undergo the suggested coupling reaction.

These considerations imply that the initial electron transfer from the reactant ion to the halomethane is energetically feasible for the reacting systems. In the absence of insight into the details of energy surfaces describing these reactions, one could utilize the difference in electron affinity between a given halomethane and the neutral species related to the electron donor to probe some features of these surfaces. Unfortunately, accurate electron affinities have not been reported for the full series of halomethanes included in the present study. Electron transmission spectroscopic studies indicate, however, that the mono- and dichloromethanes have negative vertical electron affinities.<sup>82,83</sup> In addition, electron attachment to these halomethanes may be an inherently dissociative process,<sup>84,85</sup> that is, electron transfer to these species from a negative ion in the gas phase may occur to a repulsive potential energy surface without a minimum corresponding to a radical anion of the halomethane. For the substrates,  $CH_3Cl$  and  $CH_2Cl_2$ , direct evidence is not obtained for the formation of halide ions by electron transfer. This may suggest that the attainment of such a dissociative surface is not feasible for the reactant ions and these simple halomethanes.

The details of the potential energy surfaces describing electron transfer to the halomethanes containing three or four halogen atoms are also largely unknown. Based on the formation of stable radical anions of  $CHCl_3$  and  $CCl_4$ , we reported recently that the electron affinity is likely to be between 45 and 75  $\text{kJ mol}^{-1}$  for  $CHCl_3$  and between 45 and 110  $\text{kJ mol}^{-1}$  for  $CCl_4$ .<sup>41</sup> In addition, stable radical anions are observed for  $CHBr_3$ , whereas  $CBr_4^{\cdot-}$  ions have been reported previously to arise in the reaction of the azobenzene radical anion with  $CBr_4$  in the gas phase.<sup>40</sup> Electron transfer to these halomethanes is best described, therefore, as involving the initial formation of a complex containing a halomethane radical anion and the neutral species related to the reactant ion (see also Scheme 3). As indicated by a number of theoretical studies and supported by experiments described in a previous paper,<sup>41</sup> the radical anions of  $CHCl_3$  and  $CCl_4$  are weakly bonded with respect to dissociation into a halide ion and halogen-containing methyl radical.<sup>86,87</sup> Subsequent facile dissociation of the



Scheme 3. Formation of  $AX^\cdot$  ions by initial electron transfer and subsequent halide ion transfer in the collision complexes formed in the reactions of the radical anions  $CH_2S^{\cdot-}$  and  $C_6H_4^{\cdot-}$  with the halomethanes  $CH_{4-a}X_a$  ( $X = Cl$  and  $Br$ ;  $a = 1-4$ ; see also text)

initially generated halomethane radical anion may thus occur for most reactant ions and cause halide ions to be the main or exclusive observed ionic products of an initial electron transfer to the tri- or tetrahalomethanes.

### Trends in the efficiencies of the overall reactions

The thermodynamic considerations in combination with the observed product ion distributions lead in part to a definition of the different pathways which may be of importance in the reactions of the various anions with the halomethanes. Some of these mechanistic considerations may be substantiated by the rate constants and efficiencies obtained for the overall processes (see Tables 4 and 5). With respect to the reactions with chloromethane, the trend in the efficiencies in Table 4 is in line with previous studies which indicate that  $S_N2$  substitutions in the gas phase can be associated with a significant local energy barrier causing the overall process to be slow irrespective of a favourable enthalpy change.<sup>47,49,88</sup> For example,  $\text{CH}_3\text{S}^-$  reacts with a much lower efficiency than  $\text{CH}_3\text{O}^-$  (Table 4), even though both processes are considerably exothermic. For the two allylic anions and the  $\text{C}_6\text{H}_5^-$  ion, it can be noticed that these react with chloromethane with moderate efficiencies. By contrast, the radical anion  $\text{C}_6\text{H}_4^{\cdot-}$  reacts with an efficiency that is ten times lower than the value obtained for the  $\text{C}_6\text{H}_5^-$  ion, irrespective of the fact that  $S_N2$  substitution is exceedingly exothermic in both instances.

With the dichloro- and trichloromethanes, the first series of ions react mainly or exclusively by an efficient exothermic proton abstraction. The second series of ions react with these two substrates with a lower average efficiency than the first series of ions, whereas the reverse situation applies to the reaction with  $\text{CCl}_4$ . With this substrate, the first series of ions react with a lower efficiency than the second series of ions. This indicated increase in efficiency of the overall reaction as the number of halogen atoms increases is observed for all ions of the second series. In particular, the  $\text{C}_6\text{H}_4^{\cdot-}$  radical anion reacts with an efficiency of 0.03 with chloromethane and essentially with unit efficiency if tetrachloromethane is the substrate. A similar situation holds for the allyl anion and also the  $\text{CH}_2\text{S}^-$  radical anion, which reacts only with the tri- and tetrachloromethanes. For the latter reactant ion, electron transfer is indicated to be the main or only pathway open and the high efficiencies of the overall reactions may thus indicate that this is a facile process. As a result, the increase in the efficiencies of the reactions of the other ions in the second series as the number of halogen atoms is increased in the substrate may suggest that electron transfer is also becoming more important, even though the product ion distributions indicate that the chlorine atom attack is also a pronounced process, in particular for tetrachloromethane as the substrate.

With the bromomethanes most of the ions react

readily with efficiencies approaching or equal to unity (Table 5). For bromomethane and dibromomethane, the two radical anions  $\text{CH}_2\text{S}^-$  and  $\text{C}_6\text{H}_4^{\cdot-}$  react less efficiently than the even electron negative ions, irrespective of the fact that substitution and dissociative electron transfer are thermodynamically feasible for these systems. As observed also for the chloromethanes, an increase in reaction efficiency with an increasing number of bromine atoms in the substrate is observed for the two radical anions (Table 5). The extent to which this is related to a more pronounced occurrence of electron transfer remains to be solved considering that the  $\text{Br}^-$  ions formed in these reactions may arise also by other processes (see above).

### CONCLUSIONS

The present results indicate that electron transfer is likely to be an important pathway in the reactions between the (radical) anions related to a neutral species with a relatively low electron affinity with the chloromethanes,  $\text{CHCl}_3$  and  $\text{CCl}_4$ . In the reactions of these (radical) anions with the bromomethanes, (dissociative) electron transfer may play a role even for the  $\text{CH}_2\text{Br}$  or  $\text{CH}_2\text{Br}_2$  species. For the halomethanes containing three or four halogen atoms, formation of halide ions is considered to involve initial electron transfer to give a weakly bonded radical anion of the halomethane followed by dissociation of this species into a halomethyl radical and the observed ionic products. Overall, this appears to be an efficient process, notwithstanding that the halide ions may arise also by other pathways, such as  $\alpha$ -elimination and halogen atom attack followed by dissociation of the thus generated halomethyl anions. The high efficiencies of the overall reactions with, in particular, the tetrachloro- and tetrabromomethanes in combination with the relatively high yields of the product ions of initial halogen atom attack indicate also that the latter process is facile and capable of competing effectively with the overall dissociative electron transfer process.

### ACKNOWLEDGEMENT

The authors thank the Netherlands Organization for Scientific Research (SON/NWO) for financial support.

### REFERENCES

1. L. Ebersson, *Electron Transfer Reactions in Organic Chemistry*. Springer, Berlin (1987).
2. N. Kornblum, *Angew. Chem., Int. Ed. Engl.* **14**, 734 (1975).
3. G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.* **88**, 5663 (1966).
4. G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.* **90**, 347 (1968).

- J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.* **92**, 7463 (1970).
- J. F. Bunnett, *Acc. Chem. Res.*, **11**, 413 (1978).
- R. A. Rossi and R. H. Rossi, *Aromatic Substitution by the  $S_N1$  Mechanism*. ACS Monograph 178, American Chemical Society, Washington DC (1983).
- W. L. Reynolds and R. W. Lumry, *Mechanisms of Electron Transfer*. Ronald Press, New York (1966).
- R. D. Cannon, *Electron Transfer Reactions*. Butterworths, London (1980).
- S. S. Shaik, H. B. Schlegel and S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry: the  $S_N2$  Mechanism*. Wiley, New York (1993).
- T. Lund and H. Lund, *Acta Chem. Scand.* **42**, 269 (1988).
- H. Lund, K. Daasbjerg, T. Lund and S. U. Pedersen, *Acc. Chem. Res.* **28**, 313 (1995).
- C. P. Andrieux, I. Gallardo, J.-M. Savéant and K. B. Su, *J. Am. Chem. Soc.* **108**, 638 (1986).
- J.-M. Savéant, *J. Am. Chem. Soc.* **109**, 6788 (1987).
- D. Lexa, J.-M. Savéant, K. B. Su and J. Wang, *J. Am. Chem. Soc.* **110**, 7617 (1988).
- J.-M. Savéant, *Acc. Chem. Res.* **26**, 455 (1993).
- F. G. Bordwell and J. A. Harrelson, Jr, *J. Am. Chem. Soc.* **111**, 1052 (1989).
- E. C. Ashby, *Acc. Chem. Res.* **21**, 414 (1988).
- C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd. ed. Cornell University Press, Ithaca, NY (1969).
- J. March, *Advanced Organic Chemistry*, 3rd ed. Wiley, New York (1985).
- S. S. Shaik, *Acta Chem. Scand.* **44**, 205 (1990).
- A. Pross, and S. S. Shaik, *Acc. Chem. Res.* **16**, 363 (1983).
- S. S. Shaik, *Prog. Phys. Org. Chem.* **15**, 197 (1985).
- A. Pross, *Acc. Chem. Res.* **18**, 212 (1985).
- R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).
- L. Ebersson, and S. S. Shaik, *J. Am. Chem. Soc.* **112**, 4484 (1990).
- M. Newcomb and D. P. Curran, *Acc. Chem. Res.* **21**, 206 (1988).
- M. A. Almoester Ferreira (Ed.), *Ionic Processes in the Gas Phase*. Reidel, Dordrecht (1984).
- N. M. M. Nibbering, *Adv. Phys. Org. Chem.* **24**, 1 (1988).
- D. H. Russell (Ed.), *Gas Phase Inorganic Chemistry*. Plenum Press, New York (1989).
- R. J. Schmitt, S. E. Buttrill, Jr, and D. S. Ross, *J. Am. Chem. Soc.* **106**, 926 (1984).
- M. Attina, F. Cacace and M. Speranza, *Int. J. Mass Spectrom. Ion Processes* **117**, 37 (1992).
- R. Bucci, F. Grandinetti, A. Filippi, G. Laguzzi, G. Ochiucci and M. Speranza, *J. Am. Chem. Soc.* **113**, 4550 (1991).
- A. Filippi, G. Ochiucci and M. Speranza, *Can J. Chem.* **69**, 740 (1991).
- G. Ochiucci, M. Speranza, L. J. de Koning and N. M. M. Nibbering, *J. Am. Chem. Soc.* **111**, 7387 (1989).
- F. E. Ferguson, F. C. Fehsenfeld and D. L. Albritton, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers, Vol. 1, Chapt. 2. Academic Press, New York (1979).
- W. G. Knighton and E. P. Grimsrud, *J. Am. Chem. Soc.* **114**, 2336 (1992).
- C. A. Mayhew, R. Peverall and P. Watts, *Int. J. Mass Spectrom. Ion Processes* **125**, 81 (1993).
- R. A. Morris, *J. Chem. Phys.* **97**, 2372 (1992).
- S. Ingemann, R. H. Fokkens and N. M. M. Nibbering, *J. Org. Chem.* **56**, 607 (1991).
- P. O. Staneke, G. Groothuis, S. Ingemann and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes* **142**, 83 (1995).
- P. O. Staneke, G. Groothuis, S. Ingemann and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes* **149/150**, 99 (1995).
- P. O. Staneke, S. Ingemann and N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas* **115**, 179 (1996).
- A. G. Harrison, *Chemical Ionization Mass Spectrometry*, 2nd ed. CRC Press, Boca Raton, FL (1992).
- D. K. Bohme and L. B. Young, *J. Am. Chem. Soc.* **92**, 7354 (1970).
- W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.* **99**, 4219 (1977).
- C. H. DePuy, S. Gronert, A. Mullin and V. M. Bierbaum, *J. Am. Chem. Soc.* **112**, 8650 (1990).
- K. Tanaka, G. I. Mackay, J. D. Payzant and D. K. Bohme, *Can. J. Chem.* **54**, 1643 (1976).
- J. M. Riveros, S. M. Jose and K. Takashima, *Adv. Phys. Org. Chem.* **21**, 197 (1985).
- S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
- A. G. Marshall and F. R. Verdun, *Fourier Transform in NMR, Optical, and Mass Spectrometry*. Elsevier, Amsterdam (1990).
- N. M. M. Nibbering, *Rapid Commun. Mass Spectrom.* **7**, 747 (1993).
- L. J. de Koning, C. W. F. Kort, F. A. Pinkse and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes* **95**, 71 (1989), and references cited therein.
- R. A. L. Peerboom, S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 1825 (1990), and references cited therein.
- H. E. K. Matimba, A. M. Crabbendam, S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Chem. Commun.* 664 (1991).
- Y. Guo and J. J. Grabowski, *J. Am. Chem. Soc.* **113**, 5923 (1991).
- J. Lee and J. J. Grabowski, *Chem. Rev.* **92**, 1611 (1992).
- A. J. Noest and C. W. F. Kort, *Comput. Chem.* **7**, 81 (1983).
- J. C. Kleingeld and N. M. M. Nibbering, *Tetrahedron* **39**, 4193 (1983).
- J. C. Kleingeld and N. M. M. Nibbering, *Lect. Notes Chem.* **31**, 209 (1982).
- S. E. Barlow and V. M. Bierbaum, *J. Chem. Phys.* **92**, 3442 (1990).
- R. A. Morris, A. A. Viggiano and J. F. Paulson, *J. Chem. Phys.* **92**, 3448 (1990).
- P. O. Staneke, S. Ingemann and N. M. M. Nibbering, in preparation.
- K. J. van den Berg, S. Ingemann and N.M.M. Nibbering, *Organometallics* **11**, 2389 (1992).
- S. Ingemann and N. M. M. Nibbering, *J. Org. Chem.* **48**, 183 (1983).
- F. M. Bickelhaupt, L. J. de Koning, N. M. M. Nibbering and E. V. Baerends, *J. Phys. Org. Chem.* **5**, 179 (1992).

67. T. Su and M. T. Bowers, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers, Vol. 1, Chapt. 3. Academic Press, New York (1979);
68. Y. Ikezoe, S. Matsuoka, M. Takebe and A. A. Viggiano, *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986*. Maruzen, Tokyo (1987).
69. J. E. Bartmess and R. M. Georgiadis, *Vacuum* **33**, 149 (1983).
70. G. I. Mackay, L. D. Betowski, J. D. Payzant, H. I. Schiff and D. K. Bohme, *J. Phys. Chem.* **80**, 2919 (1976).
71. T. F. Magnera and P. Kebarle, in *Ionic Processes in the Gas Phase*, edited by M. A. Almoester Ferreira, pp. 135-157. Reidel, Dordrecht (1984).
72. T. H. Morton, in *Techniques for the Study of Ion-Molecule Reactions*, edited by J. M. Farrar and W. H. Saunders, Jr, Chapt. III. Wiley-Interscience, New York (1988).
73. M. E. Jones and G. B. Ellison, *J. Am. Chem. Soc.* **111**, 1645 (1989).
74. J. E. Bartmess, *Mass Spectrom. Rev.* **8**, 297 (1989).
75. J. E. Bartmess and R. T. McIver, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers, Vol. 2, Chapt. 11. Academic Press, New York (1979).
76. J. Berkowitz, G. B. Ellison and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
77. S. W. Benson, *Thermodynamic Kinetics*, 2nd ed. Wiley, New York (1976).
78. J. L. Holmes and F. P. Lossing *J. Am. Chem. Soc.* **110**, 7343 (1988).
79. J. Hine, S. J. Ehrenson and W. H. Brader, Jr, *J. Am. Chem. Soc.* **78**, 2282 (1956).
80. J. A. Paulino and R. R. Squires, *J. Am. Chem. Soc.* **113**, 5573 (1991).
81. N. S. Zefirov and D. I. Makhon'kov, *Chem. Rev.* **82**, 615 (1982).
82. P. D. Burrow, A. Modelli, N. S. Chiu and K. D. Jordan, *J. Chem. Phys.* **77**, 2699 (1982).
83. K. D. Jordan and P. D. Burrow, *Chem. Rev.* **87**, 557 (1987).
84. R. Benassi, F. Bernardi, A. Bottoni, M. A. Robb and F. Taddei, *Chem. Phys. Lett.* **161**, 79 (1989).
85. M. Hotokka, B. O. Roos and L. Ebersson, *J. Chem. Soc., Perkin Trans. 2* 1979 (1986).
86. G. L. Gutsev, *J. Chem. Phys.* **98**, 7072 (1993), and references cited therein.
87. S. Roszak, J. J. Kaufman, W. S. Koski, M. Vijayakumar and K. Balasubramanian, *J. Chem. Phys.* **101**, 2987 (1994).
88. M. J. Pellerite and J. I. Brauman, *J. Am. Chem. Soc.* **105**, 2672 (1983).