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# Heats of Formation of Mono-Halogen-Substituted Carbenes. Stability and Reactivity of $\text{CHX}^{\cdot-}$ ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ) Radical Anions

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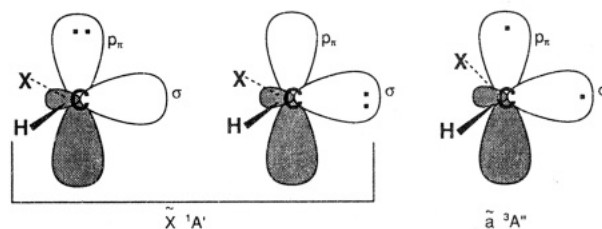
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**Abstract:** The heats of formation of mono-halogen-substituted singlet carbenes have been determined to be  $157 \pm 18$   $\text{kJ mol}^{-1}$  ( $\tilde{\text{X}}^1\text{A}'$  CHF),  $317 \pm 20$   $\text{kJ mol}^{-1}$  ( $\tilde{\text{X}}^1\text{A}'$  CHCl),  $373 \pm 18$   $\text{kJ mol}^{-1}$  ( $\tilde{\text{X}}^1\text{A}'$  CHBr), and  $428 \pm 21$   $\text{kJ mol}^{-1}$  ( $\tilde{\text{X}}^1\text{A}'$  or  $\tilde{\text{a}}^1\text{A}'$  CHI). These  $\Delta H_f^\circ$  values are based upon the following gas-phase acidities,  $\Delta H_{\text{acid}}^\circ$ , of the  $\cdot\text{CH}_2\text{X}$  radicals:  $1668 \pm 6$   $\text{kJ mol}^{-1}$  ( $\cdot\text{CH}_2\text{F}$ ),  $1610 \pm 10$   $\text{kJ mol}^{-1}$  ( $\cdot\text{CH}_2\text{Cl}$ ),  $1593 \pm 8$   $\text{kJ mol}^{-1}$  ( $\cdot\text{CH}_2\text{Br}$ ), and  $1566 \pm 11$   $\text{kJ mol}^{-1}$  ( $\cdot\text{CH}_2\text{I}$ ). The acidities were determined by observing the occurrence/nonoccurrence of proton transfer in the reactions of the  $\text{CHX}^{\cdot-}$  carbene radical anions with selected acids in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. The  $\Delta H_{\text{acid}}^\circ$  values reveal that (i) the acidity increases in the series  $\cdot\text{CH}_2\text{F}$ ,  $\cdot\text{CH}_2\text{Cl}$ ,  $\cdot\text{CH}_2\text{Br}$ , and  $\cdot\text{CH}_2\text{I}$ , i.e. the acidity increases as the halogen atom becomes heavier as observed also for the corresponding halogen-substituted methanes, and (ii) a given  $\cdot\text{CH}_2\text{X}$  radical is  $\approx 50$   $\text{kJ mol}^{-1}$  more acidic in the gas phase than the related  $\text{CH}_3\text{X}$  molecule. The reaction of a given  $\text{CHX}^{\cdot-}$  ion with the parent compound yields  $\text{X}^-$  ions in part by a direct  $\text{S}_{\text{N}}2$  substitution and in part by initial proton transfer leading to a  $[\cdot\text{CH}_2\text{X} + \cdot\text{CH}_2\text{X}]^*$  complex, which then reacts to form  $\text{X}^-$ . In addition to overall proton transfer, the reaction of the carbene radical anions with aliphatic alcohols yields  $\text{X}^-$  ions by a process which involves initial proton transfer followed by nucleophilic attack of the  $\text{RO}^-$  ion on the generated  $\cdot\text{CH}_2\text{X}$  radical.

## Introduction

The structure and reactivity of carbenes represent an important area of chemistry from both an experimental and theoretical point of view.<sup>1–9</sup> The extensive research into the properties of carbenes reflects their diverse reactivity and their capability of undergoing insertion reactions into carbon–hydrogen bonds as well as addition reactions to carbon–carbon double bonds with formation of cyclopropanes.<sup>1–3,7</sup> The reactivity of carbenes is known to depend on their spin multiplicity (see Figure 1), i.e. triplet carbenes react preferentially by two-step radical processes, for example, hydrogen atom abstraction followed by radical–radical coupling reactions, whereas singlet carbenes can react by single-step processes such as stereospecific cis-additions to alkenes.<sup>1–3</sup> The electronic configuration of the most simple carbene,  $\text{CH}_2$ , has been the subject of a number of theoretical and experimental studies, and it is now agreed upon that the triplet ground state is 40  $\text{kJ mol}^{-1}$  lower in energy than the singlet state.<sup>4–6,8</sup> The introduction of an electronegative atom or group reverses this order<sup>10–14</sup> as exemplified by CHF, which has a singlet ground state laying 62  $\text{kJ mol}^{-1}$  lower in energy than the triplet



**Figure 1.** Valence orbitals of the mono-halogen-substituted  $\text{CHX}$  carbenes. The singlet ground state is designated as  $\tilde{\text{X}}^1\text{A}'$ , whereas the triplet state is represented by  $\tilde{\text{a}}^3\text{A}''$  (see also text and ref 4, 5, and 10–12).

state as determined from the photoelectron spectrum of the  $\text{CHF}^{\cdot-}$  radical anion.<sup>11,12</sup> The  $\text{CHCl}$  and  $\text{CHBr}$  carbenes are reported also to have a singlet ground state,<sup>11,14</sup> whereas the spin multiplicity of the ground state of  $\text{CHI}$  has not been determined definitively. Upon the basis of photoelectron spectroscopy experiments with the  $\text{CHI}^{\cdot-}$  radical anion, the ground state was assigned as a triplet located 8–40  $\text{kJ mol}^{-1}$  lower in energy than the singlet state.<sup>12</sup> By contrast, recent calculations predict the singlet state of  $\text{CHI}$  to be more stable than the triplet state.<sup>10,15</sup> Irrespective of the intense research into the spin multiplicity of the  $\text{CHX}$  carbenes and their associated reactivity, consistent thermochemical data have not been published for the complete series of the mono-halogen-substituted carbenes:  $\text{CHF}$ ,  $\text{CHCl}$ ,  $\text{CHBr}$ , and  $\text{CHI}$ .

The heat of formation of  $\text{CHF}$  has been reported to be  $105 \pm 12$   $\text{kJ mol}^{-1}$  on the basis of an experimental determination of the proton affinity of  $\text{CHF}$ ,<sup>16</sup> while a study of the kinetics of the gas-phase reactions of the  $\cdot\text{CH}_2\text{F}$  radical yielded a value of  $\approx 163$

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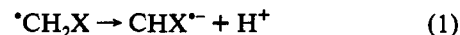
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$\text{kJ mol}^{-1}$ .<sup>17</sup> Proton affinity measurements have been used also to place the heat of formation of the  $\text{CHCl}$  carbene at  $297 \pm 20$   $\text{kJ mol}^{-1}$ ,<sup>16</sup> whereas no values have been reported previously for  $\text{CHBr}$  and  $\text{CHI}$ . In order to provide a consistent set of data based on a single experimental approach, we decided to determine the gas-phase acidities of the  $^{\circ}\text{CH}_2\text{X}$  radicals and with the use of known thermochemical relationships derive the heats of formation of the  $\text{CHX}$  carbenes.

Direct introduction of free organic radicals into a mass spectrometer is not easily achieved, and necessarily, we decided to determine the acidities of the  $^{\circ}\text{CH}_2\text{X}$  radicals by studying the proton-transfer reactions between the related  $\text{CHX}^{\ominus}$  carbene radical anions and selected molecules with a known gas-phase acidity. This approach was chosen as an entry to the heats of formation of the carbenes since the  $\text{CHX}^{\ominus}$  ions can be generated relatively easily by reacting the atomic oxygen radical anion,  $\text{O}^{\ominus}$ , with mono-halogen-substituted methanes in the gas phase.<sup>18–22</sup> Several methods, such as flowing afterglow (FA),<sup>23</sup> selected ion flow tube (SIFT),<sup>23</sup> and high-pressure mass spectrometry (HPMS)<sup>24</sup> have been developed for the study of ion/molecule reactions in the gas phase and have been applied extensively for the determination of thermochemical data. These methods utilize pressure conditions which ensure thermalization of the ions and molecules and are suited for studies of the temperature dependence of equilibrium or rate constants of gas-phase ion/molecule reactions.<sup>23–25</sup> In the present study, we have applied the low-pressure Fourier transform ion cyclotron resonance (FT-ICR)<sup>26</sup> method, which allows for a selective study of the gas-phase ion/molecule chemistry of the  $\text{CHX}^{\ominus}$  radical anions. Even though the pressure is too low in an FT-ICR instrument for the chemical system to be in thermal equilibrium with the surroundings, the reactions occurring under normal operating conditions are mostly exoergic or near-thermoneutral.<sup>18,27</sup> Moreover, thermochemical quantities, such as gas-phase acidities and proton and electron affinities, determined with the FT-ICR method are usually in agreement with the results obtained with the FA, SIFT, and HPMS methods.<sup>28–31</sup>

The gas-phase acidities of radicals and molecules provide also an experimental basis for obtaining insight into the molecular properties which determine the reactivity and stability of radical anions and anions, respectively, in the absence of solvent molecules or other indirect reactants such as counterions. Furthermore, the acidities in combination with other data can be used to derive homolytic bond dissociation energies or electron affinities of species not easily examined by other means. In this context, it should be mentioned that the gas-phase acidity of a  $^{\circ}\text{CH}_2\text{X}$  radical is defined as the enthalpy change of the reaction in eq 1 at 298

K and can be formulated as the difference between the homolytic dissociation energy of the  $\text{H}-^{\circ}\text{CHX}$  bond,  $\text{BDE}(\text{H}-^{\circ}\text{CHX})$ , and the electron affinity of the  $\text{CHX}$  carbene,  $\text{EA}(\text{CHX})$ , as shown in eq 2, where  $\text{IE}(\text{H}^{\bullet})$  denotes the ionization energy of the hydrogen atom.<sup>28</sup>



$$\Delta H^{\circ}_{\text{acid}}(^{\circ}\text{CH}_2\text{X}) = \text{BDE}(\text{H}-^{\circ}\text{CHX}) - \text{EA}(\text{CHX}) + \text{IE}(\text{H}^{\bullet}) \quad (2)$$

Previous studies from our group<sup>32,33</sup> and also by others<sup>34</sup> indicate that radicals often are more acidic than the related molecules as exemplified by the phenyl radical, which is much more acidic than benzene in the gas phase.<sup>33,35</sup> This difference in acidity is mainly a result of a  $\approx 130$   $\text{kJ mol}^{-1}$  lower dissociation energy of the C–H bonds adjacent to the radical center in  $\text{C}_6\text{H}_5^{\bullet}$  than of the C–H bonds in  $\text{C}_6\text{H}_6$ .<sup>33,35</sup> The decrease in C–H BDE going from the molecule to the radical is only partly compensated for by the larger EA of  $\text{C}_6\text{H}_5^{\bullet}$  ( $\approx 99$   $\text{kJ mol}^{-1}$ )<sup>28</sup> than of 1,2-dehydrobenzene ( $\text{EA} = 54$   $\text{kJ mol}^{-1}$ ),<sup>36</sup> and as a result, the phenyl radical is  $\approx 85$   $\text{kJ mol}^{-1}$  more acidic than benzene. The same relative order of gas-phase acidities of a radical and the related molecule has been observed for other systems, for example,  $\text{CH}_3^{\bullet}/\text{CH}_4$ ,<sup>37,38</sup>  $\text{H}_2\text{C}=\text{CH}^{\bullet}/\text{H}_2\text{C}=\text{CH}_2$ ,<sup>39–41</sup> and  $\text{Ph}-\text{N}-\text{NH}-\text{Ph}/\text{Ph}-\text{NH}-\text{NH}-\text{Ph}$ .<sup>32</sup> By contrast, the  $^{\circ}\text{CH}_2\text{CN}$  radical is as acidic as  $\text{CH}_3\text{CN}$ <sup>42</sup> and the cyclopentadienyl radical is reported to be less acidic than cyclopentadiene in the gas phase.<sup>34</sup> These contrasting observations call for more studies directed toward obtaining insight into the structural parameters, which may determine the relative acidities of radicals and the related molecules in the gas phase. In the present paper, we discuss the acidities of the  $^{\circ}\text{CH}_2\text{X}$  radicals and the corresponding  $\text{CH}_3\text{X}$  molecules.<sup>43</sup>

## Experimental Section

The experiments were performed with an FT-ICR mass spectrometer designed and constructed at the University of Amsterdam.<sup>44–46</sup> In a typical experiment, the primary negative ion,  $\text{O}^{\ominus}$ , was generated by dissociative attachment of electrons with an energy of 1.2–1.5 eV to  $\text{N}_2\text{O}$ . At these electron energies, the  $\text{O}^{\ominus}$  ions are formed with an average kinetic

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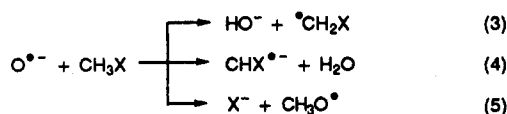
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energy of about 0.38 eV<sup>47</sup> and no precautions were taken to decrease the kinetic energy of these ions to thermal values. The duration of the electron beam pulse was normally 150 ms, and trapping of the ions was achieved by applying a voltage of  $\approx 1$  V to the trapping plates of the 1-in.<sup>3</sup> cell located in a magnetic field of 1.23 T. Subsequently and during the electron beam pulse, the O<sup>-</sup> ions reacted with one of the halogen-substituted methanes to generate the CHX<sup>-</sup> radical anions. The CHX<sup>-</sup> 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.<sup>48</sup> The reactions of the carbene 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, which increases the radius of the cyclotron motion of the ions prior to their detection. The alkoxide ions formed by proton transfer to the carbene radical anions were ejected continuously from the cell in some of the experiments, which were performed with the purpose of determining the relative abundances of the isotopic chloride or bromide ions generated in the reactions with aliphatic alcohols in the presence of a halogen-substituted methane. The continuous ejection of the alkoxide ions was achieved by applying a low-amplitude rf pulse to the excitation plates of the cell during the entire reaction period. The relative abundances of the isotopic chloride and bromide ions were determined with an accuracy better than 2% by following procedures described previously.<sup>45,49</sup> Abundant I<sup>-</sup> ions were generated by dissociative attachment of low-energy electrons to CH<sub>3</sub>I. The formation of I<sup>-</sup> ions by this process during the period in which the CHI<sup>-</sup> ion reacted with a given substrate was prevented by ejecting the low-energy electrons from the FT-ICR cell as described previously.<sup>50</sup>

The total pressure in the instrument was in most experiments (8–10)  $\times 10^{-5}$  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<sub>2</sub>O, the halogen-substituted methane, and the reference acid was mostly 1:1:1. The temperature of the trapping plate situated opposite to the filament side was measured to be  $\approx 330$  K, whereas the inlet systems, the leak valves, and the vacuum vessel of the instrument were at room temperature. Most of the chemicals used in the present study were commercially available and used without further purification. The C<sub>6</sub>H<sub>5</sub>-SCD<sub>3</sub> (>99% d<sub>3</sub>) was prepared by reacting the thiophenolate ion with CD<sub>3</sub>I and purified by preparative gas chromatography prior to use (column SE 30, temperature 150 °C).

## Results

**Formation of the CHX<sup>-</sup> Ions.** The atomic oxygen radical anion, O<sup>-</sup>, is known to be able to undergo a number of competing reactions with organic molecules, for example, hydrogen atom abstraction with formation of HO<sup>-</sup> and formal H<sub>2</sub><sup>+</sup> abstraction leading to a new radical anion and a water molecule.<sup>18,19</sup> The latter process provides a unique method for the generation of radical anions in the gas phase such as the 1,2-dehydrobenzene radical anion<sup>33,35,36</sup> and the carbene species H<sub>2</sub>C=C<sup>-</sup><sup>39,41</sup> and <sup>-</sup>CHNC.<sup>42</sup> With the mono-halogen-substituted methanes, the O<sup>-</sup> ion reacts partly by H<sub>2</sub><sup>+</sup> abstraction and partly by formation of halogen anions as well as hydroxide ions (eqs 3–5).<sup>20–22</sup> The initial relative yields of the different product ions are given in Table 1 together with the estimated reaction enthalpies.



Hydrogen atom abstraction from the halogen-substituted methanes with formation of HO<sup>-</sup> is exothermic by 30–40 kJ

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**Table 1.** Normalized Initial Abundances of the Product Ions Formed in the Reactions of O<sup>-</sup> with Mono-Halogen-Substituted Methanes and the Estimated Reaction Enthalpies (kJ mol<sup>-1</sup>)<sup>a,b</sup>

product ion	CH <sub>3</sub> F		CH <sub>3</sub> Cl		CH <sub>3</sub> Br		CH <sub>3</sub> I	
	%	$\Delta H^\circ_f$	%	$\Delta H^\circ_f$	%	$\Delta H^\circ_f$	%	$\Delta H^\circ_f$
HO <sup>-</sup>	70	-31	25	-43	10	-37	5	-30
CHX <sup>-</sup>	30	2	45	-68	55	-79	65	-99
X <sup>-c</sup>		-95	30	-238	35	-268	30	-296

<sup>a</sup> Determined by following the product ion distributions as a function of time and extrapolating to zero time. This yields the product ion distributions undisturbed by the formation of X<sup>-</sup> in the reactions of the HO<sup>-</sup> and CHX<sup>-</sup> ions with the CH<sub>3</sub>X molecules. The reactant O<sup>-</sup> ions have a kinetic energy somewhat above thermal (see the Experimental Section). <sup>b</sup> The reaction enthalpies are based on data given in refs 28 and 66 together with the  $\Delta H^\circ_f$  (CHX<sup>-</sup>) values obtained from the presently determined heats of formation of the carbenes in combination with the published electron affinities of these species, see text and Table 5. <sup>c</sup> The given reaction enthalpies refer to an S<sub>N</sub>2 substitution reaction. The formation of X<sup>-</sup> ions by an  $\alpha$ -elimination yielding HO<sup>-</sup> and CH<sub>2</sub> as the neutral products is estimated to be highly endothermic.

mol<sup>-1</sup>.<sup>28</sup> This process is observed for all four substrates and is more important than H<sub>2</sub><sup>+</sup> abstraction in the reaction with CH<sub>3</sub>F (Table 1). The H<sub>2</sub><sup>+</sup> abstraction is essentially thermoneutral for CH<sub>3</sub>F, whereas it is estimated to become increasingly exothermic as the halogen atom becomes heavier. The H<sub>2</sub><sup>+</sup> abstraction leading to the radical anions of interest is the main reaction for CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I and dominates over S<sub>N</sub>2 substitution even in the reaction with CH<sub>3</sub>I. In addition to the product ions listed in Table 1, the reaction with CH<sub>3</sub>I yields minor amounts of IO<sup>-</sup> ions, revealing the occurrence of initial attack on the iodine atom by the O<sup>-</sup> ion concomitant with or followed by methyl radical loss from the collision complex.<sup>51</sup>

**Proton Transfer to the CHX<sup>-</sup> Ions.** The main concern here is an accurate determination of the acidities of the <sup>-</sup>CH<sub>2</sub>X radicals by observing the occurrence/nonoccurrence of proton transfer in the reactions of the CHX<sup>-</sup> radical anions with selected reference acids. The results obtained for the four CHX<sup>-</sup> radical anions are collected in Table 2 together with the results of a series of experiments with the CF<sub>2</sub><sup>-</sup> ion performed with the purpose of comparing the heat of formation of CF<sub>2</sub> derived from these measurements with recent literature values (see the Discussion).

The chosen method for determination of the acidities of the radicals leads to the free energy change for deprotonation, i.e. the free energy change of the reaction in eq 1 or  $\Delta G^\circ_{\text{acid}}(\cdot\text{CH}_2\text{X})$ . The approach rests upon the assumption that exoergic processes will be observed whereas endoergic proton-transfer reactions will not occur under the experimental conditions. Several problems may be associated with the chosen method: (i) the reactant ions may contain excess internal and/or translational energy causing the occurrence of endoergic proton-transfer reactions, (ii) the occurrence of an exoergic or thermoneutral proton transfer may be hampered by a kinetic barrier for this process, and (iii) other processes can compete effectively with proton transfer and may prevent the observation of a near-thermoneutral or exoergic acid/base reaction.

In the present series of experiments, the radical anions are generated by an exothermic process (Table 1), indicating that the ions may contain initially some excess internal energy. Furthermore, the kinetic energy of the ions may be above thermal since the rf pulses applied to eject the unwanted ions can influence the motion of the radical anions in the FT-ICR cell even though care is taken to avoid off-resonance excitation (see the Experimental Section). In order to ascertain that the occurrence of proton abstraction from the reference acids is a result of an

(51) Attack of the O<sup>-</sup> ion on a halogen atom has been reported to occur also with other halogen-substituted methanes, see ref 19 and the following: (a) Mayhew, C. A.; Peverall, R.; Watts, P. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 81–93. (b) Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 8012–8020.

**Table 2.** Occurrence/Nonoccurrence of Proton Transfer in the Reactions of the  $\text{CHX}^-$  and  $\text{CF}_2^-$  Ions with Selected Reference Acids<sup>a</sup>

acid (HA)	$\Delta G^\circ_{\text{acid}}^b$ (kJ mol <sup>-1</sup> )	$\text{CHF}^-$	$\text{CHCl}^-$	$\text{CHBr}^-$	$\text{CHI}^-$	$\text{CF}_2^-$
$\text{CH}_3\text{NH}_2$	1655	-				
$\text{CH}_3\text{CH}_2\text{NH}_2$	1639	-				
$(\text{CH}_3)_2\text{NH}$	1628	+				
$\text{CH}_3\text{CH}_2\text{NHCH}_3$	1621	+				
$\text{CH}_3\text{SCH}_3$	1615	+				
$(\text{CH}_3)_3\text{P}$	1608					
$\text{H}_2\text{O}$	1607	+	-	-	-	
$\text{C}_6\text{H}_5\text{F}^c$	1586	-	-	-	-	
$\text{C}_6\text{H}_5\text{SCH}_3^d$	1566		+	-	-	
$\text{CH}_3\text{OH}$	1565	+	+	$\pm^e$	-	-
$\text{CH}_3\text{CH}_2\text{OH}$	1551		+	+	-	-
$(\text{CH}_3)_2\text{CHOH}$	1543		+	+	-	$\pm^e$
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	1540		+	+	$\pm^e$	+
$\text{CH}_3\text{CH}_2\text{CN}$	1537			+	$\pm^e$	
$\text{FCH}_2\text{CH}_2\text{OH}$	1521				+	+
$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	1512				+	

<sup>a</sup> See also text. <sup>b</sup> The values have been taken from ref 28 and refer to 298 K. The average uncertainty of the given absolute  $\Delta G^\circ_{\text{acid}}$  values is 8 kJ mol<sup>-1</sup>. Relative to each other, the values are considered to be accurate to within a few kJ mol<sup>-1</sup>. <sup>c</sup> Based on a  $\Delta H^\circ_{\text{acid}}$  value of  $1620 \pm 8$  kJ mol<sup>-1</sup> (Mautner, M. M.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6297-6303) and an estimated  $\Delta S^\circ_{\text{acid}}$  (see text and refs 29 and 65). <sup>d</sup> The given  $\Delta G^\circ_{\text{acid}}$  value refers to the methyl group of the thioether (see ref 59). <sup>e</sup> Indicates that only very minor amounts of the conjugate base of the reference acid are formed.

exoergic or near-thermoneutral nature of the process, the radical anions were allowed to react with the neutral species in the cell for 0.5–1 s. Any ions formed by proton abstraction from the reference acid during this period were then ejected from the cell whereafter the reaction between the remaining radical anions and a given acid was reexamined. This procedure may allow that part of the ion population which contains excess internal/kinetic energy to be depleted either by reactive collisions with the reference acid or by nonreactive collisions with the various neutral species present in the cell.<sup>52</sup> In addition, vibrationally excited radical anions can undergo radiative decay to the ground state during the first reaction period of 0.5–1 s.<sup>53,54</sup>

The presence of a kinetic barrier toward an exoergic to thermoneutral proton-transfer reaction is expected in particular for the reactions between charge-delocalized carbanions and carbon acids.<sup>55,56</sup> By contrast, proton-transfer reactions involving charge-localized ions and nitrogen or oxygen acids are normally relatively efficient processes in the gas phase even when near-thermoneutral or slightly exoergic.<sup>57,58</sup> For the  $\text{CHF}^-$  radical anion, proton transfer is not observed with ethylamine, whereas this process occurs readily with dimethylamine, thus placing the acidity of the  $^{\bullet}\text{CH}_2\text{F}$  radical in between the values for these species, that is,  $\Delta G^\circ_{\text{acid}}(^{\bullet}\text{CH}_2\text{F}) = 1634 \pm 6$  kJ mol<sup>-1</sup> (see Table 2). In the experiments with  $\text{CHCl}^-$ , proton transfer is not observed with water as the reference acid but occurs readily with methanol, whose  $\Delta G^\circ_{\text{acid}}$  value is  $\approx 42$  kJ mol<sup>-1</sup> lower than the value for

water. Unfortunately, ideal reference compounds with a well-established  $\Delta G^\circ_{\text{acid}}$  value in between those for water and methanol are not known, and in order to determine the acidity of the  $^{\bullet}\text{CH}_2\text{Cl}$  radical more accurately, we reacted the  $\text{CHCl}^-$  ion with methyl phenyl thioether and fluorobenzene even though proton abstraction from these carbon acids may be kinetically controlled.

The methyl group in  $\text{C}_6\text{H}_5\text{SCH}_3$  is known to be more acidic than the remaining part of the molecule,<sup>59</sup> and in an attempt to determine the site of deprotonation, the  $\text{CHCl}^-$  ion was allowed to react with  $\text{C}_6\text{H}_5\text{SCD}_3$ . However, no reaction occurs between  $\text{CHCl}^-$  and this deuterium labeled thioether, whereas a slow proton transfer is observed with the unlabeled compound. This may imply that the introduction of deuterium atoms at the methyl group decreases the acidity of this part of the molecule with the result that deuterium abstraction by  $\text{CHCl}^-$  becomes endoergic and/or proton abstraction from the methyl group is associated with such a large kinetic isotope effect that the reaction with the deuterium labeled species becomes too slow to be observed under the present experimental conditions. Nevertheless, the absence of a reaction with the deuterium-labeled compound indicates that the proton transferred in the reaction between  $\text{CHCl}^-$  and  $\text{C}_6\text{H}_5\text{SCH}_3$  originates from the methyl group. This places  $\Delta G^\circ_{\text{acid}}$  of the  $^{\bullet}\text{CH}_2\text{Cl}$  radical above the value for the methyl group of the reference acid. The absence of proton abstraction from fluorobenzene by the  $\text{CHCl}^-$  ion (Table 2) could mean that this process is hindered by a kinetic barrier in line with results of a previous study from our group in which we observed that proton abstraction from fluorobenzene by the  $\alpha$ -thio carbanion,  $\text{CH}_3\text{SCH}_2^-$ , is a slow process although exoergic by  $\approx 29$  kJ mol<sup>-1</sup>.<sup>60</sup> However, the reaction of the  $\text{CH}_3\text{SCH}_2^-$  ion with fluorobenzene yields readily detectable amounts of  $\text{C}_6\text{H}_4\text{F}^-$  ions within a reaction time of 1 s. It may be expected, therefore, that the complete absence of proton abstraction from fluorobenzene by the  $\text{CHCl}^-$  ion reflects that this process is endoergic or near-thermoneutral. In conclusion, we place  $\Delta G^\circ_{\text{acid}}(^{\bullet}\text{CH}_2\text{Cl})$  at  $1576 \pm 10$  kJ mol<sup>-1</sup>, that is, in between the values for fluorobenzene and the  $\text{CH}_3$  group in methyl phenyl thioether.

The occurrence of proton transfer between the  $\text{CHCl}^-$  ion and methyl phenyl thioether suggests that this reaction should also be observed for the other carbene radical anions if energetically feasible. Hence, the absence of proton transfer between the  $\text{CHBr}^-$  ion and the thioether is taken to mean that this process is endoergic. In combination with the occurrence of proton transfer in the reaction with ethanol (Table 2), this places  $\Delta G^\circ_{\text{acid}}(^{\bullet}\text{CH}_2\text{Br})$  at  $1559 \pm 8$  kJ mol<sup>-1</sup>. In the experiments with the  $\text{CHI}^-$  ion, proton transfer occurs readily with 2-fluoroethanol, whereas only traces of the deprotonated 2-propanol is formed with this compound as the reference acid. The  $\Delta G^\circ_{\text{acid}}$  value for the  $^{\bullet}\text{CH}_2\text{I}$  radical, therefore, is expected to be between the values for these reference acids, that is,  $1532 \pm 11$  kJ mol<sup>-1</sup>.

The assignments of the  $\Delta G^\circ_{\text{acid}}(^{\bullet}\text{CH}_2\text{X})$  values rest also upon the assumption that the observation of a near-thermoneutral or slightly exoergic proton transfer is not restrained by the occurrence of competing reactions either with the reference acid and/or the other neutral species present in the FT-ICR cell. Competing reactions proved to be relatively insignificant for the  $\text{CHF}^-$  ion, which displays no reactivity toward  $\text{N}_2\text{O}$  under the present experimental conditions and reacts only very slowly with the parent compound to form  $\text{F}^-$  ions. The other mono-halogen-substituted carbene radical anions appear also unreactive toward  $\text{N}_2\text{O}$ , whereas they react with the parent compounds to afford  $\text{X}^-$  ions (eq 6).

The  $\text{X}^-$  ions formed in the reaction with the parent compounds originate to some extent from the reactant radical anions as revealed by a selective study of the reactions of the  $\text{CH}^{35}\text{Cl}^-$  and

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(53) The radiative lifetimes of the bending modes of excited  $\text{CH}_2^-$  radical anions have been determined to be  $\approx 600$  ms ( $\nu = 1$ ),  $\approx 80$  ms ( $\nu = 2$ ), and  $\approx 10$  ms ( $\nu = 3$ ), see: Okumura, M.; Yeh, L. I.-C.; Normand, D.; van den Biesen, J. J. H.; Bustamente, S. W.; Lee, Y. T. *Tetrahedron* **1985**, *41*, 1423–1426.

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(59) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273–2281.

(60) Matimba, H. E. K.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 73–81.

**Table 3.** Normalized Abundances (%) of the RO<sup>-</sup>, <sup>35</sup>Cl<sup>-</sup>, and <sup>37</sup>Cl<sup>-</sup> Ions Formed in the Reactions of the CH<sup>35</sup>Cl<sup>-</sup> Ion with Chloromethane and Aliphatic Alcohols<sup>a</sup>

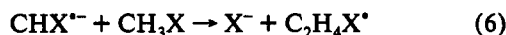
substrate	$\Delta H^{\circ}_{\text{acid}}{}^b$ (kJ mol <sup>-1</sup> )	CH <sup>35</sup> Cl <sup>-</sup>			ejection of RO <sup>-c</sup>	
		RO <sup>-</sup>	<sup>35</sup> Cl <sup>-</sup>	<sup>37</sup> Cl <sup>-</sup>	<sup>35</sup> Cl <sup>-</sup>	<sup>37</sup> Cl <sup>-</sup>
CH <sub>3</sub> Cl	1657		79	21		
CH <sub>3</sub> OH <sup>d</sup>	1592	24	53 (81) <sup>e</sup>	13 (19) <sup>e</sup>	84	16
C <sub>2</sub> H <sub>5</sub> OH <sup>d</sup>	1581	45	45 (82) <sup>e</sup>	10 (18) <sup>e</sup>	87	13
(CH <sub>3</sub> ) <sub>2</sub> CHOH <sup>d</sup>	1571	53	37 (78) <sup>e</sup>	10 (22) <sup>e</sup>	83	17
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH <sup>d</sup>	1568	23	62 (81) <sup>e</sup>	15 (19) <sup>e</sup>	80	20

<sup>a</sup> After a reaction time of 0.5–1 s. <sup>b</sup> Values taken from ref 28. <sup>c</sup> The RO<sup>-</sup> ions were ejected continuously from the FT-ICR cell during the reaction period (see the Experimental Section). <sup>d</sup> Chloromethane was also present in the cell. <sup>e</sup> Values in parentheses represent normalized relative abundances of the <sup>35</sup>Cl<sup>-</sup> and <sup>37</sup>Cl<sup>-</sup> ions.

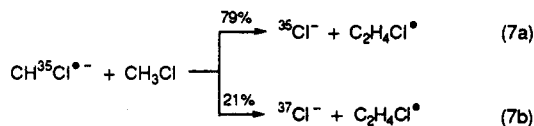
**Table 4.** Normalized Abundances (%) of the RO<sup>-</sup>, <sup>79</sup>Br<sup>-</sup>, and <sup>81</sup>Br<sup>-</sup> Ions Formed in the Reaction of the CH<sup>79</sup>Br<sup>-</sup> Ion with Bromomethane and Aliphatic Alcohols<sup>a</sup>

substrate	$\Delta H^{\circ}_{\text{acid}}{}^b$ (kJ mol <sup>-1</sup> )	RO <sup>-</sup>	CH <sup>79</sup> Br <sup>-</sup>		ejection of RO <sup>-c</sup>	
			<sup>79</sup> Br <sup>-</sup>	<sup>81</sup> Br <sup>-</sup>	<sup>79</sup> Br <sup>-</sup>	<sup>81</sup> Br <sup>-</sup>
CH <sub>3</sub> Br	1643		55	45		
CH <sub>3</sub> OH <sup>d</sup>	1592	5	80 (84) <sup>e</sup>	15 (16) <sup>e</sup>	89	11
C <sub>2</sub> H <sub>5</sub> OH <sup>d</sup>	1581	25	59 (79) <sup>e</sup>	16 (21) <sup>e</sup>	92	8
(CH <sub>3</sub> ) <sub>2</sub> CHOH <sup>d</sup>	1571	26	62 (83) <sup>e</sup>	13 (17) <sup>e</sup>		
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH <sup>d</sup>	1568	13	69 (79) <sup>e</sup>	18 (21) <sup>e</sup>	84	16

<sup>a</sup> After a reaction time of 0.5–1 s. <sup>b</sup> Values taken from ref 28. <sup>c</sup> The RO<sup>-</sup> ions were ejected continuously from the FT-ICR cell during the reaction period (see Experimental Section). <sup>d</sup> Bromomethane was also present in the cell. <sup>e</sup> Values in parentheses represent normalized relative abundances of the <sup>79</sup>Br<sup>-</sup> and <sup>81</sup>Br<sup>-</sup> ions.



CH<sup>37</sup>Cl<sup>-</sup> ions with chloromethane. For example, the reaction of the CH<sup>35</sup>Cl<sup>-</sup> ion with the parent compound yields slightly more of the <sup>35</sup>Cl<sup>-</sup> ion relative to the <sup>37</sup>Cl<sup>-</sup> ion (eq 7 and Table 3)

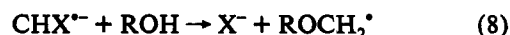


than expected for the sole occurrence of a direct S<sub>N</sub>2 substitution, which will generate the isotopic chloride ions in their natural abundance ratio (75:25). A similar result is obtained if the CH<sup>37</sup>Cl<sup>-</sup> ion is allowed to react with CH<sub>3</sub>Cl, that is, the <sup>37</sup>Cl<sup>-</sup> ion is formed in a somewhat higher relative yield (28% <sup>37</sup>Cl<sup>-</sup> and 72% <sup>35</sup>Cl<sup>-</sup>) than expected for a direct substitution reaction.<sup>49</sup>

The bromine containing ions react likewise as exemplified by the reaction of the CH<sup>79</sup>Br<sup>-</sup> ion with bromomethane. This reaction leads to 55% <sup>79</sup>Br<sup>-</sup> and 45% <sup>81</sup>Br<sup>-</sup> ions (Table 4), whereas the exclusive occurrence of a simple S<sub>N</sub>2 reaction would generate the isotopic bromide ions in an abundance ratio of 50:50.

The reaction CHCl<sup>-</sup> with CH<sub>3</sub>Cl with formation of Cl<sup>-</sup> is slow as indicated by the conversion into products, which is ≈50% after a reaction time of 1.25 s if the pressure of chloromethane is 3 × 10<sup>-5</sup> Pa (see the Experimental Section). The reactions of the CHBr<sup>-</sup> and CHI<sup>-</sup> ions with CH<sub>3</sub>Br and CH<sub>3</sub>I, respectively, are also relatively slow as indicated by the conversion into products, which is 60–70% after a reaction time of 1 s for either ion if the pressure of the parent compound is 3 × 10<sup>-5</sup> Pa. The relatively low rates suggest that the occurrence of these processes does not obscure the observation of an exoergic proton transfer.

The X<sup>-</sup> ions are generated also in the reaction of the CHX<sup>-</sup> ions with the various reference acids. This process is particularly important in the reaction with the aliphatic alcohols (eq 8). The



occurrence of this process is revealed by studying the reactions of, for example, the CH<sup>79</sup>Br<sup>-</sup> ion with methanol in the presence of bromomethane. In addition to methoxide ions, the <sup>79</sup>Br<sup>-</sup> and <sup>81</sup>Br<sup>-</sup> ions are formed in an abundance ratio (84:16, see Table 4) which is significantly different from the ratio of 55:45 obtained if only CH<sub>3</sub>Br is present in the cell. The alkoxide ions generated by proton transfer react as expected further with the bromomethane molecules by an S<sub>N</sub>2 substitution. This process proved to be of minor importance as indicated by the small effect on the abundance ratio between the <sup>79</sup>Br<sup>-</sup> and <sup>81</sup>Br<sup>-</sup> ions upon continuous ejection of the RO<sup>-</sup> ions during the reaction period (see Table 4). Similarly, the CH<sup>35</sup>Cl<sup>-</sup> ion reacts relatively readily with aliphatic alcohols in the presence of chloromethane to generate <sup>35</sup>Cl<sup>-</sup> ions in addition to alkoxide ions (Table 3). The preference for generation of X<sup>-</sup> ions originating from the reactant radical anions in the presence of an aliphatic alcohol indicates that the reaction with these substrates competes relatively effectively with the reaction between the radical anions and the parent compound also present in the FT-ICR cell.

The formation of X<sup>-</sup> ions in the reaction with the reference acids introduces some uncertainty as to whether proton transfer is energetically feasible for some of the systems studied. This relates in particular to the reaction of the CHBr<sup>-</sup> ion with methanol and the reaction of the CHI<sup>-</sup> ion with 2-methyl-1-butanol (see Table 2). However, the overall process leading to the formation of X<sup>-</sup> in the reactions with the reference acids can be described as proton transfer followed by an S<sub>N</sub>2 substitution as the final step (see the Discussion).<sup>51</sup> Several studies have provided evidence that S<sub>N</sub>2 substitutions are slow processes in the gas phase even if strongly exoergic.<sup>27,62–64</sup> This suggests that the formation of X<sup>-</sup> in the reactions with the chosen reference acids does not hamper the observation of an energetically possible proton transfer. In conclusion, it is unlikely that the competing processes suppress completely the observation of an exoergic or near-thermoneutral proton abstraction from the selected reference acids.

## Discussion

**Acidity of the <sup>•</sup>CH<sub>2</sub>X Radicals.** The occurrence/nonoccurrence of proton transfer in the reactions of the CHX<sup>-</sup> ions with various acids leads to the free energies of deprotonation of the <sup>•</sup>CH<sub>2</sub>X radicals given in Table 5. These ΔG<sup>o</sup><sub>acid</sub> values can be converted into the gas-phase acidities (ΔH<sup>o</sup><sub>acid</sub>) of the radicals if the temperature is assumed to be 298 K and provided that the entropy change associated with deprotonation of the radicals (ΔS<sup>o</sup><sub>acid</sub>) can be obtained. An experimental determination of the ΔS<sup>o</sup><sub>acid</sub> is precluded since an equilibrium situation between the carbene radical anions and one of the reference acids is unattainable. The ΔS<sup>o</sup><sub>acid</sub> values of the radicals can be estimated, however, by following the published procedures,<sup>29,65</sup> which assume this quantity to be determined largely by the entropy of the free proton and the internal and external symmetry numbers of the acid/base pair. For the present species, ΔS<sup>o</sup><sub>acid</sub> is estimated to be 114.6 J K<sup>-1</sup> mol<sup>-1</sup> or in other words the entropy of the reaction in eq 1 is determined mainly by the entropy of the free proton (108.8 J K<sup>-1</sup> mol<sup>-1</sup>). This implies that a hypothetical equilibrium between one of the carbene radical anions and the selected reference acid

(61) See also ref 43a and the following: (a) Ingemann, S.; Nibbering, N. M. M. *J. Org. Chem.* **1983**, *48*, 183–191. (b) Bickelhaupt, F. M.; de Koning, L. J.; Nibbering, N. M. M.; Baerends, E. J. *J. Phys. Org. Chem.* **1992**, *5*, 179–190.

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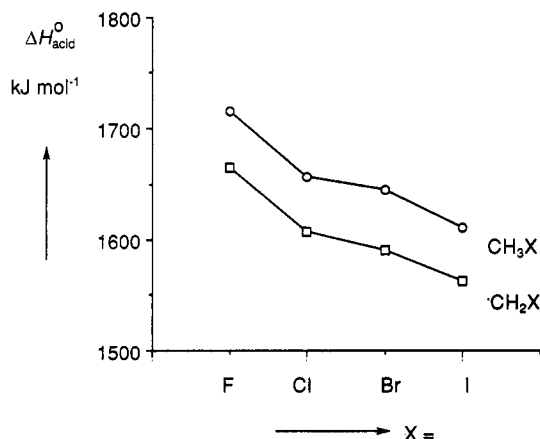
(64) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 8650–8655.

(65) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9.

**Table 5.** Gas-Phase Acidities of  $^{\bullet}\text{CH}_2\text{X}$  and  $\text{CH}_3\text{X}$  Species Together with the Appropriate C–H Bond Dissociation Energies (BDE) and Electron Affinities (EA) (All Values in  $\text{kJ mol}^{-1}$ )<sup>a</sup>

X	$\Delta G^{\circ}_{\text{acid}}(^{\bullet}\text{CH}_2\text{X})$	$\Delta H^{\circ}_{\text{acid}}(^{\bullet}\text{CH}_2\text{X})$	BDE( $^{\bullet}\text{CH}_2\text{X}$ )	EA(CHX) <sup>b</sup>	$\Delta H^{\circ}_{\text{acid}}(\text{CH}_3\text{X})^c$	BDE( $\text{CH}_3\text{X}$ )	EA( $^{\bullet}\text{CH}_2\text{X}$ )
F	1634 ± 6	1668 ± 6	408	52	≈1716	423 <sup>d</sup>	≈19
Cl	1576 ± 10	1610 ± 10	415	117	≈1657	422 <sup>e</sup>	≈77
Br	1559 ± 8	1593 ± 8	421	140	≈1643	427 <sup>d</sup>	≈96
I	1532 ± 11	1566 ± 11	416	162	≈1617	433 <sup>e</sup>	≈128

<sup>a</sup> See also text. The  $\Delta G^{\circ}_{\text{acid}}$  and  $\Delta H^{\circ}_{\text{acid}}$  values refer to 298 K. <sup>b</sup> Values from ref 12. <sup>c</sup> Values from ref 43a. <sup>d</sup> Values from ref 28. <sup>e</sup> Values based on data in ref 66.

**Figure 2.** Trend in the gas-phase acidities of the  $^{\bullet}\text{CH}_2\text{X}$  radicals and  $\text{CH}_3\text{X}$  molecules (see text and Table 5).

is predicted to be associated with a very small change in entropy, indicating that the variation in free energy of such an equilibrium within limited temperature intervals is small. Notwithstanding that the pressure in an FT-ICR instrument is too low for the reactant species to be in thermal equilibrium with the surroundings, the estimated  $\Delta S^{\circ}_{\text{acid}}$  value suggests that the possible errors in the  $\Delta H^{\circ}_{\text{acid}}$  values arise mainly from the experimental uncertainties associated with the assignment of the thermochemical onset of proton transfer and not to any significant extent from the tacit assumption that the temperature is 298 K (see also the Experimental Section).

The  $\Delta H^{\circ}_{\text{acid}}$  values in Table 5 reveal that the acidity increases in the series  $^{\bullet}\text{CH}_2\text{F}$ ,  $^{\bullet}\text{CH}_2\text{Cl}$ ,  $^{\bullet}\text{CH}_2\text{Br}$ , and  $^{\bullet}\text{CH}_2\text{I}$  with the largest difference (58  $\text{kJ mol}^{-1}$ ) observed between the fluorine- and chlorine-containing species. According to eq 2, the acidity of a given radical is determined by the difference in the homolytic C–H bond dissociation energy of the  $^{\bullet}\text{CH}_2\text{X}$  radical and the EA of the CHX species. The EA values of the singlet states of the mono-halogen-substituted carbenes have been published recently, thus allowing the C–H BDE of the radicals to be estimated.<sup>12</sup> As can be seen in Table 5, the dissociation energies are practically independent of the nature of the halogen atom whereas the EA of the carbenes increases in the series CHF, CHCl, CHBr, and CHI. The increasing acidity of the radicals with increasing size of the halogen atom is determined, therefore, by the variation in the EA of the CHX species or in other words in the stability of the radical anions with respect to the carbenes. A similar conclusion can be reached for the  $\text{CH}_3\text{X}$  molecules,<sup>43</sup> that is, the increase in acidity in the series  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  reflects the trend in the EA of the  $^{\bullet}\text{CH}_2\text{X}$  radicals since the C–H bond strengths of the methanes are almost independent of the nature of the halogen atom (Table 5).

The acidities of the radicals reveal that a given  $^{\bullet}\text{CH}_2\text{X}$  species is  $\approx 50 \text{ kJ mol}^{-1}$  more acidic than the parent molecule. Hence, the trend in the acidity of the radicals parallels the trend observed for the halogen-substituted methanes as illustrated in Figure 2. The increase in acidity on going from  $\text{CH}_3\text{X}$  to  $^{\bullet}\text{CH}_2\text{X}$  is mainly a result of the larger EA of a given CHX carbene than of the related radical and to lesser extent determined by the change in C–H BDE when a  $\text{CH}_3\text{X}$  molecule is transformed into a radical.

For example, the C–H BDE of the  $^{\bullet}\text{CH}_2\text{F}$  radical is  $\approx 15 \text{ kJ mol}^{-1}$  lower than the C–H bond strength of  $\text{CH}_3\text{F}$ ,<sup>28</sup> whereas the EA of CHF is  $\approx 33 \text{ kJ mol}^{-1}$  larger than the EA of  $^{\bullet}\text{CH}_2\text{F}$ , and as a result the radical is  $\approx 50 \text{ kJ mol}^{-1}$  more acidic than the corresponding molecule in the gas phase (see Table 5).

It is evident that a stabilization of the negative charge in the radical anions by the halogen atom will tend to increase the EA, whereas stabilizing effects in the neutral carbenes will oppose this and tend to decrease the EA. For example, the lower EA of the singlet ground state of CHF (52  $\text{kJ mol}^{-1}$ , Table 5)<sup>12</sup> than of singlet  $\text{CH}_2$  (100  $\text{kJ mol}^{-1}$ ) has been attributed to the stabilizing effect of the fluorine atom on the neutral carbene, which was considered to be more significant than the stabilization of the negative charge in the  $\text{CHF}^{\bullet}$  radical anion.<sup>11</sup> As discussed in the literature,<sup>4,5,10</sup> the stabilization of the singlet state relative to the triplet state of a halogen-containing carbene can be ascribed to two effects, which may act synergistically. First, an electronegative halogen atom can withdraw electron density from the carbon atom by an inductive effect and increase the s character of the  $\sigma$  orbital (see Figure 1). This lowers the energy of this orbital with the result that the singlet is stabilized with respect to the triplet state of the carbene. Second, the halogen atom can stabilize the singlet state by donating electron density to the unoccupied carbon  $p_x$  orbital of the carbene through the CX  $\pi$ -bonds (Figure 1). Both of these effects can be held responsible for the lower energy of the singlet state than of the triplet state of CHF, CHCl, and CHBr (vide supra).<sup>10</sup> Furthermore, the effects are particularly significant for fluorine since the electronegativity decreases in the series F, Cl, Br, and I and the carbon–halogen bond length increases as the halogen atom becomes larger, thus decreasing the importance of electron donation to the  $p_x$  orbital.

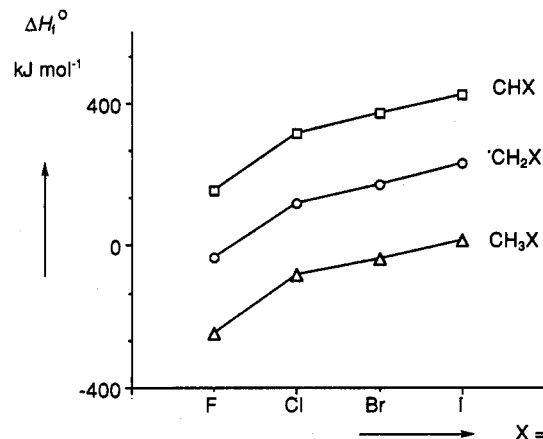
The stabilization of the negative charge in the carbene radical anions has been discussed as inductive electron withdrawal by the halogen atom.<sup>11</sup> This effect will, of course, become less important as the halogen atom becomes less electronegative and will tend to decrease the EA in the series CHF, CHCl, CHBr, and CHI. The observed increase in the EA in this series has been taken to imply, therefore, that the stabilizing effects on the neutral singlet carbenes dominate over the stabilization of the charge in the radical anions by inductive electron withdrawal.<sup>11</sup> In this respect, it should be mentioned that the trend in the EA of the CHX carbenes parallels the trend in the EA of the  $^{\bullet}\text{CH}_2\text{X}$  radicals. For the  $^{\bullet}\text{CH}_2\text{X}$  radicals, it is not anticipated that a fluorine atom exerts an influence on the radical center, which differs drastically from that of an iodine atom, suggesting that the EA of the radicals may be determined mainly by the stabilization of the charge in the  $^{\bullet}\text{CH}_2\text{X}$  ions. In qualitative terms, the trend in the EA of the  $^{\bullet}\text{CH}_2\text{X}$  radicals follows the polarizability of the halogen atoms instead of their electronegativity (see also ref 43a). A similar situation may apply to the carbene radical anions, indicating that the effects of the halogen atoms on the neutral carbenes and on the radical anions may both lead to an increase of the EA as the halogen atom becomes heavier.

**Heats of Formation of the CHX Carbenes.** The C–H bond dissociation energies of the  $^{\bullet}\text{CH}_2\text{X}$  radicals (Table 5) can be used to derive the following heats of formation of the CHX carbenes:  $157 \pm 18 \text{ kJ mol}^{-1}$  ( $\dot{\text{X}}^1\text{A}'$ , CHF),  $317 \pm 20 \text{ kJ mol}^{-1}$  ( $\dot{\text{X}}^1\text{A}'$ , CHCl),  $373 \pm 18 \text{ kJ mol}^{-1}$  ( $\dot{\text{X}}^1\text{A}'$ , CHBr), and  $428 \pm 21 \text{ kJ mol}^{-1}$  ( $\dot{\text{X}}^1\text{A}'$ , CHI).

**Table 6.** Heats of Formation ( $\Delta H_f^\circ$  in  $\text{kJ mol}^{-1}$  at 298 K) of the  $\text{CH}_3\text{X}$ ,  $\cdot\text{CH}_2\text{X}$ , and  $\text{CHX}$  Species

X	$\text{CH}_3\text{X}^a$	$\cdot\text{CH}_2\text{X}$	CHX
F	-247	-33 <sup>a</sup>	157 ± 18 <sup>c</sup>
Cl	-82	120 <sup>b</sup>	317 ± 20 <sup>c</sup>
Br	-38	170 <sup>a</sup>	373 ± 18 <sup>c</sup>
I	15	230 <sup>b</sup>	428 ± 21 <sup>c</sup>

<sup>a</sup> From ref 28. <sup>b</sup> Value from ref 66; see also text. <sup>c</sup> This work, see text.

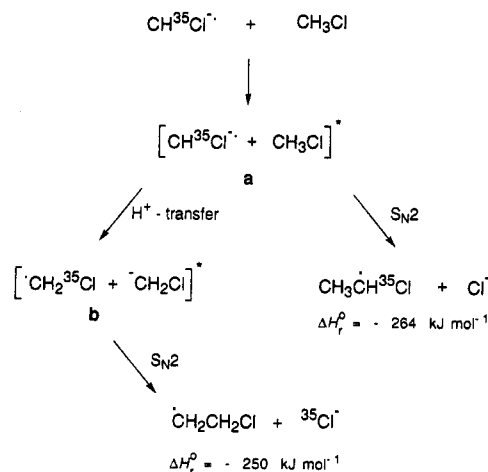
**Figure 3.** Graphical representation of the trend in the heats of formation of the  $\text{CHX}$ ,  $\cdot\text{CH}_2\text{X}$ , and  $\text{CH}_3\text{X}$  species (see text and Table 6).

$\text{mol}^{-1}$  ( $\tilde{X}^1\text{A}'$  or  $\tilde{a}^1\text{A}'\text{CHI}$ ) (Table 6). These heats of formation refer—as indicated—to the singlet ground states of the  $\text{CHF}$ ,  $\text{CHCl}$ , and  $\text{CHBr}$  carbenes as the EA values used in combination with the acidities to derive the C–H BDE values relate to this state of the carbenes. In the estimation of the heat of formation of  $\text{CHI}$ , we also used the EA value given for the singlet state even though it remains uncertain whether this is the ground state.<sup>10,12,15</sup>

The heats of formation of the carbenes are less accurate than the determined gas-phase acidities of the radicals, and the average error limit of  $\pm 20 \text{ kJ mol}^{-1}$  in Table 6 arises as the sum of the error limit of about  $8 \text{ kJ mol}^{-1}$  on the reported  $\Delta H_f^\circ$  values of the  $\cdot\text{CH}_2\text{X}$  species and the uncertainties in the  $\Delta H_f^\circ(\cdot\text{CH}_2\text{X})$  values. For example, the heat of formation of the  $\cdot\text{CH}_2\text{Cl}$  radical is quoted as  $130 \text{ kJ mol}^{-1}$  in ref 28 whereas values in between  $115$  and  $120 \text{ kJ mol}^{-1}$  are given in a recent paper by Holmes and Lossing.<sup>66</sup> Furthermore, these authors place the heat of formation of the  $\cdot\text{CH}_2\text{I}$  radical at  $230 \text{ kJ mol}^{-1}$  whereas a value of  $210 \text{ kJ mol}^{-1}$  is given in ref 28. We have used the value of  $120 \text{ kJ mol}^{-1}$  for the  $\cdot\text{CH}_2\text{Cl}$  radical and  $230 \text{ kJ mol}^{-1}$  for  $\cdot\text{CH}_2\text{I}$  because these give rise to a consistent picture of the trend in the heats of formation of the  $\text{CH}_3\text{X}$ ,  $\cdot\text{CH}_2\text{X}$ , and  $\text{CHX}$  species (Table 6). This is depicted in Figure 3, which clearly reveals that the trend in the heats of formation of the carbenes is essentially the same as the trend in the values for the radicals and the molecules. In other words, the enthalpy of dehydrogenation of a halogen-substituted methane to form a singlet carbene is independent of the nature of the halogen atom (eq 9).



The present value for the heat of formation of  $\text{CHCl}$  is within the error limit of the value ( $297 \pm 20 \text{ kJ mol}^{-1}$ ) derived on the basis of the determination of the proton affinity of this carbene.<sup>16</sup> For  $\text{CHF}$ , however, the result in Table 6 deviates significantly from the value of  $105 \text{ kJ mol}^{-1}$  obtained by studying proton-transfer reactions of the  $\text{CH}_2\text{F}^+$  ion<sup>16</sup> but is in line with the value of  $\approx 163 \text{ kJ mol}^{-1}$  based on a study of the reactivity of the  $\cdot\text{CH}_2\text{F}$  radical in the gas phase.<sup>17</sup> At present, we have no explanation for the discrepancy between our value for the heat of formation

**Scheme 1.** Proposed Mechanism for the Reaction of the  $\text{CH}^{35}\text{Cl}^-$  Ion with  $\text{CH}_3\text{Cl}$ 

of  $\text{CHF}$  and the one obtained by measuring the proton affinity of this carbene. It can be mentioned, however, that the occurrence/nonoccurrence of proton transfer in the reactions of the  $\text{CF}_2^-$  ion<sup>67</sup> with a series of aliphatic alcohols leads to a  $\Delta G_{\text{acid}}^\circ$  value of the  $\cdot\text{CHF}_2$  radical of  $1546 \pm 6 \text{ kJ mol}^{-1}$ . This value results in a  $\Delta H_{\text{acid}}^\circ(\cdot\text{CHF}_2) = 1579 \pm 6 \text{ kJ mol}^{-1}$  on the basis of an estimated  $\Delta S_{\text{acid}}^\circ(\cdot\text{CHF}_2)$  of  $109 \text{ J K}^{-1} \text{ mol}^{-1}$  and with  $T$  assumed to be 298 K. The  $\Delta H_{\text{acid}}^\circ$  value leads in combination with the reported EA of singlet difluorocarbene<sup>11</sup> of  $17 \pm 1 \text{ kJ mol}^{-1}$  to a C–H BDE of the  $\cdot\text{CHF}_2$  radical of  $\approx 284 \text{ kJ mol}^{-1}$ . With  $\Delta H_f^\circ(\cdot\text{CHF}_2) = -237 \text{ kJ mol}^{-1}$ , the heat of formation of  $\text{CF}_2$  ( $\tilde{X}^1\text{A}_1$ ) becomes  $-171 \pm 10 \text{ kJ mol}^{-1}$ . This heat of formation of  $\text{CF}_2$  is slightly lower than the upper limit of  $-165 \pm 14 \text{ kJ mol}^{-1}$  derived on the basis of measurements of the threshold energy for collision-induced dissociation of  $\text{CF}_3^-$  with formation of  $\text{F}^-$  ions<sup>68</sup> and somewhat larger than the value of  $-184 \pm 4 \text{ kJ mol}^{-1}$  determined from the photoionization threshold for  $\text{CF}_2$  loss from some fluorine-containing species.<sup>69</sup>

**Reactions of the  $\text{CHX}^-$  Ions.** The reactions of the carbene radical anions with the parent compounds yield halide ions, which to some extent originate from the reactant ions as indicated in Tables 3 and 4. A possible scheme in agreement with this finding consists of direct  $\text{S}_{\text{N}}2$  substitution competing with a process involving initial proton transfer between the radical anion and the halogen-containing methane molecule followed by a nucleophilic substitution.<sup>61</sup> The acidity measurements reveal that proton abstraction from a  $\text{CH}_3\text{X}$  molecule by the related  $\text{CHX}^-$  radical anion with formation of a free  $\cdot\text{CH}_2\text{X}$  ion is  $\approx 50 \text{ kJ mol}^{-1}$  endothermic (Table 5). However, the gain in excess internal energy upon approach of the reactants can be sufficiently large to allow for the occurrence of proton transfer within the initially formed complex<sup>18,27</sup> as illustrated in Scheme 1 for the reaction of the  $\text{CH}^{35}\text{Cl}^-$  ion with  $\text{CH}_3\text{Cl}$ . Proton transfer in complex a in Scheme 1 leads to b, which then reacts further by substitution to form a  $^{35}\text{Cl}^-$  ion and a  $\cdot\text{CH}_2\text{CH}_2\text{Cl}$  radical. The entire process is estimated to be  $250 \text{ kJ mol}^{-1}$  exothermic and is thus only  $14 \text{ kJ mol}^{-1}$  less exothermic than the direct  $\text{S}_{\text{N}}2$  substitution, which leads to a  $\text{CH}_3\text{CH}^{35}\text{Cl}$  radical (see Scheme 1).<sup>28,66</sup> The occurrence of an energetically unfavorable proton transfer in addition to a strongly exothermic  $\text{S}_{\text{N}}2$  reaction is in line with a number of other studies which have shown that substitutions often are slow in the gas phase as a result of the existence of substantial local energy barriers.<sup>27,62,63</sup>

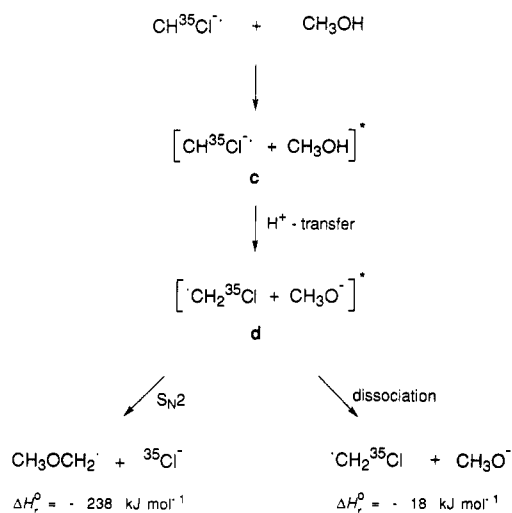
(67) This radical anion is readily formed in the reaction of the  $\text{O}^-$  ion with  $\text{CF}_2\text{H}_2$ . The  $\text{CF}_2^-$  ion reacts slowly with  $\text{N}_2\text{O}$  to afford a  $\text{CF}_2\text{N}^-$  ion: Born, M.; Ingemann, S.; Nibbering, N. M. M. Unpublished results.

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**Scheme 2.** Proposed Mechanism for the Reaction of the  $\text{CH}^{35}\text{Cl}^-$  Ion with Methanol

The formation of  $\text{X}^-$  ions by initial proton transfer between a carbene radical anion and a  $\text{CH}_3\text{X}$  molecule implies the occurrence of a nucleophilic attack of a carbanion on a  $\cdot\text{CH}_2\text{X}$  radical. A similar situation arises in the reactions of the radical anions with aliphatic alcohols (Tables 3 and 4). Here the initial proton transfer leads to a complex of a  $\cdot\text{CH}_2\text{X}$  radical and a  $\text{RO}^-$  ion as illustrated in Scheme 2 for the reaction of the  $\text{CH}^{35}\text{Cl}^-$  ion with  $\text{CH}_3\text{OH}$ . Complex d generated by proton transfer within complex c may then dissociate or react further by an  $\text{S}_{\text{N}}2$  substitution to form  ${}^{35}\text{Cl}^-$ .

In the present context, the occurrence of an  $\text{S}_{\text{N}}2$  substitution succeeding the proton-transfer step in the first complex generated upon approach of the radical anion to the alcohol molecule could be thought to influence the observation of an overall exoergic proton-transfer reaction. The  $\text{S}_{\text{N}}2$  pathway in Scheme 2 with

formation of  ${}^{35}\text{Cl}^-$  and  $\text{CH}_3\text{OCH}_2^-$  is estimated to be exothermic by  $\approx 238 \text{ kJ mol}^{-1}$ , whereas proton transfer to form  $\text{CH}_3\text{O}^-$  ions is estimated to be exothermic by  $\approx 18 \text{ kJ mol}^{-1}$  on the basis of the acidity of the  $\cdot\text{CH}_2\text{Cl}$  radical in Table 5.<sup>28</sup> Overall proton transfer to free alkoxide ions involves simple dissociation of complex d in Scheme 2, and it is not expected that this is hindered by an energy barrier, whereas the  $\text{S}_{\text{N}}2$  reaction is likely to involve a local energy barrier.<sup>27,62,63</sup> In conclusion, the  $\text{S}_{\text{N}}2$  substitution is unlikely to suppress the overall proton-transfer reaction unless this process is energetically unfeasible.

### Conclusions

We have determined the gas-phase acidities of the  $\cdot\text{CH}_2\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ) radicals by studying the ion/molecule chemistry of the  $\text{CHX}^-$  carbene radical anions. In combination with reported electron affinities of the singlet  $\text{CHX}$  carbenes, these acidities lead to the heats of formation of the  $\text{CHX}$  carbenes. The trend in the heats of formation of the  $\text{CHX}$  carbenes in the series  $\text{CHF}, \text{CHCl}, \text{CHBr}, \text{and CHI}$  is similar to the trend in the heats of formation of the halogen-substituted methanes, revealing that the energy required for dehydrogenation of a  $\text{CH}_3\text{X}$  molecule to give the related singlet carbene is essentially independent of the nature of the halogen atom. The acidity of the halogen-substituted radicals is observed to increase in the series  $\cdot\text{CH}_2\text{F}, \cdot\text{CH}_2\text{Cl}, \cdot\text{CH}_2\text{Br}, \text{and } \cdot\text{CH}_2\text{I}$ , that is, the acidity increases as the halogen atom becomes heavier as observed also for the corresponding methanes. The acidity increases by  $\approx 51 \text{ kJ mol}^{-1}$  on going from a  $\text{CH}_3\text{X}$  molecule to the related  $\cdot\text{CH}_2\text{X}$  radical. This change in acidity is mainly a result of a larger electron affinity of a given  $\text{CHX}$  carbene than of the related  $\cdot\text{CH}_2\text{X}$  radical and only to a minor extent determined by the decrease in C-H bond dissociation energy in going from a  $\text{CH}_3\text{X}$  molecule to the corresponding radical.

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