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Heats of Formation of Mono-Halogen-Substituted Carbenes: 
Stability and Reactivity of CHX+ (X = F, Cl, Br, and I) 
Radical Anions

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Abstract: The heats of formation of mono-halogen-substituted singlet carbenes have been determined to be 157 ± 18 
kJ mol−1 (X \(1^A \) CHF), 317 ± 20 kJ mol−1 (X \(1^A \) CHCl), 373 ± 18 kJ mol−1 (X \(1^A \) CHBr), and 428 ± 21 kJ mol−1 (X \(1^A \) or \(3^A \) CHI). These \(\Delta H^0\) values are based upon the following gas-phase acidities, \(\Delta H^0_{acid}\) of the \(X^1\)CHX radicals: 1668 ± 6 kJ mol−1 (X=CHF), 1610 ± 10 kJ mol−1 (X=CHCl), 1593 ± 8 kJ mol−1 (X=CHBr), and 1566 ± 11 kJ mol−1 (X=CHI). The acidities were determined by observing the occurrence/nonoccurrence of proton transfer in the reactions of the CHX+ carbone radical anions with selected acids in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. The \(\Delta H^0_{acid}\) values reveal that (i) the acidity increases in the series X=CHF, X=CHCl, X=CHBr, and X=CHI, i.e. the acidity increases as the halogen atom becomes heavier as observed also for the corresponding halogen-substituted methanes, and (ii) a given X=CHX radical is \(\approx50\) kJ mol−1 more acid in the gas phase than the related CHX molecule. The reaction of a given CHX+ ion with the parent compound yields X− ions in part by a direct Sn2 substitution and in part by initial proton transfer leading to a \(X^1\)CHX+ complex, which then reacts to form X−. In addition to overall proton transfer, the reaction of the carbone radical anions with aliphatic alcohols yields X− ions by a process which involves initial proton transfer followed by nucleophilic attack of the RO− ion on the generated X=CHX radical.

Introduction

The structure and reactivity of carbenes represent an important area of chemistry from both an experimental and theoretical point of view.1-9 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.1-3 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.1-3 The electronic configuration of the most simple carbene, CH2, 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 kJ mol−1 lower in energy than the singlet state.4-6 The introduction of an electronegative atom or group reverses this order10-14 as exemplified by CHF, which has a singlet ground state of 62 kJ mol−1 lower in energy than the triplet state as determined from the photoelectron spectrum of the CHF radical anion.11,12 The CHCl and CHBr carbenes are reported also to have a singlet ground state,11,14 whereas the spin multiplicity of the ground state of CHI has not been determined definitively. Upon the basis of photoelectron spectroscopy experiments with the CHI radical anion, the ground state was assigned as a triplet located 8-40 kJ mol−1 lower in energy than the singlet state.12 By contrast, recent calculations predict the singlet state of CHI to be more stable than the triplet state.10,15 Irrespective of the intense research into the spin multiplicity of the CHX carbenes and their associated reactivity, consistent thermochemical data have not been published for the complete series of the mono-halogen-substituted carbenes: CHF, CHCl, CHBr, and CHI.

The heat of formation of CHF has been reported to be 105 ± 12 kJ mol−1 on the basis of an experimental determination of the proton affinity of CHF,16 while a study of the kinetics of the gas-phase reactions of the CHF radical yielded a value of 163


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 \( ^* \text{CH}_2X \) radical is defined as the enthalpy change of the reaction in eq 1 at 298 K and can be formulated with respect to the homolytic dissociation energy of the \( \text{H}^+ + \text{CH}_2X \) bond.

\[
\Delta H^{\circ}_{\text{acid}} (\text{CH}_2X) = \text{BDE}(\text{H}^- \text{CH}_2X) - \text{EA}(\text{CH}_2X) + \text{IE}(\text{H}^+) \tag{1}
\]

Previous studies from our group and also by others 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. 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 \( \text{C}_6\text{H}_5^+ \) than of the C–H bonds in \( \text{C}_6\text{H}_6 \). The decrease in C–H BDE going from the molecule to the radical is only partly compensated for by the larger EA of \( \text{C}_6\text{H}_5^+ (\approx 99 \text{ kJ mol}^{-1}) \) than of 1,2-dehydrobenzene \( \text{EA} = 54 \text{ kJ mol}^{-1} \). 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, \( \text{CH}_2\text{CN} \),\( ^* \text{CH}_2\text{CN} \) and \( \text{C}_6\text{H}_5\text{CN} \) and the cyclopentadienyl radical is reported to be less acidic than cyclopentadiene in the gas phase. 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 \( ^* \text{CH}_2X \) radicals and the corresponding \( \text{CH}_3X \) molecules.

Experimental Section

The experiments were performed with an FT-ICR mass spectrometer designed and constructed at the University of Amsterdam. In a typical experiment, the primary negative ion, \( \text{O}^- \), was generated by dissociative attachment of electrons with an energy of 1–5 eV to \( \text{N}_2 \). At these electron energies, the \( \text{O}^- \) ions are formed with a variance kinetic energy.

\[
(1) \quad \text{C}_6\text{H}_5^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{H}^+ \\
(2) \quad \Delta H^{\circ}_{\text{acid}}(\text{CH}_2X) = \text{BDE}(\text{H}^- \text{CH}_2X) - \text{EA}(\text{CH}_2X) + \text{IE}(\text{H}^+) 
\]
energy of about 0.38 eV \(^{-1}\) 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. \(^3\) cell located in a magnetic field of 1.23 T. Subsequently and during the electron beam pulse, the \(O^-\) ions reacted with one of the halogen-substituted methanes to generate the \(CHX^-\) radical anions. The \(CHX^-\) 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. \(^{48}\) 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 detected continuously in 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. \(^{56,59}\) Abundant \(I^-\) ions were generated by dissociative attachment of low-energy electrons to \(CHI_3\). The formation of \(I^-\) ions by this process during the period in which the \(CHI_-\) ion reacted with a given substrate was prevented by ejecting the low-energy electrons from the FT-ICR cell as described previously. \(^{45}\)

The total pressure in the instrument was in most experiments \((8-10) \times 10^{-9}\) Torr as measured with an uncalibrated ionization gauge placed in a side arm of the main vacuum system. The ratio of the partial pressures of \(N_2\), the halogen-substituted methane, and the reference acid was 3\,-\,5:20-22.

The duration of the electron beam pulses was normalized to \(100\%\) by using \(CHI_3\) and \(CDI_3\) \((>99\%\, \delta\) and \(99\%\, \beta\) \) to prepare \(Cl_CHI_2CO\) and \(Br_CHI_2CO\) by \(CIF\), \(ClF\), and \(BrF\) as the halogen atom becomes heavier. The \(H_2^+\) abstraction leading to the radical anions of interest is the main reaction for \(CHI_3\), whereas it is estimated to become increasingly endoergic as the halogen becomes heavier. The \(H_2^+\) abstraction leading to the radical anions of interest is the main reaction for \(CHI_3\), \(CHI_2Br\), and \(CHI_2J\) and dominates over \(S_n\) substitution even in the reaction with \(CHI_1\). In addition to the product ions listed in Table 1, the reaction with \(CHI_2\) yields minor amounts of \(IO^-\) ions, revealing the occurrence of initial attack on the iodine atom by the \(O^-\) ion concomitant with or followed by methyl radical loss from the collision complex. \(^{51}\)

**Proton Transfer to the CHX^- Ions.** The main concern here is an accurate determination of the acidities of the \("CHX\) radicals by observing the occurrence/nonoccurrence of proton transfer in the reactions of the \("CHX\) radical anions with selected reference acids. The results obtained for the four \("CHX\) radical anions are collected in Table 2 together with the results of a series of experiments with the \("CF_2\) ion performed with the purpose of comparing the heat of formation of \(CF_2\) 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 \(\Delta G_{DEP}(CHX)\).

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-thermonuclear 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

### Table 1. Normalized Initial Abundances of the Product Ions Formed in the Reactions of \(O^-\) with Mono-Halogen-Substituted Methanes and the Estimated Reaction Enthalpies (kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Product</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta H^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CHF)</td>
<td>70</td>
<td>-31</td>
<td>24</td>
<td>-43</td>
</tr>
<tr>
<td>(CHCl)</td>
<td>30</td>
<td>2</td>
<td>45</td>
<td>-68</td>
</tr>
<tr>
<td>(CHBr)</td>
<td>55</td>
<td>-79</td>
<td>65</td>
<td>-99</td>
</tr>
<tr>
<td>(CHI)</td>
<td>28</td>
<td>-95</td>
<td>30</td>
<td>-238</td>
</tr>
</tbody>
</table>

\(^a\) Determined by following the product ion distributions as a function of time and extrapolating to \(t\) zero time.

\(^b\) This process is observed for all four substrates and is more important than \(H_2^+\) abstraction in the reaction with \(CHF\) (Table 1). The \(H_2^+\) abstraction is essentially thermoneutral for \(CHF\), whereas it is estimated to become increasingly endoergic as the halogen becomes heavier. The \(H_2^+\) abstraction leading to the radical anions of interest is the main reaction for \(CHCl\), \(CHBr\), and \(CHI\) and dominates even in the reaction with \(CHI_1\). In addition to the product ions listed in Table 1, the reaction with \(CHI_2\) yields minor amounts of \(IO^-\) ions, revealing the occurrence of initial attack on the iodine atom by the \(O^-\) ion concomitant with or followed by methyl radical loss from the collision complex. \(^{51}\)

(49) It can be mentioned that, with the FT-ICR instrument applied in this study, the abundance ratio between the \(W\) and \(W\) ions formed in the reaction of the \(CHI^-\) ion with \(CHI\) is measured to be \(76:24\). This ratio differs not more than 1\% from the true ratio between the natural abundances of the isotopic chloride ions. Born, M.; Engemann, S.; Nibbering, N. M. M. Unpublished results (see also ref 45).
(51) Attack of the \(O^-\) 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.; Wetsa, P. Int. J. Mass Spectrom. Ion Processes 1993, 125, 81-93. (b) Gilles, M. K.; Polak, M. L.; Linseberger, W. C. J. Chem. Phys. 1992, 96, 8012-8020.
whose AGoacid value is -42 kJ mol⁻¹ lower than the value for that is, AGoacid ('CH₂F)
with water as the reference acid but occurs readily with methanol, acidity of the 'CH₂F radical in between the values for these species.

Table 2. Occurrence/Nonoccurrence of Proton Transfer in the Reactions of the CHX⁻ and CFX⁻ Ions with Selected Reference Acids

<table>
<thead>
<tr>
<th>acid (HA)</th>
<th>ΔGoaddb (kJ mol⁻¹)</th>
<th>CHF⁻→CHCl⁻</th>
<th>CHBr⁻→CHI⁻</th>
<th>CFH⁻→CFI⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₂</td>
<td>1655</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃CH₂NH₂</td>
<td>1639</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(CH₃)₂N</td>
<td>1628</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃CH₂NHCH₃</td>
<td>1621</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃SC₃H₃</td>
<td>1615</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(CH₃)₂P</td>
<td>1608</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>1607</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃F</td>
<td>1586</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃SC₃H₃d</td>
<td>1566</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>1565</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>1551</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>(CH₃)₂CHOH</td>
<td>1543</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>(CH₃)₂CH₂CH₂OH</td>
<td>1540</td>
<td>+</td>
<td>+</td>
<td>±*</td>
</tr>
<tr>
<td>CH₃CH₂CN</td>
<td>1537</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>FCH₃CH₂OH</td>
<td>1521</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>CH₃CH₂OCH₂CH₂</td>
<td>1512</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

*See also text. a The values have been taken from ref 28 and refer to 298 K. The average uncertainty of the given absolute ΔGoadd value is 8 kJ mol⁻¹. Relative to each other, the values are considered to be accurate to within a few kJ mol⁻¹. b Based on a ΔH°acid value of 1620 ± 8 kJ mol⁻¹ (Mautner, M. M.; Kafafi, S. A. J. Am. Chem. Soc. 1985, 110, 6297-6303) and an estimated ΔS°acid (see text and refs 29 and 65). c The given ΔGoadd value refers to the methyl group of the thiocarboxylic acid (see ref 59). d 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.52 In addition, vibrationally excited radical anions can undergo radiative decay to the ground state during the first reaction period of 0.5–1 s.53,54

The presence of a kinetic barrier toward an exoergic to thermoneutral proton-transfer reaction is expected in particular for the reactions between charge-delocalized carbamions and carbon acids. 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. For the CHF⁻ radical anion, proton transfer is not observed with ethylamine, whereas this process occurs readily with dimethylamine, thus placing the acidity of the CH₃F radical in between the values for these species, that is, ΔGoadd (CH₃F) = 1634 ± 6 kJ mol⁻¹ (see Table 2). In the experiments with CHCl⁻ ion, proton transfer is not observed with water as the reference acid but occurs readily with methanol, whose ΔGoadd value is ≈ 42 kJ mol⁻¹ lower than the value for water. Unfortunately, ideal reference compounds with a well-established ΔGoadd value in between those for water and methanol are not known, and in order to determine the acidity of the CH₃Cl radical more accurately, we reacted the CHCl⁻ ion with methyl phenyl thioether and fluorobenzene even though proton abstraction from these carbon acids may be kinetically controlled.

The methyl group in CH₃HSC₃H₃ is known to be more acidic than the remaining part of the molecule,59 and in an attempt to determine the site of deprotonation, the CHCl⁻ ion was allowed to react with CH₃HSC₃H₃. However, no reaction occurs between 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 deuterion abstraction by 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 CH₃H⁺ and CH₃HSC₃H₃ originates from the methyl group. This places ΔGoadd of the CH₂Cl radical above the value for the methyl group of the reference acid. The absence of proton abstraction from fluorobenzene by the 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 α-thio carbanion, CH₃SC₃H₃⁻, is a slow process although exoergic by ≈ 29 kJ mol⁻¹. However, the reaction of the CH₃SC₃H₃⁻ ion with fluorobenzene yields readily detectable amounts of CH₃H₂F⁻ ions within a reaction time of 1 s. It may be expected, therefore, that the complete absence of proton abstraction from fluorobenzene by the CHCl⁻ ion reflects that this process is endoergic or near-thermoneutral. In conclusion, we place ΔGoadd (CH₃Cl) at 1576 ± 10 kJ mol⁻¹, that is, in between the values for fluorobenzene and the CH₃ group in methyl phenyl thioether.

The occurrence of proton transfer between the CHCl⁻ 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 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 ΔGoadd (CH₃Br) at 1559 ± 8 kJ mol⁻¹. In the experiments with the 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 ΔGoadd value for the CH₃I radical, therefore, is expected to be between the values for these reference acids, that is, 1532 ± 11 kJ mol⁻¹. The assignments of the ΔGoadd (CH₃X) 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 CHF⁻ ion, which displays no reactivity toward N₂O under the present experimental conditions and reacts only very slowly with the parent compound to form F⁻ ions. The other mono-halogen-substituted carbene radical anions appear also unreactive toward N₂O, whereas they react with the parent compounds to afford X⁻ ions (eq 6).

The 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 CH₃Cl⁻ and

(53) The radiative lifetimes of the bending modes of excited CH₂⁻ radical anions have been determined to be >600 ms (ν = 1), >80 ms (ν = 2), and >10 ms (ν = 3); see: Okumura, M.; Yeh, L. C.-C.; Normand, D.; van den Biesen, J. J. H.; Bustamante, S. W.; Lee, Y. T. Phys. Chem. 1985, 41, 1423-1426.
obscure the observation of an exoergic proton transfer. This reaction leads to also relatively slow as indicated by the conversion into products, the reaction of the CH79Br\(^{-}\) ion with bromomethane. This CH37Cl\(^{-}\) ion is allowed to react with CHpCl, that is, the 37Cl\(^{-}\) ion is formed in a somewhat higher relative yield (28% 37Cl\(^{-}\) and 72% W1\(^{-}\)) than expected for the sole occurrence of a direct sN2 substitution, the exclusive Occurrence of a simple sN2 reaction would generate the isotopic bromide ions in an abundance ratio of which will generate the isotopic chloride ions in their natural abundance. The formation of X\(^{-}\) 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\(^{-}\) ion with methanol and the reaction of the CHI\(^{-}\) ion with 2-methyl-1-butanol (see Table 2). However, the overall process leading to the formation of X\(^{-}\) in the reactions with the reference acids can be described as proton transfer followed by an Sn2 substitution as the final step (see the Discussion). Several studies have provided evidence that Sn2 substitutions are slow processes in the gas phase even if strongly exoergic. The formation of X\(^{-}\) 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\(^{-}\) ions in the reaction with the 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 CHX3 Radicals.** The occurrence/nonoccurrence of proton transfer in the reactions of the CHX3\(^{-}\) ions with various acids leads to the free energies of deprotonation of the CHX3 radicals given in Table 5. These \(\Delta G^0_{\text{acid}}\) values can be converted into the gas-phase acidities (\(\Delta H^0_{\text{acid}}\)) of the radicals if the temperature is assumed to be 298 K and provided that the entropy change associated with deprotonation of the radicals (\(\Delta S^0_{\text{acid}}\)) can be obtained. An experimental determination of the \(\Delta S^0_{\text{acid}}\) is precluded since an equilibrium situation between the carbene radical anions and one of the reference acids is unattainable. The \(\Delta S^0_{\text{acid}}\) values of the radicals can be estimated, however, by following the published procedures, 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, \(\Delta S^0_{\text{acid}}\) estimated to be 114.6 J K\(^{-1}\) mol\(^{-1}\) 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\(^{-1}\) mol\(^{-1}\)). This implies that a hypothetical equilibrium between one of the carbene radical anions and the selected reference acid is

\[
\text{CHX}^+ + \text{ROH} \rightarrow X^- + \text{ROCH}_2^+
\]

\((8)\)

The occurrence of this process is revealed by studying the reactions of, for example, the CH79Br\(^+\) ion with methanol in the presence of bromomethane. In addition to methoxide ions, the 79Br and 81Br ions are formed in an abundance ratio of 84:16, see Table 4) which is significantly different from the ratio of 55:45 obtained if only CH3Br is present in the cell. The alkoxide ions generated by proton transfer react as expected further with the bromomethane molecules by an Sn2 substitution. This process proved to be of minor importance as indicated by the small effect on the abundance ratio between the 79Br and 81Br ions upon continuous ejection of the RO\(^{-}\) ions during the reaction period (see Table 4). Similarly, the CH3Cl\(^-\) ions react relatively readily with aliphatic alcohols in the presence of chloromethane to generate 35Cl\(^-\) ions in addition to alkoxide ions (Table 3). The preference for generation of X\(^{-}\)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.

### Table 3. Normalized Abundances (% of the RO\(^{-}\), 35Cl\(^-\), and 37Cl\(^-\) Ions Formed in the Reactions of the CH3Cl\(^-\) Ion with Chloromethane and Aliphatic Alcohols

<table>
<thead>
<tr>
<th>substrate</th>
<th>(\Delta H^0_{\text{acid}}) (kJ mol(^{-1}))</th>
<th>RO(^{-})</th>
<th>35Cl(^-)</th>
<th>37Cl(^-)</th>
<th>ejection of RO(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3Cl</td>
<td>1643</td>
<td>55</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH3OH</td>
<td>1592</td>
<td>5</td>
<td>80(64)</td>
<td>15(16)</td>
<td>88</td>
</tr>
<tr>
<td>C2H5OH</td>
<td>1591</td>
<td>5</td>
<td>59(79)</td>
<td>16(21)</td>
<td>92</td>
</tr>
<tr>
<td>(CH3)2CHOH</td>
<td>1571</td>
<td>26</td>
<td>62(83)</td>
<td>13(17)</td>
<td>80</td>
</tr>
<tr>
<td>(CH3)2CHCH2OH</td>
<td>1568</td>
<td>23</td>
<td>62(81)</td>
<td>15(19)</td>
<td>80</td>
</tr>
</tbody>
</table>

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

### Table 4. Normalized Abundances (% of the RO\(^{-}\), 79Br\(^-\), and 81Br\(^-\) Ions Formed in the Reaction of the CH79Br\(^-\) Ion with Bromomethane and Aliphatic Alcohols

<table>
<thead>
<tr>
<th>substrate</th>
<th>(\Delta H^0_{\text{acid}}) (kJ mol(^{-1}))</th>
<th>RO(^{-})</th>
<th>79Br(^-)</th>
<th>81Br(^-)</th>
<th>ejection of RO(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3Br</td>
<td>1643</td>
<td>55</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH3OH</td>
<td>1592</td>
<td>5</td>
<td>80(64)</td>
<td>15(16)</td>
<td>88</td>
</tr>
<tr>
<td>C2H5OH</td>
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<td>(CH3)2CHOH</td>
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<td>80</td>
</tr>
</tbody>
</table>

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

\[\text{CHX}^- + \text{CH}_3\text{X} \rightarrow X^- + \text{CH}_2\text{H}_2\text{X}^-\]  (6)

CH79Cl\(^-\) ions with chloromethane. For example, the reaction of the CH37Cl\(^-\) ion with the parent compound yields slightly more of the 35Cl\(^-\) ion relative to the 37Cl\(^-\) ion (eq 7 and Table 3)

\[\text{CH}^\text{35Cl}^- + \text{CH}_3\text{Cl} \rightarrow 79\text{Cl}^- + \text{CH}_2\text{H}_2\text{Cl}^-\]  (7a)

\[\text{CH}^\text{37Cl}^- + \text{CH}_3\text{Cl} \rightarrow 81\text{Cl}^- + \text{CH}_2\text{H}_2\text{Cl}^-\]  (7b)
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 $\Delta S^{a\text{acid}}$ value suggests that the possible errors in the $\Delta H^{a\text{acid}}$ 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 $298 \text{ K}$ (see also the Experimental Section).

The $\Delta H^{a\text{acid}}$ values in Table 5 reveal that the acidity increases in the series $\text{CHF}, \text{CHCl}, \text{CHBr},$ and $\text{CHI}$ with the largest difference (58 kJ mol$^{-1}$) observed between the fluoride- 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 $\text{CH}_2X$ radical and the EA of the $\text{CHX}$ 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.$^{12}$ 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 $\text{CH}_2X$ molecules,$^{49}$ that is, the increase in acidity in the series $\text{CH}_2F, \text{CH}_2Cl, \text{CH}_2Br,$ and $\text{CH}_2I$ reflects the trend in the EA of the $\text{CH}_2X$ 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 $\text{CH}_2X$ 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 $\text{CH}_3X$ to $\text{CH}_2X$ is mainly a result of the larger EA of a given CHX carbone than of the related radical and to lesser extent determined by the change in C–H BDE when a $\text{CH}_3X$ molecule is transformed into a radical.

For example, the C–H BDE of the $\text{CH}_2F$ radical is $\approx 15 \text{ kJ mol}^{-1}$ lower than the C–H bond strength of $\text{CH}_3F,$$^{28}$ whereas the EA of $\text{CHF}$ is $\approx 33 \text{ kJ mol}^{-1}$ larger than the EA of $\text{CH}_2F,$ 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 $\text{CHF} (52 \text{ kJ mol}^{-1})$ than of singlet $\text{CH}_2 (100 \text{ kJ mol}^{-1})$ has been attributed to the stabilizing effect of the fluoride atom on the neutral carbone, which was considered to be more significant than the stabilization of the negative charge in the $\text{CHF}^-$ radical anion.$^{11}$ As discussed in the literature,$^{4,5,10}$ the stabilization of the singlet state relative to the triplet state of a halogen-containing carbone can be ascribed to two effects, which may act synergistically. First, an electron-negative halogen atom can withdraw electron density from the carbon atom by an inductive effect and increase the 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 carbone. Second, the halogen atom can stabilize the singlet state by donating electron density to the unoccupied carbon $p_\sigma$ orbital of the carbone through the $\beta$–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 $\text{CHF}, \text{CHCl},$ and $\text{CHBr}$ (vide supra).$^{10}$ 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 $p_\sigma$ orbital.

The stabilization of the negative charge in the carbene radical anions has been discussed as inductive electron withdrawal by the halogen atom.$^{11}$ 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 $\text{CHF}, \text{CHCl}, \text{CHBr},$ 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.$^{11}$ 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 $\text{CH}_2X$ radicals. For the $\text{CH}_2X$ 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 $\text{CH}_2X$ ions. In qualitative terms, the trend in the EA of the $\text{CH}_2X$ 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 $\text{CH}_2X$ radicals (Table 5) can be used to derive the following heats of formation of the CHX carbenes: $157 \pm 18 \text{ kJ mol}^{-1} (\text{CH}_3A', \text{CHF}), 317 \pm 20 \text{ kJ mol}^{-1} \text{ mol}^{-1} (\text{CH}_3A' \text{CHCl}), 373 \pm 18 \text{ kJ mol}^{-1} (\text{CH}_3A' \text{CHBr}),$ and $428 \pm 21 \text{ kJ mol}^{-1} (\text{CH}_3A' \text{CHI}).$
Table 6. Heats of Formation (ΔH°r in kJ mol⁻¹ at 298 K) of the CH₃X, CH₂X, and CHX Species

<table>
<thead>
<tr>
<th>X</th>
<th>CH₃X*</th>
<th>CH₂X*</th>
<th>CHX</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-247</td>
<td>-33</td>
<td>157 ± 18⁴</td>
</tr>
<tr>
<td>Cl</td>
<td>-82</td>
<td>120</td>
<td>317 ± 20⁴</td>
</tr>
<tr>
<td>Br</td>
<td>-38</td>
<td>170⁵</td>
<td>373 ± 18⁴</td>
</tr>
<tr>
<td>I</td>
<td>15</td>
<td>230⁶</td>
<td>428 ± 21⁵</td>
</tr>
</tbody>
</table>

* From ref 28. ¹ Value from ref 66; see also text. ² This work, see text.

Figure 3. Graphical representation of the trend in the heats of formation of the CHX, CH₂X, and CH₃X species (see text and Table 6).

mol⁻¹ (X A' or I A'/CHI) (Table 6). These heats of formation refer—to as indicated—to the singlet ground states of the CHF, CHCl, and 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 CHI, we also used the EA value given for the singlet state even though it remains uncertain whether this is the ground state.¹⁰,¹²,¹⁵

The heats of formation of the carbenes are less accurate than the determined gas-phase acidities of the radicalis, and the average error limit of ±20 kJ mol⁻¹ in Table 6 arises as the sum of the error limit of about 8 kJ mol⁻¹ on the reported ΔH°r values of the CHX species and the uncertainties in the ΔH°,ad(CHX) values. For example, the heat of formation of the CH₂Cl radical is quoted as 130 kJ mol⁻¹ in ref 28 whereas values in between 115 and 120 kJ mol⁻¹ are given in a recent paper by Holmes and Lossing.⁶⁶ Furthermore, these authors place the heat of formation of the CHCl radical as 230 kJ mol⁻¹ whereas a value of 210 kJ mol⁻¹ is given in ref 28. We have used the value of 120 kJ mol⁻¹ for the CH₂Cl radical and 230 kJ mol⁻¹ for CHCl because these give rise to a consistent picture of the trend in the heats of formation of the CHX, CH₂X, and 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).

CH₃X → CHX + H₂  \( \Delta H°r \approx 400 \text{ kJ mol}^{-1} \)  (9)

The present value for the heat of formation of CHCl is within the error limit of the value (297 ± 20 kJ mol⁻¹) derived on the basis of the determination of the proton affinity of this carbene. For CHF, however, the result in Table 6 deviates significantly from the value of 105 kJ mol⁻¹ obtained by studying proton-transfer reactions of the CF₂⁺ ion⁶⁶ but is in line with the value of ±163 kJ mol⁻¹ based on a study of the reactivity of the CH₂F radical in the gas phase.⁷ At present, we have no explanation for the discrepancy between our value for the heat of formation of 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 CF₂⁺ ion⁷ with a series of aliphatic alcohols leads to a ΔGo₂₉⁰ value of the ‘CHF₂ radical of 1546 ± 6 kJ mol⁻¹. This value results in a ΔH°,ad('CHF₂) = 1579 ± 6 kJ mol⁻¹ on the basis of an estimated ΔS°,ad('CHF₂) of 109 J K⁻¹ mol⁻¹ and with T assumed to be 298 K. The ΔH°,ad value leads in combination with the reported EA of singlet difluorocarbene of 17 ± 1 kJ mol⁻¹ to a C-H BDE of the ‘CHF₂ radical of ~284 kJ mol⁻¹. With ΔH°r('CHF₂) = 237 kJ mol⁻¹, the heat of formation of CHX (X A') becomes ~15 ± 10 kJ mol⁻¹. This heat of formation of CHX is slightly lower than the upper limit of ~165 ± 14 kJ mol⁻¹ derived on the basis of measurements of the threshold energy for collision-induced dissociation of CF₂⁺ with formation of F⁻ ions⁶⁸ and somewhat larger than the value of ~184 ± 4 kJ mol⁻¹ determined from the photoionization threshold for CF₂ loss from some fluorine-containing species.⁶⁹

Reactions of the 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 S-N2 substitution competing with a process involving initial proton transfer between the radical anion and the halogen-containing methane molecule followed by a nucleophilic substitution.⁶¹ The acidity measurements reveal that proton abstraction from a CHX⁺ molecule by the related CHX⁻ radical anion with formation of a free -CHX⁻ ion is ~50 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 complex⁶² as illustrated in Scheme 1 for the reaction of the CH₃Cl⁻ ion with CH₃Cl. Proton transfer in complex a in Scheme 1 leads to b, which then reacts further by substitution to form a 35Cl⁻ ion and a 'CH₂CH₂Cl radical. The entire process is estimated to be 250 kJ mol⁻¹ exothermic and is thus only 14 kJ mol⁻¹ less exothermic than the direct S-N2 substitution, which leads to a CH₃CH₂Cl radical (see Scheme 1). The occurrence of an energetically unfavorable proton transfer in addition to a strongly exothermic S-N2 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.⁷⁰,⁶²,⁶³

Scheme 1. Proposed Mechanism for the Reaction of the CH₃Cl⁻ Ion with CH₃Cl
Heats of Formation of Mono-Halogen-Substituted Carbenes

Scheme 2. Proposed Mechanism for the Reaction of the CH$_3^+$Cl$^-$ Ion with Methanol

\[
\begin{align*}
\text{CH}_3^+\text{Cl}^- & + \text{CH}_3\text{OH} \\
\text{c} & \quad \text{H}^+ \text{- transfer} \\
\left[\text{CH}_3^+\text{Cl}^- + \text{CH}_3\text{OH}\right] & \\
\text{d} & \quad \text{dissociation} \\
\text{CH}_3\text{OCH}_2^- + ^{35}\text{Cl}^- & \quad \text{CH}_2^+\text{Cl}^- + \text{CH}_3\text{O}^- \\
\Delta H^\circ & = -238 \text{ kJ mol}^{-1} \\
\Delta H^\circ & = -18 \text{ kJ mol}^{-1}
\end{align*}
\]

The formation of X$^-$ ions by initial proton transfer between a carbene radical anion and a CH$_3$X molecule implies the occurrence of a nucleophilic attack of a carbanion on a $^+$CH$_2$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 $^+$CH$_2$X radical and a RO$^-$ ion as illustrated in Scheme 2 for the reaction of the CH$_3^+$Cl$^-$ ion with CH$_3$OH. Complex d generated by proton transfer within complex c may then dissociate or react further by an S$_{N}2$ substitution to form $^{35}$Cl$^-$. In conclusion, the S$_{N}2$ 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 $^+$CH$_2$X (X = F, Cl, Br, and I) radicals by studying the ion/molecule chemistry of the CHX$^-$ carbene radical anions. In combination with reported electron affinities of the singlet CHX carbenes, these acidities lead to the heats of formation of the CHX carbenes. The trend in the heats of formation of the CHX carbenes in the series CHF, CHCl, CHBr, 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 CH$_3$X molecules 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 $^+$CH$_2$F, $^+$CH$_2$Cl, $^+$CH$_2$Br, and $^+$CH$_2$I, that is, the acidity increases as the halogen atom becomes heavier as observed also for the corresponding methanes. The acidity increases by $\approx51$ kJ mol$^{-1}$ on going from a CH$_3$X molecule to the related $^+$CH$_2$X radical. This change in acidity is mainly a result of a larger electron affinity of a given CHX carbene than of the related $^+$CH$_2$X radical and only to a minor extent determined by the decrease in C–H bond dissociation energy in going from a CH$_3$X molecule to the corresponding radical.

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