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Thermochemical properties of halogen-substituted methanes, methyl radicals, and carbenes in the gas phase

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Abstract

The thermochemical properties of a series of chlorine- and bromine-substituted methanes, methyl radicals, and carbenes have been (re)examined on the basis of ion–molecule reactions as performed with the use of Fourier transform ion cyclotron resonance mass spectrometry. In particular, the occurrence of reversible proton transfer in the reactions of the $CHClBr^-$, $CHBr_2^-$, and CBr_3^- anions with selected reference acids has been used to obtain the following gas-phase acidities: $\Delta H^\circ_{acid}(CH_2ClBr) = 1560 \pm 8$ kJ mol^{-1}, $\Delta H^\circ_{acid}(CH_2Br_2) = 1544 \pm 8$ kJ mol^{-1}, and $\Delta H^\circ_{acid}(CHBr_3) = 1463 \pm 8$ kJ mol^{-1}. In addition, the gas-phase acidities of the $^{\cdot}CHCl_2$, $^{\cdot}CHClBr$, and $^{\cdot}CHBr_2$ radicals have been placed at 1524 ± 10, ~1509, and ~1494 kJ mol^{-1}, respectively. The values for the $^{\cdot}CHClBr$ and $^{\cdot}CHBr_2$ radicals have been derived on the basis of the occurrence/nonoccurrence of proton transfer in the reactions of the $CClBr^{-\cdot}$ and $CBr_2^{-\cdot}$ carbene radical anions with various reference acids in combination with the trend in the gas-phase acidities of bromine containing methanes and methyl radicals. The present gas-phase acidities together with experimentally determined electron affinities of the dihalogen-substituted carbenes have been used to estimate the enthalpies of formation of the CCl_2, CClBr, and CBr_2 carbenes [$\Delta H^\circ_f(CCl_2) = 226 \pm 25$ kJ mol, $\Delta H^\circ_f(CClBr) \sim 267$ kJ mol, and $\Delta H^\circ_f(CBr_2) \sim 324$ kJ mol^{-1}). (Int J Mass Spectrom 194 (2000) 103–113) © 2000 Elsevier Science B.V.

Keywords: Gas-phase acidities; Enthalpies of formation; Radical anions; Halogen-substituted carbenes; Fourier transform ion cyclotron resonance

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1. Introduction

The thermochemical properties of various halogen-substituted organic compounds are of general importance in view of the common usage of these species and their role in, e.g. the ion chemistry occurring in the upper atmosphere [1–3]. In addition, simple organic halogen-containing species are used frequently in more fundamental studies of chemical reactivity in condensed phases [4] as well as in studies of ion-molecule reactions in the gas phase [5–11]. In this respect, simple halogen-substituted carbenes are of particular interest largely because the reactivity of carbenes is determined by their spin multiplicity, i.e. singlet carbenes prefer to react in single-step processes, whereas triplet carbenes prefer to react in two-step processes [12,13].

For monohalogen-substituted carbenes (CHX; X = F, Cl, Br and I) a number of reports indicate that they all have a singlet ground state and that the

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Dedicated to Professor Jim Morrison on the occasion of his 75th birthday and for his important contributions to mass spectrometry.

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singlet–triplet energy gap decreases as the halogen atom becomes heavier [14–19]. A similar trend is indicated also for dihalogen-substituted carbenes as revealed by the reported singlet–triplet differences for CF_2 (237 kJ mol^{-1}), CCl_2 (86 kJ mol^{-1}), and CBr_2 (52 kJ mol^{-1}) [14,15]. Irrespective of the insight into the electronic properties of simple carbenes, the enthalpies of formation, ΔH_f°, of most halogen-substituted carbenes are less certain mainly as a result of the fact that different experimental methods have been used to determine the thermochemical properties of these species in various independent studies. For example, the enthalpy of formation of the CCl_2 carbene has been determined experimentally in a number of instances [20–24] ever since it was indicated to be formed as an intermediate species in the gas-phase pyrolysis of trichloromethane and tetrachloromethane [25]. In the different studies, the enthalpy of formation of CCl_2 has been placed at values ranging from 125 to 239 kJ mol^{-1}, with one of the most recent values being 218 ± 14 kJ mol^{-1} as obtained with the use of the flowing afterglow (FA) method [23]. Another mass spectrometric method that has been used for the determination of the enthalpies of formation of carbenes is Fourier transform ion cyclotron resonance (FTICR) [26]. Notably, in a previous study from our group we applied the FTICR method in order to obtain the enthalpies of formation of the monohalogen-substituted carbenes, CHX (X = F, Cl, Br, and I) by determining experimentally the gas-phase acidities, ΔH_{acid}°, of the $^{\cdot}CH_2X$ radicals and combining these values with reported thermochemical properties of the appropriate species [27].

In the present study, this approach has been extended to a (re)determination of the enthalpies of formation of the dihalogen substituted carbenes, CCl_2, CClBr, and CBr_2; that is, the gas-phase acidities of the $^{\cdot}CHCl_2$, $^{\cdot}CHBrCl$, and $^{\cdot}CHBr_2$ radicals have been obtained together with the electron affinities (EAs) of the related carbenes and radicals. In addition, the gas-phase acidities of CH_2ClBr, CH_2Br_2, and $CHBr_3$ have been determined in order to obtain a relatively complete picture of the trend in the gas-phase acidities of the simple halomethanes as well as halomethyl radicals as the number and nature of the halogen atoms is altered. The combination of these results with known data for the related fluorine-substituted species provides a basis for a coherent discussion of thermochemical properties of halogen-substituted methanes, methyl radicals, and carbenes.

2. Experimental

The experiments were performed with the use of a FTICR mass spectrometer designed and constructed at the University of Amsterdam [28]. The general operating procedure of this instrument has been described in previous publications [29,30]. The $O^{-\cdot}$ ions, necessary to form the (radical) anions of interest, were generated by dissociative electron capture of N_2O (electron energy ~ 1.2 eV). Unwanted ions were ejected from the FTICR cell by applying appropriate radio-frequency pulses to the excitation plates of the cell. During the experiments, the presence of free electrons in the cell was avoided by continuously applying a high frequency pulse to the trapping plates as described elsewhere [31]. The total pressure was usually about 8×10^{-5} Pa as measured with an uncalibrated ionization gauge placed in a sidearm of the main vacuum system. The ratio of the partial pressures of N_2O, the halogen-substituted methane, and the reference acid or electron acceptor was in most experiments 1:1:1. The temperature of the trapping plate situated opposite the filament side was measured to be about 330 K. The inlet systems, leak valves and the vacuum vessel were at room temperature.

3. Results

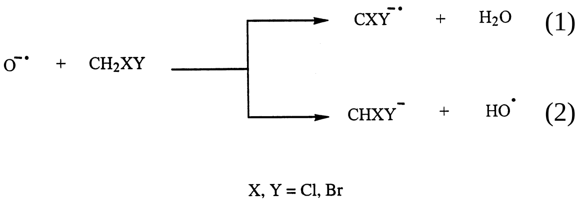
The appropriate dihalogen-substituted (radical) anions were generated by allowing the $O^{-\cdot}$ radical anion to react with CH_2Cl_2, CH_2ClBr, or CH_2Br_2, respectively. The reaction with these halomethanes is known to involve competing $H_2^{+\cdot}$-abstraction with formation of a dihalogen substituted carbene radical anion [Eq. (1)] and proton transfer leading to a halogen containing methyl anion [Eq. (2)] [11,32]. Likewise, the $O^{-\cdot}$

Table 1
Determination of the electron affinities of the chlorine- and bromine-substituted carbenes and methyl radicals (see text)[a]

M	EA[b]	$CCl_2^{-\cdot}$	$CClBr^{-\cdot}$	$CBr_2^{-\cdot}$	$CHCl_2^-$	$CHClBr^-$	$CHBr_2^-$
$C_6H_5NO_2$	97				−	−	−
CF_3COCF_3	138[c]				−	−	−
2-$NO_2C_6H_4$(CHO)	146	−	−	−	+	+	−
3-$NO_2C_6H_4$(CHO)	157			−			−
3,5-$(CF_3)_2C_6H_3NO_2$	173	+	−	−	+	+	+
2-$CH_3C_6H_3O_2$[d]	178		+/−	−		+	+
4-$NO_2C_6H_4NO_2$	193		+	+			+
EA (related neutral)		160 ± 14	178 ± 10	186 ± 8	142 ± 4	142 ± 4	165 ± 8

[a] All values are in kJ mol^{-1}.
[b] The values have been taken from [33,36].
[c] This value has been taken from [34].
[d] 2-methyl-1,4-benzoquinone.

ion was reacted with $CHCl_3$ and $CHBr_3$ in order to form the CCl_3^- and CBr_3^- ions, respectively



The (radical) anions were reacted subsequently with a series of selected electron acceptors in order to determine the electron affinities of the related neutral species by observing the occurrence/nonoccurrence of electron transfer as exemplified in Eq. (3) for a dihalogen carbene radical anion. Similarly, the (radical) anions were reacted with a series of reference acids for the purpose of determining the gas-phase acidities of the related halogen-substituted methanes or methyl radicals as illustrated in Eq. (4)

$$CXY^{-\cdot} + M \rightarrow CXY + M^{-\cdot} \qquad (3)$$

$$CXY^{-\cdot} + HA \rightarrow CHXY^{\cdot} + A^- \qquad (4)$$

3.1. Electron affinities

The occurrence/nonoccurrence of electron transfer in the reactions between the (radical) anions and selected electron acceptors with a known EA [33,34] is indicated in Table 1. The EA values of the halomethyl radicals and carbenes can be obtained directly from the results in Table 1 in keeping with the facts that (1) only exoergic to thermoneutral reactions are observed under normal operating conditions with the present instrumental method [27], and (2) the entropy change for electron transfer reactions involving simple species in the gas phase is often negligible [33]. In other words, the reaction Gibbs energy, ΔG_r°, of a given electron transfer reaction is considered to be equal to the reaction enthalpy, ΔH_r°. As a result, the occurrence/nonoccurrence of electron transfer leads to the enthalpy change for removal of an electron from a given (radical) anion. Upon the assumption that the constant pressure heat capacities (and their temperature dependence) are similar for a given (radical) anion and related neutral species, the enthalpy change for detachment of an electron can be equated with the EA of the halogen-substituted carbene or methyl radical. In the present context, this implies that the EA of the species of interest is given as the mean of the values of the reference compounds with the smallest interval for which an electron transfer occurs and does not occur.

The results given in Table 1 indicate that the EA of the $^{\cdot}CHCl_2$ radical is 142 ± 4 kJ mol^{-1} and thus somewhat lower than an earlier value of 152 ± 14 kJ mol^{-1} [35,36]. Based on the occurrence/nonoccurrence of electron transfer in the reactions of the $CHClBr^-$ anion, the EA of the $^{\cdot}CHClBr$ radical

Table 2
Occurrence/nonoccurrence of proton transfer to the chlorine- and bromine-substituted carbene radical anions and methyl carbanions (see text)

HA	$\Delta G^{\circ}_{\text{acid}}$ [a]	$CCl_2^{-\cdot}$	$CClBr^{-\cdot}$	$CBr_2^{-\cdot}$	$CHCl_2^-$	$CHClBr^-$	$CHBr_2^-$	CCl_3^-	CBr_3^-
$(CH_3)_3COH$	1540				rev.[b]		−		
CH_2Cl_2	1535					−			
CH_3CN	1528					rev.[b]	−		
CH_3COCH_3	1514	−					rev.[b]	−	
$CH_3COC_2H_5$	1508						rev.[b]		
CH_3CH_2CHO	1501	−					+		
CF_3CH_2OH	1482	+		−					
CH_3SH	1467		−	−					
CH_3NO_2	1464	+						rev.[b]	
CH_3CH_2SH	1460		−	−					
$(CH_3)_2CHSH$	1452		−[c]						
$C_6H_5NO_2$	1450		−						
$(CH_3)_3CSH$	1449		−	−				+	
4-$CH_3C_6H_4NO_2$	1445		+						
indene	1442		+	−					−
CF_3COCH_3	1431		+	+				+	rev.[b]
CH_3CO_2H	1429		+						+
HCO_2H	1415		+	+					

[a] The values have been taken from [36,39] and are in kJ mol^{-1}.
[b] Proton transfer is observed to be reversible.
[c] Traces of $(CH_3)_2CHS^-$ ions are formed.

becomes the same as the value for $^{\cdot}CHCl_2$; that is, the EA of both of these radicals is indicated to be 142 ± 4 kJ mol^{-1}. The EA of $^{\cdot}CHClBr$ has not been reported previously but the present value may be considered to be somewhat too low since the EA of this radical is likely to be in between the values of the $^{\cdot}CHCl_2$ and $^{\cdot}CHBr_2$ species (Table 1) in line with the finding for the related carbenes (vide infra).

The present results indicate that the EA of CCl_2 is between 146 and 173 kJ mol^{-1}; that is, in between the values for 2-$NO_2C_6H_4(CHO)$ and 3,5-$(CF_3)_2C_6H_3NO_2$, respectively (Table 1). This places the EA of the CCl_2 carbene at 160 ± 14 kJ mol^{-1} in agreement with a value of 155 ± 1 kJ mol^{-1} obtained with the use of photoelectron spectroscopy [14]. The EA values of the bromo-containing carbenes, CClBr and CBr_2, are determined to be 178 ± 10 and 186 ± 8 kJ mol^{-1}, respectively; that is, the EA of CClBr is determined to be in between the values for the CCl_2 and CBr_2 carbenes.

The present EA of the CBr_2 carbene is significantly lower than suggested on the basis of the failure to obtain the photoelectron spectrum of the $CBr_2^{-\cdot}$ radical anion by electron detachment with photons with an energy of 245 kJ mol^{-1} [14]. In combination with the instrumental aspects of the experiments, the absence of photodetachment of an electron was taken to mean that the EA of the CBr_2 carbene should be larger than 222 kJ mol^{-1}. We have no explanation for the reported failure to record the photoelectron spectrum of the $CBr_2^{-\cdot}$ radical anion but emphasize that the present EA value is not in disagreement with the trend in the EA values of various halogen-substituted carbenes and methyl radicals (see also Sec. 4).

3.2. Gas-phase acidities

The results of the experiments concerned with the occurrence of proton transfer in the reactions of the (radical) anions with a series of selected reference acids are given in Table 2. For the halogen substituted methanes, reversible proton transfer is observed with an appropriate reference acid as exemplified in Eq. (5) for the $CHClBr^-$ species

$$CHClBr^- + CH_3CN \rightleftharpoons CH_2ClBr + CH_2CN^- \tag{5}$$

Table 3
Gibbs energies for deprotonation (ΔG°_{acid}), gas-phase acidities (ΔH°_{acid}), C–H bond dissociation enthalpies (BDE) and electron affinities (EA) of fluoro-, chloro-, and bromo-containing methanes, methyl radicals, and carbenes (values in kJ mol^{-1}, the average uncertainty on the acidity values is ±8 kJ mol^{-1}, see also text and Tables 1 and 2)

Halomethane	ΔG°_{acid}	ΔH°_{acid}	C–H BDE	EA halomethyl-radical	Halomethyl-radical	ΔG°_{acid}	ΔH°_{acid}	C–H BDE	EA halocarbene
CH_3F	1676[a,b]	1711[a,b]	419[c]	19[a]	$^{\cdot}CH_2F$	1634[d]	1668[d]	400[e]	52[f]
CH_2F_2	1595[a]	1628[a]	432[c]	116[a]	$^{\cdot}CHF_2$	1547[d]	1579[d]	276[e]	17[f]
CHF_3	1545[a]	1577[a]	445[c]	176[a]					
CH_3Cl	1625[a,b]	1657[a,b]	418[e]	81[a]	$^{\cdot}CH_2Cl$	1576[d]	1610[d]	406[e]	116[f]
CH_2Cl_2	1540[g]	1572[g]	394[e]/407[h]	142[a]	$^{\cdot}CHCl_2$	1492[g]	1524[g]	364[e]	160[g]
$CHCl_3$	1464[g]	1496[g]	386[e]/397[h]	210[a]					
CH_3Br	1611[a,b]	1643[a,b]	420[e]	97[a]	$^{\cdot}CH_2Br$	1559[d]	1593[d]	413[e]	140[f]
CH_2Br_2	1512[g]	1544[g]	389[e]/411[h]	165[g]	$^{\cdot}CHBr_2$	1437[i]; 1462[j]	1469[i]; 1494[j]	360[k]	186[g]
$CHBr_3$	1431[g]	1463[g]	368[e]/399[h]	225[l]/256[m]					
CH_2ClBr	1528[g]	1560[g]	382[e]; 393[n]	142[g]	$^{\cdot}CHClBr$	1447[i]; 1477[j]	1479[i]; 1509[j]	366[k]	178[g]

[a] Taken from [36].
[b] Taken from [37].
[c] Estimated on the basis of data given in [36].
[d] Taken from [27].
[e] Estimated on the basis of the gas-phase acidity and the EA value given.
[f] Taken from [14,15].
[g] Obtained in this study; see text.
[h] Estimated on the basis of data given in [36,41].
[i] Value indicated by the results in Table 2 (see text).
[j] Corrected value (see text).
[k] Estimated on the basis of the corrected gas-phase acidity and the EA value given.
[l] Estimated with the use of a C–H BDE of 368 kJ mol^{-1}.
[m] Estimated with the use of a C–H BDE of 399 kJ mol^{-1}.
[n] Based on an EA of the $^{\cdot}CHClBr$ radical of 153 kJ mol^{-1} (see text).

The observation of reversibility in the proton transfer reaction places the ΔG°_{acid} value for deprotonation of a given halomethane close to the value for the reference acid. Subsequently, the ΔG°_{acid} values have been converted into the gas-phase acidities, ΔH°_{acid}, with the use of an estimated $T\Delta S^\circ_{acid}$ term of 32 kJ mol^{-1} and the final values are collected in Table 3. The present value of the $T\Delta S^\circ_{acid}$ term is based on data given in the literature which indicates that the entropy change associated with deprotonation of halogen-substituted methanes is in between 97 and 117 J K^{-1} mol^{-1}. In other words, the average value of ΔS°_{acid} for a number of halomethanes is indicated to be close to the entropy of the free proton (108.8 J K^{-1} mol^{-1}) [27,36,37]. Upon the assumption that ΔS°_{acid} is 109 J K^{-1} mol^{-1} for the present series of halomethanes, the $T\Delta S^\circ_{acid}$ term becomes 32 kJ mol^{-1} if the temperature is presumed to be close to 298 K as discussed in previous reports from our group [27,38].

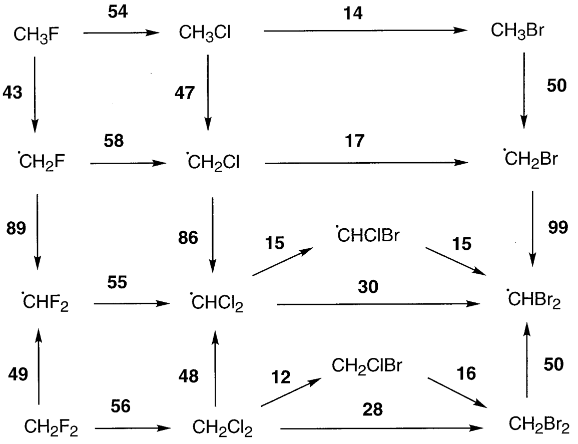
For some of the halomethanes included in this study, the present gas-phase acidities are in agreement with values reported previously. For example, the value of the gas-phase acidity of CH_2Cl_2 (1572 ± 8 kJ mol^{-1}) as based on the reversibility of proton transfer in the reaction with $(CH_3)_3COH$ leads to essentially the same value as reported (1567 ± 13 kJ mol^{-1}) [36]. With respect to $CHCl_3$, the observation of a reversible proton transfer in the reaction with CH_3NO_2 (Table 2) leads to a gas-phase acidity of 1496 ± 8 kJ mol^{-1}. This value is likewise essentially indistinguishable from the most recently published value of 1497 ± 8 kJ mol^{-1} as determined by observing the occurrence/nonoccurrence of proton transfer in reactions of the CCl_3^- ion in a FA instrument [23]. For the bromomethane, CH_2Br_2, the observation of reversibility in the proton transfer reaction between the $CHBr_2^-$ ion and CH_3COCH_3 as well as $CH_3COCH_2CH_3$ (Table 2) places the gas phase acidity of CH_2Br_2 at 1544 ± 8 kJ mol^{-1}. Likewise, the occurrence of a reversible proton transfer between CBr_3^- and CF_3COCH_3 leads to a gas phase acidity of 1463 ± 8 kJ mol^{-1} for the $CHBr_3$ methane. This latter value is significantly different from the literature value (1546 ± 34 kJ mol^{-1}) which was obtained with the so-called magnetron method [36,39]. However, the literature value would suggest that $CHBr_3$ is less acidic than $CHCl_3$ in the gas phase, in contrast to the data in Table 3 and the common observation that bromo-containing halomethanes are more acidic than the related chloro-containing species. In other words, the present value as obtained on the basis of the occurrence of reversible proton transfer is considered to be more reliable.

The results of the experiments concerned with the occurrence/nonoccurrence of proton transfer in the reactions of a carbene radical anion with a series of selected reference acids are also given in Table 2. From these results, the change in Gibbs energy, $\Delta G^{\circ}_{\text{acid}}$, for the conversion of the $^{\cdot}$CHXY radical into the $CXY^{-\cdot}$ radical anion and a proton may be obtained thus allowing for the subsequent estimation of the $\Delta H^{\circ}_{\text{acid}}$ values with the use of the same $T\Delta S^{\circ}_{\text{acid}}$ (32 kJ mol^{-1}) term as for the halogen substituted methane molecules and also for the $^{\cdot}CHF_2$ radical [23,27]. For the $^{\cdot}CHCl_2$ radical this procedure leads to a $\Delta H^{\circ}_{\text{acid}}$ value of 1524 ± 10 kJ mol^{-1} in close agreement with the most recent literature value of 1516 ± 12 kJ mol^{-1} [23]. For the $^{\cdot}$CHClBr and $^{\cdot}CHBr_2$ radicals, this approach leads to indicated $\Delta H^{\circ}_{\text{acid}}$ values of 1479 and 1469 kJ mol^{-1}, respectively (see Table 3 and Sec. 4).

4. Discussion

4.1. Trend in the gas-phase acidities

The gas-phase acidities determined in the present study are summarized in Table 3 together with the values for the appropriate fluoromethanes and fluoromethyl radicals. The acidities of the latter series of species have been included in order to discuss concisely the variation in the gas-phase acidities with a change in the number as well as the nature of the halogen atoms.



Scheme 1. Overview of the differences in gas-phase acidities, $\Delta H^{\circ}_{\text{acid}}$, of the halogen-substituted methanes and methyl radicals. The numbers given in the scheme are in kJ mol^{-1} and represent increases in gas-phase acidity (see Table 3). For the $^{\cdot}$CHClBr and $^{\cdot}CHBr_2$ radicals, the numbers in the scheme are associated with the correction of the gas-phase acidities as detailed in the text.

For all three series of halomethanes, the increase in acidity going from the monohalogen substituted species to the dihalomethane is somewhat larger than the increase in acidity going from the dihalogen-substituted methane to the trihalomethane. For example, the difference between CH_3F and CH_2F_2 is 83 kJ mol^{-1}, whereas the increase in acidity going from CH_2F_2 to CHF_3 is 51 kJ mol^{-1}. For the chloromethanes, the difference in acidity between CH_3Cl and CH_2Cl_2 is 85 kJ mol^{-1} and thus slightly larger than the difference of 76 kJ mol^{-1} observed for CH_2Cl_2 and $CHCl_3$. A comparable situation applies to the bromomethanes; that is, substitution of a hydrogen atom for a bromine atom in CH_3Br increases the acidity by 99 kJ mol^{-1}, whereas a slightly smaller increase (81 kJ mol^{-1}) is obtained upon the introduction of a third bromine atom (Table 3).

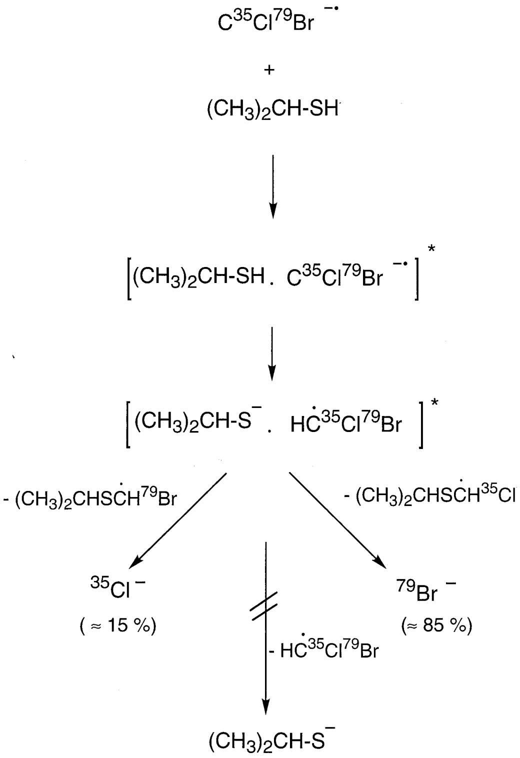
As discussed in previous reports [27,37], halomethanes become more acidic as a given halogen atom is substituted for a heavier one. For example, CH_3F is 54 kJ mol^{-1} less acidic than CH_3Cl and essentially the same difference is observed for CH_2F_2 and CH_2Cl_2 (56 kJ mol^{-1}), whereas a significantly larger difference in acidity is obtained for CHF_3 and $CHCl_3$ (81 kJ mol^{-1}) (see also Scheme 1).

As can be seen in Scheme 1, a different trend is obtained if the chloromethanes are compared with the bromomethanes. For example, the difference in gas-phase acidity between CH_3Cl and CH_3Br is 14 kJ mol^{-1} and thus the half of the difference observed for the CH_2Cl_2 and CH_2Br_2 species (28 kJ mol^{-1}). For the trichloro- and tribromomethanes, the difference of 33 kJ mol^{-1} (see Table 3) is somewhat less than expected for a simple trend in the acidity values. Nevertheless, the differences in acidities between the chloro- and bromomethanes suggest that replacing a chlorine atom for a bromine results in an increase in acidity of 11–15 kJ mol^{-1}. In agreement herewith, the experimentally obtained acidity of CH_2ClBr (1560 ± 8 kJ mol^{-1}) is close to the mean value (1558 kJ mol^{-1}) of the gas-phase acidities of CH_2Cl_2 and CH_2Br_2 (Table 3 and Scheme 1).

With respect to the monohalogen substituted species, it was concluded in a previous study that the difference in acidity between a given halomethane and the related radical is almost independent of the nature of the halogen atom; that is, the monohalogen substituted methanes were observed to be 43–51 kJ mol^{-1} less acidic than the related radicals [27,40]. As shown in Scheme 1, a similar situation applies to the dihalogen substituted species in the sense that a given halomethane is less acidic in the gas phase than the related radical. For the difluorine-substituted species, the CH_2F_2 methane is indicated to be 49 kJ mol^{-1} less acidic than the $^{\cdot}CHF_2$ radical. Essentially the same difference is obtained for the chlorine-substituted species; that is, the CH_2Cl_2 methane is 48 kJ mol^{-1} less acidic than the $^{\cdot}CHCl_2$ radical in the gas phase. For the bromine containing species the results of the occurrence/nonoccurrence of proton transfer in reactions with reference acids suggest that a different situation may arise for these species. For example, the gas-phase acidity of the $^{\cdot}CHBr_2$ radical is indicated to be 1469 kJ mol^{-1} by the bracketing experiments thus suggesting that the CH_2Br_2 methane is 75 kJ mol^{-1} less acidic than the related radical (Table 3). This seems to be inconsistent with the findings for the difluoro and related methyl radicals and also to be in disagreement with the effect on the acidity by changing a chlorine atom for a bromine atom in a methane molecule (vide supra). More explicitly, the difference in acidity between $^{\cdot}CH_2Cl$ and $^{\cdot}CH_2Br$ is 17 kJ mol^{-1} whereas an acidity value of 1469 kJ mol^{-1} for the dibromomethyl radical implies that the difference between $^{\cdot}CHCl_2$ and $^{\cdot}CHBr_2$ should be 55 kJ mol^{-1} (see Table 3). These discrepancies (possible origins to be discussed further) can be avoided if it is assumed that the increase in acidity going from CH_2Br_2 to $^{\cdot}CHBr_2$ is the same as the increase in acidity going from CH_3Br to $^{\cdot}CH_2Br$ (50 kJ mol^{-1}). As a result, the gas-phase acidity of the $^{\cdot}CHBr_2$ radical may be placed at a value of 1494 kJ mol^{-1} (Table 3). With this correction of gas-phase acidity of the $^{\cdot}CHBr_2$ radical, the difference in acidity between the $^{\cdot}CHCl_2$ and $^{\cdot}CHBr_2$ radicals becomes 30 kJ mol^{-1} and thus more in line with the findings for the related methanes (see Scheme 1).

The adjustment of the gas-phase acidity for the $^{\cdot}CHBr_2$ radical necessitates that the value for $^{\cdot}CHClBr$ is also corrected in order to avoid the situation that this latter radical becomes more acidic than the former species. In keeping with the observation that the gas-phase acidity of CH_2ClBr is close to the mean value of the acidities for CH_2Cl_2 and CH_2Br_2, a similar situation can be anticipated for the related radicals. In other words, the gas-phase acidity of the $^{\cdot}CHClBr$ radical is placed at a value of 1509 kJ mol^{-1} (Table 3) which is the mean value of the gas-phase acidity of the $^{\cdot}CHCl_2$ radical and the corrected value for the $^{\cdot}CHBr_2$ radical (see also Scheme 1).

The suggested corrections of the gas-phase acidities of the $^{\cdot}CHClBr$ and $^{\cdot}CHBr_2$ radicals indicate that the observation of occurrence/nonoccurrence of proton transfer to the related carbene radical anions may not be thermodynamically controlled. The failure to obtain consistent gas-phase acidities of these species may be thought to be related to the existence of an energy barrier for proton transfer and/or the occurrence of a competing process. In this respect, it should



Scheme 2. Proposed mechanism for the reaction of the $C^{35}Cl^{79}Br^{-\cdot}$ radical anion with $(CH_3)_2CH\text{–}SH$ in the gas phase (see text).

be noted that halide anions originating from the reactant $CClBr^{-\cdot}$ or $CBr_2^{-\cdot}$ radical anions are formed to some extent in the reactions with the reference acids. Such a process has been observed and discussed previously for the reactions of monohalogen substituted radical anions with different reference acids [27]. For the present species, this halide anion forming process is exemplified in Scheme 2 for the reaction of the $C^{35}Cl^{79}Br^{-\cdot}$ radical anion with $(CH_3)_2CHSH$. The central step in the process involves proton transfer with formation of an ion-molecule complex which may either dissociate giving rise to the deprotonated reference acid or react further by S_N2 substitution to afford mainly $^{79}Br^-$ ions (Scheme 2). In a situation that the overall proton transfer to the deprotonated reference acid is only slightly exothermic, the complex could be thought to prefer to react by the substitution pathway with the formation of free halide anions, thus invalidating the proton transfer bracketing. Irrespective of the precise mechanism and dynamics of the overall reaction it may be expected that halide anion formation is a more facile process for bromine containing radical anions than for chlorine-substituted species in line with the fact that our gas-phase acidity of the $^\cdot CHCl_2$ radical is close to the value given in the literature [23].

4.2. C–H bond dissociation enthalpies and electron affinities

The gas-phase acidity of a species can be formulated as indicated in Eq. (6); that is, the gas-phase acidity of a H_2A molecule can be written as the difference in the HA–H bond dissociation enthalpy (BDE) and the EA of the $HA^\cdot$ radical plus the ionization energy (IE) of the hydrogen atom.

$$\Delta H^\circ_{acid}(H_2A) = BDE(HA\text{–}H) - EA(HA^\cdot) + IE(H^\cdot) \tag{6}$$

This reveals that gas-phase acidities in combination with electron affinities can be used to estimate C–H BDE values. For the CH_2Br_2 methane, we obtain a C–H BDE of 389 kJ mol^{-1} with the use of an EA value of 165 kJ mol^{-1} for the $^\cdot CHBr_2$ radical and an acidity of 1544 kJ mol^{-1} for the parent methane (Table 3). In the literature, the C–H BDE of the CH_2Br_2 methane is given as 410 kJ mol^{-1} as based on $\Delta H^\circ_f(^\cdot CHBr_2) = 186$ kJ mol^{-1} and an estimated ΔH°_f value of -6 kJ mol^{-1} for the CH_2Br_2 methane [41]. However, the estimation of the latter quantity was achieved with an enthalpy of formation of the $CHBr_3$ methane of 24 kJ mol^{-1} [39], whereas a value of 55 kJ mol^{-1} is given in [36]. (Provided that this latter value is correct this implies evidently that the enthalpy of formation of CBr_4 is more likely to be 84 kJ mol^{-1} than 50 kJ mol^{-1}; both values are given in [36].) If the value of 55 kJ mol^{-1} for $\Delta H^\circ_f(CHBr_3)$ is accepted, the mean of the values for CH_3Br (-34 kJ mol^{-1}) and $CHBr_3$ becomes 11 kJ mol^{-1}. With $\Delta H^\circ_f(CH_2Br_2)$ equal to 11 kJ mol^{-1}, the C–H BDE of CH_2Br_2 becomes 393 kJ mol^{-1} and thus close to the value obtained from the present gas-phase acidity and EA values. In addition, an enthalpy of formation of

$CHBr_3$ of 55 kJ mol^{-1} results in a C–H BDE of 368 kJ mol^{-1} for this bromomethane. This value is evidently lower than the value of 399 kJ mol^{-1} obtained with an enthalpy of formation of $CHBr_3$ of 24 kJ mol^{-1} (vide infra).

In summary, the C–H BDE increases somewhat for the fluoromethanes as the number of fluorine atoms is increased (see Table 3), whereas a slight decrease in the C–H BDE is observed for the chloromethanes. A similar situation applies to the bromomethanes even though the C–H BDE may decrease more significantly in the series CH_3Br, CH_2Br_2, and $CHBr_3$ than in the series of chloromethanes (see also Table 3).

With respect to the electron affinities of the halogen-substituted methyl radicals, a significant increase in EA is observed as the number of halogen atoms is enlarged. For the chlorine-substituted methyl radicals, the EA of $^{\cdot}CHCl_2$ is 61 kJ mol^{-1} larger than of the $^{\cdot}CH_2Cl$ radical (Table 3). In turn, the EA of the $^{\cdot}CCl_3$ is 68 kJ mol^{-1} larger than the value for the $^{\cdot}CHCl_2$ species. For the bromine-containing radicals, it may be noted that the electron affinity of $^{\cdot}CHBr_2$ is 68 kJ mol^{-1} greater than of $^{\cdot}CH_2Br$. Unfortunately, the EA of the $^{\cdot}CBr_3$ radical is not given in the literature but with a C–H BDE of 368 kJ mol^{-1}, a value of 225 kJ mol^{-1} can be obtained with the use of the relationship between the gas-phase acidity and the appropriate C–H BDE and EA values as illustrated in Eq. (6) for a H_2A species. The thus estimated EA of $^{\cdot}CBr_3$ is 60 kJ mol^{-1} larger than the value for the $^{\cdot}CHBr_2$ radical, whereas a difference of 91 kJ mol^{-1} is obtained if a C–H BDE of the $CHBr_3$ species of 399 kJ mol^{-1} is used in order to estimate the electron affinity of the $^{\cdot}CBr_3$ radical (vide supra).

In terms of gas-phase acidity, the present discussion supports the conclusion that the most important element in determining the increase in acidity with the number of halogens is the change in the EA of the halogen-substituted radicals. For the species included in this study, a somewhat less straightforward situation arises with respect to the difference in acidity between a monohalogen-substituted methyl radical and the disubstituted radical (Table 3). For the fluorine substituted species, the C–H BDE of the $^{\cdot}CHF_2$ radical is 124 kJ mol^{-1} lower than the value of the $^{\cdot}CH_2F$ radical. The electron affinity of the CF_2 carbene, however, is 35 kJ mol^{-1} lower than that of the CHF carbene and, as a result, the difluoro-substituted radical becomes 89 kJ mol^{-1} more acidic than the parent methane (see also Scheme 1). For the chloro- and bromo-substituted radicals, the changes in the C–H BDE and the electron affinities of the involved species act in concert in the sense that not only are the C–H BDE of the dihalogen substituted radicals significantly lower than those of the monohalogen containing species but the electron affinities of a dihalogen-substituted carbene are also larger than those of the related monohalogen containing species. For example, the C–H BDE of $^{\cdot}CHCl_2$ is 42 kJ mol^{-1} lower than that of $^{\cdot}CH_2Cl$ and the EA of the CCl_2 carbene is 44 kJ mol^{-1} larger than that of CHCl. Overall, the $^{\cdot}CHCl_2$ radical becomes 86 kJ mol^{-1} more acidic than $^{\cdot}CH_2Cl$. For the bromomethyl radicals, the decrease in the C–H BDE going from $^{\cdot}CH_2Br$ to $^{\cdot}CHBr_2$ becomes 53 kJ mol^{-1} if a value of 360 kJ mol^{-1} for the C–H BDE of the $^{\cdot}CHBr_2$ radical is used (Table 3). In combination with the 46 kJ mol^{-1} larger EA of CBr_2 than of CHBr, the $^{\cdot}CHBr_2$ radical turns out to be 99 kJ mol^{-1} more acidic than $^{\cdot}CH_2Br$ (see also Scheme 1).

4.3. Enthalpies of formation

The present gas-phase acidities and electron affinities can be used to estimate the enthalpies of formation of the $^{\cdot}CHCl_2$, $^{\cdot}CHBrCl$, and $^{\cdot}CHBr_2$ radicals as well as of the carbenes, CCl_2, CClBr, and CBr_2. The present gas-phase acidity of CH_2Cl_2 and the experimentally obtained EA of $^{\cdot}CHCl_2$ results in a ΔH_f° of the radical of 80 ± 12 kJ mol^{-1}; that is, our value is somewhat lower than the enthalpy of formation given in the literature (93 ± 8 kJ mol^{-1}) [41,42]. For the $^{\cdot}CHBr_2$ radical, the ΔH_f° becomes ~182 kJ mol^{-1} on the basis of the appropriate gas-phase acidity and EA value in combination with $\Delta H_f^\circ(CH_2Br_2) = 11$ kJ mol^{-1} (vide supra). This present value for the $^{\cdot}CHBr_2$ radical is close to the enthalpy of formation of 187 ± 8 kJ mol^{-1} given in [41] even though this value was obtained with an enthalpy of formation of CH_2Br_2 of −6 kJ mol^{-1}. For the $^{\cdot}CHClBr$ radical, an EA of 141 kJ mol^{-1} leads to an enthalpy of formation for this

Table 4
Enthalpies of formation (ΔH_f° in kJ mol^{-1}) of dihalogen substituted methanes, methyl radicals and carbenes (see text)

Halomethane	ΔH_f°	Halomethyl radical	ΔH_f°	Halocarbene	ΔH_f°
CH_2F_2	-451 ± 1^a	$^{\cdot}CHF_2$	-237 ± 8^a	CF_2	-165 ± 14^b -179 ± 10^c -182^d
CH_2Cl_2	-96 ± 1^a	$^{\cdot}CHCl_2$	80 ± 12^e 93 ± 8^f	CCl_2	226 ± 25^e 218 ± 14^b 238 ± 16^g
CH_2ClBr	-45^h	$^{\cdot}CHClBr$	119 ± 12^e	CClBr	$\approx 267^e$
CH_2Br_2	11^i -6^f	$^{\cdot}CHBr_2$	182 ± 20^e 187 ± 8^f	CBr_2	$\approx 324^e$

[a] Taken from [36].
[b] Taken from [23].
[c] Estimated with the use of data given in Table 3; see also [27].
[d] Cited in [36] with no indication of error limits.
[e] Obtained in the present study.
[f] Taken from [41].
[g] Cited in [23,36].
[h] Taken from [39].
[i] Estimated in the present study (see text).

radical of 119 kJ mol^{-1} and thus somewhat lower than the mean value for the $^{\cdot}CHCl_2$ and $^{\cdot}CHBr_2$ radicals. Obviously, if the electron affinity of the $^{\cdot}$CHClBr radical is assumed to be in between the values for the $^{\cdot}CHCl_2$ and $^{\cdot}CHBr_2$ radicals (mean value 153 kJ mol^{-1}), this increases the enthalpy of formation of the $^{\cdot}$CHClBr to a value of 130 kJ mol^{-1} (the mean value of the enthalpies of formation of the dichloro- and dibromomethyl radicals).

For the carbenes, the C–H BDE values obtained from the gas-phase acidities of the radicals and the EA values of the carbenes lead to the enthalpies of formation of the CCl_2, CClBr, and CBr_2 species. For CCl_2, an enthalpy of formation of the $^{\cdot}CHCl_2$ radical of 80 kJ mol^{-1} results in a ΔH_f° value of CCl_2 of 226 ± 25 kJ mol^{-1}. This outcome is close to the reported value of 218 ± 14 kJ mol^{-1} as obtained by collision-induced dissociation studies of the CCl_3^- ion [23] but somewhat lower than the value of 238 ± 16 kJ mol^{-1} derived from previous acidity measurements of the $^{\cdot}CHCl_2$ radical [23]. However, if the enthalpy of formation of the $^{\cdot}CHCl_2$ radical is placed at 93 kJ mol^{-1}, our experimentally obtained acidity (Table 3) leads to an enthalpy of formation for CCl_2 of 239 kJ mol^{-1} and thus essentially the same as given in [23,36]. For the CClBr carbene, the enthalpy of formation estimated with the use of ΔH_f°($^{\cdot}$CHClBr) = 119 ± 12 kJ mol^{-1} becomes 267 kJ mol^{-1}. This value is slightly lower than the mean value (275 kJ mol^{-1}) of the enthalpies of formation of the CCl_2 and CBr_2 carbenes (Table 4).

For the CBr_2 carbene, the present value of 324 kJ mol^{-1} is based on an enthalpy of formation of the CH_2Br_2 carbene of 11 kJ mol^{-1} and a corrected gas-phase acidity for the $^{\cdot}CHBr_2$ radical (vide supra). Of course, with other starting values or with the gas-phase acidity indicated by the occurrence/nonoccurrence of proton transfer in the reactions of the $CBr_2^{-\cdot}$ radical anion (Tables 2 and 3) other final values will be obtained for the enthalpy of formation of the CBr_2 carbene. It should be noted, however, that the difference in enthalpy of formation between CHBr (373 kJ mol^{-1}) [27] and CBr_2 (324 kJ mol^{-1}) is 49 kJ mol^{-1} and that a similar difference (51 kJ mol^{-1}) is observed between the enthalpies of formation of the CHCl (317 kJ mol^{-1}) [27] and CClBr (266 kJ mol^{-1}) in line with the thought that the introduction of a bromine atom may lead to approximately the same change in the enthalpy of formation for closely related species.

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References

[1] D. Smith, N.G. Adams, Topics Curr. Chem. 89 (1980) 1.
[2] E.E. Ferguson, F.C. Fehsenfeld, D.L. Albritton, Gas Phase Ion Chemistry, M.T. Bowers (Ed.), Academic, New York, 1979, Chap. 2, p. 45.
[3] E.E. Ferguson, F. Arnold, Acc. Chem. Res. 14 (1981) 327.
[4] S.S. Shaik, H.B. Schegel, S. Wolfe, Theoretical Aspects of Physical Organic Chemistry, The S_N2 Mechanism, Wiley, New York, 1992.
[5] K. Tanaka, G.I. Mackay, J. Payzant, D.K. Bohme, Can. J. Chem. 54 (1976) 1643.
[6] M.J. Pellerite, J.I. Brauman, J. Am. Chem. Soc. 105 (1983) 2672.
[7] A.A. Viggiano, R.A. Morris, J.S. Paschkewitz, J.F. Paulson, J. Am. Chem. Soc. 114 (1992) 10477.
[8] R.A. Morris, J. Phys. Chem. 97 (1992) 2372.
[9] C.A. Mayhew, R. Peverall, P. Watts, Int. J. Mass Spectrom. Ion Processes 125 (1993) 81.
[10] P.O. Staneke, G. Groothuis, S. Ingemann, N.M.M. Nibbering, J. Phys. Org. Chem. 9 (1996) 471.
[11] P.O. Staneke, J. Kauw, M. Born, S. Ingemann, N.M.M. Nibbering, Rapid Commun. Mass Spectrom. 11 (1997) 124.
[12] W. Kirmse, Carbene Chemistry, Academic, New York, 1971.
[13] R.A. Moss, M. Jones Jr., Reactive Intermediates, M. Jones Jr., R.A. Moss (Eds.), Wiley, New York, 1978, Vol. 1, Chap. 3, p. 69.
[14] K.K. Murray, D.G. Leopold, T.M. Miller, W.C. Lineberger, J. Phys. Chem. 89 (1988) 5442.
[15] M.K. Gilles, K.M. Erwin, J. Ho, W.C. Lineberger, J. Phys. Chem. 96 (1992) 1130.
[16] K.K. Irikura, W.A. Goddard III, J.L. Beauchamp, J. Am. Chem. Soc. 114 (1992) 48.
[17] N. Russo, E. Sicilia, M. Toscano, Chem. Phys. Lett. 213 (1993) 245.
[18] A. Gobbi, G. Frenking, J. Chem. Soc. Chem. Commun. (1993) 1162.
[19] S.E. Worthington, C.J. Cramer, J. Phys. Org. Chem. 10 (1997) 755.
[20] S.G. Lias, Z. Karpas, J.F. Liebman, J. Am. Chem. Soc. 107 (1985) 6089.
[21] J.S. Shapiro, F.P. Lossing, J. Phys. Chem. 72 (1968) 1552.
[22] B.A. Levi, R.W. Taft, W.J. Hehre, J. Am. Chem. Soc. 99 (1977) 8454.
[23] J.A. Paulino, R.R. Squires, J. Am. Chem. Soc. 113 (1991) 5573.
[24] D.W. Kohn, E.S.J. Robles, C.F. Logan, P. Chen, J. Phys. Chem. 97 (1993) 4936.
[25] G.P. Semeluk, R.B. Bernstein, J. Am. Chem. Soc. 79 (1957) 44.
[26] A.G. Marshall, F.R. Verdun, Fourier Transform in NMR, Optical, and Mass Spectrometry, Elsevier, Amsterdam, 1990.
[27] M. Born, S. Ingemann, N.M.M. Nibbering, J. Am. Chem. Soc. 116 (1994) 7210.
[28] N.M.M. Nibbering, Rapid Commun. Mass Spectrom. 7 (1993) 747.
[29] L.J. de Koning, C.W.F. Kort, F.A. Pinkse, N.M.M. Nibbering, Int. J. Mass Spectrom. Ion Processes 95 (1989) 71, and references cited therein.
[30] R.A.L. Peerboom, S. Ingemann, N.M.M. Nibbering, J. Chem. Soc., Perkin Trans. 2, (1990) 1825, and references cited therein.
[31] J.C. Kleingeld, N.M.M. Nibbering, Lect. Notes Chem. 31 (1982) 209.
[32] J. Lee, J.J. Grabowski, Chem. Rev. 92 (1992) 1611.
[33] P. Kebarle, S. Chowdhury, Chem. Rev. 87 (1987) 513.
[34] R.N. McDonald, A.K. Chowdhury, J. Am. Chem. Soc. 105 (1983) 198.
[35] D.K. Bohme, E. Lee-Ruff, L.B. Young, J. Am. Chem. Soc. 94 (1972) 5153.
[36] NIST Chemistry Webbook, NIST Standard Reference Database Number 69, November 1998, W.G. Mallard, P.J. Lindstrom (Eds.), National Institute of Standards and Technology, Gaithersburg, MD, 20899.
[37] S. Ingemann, N.M.M. Nibbering, J. Chem. Soc., Perkin Trans. 2 (1985) 837.
[38] M. Born, S. Ingemann, N.M.M. Nibbering, J. Phys. Chem. 100 (1996) 17662.
[39] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) Suppl. 1.
[40] M. Born, S. Ingemann, N.M.M. Nibbering, Mass Spectrom. Rev. 16 (1997) 181.
[41] J.L. Holmes, F.P. Lossing, J. Am. Chem. Soc. 110 (1988) 7343.
[42] C.F. Rodriquez, D.K. Bohme, A.C. Hopkinson, J. Phys. Chem. 100 (1996) 2942.