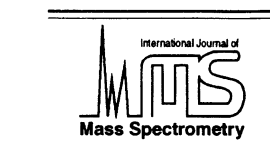




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The methylene chloride radical cation and its distonic isomers in the gas phase

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Abstract

Metastable methylene chloride radical cations react spontaneously by loss of a chlorine atom with an apparent kinetic isotope effect of 9 ± 1 and a kinetic energy release of <1 meV. It is difficult to account for an isotope effect of this magnitude, inasmuch as the zero-point vibrational energy differences are very small; the decay of an electronically excited state to the ground state may be involved. The stable molecular ions are very reactive toward collision induced dissociation, and the predominant reactions are collision induced even at very high vacuum. Similar behavior is observed for 1,1-dibromoethane radical cations, whose spontaneous reactions almost exclusively result in loss of ^{79}Br . The H-Cl-CHCl^+ distonic isomer of the methylene chloride radical cation reacts exclusively by loss of a chlorine atom, presumably after rearrangement to the methylene chloride radical cation. The $^{35}\text{Cl}/^{37}\text{Cl}$ ratio observed is 1.27 ± 0.01 . The kinetic energy release associated with this reaction is moderate. It did not prove possible to prepare the $\text{CH}_2\text{-Cl-Cl}^+$ distonic isomer of the methylene chloride radical cation. (Int J Mass Spectrom 210/211 (2001) 403–415) © 2001 Elsevier Science B.V.

Keywords: Heavy atom isotope effects; isomerization; ab initio calculations

1. Introduction

Measurement of the relative rates of competing reactions in the field-free regions of a mass spectrometer requires that the magnitude of any instrumentation-dependent mass discrimination effects can be assessed with reasonable accuracy. Derrick and co-workers [1] showed that even moderate release of kinetic energy in unimolecular reactions could give rise to appreciable mass discrimination, owing to differences in collection efficiency. Ia Lau [2] dis-

cussed how detector response in multiplier systems could introduce mass discrimination.

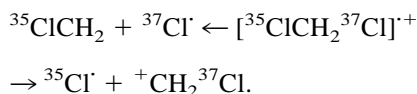
The effects discussed by these investigators would not be expected to introduce serious errors when the products of the reactions in question differ by only a few mass units, as in, for example, studies of secondary kinetic isotope effects [3]. To verify this assumption, we decided to examine the halogen atom loss from chlorine and bromine containing aliphatic radical cations. These species often lose halogen atoms and/or hydrogen halide molecules in the ion source and field free regions of mass spectrometers [4,5]. Expecting that intramolecular heavy-atom isotope effects on the simple cleavage of carbon–halogen bonds would be negligible, we measured the relative

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Dedicated to professor Nico M. M. Nibbering, a leading figure in European mass spectrometry for more than 30 years.

rates of loss of ^{35}Cl and ^{37}Cl atoms from a variety of isotopically mixed metastable dichloroalkane radical cations (molecular ions incorporating one ^{35}Cl and one ^{37}Cl) and the relative rate of loss of ^{79}Br and ^{81}Br from isotopically mixed dibromoalkane radical cations. Previously reported examples of $^{35}\text{Cl}/^{37}\text{Cl}$ kinetic isotope effects in gas-phase reactions include values as high as 1.90 for loss of Cl^\cdot from $\text{Si}^{37}\text{Cl}_3^{35}\text{Cl}$ measured in a MIKE experiment [6]; 1.06 for Cl^\cdot loss from $^{35}\text{Cl}^{37}\text{Cl}^+$ [7]; and other values close to unity obtained by multiple reaction monitoring [8].

Surprisingly, some of our initial results showed quite remarkable peak shape and intensity differences between the signals arising from loss of the isotopically different halogen atoms, which prompted us to undertake a more thorough investigation of the properties of these systems. This article examines the dissociation of distonic and conventional CH_2Cl_2 radical cations and related species.



The halogen atom loss from isotopically mixed dihaloalkane ions will be accompanied by heavy-atom kinetic isotope effects that will directly influence the ratio between the intensities of the signals due to the competing halogen loss reactions [9]. However, it is, strictly speaking, not entirely correct to consider this ratio to be a measure of a primary isotope effect on the halogen atom loss, as the fragment ions formed are not identical but are each other's isotopomers. The ratio actually measured will reflect a combination of primary and secondary effects.

It is convenient to think of the expulsion of the halogen atom as a simple cleavage reaction, but polyhalogenated methanes can be brought to isomerize [10] to isohalomethanes, as demonstrated [10–14] in reports on IR-spectroscopy studies of these systems trapped in noble gas matrices. Furthermore, the presence of the methylene chloride radical cation and its distonic isomer $\text{H}-\text{Cl}-\text{CHCl}^{\cdot+}$ as well as a (CH_2Cl^+) Cl^\cdot complex (Cl^\cdot presumed to be coordinated to a hydrogen atom) has been suggested in order to interpret IR spectra recorded after electron bombardment

of methylene chloride and subsequent matrix isolation [10]. We have, therefore, included two distonic isomers of the methylene chloride radical cations in the present investigation, one corresponding to formal protonation of a chlorine atom in the dichloromethyl radical, and one corresponding to the formal attachment of Cl^+ to the chlorine atom in the chloromethyl radical. The former, $\text{H}-\text{Cl}-\text{CHCl}^{\cdot+}$, has been characterized experimentally in the gas phase [15,16], and a report by Schwarz et al. [17] on the isomerism of CCl_4^+ suggests that also the $\text{CH}_2-\text{Cl}-\text{Cl}^{\cdot+}$ distonic isomer may exist in the gas phase, even though it is not clear whether the nonclassical CCl_4^+ isomer reported by Schwarz is a covalently bonded system or a complex held together by ion-induced dipole forces.

Loss of Cl^\cdot from the CH_2Cl_2 molecular ion with a kinetic energy release of 20 ± 3 meV has been observed in a photoelectron-photoion coincidence experiment [18]; that is, for reactions occurring in the ion source. Voyksner et al. [19] reported a value of 11.5 meV for the unimolecular loss of a chlorine atom from the metastable molecular ions, increasing to 15.9 meV under CID conditions. Cooks et al. [20] reported 15 meV as an upper limit for the kinetic energy released on loss of a chlorine atom from the metastable methylene chloride radical cation and noted the presence of a collision-induced component. Collisional dissociation was also observed in a photoionization study of the ionization and fragmentation of methylene chloride [21]. Bortolini et al. [22] reported the MIKE and CID spectra of methylene chloride, bromide, and iodide. They found that H^\cdot loss is the dominating reaction, accompanied in all three cases by loss of a halogen atom. In a second paper, Bortolini et al. [23] suggested the existence of long-lived electronically excited states of the radical cations of methylene bromide and iodide, whereas no reproducible results were obtained for methylene chloride.

To complement our experimental studies of the metastable radical cations, we have examined the properties and reactions of the various CH_2Cl_2^+ isomers with high-level ab initio calculations. A previous study by Lewars [24] described the results of a computational investigation of the isomers of neutral methylene chloride and its radical cation. For the

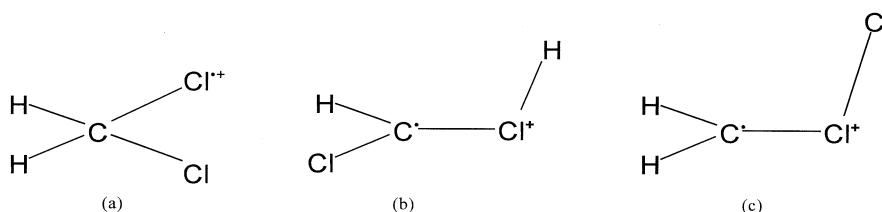


Fig. 1. Connectivity of the CH_2Cl_2^+ isomers. (a) The radical cation of methylene chloride, (b) H-Cl-CHCl^+ , (c) $\text{CH}_2\text{-Cl-Cl}^+$

latter, Lewars found five minima: the classical radical cation, its H-Cl-CHCl^+ distonic isomer, and three loosely bonded isomers that are probably best considered as ion–molecule complexes: ionized dichlorocarbene and H_2 , a chlorine atom attached to a hydrogen atom of the chloromethyl cation, and a chlorine atom attached to the chlorine atom of the chloromethyl cation. The last would, if covalently bonded, be the $\text{CH}_2\text{-Cl-Cl}^+$ distonic isomer of the methylene chloride radical cation (Fig. 1).

2. Methods

MIKE and CID experiments were carried out on a Jeol JMS-HX110/110A four-sector (EBEB) mass spectrometer operated in three-sector mode (EBE). The precursor ions were selected with the first two sectors, and daughter ion spectra were obtained by scanning the second electrostatic sector. The collector slit was sufficiently wide to accept the full width of the precursor ion beam to ensure maximal energy resolution without limiting the signal intensities. The detector had an off-axis conversion dynode at 20 kV postacceleration potential opposite a 16-stage electron multiplier at 2 kV attenuation (125 V stage^{-1}).

The radical cation of methylene chloride and its labeled analogs was formed by electron ionization of CH_2Cl_2 , $^{13}\text{CH}_2\text{Cl}_2$, and CD_2Cl_2 . The H-Cl-CHCl^+ isomer was formed by loss of CO_2 from the dichloroacetic acid radical cation as described by Holmes et al. [15].

Attempts to form the $\text{CH}_2\text{-Cl-Cl}^+$ distonic isomer by decarbonylation of the chloroacetylchloride radical cation as described for the CCl_4^+ system [17] were not successful; the $\text{CH}_2\text{Cl}_2^{++}$ ions obtained in this manner

appeared to be identical to the methylene chloride radical cation.

Deconvolution of composite daughter ion signals was performed with the Origin 4.1 program package from Microcal. Fig. 3a, 3b, 5a, and 5b illustrate the deconvolution procedure described in the discussion of the experimental results.

Isotope effects were determined from MIKE spectra of the isotopomer containing one atom of each chlorine isotope, and the kinetic isotope effect was determined as the ratio between the product ion signal intensities, by measuring peak heights.

The relatively small difference in mass between the isotopomeric product ions as well as the very low kinetic energy release associated with the spontaneous reactions suggest that the mass discrimination caused by differences in collection efficiency [1] amounts to approximately 0.4%, the heavier isotopomer being collected slightly more efficiently.

Mass discrimination as a result of detector response to various isotopes of the elements Kr, Xe, and Cl was reviewed by la Lau [2], who concluded that, in general, isotope effects on detector response caused by isotope pairs like ^{35}Cl and ^{37}Cl or ^{79}Br and ^{81}Br in organic ions will be slight, if noticeable at all. Furthermore, for equal ion velocities (i.e., most ions formed in the field free regions), the responses caused by the isotopic ions will be much more alike [2] than those of ions formed in the ion source, and it is, therefore, unlikely that our results are significantly influenced by detector response discrimination.

The pressure in the field free region during MIKE experiments was below 5×10^8 Torr; during CID experiments it was $\approx 2 \times 10^6$ Torr, corresponding to a barely measurable ($\sim 2\%$) reduction of the precursor

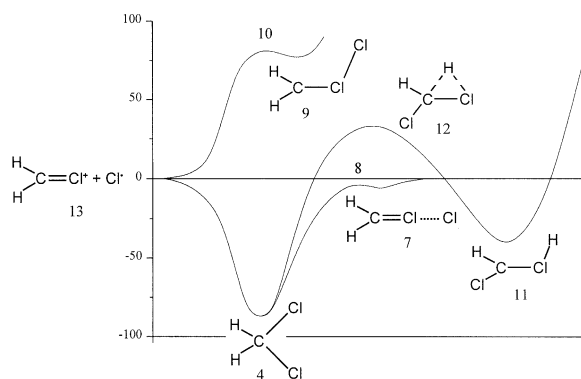


Fig. 2. CH_2Cl_2^+ potential energy surface at the MP2 (full)/6-311++G(2d,2p) level, energies including scaled zero-point vibrational energy contributions relative to the energy of the dissociation products.

sor ion signal. Pressures were measured with a Balzers IMG 300 ion gauge control placed in the field free region ≈ 20 cm from the collision chamber and from the nearest diffusion pumps. The MIKE-spectra of the methylene chloride radical cation and of the 1,1-dibromoethane radical cation were reproduced on a VG Autospec instrument at the University of Bielefeld, Germany.

Ab initio calculations were performed with the Gaussian 94 program package on an SGI Power Challenge computer. Computational results including frequency calculations were obtained at the MP2(full)/6-311++G(2d,2p) level. The zero-point vibrational energy contributions were scaled by the factor of 0.9496 recommended by Scott and Radom [25] for MP2(fc)/6-311G(d,p) frequencies.

3. Results and discussion

3.1. Computational studies

Relative energies including zero-point vibrational energy contributions of stationary points on the CH_2Cl_2^+ potential energy surface are reported in Table 1. Fig. 2 shows the relative energies of the states and geometries relevant for the discussion of the experimental results.

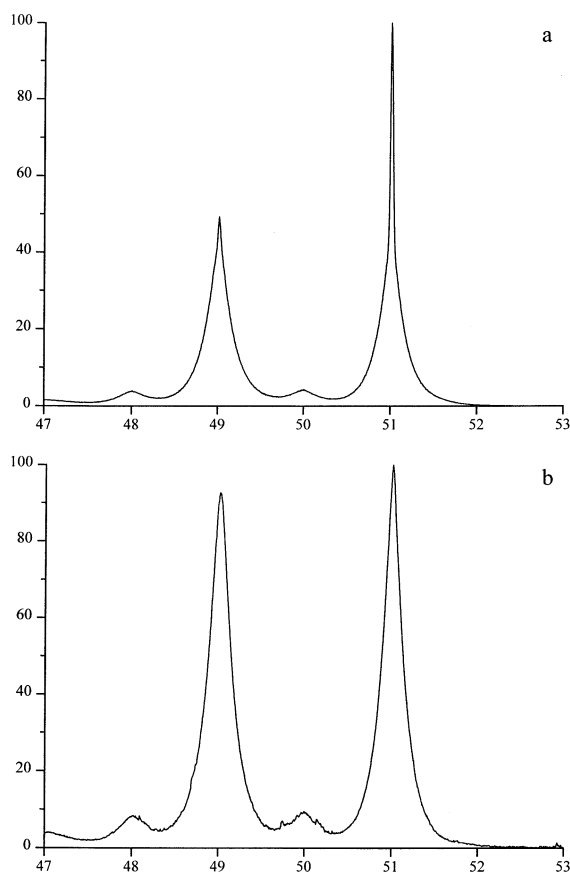


Fig. 3. Signals due to loss of Cl^+ from $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$ obtained (a) in the MIKE experiment and (b) by collisionally induced dissociation.

3.1.1. The methylene chloride radical cation

The methylene chloride radical cation can occupy four different electronic states in the C_{2v} point group [26]: A1 (1), A2 (2), B1 (3), and B2 (4). An A'' state (5) with C_s geometry was also found to constitute a local minimum. Our calculations suggest that Cl^+ loss from the B1, B2, and A'' states will proceed without an energy barrier toward the reverse reaction, while loss of Cl^+ from the A1 state involves an intermediate energy barrier (6). We were not able to model the dissociation of the A2 state. The A1, A2, and A'' states are considerably higher in energy than the B1 and B2 states, and it is perhaps not likely that molecular ions initially formed in these states will survive long enough to be of relevance to our experiment. These

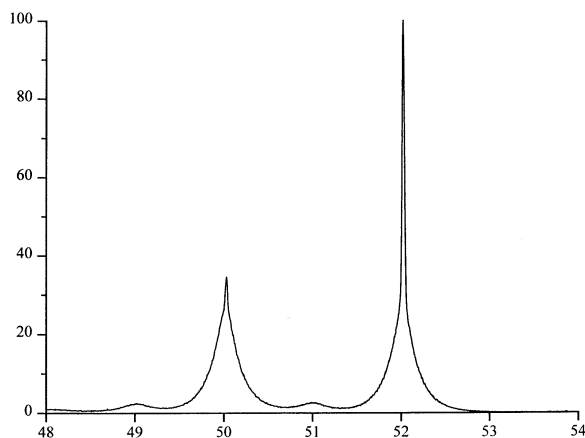


Fig. 4. Signals caused by loss of Cl⁻ from ¹³CH₂³⁵Cl³⁷Cl⁺, obtained in the MIKE experiment.

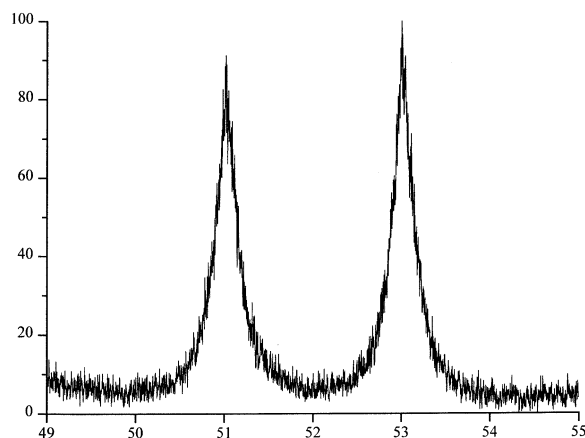


Fig. 5. Signals caused by loss of Cl⁻ from CD₂³⁵Cl³⁷Cl⁺, obtained in the MIKE experiment.

states are therefore not considered further. We find the B2 state to be slightly lower in energy than the B1 state, which has the geometry reported by Lewars [24], but the calculated energy difference depends on the choice of basis set. However, dissociation from either state can take place without a barrier toward the reverse reaction, and it is, therefore, not crucial to the

Table 1

Calculated energies of the stationary points on the CH₂³⁵Cl₂⁺ potential energy surface^a

	Isomer, description	E _{rel} (kJ/mol)
1	CH ₂ Cl ₂ ⁺ , A1	1
2	CH ₂ Cl ₂ ⁺ , A2	5
3	CH ₂ Cl ₂ ⁺ , B1	-77
4	CH ₂ Cl ₂ ⁺ , B2	-87
5	CH ₂ Cl ₂ ⁺ , A''	-40
6	TS (cleav. 1)	35
7	CH ₂ -Cl-Cl ⁺ (linear)	-6
8	TS (rearr. 7)	-4
9	CH ₂ -Cl-Cl ⁺ (bent)	77
10	TS (cleav. 9)	81
11	H-Cl-CHCl ⁺	-40
12	TS (rearr. 11)	33
13	⁺ CH ₂ ³⁵ Cl + Cl ⁻	0 ^b

^a0 K, energies relative to ⁺CH₂³⁵Cl + Cl⁻. Geometries optimized and vibrational frequencies calculated at the MP2(full)/6-311++g(2d,2p) level. Zero-point vibrational energy contributions are calculated for the CH₂³⁵Cl₂⁺ isotopomers and scaled with a factor 0.9496 [25].

^bThe zero-point vibrational energy of ⁺CH₂³⁵Cl is 4.6 cm⁻¹ higher than that of ⁺CH₂³⁷Cl.

discussion of our experimental results to know whether the B1 or B2 state is of lower energy. In Fig. 2, only the position of the B2 state is shown.

Loss of Cl⁻ from the molecular ion can take place by direct cleavage of the C–Cl bond or via the shallow minimum **7** (see below); the energy required for rearrangement to form **7** is less than that required for dissociation, and loss of Cl⁻ from **7** would not be associated with an energy barrier for the reverse reaction. The possible intermediacy of **7** may influence the rate of dissociation.

Characteristic bond lengths and angles for the stationary points **1–4** of the C_{2v} point group are summarized in Table 2. Characteristics of the stationary points **5** and **6** are given in Table 3.

Table 2

Stationary points on the CH₂Cl₂⁺ potential energy surface with C_{2v} symmetry^a

Stationary point number	State	C–Cl distance	Cl–C–Cl angle	C–H distance	H–C–Cl angle
1	B2	1.781	90.4	1.078	111.5
2	B1	1.717	119.7	1.109	108.6
3	A2	1.803	106.2	1.080	109.1
4	A1	1.767	122.6	1.089	104.5
7	B1	1.592	4.938		
13	A1	1.592		1.082	119.0

^aDistances in Ångströms, angles in degrees.

Table 3
Stationary points on the CH_2Cl_2^+ potential energy surface with C_s symmetry^a

Stationary point number	State	C–C [−] distance	C–Cl ² distance	Cl–C–Cl angle	C–H distance	H–C–Cl ¹ angle	H–C–Cl ¹ –Cl ² dihedral
5	A''	1.708	1.837	114.5	1.091	114.5	±115.8
6 (TS)	A'	1.639	2.162	110.1	1.083	116.4	±101.8
8 (TS)	A'	1.706	3.012	41.0	1.075	115.8	±86.7
9	A'	1.648	3.106	41.7	1.078	117.5	±87.8
10 (TS)	A'	1.590	3.969	63.2	1.082	119.0	±89.9

^aDistances in Ångströms, angles and dihedral angles in degrees.

3.1.2. The $\text{CH}_2\text{–Cl–Cl}^+$ distonic isomer

Two minima were found with $\text{CH}_2\text{–Cl–Cl}^+$ connectivity: an isomer with C_{2v} geometry, **7** (B1), in which the heavy atoms are on a line (this isomer was also reported by Lewars [24]), and a bent isomer with C_s geometry, **9** (A'), with the mirror plane being defined by the heavy atoms. A classical transition state, **10**, for Cl[−] loss from **9** was found, whereas Cl[−] loss from **7** appeared to proceed without an intermediate energy barrier. Rearrangement of the linear species to the methylene chloride radical cation is associated with an energy barrier, **8**, while no reaction path was found to connect the bent species with the methylene chloride radical cation, dissociation being more favorable.

The linear $\text{CH}_2\text{–Cl–Cl}^+$ distonic isomer suggested by Lewars [24] is best described as an ion–atom complex: a chloromethyl cation, whose chlorine atom interacts electrostatically with a relatively remote chlorine atom. A bond with significant covalent character between the two chlorine atoms appears not to be involved. The Cl–Cl distance, 3.46 Å, is close to the sum of the van der Waals radii of two chlorine atoms (3.60 Å); furthermore, the energy of the complex is lower than that of the separated fragments by

only 6 kJ mol^{−1}, which corresponds reasonably well to purely electrostatic interactions between a chlorine atom and a point charge. We find that rearrangement to the methylene chloride radical cation is associated with a quite low barrier (2 kJ mol^{−1}, considerably lower than the previously estimated [10] upper limit of 43 kJ mol^{−1}). Furthermore, the geometry of the CH_2Cl unit in **7** is very close to that of the isolated chloromethyl cation, **13**. This suggests that the carbon–chlorine bond in the chloromethyl part is as strong as in the isolated chloromethyl cation and not appreciably affected by the presence of the attached chlorine atom; a covalent bond between the two chlorine atoms would presumably weaken and, thus, elongate the carbon–chlorine bond.

Our calculations indicate the existence of a higher-energy isomer with C_s geometry in which the mirror plane is defined by the heavy atoms. In this species, the Cl–Cl bond is 2.06 Å, the C–Cl bond is 1.71 Å, and the C–Cl–Cl angle is 106°, implying that the heavy atoms are connected by covalent bonds. This isomer would appear to be an alternative $\text{CH}_2\text{–Cl–Cl}^+$ distonic isomer, but it is quite high in energy (83 kJ/mol^{−1} over the atom–ion complex **7**). The geometry of this species resembles that calculated by

Table 4
Stationary points on the CH_2Cl_2^+ potential energy surface with C_1 symmetry^a

Stationary point number	State	C–Cl ¹ distance	C–Cl ² distance	Cl–C–Cl angle	C–H distance	H–C–Cl ¹ angle	H–C–Cl ¹ –Cl ² dihedral
11	–	1.855	1.647	116.8	1.078 2.381	107.0 32.7	143.1 −69.5
12 (TS)	–	1.869	1.634	118.3	1.078 1.499	110.1 48.1	152.2 −106.2

^aDistances in Ångströms, angles and dihedral angles in degrees.

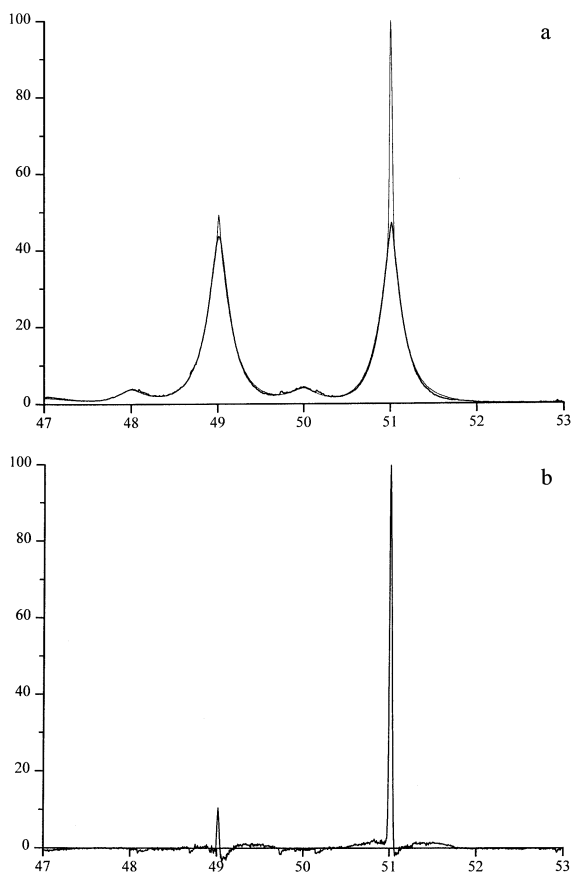


Fig. 6. Comparison of the renormalized CID spectrum of $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$ and the broad component observed for loss of Cl⁻ in the MIKE spectrum of $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$. (b) Difference spectrum (normalized) obtained upon subtraction of the renormalized CID spectrum from the MIKE spectrum of $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$, both shown in (a).

Lewars [24] for the (neutral) isomethylene chloride, but the computational results suggest that the $\text{CH}_2\text{-Cl-Cl}^+$ distonic isomer, **9**, of the methylene chloride radical cation can not be prepared in the gas phase by vertical ionization of isomethylene chloride, as the Cl–Cl distance (2.40 Å) in isomethylene chloride is beyond the Cl–Cl distance (2.17 Å) in the transition state **10** for the dissociation of **9**. Because our computational results imply that the methylene chloride radical cation also cannot be brought to rearrange into **9**, it is not likely that this isomer can be characterized experimentally in the gas phase.

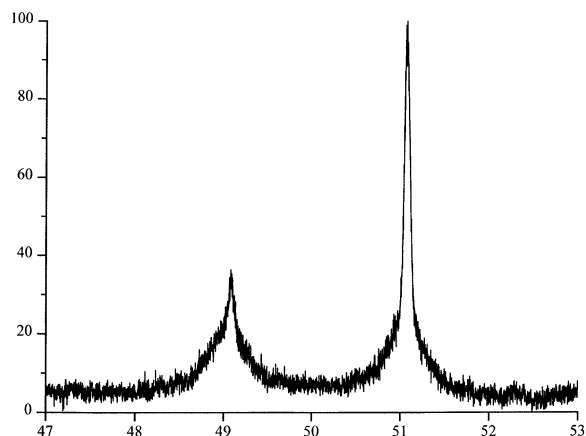


Fig. 7. MIKE spectrum of $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$ obtained at a 2-kV accelerating potential. The broad component is shifted ~ 1 eV toward lower energy relative to the slim component.

3.1.3. The H-Cl-CHCl^+ distonic isomer

The H-Cl-CHCl^+ distonic isomer, **11**, is the same as that discussed by Lewars [24]. We were not able to locate a transition state for direct loss of Cl⁻ from this isomer, but a transition state, **12**, for rearrangement into the methylene chloride radical cation was found (Table 4). The major dissociation reaction of **11** is loss of a chlorine atom. Our calculations suggest that this reaction proceeds via rearrangement by 1,2-hydrogen atom migration; direct dissociation by stretching of the C–Cl bond requires considerable energy. The transition state (Fig. 2) is higher in energy than $\text{CH}_2\text{Cl}^+ + \text{Cl}^-$ which implies that a H-Cl-CHCl^+ distonic ion with sufficient internal energy to rearrange would also have sufficient excess energy to dissociate. The transition state for this rearrangement was also reported by Lewars [24] but was associated by him with another isomerization process.

3.2. Experimental studies

The MIKE and CID spectra of the monoisotopic radical cations of methylene chloride and its H-Cl-CHCl^+ distonic isomer are tabulated in Table 5. We were unable to reproduce the results reported by Bortolini et al. [22] with regard to the reactions of the radical cation of methylene chloride. The base peak in the MIKE spectrum of the methylene chloride radical

Table 5
MIKE and CID spectra, relative intensity

<i>m/z</i> 84:	CH ₂ Cl ₂ ⁺		H-Cl-CHCl ⁺ ^a		¹³ CHCl ₂ ⁺ ^b	
	MIKE	CID	MIKE	CID	MIKE	CID
83	5	10	—	9	2	45
82	—	1	—	2	—	—
70	—	0.5	—	—	—	1
49	100	100	100	100	5	100
48	3	8	—	23	100	70
47	1	4	—	11	—	—
42	—	0.2	—	5	—	11
41.5	—	0.05	—	—	—	3
41	—	2	—	—	—	0.5
36	—	0.4	—	1	—	2
35	—	0.8	—	1	—	4
14	—	0.2	—	—	—	0.5
13	—	0.1	—	—	—	—
12	—	0.03	—	—	—	—

^a From dichloroacetic acid [15].

^b From ¹³C-labeled methylene chloride.

cation recorded in this present study corresponds to loss of Cl[•]; H[•] loss amounts to 4%–5%, and no loss of H₂ is observed. A small signal (3%) corresponding to loss of HCl may originate from the molecular ion as well as from a contamination of the precursor ion beam by the ¹³C contribution to (M–H)⁺, as the base signal in the MIKE spectrum of the latter corresponds to loss of HCl. The small (M–37)⁺ signal presumably corresponds to loss of H[•] and HCl from the molecular ion. An alternative possibility would be loss of ³⁷Cl[•] from an ion-beam contamination by CCl₂⁺, but the abundance of these ions in the ion source is negligible.

Only a few of the surviving methylene chloride radical cations react spontaneously in the field free regions; the signals are extraordinarily weak relative to the intensity of the precursor ion signal. Furthermore, the signal caused by loss of Cl[•] consists of two components, as also noted by Cooks et al. [20]: one is very slim, corresponding to a kinetic energy release of 1 meV or less, and the other is Gaussian shaped and corresponds to a moderate kinetic energy release (~25 meV).

The composite signals caused by Cl[•] loss from CH₂³⁵Cl³⁷Cl⁺ are shown in Fig. 3a. The intensity ratio of the slim components is 9 ± 1, whereas the intensity ratio of the broad components is 1.0 ± 0.05.

The CID spectrum of the methylene chloride radical cation resembles the MIKE spectrum with one significant exception: the slim component of the Cl[•] loss signal is absent (Fig. 3b). CID spectra obtained at very low collision gas pressures shows that the slim component in the Cl[•] loss signal quickly disappears under the broader component; at high-pressure CID, the ratio of the broad components is 1.04 ± 0.01.

To further examine the nature of the observed composite signals, and to avoid interference from the

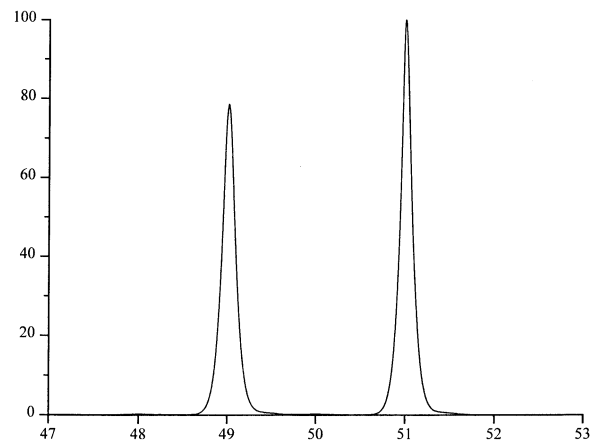


Fig. 8. MIKE signal caused by loss of Cl⁺ from the H-Cl-CHCl⁺ distonic isomer (precursor: dichloroacetic acid).

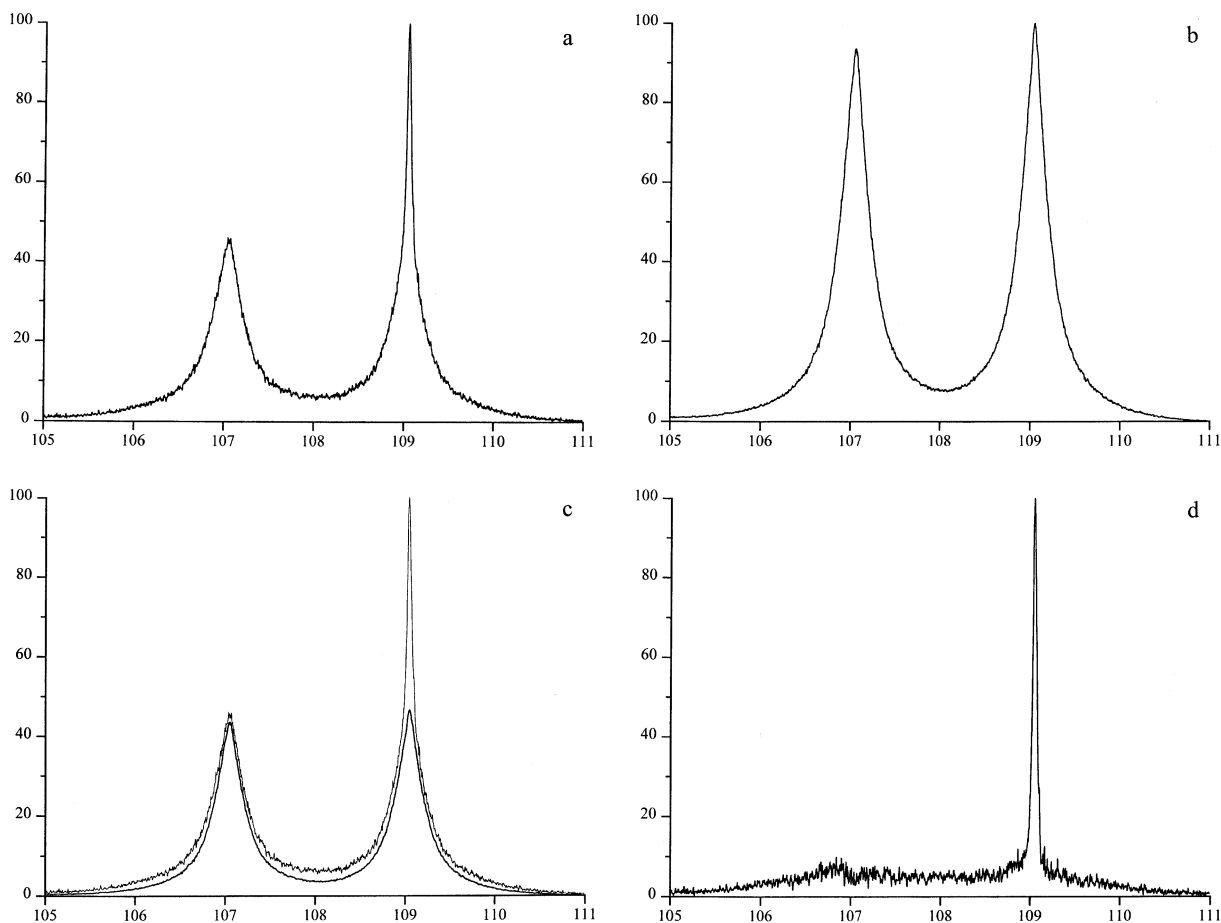


Fig. 9. Loss of Br^+ from $\text{CH}_3\text{CH}^{79}\text{Br}^{81}\text{Br}^+$: MIKE spectrum (a), CID spectrum (b), comparison (c), and difference spectrum (d).

ion beam contamination by $^{13}\text{CHCl}_2^+$, the MIKE spectra of ^{13}C -labeled methylene chloride (99% ^{13}C purity) and CD_2Cl_2 , (99.9% D purity) were also recorded. The behavior of the ^{13}C -containing ions resembles that of the unlabeled species; the composite signals caused by Cl^- loss from $^{13}\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$ are shown in Fig. 4. The intensity ratio of the slim components is 8 ± 1 , while the intensity ratio of the broad components is 1.1 ± 0.05 . The spectrum of the deuterium-labeled methylene chloride molecular ion, however, does not exhibit any slim components (Fig. 5). It appears that the daughter-ion signal intensity relative to the precursor ion signal intensity is noticeably smaller than for the H and ^{13}C isotopomers.

The two-component signals observed in the MIKE

spectra of the unlabeled and ^{13}C -labeled methylene chloride radical cations (Fig. 3a and 4) indicate that loss of Cl^- occurs by two distinct processes. Contributions from collisionally induced reactions are ordinarily negligible under the high-vacuum conditions of the MIKE experiment, but we find that CID processes cannot be disregarded when the daughter-ion signal is unusually weak relative to the precursor ion signal, particularly when the precursor ions are sensitive towards CID, as noted previously [20,21]. By comparing the MIKE spectrum (Fig. 3a) with the CID spectrum (Fig. 3b), we are able to assign the broad component in the MIKE spectrum to collisionally induced reactions. In Fig. 6a, the CID spectrum has been renormalized by a factor of 0.47 to fit the MIKE

spectrum, which yields a very good fit of the broad component in the MIKE signal to the renormalized CID signal. Fig. 6b shows that subtraction of the renormalized CID signal from the MIKE signal, (i.e., on correction of the MIKE spectrum for the CID contribution) leaves two distinct and very sharp signals, which we believe correspond to the spontaneous reactions of metastable molecular ions. The assignment of the broad component to collision-induced processes is further confirmed by the following observations: the broad component is slightly shifted toward lower energy relative to the slim component, a so-called Derrick-shift, which arises because the CID process involves conversion of kinetic energy to internal energy [27,28]; the shift becomes more pronounced when the accelerating voltage is reduced (Fig. 7). Furthermore, the intensity of the slim component is increased relative to that of the broad component on lowering the accelerating voltage. When the precursor ion velocity is lowered, the reaction probability for the metastable ions increases, which contributes to the intensity of the slim component, whereas the probability of collision is, to a good approximation, proportional to the background pressure and the length of the field free region, both of which do not vary with the accelerating voltage. This assumes that the probability that collision-induced reactions will occur is independent of the kinetic energy of kilovolt ions. Baer et al. [29] have shown that CH_2Br_2^+ can efficiently convert relatively large amounts of kinetic energy to internal energy on collision; our results suggest that this is also the case for CH_2Cl_2^+ .

Taking the slim components to represent the spontaneous reactions, we note that the isotope effect on the spontaneous cleavage is 9 ± 1 , a controversially large value. The kinetic energy release associated with the spontaneous reaction is very small ($T_{0.5} = 1$ meV). The computational results indicate that the reaction is not associated with an energy barrier for the reverse reaction, and the kinetic energy released on dissociation indicates that the excess energy in the transition state is low. The low number of degrees of freedom causes the $k(E)$ curve for Cl loss to be very steep; that is, the metastable radical cations of meth-

ylene chloride possess a quite narrow interval of internal energies at the threshold for dissociation. These are conditions that would be expected to result in respectable kinetic isotope effects. However, the difference in zero-point vibrational energy between the $^+\text{CH}_2^{35}\text{Cl}$ and $^+\text{CH}_2^{37}\text{Cl}$ product ions is <0.1 kJ mol $^{-1}$, which does not seem to explain or justify an isotope effect of the observed magnitude (assuming that the properties of the products resemble those of the transition state, in the absence of an energy barrier).

The complete absence of a slim component in the MIKE spectrum of the CD_2Cl_2 molecular ions would seem to indicate that the incorporation of deuterium causes the molecular ions to not undergo spontaneous dissociation at all. This is puzzling inasmuch it does not seem likely that the energy distribution of the CD_2Cl_2 molecular ions would be very different from that of the CH_2Cl_2 molecular ions. An intriguing alternative would be that the spontaneous reactions are caused by the presence of long-lived electronically excited CH_2Cl_2 molecular ions. The results obtained by Bortolini et al. [23], although inconclusive for CH_2Cl_2^+ point to a similar conclusion. The conversion to ground state molecular ions would be symmetry forbidden and hence slow, but dissociation after conversion could possibly contribute to the observed reactions of the metastable ions if dissociation by chlorine atom loss of the excited state was significantly slower than dissociation of the ground-state ions. The difference between the behavior of the CH_2Cl_2 and CD_2Cl_2 molecular ions could, in turn, originate in different rates of intersystem crossing for these systems. Isotope-dependent effects on the rates of intramolecular single electron transfer have been suggested for the bismethyleneadamantane radical cation [30], a system that, with regard to symmetry, resembles the methylene chloride radical cation. The excited state in question could be either of the A1 and A2 states; they are both sufficiently high in energy and the calculations suggest that neither of the two states dissociates readily. Respectable geometry changes would accompany the intersystem crossing, which would contribute to the lifetime of the excited states. Conversion to the dissociative state (which

could be either B1 or B2) would require active vibrational modes with B1 or B2 symmetry, of which there are several in the methylene chloride system. The molecular dynamics model [31] employed by Jones et al. [30] to describe the properties of bismethyleneadamantane radical cation could presumably be successfully applied to the methylene chloride radical cation system.

The MIKE spectrum of the H-Cl-CHCl^+ distonic isomer shows a simple Gaussian signal for Cl^- loss with an associated moderate kinetic energy release (≈ 8 meV). The relative signal intensity shown in Fig. 8 for spontaneous Cl^- loss from the $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}^+$ isotopomer is 1.27 ± 0.01 .

We have investigated the halogen atom expulsion from several other small dichloro- and dibromoalkane radical cations and found that only geminally dihalogenated compounds give rise to composite peak shapes in the MIKE experiments because of CID processes.

Compared with methylene chloride, methylene bromide yields an even weaker daughter-ion signal and is more sensitive toward CID; the slim component of the daughter-ion signal can only be identified with certainty in difference spectra. We have not been able to obtain a MIKE spectrum with a signal-to-noise ratio sufficient to determine the isotope effect on spontaneous loss of Br^- better than an approximate value of 3 ± 1 . In the case of methylene iodide, the signal obtained appears to be 100% collisionally induced.

Although metastable CH_2F_2^+ ions mainly react ($>99\%$) by loss of a hydrogen atom, a weak signal corresponding to loss of a fluorine atom is also observed. This is, in fact, a two-component signal, that corresponds to kinetic energy releases of ~ 1 eV (>95 area%) and 40 meV (<5 area%), respectively. Similar composite signals have been described [32] for spontaneous loss of a fluorine atom from a mixture of electronically excited and ground state CF_3^+ cations.

1,1-Dichloro- and 1,1-dibromoethane give rise to stronger daughter-ion signals than do the methylene halides, as is expected because of the increased number of internal degrees of freedom. The behavior

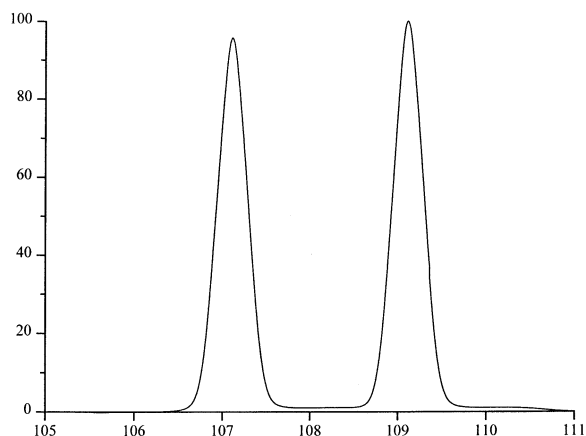


Fig. 10. MIKE spectrum of $^{79}\text{BrCH}_2\text{CH}_2^{81}\text{Br}^+$ (spectrum contains no other peaks).

of the radical cation of 1,1-dichloroethane is complex, and a direct comparison with methylene chloride is not possible; one problem being that HCl elimination is an important competing reaction. The MIKE spectrum (Fig. 9a) of the radical cation of 1,1-dibromoethane, however, is quite similar to that of methylene chloride. These ions are also very sensitive towards CID, and the preference for spontaneous loss of $^{79}\text{Br}^-$ over $^{81}\text{Br}^-$ is quite pronounced. In fact, only one slim component can be identified; namely, that corresponding to spontaneous loss of $^{79}\text{Br}^-$ (Fig. 9a–d). This observation suggests that the kinetic isotope effect on loss of Br^- from metastable $\text{CH}_3\text{CH}^{79}\text{Br}^{81}\text{Br}^+$ ions is very large. For comparison, the kinetic isotope effect on loss of Br^- from metastable 1,2-dibromoethane radical cations (Fig. 10) is only a few percent (1.045 ± 0.005). That, however, is in itself a remarkably large heavy-atom isotope effect.

4. Conclusion

We have measured heavy-atom isotope effects of surprising magnitude for loss of halogen atoms from the radical cations of small aliphatic dichloro- and dibromoalkanes. These results can not be attributed to instrumental effects. Any such effects would influence equally the signals caused by the spontaneous

and collisionally induced reactions, but only the signals caused by the spontaneous reactions exhibit large isotope-dependent differences. Likewise, any instrumental discrimination will influence the signals of isomeric compounds equally: we observe large $^{79}\text{Br}/^{81}\text{Br}$ differences on the spontaneous reactions of the 1,1-dibromoethane radical cation but not on the reactions of 1,2-dibromoethane, and we observe much larger $^{35}\text{Cl}/^{37}\text{Cl}$ differences for the methylene chloride radical cation than for its distonic isomer.

The observed differences, therefore, must have chemical reasons, and it is, in turn, reasonable to see them as reflecting proper isotope effects. However, we hesitate to ascribe the effects observed to transition-state zero-point vibrational energy differences if it is assumed that the properties of the transition state for halogen atom loss, a simple cleavage with no energy barrier toward the reverse process, can be approximated by the properties of the products of the reaction. The calculated zero-point energy difference would appear to be much too small to account for isotope effects as large as those observed considering that the dissociation of the methylene chloride radical cation is $\sim 80 \text{ kJ mol}^{-1}$ endothermic and that the excess energy of the transition state, therefore, cannot be exceedingly low.

We are, therefore, forced to assume that the transition states for halogen atom loss from geminal dihaloalkane radical cations are located earlier on the reaction coordinate and, given the magnitude of the effects observed, that the transition states exhibit strong halogens-halogen interactions. However, we have not been able to identify the nature of these transition states. An alternative would be to take the very large effects to reflect a chlorine isotope effect on the conversion of a long-lived excited electronic state to the ground state. The pronounced influence of deuterium on the spontaneous chlorine atom loss could be taken to imply that the C–Cl cleavage reaction takes place subsequent to intersystem crossing from a relatively long-lived excited state and that the rate of conversion is quite different for CD_3Cl_3^+ and CH_2Cl_2^+ ; a more rapid decay of excited CD_2Cl_2^+ ions would possibly be virtually complete before the ions reach the mass spectrometer field free regions,

and a considerably slower process might not contribute noticeably to the reactions observed. The remarkable $^{35}\text{Cl}/^{37}\text{Cl}$ isotope effect on the spontaneous loss of a chlorine atom from the CH_2Cl_2 and $^{13}\text{CH}_2\text{Cl}_2$ molecular ions could, in turn, be the result of a chlorine isotope effect on the decay of the excited state. Further investigation is required to clarify these matters.

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