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Chemical and Thermodynamic Properties of Methyl Chloride Dimer Radical Cations in the Gas Phase

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Abstract: Dimer radical cations of methyl chloride have been prepared in a Fourier transform ion cyclotron resonance mass spectrometer using a consecutive exchange reaction of the xenon dimer radical cation with methyl chloride. Both theory and experiment have indicated the existence of two different stable methyl chloride dimer radical cations, that is a two-center three-electron (2c/3e) bonded dimer radical cation, $CH_3Cl\therefore ClCH_3^{\bullet +}$, with C_2 symmetry and a methyl chloride chloronium ylidion structure, $CH_3Cl\cdot H\cdot ClCH_2^{\bullet +}$, with C_s symmetry. The $CH_3Cl\therefore ClCH_3^{\bullet +}$ species has been observed to react both as an electron acceptor and as a proton donor. The $CH_3Cl\cdot H\cdot ClCH_2^{\bullet +}$ structure, however, reacts only as an electron acceptor. Calculations of the $CH_3Cl\therefore ClCH_3^{\bullet +}$ structure at the MP2/6-311G(d,p) level of theory indicate a bond dissociation energy of 105.4 kJ mol^{-1} relative to its ionized and neutral monomer products, while experiments show a bond dissociation energy of 109 ± 5 kJ mol^{-1}. The bond dissociation energy of the $CH_3Cl\cdot H\cdot ClCH_2^{\bullet +}$ species has been determined to be 62.8 kJ mol^{-1} at the MP2/6-311G(d,p) level of theory, whereas experiments indicate 76 kJ mol^{-1} relative to the radical cation of methyl chloride and its neutral counterpart as products. These results indicate that $CH_3Cl\therefore ClCH_3^{\bullet +}$ is the intermediate complex in the electron transfer reaction and $CH_3Cl\cdot H\cdot ClCH_2^{\bullet +}$ the intermediate complex in the proton transfer reaction between the methyl chloride radical cation and neutral methyl chloride.

Introduction

It is well-known that ion−molecule reactions in the gas phase proceed via intermediate complexes separated by energy barriers, as has been described by Brauman and co-workers.[1−5] First the ion approaches the molecule as a result of long range ion−dipole moment interactions until the repulsive charge distributions of the electrons of both the ion and molecule prevent a smaller distance. Then the generated ion−molecule complex can undergo rearrangement of the atoms or groups of atoms and via a transition state can convert into another complex *etc.*, followed by eventual dissociation into products provided that the overall reaction is exothermic or thermoneutral.

Information about the chemical and thermodynamic properties of the intermediate complexes is essential to complete the picture of the reaction dynamics of a gas-phase ion−molecule reaction. Such properties determine the efficiency and rate of reaction. If a molecular radical cation reacts with its neutral counterpart, then the reaction proceeds via formation of a dimer radical cation complex.

A typical example is the proton transfer reaction between the methyl chloride radical cation and neutral methyl chloride involving the intermediate dimer radical cation complex $C_2H_6Cl_2^{\bullet +}$, reaction 1.

$$CH_3Cl^{\bullet +} + CH_3Cl \rightarrow [C_2H_6Cl_2^{\bullet +}]^* \rightarrow CH_3ClH^+ + CH_2Cl^\bullet \qquad (1)$$

Although this proton transfer reaction has been studied extensively,[6−8] the literature concerning the intermediate complex, $C_2H_6Cl_2^{\bullet +}$, and also $C_2H_6X_2^{\bullet +}$ with X = F, Br, and I in the gas phase is scarce. The minimum energy structure of the $C_2H_6X_2^{\bullet +}$ dimer radical cations (X = Cl, Br, or I) has been calculated to have a two-center three-electron (2c/3e) bond,[9−11] located between the two halogens. This type of bonding has been shown for the methyl chloride dimer radical cation[12] and for the methyl bromide dimer radical cation[13] using AM1 calculations. Zahradnik *et al.*[14,15] have attempted to optimize the methyl chloride dimer radical cation using *ab initio* calculations but have not succeeded in finding a minimum energy structure, rather they found a proton transfer process.

In contrast, theoretical studies[14,15] have shown that the minimum energy structure of the methyl fluoride dimer radical cation is not a 2c/3e bonded species but a hydrogen bonded complex, $H_2FCH{\cdot\cdot}HCFH_2^{\bullet +}$, with a C_{2h} symmetry.

Experimentally, only a few studies of $C_2H_6X_2^{\bullet +}$ radical cations in the gas phase are known. Booze and Baer[16] prepared

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the methyl chloride dimer radical cation by photoionizing clusters generated with use of a molecular beam apparatus. Their time-of-flight spectra indicated that the $C_2H_6Cl_2^{\bullet+}$ species was formed via two different processes, namely dissociative ionization of higher order clusters or direct ionization of methyl chloride dimers. The $C_2H_6I_2^{\bullet+}$ radical cation has been studied by Livant and Illies,[17] who have determined its 2c/3e bond strength to be between 96 and 109 kJ mol^{-1} relative to the radical cation of methyl iodide and neutral methyl iodide as products using high pressure mass spectrometry. To our knowledge, experimental studies of $C_2H_6F_2^{\bullet+}$ and $C_2H_6Br_2^{\bullet+}$ in the gas phase have not been reported. The present study has been undertaken to verify experimentally the theoretically predicted 2c/3e bonding of the radical cation dimer of methyl chloride and to determine its bond strength relative to ionized and neutral monomer products. In addition, *ab initio* calculations have been performed to support the experimental data obtained. It has been possible to generate also the radical cation dimers of methyl fluoride and methyl bromide. However, their abundances were too low for further experiments.

Experimental Section

The experiments have been performed using a Bruker CMS-47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source and a 4.7 T superconducting magnet. The instrument has been described previously.[18−20]

Xenon dimer radical cations were generated in the external ion source in the chemical ionization (CI) mode using 90 eV electrons and transported to the FT-ICR cell where they were trapped. In the cell, methyl chloride was present at a pressure of 1×10^{-8} mbar (ion gauge manometer reading). The background pressure was below 1×10^{-9} mbar. The xenon dimer radical cations were thermalized by collisions with nitrogen gas, which was introduced through a pulsed valve for 100 ms with a pump-down delay of 3 s. The ligand exchange reaction of the xenon dimer radical cations with methyl chloride produced the methyl chloride dimer radical cation (*vide infra*). Subsequently, the methyl chloride dimer radical cations were isolated.[20] The reactivity of the methyl chloride dimer radical cations with various reference compounds was monitored as a function of time.

The collisionally activated dissociation (CAD) experiments were performed, and the data obtained were processed as previously described.[21−24] In general these experiments have been shown to be suitable for the determination of bond dissociation energies (BDEs) from threshold center-of-mass kinetic energy measurements.[21−24] In these types of experiments the $C_2H_6Cl_2^{\bullet+}$ ions were selected in the FT-ICR cell and thermalized by pulsed-valve addition of nitrogen gas. After a pump-down delay of 4 s in order to remove the nitrogen gas, the selected $C_2H_6Cl_2^{\bullet+}$ ions were translationally excited with an on-resonance single-frequency excitation field of variable duration with an electric field strength (E_0) of 286 V m^{-1}. Subsequently, the ions were allowed to collide with neon gas for 0.050 s. This collision time was chosen such that single-collision conditions were maintained. The pressure of the target gas neon was about 2.5×10^{-8} mbar (ionization gauge manometer reading). For the determination of the threshold values, the kinetic energy in the laboratory frame, E_{lab}, was converted into the center-of-mass energy, E_{cm}, with the use of eq 2, with m_t the mass of the target molecule (neon), and m_p the mass of the selected dimer radical cation.

$$E_{cm} = E_{lab}\frac{m_t}{m_p + m_t} \qquad (2)$$

The kinetic energy was determined with the use of eq 3.

$$E_{lab} = T_{exc}^2\frac{q\omega_{eff}E_0^2}{8B} \qquad (3)$$

In eq 3, q represents the charge of the ion, ω_{eff} is the angular cyclotron frequency of the dimer radical cation, B is the magnetic field strength, and T_{exc} is the excitation time. The collected data obtained were fitted to a model,[25] described with eq 4.

$$\sigma(E_{cm}) = \sigma_0\frac{(E_{cm} - E_{th})^n}{E_{cm}^m} \qquad (4)$$

The product ion abundance, $\sigma(E_{cm})$, was fitted as a function of the center-of-mass kinetic energy for different values of the parameters σ_0, n, and E_{th}. The analysis was restricted to $m = 1$ since it was shown that this form is one of the most useful in deriving accurate thermodynamic data.[25] The threshold energies, E_{th}, obtained from the analysis were collected for Doppler broadening by adding $3[m_p/(m_p + m_t)]kT$, where k is the Boltzmann constant and T is the estimated temperature (298 K).[26]

Materials. All chemicals employed here were commercially available and used without further purification.

Computational Procedures. Calculations were performed on an RS/6000 workstation using the Gaussian 94 program packages.[27] The geometry optimization and the frequency calculation were performed at the MP2/6-311G(d,p) level. Gauld and Radom[28] found that the minimal basis set suitable for these systems was 6-311G(d,p) at the MP2 level of theory. The relative energies were calculated with scaled (by 0.9496)[29] zero-point energies. In addition, G2 calculations were performed for $CH_2Cl^{\bullet}$, CH_3Cl, $CH_3Cl^{\bullet+}$, CH_3ClH^{+}, and $CH_2ClH^{\bullet+}$. Since there is a discussion about the enthalpy of formation of these compounds,[30] we have calculated the enthalpy of formation of these species. Enthalpies of formation were calculated from the atomization energies at the G2 level with the standard experimental enthalpies of formation of the elements from Lias *et al.*[31] The geometry of the dimer radical cations was first optimized with AM1 semiempirical calculations, which were used as an input for the *ab initio* calculations.

Results

Noble gas dimer radical cations are known to react by ligand exchange.[19,32−34] A consecutive exchange reaction of a noble

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Table 1. Occurrence (+) and Nonoccurrence (−) of Single Electron Transfer (SET) and Proton Transfer (PT) of $(CH_3Cl)_2^{\bullet+}$ with Various Compounds

compound	IE[a] (eV)	SET	PA[b] (kJ mol^{-1})	PT
propene	9.73	+	751	−
dimethyl ether	10.025	+	804	+
n-hexane	10.13	+	*c*	−
n-pentane	10.22	+	*c*	−
acetaldehyde	10.2298	+	781	+
propyne	10.36	+	748	−
ethanol	10.41	+	788	+
ethene	10.5138	−	680	−
methyl bromide	10.541	−	662[d]	−
isobutane	10.57	−	683	−
acetic acid	10.66	−	796	+
methanol	10.82	−	761	+
methyl chloride	11.25	−	682	−
water	12.61	−	697	−

[a] Ionization energy from ref 38. [b] Proton affinity from ref 31. [c] Unknown. [d] Reference 30.

gas dimer radical cation with a small molecule (M) with an ionization energy higher than 11 eV has been shown to produce dimer radical cations of M. This procedure has been employed previously[19,34] to generate $(H_2O)_2^{\bullet+}$ and has been used here to generate the methyl chloride dimer radical cation.

In the FT-ICR cell the xenon dimer radical cations react with methyl chloride giving the $Xe{-}CH_3Cl^{\bullet+}$ complex, reaction 5.

$$Xe_2^{\bullet+} + CH_3Cl \rightarrow Xe\text{-}CH_3Cl^{\bullet+} + Xe \qquad (5)$$

A subsequent exchange reaction between the $Xe\text{-}CH_3Cl^{\bullet+}$ radical cation and CH_3Cl leads to the methyl chloride dimer radical cation, reaction 6.

$$Xe\text{-}CH_3Cl^{\bullet+} + CH_3Cl \rightarrow (CH_3Cl)_2^{\bullet+} + Xe \qquad (6)$$

After selection the reactivity of $(CH_3Cl)_2^{\bullet+}$ has been studied with use of a set of reference compounds with well-known thermochemical properties. Two typical reactions between the $(CH_3Cl)_2^{\bullet+}$ ion and the reference compounds have been observed, that is, single electron transfer (SET, reaction 7) and proton transfer (PT, reaction 8). Because only exothermic or thermoneutral processes occur in an FT-ICR cell, the occurrence of a reaction indicates an energetically accessible process. The observed occurrence (+) or nonoccurrence (−) of the two processes has been listed in Table 1. Analogously to the results

$$(CH_3Cl)_2^{\bullet+} + M \rightarrow M^{\bullet+} + 2CH_3Cl \qquad (7)$$

$$(CH_3Cl)_2^{\bullet+} + M \rightarrow MH^+ + CH_3Cl + CH_2Cl^{\bullet} \qquad (8)$$

obtained for the water dimer radical cation[34] it may be assumed that in reaction 7 two methyl chloride molecules are generated and no $(CH_3Cl)_2$ dimer. Propene, *n*-hexane, *n*-pentane, and propyne react with $(CH_3Cl)_2^{\bullet+}$solely via SET. In the case of dimethyl ether, acetaldehyde, and ethanol competing processes of SET and PT are observed. $(CH_3Cl)_2^{\bullet+}$ shows no reactivity with respect to any of the compounds: ethene, isobutane, methyl chloride, and water. Only PT is observed in reaction with either acetic acid and methanol. No dissociative electron transfer has been observed for any of the studied reference compounds.

Interestingly, the reaction between $(CH_3Cl)_2^{\bullet+}$ and methyl bromide shows neither SET nor PT but ligand exchange instead.

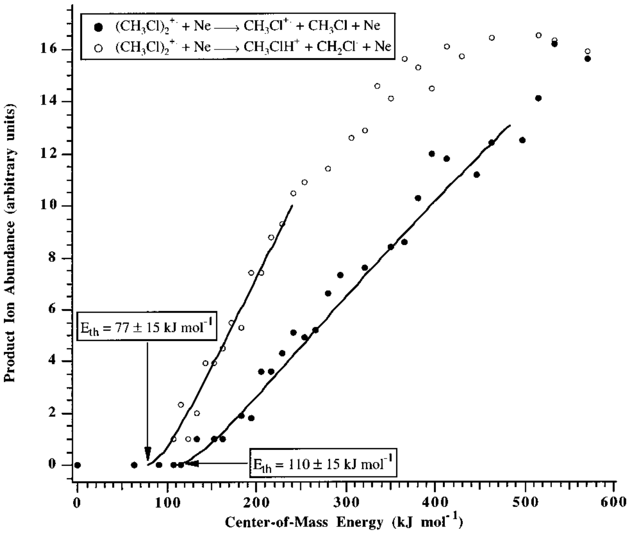

Figure 1. Collisionally activated dissociation of translationally excited $C_2H_6Cl_2^{\bullet+}$ radical cations with neon (2.5 × 10^{-8} mbar, ionization gauge manometer reading) as collision gas. The open and closed circles are experimental data obtained with a delay of 0.050 s between the CAD radio frequency pulse and the detection of the product ions. The full lines have been obtained with use of the fitting procedure described earlier.[21−24]

Initially only the ligand exchange product ions $[CH_3Cl, CH_3Br]^{\bullet+}$ are observed. Thereafter, a consecutive exchange reaction occurs yielding $(CH_3Br)_2^{\bullet+}$ in very low abundance. This exchange reaction has been found to be a very slow process, indicating an energy barrier.

In contrast to the reactivity of the water dimer radical cation,[34] $(H_2O)_2^{\bullet+}$, which reacts with water to yield the protonated water dimer, $(H_2O)_2H^+$, the $(CH_3Cl)_2^{\bullet+}$ ion has not been found to react with any substance to generate $(CH_3Cl)_2H^+$.

Apart from the above mentioned single electron transfer and proton transfer bracketing also collisionally activated dissociation (CAD) experiments have been performed in order to elucidate the nature of the dimer bond of the $C_2H_6Cl_2^{\bullet+}$ dimer radical cations. Two independent fragmentation channels have been observed for the translationally excited $C_2H_6Cl_2^{\bullet+}$ ions in collision with neon, reactions 9 and 10. The product ion

$$C_2H_6Cl_2^{\bullet+} + Ne \rightarrow CH_3ClH^+ + CH_2Cl^{\bullet} + Ne \qquad (9)$$

$$C_2H_6Cl_2^{\bullet+} + Ne \rightarrow CH_3Cl^{\bullet+} + CH_3Cl + Ne \qquad (10)$$

abundance of $CH_3Cl^{\bullet+}$ and CH_3ClH^+ have been plotted as a function of the center-of-mass energy of the translationally excited $(CH_3Cl)_2^{\bullet+}$ ions in Figure 1. The data points have been recorded at a steady neon pressure of 2.5 × 10^{-8} mbar and a collision time of 0.050 s determined to be single collision conditions. From Figure 1, the threshold energy, E_{th}, for the process leading to $CH_3ClH^+ + CH_2Cl^{\bullet}$ formation has been derived to be 77 ± 15 kJ mol^{-1}, while the E_{th} for the process leading to $CH_3Cl^{\bullet+} + CH_3Cl$ has been determined to be 110 ± 15 kJ mol^{-1} using the procedure described earlier.[21−24]

Calculations. Monomers. Geometry optimizations of $CH_2Cl^{\bullet}$ (**I**), CH_3Cl (**II**), $CH_3Cl^{\bullet+}$ (**III**), CH_3ClH^+ (**IV**), and $^{\bullet}CH_2ClH^+$ (**V**) have been performed, and the results are shown in Figure 2 and Table 2. In addition enthalpies of formation calculated at the G2 level of theory are listed in Table 2. The energies and geometries of **II**, **III**, and **V** are in excellent agreement with those obtained by Gauld and Radom.[28]

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Table 2. Energies (hartrees) and Enthalpies of Formation (kJ mol^{-1}) Calculated in the Present Study for Monomers **I**−**V** (see Figure 2)

	species	symmetry	electronic state	energy MP2/6-311G(d,p) (hartree)	ZPE[a] (hartree)	no. of imaginary freq	ΔH_f° [b] calcd (kJ mol^{-1})	ΔH_f° expt (kJ mol^{-1})
I	$CH_2Cl^\bullet$	C_s	$^2A'$	−498.761 231 5	0.023 480	0	118.7	120[c]
II	CH_3Cl	C_{3v}	$^1A_1$	−499.426 279 5	0.038 544	0	−85.2	−82.0[d]
III	$CH_3Cl^{\bullet+}$	C_s	$^2A'$	−499.016 863 3	0.035 491	0	1006.3	1003.4[d]
IV	CH_3ClH^+	C_s	$^1A'$	−499.680 137 8	0.047 502	0	796.9	797[e]
V	$^\bullet CH_2ClH^+$	C_1		−498.998 931 6	0.032 784	0	1048.8	1029[f]

[a] Unscaled. [b] Calculated enthalpy of formation; G2 level of theory, explanation see text. [c] Reference 35. [d] Reference 38. [e] Reference 30. [f] Reference 31.

Table 3. Calculated Energies (hartrees) for the $(CH_3Cl)_2^{\bullet+}$ Dimer Radical Cations **VI** to **IX** (See Figure 3)[a]

	species	symmetry	electronic state	energy MP2/6-311G(d,p) (hartree)	ZPE[b] (hartree)	no. of imaginary freq	rel energy (kJ mol^{-1})
VI	$CH_3Cl^{\bullet+}{\cdot}ClCH_3$	C_2	^2B	−998.487 124 9	0.078 066	0	0.0
IX	$CH_3Cl{\cdot}H{\cdot}ClCH_2^{\bullet+}$	C_s	$^2A'$	−998.464 619 4	0.071 459	0	42.6
II + III	$CH_3Cl^{\bullet+} + CH_3Cl$						105.4
I + IV	$CH_3ClH^+ + {}^\bullet CH_2Cl$						102.5
II + V	$^\bullet CH_2ClH^+ + CH_3Cl$						145.8

[a] In addition, the relative energies of dimer radical cations are estimated and compared to the sum of the energies of the possible fragmentation products. [b] Unscaled.

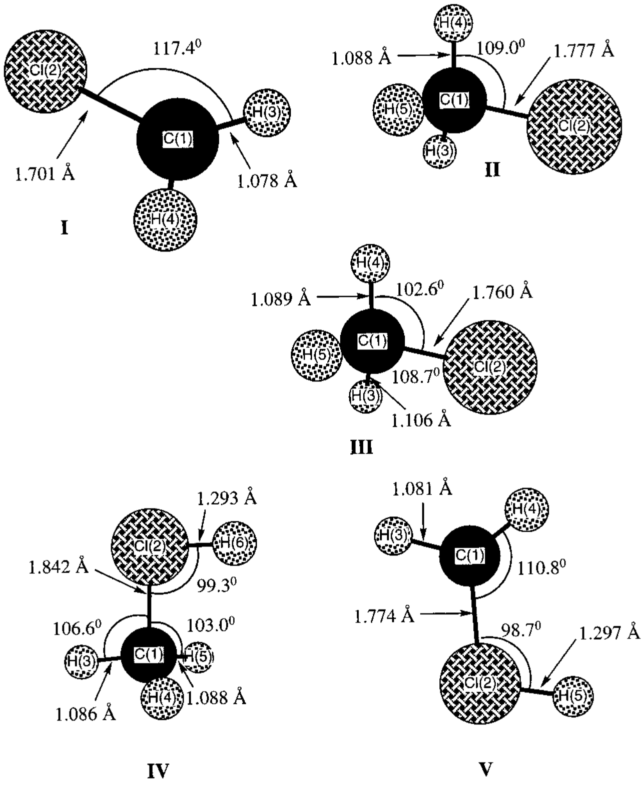

Figure 2. Optimized geometries of the structures of the monomers **I**−**V** at the MP2/6-311G(d,p) level of theory.

Dimers. Five isomeric structures of the $C_2H_6Cl_2^{\bullet+}$ dimer radical cation have been considered, three having a 2c/3e chloride chloride bond (**VI**, **VII**, and **VIII**), one with an ylide structure $CH_3Cl{\cdot\cdot}HClCH_2^{\bullet+}$ (**IX**), and one with a proton bonded structure (**X**). The results appear in Figure 3 and Table 3. No *ab initio* minimum for the proton bonded structure has been found, although AM1 semiempirical calculations indicate that it is a stable species. Structure **X** in Figure 3b represents the AM1 optimized structure.

Of the three 2c/3e bonded methyl chloride dimer radical cations which have been examined, **VI** has been found to be a minimum energy structure, although only slightly lower in energy than **VII** (0.6 kJ mol^{-1}). Furthermore, one negative frequency indicates that **VII** is a transition state. Structure **VIII** is 14.9 kJ mol^{-1} less stable and has three imaginary frequencies. At the HF/6-311G(d,p) level **VII** was found to be lower in energy than **VI** with only 0.2 kJ mol^{-1}. The ylide bound structure **IX** has been found to be a minimum at the potential energy surface, 42.6 kJ mol^{-1} higher in energy than **VI**.

Discussion

Enthalpies of Formation and Structures of $C_2H_6Cl_2^{\bullet+}$. In order to estimate the enthalpy of formation of the $C_2H_6Cl_2^{\bullet+}$ dimer radical cation from eqs 7−10 one needs to know the enthalpies of formation of one of the reactants and all products. In the cases of CH_3ClH^+ and $CH_2Cl^\bullet$ there is some discussion in the literature about their enthalpy of formation (*vide infra*).

Recently, the proton affinity (PA) of methyl chloride has been found[30] to be 650.6 kJ mol^{-1}. This new value is significantly lower than the accepted[31] value of 682 kJ mol^{-1} but is in excellent agreement with *ab initio* calculations[30] and therefore has been used here in order to calculate the enthalpy of formation of CH_3ClH^+, giving $\Delta H_f^{\circ} = 797$ kJ mol^{-1}.

In the case of $CH_2Cl^\bullet$, the experimental enthalpy of formation of 120 kJ mol^{-1} determined by Holmes and Lossing[35] has been used here instead of the value of 130 kJ mol^{-1} given in the giant tabulated data set.[31] It was shown that this value is more consistent with trends in the values of the enthalpies of formation of the series of $CH_2X^\bullet$ (X = F, Cl, Br, and I) radicals.[36] Furthermore, Rodriguez *et al.*[37] performed *ab initio* calculations on the $CH_2Cl^\bullet$ radical and obtained an enthalpy of formation, ΔH_f°, of 118.8 kJ mol^{-1}. This calculated enthalpy of formation is in excellent agreement with the experimentally determined value[35] of 120 kJ mol^{-1}, see Table 2.

The enthalpy change of the proton transfer reaction 11 has been estimated to be −2.9 kJ mol^{-1} at the MP2/6-311G(d,p) level of theory and −5.5 kJ mol^{-1} at the G2 level of theory.

$$CH_3Cl^{\bullet+} + CH_3Cl \rightarrow CH_3ClH^+ + CH_2Cl^\bullet \qquad (11)$$

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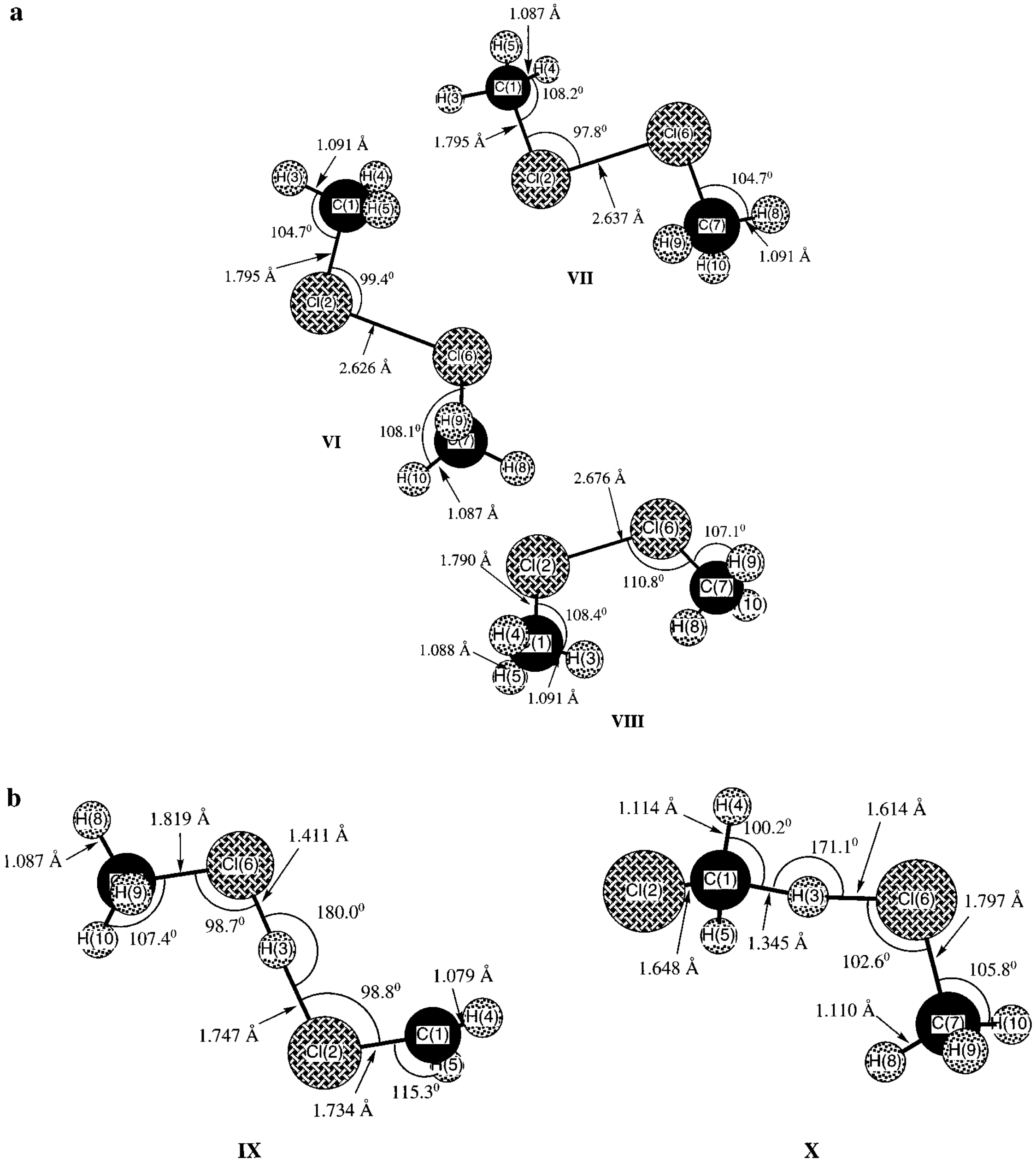

Figure 3. (a) Optimized geometries of the isomeric structures **VI**−**VIII** of the $C_2H_6Cl_2^{\bullet+}$ dimer radical cation at the MP2/6-311G(d,p) level of theory. (b) Optimized geometries of the isomeric structures **IX** and **X** of the $C_2H_6Cl_2^{\bullet+}$ dimer radical cations obtained at the MP2/6-311G(d,p) (structure **IX**) and AM1 semiempirical (structure **X**) level of theory; explanation see text.

Using the experimentally determined enthalpies of formation of the species in this reaction (see Table 2), it can be estimated that reaction 11 is 4 kJ mol^{-1} exothermic. The calculated and experimental reaction enthalpy are thus in excellent agreement with each other. Furthermore, it supports the proposition that the enthalpy of formation of $CH_2Cl^{\bullet}$, as determined by Holmes and Lossing[35] is accurate.

From the experimental results (Table 1) it follows that a thermoneutral electron transfer reaction between the $C_2H_6Cl_2^{\bullet+}$ ion and a compound with an ionization energy between 10.41 and 10.51 eV may be expected. Because the enthalpy of formation of CH_3Cl (Table 2) and the enthalpies of formation of both the neutral and corresponding radical cations of the compounds listed in Table 1 are known,[38] the enthalpy of formation of $C_2H_6Cl_2^{\bullet+}$ can be estimated from eq 7. This leads to an enthalpy of formation of $C_2H_6Cl_2^{\bullet+}$ between 840 and 850 kJ mol^{-1}.

The proton transfer reaction, on the other hand, is thermoneutral in reactions with compounds having a proton affinity between 751 and 761 kJ mol^{-1}. From eq 8, using the enthalpies of formation of CH_3Cl and $CH_2Cl^{\bullet}$ from Table 2 and the enthalpies of formation of M and MH^+ from the literature,[31] an enthalpy of formation between 807 and 817 kJ mol^{-1} is derived for $C_2H_6Cl_2^{\bullet+}$.

These different enthalpies of formation obtained strongly suggest two stable $C_2H_6Cl_2^{\bullet+}$ isomers, designated here as isomer **A** (ΔH_f = 840−850 kJ mol^{-1}) and isomer **B** (ΔH_f = 807−817 kJ mol^{-1})

Consider isomer **A** which only reacts via SET and has a ΔH_f = 840−850 kJ mol^{-1}. If isomer **A** would undergo a thermoneutral PT, such a reaction would have been observed with a

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[38] Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database 19A*, Version 2-01, January 1994; National Institute of Standards and Technology; Washington, DC, 1994.

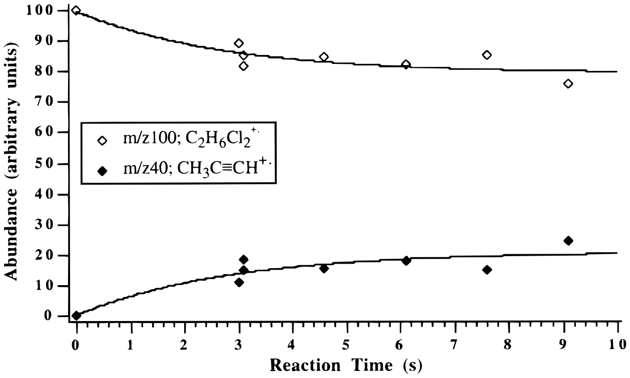

Figure 4. Abundance of the $C_2H_6Cl_2^{\bullet+}$ (◇) and $CH_3C{\equiv}CH^{\bullet+}$ (◆) ions as a function of the reaction time. The pressure of CH_3Cl and propyne were 1×10^{-8} mbar (ion gauge manometer reading).

compound having a proton affinity (PA) between 718−728 kJ mol^{-1}. As no proton transfer reaction between $C_2H_6Cl_2^{\bullet+}$ and either propyne (PA = 748 kJ mol^{-1}) or propene (751 kJ mol^{-1}) has been observed, this implies that isomer **A** cannot react via a proton transfer but only through an electron transfer. Moreover, the proton transfer reaction may be hampered due to steric hindrance and the geometry of the dimer radical cation.

The second isomer designated **B** has a $\Delta H_f^\circ = 807-817$ kJ mol^{-1} as indicated by the PT reactions. Such an isomer would undergo SET with compounds with an ionization energy between 10.07 and 10.17 eV. However, isomer **A** also reacts with compounds having an ionization energy below 10.41 eV via SET, so that distinction between the two isomers has been found to be very difficult. The reagent used in this study which is intermediate between these two regions of ionization energies is propyne. In the reaction between $C_2H_6Cl_2^{\bullet+}$ and propyne (IE = 10.36 eV) there is still 80% of the selected $C_2H_6Cl_2^{\bullet+}$ ions left after a sufficient long reaction time (see Figure 4). This implies that isomer **B** indeed is unreactive toward propyne, while isomer **A** is reactive.

The existence of two stable $C_2H_6Cl_2^{\bullet+}$ isomers is supported by the CAD experiments, which show two different fragmentation channels. In the low energy fragmentation channel the $C_2H_6Cl_2^{\bullet+}$ dissociates into $CH_3ClH^+ + CH_2Cl^\bullet$, whereas in the higher energy fragmentation channel the $C_2H_6Cl_2^{\bullet+}$ dissociates into $CH_3Cl^{\bullet+} + CH_3Cl$. The first process is 77 ± 15 kJ mol^{-1} endothermic, yielding an enthalpy of formation of $C_2H_6Cl_2^{\bullet+}$ of 840 ± 15 kJ mol^{-1}. The latter dissociation channel is 110 ± 15 kJ mol^{-1} endothermic, resulting in an enthalpy of formation of $C_2H_6Cl_2^{\bullet+}$ of 811 ± 15 kJ mol^{-1}. These two enthalpies of formation are in excellent agreement with the results obtained from the electron and proton transfer bracketing experiments. Apparently, the $C_2H_6Cl_2^{\bullet+}$ isomer which dissociates into $CH_3ClH^+ + CH_2Cl^\bullet$ corresponds to isomer **A**, while the $C_2H_6Cl_2^{\bullet+}$ isomer which dissociates into $CH_3Cl^{\bullet+} + CH_3Cl$ corresponds to isomer **B**.

Based upon the performed calculations (*vide supra*) it is now possible to assign structures to the isomers **A** and **B**. These calculations indicate that the lowest energy structure for the $C_2H_6Cl_2^{\bullet+}$ dimer radical cation is **VI**, which has a bond dissociation energy of 105.4 kJ mol^{-1} relative to the products $CH_3Cl^{\bullet+}$ and CH_3Cl. Thus, isomer **B** determined to have a bond dissociation energy of 109 ± 5 kJ mol^{-1} corresponds to dimer **VI** and has a 2c/3e chloride chloride bond. A second stable structure is **IX**, calculated to have a bond dissociation energy of 62.8 kJ mol^{-1}. This would correspond with isomer **A**, for which a bond dissociation energy of 76 ± 5 kJ mol^{-1} has been measured.

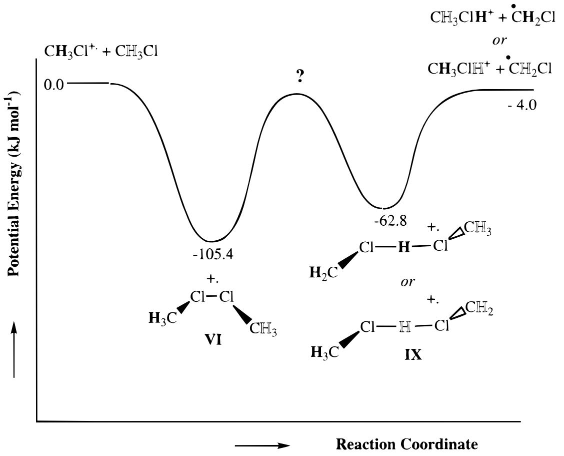

Figure 5. Proposed potential energy surface for the reaction between methyl chloride and its molecular ion. The indicated relative energies have been obtained from calculations at the MP2/6-311G(d,p) level of theory (see text).

Mechanism of Reaction between $CH_3Cl^{\bullet+}$ and CH_3Cl. Both experimental and theoretical results are consistent with a proposed potential energy surface for the reaction between methyl chloride and its radical cation, outlined in Figure 5. In Figure 5 the hydrogen atoms originating from the methyl chloride radical cation are depicted by **H**, while the hydrogen atoms of the reactant methyl chloride molecule are depicted by H. Since it is found that threshold dissociation of complex **IX** leads to $[CH_3ClH^+ + {}^\bullet CH_2Cl]$ rather than to the more stable $[CH_3Cl^{\bullet+} + CH_3Cl]$ products, it is asumed that the energy of the interconversion barrier associated with the two reaction complexes **VI** and **IX** is close to the energy of the products $[CH_3ClH^+ + {}^\bullet CH_2Cl]$. It is considered that the overall reaction shown in Figure 5 takes place through interconversion of the initially formed intermediate reactant complex **VI** into the product complex **IX**. This interconversion can be assumed to proceed via a route similar to the conversion of $CH_3OH^{\bullet+}$ into ${}^\bullet CH_2OH_2^+$, assisted by an associated molecule of water.[39−41] Since complex **VI** has C_2 symmetry, all hydrogen atoms are chemically equivalent. Consequently, isomerization leads to product complex **IX** in which the hydrogen, bonding the two chlorine atoms, can originate from the original methyl chloride molecule or from the original methyl chloride radical cation, yielding $C\mathbf{H}_2Cl{\cdot}\mathbf{H}{\cdot}ClCH_3^{\bullet+}$ and $C\mathbf{H}_3Cl{\cdot}H{\cdot}ClCH_2^{\bullet+}$ with equal probability (see Figure 5). As a result, a formal proton transfer from the radical cation to the methyl chloride molecule and a formed hydrogen abstraction from the methyl chloride molecule to its radical cation is anticipated to be equally feasible. This is consistent with the results of a TESICO study of the reaction between methyl chloride and its molecular ion, reported by Suzuki and Koyano,[7] who concluded that the competing proton transfer and hydrogen atom abstraction occur with an almost equal abundance.

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