The salts of chloronium ions $R^+ - Cl^-$ ($R = CH_3$ or $CH_2Cl$): formation, thermal stability, and interaction with chloromethanes†

Evgenii S. Stoyanov

The interaction of CH$_3$Cl/CD$_3$Cl or CH$_2$Cl$_2$/CD$_2$Cl$_2$ with the carborane acid H(CHB$_{11}$Cl$_{11}$) (abbreviated as H(Cl$_{11}$)) generates the salts of CH$_3$-(Cl$_{11}$) and CH$_2$Cl-(Cl$_{11}$) and their deuterio analogs, respectively, which are analogs of the salts of asymmetric chloronium cations. Next, salts of chloronium cations CH$_3$-Cl$^+$-CH$_2$, ClCH$_2$-Cl$^+$-CH$_2$Cl, and CIC$_2$H$_2$-Cl$^+$-CH$_3$ and their deuterio analogs were obtained from the above compounds. The asymmetric ClCH$_2$-Cl$^+$-CH$_3$ cation was found to be unstable, and at ambient temperature, slowly disproportionated into symmetric cations (CH$_2$)Cl$^+$ and (CH$_2$Cl)$_2$Cl$^+$. At a high temperature (150 °C), disproportionation was completed within 5 minutes, and the resulting cations further decomposed into CH$_3$-(Cl$_{11}$) and CH$_2$Cl-(Cl$_{11}$). The molecular fragment CICH$_2$-X of the compounds (X = Cl$_{11}$, -Cl$^+$-CH$_2$Cl, or -Cl$^+$-CH$_3$) is involved in exchange reactions with CH$_2$Cl$_2$ and CHCl$_3$, converting into CH$_3$-(X) with the formation of chloroform and CCl$_4$, respectively.

Halonium ions (R$_2$Hal$^+$) are well-recognized reactive intermediates in electrophilic chemistry.$^{1,2}$ Their stability increases in the order Hal = F, Cl, Br, I. Recently, the evidence of the formation of the symmetrical fluoronium ions in solutions was obtained,$^{3,4}$ and the nature of carbon–halogen bonds in the halonium ions was studied.$^5$ Mostly stable dimethylbromonium and -iodonium salts are presently commercialized and widely used in chemical ionization mass spectroscopy (gas phase chemistry) as effective methylating$^{6–12}$ and protonating agents$^{13,14}$ for a variety of compounds. Nevertheless, the chemistry of dialkylhalonium ions in condensed phases is virtually unknown. Recently, the salts of (CH$_3$)$_2$Cl$^+$ and (C$_2$H$_5$)$_2$Cl$^+$ with the exceptionally stable and inert toward reactive cations undecachlorocarborane ions, CHB$_{11}$Cl$_{11}^-$, were obtained and studied using X-ray and infrared (IR) spectroscopy.$^{15}$ The solid salt [CH$_3$]Cl(CHB$_{11}$Cl$_{11}$)$^-$ is stable even at elevated temperatures and decomposes at 140 °C releasing CH$_3$(CHB$_{11}$Cl$_{11}$) and CH$_2$Cl$_2$. This is an important method for the isolation of pure CH$_3$(CHB$_{11}$Cl$_{11}$), which can be viewed as a neutral analogue of an asymmetric chloronium ion related to the dimethylchloronium ylide, CH$_3$ClCH$_2$.$^{16,17}$

In the present work we obtained the salts of symmetric and asymmetric chloronium cations, CH$_3$-Cl$^+$-CH$_3$ and CH$_2$Cl-Cl$^+$-CH$_2$Cl, both protio and deuterio analogs, with the CHB$_{11}$Cl$_{11}^-$ counterion (hereafter abbreviated as {Cl$_{11}$}$.^-$), Fig. S1, ESI†). We also explored their thermal stability and interaction with some simple chloromethanes. The carborane ion {Cl$_{11}$}$.^-$ was chosen as a counterion for chloronium salts because of its exceptionally low basicity and high thermal stability, which ensure the stability of chloronium salts at room temperature and above.$^{15}$

**Experimental**

Carborane acid H(Cl$_{11}$) was prepared as previously described.$^{18}$ The acid was sublimed at 150–160 °C under a pressure of 10$^{-5}$ Torr on cold Si windows of a specially designed IR cell-reactor as a very thin translucent layer.$^{19}$ The spectrum of the sublimed acid showed no traces of the H$_2$O$^+$ cation.$^{20}$ Dry gaseous chloromethanes (CH$_3$Cl, CH$_2$Cl$_2$, and CHCl$_3$) were injected anaerobically into the IR cell. The values of their partial pressure were calculated as the ratio of absorption intensity to that of the standard spectrum recorded in the same cell filled with vapors at atmospheric pressure.

All procedures were performed in a Vacuum Atmospheres Corp. glovebox in the atmosphere of N$_2$ (O$_2$ and H$_2$O < 0.5 ppm). The IR spectra were recorded on a PerkinElmer Spectrum-100 spectrometer inside a dry box in the transmission mode (400–4000 cm$^{-1}$). The IR data were processed in the GRAMMS/A1 (7.00) software program from Thermo Fisher Scientific.

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Results and discussion

To explore the chemical processes involving chloronium ions by means of IR spectroscopy, their detailed IR spectra must be obtained and interpreted.

Chloronium salts and IR spectra

The CH$_3$–Cl$^+$–CH$_2$Cl cation was obtained by introducing the CH$_2$Cl$_2$ vapors at a partial pressure ($P_{CH_2Cl_2}$) of 0.4 atm into an evacuated IR cell containing a film of CH$_2$–{Cl$_{11}$} sublimed on their Si-windows. Reaction (1) of CH$_3$–Cl$^+$–CH$_2$Cl formation proceeds very slowly, without a release of HCl.

$$\text{CH}_3\{{\text{Cl}_{11}\}} + \text{CH}_2\text{Cl}_2 \rightarrow \{\text{CH}_3\text{–Cl}^+\text{–CH}_2\text{Cl}\}\{{\text{Cl}_{11}\}}$$

After 40 minutes, the spectrum of the cation was isolated by subtracting the original spectrum of CH$_3$–{Cl$_{11}$} multiplied by the scaling factor $f = 0.933$ (Fig. 1, red). This means that only 6.7% of the CH$_3$–{Cl$_{11}$} salt (100–93.3%) has reacted.

If the partial pressure of the injected CH$_2$Cl$_2$ vapors was twofold higher (1 atm), then the reaction was accelerated significantly and completed within 6 minutes. The spectrum of the resultant CH$_3$–Cl$^+$–CH$_2$Cl cation slightly differs from that of the previous sample (Fig. 1), indicating that the cation is sensitive to changes in the environment.

The CH$_3$–Cl$^+$–CD$_2$Cl cation is formed when the vapors of CD$_2$Cl$_2$ are introduced into the IR cell with sublimed CH$_3$–{Cl$_{11}$}. The IR spectrum of the salt of this cation is shown in Fig. 2 (red; the gas phase was evacuated).

Interpretation of the IR spectra

IR spectra of the salts of the cations CH$_3$–Cl$^+$–CH$_2$Cl (red), CD$_3$–Cl$^+$–CH$_3$Cl (blue), and CH$_3$–Cl$^+$–CD$_2$Cl (green) that are normalized to the intensity of the anion are shown in Fig. 3. The figure shows that in the frequency range of CH stretch vibrations, the sum of the spectra of the fragments CH$_3$C–{Cl$^-$} (blue) and CH$_3$–{Cl$^-$} (green) matches the spectrum of the CH$_3$–Cl$^+$–CH$_2$Cl cation. The same result was observed in the frequency range of the CH bend vibrations (Fig. 3, right).

Interpretations of the IR spectra for all cations follow from the above data (Tables 1 and 2), taking into account that spectra of CH$_3$–{Cl$_{11}$} and (CH$_3$–Cl$^+$–CH$_3$){Cl$_{11}$} were interpreted earlier. It was important to determine the existence of specific absorption bands for each compound under study; we will use these bands (shown in Tables 1 and 2) as markers for the identification of these compounds in the mixtures. Intensity of the marked bands allowed us to estimate relative amounts of the compounds.
Interaction of mono- and dichloromethane with H(\text{Cl}_{11}) and chloronium cations

CH₃Cl interacts with the H(\text{Cl}_{11}) acid in two stages. At first, it is protonated with the release of HCl and the formation of CH₃\{\text{Cl}_{11}\} (eqn (2)):

\[
\text{CH₃Cl} + \text{H(\text{Cl}_{11})} \rightarrow \text{CH₃ClH}^+\{\text{Cl}_{11}\} \rightarrow \text{CH₃}\{\text{Cl}_{11}\} + \text{HCl}
\]

(eqn (2))

\[
\text{CH₃}\{\text{Cl}_{11}\} + \text{CH₃Cl} \rightarrow \text{CH₃₂Cl}^+\{\text{Cl}_{11}^-\}
\]

(eqn (3)). Then, CH₃Cl binds to CH₃\{\text{Cl}_{11}\}, thus forming (CH₃₂Cl)⁺\{\text{Cl}_{11}⁻\} (eqn (3)). The formation of the resultant CH₃\{\text{Cl}_{11}\} can be observed by monitoring the intensity of the IR absorption of the released HCl (I\text{HCl}). The amount of the resulting ion (CH₃₂Cl)⁺ can be traced from the intensity of its band νₐs(CCl₂/C) at 636 cm⁻¹ (I₆₃₆; Fig. S4, ESI†). Dependence of I₆₃₆ on I\text{HCl} was initially proportional (Fig. 4), which means that both reactions proceed at constant speeds. When the thickness of the layer of the formed surface products increases sufficiently to slow down the diffusion of CH₃Cl molecules to the acid, the rate of

![Image](https://example.com/image.png)

**Fig. 3** IR spectra of salts of cations: CH₃–Cl⁺–CH₂Cl (red), CD₃–Cl⁺–CH₂Cl (blue) and CH₃–Cl⁺–CD₂Cl (green).

**Fig. 4** Dependence of the intensity of band νₐs(CCl₂/C) at 636 cm⁻¹ of the (CH₃₂Cl)⁺ cation on the intensity of HCl absorption [reflects the dependence of the (CH₃₂Cl)⁺ formation on the CH₃(\text{Cl}_{11}) formation].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>IR frequencies of the methyl and bridged C–Cl⁺–C groups of the compounds analyzed, in comparison with the IR spectrum of CH₃Cl (the most characteristic or intense bands, used as markers to identify the cations in their mixtures, are underlined)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>νₐsCH₃</td>
</tr>
<tr>
<td>CH₃Cl (gas)²¹</td>
<td>3043</td>
</tr>
<tr>
<td>CH₃–{Cl₁₁}₁⁵</td>
<td>3083</td>
</tr>
<tr>
<td>CH₃–Cl⁺–CH₃₁⁵</td>
<td>3068</td>
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<tr>
<td>H₃C–Cl⁺–CD₂Cl</td>
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</table>

<table>
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<th>Table 2</th>
<th>IR frequencies of the methylene chloride and bridged C–Cl⁺–C groups of the compounds analyzed, in comparison with the IR spectrum of CH₂Cl₂ (the most characteristic or intense bands, used as markers to identify the cations in their mixtures, are underlined)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>νₐsCH₂</td>
</tr>
<tr>
<td>CH₂Cl₂ (liquid)²³</td>
<td>3045</td>
</tr>
<tr>
<td>ClH₂C–{Cl₁₁}</td>
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<tr>
<td>ClH₂C–Cl⁺–CH₂Cl IIa</td>
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<tr>
<td>ClH₂C–Cl⁺–CD₂Cl IIb</td>
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<tr>
<td>ClH₂C–Cl⁺–CH₄</td>
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</tr>
<tr>
<td>ClH₂C–Cl⁺–CD₄</td>
<td>3044</td>
</tr>
</tbody>
</table>

a Not determined.

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**Interaction of mono- and dichloromethane with H(\text{Cl}_{11}) and chloronium cations**

CH₃Cl interacts with the H(\text{Cl}_{11}) acid in two stages. At first, it is protonated with the release of HCl and the formation of CH₃\{\text{Cl}_{11}\} (eqn (2)):

\[
\text{CH₃Cl} + \text{H(\text{Cl}_{11})} \rightarrow \text{CH₃ClH}^+\{\text{Cl}_{11}\} \rightarrow \text{CH₃}\{\text{Cl}_{11}\} + \text{HCl}
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\text{CH₃}\{\text{Cl}_{11}\} + \text{CH₃Cl} \rightarrow \text{CH₃₂Cl}^+\{\text{Cl}_{11}^-\}
\]

(eqn (3)). Then, CH₃Cl binds to CH₃\{\text{Cl}_{11}\}, thus forming (CH₃₂Cl)⁺\{\text{Cl}_{11}⁻\} (eqn (3)). The formation of the resultant CH₃\{\text{Cl}_{11}\} can be observed by monitoring the intensity of the IR absorption of the released HCl (I\text{HCl}). The amount of the resulting ion (CH₃₂Cl)⁺ can be traced from the intensity of its band νₐs(CCl₂/C) at 636 cm⁻¹ (I₆₃₆; Fig. S4, ESI†). Dependence of I₆₃₆ on I\text{HCl} was initially proportional (Fig. 4), which means that both reactions proceed at constant speeds. When the thickness of the layer of the formed surface products increases sufficiently to slow down the diffusion of CH₃Cl molecules to the acid, the rate of
CH$_3$[Cl$_{11}$] formation decreases and the slope increases (Fig. 4). The cation of the ultimate salt (CH$_3$)$_2$Cl$^+$[Cl$_{11}$] does not show any further interaction with CH$_3$Cl.

Dichloromethane vapors (at a partial pressure of 0.65 atm) interacted with sublimed acid in the same way as chloromethane did. At the first stage, IR spectra registered the emergence of absorbance of the gaseous HCl and the surface CH$_2$Cl–[Cl$_{11}$] compound, which are formed in accordance with eqn (4):

$$\text{CH}_2\text{Cl}_2 + \text{H}[\text{Cl}_{11}] \rightarrow \text{CH}_2\text{Cl}–[\text{Cl}_{11}] + \text{HCl} \quad (4)$$

The IR spectrum of CH$_2$Cl–[Cl$_{11}$] showed the characteristic band of the C–Cl stretch at 793 cm$^{-1}$, and the absence of the bands of C–Cl–C group vibrations in the frequency range 650–500 cm$^{-1}$ (Fig. 5 and Table 2). Intensity of HCl absorption ($I_{\text{HCl}}$) was used to quantify the total amount of the formed CH$_2$Cl–[Cl$_{11}$], whereas intensity of the band of the terminal C–Cl stretch ($I_{\text{CCl}}$) reflects the current amount of this compound. Dependence of $I_{\text{CCl}}$ on $I_{\text{HCl}}$ was linear for the first 5 hours of the reaction (Fig. 6); this result means that only CH$_2$Cl–[Cl$_{11}$] was formed. Then, the dependence started to drop (point 22 in Fig. 6), indicating the second stage of the reaction: involvement of CH$_2$Cl–[Cl$_{11}$] in the formation of the ClH$_2$C–Cl$^+$–CH$_2$Cl cation (eqn (5)).

$$\text{CH}_2\text{Cl}–[\text{Cl}_{11}] + \text{CH}_2\text{Cl}_2 \rightarrow \text{ClH}_2\text{C}–\text{Cl}^+–\text{CH}_2\text{Cl}. \quad (5)$$

Extrapolation of $I_{\text{CCl}}$ from $I_{\text{HCl}}$ to the moment of the reaction stoppage (at the 1380th minute, when CH$_2$Cl$_2$ was pumped out) yields $I_{\text{CCl}} = 0.084$ (arbitrary units; Fig. 6). This value corresponds to the amount of CH$_2$Cl–[Cl$_{11}$] that was formed in accordance with the amount of HCl production (eqn (4)). Nevertheless, because CH$_2$Cl–[Cl$_{11}$] is further consumed (reaction (5)), $I_{\text{CCl}}$ decreases to 0.040 arbitrary units (Fig. 6), meaning that 48% (0.040/0.084) of this compound survived, and 52% was converted to the chloronium ion.

An IR spectrum of (CH$_2$Cl)$_2$Cl$^+$ was obtained by subtracting the spectrum of CH$_2$Cl–[Cl$_{11}$] from the spectrum of the mixture of (CH$_2$Cl)$_2$Cl$^+$ with the CH$_2$Cl–[Cl$_{11}$] up to complete compensation of the bands $\nu$C–Cl = 792 cm$^{-1}$ and $\delta$CH$_2 = 1243$ cm$^{-1}$, which are specific to CH$_2$Cl–[Cl$_{11}$] (Fig. 5, blue; Table 2). The frequencies of the (CH$_2$Cl)$_2$Cl$^+$ cation are very close to those of CH$_2$Cl–[Cl$_{11}$] except for one intense band at 1284 cm$^{-1}$, which can be used as a marker of this cation (Table 2). Furthermore, we will denote CH$_2$Cl–[Cl$_{11}$] as compound I and the (CH$_2$Cl)$_2$Cl$^+$ salt as compound II.

After stoppage of the reaction at minute 1380, an IR spectrum of the sample retained a strong absorption pattern of the unreacted acid, which constituted 70% of the original spectrum of the acid.

To continue reactions (4) and (5) at a higher speed, the CH$_2$Cl$_2$ vapors were reintroduced into our IR cell at higher partial pressure (1 atm). Under these conditions, the formation of compound I was completed after 8 minutes with full utilization of the acid and termination of the HCl release (point 30 in Fig. 7). An IR spectrum of this sample is shown in Fig. 8 (black).

Further interaction of compound I with CH$_2$Cl$_2$ and the formation of II is manifested in IR spectra as a decrease in the intensity of compound I and the upregulation of compound II with the appearance of isosbestic points (Fig. 8 and Fig. S5, ESI†).

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**Fig. 5**  IR spectra of the CH$_2$Cl–[Cl$_{11}$] compound (red) and the salt of CH$_2$Cl–Cl$^+$–CH$_2$Cl cation (blue). The spectra of unreacted H[Cl$_{11}$] acid, gaseous HCl and CH$_2$Cl$_2$ were subtracted. The region of strong absorption of gaseous CH$_2$Cl$_2$ (C–Cl stretches), where compensation does not work, is shaded.
The spectrum of the resultant cation II differed from that of the same cation formed during a slow reaction of CH₂Cl–{Cl₁₁} with CH₂Cl₂ (Fig. 9 and Table 2). Thus, two isomers of CH₂Cl–Cl⁺–CH₂Cl are formed: compound IIa from the slowly proceeding reaction (5) and compound IIb from the rapid reaction (5). They differ in frequencies of stretches CH and CCl. Nonetheless, their bend CH vibrations are very similar and have one specific band \( \delta \text{CH}_2 \) (1284 cm\(^{-1}\)), which does not overlap with the bands of other types of cations. Therefore, the intensity of this band \( I_{1284} \) can be used for the estimation of the amount of the IIa + IIb mixture.

Fig. 10 shows the time dependence of the intensity of absorption bands of compounds I \( I_{3063} \) and II \( I_{1284} \) that reflects the formation of the corresponding cations. One can see that the formation of compound II passes through a maximum at point 34, when compound I disappears, and then decreases.

Simultaneously, the bands indicative of the cation CH₃–Cl⁺–CH₂Cl at 1261 and 1248 cm\(^{-1}\) made an appearance (Table 2) and increased in intensity. We will denote this cation as compound III. Its narrow band \( \delta \text{CH}_2 = 1248 \text{ cm}^{-1} \) \( I_{1248} \) does not overlap with the bands of other cations and can be used for the assessment of the relative amount of compound III (Fig. 10, green). Along with the spectrum of compound III, the absorption bands of the cation \( (\text{CH}_3)_2\text{Cl}^+ \) also develop (hereafter denoted as compound IV). Intensity of its single band at 1324 cm\(^{-1}\) \( I_{1324} \) was used to assess the formation of compound IV. Fig. 10 summarizes the sequence of the formation of compounds I, II, III, and IV and the relative amounts of each compound, but does not describe the quantitative relations among them.

Cations III and IV can be formed only if the reaction of I or II with CH₂Cl₂ is accompanied by the formation of gaseous products. The spectra of the gas phase revealed the band of H–C–Cl bend vibration of chloroform at 1219 cm\(^{-1}\). The time dependence of its intensity shows that the formation of chloroform is associated with the formation of compounds I and II (Fig. 10).
In the situation when only I is formed ($P_{CHCl_2} = 0.65$ atm), the dependence of the chloroform formation ($I_{1219}$) on the formation of I ($I_{1242}$) increases both with an increase in the amount of compound I and with an increase in the contact time of I with dichloromethane (Fig. 11). Subtraction of the spectrum of compound I from the spectrum of the products (at point 18 in Fig. 11) leads to the manifestation of the spectrum of compound $\text{CH}_3\text{Cl}_{11}$ (Fig. S6, ESI†). Hence, $\text{CH}_2\text{Cl}_2$ reacts with $\text{CH}_2\text{Cl}\{\text{Cl}_{11}\}$ according to eqn (6):

$$\text{CH}_2\text{Cl}\{\text{Cl}_{11}\} + \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\{\text{Cl}_{11}\} + \text{CHCl}_3$$  

Confusing reaction (6). In contrast, starting from point 32, chloroform formation stopped, whereas from point 34, it begins to decrease, when the amount of II passes through a maximum, and compound I is exhausted (Fig. 10). The subsequent expenditure of chloroform occurs simultaneously with the consumption of compound II and the increasing amount of III. This finding points to reaction (7):

$$\text{CH}_2\text{Cl}\{\text{Cl}_{11}\} + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}\text{Cl}^+\text{Cl}_2 + \text{CHCl}_3$$  

The detection of CCl$_4$ was carried out as follows. After the completion of the reaction, the gaseous phase and all surface-adsorbed molecules were removed by pumping. The difference in IR spectra before and after the evacuation represented the spectrum of removed molecules. It consists of a strong absorption pattern of the original dichloromethane, the characteristic band at 1219 cm$^{-1}$ of chloroform, and a weak band at 790 cm$^{-1}$, which may belong to the C-Cl stretch of CCl$_4$. The latter frequency is lower than that of gaseous CCl$_4$ (795 cm$^{-1}$), but equals that of CCl$_4$ solvated with dichloromethane in its solutions (789 cm$^{-1}$). Therefore, the traces of the formed CCl$_4$ are adsorbed by superficial chloronium salts.

To sum up, we can conclude that $\text{CH}_2\text{Cl}_2$ and $\text{CHCl}_3$ interact with the molecular fragment $\text{CH}_2\text{Cl}\{\text{Cl}_{11}\}$, whose reactivity is highest in $\text{CH}_2\text{Cl}\{\text{Cl}_{11}\}$ and is consistently reduced in cations II and III. In general, these interactions can be expressed as:

$$\text{CH}_2\text{Cl}\{\text{Cl}_{11}\} + \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\{\text{Cl}_{11}\} + \text{CHCl}_3$$  

$$\text{CH}_2\text{Cl}\text{Cl}^+\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}\text{Cl}^+\text{Cl}_2 + \text{CHCl}_3$$  

$$\text{CH}_2\text{Cl}\{}\text{Cl}_{11}\} + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}\{}\text{Cl}_{11}\} + \text{CHCl}_3$$  

$$\text{CH}_2\text{Cl}\{}\text{Cl}_{11}\} + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}\{}\text{Cl}_{11}\} + \text{CHCl}_3$$  

Decreasing the reactivity of the molecular fragment $\text{CH}_2\text{Cl}$- in compounds I, II, and III is correlated with its decreasing polarizability, which in turn is determined by the change in ionicity of the bonds in chloronium bridge C-Cl$^+$-C.

**Ionicity/covalency of the bonds in the C-Cl$^+$-C bridge of chloronium ions**

The stretch frequencies of the methyl group, especially $\nu_{as}\text{CH}_3$, are sensitive to $\text{CH}_3$ polarization: the higher these frequencies, the stronger the $\text{CH}_3$ group is polarized and the higher is ionicity of the $\text{CH}_3$-Cl(X) bond. In compounds $\text{CH}_3\{}\text{Cl}_{11}\}$ and $\text{CH}_2\text{Cl}^+\text{Cl}_2\text{CH}_3$, the $\text{CH}$ stretches differ insignificantly (Table 1), pointing to almost the same ionicity of $\text{CH}_3^+$ bonding to $\text{Cl}^-$ and Cl-$\text{CH}_3$, respectively. Nonetheless, one would expect weaker ionicity (stronger covalency) of the bonds in $\text{CH}_3^+$-Cl$^-$ than in $\text{CH}_3^+\{}\text{Cl}_{11}\}$. The crystal structure of the $\text{CH}_2\text{Cl}^+\text{Cl}_2\text{CH}_3\{}\text{Cl}_{11}\}^-$ salt shows (Fig. S7 in ESI†) that the chloronium Cl-atom forms six ionic bonds with Cl-atoms of the four $\{\text{Cl}_{11}\}^-$ anions of its...
environment. This situation favors an increase in the ionicity of C–Cl+–C bonds and contributes to the convergence of polarizability of CH2 groups in CHH2–{Cl11} and (CH3–Cl+–CH2){Cl11} salts. If we now examine the salt (CH3–Cl+–CD2Cl){Cl11}, one can see that CH stretches significantly decrease (Table 1). It is evident that this salt is amorphous and has a disordered structure that may reduce the number of linkages between the chloronium Cl atom and neighboring {Cl11} anions, thus increasing the covalency of the C–Cl+–C group. In any case, the ionicity of the CH2Cl{X} bond decreases in the following order:

\[
\nu_{\text{asCH}_2\text{Cl}} \text{ cm}^{-1} \\
\begin{align*}
\text{CH}_2\text{Cl}–\{\text{Cl}_{11}\} &\sim \text{CH}_3–\text{Cl}^+–(–\text{CH}_3) \\
> \text{CH}_3–\text{Cl}^+–(–\text{CD}_2\text{Cl}) &> \text{CH}_3\text{Cl}
\end{align*}
\]

Just as the methyl group in salts CH3–{Cl11} and (CH3–Cl+–CH3){Cl11}, the CH2Cl group in salts CH2C–{Cl11} and IIa shows identical CH stretch frequencies (Table 2). Probably, in the case of the slow formation (hours) of the (ClH2C–Cl+–CH2Cl){Cl11} cation, the CH2Cl group in salts CH2C–{Cl11} and IIa shows identical CH stretch frequencies (Table 2). Probably, in the case of quick formation (minutes), the (CH3–Cl+–CD2Cl){Cl11} salt (IIa), its structure is the densest, close to that of the single crystal with a maximal number of interactions between the chloronium Cl atom and atoms of the nearest {Cl11} anions. In the case of quick formation (minutes), the (CH2C–Cl+–CH2Cl){Cl11} salt is amorphous with a loose structure and fewer contacts between the chloronium Cl atom and Cl atoms of the neighboring anions. This situation increases the covalency of the bonds in the C–Cl+–C bridge and decreases the polarizability of CH2Cl groups and their CH stretches. We named this salt “isomer IIb”. Polarizability and CH frequencies of the CH2Cl group of IIb coincide with those of the salt (CH2C–Cl+–CH2Cl){Cl11}. Thus, ionicity of the CH2C–Cl{X} bond decreases in the following order:

\[
\nu_{\text{asCD}_3} \text{ cm}^{-1} \\
\begin{align*}
\text{CD}_3–\text{Cl}^+–\text{CH}_2\text{Cl} &\sim \text{IIa} > \text{IIb} \\
> \text{CH}_2\text{C}–\text{Cl}^+–(–\text{CH}_3) &> \text{IIb}
\end{align*}
\]

in accordance with decreasing frequencies of CH stretches, which indicate the polarization of the CH2C group. Isomers IIa and IIb differ in frequencies of stretch vibrations of C–Cl+–C bridges (Table 2); this observation confirms that this is the starting point of their differences.

The proposed model seems to be a reasonable explanation for the existence of IIa and IIb isomers when they are formed slowly (within hours) or quickly (in minutes), respectively.

**Thermal stability of chloronium cations**

**Ambient temperature.** The salt of the symmetric cation (CH3)2Cl+ can be stored indefinitely (weeks or months) without any changes in the IR spectrum. The spectra of the salts of asymmetric cations are time dependent at ambient temperature: exposure of freshly prepared salt (CD3–Cl+–CH2Cl){Cl11} to vacuum for one day results in disappearance of the bands of its cation (Fig. 13, blue). They are replaced with the bands of cation IIa: CH2Cl–Cl+–CH2Cl [labeled (2) in Fig. 13, red]. Weak bands of cations CD3Cl–Cl+–CD2Cl and (CH3)2Cl+ also appeared (labeled 2 and 3 respectively), as did the traces of HCl absorption.

In the range of CD stretch vibrations, the band \(\nu_{\text{asCD}_3} = 2297 \text{ cm}^{-1}\) of the cation CD3–Cl+–CH2Cl was replaced with the intense \(\nu_{\text{asCD}_3}\) band at 2307 cm\(^{-1}\) of the cation CD3–Cl+–CD3. Thus, the CD3–Cl+–CH2Cl cation in the solid phase at ambient temperature is unstable, and during the day, disproportionates into symmetrical cations, predominantly according to eqn (9) and to a slight extent, according to eqn (10)

\[
\begin{align*}
2\text{CD}_3–\text{Cl}^+–\text{CH}_2\text{Cl} &\rightarrow \text{CH}_2\text{Cl}–\text{Cl}^+–\text{CH}_2\text{Cl} + \text{CD}_3–\text{Cl}^+–\text{CD}_3 \\
(9) \\
2\text{CD}_3–\text{Cl}^+–\text{CH}_2\text{Cl} &\rightarrow \text{CH}_3–\text{Cl}^+–\text{CH}_3 + \text{CD}_3–\text{Cl}^+–\text{CD}_3 \\
(10)
\end{align*}
\]

The disproportionation looks as if at the chlorine atom, there is an intramolecular exchange of groups CD3– and –CH2Cl that is difficult to imagine for the solid phase. Intermediates with the molecular fragments CHDCl– and CH2D– were not detected by IR spectroscopy.

**Increased temperature.** Heating of the salt (CH3–Cl+–CH2Cl){Cl11} to \(-100 \text{ °C}\) for 5 min in a sealed cell led to disappearance of its spectrum (Fig. 14 and Fig. S8, ESI,† blue) and to the emergence of overlapping spectra of the symmetric cation (CH3)2Cl+ and isomer (CH3)2Cl+, IIa (with the marked

![Fig. 13](image-url) IR spectra of the freshly prepared salt (CD3–Cl+–CH2Cl){Cl11} (blue) and after one or three days of storage (red). The bands of the cations (CH2Cl)2Cl+, CD3Cl–Cl+–CD2Cl and (CH3)2Cl+ are marked respectively as (1), (2) and (3).
bands a and b, respectively, Fig. 14 and Fig. S8, ESI, red). The absorption bands of gaseous HCl did not appear.

Therefore, at 100 °C, the asymmetric cation CH₃Cl⁺–CH₂Cl quickly disproportionates into the more stable symmetric cations:

\[ 2\text{CH}_3\text{Cl}^+\text{–CH}_2\text{Cl} \rightarrow \text{CH}_3\text{Cl}^+\text{–CH}_2\text{Cl} + \text{CH}_3\text{Cl}^+\text{–CH}_3 \] (11)

Further heating of the sample for 5 minutes at 150 °C led to an equal (threefold) reduction in intensity of the bands at 1324 and 1284 cm⁻¹ of the cations (CH₃)₂Cl⁺ and (CH₂Cl)₂Cl⁺, respectively, and appearance and an increase in intensity of the bands of CH₃Cl⁺ (1335 cm⁻¹: Fig. 14, green) and CH₂Cl⁻{Cl₁₁} (νCCl_term = 793 cm⁻¹). Additionally, bands with a rotational structure at 1270 and 761 cm⁻¹ of gaseous CH₂Cl₂ were observed. Consequently, an increase in temperature facilitates the decomposition of chloronium ions according to eqn (12) and (13); this change should lead to increasing intensity of the IR spectrum of released dichloromethane.

\[
\begin{align*}
\text{(CH}_3\text{Cl}^+\text{–CH}_2\text{Cl)}\{\text{Cl}_{11}\} & \rightarrow \text{CH}_3\text{Cl}+\text{Cl}^-+\text{CH}_2\text{Cl}_2, \\
\text{(CH}_3\text{H}_2\text{Cl}^+\text{–CH}_2\text{Cl})\{\text{Cl}_{11}\} & \rightarrow \text{CH}_3\text{H}_2\text{Cl}^+\text{–Cl}^-+\text{CH}_2\text{Cl}_2
\end{align*}
\] (12) (13)

Longer heating of the sample at 150 °C did not enhance the spectrum of CH₂Cl₂. It remained virtually unchanged. In contrast, the bands of CHCl₃ appeared (1219 and 772 cm⁻¹) and were enhanced with heating and a very weak absorption pattern of gaseous HCl developed. The solid-phase spectrum shows increased intensity of the CH₃{Cl₁₁} band at 1335 cm⁻¹ and disappearance of the adsorption of CH₂Cl⁻{Cl₁₁}. Taken together, our data indicate that the CHCl₃ formation is caused by the interaction of CH₂Cl⁻{Cl₁₁} with dichloromethane:

\[ \text{CH}_2\text{Cl}^-\text{–Cl}^-+\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\text{Cl}^-\text{–Cl}^-+\text{CHCl}_3. \]

To determine the reason for the formation of trace amounts of HCl, additional studies are needed.

Conclusions

The salts of symmetric methylchloronium cations, \((\text{CH}_3)_2\text{Cl}^+\{\text{Cl}_{11}\}^{-}\) and \((\text{CH}_2\text{Cl})_2\text{Cl}^+\{\text{Cl}_{11}\}^{-}\), and their neutral analogs CH₃{Cl₁₁} and CH₂Cl⁻{Cl₁₁}, are stable at ambient and increased temperatures. Nevertheless, the asymmetric cation \(\text{CH}_3\text{H}_2\text{Cl}^+\text{–CH}_2\text{Cl}\) even at ambient temperature disproportionates into symmetrical \((\text{CH}_3)_2\text{Cl}^+\) and \((\text{CH}_2\text{Cl})_2\text{Cl}^+\). The molecular fragment CH₂Cl⁻ of the chloronium ions enters exchange reactions with CH₂Cl₂ and CHCl₃ with increasing reactivity in the order CH₂Cl⁻–CH₃ > CH₂Cl⁻–CH₂Cl, CHCl₂⁻–CH₃, and CHCl₂⁻–(Cl₁₁), yielding more stable and less reactive \((\text{CH}_2\text{Cl})_2\text{Cl}^+\{\text{Cl}_{11}\}^{-}\) and \(\text{CH}_3\text{Cl}^-\text{–Cl}^-\) compounds.

If we take into account the reactivity of \(\text{H}\{\text{Cl}_{11}\}^{-}\) acid or its chloronium salts with CH₂Cl₁₁, and the simultaneous disproportionation of the CH₃Cl⁻–CH₂Cl cation (eqn (11); initiated by the elevated temperature), then the end products of interactions at ambient, or slightly evaluated temperature, are the chemically inert CH₃Cl⁻–CH₃ and CCl₄:

\[
\text{H}\{\text{Cl}_{11}\}^{-}+\text{CH}_2\text{Cl}_2
\]

Starting compounds

\[
\rightarrow [\text{CH}_3\text{Cl}^-\text{–Cl}^-+\text{CH}_2\text{Cl}_2, \text{CH}_3\text{Cl}^-\text{–Cl}^-+\text{CH}_2\text{Cl}, \text{CH}_2\text{Cl}^-\text{–Cl}^-+\text{CH}_3] \quad \text{Intermediates}
\]

\[
\rightarrow \text{CH}_3^-\text{–Cl}^-+\text{CH}_3+\text{CCl}_4/\text{CHCl}_3 \quad \text{End products}
\]

Reactions (9)–(13) (as determined in this study) proceed with the formation of a trace amount of HCl, thus indicating the negligible presence of parallel reactions. Under the other conditions, they may appear to be significant and interesting for future research.

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