The salts of chloronium ions \( R-\text{Cl}^+ - R \) (\( R = \text{CH}_3 \) or \( \text{CH}_2\text{Cl} \)): formation, thermal stability, and interaction with chloromethanes†

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The interaction of \( \text{CH}_3\text{Cl/CD}_3\text{Cl} \) or \( \text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2 \) with the carborane acid \( \text{H(\text{CHB}_{11}\text{Cl}_{11})} \) (abbreviated as \( \text{H(Cl}_{11} \)) generates the salts of \( \text{CH}_3-\{\text{Cl}_{11}\} \) and \( \text{CH}_2\text{Cl}-\{\text{Cl}_{11}\} \) and their deuterio analogs, respectively, and the nature of carbon–halogen bonds in the halonium ions was studied.5 Mostly stable dimethylbromonium and -iodonium ions in solutions was obtained,3,4 and halonium ions (\( R_2\text{Hal}^+ \)) are well-recognized reactive intermediates in electrophilic chemistry.1,2 Their stability increases in the order \( \text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{I} \). Recently, the evidence of the formation of the symmetrical fluoronium ions in solutions was obtained,3,4 and the interaction with chloromethanes. The carborane ion \( \{\text{Cl}_{11}\} \) 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 \( \text{H}\{\text{Cl}_{11}\} \) 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 \( \text{H}_2\text{O}^+ \) cation.20 Dry gaseous chloromethanes (\( \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \) and \( \text{CHCl}_3 \)) 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 \( \text{N}_2 \) (\( \text{O}_2 \) and \( \text{H}_2\text{O} < 0.5 \) 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.
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 CH₃–Cl+–CH₂Cl cation was obtained by introducing the CH₂Cl₂ vapors at a partial pressure \( P_{\text{CH}_2\text{Cl}_2} \) of 0.4 atm into an evacuated IR cell containing a film of CH₃–{Cl₁₁} sublimed on their Si-windows. Reaction (1) of CH₃–Cl+–CH₂Cl formation proceeds very slowly, without a release of HCl.

\[
\text{CH}_3\{\text{Cl}_{11}\} + \text{CH}_2\text{Cl}_2 \rightarrow \{\text{CH}_3\text{Cl}^+–\text{CH}_2\text{Cl}\}\{\text{Cl}_{11}^-\}
\]  

(1)

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

If the partial pressure of the injected CH₂Cl₂ vapors was twofold higher (1 atm), then the reaction was accelerated significantly and completed within 6 minutes. The spectrum of the resultant CH₃–Cl⁺–CH₂Cl cation slightly differs from that of the previous sample (Fig. 1), indicating that the cation is sensitive to changes in the environment.

The CH₃–Cl⁺–CD₂Cl cation is formed when the vapors of CD₂Cl₂ are introduced into the IR cell with sublimed CH₃–{Cl₁₁}. The IR spectrum of the salt of this cation is shown in Fig. 2 (red; the gas phase was evacuated).

The IR spectrum of the salt of this cation is shown in Fig. 2 (red; the gas phase was evacuated). The CD₃–Cl⁺–CH₂Cl and CD₃–Cl⁺–CD₂Cl cations were formed when vapors of CH₂Cl₂ or CD₂Cl₂ respectively, were injected into the IR cell with a film of sublimed CD₃–{Cl₁₁} salt on the Si windows. Their IR spectra are presented in Fig. S2 and S3 (ESI†) and in Table 1.

Interpretation of the IR spectra

IR spectra of the salts of the cations CH₃–Cl⁺–CH₂Cl (red), CD₃–Cl⁺–CH₂Cl (blue), and CH₃–Cl⁺–CD₂Cl (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 CH₃C–{Cl⁻} (blue) and CH₃–{Cl⁻} (green) matches the spectrum of the CH₃–Cl⁺–CH₂Cl 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 \( \text{CH}_3\{\text{Cl}_{11}\} \) and \( \{\text{CH}_3\text{Cl}^+–\text{CH}_3\}\{\text{Cl}_{11}^-\} \) were interpreted earlier.₁⁵ 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{Cl11} and chloronium cations

CH3Cl interacts with the H{Cl11} acid in two stages. At first, it is protonated with the release of HCl and the formation of CH3{Cl11} (eqn (2)):

$$\ce{CH3Cl + H{Cl11} -> [CH3Cl-H{Cl11}] -> CH3{Cl11} + HCl}$$  \hspace{1cm} (2)

$$\ce{CH3{Cl11} + CH3Cl -> [CH3]2Cl+{Cl11^-}}$$  \hspace{1cm} (3)

Then, CH3Cl binds to CH3{Cl11}, thus forming (CH3)2Cl+{Cl11−} (eqn (3)). The formation of the resultant CH3{Cl11} can be observed by monitoring the intensity of the IR absorption of the released HCl \(I_{HCl}\). The amount of the resulting ion \((\ce{CH3})_2\text{Cl}^+\) can be traced from the intensity of its band \(\nu_{as}(\text{CCI})\) at 636 cm\(^{-1}\) \((I_{636}; \text{Fig. S4, ESI}^\dagger)\). Dependence of \(I_{636}\) on \(I_{HCl}\) 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

### Table 1

| Compound          | \(\nu_{as}\text{CH3}\) | \(\nu_s\text{CH3}\) | \(\delta\text{CH3}\) | \(\delta\text{CH4}\) | \(\nu_{as}\text{CH3}\) | \(\nu_s\text{CH3}\) | \(\nu_{as}\text{CH2}\) | \(\nu_s\text{CH2}\) | \(\nu_{as}\text{CCI}\) |
|-------------------|------------------------|---------------------|---------------------|---------------------|------------------------|---------------------|------------------------|---------------------|------------------------|
| CH3Cl (gas) \(^{21}\) | 3043                   | 3039                | 2968                | 2879                | 1452                   | 1355                | 1017                   | 732                 |
| CH3{Cl11} \(^{15}\) | 3083                   | 3071                | 2962                | 1409                | 1335                   | 1324                | 636                    |
| CH3{Cl11}-CH3 \(^{15}\) | 3068                   | 3054                | 2947                | 1406                | 1330                   | 934                 | 632                    | 522                 |

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

### Table 2

| Compound          | \(\nu_{as}\text{CH2}\) | \(\nu_s\text{CH2}\) | \(\nu_{as}\text{CCI}\) | \(\nu_s\text{CCI}\) |
|-------------------|------------------------|---------------------|------------------------|---------------------|
| CH2Cl2 (liquid) \(^{23}\) | 3045                   | 2990                | 1424                   | 739                 |
| ClH2C–{Cl11} \(^{15}\) | 3079                   | 3063                | 2978                   | 1391                |
| ClH2C–{Cl11}–CH2Cl IIa | 3073                   | 3064                | 2980                   | 1416                |
| ClH2C–{Cl11}–CH2Cl IIb | 3044                   | 2964br              | 1409                   | 1338                |
| ClH2C–Cl+–CH2Cl IIa | 3044                   | 2962                | 1407                   | 1338                |
| ClH2C–Cl+–CH2Cl IIb | 3044                   | 2962                | 1398                   | 1387                |
| a Not determined. |

Fig. 4 Dependence of the intensity of band \(\nu_{as}(\text{CCI})\) at 636 cm\(^{-1}\) of the (CH3)2Cl+ cation on the intensity of HCl absorption [reflects the dependence of the (CH3)2Cl+ formation on the \(\text{CH3Cl}_{\text{II}}\) formation].
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):

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

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–C–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 ($I_{\text{C}\text{Cl}}$) reflects the current amount of this compound. Dependence of $I_{\text{C}\text{Cl}}$ 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 $I_{\text{C}\text{Cl}}$ from $I_{\text{HCl}}$ to the moment of the reaction stoppage (at the 1380th minute, when CH$_2$Cl$_2$ was pumped out) yields $I_{\text{C}\text{Cl}} = 0.084$ (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)), $I_{\text{C}\text{Cl}}$ 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 $\delta\text{CCl} = 792$ cm$^{-1}$ and $\delta\text{CH}_2 = 1243$ 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$^\dagger$).
The spectrum of the resultant cation II differed from that of the same cation formed during a slow reaction of CH$_2$Cl–{Cl$_{11}$} with CH$_2$Cl$_2$ (Fig. 9 and Table 2). Thus, two isomers of CH$_2$Cl–Cl$^+$–CH$_2$Cl 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 $\delta$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 CH$_3$–Cl$^+$–CH$_2$Cl 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 $\delta$CH$_2$ = 1248 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 (CH$_3$)$_2$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 CH$_2$Cl$_2$ 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).

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In the situation when only I is formed ($P_{CH_2Cl} = 0.65 \text{ atm}$), 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 CH$_2Cl$Cl$_{11}$ (Fig. S6, ESI†). Hence, CH$_2Cl_2$ reacts with CH$_2Cl$Cl$_{11}$ according to eqn (6):

$$\text{CH}_2\text{Cl}\{\text{Cl}_{11}\} + \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\{\text{Cl}_{11}\} + \text{CHCl}_3$$  \hspace{1cm} (6)

Confirming 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):

$$\text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CH}_3\{\text{Cl}_{11}\} \rightarrow \text{CH}_3\{\text{Cl}^-\} + \text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{CCl}_4,$$  \hspace{1cm} (7)

(anions are omitted), which is suggestive of CCl$_4$ formation.

In the same way, compound IV can form:

$$\text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CHCl}_3 + \text{CCl}_4,$$  \hspace{1cm} (8)

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 CH$_2Cl_2$ and CHCl$_3$ interact with the molecular fragment CH$_2Cl$-, whose reactivity is highest in CH$_2Cl$Cl$_{11}$ and is consistently reduced in cations II and III. In general, these interactions can be expressed as:

$$
\begin{align*}
\text{CH}_2\text{Cl}\{\text{Cl}_{11}\} + \text{CH}_2\text{Cl}_2 & \rightarrow \text{CH}_3\{\text{Cl}_{11}\} + \text{CHCl}_3 \\
\text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CH}_2\text{Cl}_2 & \rightarrow \text{CH}_3\{\text{Cl}^-\} + \text{CHCl}_3 + \text{CCl}_4 \\
\text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CHCl}_3 & \rightarrow \text{CH}_2\text{Cl}\{\text{Cl}^-\} + \text{CHCl}_3 + \text{CCl}_4
\end{align*}
$$

With the rapid formation of CH$_2Cl$Cl$_{11}$ in reaction (4) at $P_{CH_2Cl} = 1 \text{ atm}$, chloroform is formed symbatically (Fig. 12), decreasing the reactivity of the molecular fragment CH$_2Cl$- 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 CH$_3$ polarization: the higher these frequencies, the stronger the CH$_3$ group is polarized and the higher is ionicity of the CH$_3$-Cl(X) bond. In compounds CH$_3$-{Cl$_{11}$} and CH$_2$Cl-Cl$^-$-CH$_3$, the CH stretches differ insignificantly (Table 1), pointing to almost the same ionicity of CH$_3^+$ bonding to {Cl$^-$} and Cl-CH$_3$, respectively. Nonetheless, one would expect weaker ionicity (stronger covalency) of the bonds in CH$_3$-Cl$^-$/CH$_3$ than in CH$_3$-{Cl$_{11}$}. The crystal structure of the (CH$_3$-Cl$^-$/CH$_3$){Cl$_{11}$} salt shows (Fig. S7 in ESI†) that the chloronium Cl-atom forms six ionic bonds with Cl-atoms of the four {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 CH3 groups in CH3–{Cl11} and (CH3–Cl+–CH3){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 CH3–Cl(–X) bond decreases in the following order: 

\[ \nu_{\text{asCH3}} \text{ cm}^{-1} \]

\[ \text{CH3} - \{\text{Cl11}\} \sim \text{CH3} - \text{Cl}^+ (\text{-CH3}) \]

\[ > \text{CH3} - \text{Cl}^+ (\text{-CD2Cl}) > \text{CH3Cl} \]

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+–CH3){Cl11} 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 CH3–Cl(–X) bond decreases in the following order:

\[ \nu_{\text{asCH2Cl}} \text{ cm}^{-1} \]

\[ \text{CH2Cl} - \{\text{Cl11}\} \sim \text{IIa} > \text{IIb} \]

\[ > \text{CH2Cl} - \text{Cl}^+ (\text{-CH3}) \]

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: CH3Cl–Cl+–CH3Cl [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 \( \nu_{\text{asCD3}} = 2297 \text{ cm}^{-1} \) of the cation CD3–Cl+–CH2Cl was replaced with the intense \( \nu_{\text{asCD3}} \) band at 2307 cm\(^{-1}\) of the cation CD3–Cl+–CD3. Thus, the CD3–Cl+–CH3Cl 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)

\[ 2\text{CD3–Cl+–CH2Cl} \rightarrow \text{CH3Cl–Cl+–CH3Cl} + \text{CD3–Cl+–CD3} \]  
\[ (9) \]

\[ 2\text{CD3–Cl+–CH3Cl} \rightarrow \text{CD3Cl–Cl+–CD2Cl} + \text{CH3Cl–Cl+–CH3Cl} \]  
\[ (10) \]

The disproportionation looks as if at the chlorine atom, there is an intermolecular 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 \(-100^\circ\text{C}\) 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 (CH3)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 CH₃–Cl⁺–CH₂Cl quickly disproportionates into the more stable symmetric cations:

$$2\text{CH}_3\text{Cl}^- \text{–CH}_2\text{Cl} \rightarrow \text{CICH}_2\text{Cl}^- \text{–CH}_2\text{Cl} + \text{CH}_3\text{Cl}^- \text{–CH}_3$$ (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 CH₃–Cl⁻ (1335 cm⁻¹; Fig. 14, green) and CH₂Cl–Cl⁻ (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.

$$\text{CH}_3\text{Cl}^- \text{–CH}_2\text{Cl} \rightarrow \text{CH}_3\text{Cl}^- \text{–Cl}^- + \text{CICH}_2\text{Cl}^- \text{–CH}_2\text{Cl}$$ (12)
$$\text{CICH}_2\text{Cl}^- \text{–Cl}^- \rightarrow \text{CICH}_2\text{Cl}^- \text{–Cl}^- + \text{CH}_3\text{Cl}^- \text{–CH}_2\text{Cl}$$ (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 CH₃Cl⁻ band at 1335 cm⁻¹ and disappearance of the adsorption of CH₂Cl–Cl⁻. Taken together, our data indicate that the CHCl₃ formation is caused by the interaction of CH₂Cl–Cl⁻ with dichloromethane:

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

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

Conclusions

The salts of symmetric methylichloronium cations, (CH₃)₂Cl⁺[Cl⁻] and (CH₂Cl)₂Cl⁺[Cl⁻], and their neutral analogs CH₃–{Cl₁₁} and CH₂Cl–{Cl₁₁}, are stable at ambient and increased temperatures. Nevertheless, the asymmetric cation CICH₂–Cl⁺–CH₃ even at ambient temperature disproportionate into symmetrical (CH₃)₂Cl⁺ and (CH₂Cl)₂Cl⁺. The molecular fragment CHCl–Cl⁻ of the chloronium ions enters exchange reactions with CH₂Cl₂ and CHCl₃ with increasing reactivity in the order CICH₂–Cl⁺–CH₃, CICH₂–Cl⁺–CH₂Cl, and CH₂Cl–Cl⁻{Cl₁₁}, yielding more stable and less reactive (CH₂Cl)₂Cl⁺{Cl₁₁} and CH₃{Cl₁₁} compounds. If we take into account the reactivity of H[Cl₁₁] acid or its chloronium salts with CH₂Cl₂, and the simultaneous disproportionation of the CH₃–Cl⁻–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 CH₃–Cl⁺–CH₃ and CCl₄:

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

Starting compounds

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

Intermediates

$$\rightarrow \text{CH}_3^- + \text{Cl}^- + \text{CH}_3 + \text{CCl}_4/\text{CHCl}_3$$

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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