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

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The interaction of CH_3Cl/CD_3Cl or CH_2Cl_2/CD_2Cl_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_2Cl–{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_3, $ClCH_2$–Cl$^+$–CH_2Cl, and $ClCH_2$–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 $(CH_3)_2Cl^+$ and $(CH_2Cl)_2Cl^+$. 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_2Cl–{Cl_{11}}. The molecular fragment $ClCH_2$–(X) of the compounds (X = {Cl_{11}}, –Cl$^+$–CH_2Cl, or –Cl$^+$–CH_3) is involved in exchange reactions with CH_2Cl_2 and $CHCl_3$, converting into CH_3–(X) with the formation of chloroform and CCl_4, respectively.

Halonium ions (R_2Hal^+) 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 $(CH_3)_2Cl^+$ and $(C_2H_5)_2Cl^+$ 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 $(CH_3)_2Cl^+(CHB_{11}Cl_{11}^-)$ is stable even at elevated temperatures and decomposes at 140 °C releasing $CH_3(CHB_{11}Cl_{11})$ and CH_3Cl. 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_3ClCH_2.[16,17]

In the present work we obtained the salts of symmetric and asymmetric chloronium cations, CH_3–Cl$^+$–CH_2Cl and CH_2Cl–Cl$^+$–CH_2Cl, 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_3O^+ cation.[20] Dry gaseous chloromethanes (CH_3Cl, CH_2Cl_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_2O < 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 $CH_3–Cl^+–CH_2Cl$ cation was obtained by introducing the CH_2Cl_2 vapors at a partial pressure ($P_{CH_2Cl_2}$) of 0.4 atm into an evacuated IR cell containing a film of $CH_3–\{Cl_{11}\}$ sublimed on their Si-windows. Reaction (1) of $CH_3–Cl^+–CH_2Cl$ formation proceeds very slowly, without a release of HCl.

$$CH_3\{Cl_{11}\} + CH_2Cl_2 \rightarrow (CH_3–Cl^+–CH_2Cl)\{Cl_{11}{}^-\} \qquad (1)$$

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_2Cl_2 vapors was twofold higher (1 atm), then the reaction was accelerated significantly and completed within 6 minutes. The spectrum of the resultant $CH_3–Cl^+–CH_2Cl$ cation slightly differs from that of the previous sample (Fig. 1), indicating that the cation is sensitive to changes in the environment.

The $CH_3–Cl^+–CD_2Cl$ cation is formed when the vapors of CD_2Cl_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).

The $CD_3–Cl^+–CH_2Cl$ and $CD_3–Cl^+–CD_2Cl$ cations were formed when vapors of CH_2Cl_2 or CD_2Cl_2 respectively, were injected into the IR cell with a film of sublimed $CD_3–\{Cl_{11}\}$ 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 $CH_3–Cl^+–CH_2Cl$ (red), $CD_3–Cl^+–CH_2Cl$ (blue), and $CH_3–Cl^+–CD_2Cl$ (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 $ClH_2C–(Cl^+–)$ (blue) and $CH_3–(Cl^+–)$ (green) matches the spectrum of the $CH_3–Cl^+–CH_2Cl$ 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.[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.

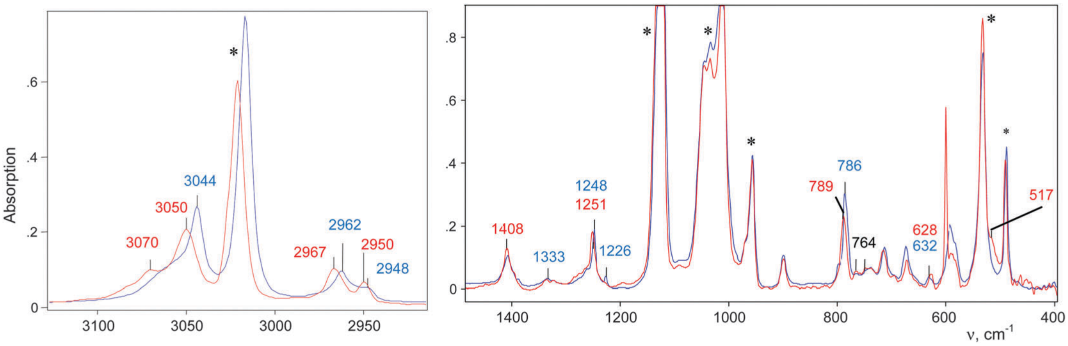

Fig. 1 Red: IR spectra of $(CH_3–Cl^+–CH_2Cl)\{Cl_{11}{}^-\}$ formed at low (red) and high (blue) partial pressure of CH_2Cl_2 (0.4 and 1 atm respectively). Both spectra are normalized to intensity of the anion. The red spectrum was isolated after subtracting the spectrum of the unreacted $CH_3–\{Cl_{11}\}$. Intense bands (marked by an asterisk) belong to the $\{Cl_{11}{}^-\}$ anion.

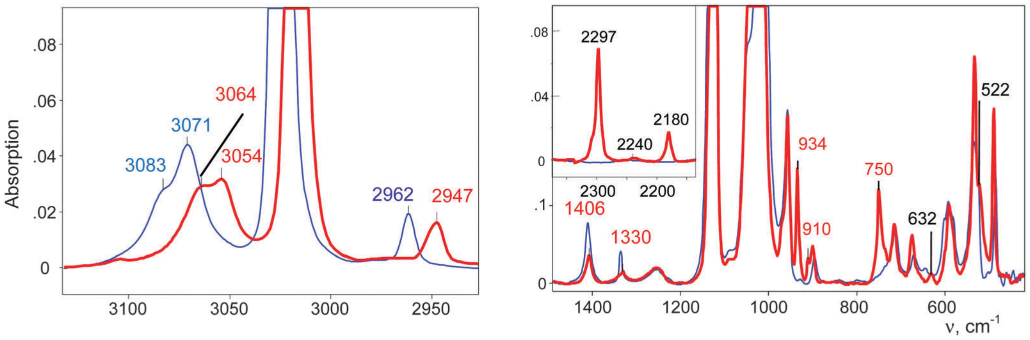

Fig. 2 IR spectra of the initial $CH_3–\{Cl_{11}\}$ salt (blue) and the salt of the $CH_3–Cl^+–CD_2Cl$ cation (red).

Table 1 IR frequencies of the methyl and bridged C–Cl$^+$–C groups of the compounds analyzed, in comparison with the IR spectrum of CH_3Cl (the most characteristic or intense bands, used as markers to identify the cations in their mixtures, are underlined)

Compound	$\nu_{as}CH_3$		ν_sCH_3		$\delta_{as}CH_3$	δ_sCH_3	CH_3 rock	$\nu_{as}(CClC)$	$\nu_s(CClC)$
CH_3Cl (gas)[21]	3043	$\underline{3039}$	2968	2879	1452	1355	1017m	732 (νCCl)	
CH_3–{Cl_{11}}[15]	3083	$\underline{3071}$	2962		1409	1335	—	—	
CH_3–Cl^+–CH_3[15]		$\underline{3068}$	2957		1417	1324		$\underline{636}$	
H_3C–Cl^+–CD_2Cl	3064	$\underline{3054}$	2947		1406	1330	934	632	522

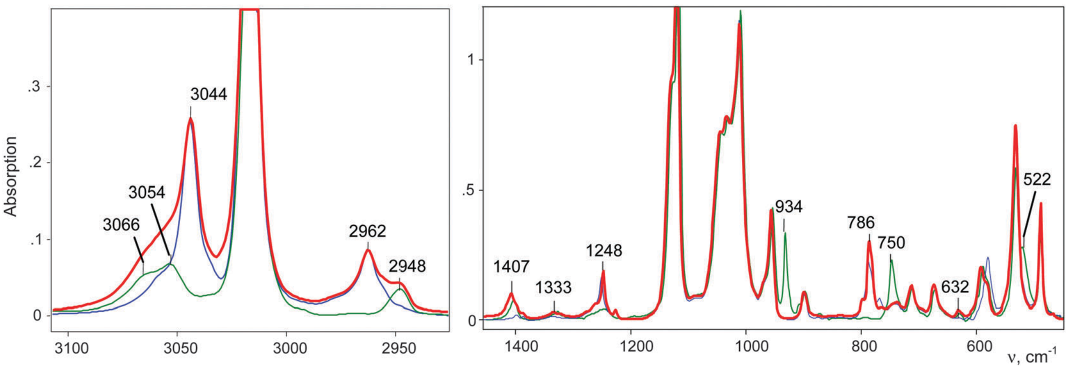

Fig. 3 IR spectra of salts of cations: CH_3–Cl^+–CH_2Cl (red), CD_3–Cl^+–CH_2Cl (blue) and CH_3–Cl^+–CD_2Cl (green).

Table 2 IR frequencies of the methylene chloride and bridged C–Cl$^+$–C groups of the compounds analyzed, in comparison with the IR spectrum of CH_2Cl_2 (the most characteristic or intense bands, used as markers to identify the cations in their mixtures, are underlined)

Compound	$\nu_{as}CH_2$			ν_sCH_2	δCH_2 scissor		δCH_2 waggle			$\nu_{as}CCl_2/\nu C$–Cl		$\nu_{as}(CClC)$	
CH_2Cl_2 (liquid)[22]		3045		2990	1424			1265vs			$\underline{739}$	—	
ClH_2C–{Cl_{11}}	3079	$\underline{3063}$		2978	1391	$\underline{1385}$		$\underline{1243}$vs			$\underline{793}$	—	
ClH_2C–Cl^+–CH_2Cl **IIa**	3073	$\underline{3064}$	3048	2980	1416 1409	1324		$\underline{1284vs}$	1248		$\underline{770}$	635	
ClH_2C–Cl^+–CH_2Cl **IIb**		$\underline{3044}$		2964br	1406	1338		$\underline{1283vs}$	1248 1226	798	$\underline{783}$	672	593
ClH_2C–Cl^+–CH_3		3044		2962	$\underline{1407}$	1386	1261	$\underline{1248s}$	1226		$\underline{786}$	[a]	
ClH_2C–Cl^+–CD_3		3044		2962	$\underline{1398}$	1387	1263	$\underline{1251s}$	1226		$\underline{787}$	[a]	

[a] Not determined.

Interaction of mono- and dichloromethane with H{Cl_{11}} and chloronium cations

CH_3Cl interacts with the H{Cl_{11}} acid in two stages. At first, it is protonated with the release of HCl and the formation of CH_3{Cl_{11}} (eqn (2)):

$$CH_3Cl + H\{Cl_{11}\} \rightarrow [CH_3Cl\text{–}H^+\{Cl_{11}\}] \rightarrow CH_3\{Cl_{11}\} + HCl \quad (2)$$

$$CH_3\{Cl_{11}\} + CH_3Cl \rightarrow (CH_3)_2Cl^+\{Cl_{11}{}^-\} \quad (3)$$

Then, CH_3Cl binds to CH_3{Cl_{11}}, thus forming $(CH_3)_2Cl^+${$Cl_{11}{}^-$} (eqn (3)). The formation of the resultant CH_3{Cl_{11}} can be observed by monitoring the intensity of the IR absorption of the released HCl (I_{HCl}). The amount of the resulting ion $(CH_3)_2Cl^+$ can be traced from the intensity of its band $\nu_{as}(CCl^+C)$ at 636 cm^{-1} (I_{636}; Fig. S4, ESI†). 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 CH_3Cl molecules to the acid, the rate of

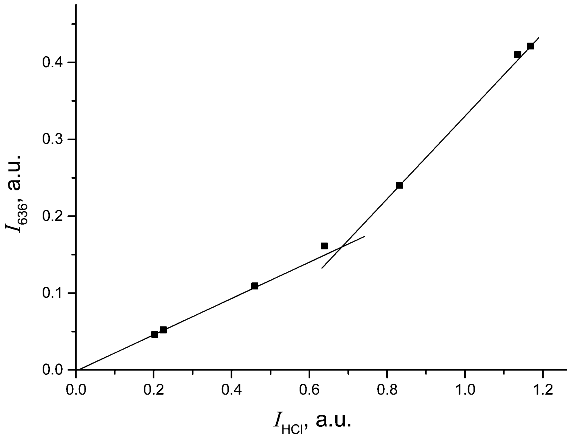

Fig. 4 Dependence of the intensity of band ν_{as}(CClC) at 636 cm^{-1} of the $(CH_3)_2Cl^+$ cation on the intensity of HCl absorption [reflects the dependence of the $(CH_3)_2Cl^+$ formation on the CH_3{Cl_{11}} formation].

$CH_3^+\{Cl_{11}^-\}$ formation decreases and the slope increases (Fig. 4). The cation of the ultimate salt $(CH_3)_2Cl^+\{Cl_{11}^-\}$ does not show any further interaction with CH_3Cl.

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 $CH_2Cl–\{Cl_{11}\}$ compound, which are formed in accordance with eqn (4):

$$CH_2Cl_2 + H\{Cl_{11}\} \rightarrow CH_2Cl–\{Cl_{11}\} + HCl \qquad (4)$$

The IR spectrum of $CH_2Cl–\{Cl_{11}\}$ 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_{HCl}) was used to quantify the total amount of the formed $CH_2Cl–\{Cl_{11}\}$, whereas intensity of the band of the terminal C–Cl stretch (I_{CCl}) reflects the current amount of this compound. Dependence of I_{CCl} on I_{HCl} was linear for the first 5 hours of the reaction (Fig. 6); this result means that only $CH_2Cl–\{Cl_{11}\}$ was formed. Then, the dependence started to drop (point 22 in Fig. 6), indicating the second stage of the reaction: involvement of $CH_2Cl–\{Cl_{11}\}$ in the formation of the $ClH_2C–Cl^+–CH_2Cl$ cation (eqn (5)).

$$CH_2Cl–\{Cl_{11}\} + CH_2Cl_2 \rightarrow ClH_2C–Cl^+–CH_2Cl. \qquad (5)$$

Extrapolation of I_{CCl} from I_{HCl} to the moment of the reaction stoppage (at the 1380th minute, when CH_2Cl_2 was pumped out) yields I_{CCl} = 0.084 (arbitrary units; Fig. 6). This value corresponds to the amount of $CH_2Cl–\{Cl_{11}\}$ that was formed in accordance with the amount of HCl production (eqn (4)). Nevertheless, because $CH_2Cl–\{Cl_{11}\}$ is further consumed (reaction (5)), I_{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 $(CH_2Cl)_2Cl^+$ was obtained by subtracting the spectrum of $CH_2Cl–\{Cl_{11}\}$ from the spectrum of the mixture of $(CH_2Cl)_2Cl^+$ with the $CH_2Cl–\{Cl_{11}\}$ up to complete compensation of the bands νCCl = 792 cm^{-1} and δCH_2 = 1243 cm^{-1}, which are specific to $CH_2Cl–\{Cl_{11}\}$ (Fig. 5, blue; Table 2). The frequencies of the $(CH_2Cl)_2Cl^+$ cation are very close to those of $CH_2Cl–\{Cl_{11}\}$ 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 $CH_2Cl–\{Cl_{11}\}$ as compound **I** and the $(CH_2Cl)_2Cl^+$ salt as compound **II.**

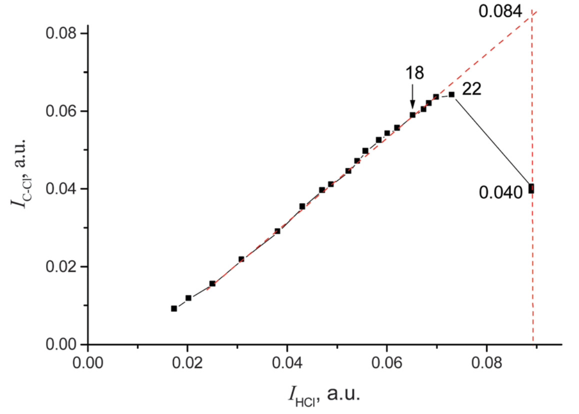

Fig. 6 Dependence of I_{CCl} on I_{HCl}, pointing to $ClH_2C–\{Cl_{11}\}$ formation and its further consumption on the formation of the $ClH_2C–Cl^+–CH_2Cl$ cation.

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_2Cl_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_2Cl_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†).

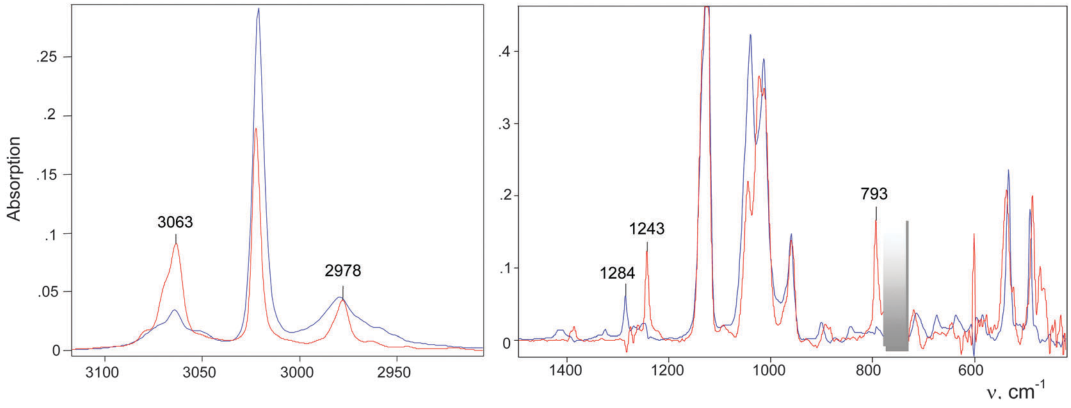

Fig. 5 IR spectra of the $CH_2Cl–\{Cl_{11}\}$ compound (red) and the salt of $CH_2Cl–Cl^+–CH_2Cl$ cation (blue). The spectra of unreacted $H\{Cl_{11}\}$ acid, gaseous HCl and CH_2Cl_2 were subtracted. The region of strong absorption of gaseous CH_2Cl_2 (C–Cl stretches), where compensation does not work, is shaded.

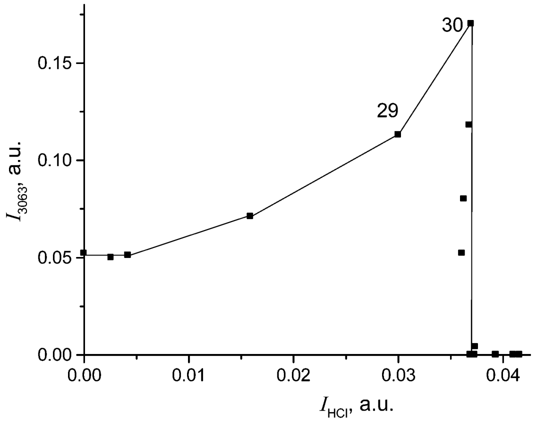

Fig. 7 Dependence of $CH_2Cl–\{Cl_{11}\}$ formation (determined by means of intensity of its band $\nu_{as}CH_2$ at 3063 cm^{-1}) on the amount of released HCl (determined by means of intensity of the νHCl band).

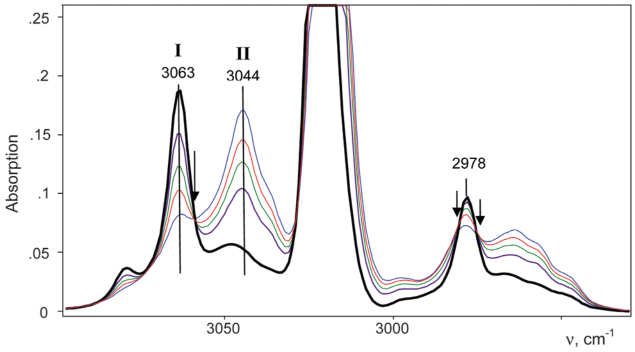

Fig. 8 A change in intensity of the IR spectra of compounds $CH_2Cl–\{Cl_{11}\}$ and $(CH_2Cl–Cl^+–CH_2Cl)\{Cl_{11}{}^-\}$ as reaction (5) proceeds. The arrows indicate isosbestic points. The spectrum of gaseous CH_2Cl_2 was subtracted.

The spectrum of the resultant cation **II** differed from that of the same cation formed during a slow reaction of $CH_2Cl–\{Cl_{11}\}$ with CH_2Cl_2 (Fig. 9 and Table 2). Thus, two isomers of $CH_2Cl–Cl^+–CH_2Cl$ 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 δCH_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 $CH_3–Cl^+–CH_2Cl$ 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 δCH_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 $(CH_3)_2Cl^+$ 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_2Cl_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).

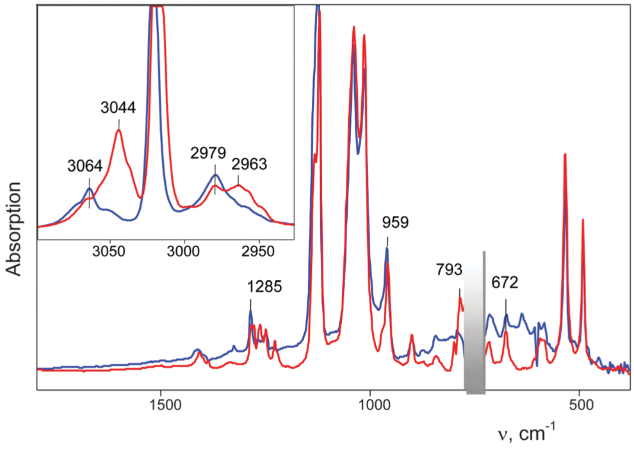

Fig. 9 IR spectra of $(CH_2Cl)_2Cl^+\{Cl_{11}\}$, formed by slow (**IIa**, some hours, blue) and quick interaction of $CH_2Cl–\{Cl_{11}\}$ with CH_2Cl_2 (**IIb**, some minutes, red). The region of strong absorption of gaseous CH_2Cl_2 (C–Cl stretches), where compensation does not work, is shaded.

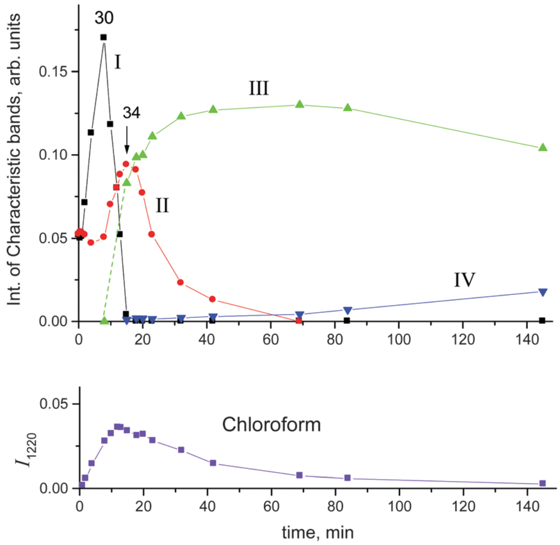

Fig. 10 Kinetic curves of the formation of compounds **I–IV** and chloroform; these curves were constructed by means of the intensity values of their bands at 3068 (compound **I**), 1284 (**II**), 1248 (**III**), 1322 (**IV**), and 1220 cm^{-1} (chloroform). Curves **I–IV** do not quantitatively indicate the proportion of a cation in the mixture of compounds **I–IV**.

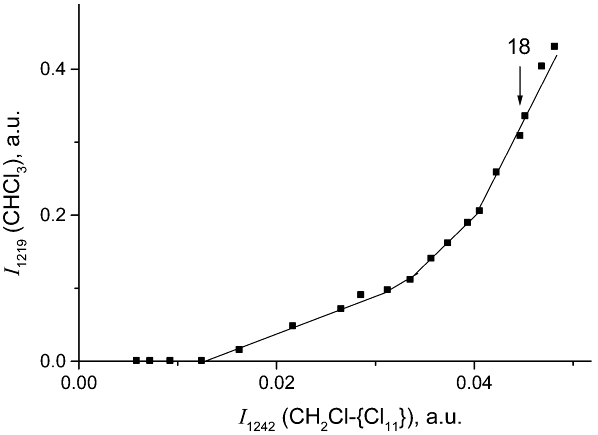

Fig. 11 Dependence of $CHCl_3$ formation (shown as intensity of the band at 1219 cm^{-1}) on CH_2Cl–{Cl_{11}} formation (indicated by intensity of its band at 1242 cm^{-1}) under the conditions when only compound **I** is formed. Cation **II** starts to form after point 18.

In the situation when only **I** is formed ($P_{CH_2Cl_2}$ = 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 $CH_3\{Cl_{11}\}$ (Fig. S6, ESI†). Hence, CH_2Cl_2 reacts with $CH_2Cl\{Cl_{11}\}$ according to eqn (6):

$$\underset{\text{Compound I}}{CH_2Cl\{Cl_{11}\}} + CH_2Cl_2 \rightarrow CH_3\{Cl_{11}\} + CHCl_3 \qquad (6)$$

With the rapid formation of $CH_2Cl\{Cl_{11}\}$ in reaction (4) at $P_{CH_2Cl_2}$ = 1 atm, chloroform is formed symbatically (Fig. 12), 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):

$$CH_2Cl–Cl^+–CH_2Cl + CHCl_3 \rightarrow CH_2Cl–Cl^+–CH_3 + CCl_4, \qquad (7)$$

(anions are omitted), which is suggestive of CCl_4 formation.

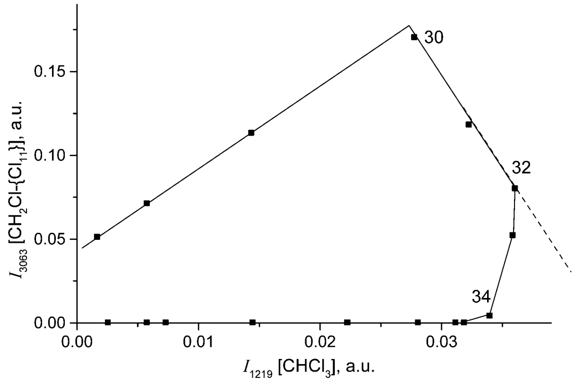

Fig. 12 The link between formation of CH_2Cl–{Cl_{11}} (indicated by intensity of its band at 3063 cm^{-1}) and $CHCl_3$ (indicated by intensity of its band at 1219 cm^{-1}).

In the same way, compound **IV** can form:

$$CH_2Cl–Cl^+–CH_3 + CHCl_3 \rightarrow CH_3–Cl^+–CH_3 + CCl_4, \qquad (8)$$

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:

$$\left.\begin{array}{ll}\mathbf{I} & \mathbf{CH_2Cl}–\{Cl_{11}\} \\ \mathbf{II} & \mathbf{CH_2Cl}–Cl^+–CH_2Cl \\ \mathbf{III} & \mathbf{CH_2Cl}–Cl^+–CH_3\end{array}\right\} + CH_2Cl_2/CHCl_3 \rightarrow \left.\begin{array}{ll} & \mathbf{CH_3}–\{Cl_{11}\} \\ \mathbf{III} & \mathbf{CH_3}–Cl^+–CH_2Cl \\ \mathbf{IV} & \mathbf{CH_3}–Cl^+–CH_3\end{array}\right\} + CHCl_3/CCl_4$$

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 $\nu_{as}CH_3$, 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_3–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 CH_3 groups in CH_3–{Cl_{11}} and (CH_3–Cl$^+$–CH_3){Cl_{11}^-} salts. If we now examine the salt (CH_3–Cl$^+$–CD_2Cl){Cl_{11}^-}, 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 {Cl_{11}^-} anions, thus increasing the covalency of the C–Cl$^+$–C group. In any case, the ionicity of the CH_3–Cl(–X) bond decreases in the following order:

$$\nu_{as}\mathrm{CH_3,\,cm^{-1}}\quad \underset{3071}{\mathrm{CH_3-\{Cl_{11}\}}} \sim \underset{3068}{\mathrm{CH_3-Cl^+(-CH_3)}}$$

$$> \underset{3054}{\mathrm{CH_3-Cl^+(-CD_2Cl)}} > \underset{3039}{\mathrm{CH_3Cl}}$$

Just as the methyl group in salts CH_3–{Cl_{11}} and (CH_3–Cl$^+$–CH_3){Cl_{11}^-}, the CH_2Cl group in salts ClH_2C–{Cl_{11}} and **IIa** shows identical CH stretch frequencies (Table 2). Probably, in the case of the slow formation (hours) of the (ClH_2C–Cl$^+$–CH_2Cl){Cl_{11}^-} 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 {Cl_{11}^-} anions. In the case of quick formation (minutes), the (ClH_2C–Cl$^+$–CH_2Cl){Cl_{11}^-} 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 CH_2Cl groups and their CH stretches. We named this salt "isomer **IIb**". Polarizability and CH frequencies of the CH_2Cl group of **IIb** coincide with those of the salt (ClH_2C–Cl$^+$–CH_3){Cl_{11}^-}. Thus, ionicity of the ClH_2C–Cl(–X) bond decreases in the following order:

$$\nu_{as}\mathrm{CH_2Cl,\,cm^{-1}}\quad \underset{3063}{\mathrm{ClH_2C-\{Cl_{11}\}}} \sim \underset{3064}{\mathbf{IIa}} > \underset{3044}{\mathbf{IIb}}$$

$$\sim \underset{3044}{\mathrm{ClH_2C-Cl^+(-CH_3)}}$$

in accordance with decreasing frequencies of CH stretches, which indicate the polarization of the ClH_2C 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 $(CH_3)_2Cl^+$ 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 (CD_3–Cl$^+$–CH_2Cl){Cl_{11}} 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**: CH_2Cl–Cl$^+$–CH_2Cl [labeled (2) in Fig. 13, red]. Weak bands of cations CD_2Cl–Cl$^+$–CD_2Cl and $(CH_3)_2Cl^+$ also appeared (labeled 2 and 3 respectively), as did the traces of HCl absorption.

In the range of CD stretch vibrations, the band $\nu_{as}CD_3$ = 2297 cm^{-1} of the cation CD_3–Cl$^+$–CH_2Cl was replaced with the intense $\nu_{as}CD_3$ band at 2307 cm^{-1} of the cation CD_3–Cl$^+$–CD_3. Thus, the CD_3–Cl$^+$–CH_2Cl 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)

$$2\mathrm{CD_3{-}Cl^+{-}CH_2Cl} \rightarrow \mathrm{CH_2Cl{-}Cl^+{-}CH_2Cl} + \mathrm{CD_3{-}Cl^+{-}CD_3} \tag{9}$$

$$2\mathrm{CD_3{-}Cl^+{-}CH_2Cl} \rightarrow \mathrm{CD_2Cl{-}Cl^+{-}CD_2Cl} + \mathrm{CH_3{-}Cl^+{-}CH_3} \tag{10}$$

The disproportionation looks as if at the chlorine atom, there is an intermolecular exchange of groups CD_3– and –CH_2Cl that is difficult to imagine for the solid phase. Intermediates with the molecular fragments CHDCl– and CH_2D– were not detected by IR spectroscopy.

Increased temperature. Heating of the salt (CH_3–Cl$^+$–CH_2Cl){Cl_{11}^-} to −100 °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 $(CH_3)_2Cl^+$ and isomer $(CH_2Cl)_2Cl^+$, **IIa** (with the marked

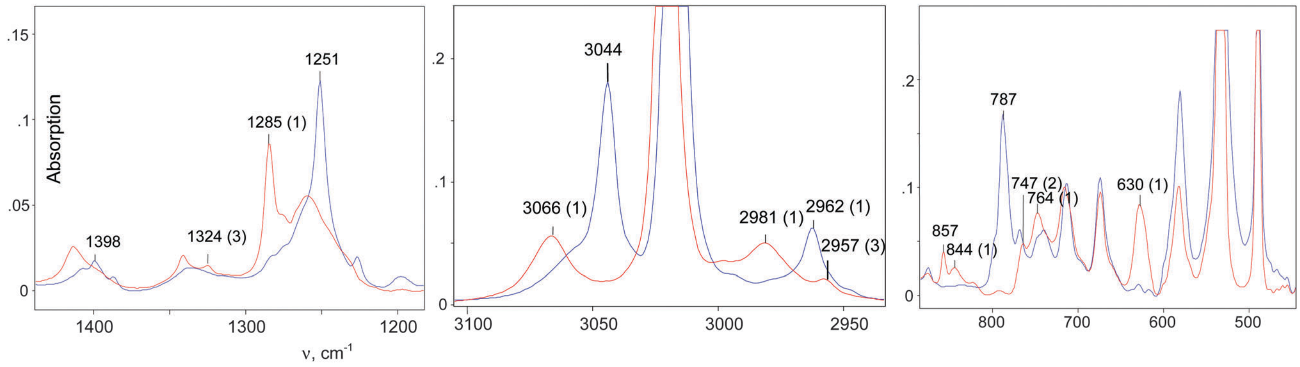

Fig. 13 IR spectra of the freshly prepared salt (CD_3–Cl$^+$–CH_2Cl){Cl_{11}} (blue) and after one or three days of storage (red). The bands of the cations $(CH_2Cl)_2Cl^+$, CD_2Cl–Cl$^+$–CD_2Cl and $(CH_3)_2Cl^+$ are marked respectively as (1), (2) and (3).

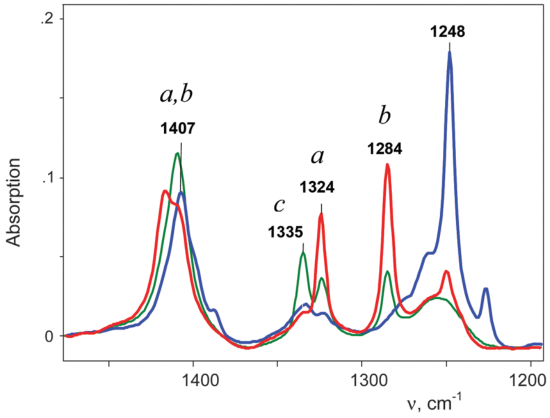

Fig. 14 IR spectra in the frequency region of CH bend vibrations of the salt $(CH_3{-}Cl^+{-}CH_2Cl)\{Cl_{11}^-\}$ before (blue) and after heating for 5 minutes at 100 °C (red) and 150 °C (green). The most characteristic bands of the formed compounds are marked with (a) for $(CH_3)_2Cl^+$, (b) for $(CH_2Cl)_2Cl^+$ (**IIa**) and (c) for $CH_3{-}\{Cl_{11}\}$.

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 $CH_3{-}Cl^+{-}CH_2Cl$ quickly disproportionates into the more stable symmetric cations:

$$2CH_3{-}Cl^+{-}CH_2Cl \rightarrow ClH_2C{-}Cl^+{-}CH_2Cl + CH_3{-}Cl^+{-}CH_3 \quad (11)$$

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 $(CH_3)_2Cl^+$ and $(CH_2Cl)_2Cl^+$, respectively, and appearance and an increase in intensity of the bands of $CH_3{-}\{Cl_{11}\}$ (1335 cm^{-1}: Fig. 14, green) and $ClH_2C{-}\{Cl_{11}\}$ (νCCl_{term} = 793 cm^{-1}). Additionally, bands with a rotational structure at 1270 and 761 cm^{-1} of gaseous CH_2Cl_2 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.

$$(CH_3{-}Cl^+{-}CH_2Cl)\{Cl_{11}^-\} \rightarrow CH_3{-}\{Cl_{11}\} + CH_2Cl_2 \quad (12)$$

$$(ClH_2C{-}Cl^+{-}CH_2Cl)\{Cl_{11}^-\} \rightarrow ClH_2C{-}\{Cl_{11}\} + CH_2Cl_2 \quad (13)$$

Longer heating of the sample at 150 °C did not enhance the spectrum of CH_2Cl_2. It remained virtually unchanged. In contrast, the bands of $CHCl_3$ 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 $CH_3\{Cl_{11}\}$ band at 1335 cm^{-1} and disappearance of the adsorption of $ClH_2C{-}\{Cl_{11}\}$. Taken together, our data indicate that the $CHCl_3$ formation is caused by the interaction of $ClH_2C{-}\{Cl_{11}\}$ with dichloromethane:

$$ClH_2C{-}\{Cl_{11}\} + CH_2Cl_2 \rightarrow CH_3{-}\{Cl_{11}\} + CHCl_3.$$

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

Conclusions

The salts of symmetric methylchloronium cations, $(CH_3)_2Cl^+\{Cl_{11}^-\}$ and $(CH_2Cl)_2Cl^+\{Cl_{11}^-\}$, and their neutral analogs $CH_3{-}\{Cl_{11}\}$ and $CH_2Cl{-}\{Cl_{11}\}$, are stable at ambient and increased temperatures. Nevertheless, the asymmetric cation $ClCH_2{-}Cl^+{-}CH_3$ even at ambient temperature disproportionates into symmetrical $(CH_3)_2Cl^+$ and $(CH_2Cl)_2Cl^+$. The molecular fragment $CH_2Cl{-}$ of the chloronium ions enters exchange reactions with CH_2Cl_2 and $CHCl_3$ with increasing reactivity in the order $ClCH_2{-}Cl^+{-}CH_3$, $ClCH_2{-}Cl^+{-}CH_2Cl$, and $CH_2Cl{-}\{Cl_{11}\}$, yielding more stable and less reactive $(CH_3)_2Cl^+\{Cl_{11}^-\}$ and $CH_3\{Cl_{11}\}$ compounds.

If we take into account the reactivity of $H\{Cl_{11}\}$ acid or its chloronium salts with CH_2Cl_2, and the simultaneous disproportionation of the $CH_3{-}Cl^+{-}CH_2Cl$ cation (eqn (11); initiated by the elevated temperature), then the end products of interactions at ambient, or slightly evaluated temperature, are the chemically inert $CH_3{-}Cl^+{-}CH_3$ and CCl_4:

$$\underset{\text{Starting compounds}}{H\{Cl_{11}\} + CH_2Cl_2}$$

$$\rightarrow \underset{\text{Intermediates}}{[CH_2Cl - \{Cl_{11}\}, CH_2Cl - Cl^+ - CH_2Cl, CH_2Cl - Cl^+ - CH_3]}$$

$$\rightarrow \underset{\text{End products}}{CH_3 - Cl^+ - CH_3 + CCl_4/CHCl_3}$$

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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