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Chemical Ionization Mass Spectrometry of Halomethanes with Tetramethylsilane as Reagent Gas

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Chemical ionization mass spectra of halomethanes measured using tetramethylsilane as reagent gas exhibit three major peaks corresponding to $[M + SiMe_3]^+$, $[M - X]^+$ and $(MeSi)_2X^+$ ions (X = Cl, Br or I). Dihalomethanes CH_2X_2 form the most stable silylated molecular ions, whereas in the mass spectra of tetrahalomethanes (CX_4) these ions have not been detected and the ions CX_3^+ are the most abundant. Production of bistrimethylsilylhalonium ions is the most pronounced process for haloforms (CHX_3).

INTRODUCTION

Tetramethylsilane has been widely used as a specific reagent gas in chemical ionization (CI) experiments with various organic compounds including haloalkanes.[1] Continuing these studies, we have examined reactions of the trimethylsilyl ion with halomethanes **1**–**8**:

CH_2X_2	CHX_3	CX_4
1 X = Cl	**4** X = Cl	**7** X = Cl
2 X = Br	**5** X = Br	**8** X = Br
3 X = I	**6** X = I	

EXPERIMENTAL

Mass spectra were obtained with a Kratos MS-30 double-beam instrument as described as previously.[1] Specimens were introduced through a gas chromatograph with a column temperature of 150 °C.

RESULTS AND DISCUSSION

The mass spectra of halomethanes **1**–**8** are presented in Table 1. Mainly the mass spectra exhibit two or three peaks, corresponding to ions $[M + SiMe_3]^+$, $[M - X]^+$ and $(Me_3Si)_2X^+$ (where X = Cl, Br or I). The relative abundances of the ions depend on the nature of halogen and number of halogen atoms in the molecule. The following regularities can be mentioned. The adduct ions $[CH_2X_2 + SiMe_3]^+$ formed from dihalomethanes do not eliminate trimethylsilyl halides yielding CH_2X^+ ions. Reactions (1)–(3) according to calculations[2] are endothermic. The heats of reactions differ insignificantly.

$$CH_2Cl_2 + Me_3Si^+ \rightarrow \overset{+}{C}H_2Cl + ClSiMe_3 + Q \qquad (1)$$
$$\Delta H_f^\circ \; -95.0 \quad 629.7 \quad 954.7 \quad -353.8$$
$$Q_{(1)} = (-95.0 + 629.7) - (954.7 - 353.8) = -66.2 \text{ kJ mol}^{-1}$$

$$CH_2Br_2 + Me_3Si^+ \rightarrow \overset{+}{C}H_2Br + BrSiMe_3 + Q \qquad (2)$$
$$\Delta H_f^\circ \; 10.0 \quad 629.7 \quad 938.1 \quad -293.2$$
$$Q_{(2)} = (10.0 + 629.7) - (938.1 - 193.2) = -50.2 \text{ kJ mol}^{-1}$$

$$CH_2I_2 + Me_3Si^+ \rightarrow \overset{+}{C}H_2I + ISiMe_3 + Q \qquad (3)$$
$$\Delta H_f^\circ \; 121.0 \quad 629.7 \quad 1034.2 \quad 218.0$$
$$Q_3 = (121.0 + 629.7) - (1034.2 - 218.0) = -65.55 \text{ kJ mol}^{-1}$$

Dihalomethanes in a tetramethylsilane plasma also form bis (trimethylsilyl)halonium ions, $(Me_3Si)_2X^+$, the abundance of which increases in the order **1** > **2** > **3**. Since $[CH_2X_2 + SiMe_3]^+$ ions do not decompose to produce CH_2X^+ (the corresponding peaks were not observed in the mass spectra presented in Table 1) and neutral trimethylsilyl halides, bis(trimethylsilyl)-

Table 1. Chemical ionization mass spectra of halomethanes 1–8 with tetramethylsilane as reagent gas

Ions	Relative abundance (%)[a]							
	CH_2Cl_2 (1)	CH_2Br_2 (2)	CH_2I_2 (3)	$CHCl_3$ (4)	$CHBr_3$ (5)	CHI_3 (6)	CCl_4 (7)	CBr_4 (8)
$[M + SiMe_3]^+$	100	100	100	8	50	50	—	—
$[M - X]^+$	—	—	—	5	5	100	100	100
$(Me_3Si)_2X^+$	13	46	55	100	100	100	12	60

[a] Sum of intensities of isotopic peaks for chloro and bromo derivatives.

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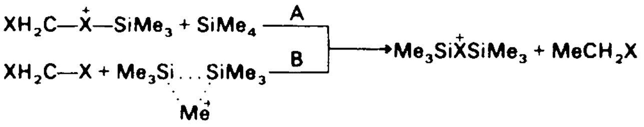
halonium ions could hardly be formed through trimethylsilylation of the latter. Possibly halonium ions $(Me_3Si)_2X^+$ result either through collisions of $[M + SiMe_3]^+$ adducts with neutral tetramethylsilane molecules or through reaction of $Si_2Me_7^+$ ions (*m/z* 161), which are present in the tetramethylsilane plasma,[3] with substrate molecule CH_2X_2, shown on Scheme 1.



Scheme 1

To eliminate this ambiguity, some experiments were undertaken. An attempt to use ion cyclotron resonance (ICR) to solve this problem (with the aid of the double resonance technique) proved to be unsuccessful, because at the low pressure necessary for normal work with the ICR cell, no the halonium ions $(Me_3Si)_2X^+$ were produced.

A decrease in the reagent gas pressure in the ionization chamber in CI experiments led to a decrease in the abundances of both ions. The abundance of the halonium ions decreased more sharply with decrease in pressure, and the corresponding peaks disappeared earlier than the peaks of the $Me_7Si_2^+$ ions. This result seemed to indicate that path B in Scheme 1 is operative. However, the observations may also be interpreted in terms of instability of both types of ions at low pressures. The ions can dissociate at a high rate because an insufficient number of collisions with neutral molecules does not provide an efficient route for the dissipation of the excess internal energy of the ions. To test this possibility, the pressure in the ionization chamber was increased by means of the additional introduction of methane. An increase in the abundances of both ions resulted, thus confirming the above considerations. We conclude that both mechanisms can be responsible for the halonium ion formation under the CI conditions used.

Haloforms CHX_3 (**4**–**6**) in a tetramethylsilane plasma afford mainly bis(trimethylsilyl)halonium ions. Adducts $[CHX_3 + SiMe_3]^+$ are less abundant and eliminate Me_3SiX, yielding $[M - X]^+$ ions. Calculations of the heats of reactions (4) and (5) show that they are slightly exothermic. Unfortunately, a lack of corresponding thermochemical data does not allow the heat of reaction between iodoform and trimethylsilyl cation to be detected.

$$\begin{array}{lllll} & CHCl_3 + Me_3Si^+ & \rightarrow CHCl_2^+ & + ClSiMe_3 & + Q \quad (4) \\ \Delta H_f^\circ & -102.7 \quad 629.7 & \quad 862.5 & -353.8 & \end{array}$$

$$Q_{(4)} = (-102.7 + 629.7) - (862.5 - 353.8) = 18.3 \text{ kJ mol}^{-1}$$

$$\begin{array}{lllll} & CHBr_3 + Me_3Si^+ & \rightarrow CHBr_2^+ & + BrSiMe_3 & + Q \quad (5) \\ \Delta H_f^\circ & 60.0 \quad 629.7 & \quad 971.4 & -293.2 & \end{array}$$

$$Q_{(5)} = (60 + 629.7) - (971.4 - 293.2) = 11.5 \text{ kJ mol}^{-1}$$

For carbon tetrachloride and carbon tetrabromide, $[M + SiMe_3]^+$ ions are unstable and the corresponding peaks are absent from the mass spectra. The CX_3^+ ions are the most abundant. Their abundances are significantly higher than those of bis(trimethylsilyl)halonium ions. Reactions (6) and (7), as demonstrated by thermochemical calculations, are strongly exothermic

$$\begin{array}{lllll} & CCl_4 + Me_3Si^+ & \rightarrow {}^+CCl_3 & + ClSiMe_3 & + Q \quad (6) \\ \Delta H_f^\circ & -95.6 \quad 629.7 & \quad 833.2 & -353.8 & \end{array}$$

$$Q_{(6)} = (-95.6 + 629.7) - (833.2 - 353.8) = 54.7 \text{ kJ mol}^{-1}$$

$$\begin{array}{lllll} & CBr_4 + Me_3Si^+ & \rightarrow {}^+CBr_3 & + BrSiMe_3 & + Q \quad (7) \\ \Delta H_f^\circ & 120.0 \quad 629.7 & \quad 983.1 & -293.2 & \end{array}$$

$$Q_{(7)} = (120.0 - 629.7) - (983.1 - 293.2) = 59.8 \text{ kJ mol}^{-1}$$

Thus, the chemical ionization mass spectra of di-, tri- and tetrahalomethanes are very characteristic: for CH_2X_2 the base peak corresponds to $[M + SiMe_3]^+$ ions, for CHX_3 to bis(trimethylsilyl)halonium ions and for CX_4 to fragments $[M - X]^+$.

In the same mass spectra very faint peaks of $(Me_3Si)_2X_2^{+\cdot}$ ions (less than 1%) were observed. Possibly these ions are formed by reaction of bis(trimethyl)-halonium ions with substrates, e.g. according to

$$Me_3Si\overset{+}{Br}SiMe_3 + CH_2Br_2 \rightarrow Si_2Br_2Me_6^{+\cdot} + CH_2Br^\cdot$$

To characterize semiquantitatively the reactivities of various halomethanes toward trimethylsilyl cation, we used the method described previously,[1] i.e. measuring the chemical ionization mass spectra for equal concentrations of dichloromethane and halides **2**–**8**. The results are presented in Table 2.

Table 2. Intensity ratios $I_{[M+SiMe_3]^+}/I_{[CH_2Cl_2+SiMe_3]^+}$, $I_{(SiMe_3)_2X^+}/I_{[CH_2Cl_2+SiMe_3]^+}$ and $I_{([M+SiMe_3]^+ + (SiMe_3)_2X^+ + [M-X]^+)}/I_{([CH_2Cl_2+SiMe_3]^+ + (SiMe_3)_2X^+)}$ obtained for equal concentrations of halomethanes 1–8 in the ionization chamber

Compound	$\frac{I_{[M+SiMe3]^+}}{I_{[CH2Cl2+SiMe3]^+}}$	$\frac{I_{(SiMe3)2X^+}}{I_{[CH2Cl2+SiMe3]^+}}$	$\frac{I_{([M+SiMe3]^+ + (SiMe3)2X^+ + [M-X]^+)}}{I_{([CH2Cl2+SiMe3]^+ + (SiMe3)2Cl^+)}}$
CH_2Cl_2 (**1**)	1	0.1	1
$CHCl_3$ (**4**)	0.8	10	10
CCl_4 (**7**)	—	12	100
CH_2Br_2 (**2**)	18	8.4	24
$CHBr_3$ (**5**)	5	10	15
CBr_4 (**8**)	—	35	75
CH_2I_2 (**3**)	21	12	29
CHI_3 (**6**)	15	30	67

As mentioned above, in the mass spectra of dihalomethanes only two peaks corresponding to $[M + SiMe_3]^+$ and $(Me_3Si)_2X^+$ ions were detected, two pathways being possible for the formation of the latter (Scheme 1). If halonium ions arise only by path B, the ratios $I_{[CH_2X_2+SiMe_3]^+}/I_{[CH_2Cl_2+SiMe_3]^+}$ should not be affected by this process and these values should be approximately equal to the relative basicities of the dihalomethanes. If the formation of halonium ions were to proceed to some extent along path A, some of the ions $[CH_2X_2 + SiMe_3]^+$ could be converted into halonium ions, and the observed relative abundances would be lower than the relative basicities. In this case the ratio $I_{\Sigma M}/I_{\Sigma CH_2Cl_2}$ should be closer to the real value. The first assumption led to a ratio of 1:18:21 for the relative basicities of dichloromethane, dibromomethane and diiodomethane toward Me_3Si^+ ion, whereas the ratio would be 1:24:29 (Table 2) if the second assumption is valid. Both estimations give similar results, indicating a large difference in basicity between dichloromethane and dibromomethane, whereas the basicities of dibromomethane and diiodomethane are close.

An estimation of the relative basicities of haloforms from the data in Table 2 is more difficult, since the formation of $[CHX_3 + SiMe_3]^+$ ions is only a minor process for these compounds. However, comparison of the data in the first and third columns gives a ratio from 1:6.25:18.75 to 1:1.5:6.7 for the relative basicities of chloroform, bromoform and iodoform. Hence the basicities of haloforms qualitatively follow the same pattern as those of dihalomethanes.

Since tetrachloromethane and tetrabromomethane form very unstable $[CX_4 + SiMe_3]^+$ ions, the data in Table 2 cannot be used for the estimation of the relative basicities of these compounds. However, it should be noted that the total ion current increases by approximately two orders of magnitude on passing from CH_2Cl_2 to CCl_4 and CBr_4 (column 3 in Table 2). Hence the low critical energy of decomposition of $[CX_4 + SiMe_3]^+$ ions leads to a significant increase in the sensitivity of detection of tetrahalomethanes by chemical ionization mass spectrometry with tetramethylsilane as reagent gas.

REFERENCES

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