Investigations of Halonium lons in the Gas Phase

Jane Hollis, John M. Tedder and G. Stewart Walker *,†

Department of Chemistry, St. Andrews University, St. Andrews, Fife, KY16 9ST, Scotland

The mechanisms involved in the formation of monomethyl halonium and dimethyl halonium ions in the gas phase have been investigated using a triple quadrupole mass spectrometer and a quinqua quadrupole mass spectrometer. The results indicate that the mechanism for formation of the halonium ions is analogous to the $S_N 2$ nucleophilic addition with elimination mechanism previously reported for the formation of oxonium ions.

In a recent paper¹ the mechanism involved in the formation of oxonium ions was discussed. A general reaction scheme, Fig. 1, was found to apply where R^1 , R^2 , R^3 , R^4 and R^5 were CH_3^- , CD_3^- , $C_2H_5^-$, H or D, O¹ and O² were ¹⁶O or ¹⁸O.

This work has been extended to include the investigation of the reactions of halogenomethanes.

Alkyl halonium ions, $R-X-H^+$ and dialkyl halonium ions $(R^1-X-R^2)^+$, have been observed as rearrangement products from electron impact mass spectrometer ² and in ion cyclotron resonance studies of ion reactions.³

The detection of an additional NMR signal in superacids has revealed the formation of dialkyl halonium ions.⁴

$$2RX + SbF_5 - SO_2 \xrightarrow[-60°C]{SO_2} R - X^+ - RSbF_5 X^-$$

excess (X = Cl, Br or I)

Dimethyl and diethyl halonium ions, prepared in this way, have been found to be effective alkylating agents in the solution phase. $^{5-12}$

Gas-phase studies of alkyl halonium ions have developed over the last twenty years. McAskill studied the energy dependence of ion-molecule reactions of methane and halogenomethanes using a high pressure ion cyclotron resonance mass spectrometer.¹³⁻¹⁵ In addition to CH_2Cl^+ , CH_3Cl^+ and CH_3ClH^+ ions very small quantities of $C_2H_3^+$ and $C_2H_5^+$ ions and an ion that was assigned the structure of protonated ethyl chloride, $C_2H_5Cl-H^+$, were observed. Similar results were reported for fluoromethane and the ion, $C_2H_6F^+$, was described as protonated fluoroethane.

Kebarle and co-workers, in a series of papers from 1978 to 1986, have studied the gas-phase binding energy and stability of chloronium ions from consideration of the gas-phase equilibria.¹⁶⁻²² In all papers they considered the $C_2H_6Cl^+$ ion to be dimethyl chloronium ion rather than protonated chloroethane.

In 1986 a report of dimethyl fluoronium ions and the protonbound dimer of fluoromethane in the gas phase was presented by McMahon and Kebarle.²³

Dimethyl iodonium ions have been reported and used for gas-phase methylation of organic functional groups.²⁴

In these reports the methyl halonium ions were formed by electron impact on halogenomethane and methane gases at a pressure of ca. 1 Torr.[‡]

Using the triple and quinqua quadrupole mass spectrometers the reactions involved in the formation of methyl halonium ions at low pressures, and the subsequent reactions of methyl



Fig. 1 General reaction scheme



Fig. 2 Schematic diagram of triple quadrupole mass spectrometer



Fig. 3 Schematic diagram of quinqua quadrupole mass spectrometer

halonium ions with other molecules, can be studied. Because of the ability of the multi-quadrupole mass spectrometers to isolate ions and react them with other gases, reactions involving different halonium ions and oxonium ions could be used to help elucidate the mechanisms involved. The purpose of the work described in this paper was to investigate the formation and reactions of methyl halonium ions.

Experimental

The triple quadrupole mass spectrometer, Fig. 2, and the quinqua quadrupole mass spectrometer, Fig. 3, that were used have been described in the literature.^{1,25}

Ions formed in the ionisation chamber were analysed by using the first quadrupole as a mass analyser. Ions of one mass were separated and allowed into the second quadrupole by

[†] Present address: CSIRO, Division of Coal and Energy Technology Private Mail Bag 7, Menai, 2234 NSW, Australia.

 $[\]ddagger 1 \text{ Torr} = 133.322 \text{ Pa.}$



Fig. 4 Fragments ions from CH₃ClH⁺



Fig. 5 Fragments ions from CH₃ClD⁺

operating the first quadrupole as a mass filter. An α -target gas was allowed into the second quadrupole by means of the α -gas inlet. The ions produced in the reaction of the α -primary ion with the α -target gas were called α -secondary ions and were analysed in the third quadrupole. In the quinqua quadrupole mass spectrometer these α -secondary ions could be separated from the other ions, by operating the third quadrupole as a mass filter, and passed into the fourth quadrupole in which a β -target gas had been admitted through the β -gas inlet. The products from this reaction, β -secondary ions, were analysed by operating the fifth quadrupole as a mass analyser. In this way sequential ion-molecule reactions were investigated in the pressure range of $10^{-6}-10^{-3}$ Torr.

All gases and liquids used were commercially available at >99% purity and were used without further purification, except fluoromethane which was synthesised using the method of Kamm and Marvel.²⁶

Results

The results of these experiments are presented in Tables 1 to 10. In these tables the amounts of each product ion (as a percentage of the total amount of product ions) and the amounts of unreacted primary ion are given at a range of pressures as monitored by a Penning Gauge mounted in the second quadrupole mass spectrometer. These pressures should not be taken as absolute values but can be used for internal comparison of results. The results are corrected to incorporate the isotopes of chlorine and bromine unless the relative amount of the isotopes was relevant to the experiment.

Discussion

The reaction of CHO⁺, CDO⁺, CH¹⁸O⁺ and CH₂N⁺ ions with the halogenomethanes, CH₃X, produced similar, but not identical, results. The formation of CH₂X⁺, CH₃⁺ and CH₃XH⁺ ions indicated that the first reaction was the protonation of the halogenomethane to form CH₃XH⁺ which subsequently fragmented.



The reaction of ions with chloromethane will be discussed in detail below. The reactions of the other halogenomethanes will be summarised.

Protonation of Chloromethane.—The reaction of CDO^+ and CH_2N^+ ions with chloromethane produced deuteronated and protonated CH_3Cl respectively. The fragments from the ions CH_3ClH^+ and CH_3ClD^+ were studied in order to determine the site of protonation. If the halogen was the site of protonation a 1,2 elimination would result in a preference for the formation of CH_2Cl^+ ions and HD as a neutral compound.

 $CH_3Cl - D^+ \longrightarrow CH_2Cl^+ + HD$

If the extra proton was attached not to the halogen, but to the carbon in a pentacoordinate structure, such as those suggested for CH_5^+ ions, then elimination of H_2 or HD could occur to give $CHDCl^+$ or CH_2Cl^+ respectively, and one would expect to observe a mixture of product ions.



If the deuterium was on the chlorine the elimination of DCl would produce CH_3^+ (m/z = 15), whereas, if the deuterium was on the carbon, or was mobile, then the elimination of HCl and production of CH_2D^+ ions (m/z = 16) would also be observed.

The results of these experiments are presented in Figs. 4 and 5. They show that, apart from a small amount of CHDCl⁺ ion formation, which could arise from H/D exchange prior to fragmentation, almost all of the CH₃ClD⁺ ions produced CH₂Cl⁺ ions with the elimination of HD. In addition the production of CH₂D⁺ ions was found to be minimal (0.6%) compared with CH₃⁺ ions (32%). These results support the initial protonation taking place on the halogen to produce (CH₃-Cl-H)⁺ ions.

Reactions of Ions with Chloromethane.—The reaction of CDO⁺ and CH₂N⁺ ions with chloromethane produced CH₂Cl⁺, CH₃⁺ and CH₃ClH⁺ ions at the lower pressures (Table 1). Dimethyl chloronium ions were observed at the higher pressures. Two mechanisms were proposed to account for the formation of dimethyl chloronium ions. Mechanism (1) involved the direct addition of the methyl cation to a neutral chloromethane molecule and collision deactivation to form a stable addition complex.

Mechanism (1)

$$CHO^{+} + CH_{3}CI \longrightarrow CO + CH_{3}CIH^{+}$$
$$CH_{3}CIH^{+} \longrightarrow HCI + CH_{3}^{+}$$

Table 1 % Ion current for $CH_2N^+ + CH_3Cl$ at various pressures

| | Ion | | Unchanged | | | |
|--------------------------------|------------------------------|---------------------------------|----------------------------------|---|------------------------|---------------|
| Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | CH ₂ Cl ⁺ | CH ₃ ClH ⁺ | (CH ₃) ₂ Cl ⁺ | Impurity (O^+/O_2^+) | CH_2N^+ (%) |
| 2.3 | 89.4 | 2.8 | 6.4 | 0.0 | 1.4 | 98.1 |
| 5.3 | 73.7 | 8.1 | 14.6 | 1.7 | 1.9 | 92.3 |
| 7.5 | 54.7 | 15.9 | 21.6 | 4.7 | 3.1 | 86.5 |
| 45 | 22.5 | 28.0 | 20.9 | 23.9 | 4.7 | 73.2 |
| 75 | 6.0 | 24.9 | 16.1 | 47.7 | 5.4 | 61.7 |

Table 2 % Ion current for $CH_3^+ + CH_3Cl$ at various pressures

| | Ion | | | | | |
|--------------------------------|---|---------------------------------|----------------------------------|---|---------------|---|
| Pressure/10 ⁻⁵ Torr | $\frac{C_2 H_n^+}{(n=3 \text{ or } 5)}$ | CH ₂ Cl ⁺ | CH ₃ ClH ⁺ | (CH ₃) ₂ Cl ⁺ | Minor ions | Unchanged CH ₃ ⁺ (%) |
| 1.5 | 22.8 | 73.4 | 3.4 | 0.0 | 0.4 | 99.7 |
| 3.0 | 17.9 | 77.9 | 3.3 | 0.2 | 0.8 | 99.3 |
| 4.5 | 15.3 | 79.9 | 4.0 | 0.3 | 0.6 | 98.6 |
| 6.0 | 14.4 | 80.8 | 3.8 | 0.5 | 0.6 | 97.8 |
| 7.5 | 12.9 | 81.5 | 4.3 | 0.7 | 0.6 | 96.7 |



Fig. 6 % Secondary ion current vs. pressure for CDO⁺ into CH₃Cl

$$CH_3^+ + CH_3Cl \longrightarrow [C_2H_6Cl]^{*+}$$
$$[C_2H_6Cl]^{*+} + M \longrightarrow CH_3^+CH_3^+CH_3 + M^*$$

Mechanism (2) involved the addition of a monomethyl chloronium ion to a neutral chloromethane molecule with elimination of HCl.

Mechanism (2)

$$CHO^{+} + CH_{3}Cl \longrightarrow CO + CH_{3}ClH^{+}$$
$$CH_{3}ClH^{+} + CH_{3}Cl \longrightarrow CH_{3}-Cl-CH_{3}^{+} + HCl$$

It would be expected that an increase in the amount of the product ion, $CH_3ClCH_3^+$, would be matched by a decrease in the amount of the parent ion, either CH_3^+ , in the case of mechanism (1), or CH_3ClH^+ , in the case of mechanism (2). But, as both CH_3^+ and CH_3ClH^+ ions were present as secondary ions (see Fig. 6 and Table 1) and diminished with the increase of $CH_3ClCH_3^+$ ions, it was not possible to ascertain from these results which of the two proposed mechanisms was operating.

One of the constraints of the multiple quadrupole system is that ions can take between 30 and 60 μ s to travel from the point of reaction to the detector. This is a drawback of the quadrupole system which prevents the elucidation of the mechanism by probing the early stages of the reaction. However, one of the advantages of the multiple quadrupole system is its ability to separate specific ions for reaction with specific neutral molecules. This was used to advantage in the following experiments to determine which mechanism was responsible for the formation of dimethyl halonium ions.

(a) $CH_3^+ + CH_3Cl$. The dominant reaction was a hydride abstraction to form methane and CH_2Cl^+ ions. (See Table 2.)

$$CH_3^+ + CH_3Cl \longrightarrow CH_4 + CH_2Cl^+ max = 90\%$$

(A halide abstraction would not be detected because the product ion would be the same as the primary ion.)

$$CH_3^+ + CH_3Cl \longrightarrow CH_3Cl + CH_3^+$$

Also present were ions of m/z 27 (C₂H₃⁺; max = 12%), 29 (C₂H₅⁺; max = 3%), 39 (C₃H₃⁺; max = 0.4%), 41 (C₃H₅⁺; max = 0.1%), 49/51 (CH₂Cl⁺; max = 90%), 51/53 (CH₃ClH⁺; max = 5%) and 65/67 (C₂H₆Cl⁺; max = 2%).

(b) $CD_3^+ + CH_3Cl$. Monomethyl chloronium ions and dimethyl chloronium ions were observed, but with no deuterium incorporated. That the reaction of CD_3^+ with chloromethane did not produce any deuteronated dimethyl chloronium ions, $CD_3ClCH_3^+$ indicates that dimethyl chloronium ions are not formed by direct addition of methyl cations to chloromethane.

$$CD_3^+ + CH_3Cl \longrightarrow CD_3 - CD_3 - CH_3$$

The most abundant ion was CH_2Cl^+ , formed by hydride abstraction. This is analogous to the initial stages of the reaction of methyl cations with methanol.

$$CH_3^+ + CH_3X \longrightarrow CH_4 + CH_2X^+ (X = OH \text{ or } CI)$$

With X = OH the product ion CH_2OH^+ goes on to protonate methanol to produce the monomethyl oxonium ion (protonated methanol) which reacts with another molecule of methanol to produce the dimethyl oxonium ion (protonated dimethyl ether).

$$CH_2OH^+ + CH_3OH \longrightarrow H_2CO + CH_3OH_2^+$$

 $CH_3OH_2^+ + CH_3OH \longrightarrow H_2O + (CH_3)_2OH^+$

| | Ion | | | | | |
|--------------------------------|------------------------------|--------------------------------|---------------------------------|--|------------|--|
| Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | CH ₂ F ⁺ | CH ₃ FH ⁺ | (CH ₃) ₂ F ⁺ | Minor ions | Unchanged CH ¹⁸ O ⁺ (%) |
| 0.75 | 60.0 | 12.5 | 27.5 | 0.0 | 0.0 | 99.6 |
| 2.3 | 51.0 | 17.5 | 23.5 | 8.1 | 0.0 | 98.5 |
| 6.0 | 42.9 | 22.8 | 19.7 | 14.6 | 0.0 | 97.1 |
| 7.5 | 38.3 | 25.9 | 17.9 | 17.9 | 0.0 | 96.3 |
| 45.0 | 12.5 | 31.8 | 7.9 | 33.7 | 14.1 | 69.5 |

Table 3 % Ion current for $CH^{18}O^+ + CH_3F$ at various pressures

This latter reaction is not feasible with X = Cl because CH_2Cl^+ does not protonate chloromethane.

$$CH_2Cl^+ + CH_3Cl \longrightarrow [HCCl] + CH_3ClH^+$$

The reaction of CH_2Cl^+ with CH_3Cl was carried out using $CH_2^{35}Cl^+$ and $CH_2^{37}Cl^+$ ions. With $CH_2^{35}Cl^+$ ions the only two ions observed were primary ion $CH_2^{35}Cl^+$ (m/z = 49) and $CH_2^{37}Cl^+$ (m/z = 51) formed by a hydride abstraction reaction.

$$CH_2{}^{35}Cl^+ + CH_3{}^{35/37}Cl \longrightarrow CH_3{}^{35}Cl + CH_2{}^{35/37}Cl^+$$

 $m/z = 49$ $m/z = 49/51$

With $CH_2^{37}Cl^+$ ions the same two ions were observed: primary ion $CH_2^{37}Cl^+$ (m/z = 51) and $CH_2^{35}Cl^+$ (m/z = 49) formed by a hydride abstraction reaction.

$$CH_2{}^{37}Cl^+ + CH_3{}^{35/37}Cl \longrightarrow CH_3{}^{37}Cl + CH_2{}^{35/37}Cl^+$$

 $m/z = 51$ $m/z = 49/51$

The question remains as to the mechanism of formation of the monomethyl and dimethyl chloronium ions in the reaction of methyl ions and chloromethane. The direct addition of methyl cation to chloromethane and the protonation of chloromethane by CH_2Cl^+ ions have been ruled out. The other ions present in the system that could be responsible for the formation of the monomethyl chloronium ions were the $C_2H_3^+$ and the $C_2H_5^+$ ions. In subsequent experiments the $C_2H_3^+$ and the $C_2H_5^+$ ions were generated from ethane in the ion source of the triple quadrupole mass spectrometer and reacted with chloromethane. In both reactions monomethyl chloronium ions were major ionic products at lower pressures.

$$C_{2}H_{5}^{+} + CH_{3}Cl \longrightarrow C_{2}H_{4} + CH_{3}ClH^{+}$$
$$C_{2}H_{3}^{+} + CH_{3}Cl \longrightarrow C_{2}H_{2} + CH_{3}ClH^{+}$$

Dimethyl chloronium ions were observed and became the largest product at the highest pressures. This leads to the conclusion that dimethyl chloronium ions are formed by the reaction of methyl cations with chloromethane by the reaction route outlined below.



Reactions of Ions with Halogenomethanes.—The reactions of $CH^{18}O^+$, CH_2N^+ , CH_3^+ and CD_3^+ ions with the other halogenomethanes were studied (see Table 3). The results were essentially identical with those for chloromethane and involved the protonation of halogenomethane, the fragmentation of monomethyl halonium ion and the reaction of monomethyl halonium ions with halogenomethane to form dimethyl halonium ions and HX.





The main difference between the reactions of the halogenomethanes are outlined below.

(a) Fluoromethane. The main difference in the reactions of fluoromethane was that the CH_2F^+ ion reacted with CH_3F to produce some minor ions whereas CH_2Cl^+ ions were shown to be effectively unreactive towards CH_3Cl .

The reaction of CH_2F^+ (isolated from other ions in the first quadrupole) with CH_3F (in the second quadrupole) produced many of the minor ions that had been present in the previous experiments. The most abundant ion was CH_3^+ which could arise from halide abstraction.

$$CH_2F^+ + CH_3F \longrightarrow CH_2F_2 + CH_3^+$$

The CH_3^+ ions went on to react with more fluoromethane to produce $C_2H_5^+$ and $C_2H_3^+$ ions.

$$CH_3^+ + CH_3F \longrightarrow HF + C_2H_5^+ \longrightarrow H_2 + C_2H_3^+$$

The ions of m/z 31 arose from the fragmentation of the CH_2F^+ ions to CF^+ ions.

 $CH_2F^+ \longrightarrow CF^+ + H_2$

Other ions arose from the addition with fragmentation reactions of CH_2F^+ ions with CH_3F .

Ions of m/z 61 and 77 were observed at higher pressures indicating that they were tertiary ions. They can be accounted for by the reactions of secondary ions with fluoromethane.

Table 4 % Ion current for $CH_2N^+ + CH_3Br$ at various pressures

| | | Ion | | | Unchanged | | |
|---------|--------------------------------|------------------------------|-------------------------------|---------------------------------|----------------------------------|-------------------|----------------------|
| | Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | H ₃ O ⁺ | CH ₂ Br ⁺ | CH ₃ BrH ⁺ | $(CH_3)_2Br^+$ | CH_2N^+ (%) |
| <u></u> | 5.3 11.0 45.0 | 37.1 29.1 16.9 | 42.0 52.1 62.0 | 2.9 5.3 5.5 | 18.0 13.5 11.4 | 0.0 0.0 4.2 | 99.2 98.1 95.3 |

Table 5 % Ion current for $CH_3^+ + CH_3Br$ at various pressures

| | | Ion | | | | | | |
|--------------------------------|-----------------------------|---------------------------------|----------------------------------|----------------------------------|---|---------------|------------------------|--|
| Pressure/10 ⁻⁵ Torr | $C_2 H_n^+$ (n = 3 or 5) | CH ₂ Br ⁺ | CH ₃ Br ^{+•} | CH ₃ BrH ⁺ | (CH ₃) ₂ Br ⁺ | Minor ions | Unchanged CH_3^+ (%) | |
| 2.3 | 42.1 | 31.6 | 21.1 | 0.0 | 0.0 | 5.2 | 99.8 | |
| 5.3 | 34.8 | 40.7 | 21.2 | 0.0 | 0.0 | 3.3 | 98.8 | |
| 11.0 | 33.5 | 39.5 | 19.7 | 2.6 | 0.0 | 4.7 | 98.5 | |
| 45.0 | 28.5 | 38.5 | 19 | 2.8 | 2.62 | 8.6 | 96.4 | |

Table 6 % Ion current for $CH_2N^+ + CH_3I$ at various pressures

| | Ion | | | | Unchenned |
|--------------------------------|------------------------------|------|--------------------------------|---------------------------------|---------------|
| Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | I+ | CH ₃ I ⁺ | CH ₃ IH ⁺ | CH_2N^+ (%) |
| 3.8 | 16.4 | 0.00 | 27.9 | 55.8 | 99.4 |
| 7.5 | 9.73 | 14.2 | 23.9 | 52.2 | 98.9 |
| 26.0 | 0.00 | 0.00 | 25.2 | 74.9 | 98.4 |

$$CH_{2}F^{*} + CH_{3}F \longrightarrow [C_{2}H_{5}F_{2}]^{*} \longrightarrow CHF_{2}^{*} (m/z = 51) + CH_{4}$$

$$C_{2}H_{4}F^{*} (m/z = 47) + HF$$

$$\downarrow$$

$$C_{2}H_{2}F^{*} (m/z = 45) + H_{2}$$

$$\downarrow$$

$$C_{2}F^{*} (m/z = 43) + H_{2}$$

$$C_{2}H_{4}F^{+} + CH_{3}F \longrightarrow [C_{3}H_{7}F_{2}]^{*+} \longrightarrow C_{3}H_{6}F^{+}$$

$$(m/z = 61) + HF$$

$$C_{2}H_{2}F^{+} + CH_{3}F \longrightarrow [C_{3}H_{5}F_{2}]^{*+} \longrightarrow C_{3}H_{3}F_{2}^{+}$$

$$(m/z = 77) + H_{2}$$

(b) Bromomethane. Because of the relatively high reactivity of bromomethane vapour these reactions were kept to a minimum. Only two ions were investigated, CH_2N^+ and CH_3^+ (Tables 4 and 5). Nonetheless it is thought that they represent the first reports of such experiments. The isotopes of bromine aided the identification of CH_3XH^+ and $(CH_3)_2X^+$ species.

(c) Iodomethane. The reaction of iodomethane followed a similar pattern to fluoromethane and bromomethane with a few exceptions.

The methyl iodonium ion was produced by the reaction of CH_2N^+ with iodomethane (Table 6). A fragment ion of m/z 15 was observed but no ion corresponding to CH_2I^+ was detected. Also present in these reactions were the ions due to iodomethane radical cations and iodine cations. Iodine cations could arise from cleavage of the iodomethane radical cations or from elimination of methane from the methyl iodonium ions.

$$CH_{3}I^{+} \longrightarrow CH_{3} + I^{+}$$
$$CH_{3}-I-H^{+} \longrightarrow CH_{4} + I^{+}$$

In the reaction carried out at higher pressure the dimethyl iodonium ion of m/z 157 was produced.

$$CH_3-I-H^+ + CH_3I \longrightarrow CH_3-I-CH_3^+ + HI$$

The products of the reaction of CH_3^+ and CD_3^+ with iodomethane were as for the other halides except that the iodomethane cation, produced by charge exchange reaction, was the dominant ion. CH_2I^+ , $C_2H_n^+$ (n = 3, 4 or 5), CH_3IH^+ and $(CH_3)_2I^+$ ions were also present.

It should be noted that the large quantity of iodomethane ions obtained in this experiment was not matched by a correspondingly large quantity of iodine cations. This would suggest that the I^+ ions observed, in this and in the previous experiment, arise from the rearrangement and fragmentation of the monomethyl iodonium ion, and not from the cleavage of the iodomethyl cation.

$$CH_3I^{+*} \longrightarrow CH_3^{*} + I^+$$

 $CH_3-I-H^+ \longrightarrow CH_4 + I^+$

The reaction of $C_2H_3^+$ and $C_2H_5^+$ ions with iodomethane produced large amounts of monomethyl iodonium and dimethyl iodonium ions (see Table 7).

The general conclusion to be drawn from the reactions of protonating ions with halogenomethanes is that the reaction of methyl halonium ions with halogenomethane produces dimethyl halonium ions and HX. To investigate these ions further 'cross reactions' were attempted. These involve reacting one species of methyl oxonium or methyl halonium ion with a different neutral molecule.

Reaction of Methyl Chloronium Ions with Dimethyl Ether.— Using the quinqua quadrupole mass spectrometer it was possible to form methyl chloronium ions in the second quadrupole.

| | Ion | | | | |
|--------------------------------|------------------------------|--------------------|--|----------------------------|--|
| Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | CH₃IH ⁺ | (CH ₃) ₂ I ⁺ | - Unchanged $C_2H_5^+$ (%) | |
| 3.0 | 5.4 | 92.2 | 2.4 | 96.7 | |
| 7.5 | 2.5 | 87.6 | 9.9 | 84.1 | |
| 15.0 | 0.00 | 77.6 | 22.5 | 73.5 | |
| 23.0 | 0.00 | 63.4 | 36.6 | 61.8 | |

Table 7 % Ion current for $C_2H_5^+ + CH_3I$ at various pressures

Table 8 % Ion current for $CH_3ClH^+ + (CH_3)_2O$ at various pressures

| | Ion | | | | |
|--------------------------------|-------------|---|--|---|--|
| Pressure/10 ⁻⁵ Torr | $C_2H_5O^+$ | (CH ₃) ₂ OH ⁺ | (CH ₃) ₃ O ⁺ | Changed CH ₃ ClH ⁺ (%) | |
| 17.0 | 39.1 | 60.9 | 0.0 | 92.9 | |
| 35.0 | 43.3 | 40.0 | 16.7 | 55.6 | |
| 48.0 | 44.3 | 36.1 | 19.7 | 51.2 | |
| 53.0 | 44.6 | 36.5 | 18.9 | 48.6 | |

Table 9 % Ion current for $CH_3OH_2^+ + CH_3Cl$ at various pressures

| | Ion | | | | | |
|--------------------------------|------------------------------|---------------------------------|----------------------------------|---|--|---|
| Pressure/10 ⁻⁵ Torr | CH ₃ ⁺ | CH ₂ Cl ⁺ | CH ₃ ClH ⁺ | (CH ₃) ₂ Cl ⁺ | CH ₃ OH ₂ ⁺ ion fragments | Unchanged CH ₃ OH ₂ ⁺ (%) |
| 1.5 | 45.7 | 2.9 | 13.0 | 2.2 | 36.2 | 99.3 |
| 6.0 | 38.5 | 7.9 | 20.5 | 6.8 | 26.3 | 97.1 |
| 11.0 | 27.9 | 15.6 | 17.6 | 14.7 | 24.2 | 94.3 |
| 30.0 | 21.3 | 22.2 | 14.2 | 18.8 | 23.5 | 89.4 |
| 60.0 | 17.8 | 22.7 | 13.9 | 22.4 | 23.2 | 86.5 |

$$CH_3NH_2 \xrightarrow{e^-} CH_2N^+ + CH_3Cl \longrightarrow HCN + CH_3ClH^+$$

The most abundant ion, $CH_3^{35}ClH^+$, was separated and mixed with dimethyl ether in the fourth quadrupole. The ions produced in this reaction were $(CH_3)_2OH^+$ (dimethyl oxonium), $C_2H_5O^+$ (a fragment of dimethyl oxonium) and $(CH_3)_3O^+$ (trimethyl oxonium) ions. Table 8 shows that the trimethyl oxonium ions are tertiary fragment ions and are formed either by the reaction of methyl chloronium ion with dimethyl ether

$$CH_3ClH^+ + (CH_3)_2O \longrightarrow (CH_3)_3O^+ + CH_3Cl$$

or by the reaction of dimethyl oxonium ions with dimethyl ether.



Without labelled methyl groups on the methyl chloronium ions or the dimethyl ether it was not possible to repeat this experiment to determine whether one or other, or both, of these reactions was responsible for the production of the trimethyl oxonium ions. Reactions of Methyl Oxonium Ions with Chloromethane.— Methyl oxonium ions, formed by reaction within the ionisation chamber of the triple quadrupole mass spectrometer, were separated from the other ions in the first quadrupole and passed into chloromethane gas. The main products detected at the end of the third quadrupole were methyl chloronium ions and fragment ions CH_2Cl^+ and CH_3^+ . Dimethyl chloronium ions were observed at higher pressures (Table 9). The chloronium ions could be formed via two routes, one involving the methylation of chloromethane by the methyl oxonium ions, and the other involving the methylation of chloromethane by the methyl chloronium ions.



To investigate these possibilities the experiment was repeated using deuteriated methyl oxonium ions as the primary ion. If methylation by the methyl oxonium ions was occurring the dimethyl chloronium would have one deuteriated methyl group $(CD_3-Cl-CH_3^+)$ and a corresponding m/z of 68/70. If methylation by the methyl chloronium ions was occurring the dimethyl chloronium ion would have no deuteriated methyl group $(CH_3-Cl-CH_3^+)$ and a corresponding m/z of 65/67.



Fig. 7 Reaction pathways in methanol





Fig. 8 Reaction pathways in halogenomethanes

$$\mathrm{CD_3}_{38}^{\mathrm{OD}_2^+} + \mathrm{CH_3Cl} \longrightarrow \mathrm{CD_3-Cl-CH_3^+}_{68/70} + \mathrm{D_2O}$$

As can be seen in Table 10 secondary ions of m/z 68/70 were obtained in high yields at lower pressures.



At the highest pressures a trace amount of tertiary ions of m/z 65/67 appeared, indicating that both routes are in operation.

These 'cross experiments' have shown that the mechanism proposed for the reaction of oxonium ions and for the reaction of halonium ions is also applicable to the reactions of halonium ions with dimethyl ether and oxonium ions with halogenomethanes.

Conclusions

Halogenomethane molecules can be protonated to form monomethyl halonium ions, CH_3XH^+ . These ions react with another molecule of halogenomethane to produce the dimethyl halonium ions $CH_3-X-CH_3^+$. It is thought that these reactions follow the same S_N^2 mechanism that was found to occur for the formation of oxonium ions.¹ The reactions studied can be combined and represented by the reaction pathways in Figs. 7 and 8. The mechanisms for the formation of oxonium ions and halonium ions can be represented in the following general reaction schemes.

The monomethyl and dimethyl halonium ions of chlorine, fluorine and iodine have been used as gas-phase methylating agents.^{13–24,27} The advantages of using methyl halonium ions rather than free methyl ions in ion-molecule reactions are twofold: (1) methylation by methyl halonium ions is a much milder form of methylation and will produce less fragmentation of the methylated species than would a direct methylation. (2) There are fewer side reactions with the methyl halonium ions than with direct methylation. For example, hydride abstraction,

| | Ion | | | | | | | | | | | |
|--------------------------------|------|------------------------------|---------------------------------|---------|----------------------------------|---|--|----------------------------------|--------------------------|--|--|--|
| Pressure/10 ⁻⁵ Torr | CH₃⁺ | CD ₃ ⁺ | CH ₂ Cl ⁺ | CH₃ClH⁺ | CH ₃ ClD ⁺ | (CH ₃) ₂ Cl ⁺ | CH ₃ ClCD ₃ ⁺ | $CD_3OD_2^+$ ion fragments | Unchanged reagents(%) | | | |
| 6.0 | 13.7 | 59.6 | 7.1 | 3.0 | 3.0 | 0.0 | 5.0 | 8.6 | 96.4 | | | |
| 7.5 | 15.2 | 55.3 | 9.7 | 2.9 | 2.9 | 0.0 | 5.8 | 8.2 | 95.7 | | | |
| 15.0 | 14.5 | 40.2 | 20.4 | 6.5 | 3.2 | 0.0 | 8.0 | 7.2 | 92.0 | | | |
| 34.0 | 11.2 | 26.9 | 32.2 | 5.0 | 2.9 | trace | 12.1 | 9.7 | 89.3 | | | |
| 56.0 | 9.5 | 14.2 | 39.5 | 7.9 | 3.2 | trace | 15.8 | 9.9 | 85.6 | | | |

General reaction scheme for halonium ions:

-

$$CH_3 - X - H^+$$

 $CH_3 - X - CH_3 - X - CH_3^+ + HX$
 $CH_3 - X = F, Cl, Br and I$

General reaction scheme for 'cross reactions':





which tends to occur with free methyl ions, does not occur so readily with the methyl halonium ions.

The triple and quinqua quadrupole mass spectrometers, with their ability to form and isolate methyl halonium ions, have been shown to be effective tools in the pursuance of investigations of ion-molecule reactions in the gas phase.

Acknowledgements

We thank Emeritus Professor J. D. Morrison of La Trobe University, Australia, Dr. S. R. Wade of BP Research, London, J. Rennie, J. Ward and C. Smith of St. Andrews University, Scotland for their help and advice and F. van Tiggelin of Belgium for her assistance in some of the experiments. One of us, G. S. W., acknowledges the Woonona/Bulli R.S.L., Australia, for providing facilities used to write this paper.

References

- 1 J. M. Tedder and G. S. Walker, J. Chem. Soc., Perkin Trans. 2, 1991, 317.
- 2 F. W. McLaffery, Anal. Chem., 1962, 34, 2.
- 3 F. W. McLaffery, Anal. Chem., 1962, 34, 16.
- 4 G. A. Olah, Y. Yamada and R. J. Spear, J. Am. Chem. Soc., 1975, 97, 680.
- 5 G. A. Olah and J. J. Svoboda, Synthesis, 1973, 203.
- 6 G. A. Olah and J. M. Bollinger, J. Am. Chem. Soc., 1967, 89, 4744.
- 7 G. A. Olah and J. M. Bollinger, J. Am. Chem. Soc., 1968, 90, 947.
- 8 G. A. Olah, J. M. Bollinger and J. Brinich, J. Am. Chem. Soc., 1968, 90, 2587.
- 9 G. A. Olah and P. E. Peterson, J. Am. Chem. Soc., 1968, 90, 4675.
- 10 G. A. Olah, J. M. Bollinger and J. Brinich, J. Am. Chem. Soc., 1968, 90, 6988.
- 11 G. A. Olah, J. R. DeMember and R. H. Schlosberg, J. Am. Chem. Soc., 1969, 91, 2112.
- 12 G. A. Olah and J. R. DeMember, J. Am. Chem. Soc., 1969, 91, 2114.
- 13 N. A. McAskill, Aust. J. Chem., 1969, 22, 2275.
- 14 N. A. McAskill, Aust. J. Chem., 1970, 23, 893.
- 15 N. A. McAskill, Aust. J. Chem., 1970, 23, 2301.
- 16 D. K. Sen Sharma and P. Kebarle, J. Am. Chem. Soc., 1978, 100, 5826.
- 17 D. K. Sen Sharma and P. Kebarle, J. Am. Chem. Soc., 1982, 104, 19.
- 18 K. Hiraoka and P. Kebarle, Can. J. Chem., 1985, 63, 3160.
- 19 G. Caldwell, T. F. Magnera and P. Kebarle, J. Am. Chem. Soc., 1984, 106, 959.
- 20 T. B. McMahon and P. Kebarle, Can. J. Chem., 1985, 63, 3160.
- 21 R. B. Sharma, D. K. Sen Sharma, K. Hiraoka and P. Kebarle, J. Am. Chem. Soc., 1985, 107, 3755.
- 22 D. K. Sen Sharma, S. Meza de Hojer and P. Kebarle, J. Am. Chem. Soc., 1985, 107, 3757.
- 23 T. B. McMahon and P. Kebarle, J. Am. Chem. Soc., 1986, 108, 6502.
- 24 C. Jortay, R. Flammang and A. Maquestiau, Bull. Soc. Chim. Belg.,
- 1985, **94**, 727 (Chem. Abstr. **105**, 152217a).
- 25 J. H. Batey and J. M. Tedder, J. Chem. Soc., Perkin Trans. 2, 1983, 1263.
- 26 W. F. Edgell and L. Parts, J. Am. Chem. Soc., 1955, 77, 4899.
- 27 N. A. McAskill, Aust. J. Chem., 1969, 22, 2267.

Paper 0/04152A Received 11th September 1990 Accepted 25th March 1991