

Investigations of Halonium Ions 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

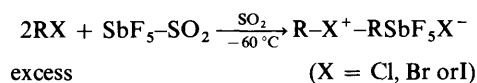
The mechanisms involved in the formation of monomethyl halonium and dimethyl halonium ions in the gas phase have been investigated using a triple quadrupole mass spectrometer and a quinquadrupole mass spectrometer. The results indicate that the mechanism for formation of the halonium ions is analogous to the S_N2 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 R¹, R², R³, R⁴ and R⁵ were CH₃⁻, CD₃⁻, C₂H₅⁻, 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 (R¹-X-R²)⁺, have been observed as rearrangement products from electron impact mass spectrometer² 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



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 CH₂Cl⁺, CH₃Cl⁺ and CH₃ClH⁺ ions very small quantities of C₂H₃⁺ and C₂H₅⁺ ions and an ion that was assigned the structure of protonated ethyl chloride, C₂H₅Cl-H⁺, were observed. Similar results were reported for fluoromethane and the ion, C₂H₆F⁺, was described as protonated fluoroethane.

Kearle 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 C₂H₆Cl⁺ ion to be dimethyl chloronium ion rather than protonated chloroethane.

In 1986 a report of dimethyl fluoronium ions and the proton-bound dimer of fluoromethane in the gas phase was presented by McMahon and Kearle.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 quinquadrupole mass spectrometers the reactions involved in the formation of methyl halonium ions at low pressures, and the subsequent reactions of methyl

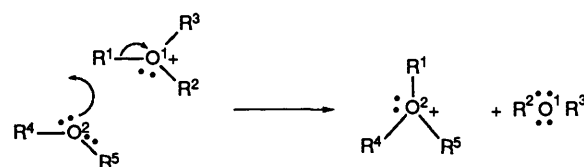


Fig. 1 General reaction scheme

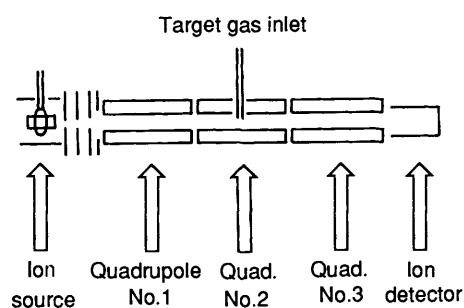


Fig. 2 Schematic diagram of triple quadrupole mass spectrometer

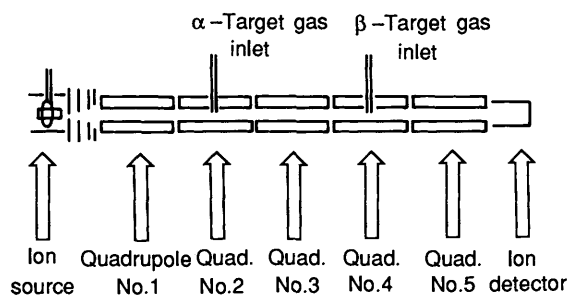


Fig. 3 Schematic diagram of quinquadrupole mass spectrometer

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.

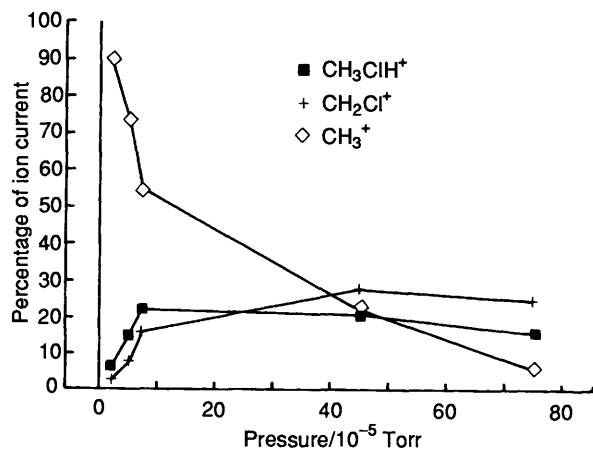
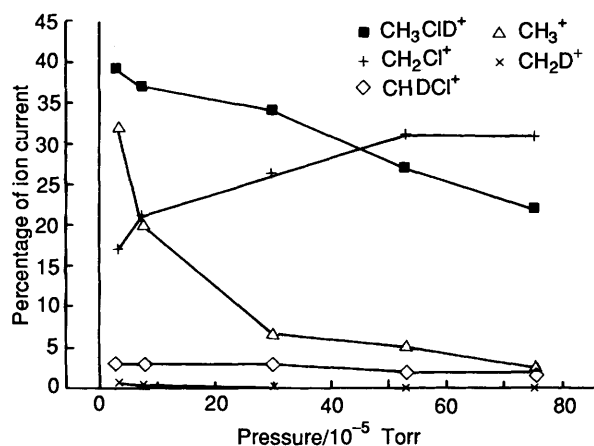
Experimental

The triple quadrupole mass spectrometer, Fig. 2, and the quinquadrupole 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.

[‡] 1 Torr = 133.322 Pa.

Fig. 4 Fragments ions from CH_3CIH^+ Fig. 5 Fragments ions from CH_3CID^+

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 quinquadrupole 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.

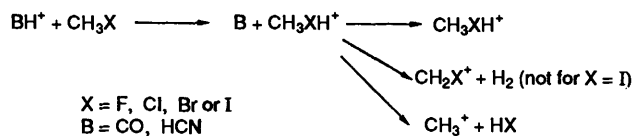
All gases and liquids used were commercially available at >99% purity and were used without further purification, except fluoromethane which was synthesised using the method of Kamm and Marvel.²⁶

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.

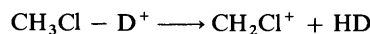
Discussion

The reaction of CHO^+ , CDO^+ , CH^{18}O^+ and CH_2N^+ ions with the halogenomethanes, CH_3X , produced similar, but not identical, results. The formation of CH_2X^+ , CH_3^+ and CH_3XH^+ ions indicated that the first reaction was the protonation of the halogenomethane to form CH_3XH^+ which subsequently fragmented.

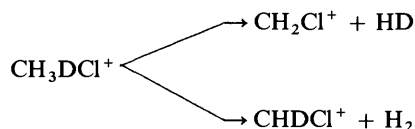


The reaction of ions with chloromethane will be discussed in detail below. The reactions of the other halogenomethanes will be summarised.

Protonation of Chloromethane.—The reaction of CDO^+ and CH_2N^+ ions with chloromethane produced deuterated and protonated CH_3Cl respectively. The fragments from the ions CH_3CIH^+ and CH_3CID^+ 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.



If the extra proton was attached not to the halogen, but to the carbon in a pentacoordinate structure, such as those suggested for CH_3^+ 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 CH_3CID^+ ions produced CH_2Cl^+ ions with the elimination of HD. In addition the production of CH_2D^+ ions was found to be minimal (0.6%) compared with CH_3^+ ions (32%). These results support the initial protonation taking place on the halogen to produce $(\text{CH}_3\text{-Cl-H})^+$ ions.

Reactions of Ions with Chloromethane.—The reaction of CDO^+ and CH_2N^+ ions with chloromethane produced CH_2Cl^+ , CH_3^+ and CH_3CIH^+ 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)

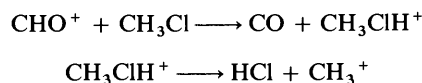
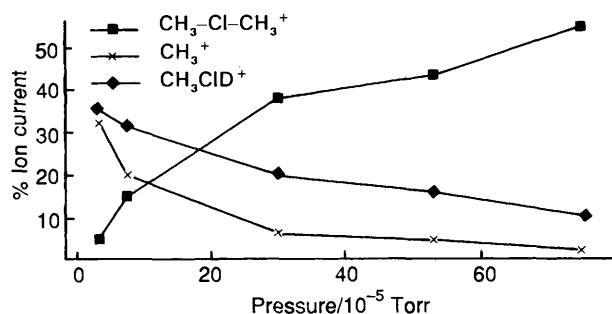
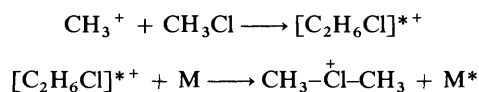


Table 1 % Ion current for $\text{CH}_2\text{N}^+ + \text{CH}_3\text{Cl}$ at various pressures

Pressure/ 10^{-5} Torr	Ion					Unchanged CH_2N^+ (%)
	CH_3^+	CH_2Cl^+	CH_3ClH^+	$(\text{CH}_3)_2\text{Cl}^+$	Impurity (O^+/O_2^+)	
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

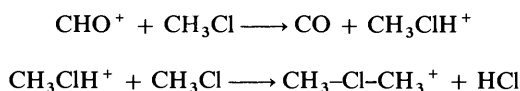
Table 2 % Ion current for $\text{CH}_3^+ + \text{CH}_3\text{Cl}$ at various pressures

Pressure/ 10^{-5} Torr	Ion					Unchanged CH_3^+ (%)
	C_2H_n^+ ($n = 3$ or 5)	CH_2Cl^+	CH_3ClH^+	$(\text{CH}_3)_2\text{Cl}^+$	Minor ions	
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 CH_3Cl 

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

Mechanism (2)



It would be expected that an increase in the amount of the product ion, $\text{CH}_3\text{ClCH}_3^+$, 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 $\text{CH}_3\text{ClCH}_3^+$ ions, it was not possible to ascertain from these results which of the two proposed mechanisms was operating.

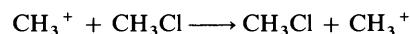
One of the constraints of the multiple quadrupole system is that ions can take between 30 and 60 μs to travel from the point of reaction to the detector. This is a drawback of the quadrupole system which prevents the elucidation of the mechanism by probing the early stages of the reaction. However, one 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) $\text{CH}_3^+ + \text{CH}_3\text{Cl}$. The dominant reaction was a hydride abstraction to form methane and CH_2Cl^+ ions. (See Table 2.)

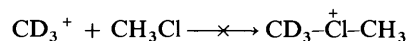


(A halide abstraction would not be detected because the product ion would be the same as the primary ion.)

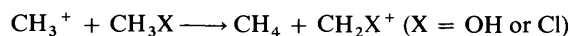


Also present were ions of m/z 27 (C_2H_3^+ ; max = 12%), 29 (C_2H_5^+ ; max = 3%), 39 (C_3H_3^+ ; max = 0.4%), 41 (C_3H_5^+ ; max = 0.1%), 49/51 (CH_2Cl^+ ; max = 90%), 51/53 (CH_3ClH^+ ; max = 5%) and 65/67 ($\text{C}_2\text{H}_6\text{Cl}^+$; max = 2%).

(b) $\text{CD}_3^+ + \text{CH}_3\text{Cl}$. 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 deuterated dimethyl chloronium ions, $\text{CD}_3\text{ClCH}_3^+$ indicates that dimethyl chloronium ions are not formed by direct addition of methyl cations to chloromethane.



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.



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).

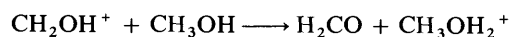
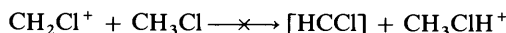


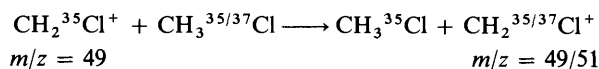
Table 3 % Ion current for $\text{CH}^{18}\text{O}^+ + \text{CH}_3\text{F}$ at various pressures

Pressure/ 10^{-5} Torr	Ion					Unchanged CH^{18}O^+ (%)
	CH_3^+	CH_2F^+	CH_3FH^+	$(\text{CH}_3)_2\text{F}^+$	Minor ions	
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

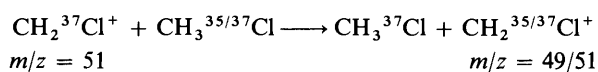
This latter reaction is not feasible with $\text{X} = \text{Cl}$ because CH_2Cl^+ does not protonate chloromethane.



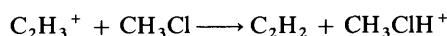
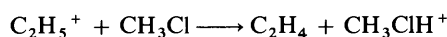
The reaction of CH_2Cl^+ with CH_3Cl was carried out using $\text{CH}_2^{35}\text{Cl}^+$ and $\text{CH}_2^{37}\text{Cl}^+$ ions. With $\text{CH}_2^{35}\text{Cl}^+$ ions the only two ions observed were primary ion $\text{CH}_2^{35}\text{Cl}^+$ ($m/z = 49$) and $\text{CH}_2^{37}\text{Cl}^+$ ($m/z = 51$) formed by a hydride abstraction reaction.



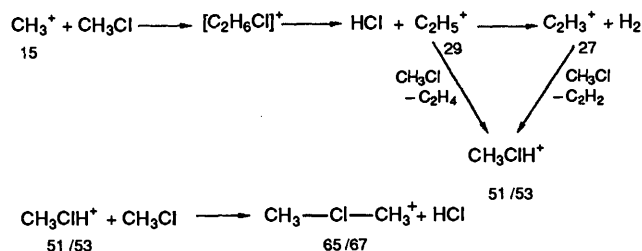
With $\text{CH}_2^{37}\text{Cl}^+$ ions the same two ions were observed: primary ion $\text{CH}_2^{37}\text{Cl}^+$ ($m/z = 51$) and $\text{CH}_2^{35}\text{Cl}^+$ ($m/z = 49$) formed by a hydride abstraction reaction.



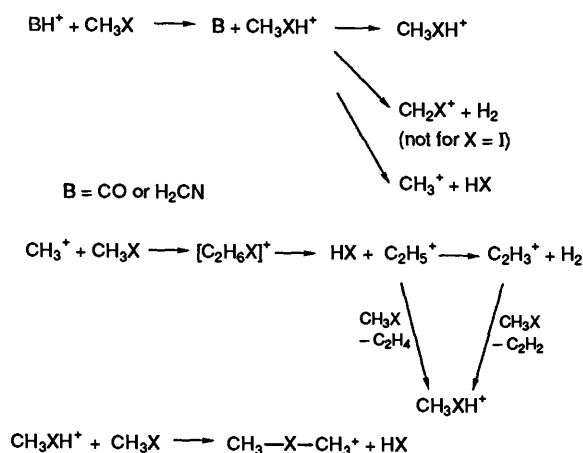
The question remains as to the mechanism of formation of the monomethyl and dimethyl chloronium ions in the reaction of methyl ions and chloromethane. The direct addition of methyl cation to chloromethane and the protonation of chloromethane by CH_2Cl^+ ions have been ruled out. The other ions present 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.



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.



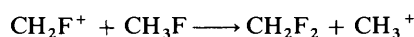
Reactions of Ions with Halogenomethanes.—The reactions of CH^{18}O^+ , CH_2N^+ , CH_3^+ and CD_3^+ ions with the other halogenomethanes were studied (see Table 3). The results were essentially identical with those for chloromethane and involved the protonation of halogenomethane, the fragmentation of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



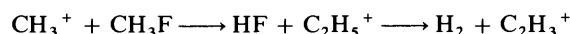
The main difference between the reactions of the halogenomethanes are outlined below.

(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 .

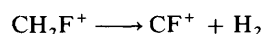
The reaction of CH_2F^+ (isolated from other ions in the first quadrupole) with CH_3F (in the second quadrupole) produced many of the minor ions that had been present in the previous experiments. The most abundant ion was CH_3^+ which could arise from halide abstraction.



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



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



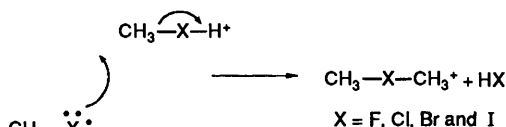
Other ions arose from the addition with fragmentation reactions of CH_2F^+ ions with CH_3F .

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.

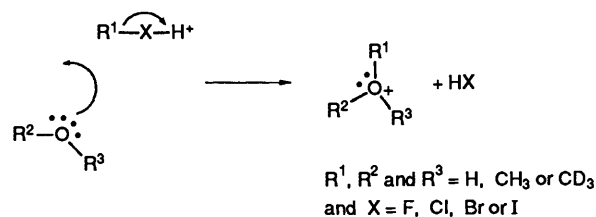
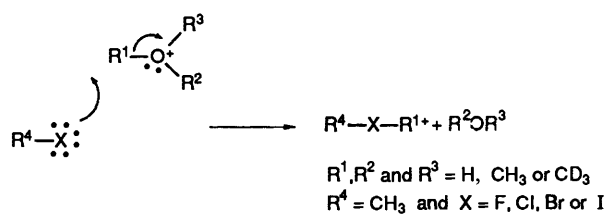
Table 10 % Ion current for $\text{CD}_3\text{OD}_2^+ + \text{CH}_3\text{Cl}$ at various pressures

Pressure/ 10^{-5} Torr	Ion							CD_3OD_2^+ ion fragments	Unchanged reagents(%)
	CH_3^+	CD_3^+	CH_2Cl^+	CH_3CH^+	CH_3CID^+	$(\text{CH}_3)_2\text{Cl}^+$	$\text{CH}_3\text{ClCD}_3^+$		
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:



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 quinquadrupole 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