A Study of Ion–Molecule Reactions in the Gas Phase. Part 3.† The Reactions of Methyl and Fluoromethyl Cations with Alkenes and Fluoroalkenes in the Gas Phase

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The reactions of CH_3^+, CH_2F^+, CHF_2^+, and CF_3^+ with ethene, fluoro-, 1,1-difluoro-, trifluoro-, and tetrafluoro-ethene and with propene, but-1-ene, but-2-ene, and 2-methylpropene have been studied in the gas phase. As well as simple charge exchange, addition reactions were observed in which the initial adduct broke down to yield neutral fragments and ions of either general formula $(C_nX_{2n+1})^+$ or $(C_nX_{2n-1})^+$, where X = H and/or F. The fragmentation of the initial transient adduct ion was often associated with hydrogen atom and/or fluorine atom migration.

Part 1[1] described a study of the reactions of methyl cations with ethene and other simple olefins in the gas phase. The present paper describes the extension of this work to include the reactions of fluoromethyl cations with ethene, polyfluoroethenes, propene, and the three butenes. The apparatus has been described in earlier papers.

There is surprisingly little in the literature describing ion–molecule reactions which involve the reactions of alkyl cations with olefins.[1–3] There is an extensive literature on the mass spectra of fluorocarbon derivatives,[4] but again relatively little concerned with ion–molecule reactions of fluorine-containing alkyl cations with fluorine-containing olefins.[5]

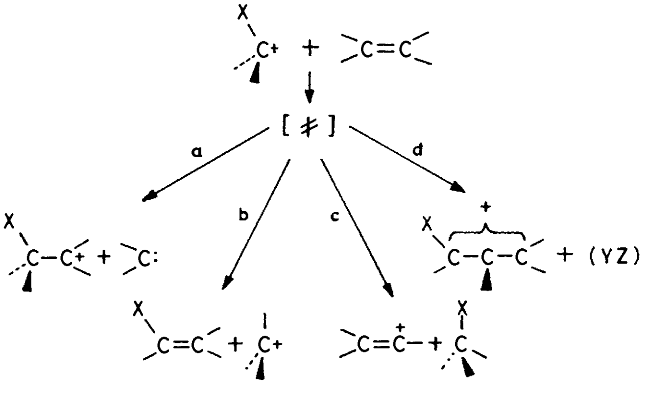
Experimental

Details of the apparatus have been described in an earlier paper.[1] The relative flux of secondary ions was determined by measuring the primary ion current when there was no collision gas in the second quadrupole and this was compared with the ion currents attributable to specific product ions and the results are all expressed as $(I_s/I_p) \times 10^3$ (where I_s is the measured current attributable to a particular secondary ion and I_p is the total primary ion current).

The methyl cation was prepared by electron impact on methane or chloromethane; the fluoromethyl cation came from electron impact on symmetrical difluoroacetone, the difluoromethyl cation from electron impact on difluoromethane, and the trifluoromethyl cation from electron impact on tetrafluoromethane. The olefins were commercial materials used without further purification. The reactions were performed at four pressures and it is possible to distinguish between those ions whose concentration increases regularly with increasing olefin pressure, and those ions whose concentration initially increases with increasing olefin pressure, but whose concentration levels off or even decreases as more olefin is added. These latter ions must be reacting further with the olefin.

Discussion

(a) *The Reactions of Methyl and Fluoromethyl Cations with Ethene and Fluoroethenes.*—The addition of methyl and fluoromethyl cations to ethene and to fluoroethenes are exothermic processes. The initial addition leads to an activated complex which can fragment in four principal ways. As we shall see, the allyl cation (Scheme 1, reaction **d**) may involve a composite step in the reactions of the methyl cation with ethene.



Scheme 1.

Reaction pathway **a** leads to the formation of a carbene and a substituted ethyl cation (Scheme 2). In all the examples cited the ejected neutral fragment is difluorocarbene (CH_2 and CHF occur in minor reactions). Three of the reactions could be regarded as 'knock on' processes (Scheme 3). The others involve hydride or fluoride transfer (Scheme 4).

Reaction **b** is also a concerted addition–elimination, but a rearrangement is involved. In this series the difluoromethyl cation (CHF_2^+) is the predominant ionic product (Scheme 5). These reactions all involve hydride transfer (Scheme 6). A closely related reaction involves fluoride transfer (Scheme 7).

Reaction **c** leads to the formation of $C_2X_3^+$ ions. There are a few reactions in which the initial addition complex expels H_2 or HF leaving a three-carbon fragment (*i.e.* an allyl cation) (Scheme 9). Notice that the three examples involve addition to ethene. These reactions have been depicted in Scheme 10 as proceeding through the same 'addition complex' as the other ions; it is possible however that in reality many of these reactions involve tertiary ions.

A considerable effort was expended in attempting to estimate the ΔH value for each process. However, the data for the fluorine-containing species are so scattered and contradictory that attempts to do this have been abandoned.

It has been assumed so far that all the products are derived from a one-step reaction between cation and alkene. There is however good evidence that a number of the products are tertiary ions. Thus the reaction of methyl cations with 1,1-difluoroethene yields no $C_2H_3F_2^+$ ions at the lowest difluoroethene pressures, but as the pressure of difluoroethene is increased the yield of $C_2H_3F_2^+$ increases very rapidly, *i.e.*

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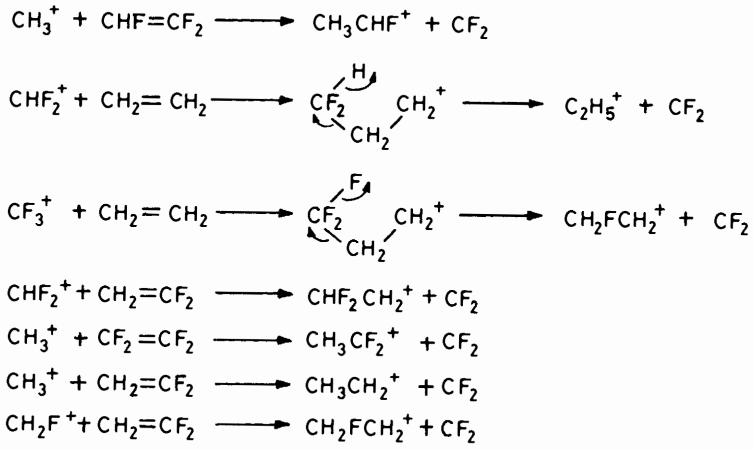
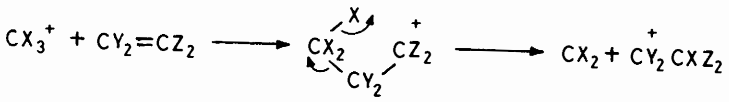
† Part 2, A. L. Mitchell and T. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1984, 667.



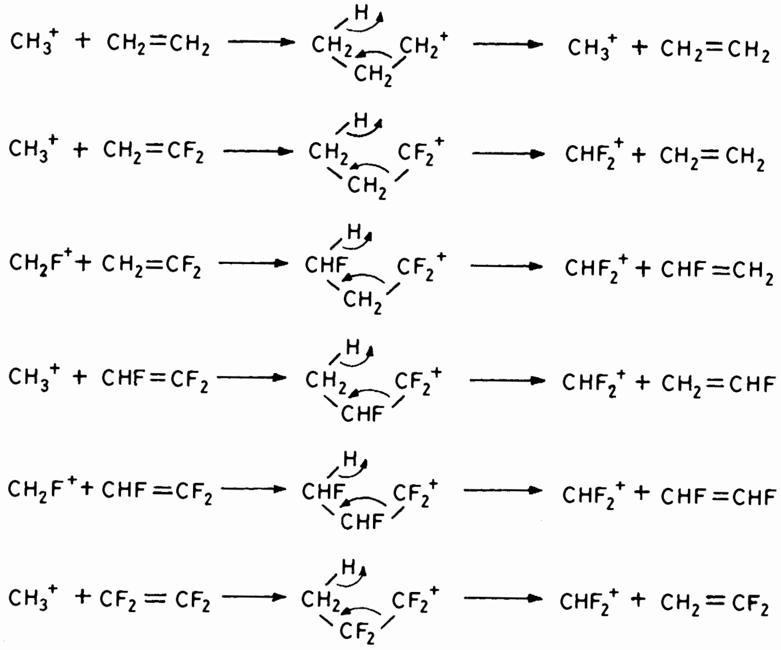
Scheme 2.

$$CX_3^+ + CY_2{=}CZ_2 \longrightarrow (CX_3CY_2CZ_2)^{*+} \longrightarrow CX_3CY_2^+ + CZ_2$$

Scheme 3.



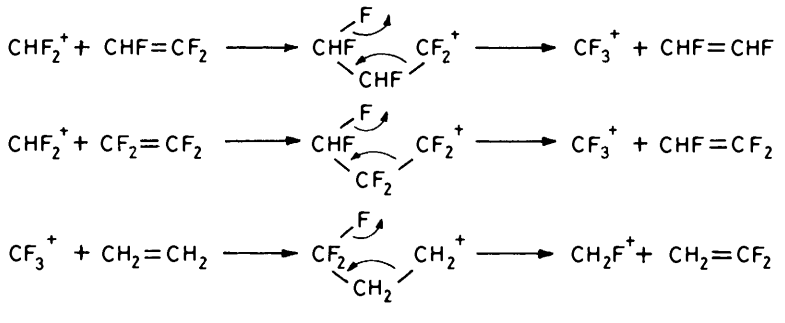
Scheme 4.



Scheme 5.

$$CHX_2^+ + CY_2{=}CZ_2 \longrightarrow CX_2{=}CY_2 + CHZ_2^+$$

Scheme 6.



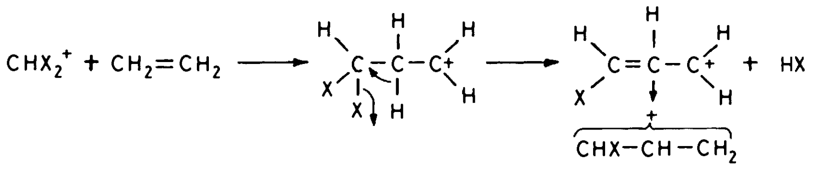
Scheme 7.

$$CH_3^+ + CH_2{=}CH_2 \longrightarrow CH_4 + C_2H_3^+$$
$$CH_3^+ + CH_2{=}CF_2 \longrightarrow CH_3F + C_2H_2F^+$$
$$CF_3^+ + CH_2{=}CF_2 \longrightarrow CF_4 + C_2H_2F^+$$

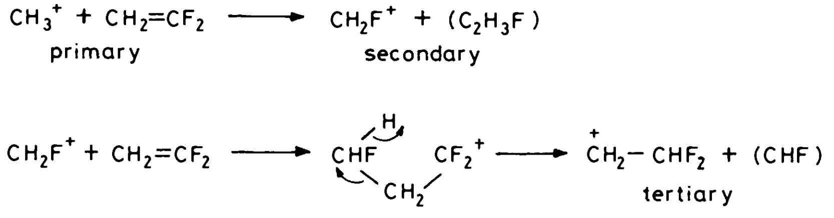
Scheme 8.

$$CH_2F^+ + CH_2{=}CH_2 \longrightarrow C_3H_4F^+ + H_2$$
$$CH_2F^+ + CH_2{=}CH_2 \longrightarrow C_3H_5^+ + HF$$
$$CHF_2^+ + CH_2{=}CH_2 \longrightarrow C_3H_4F^+ + HF$$

Scheme 9.

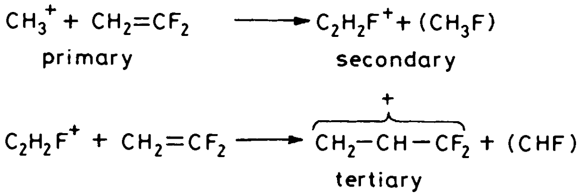


Scheme 10.



Scheme 11.

$C_2H_3F_2^+$ is a tertiary ion. It seems probable that the sequence in Scheme 11 is involved. The ion $C_3H_3F_2^+$ is also unobserved at the lowest pressures and the $C_2H_2F^+$ ions initially increase in concentration as the pressure of the starting difluoroethene increases, then decrease at the highest pressure studied. The probable sequence is in Scheme 12. The stability of the allyl cations probably accounts for the appearance of these as tertiary ions. Notice that the reactions of CH_2F^+ with ethene are described in reaction sequences in which it is a secondary ion



Scheme 12.

Table 1. The reaction of methyl and fluoromethyl cations with ethene and the fluoroethenes

$C_3H_7^+$ $(I_s/I_p) \times 10^3$

	$CH_3^+ + CH_2{=}CH_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5} Torr
Product			
c $C_2H_3^+$ (CH_4)	22	81	91
a $C_2H_5^+$ (CH_2)	2	28	58
$C_3H_3^+$ $(2H_2)$	5	21	28
d $C_3H_5^+$ (H_2)	5	35	86

$C_3H_6F^+$ $(I_s/I_p) \times 10^3$

	$CH_2F^+ + CH_2{=}CH_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5} Torr
Product			
c $C_2H_3^+$ (CH_3F)	2	3	4
a $C_2H_5^+$ (CHF)	1	2	3
b CH_2F^+ (C_2H_4)	χ	χ	χ
d $C_3H_5^+$ (HF)	9	14	28
d $C_3H_4F^+$ (H_2)	7	12	15

$C_3H_5F_2^+$ $(I_s/I_p) \times 10^3$

	$CH_3^+ + CH_2{=}CF_2$			$CHF_2^+ + CH_2{=}CH_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5} Torr
Product						
c $C_2H_3^+$ (CH_2F_2)	7	24	43	3	4	5
a $C_2H_5^+$ (CF_2)	7	29	49	11	22	26
b CH_2F^+ (C_2H_3F)	8	24	19	6	8	9
d $C_3H_5^+$ (F_2)				3	10	34
c $C_2H_2F^+$ (CH_3F)	21	55	51			
b CHF_2^+ (C_2H_4)	41	140	170	χ	χ	χ
d $C_3H_4F^+$ (HF)	4	15	31	9	22	60
a $C_2H_3F_2$ (CH_2)		39	120			
d $C_3H_3F_2^+$ (H_2)		9	18		1	4

$C_3H_4F_3^+$ $(I_s/I_p) \times 10^3$

	$CH_3^+ + CHF{=}CF_2$			$CH_2F^+ + CH_2{=}CF_2$			$CF_3^+ + CH_2{=}CH_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5} Torr
Product									
d $C_2H_3^+$ (CHF_3)	5	15	27	1	2	5	10	13	16
b CH_2F^+ $(C_2H_2F_2)$	6	8	10	χ	χ	χ	12	16	18
d $C_2H_2F^+$ (CH_2F_2)		8	19	2	5	8			
a $C_2H_4F^+$ (CF_2)	30	96	121	2	3	7	17	30	49
b CHF_2^+ (C_2H_3F)	20	68	87	4	7	15	17	25	39
c $C_3H_4F^+$ (F_2)		4	7					5	15
a $C_2H_3F_2^+$ (CHF)		7	14	1	3	9			
b CF_3^+ (C_2H_4)	7	31	54	3	5	8	χ	χ	χ
c $C_3H_3F_2^+$ (HF)		12	40	1	3	8	11	23	52

$C_3H_3F_4^+$ $(I_s/I_p) \times 10^3$

	$CH_3^+ + CF_2{=}CF_2$			$CH_2F^+ + CHF{=}CF_2$			$CHF_2^+ + CH_2{=}CF_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5} Torr
Product									
d $C_2H_3^+$ (CF_4)							4	7	16
d $C_2H_2F^+$ (CHF_3)	4	15	29				4	7	13
b CHF_2^+ $(C_2H_2F_2)$		9	12	6	7	8	χ	χ	χ
a $C_2H_3F_2^+$ (CF_2)	23	95	162	2	2	2	15	28	105
b CF_3^+ (C_2H_3F)	4	12	26	1	2	4	2	5	8

$C_3H_2F_5^+$ $(I_s/I_p) \times 10^3$

	$CH_2F^+ + CF_2{=}CF_2$			$CHF_2^+ + CHF{=}CF_2$			$CF_3^+ + CH_2{=}CF_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5} Torr
Product									
d $C_2H_2F^+$ (CF_4)				4	7	13	13	27	46
b CF_3^+ $(C_2H_2F_2)$				35	103	202	χ	χ	χ
c $C_3H_2F_2^{+\cdot}$ $(F_2,F^{\cdot})$					2	3		11	31

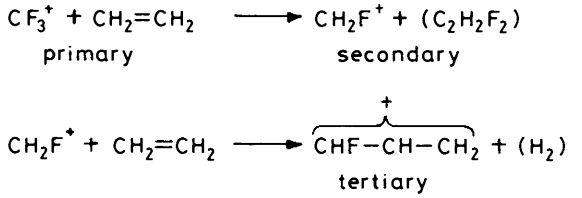
Table 1 (*continued*)

$C_3HF_6^+$ $(I_s/I_p) \times 10^3$

	$CHF_2^+ + CF_2{=}CF_2$			$CF_3^+ + CHF{=}CF_2$		
Secondary gas pressure	10^{-6}	5×10^{-6}	10^{-5}	10^{-6}	5×10^{-6}	10^{-5} Torr
Product						
b CHF_2^+ $(CF_2{=}CF_2)$	χ	χ	χ	2	4	7
b CF_3^+ $(CHF{=}CF_2)$	5	14	51	χ	χ	χ

Table 2. The reactions of methyl and fluoromethyl cations with hydrocarbon olefins

	$(I_s/I_p) \times 10^3$													
	c $C_2H_3^+$ 27	**a** $C_2H_5^+$ 29	**d** $C_3H_5^+$ 41	**a** $C_3H_7^+$ 43	**a** $C_2H_4F^+$ 47	**c** $C_4H_7^+$ 55	**a** $C_4H_9^+$ 57	**c** $C_3H_4F^+$ 59	**a** $C_3H_6F^+$ 61	**a** $C_2H_3F_2^+$ 65	**b** CF_3^+ $C_5H_9^+$ 69	**a** $C_3H_3F_2^+$ 77	Charge exchange	Total observed ion current
Ethene													(28)	
CH_3^+	81	28	85										17	211
CH_2F^+	7	3	12					10						32
CHF_2^+	4	18	5					20						47
CF_3^+	9		7		21							11		48
Propene													(42)	
CH_3^+	7	33	31	17		10	3				10		44	155
CH_2F^+	4	31	13	13	8	4							5	78
CHF_2^+	3	8	20	31	31	9	3			6			8	119
CF_3^+			10	10	45	4		3	3	3			13	91
But-1-ene													(56)	
CH_3^+	5	25	16	5		18	11				3		55	137
CH_2F^+	3	16	12	9	6	9	3				2		5	65
CHF_2^+		8	19	8	8	23	18	10	5	4	4		16	123
CF_3^+		7	15	3	7	20	5	5	15	3		11	16	104
But-2-ene													(56)	
CH_3^+	6	20	14	6		25	8				2		98	179
CH_2F^+	2	7	8	6	6	15	4				2		39	89
CHF_2^+		9	13	4	11	35	19	9	4	7	5		57	173
CF_3^+		13	8		12	29	9	5	9	3	9		68	165
2-Methylpropene													(56)	
CH_3^+	7	21	15	4		21	32				5		70	175
CH_2F^+		8	11	8	5	13	12				2		23	82
CHF_2^+		7	15	4	8	25	39	11	11	3	5		35	163
CF_3^+		4	10	3	4	17	22	4	18		8		23	113



Scheme 13.

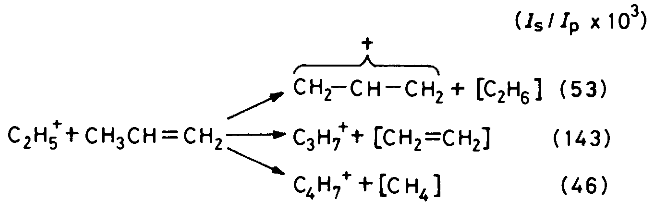
(Scheme 13), and $C_3H_4F^+$ a tertiary ion, but as the data show CH_2F^+ can be the primary ion and $C_3H_4F^+$ the secondary ion. Nonetheless it seems probable that the majority of the C_3 cations are formed as a result of a tertiary reaction rather than directly in a secondary reaction.

The second general feature of results is that as the fluorine content of both cation and the olefin increases so the extent of reaction decreases. In particular the addition of the fluoromethyl cations to the CF_2 end of a polyfluoroethene is very restricted.

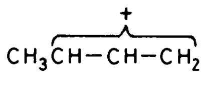
(b) *The Reactions of Methyl and Fluoromethyl Cations with Propene and the Butenes.*—The major difference in the reactions of fluoromethyl cations with propene and the butenes compared with the reaction of the same ions with fluoroethenes is that in the latter reactions tertiary and even quaternary ions are observed. The second feature of reactions with propene or the butenes is the importance of hydrogen atom transfer to yield allyl radicals.

For discussion of the results involving fluoroethenes it was convenient to treat reaction sequences **a** and **b** (see Scheme 1) as separate, but in systems involving four or more atoms the products are better regarded as belonging to the same family $(C_nH_{2n+1})^+$. Similarly the reaction sequences **c** and **d** lead to products belonging to the family $(C_nH_{2n-1})^+$. We will designate the first family *a* and indicate the higher homologues as *a*′, *a*″ *etc.*; similarly, the C_nH_{2n-1} family we will designate *c* (Table 1).

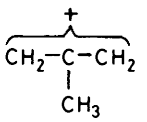
The principal secondary ions in the reaction of methyl cations with propene are $C_2H_5^+$ and $C_3H_5^+$. The further reactions of these two ions were therefore investigated. Both ions were prepared in the primary source, selected by the first quadrupole and allowed to react with propene in the second quadrupole. Both reactions resulted in a plethora of further ions. The pre-



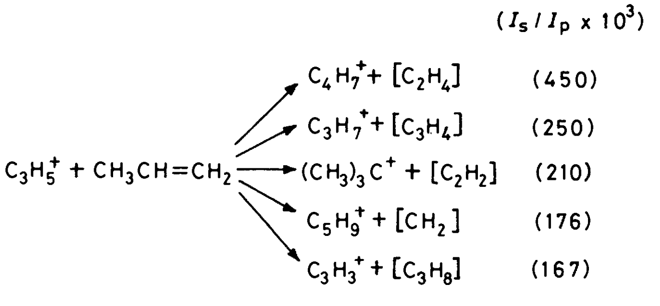
Scheme 14. The principal product ions from the reaction of $C_2H_5^+$ with propene



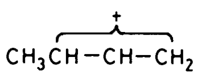
(1)



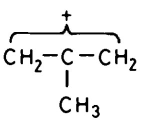
(2)



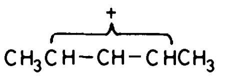
Scheme 15. The principal product ions from the reaction of $C_3H_5^+$ with propene



(3)



(4)



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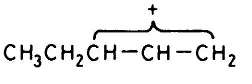

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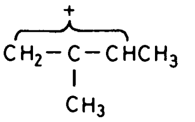

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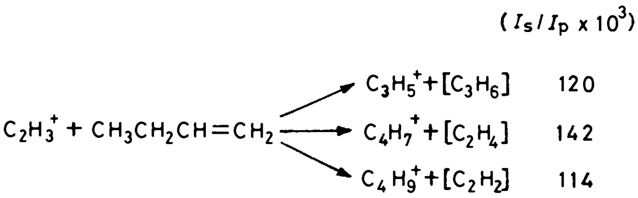
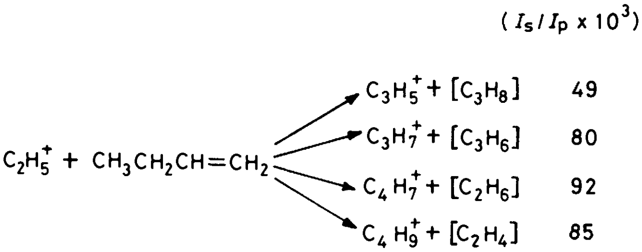
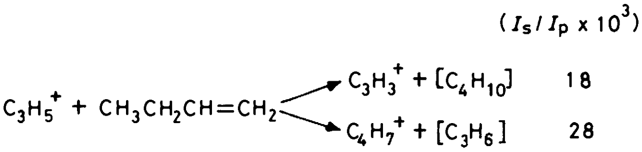


Scheme 16. The principal product ions from the reaction of $C_2H_3^+$ ions with but-1-ene



Scheme 17. The principal product ions from the reaction of $C_2H_5^+$ ions with but-1-ene



Scheme 18. The principal product ions from the reaction of $C_3H_5^+$ ions with but-1-ene

dominant ions are shown in Scheme 14 and 15. The fine structure of the substituted allyl ion is uncertain; it could be (**1**) or (**2**). The fine structure of the substituted allyl ions is uncertain; $C_4H_7^+$ could be (**3**) or (**4**) and $C_5H_9^+$ could be one of (**5**)—(**7**).

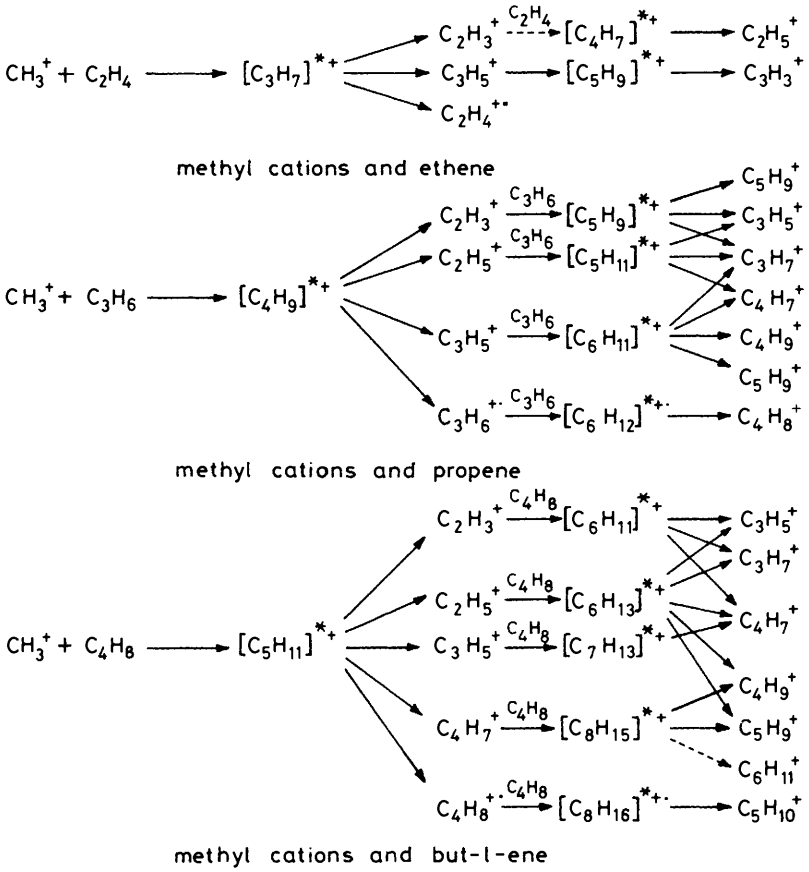
In addition to simple tertiary ions, there are ions which may be simultaneously secondary and tertiary. Thus in the reaction of methyl ions with propene, secondary ions (*m/e* 43; $C_3H_7^+$) are formed. Ions of the same mass (*m/e* 43) can also be derived from the reactions of $C_2H_5^+$ and of $C_3H_5^+$ with propene.

The principal ions from the reaction of methyl cations with the three butenes were *m/e* 29 ($C_2H_5^+$), 41 ($C_3H_5^+$), and 55 ($C_4H_7^+$). The reaction of methyl cations with 2-methylpropene (isobutene) also differed from the reaction with the other two butenes in the larger size of the *m/e* 57 ($C_4H_9^+$) peak. Unlike the other major secondary ions derived from but-1-ene and but-2-ene which give evidence of further reaction as the olefin concentration is increased, the *m/e* 57 ($C_4H_9^+$) ion derived from 2-methylpropene increases regularly with olefin concentration, *i.e.* the $C_4H_9^+$ ion once formed is relatively unreactive. The ion *m/e* 57 derived from 2-methylpropene is undoubtedly the t-butyl cation.

The forward reaction sequences of methyl cations with ethene, propene, and but-1-ene are summarised in Scheme 19. All the individual steps have been observed in isolation. Not included (except with ethene) are steps which involve the formation of smaller ions (Scheme 20). The notable feature of Scheme 19 is the number of ways in which the secondary activated complexes fragment; this is all the more striking when it is remembered that only the major ions are shown.

Turning to the results when fluoromethyl cations are the primary ions, we have seen that major ions from the reaction of CH_3^+ with ethene in order of abundance are *m/e* 27 ($C_2H_3^+$), 41 ($C_3H_5^+$), and 29 ($C_2H_5^+$). The same ions predominate in the reaction between CH_2F^+ and ethene together with the addition of *m/e* 59 ($C_3H_4F^+$). The identical ions also appear in the reaction between CHF_2^+ and ethene with the addition of *m/e* 33 (CH_2F^+). In the reaction of CF_3^+ with ethene, *m/e* 27 ($C_2H_3^+$) and 41 ($C_3H_5^+$) remain but all the other secondary ions contain fluorine: *m/e* 33 (CH_2F^+), 47 ($C_2H_4F^+$), 51 (CHF_2^+), and 77 ($C_3H_3F_2^+$).

The major ions from the reaction of methyl and the fluoromethyl cations with propene have the formula C_2H_4X where X = H or F, together with fluoro- or difluoro-ethene as the neutral fragment (Scheme 21). The second most important process was hydride transfer from propene to the primary methyl cation (Scheme 22). The *m/e* 43 ($C_3H_7^+$) ion is an important ion in the reactions of propene with CHF_2^+,



Scheme 19. The reaction sequences observed between methyl cations and ethene, propene, and but-1-ene

$$C_3H_5^+ + C_4H_8 \longrightarrow C_3H_3^+ + C_4H_{10}$$

Scheme 20.

$$CH_3^+ + CH_2{=}CHCH_3 \longrightarrow C_2H_5^+ + C_2H_4 \qquad I_s/I_p \quad 33 \times 10^{-3}$$

$$CH_2F^+ + CH_2{=}CHCH_3 \longrightarrow C_2H_5^+ + C_2H_3F \qquad I_s/I_p \quad 31 \times 10^{-3}$$

$$CHF_2^+ + CH_2{=}CHCH_3 \longrightarrow C_2H_4F^+ + C_2H_3F \qquad I_s/I_p \quad 31 \times 10^{-3}$$

$$CF_3^+ + CH_2{=}CHCH_3 \longrightarrow C_2H_4F^+ + C_2H_2F_2 \qquad I_s/I_p \quad 45 \times 10^{-3}$$

Scheme 21.

CH_2F^+, and CF_3^+. In the latter reaction $C_3H_7^+$ must be a tertiary ion (Scheme 23). If this mechanism is correct then it is extremely likely that the high yield of *m/e* 43 ($C_3H_7^+$) in the reaction products of *m/e* 51 (CHF_2^+) with propene is partly due to the corresponding tertiary reaction (Scheme 24). The reactions of the fluoromethyl cations with the three butenes are best discussed together. The ion *m/e* 29 ($C_2H_5^+$) is quite strong in each of the product spectra. The most interesting region includes the ions *m/e* 55 ($C_4H_7^+$), 56 ($C_4H_8^+$), and 57 ($C_4H_9^+$). When but-1-ene is the neutral species the predominant ion in this region is $C_4H_7^+$ and indeed, when CHF_2^+ and CF_3^+ are primary ions, $C_4H_7^+$ is the largest peak in the whole spectrum. When but-2-ene is the neutral

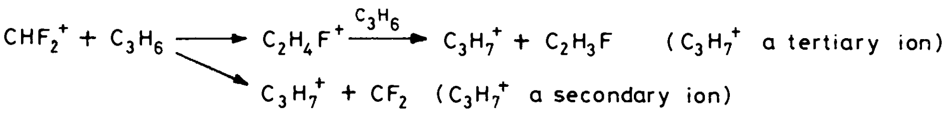
$$CX_3^+ + CH_3CH{=}CH_2 \longrightarrow C_3H_5^+ + CX_3H \qquad \text{(where X = F and/or H)}$$

$$(I_s/I_p \times 10^3;\ CH_3^+\ 31;\ CH_2F^+\ 13;\ CH_2F^+\ 20;\ \text{and}\ CF_3^+\ 31)$$

Scheme 22.

$$CF_3^+ + C_3H_6 \longrightarrow C_2H_4F^+ \xrightarrow{C_3H_6} C_3H_7^+ + C_2H_3F$$

Scheme 23.



$$CHF_2^+ + C_3H_6 \longrightarrow C_2H_4F^+ \xrightarrow{C_3H_6} C_3H_7^+ + C_2H_3F \qquad (C_3H_7^+\ \text{a tertiary ion})$$

$$CHF_2^+ + C_3H_6 \longrightarrow C_3H_7^+ + CF_2 \qquad (C_3H_7^+\ \text{a secondary ion})$$

Scheme 24.

Table 3. Fluorine incorporation in the secondary ions derived from the reaction of fluoromethyl cations with but-1-ene

$(I_S/I_P \times 10^3)$						
$CH_3^+ + C_4H_8 \longrightarrow$	$C_2H_5^+$	(25)	$C_3H_5^+$	(16)	$C_3H_7^+$	(5)
$CH_2F^+ + C_4H_8 \longrightarrow$	$C_2H_5^+$	(16)	$C_3H_5^+$	(12)	$C_3H_7^+$	(9)
$\longrightarrow$	$C_2H_4F^+$	(16)				
$CHF_2^+ + C_4H_8 \longrightarrow$	$C_2H_5^+$	(8)	$C_3H_5^+$	(19)	$C_3H_7^+$	(8)
$\longrightarrow$	$C_2H_4F^+$	(8)	$C_3H_4F^+$	(10)	$C_3H_6F^+$	(5)
$\longrightarrow$	$C_2H_3F_2^+$	(4)				
$CF_3^+ + C_4H_8 \longrightarrow$	$C_2H_5^+$	(7)	$C_3H_5^+$	(15)	$C_3H_7^+$	(3)
$\longrightarrow$	$C_2H_4F^+$	(7)	$C_3H_4F^+$	(5)	$C_3H_6F^+$	(15)
$\longrightarrow$	$C_2H_3F_2^+$	(11)	$C_3H_3F_2^+$	(11)		

$$C_2H_5^+ + C_4H_8 \longrightarrow C_2H_4 + C_4H_9^+$$

$$C_2H_5^+ + C_4H_8 \longrightarrow C_2H_6 + C_4H_7^+$$

Scheme 25.

olefin the predominant product ion from all the primary ions is $C_4H_8^+$, *i.e.* the charge-exchange product. When 2-methylpropene is the neutral and the methyl cation is the primary ion, $C_4H_8^+$ is still the predominant product ion, but the peaks corresponding to $C_4H_7^+$ and $C_4H_9^+$ are of comparable intensity. The proportion of the $C_4H_9^+$ ion decreases very rapidly when the pressure of the collision gas is very low. This strongly suggests that this ion is a tertiary species, and indeed when CF_3^+ is the primary ion, $C_4H_9^+$ must be tertiary. This ion, the t-butyl cation [$(CH_3)_3C^+$], is formed by disproportionation (Scheme 25). The $C_4H_7^+$ ion may be formed by a similar disproportionation reaction. The relatively high concentration of the $C_4H_7^+$ suggests that this ion is probably the delocalised methyl allyl [$CH_3\overbrace{CH\text{–}CH\text{–}CH_2}^{+}$ from $CH_3CH_2CH{=}CH_2$ and $\overbrace{CH_2\text{–}C(CH_3)\text{–}CH_2}^{+}$ from $CH_2{=}C(CH_3)CH_3$].

The ion $C_5H_9^+$ (*m*/*e* 69) occurs in the reaction of CH_3^+ with propene and the reactions of CH_2F^+ and CHF_2^+ with butenes, where the olefin concentration is high (*i.e.* it is a tertiary ion).

The incorporation of fluorine into the secondary ions is in Table 3. A very similar pattern of ions was obtained when propene was the target gas. Even when the primary ion was CF_3^+, fluorine atoms were incorporated more into the neutral fragments than into the secondary ions. The increasing fluorine incorporation in the fragment ions as the fluorine content of the primary ion increases shows that there is appreciable scrambling of the fluorine atoms. We have previously noted that hydrogen atom scrambling is very extensive in the addition complexes formed by alkyl radicals interacting with olefins.

Table 2 shows the total observed ion current in the exothermic reactions varies according to the nature of the primary ion. The order is $CH_2F^+ \ll CF_3^+ < CHF_2^+ < CH_3^+$. The fluoromethyl cation appears out of order. The fluoromethyl cation was derived from electron bombardment of symmetrical difluoroacetone whereas the primary ions were derived from electron bombardment of halogenomethane (CHF_2^+ from CH_2F_2; CF_3^+ from CF_4; and CH_3^+ from CH_4). The possibility that the fluoromethyl cation formed from a ketone may be in different electronic state to the cations formed from substituted methanes needs further investigation.

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