Studies of Ion Molecule Reactions using a Multiple Quadrupole Mass Spectrometer. Part 3.[1] The Reactions of Alkenyl Radical Cations $C_nH_{2n}^+$ with Alkenes

Alan L. Mitchell and John M. Tedder
Department of Chemistry, The University of St. Andrews, Fife KY16 9ST, Scotland

---

The gas-phase reactions of ethenyl ($C_2H_4^{+\cdot}$), propenyl ($C_3H_6^{+\cdot}$), and butenyl ($C_4H_8^{+\cdot}$) with each of ethene, propene, but-1-ene, *cis*-but-2-ene, and 2-methylpropene have been reinvestigated using a triple quadrupole mass spectrometer. The present results are on the whole in good agreement with earlier studies, but the triple quadrupole enables reactions to be studied over a wider pressure range than the majority of previous investigations. It is particularly easy to isolate proposed sequences and thus to confirm (or disprove) particular reaction pathways.

The literature describing studies of the reactions of alkene radical cations is very extensive and only major investigations will be discussed here. The earliest significant work involved relatively high pressures using α-particle radiolysis of ethene;[2] high-pressure mass spectrometry of ethene was studied by Wexler and Marshall;[3] Myher and Harrison studied ion–molecule reactions in which $C_2H_4^{+\cdot}$ was the only primary ion;[4] Tiernan and Futrell used a time of flight mass spectrometer to study ethene at low pressures;[5] and Bowers *et al.* used ion cyclotron resonance to study ion–molecule reactions in ethene at very low pressures.[6] Studies of larger ions and molecules include propene radical cations reacting with propene,[7] and with butenes;[8] the effect of kinetic energy on ionic reactions;[9] further studies on ion–molecule reactions in propene;[10] and evidence that the distribution of product ions is strongly dependent on kinetic energy.[11]

It can be seen that studies have been made at high pressure (> 1 Torr) and at very low pressure (10^{-6} Torr); the present apparatus is particularly well suited to studying the intermediate pressure range. For example $C_3H_5^+$ is the predominant product ion in the reaction of $C_2H_4^{+\cdot}$ with C_2H_4 at the lowest pressures 5×10^{-6} Torr, while $C_5H_9^+$ is the predominant ion at 2.0 Torr. The present study as far as possible straddles these two studies and shows in fact that $C_5H_9^+$ is a tertiary ion derived from the reaction of the secondary ion $C_3H_5^+$ with ethene (C_2H_4). Unlike much of the previous work the study of the cross-reaction between an alkene radical cation with a different alkene presents no experimental difficulties. Thus the information easily obtained from a triple quadrupole is often greater than that of most of the earlier techniques.

The apparatus has been described in previous papers. The reactants were all commercial materials used without purification beyond 'degassing' to remove air. All the reactions were studied over a wide range of secondary reactant pressures and over several primary ion fluxes. The results are all at constant pressure; Tables listing mass spectra at different pressures are in Supplementary Publication No. SUP 56558 (13 pp.).†

$$C_2H_4^{+\cdot} + C_2H_4 \longrightarrow [C_4H_8]^{*+\cdot} \longrightarrow C_3H_5^+ + CH_3^{\cdot} \quad (1)$$

$$C_2H_4^{+\cdot} + C_2H_4 \longrightarrow [C_4H_8]^{*+\cdot} \longrightarrow C_4H_7^+ + H^{\cdot} \quad (2)$$

$$C_3H_5^+ + C_2H_4 \longrightarrow [C_5H_9]^{*+} \xrightarrow{M} C_5H_9^+ \quad (3)$$

$$C_4H_7^+ + C_2H_4 \longrightarrow [C_6H_{11}]^{*+} \xrightarrow{M} C_6H_{11}^+ \quad (4)$$

The Interaction between the Ethenyl Radical Cation $C_2H_4^{+\cdot}$ *and Ethene.*—The principal reaction between the ethenyl radical ion $C_2H_4^{+\cdot}$ and ethene is disproportionation (1) to yield $C_3H_5^+$ (*m/e* 41) and neutral methyl radicals. The only other secondary ion formed in appreciable yield is $C_4H_7^+$ (*m/e* 55) with hydrogen atoms being ejected [reaction (2)]. Figures 1a and b show clearly that these two ions are the only major secondary ions. The principal tertiary ion is $C_5H_9^+$ (*m/e* 69). In separate experiments the ion $C_3H_5^+$ (prepared from a variety of sources) was treated with ethene and gave $C_5H_9^+$ in high yield. Hence in the present study this ion is chiefly formed by the addition of $C_3H_5^+$ ions with ethene [reaction (3)]. The corresponding tertiary ion $C_6H_{11}^+$ (*m/e* 83) derived from $C_4H_7^+$ (*m/e* 55) is also observed but in very low concentration. As the pressure of ethene increased so the proportion of $C_6H_{11}^+$ increased while the proportion of $C_4H_7^+$ decreased. In separate experiments reaction (4) of $C_4H_7^+$ with ethene gave $C_6H_{11}^+$ in high yield. The alternative fate of the two secondary ions is fragmentation.

The c.i.d. (collision-induced decomposition) spectrum of $C_3H_5^+$ consists of a single fragment $C_3H_3^+$ but the c.i.d. spectrum of $C_4H_7^+$ consists of $C_2H_5^+$, $C_3H_3^+$, and $C_4H_5^+$, in relative proportions which vary slightly depending on the nature of the collision gas (0.4:0.3:0.3).

The remaining product ions occurring in appreciable concentration were quaternary ions and their origin was established by a series of independent experiments: (i) $C_5H_7^+$ whose concentration increased as the concentration of $C_5H_9^+$ increased, was formed in the c.i.d. of $C_5H_9^+$ (the $C_5H_9^+$ ions were prepared by electron impact on cyclopentane and cyclohexane): (ii) $C_7H_{13}^+$ was formed by the addition of $C_5H_9^+$ to C_2H_4 (other ions observed included $C_3H_3^+$ 62%, $C_5H_2^+$ 9%); (iii) C_8H_{15} was formed similarly.

$$C_5H_9^+ + M \longrightarrow C_5H_7^+(H_2)\ 25\%,\ C_3H_5^+(C_2H_4)\ 75\% \quad (5)$$

$$C_5H_9^+ + C_2H_4 \longrightarrow C_7H_{13}^+\ 6\% \quad (6)$$

$$C_6H_{11}^+ + C_2H_4 \longrightarrow C_8H_{15}^+ \quad (7)$$

---

† For details of Supplementary Publications, see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1.

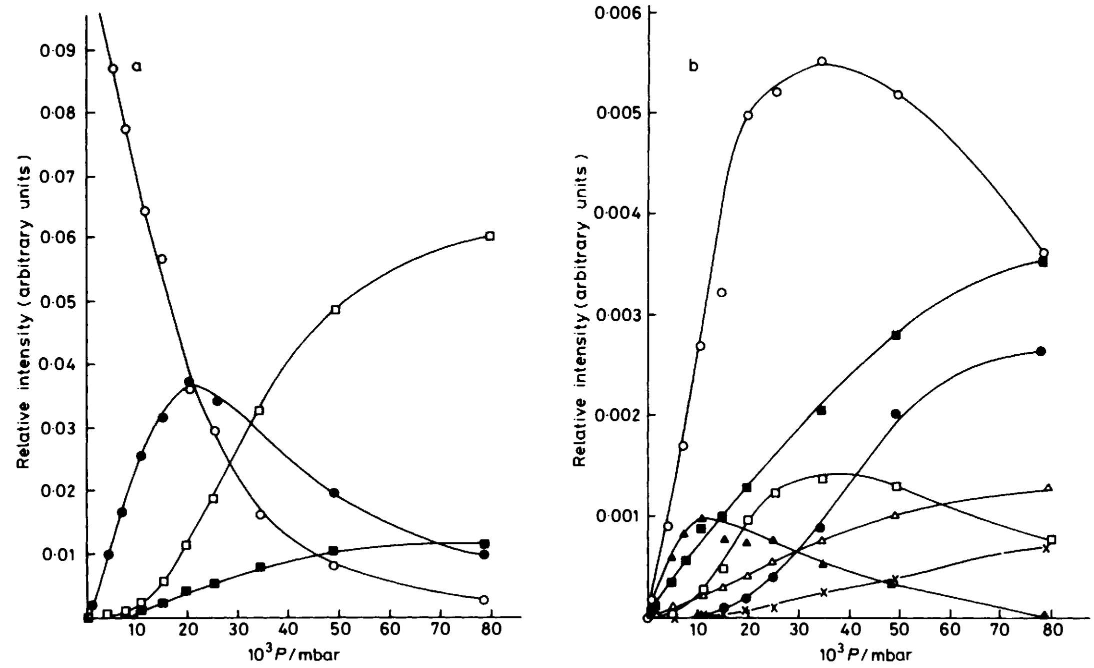
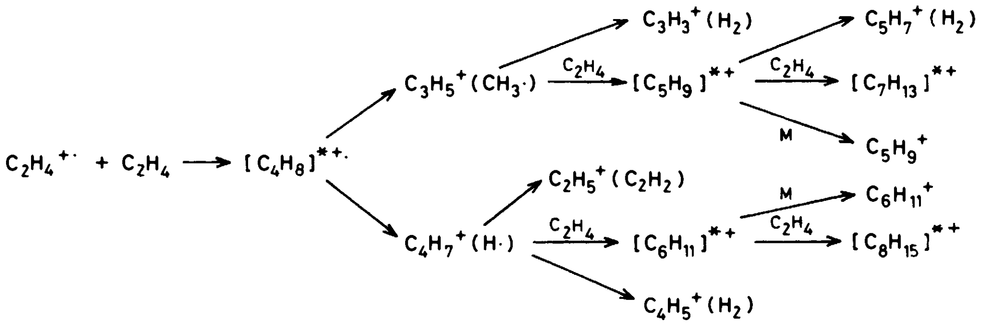
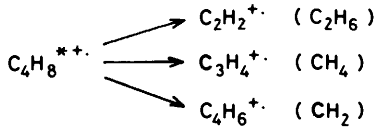


Figure 1. a: ○, *m/e* 28; ●, *m/e* 41; □, *m/e* 69; ■, 67. b: ○, *m/e* 55; ●, *m/e* 83; □, *m/e* 29; ■, *m/e* 39; ▲, *m/e* 26; △, *m/e* 53; ×, *m/e* 56

We can now draw on Scheme 1 for the principal forward interactions of $C_2H_4^{+\cdot}$ with C_2H_4 (many of the steps are reversible but these are not shown).



Scheme 1. The forward reaction sequences of $C_2H_4^{+\cdot}$ with C_2H_4.



Scheme 2.

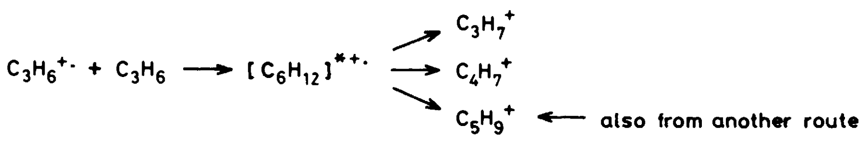
In addition there were trace amounts (*i.e.* < 10^{-2} of the principal secondary ions) of odd-electron ions *m/e* $C_4H_6^{+\cdot}$, $C_3H_4^{+\cdot}$, and $C_2H_2^{+\cdot}$. These three ions are probably secondary ions derived directly from $[C_4H_8]^{*+\cdot}$ (Scheme 2). Another very minor ion is $C_2H_3^+$ which may also be derived from the initial adduct [reaction (8)].

$$C_4H_8^{*+\cdot} \longrightarrow C_2H_3^+ + C_2H_5\cdot \qquad (8)$$

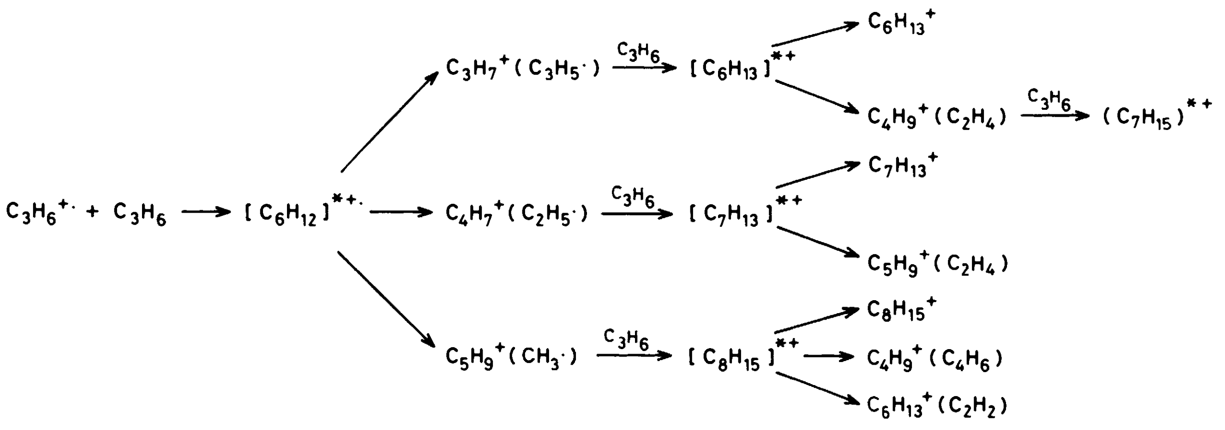
Unlike the odd-electron ions whose concentration decreases rapidly with increasing ethylene pressure, the concentration of $C_2H_3^+$ only decreases slowly. It is important to appreciate that in the triple quadrupole apparatus the yield of these minor ions in Figure 1b is an order of magnitude lower than the principal ions depicted in Figure 1a.

The Interaction between Propenyl Radical Cations $C_3H_6^{+\cdot}$ and Propene.—The very striking feature of the series of reactions initiated by the interaction of $C_3H_6^{+\cdot}$ with C_3H_6 is the occurrence of two reaction sequences, one involving even-electron ions and the other involving odd-electron ions. This is in sharp contrast with the ethenyl–ethene system where all the major ions were even-electron species. We will consider the even-electron reactions first.

There are three secondary even-electron ions $C_3H_7^+$ (*m/e* 43), $C_4H_7^+$ (*m/e* 55), and $C_5H_9^+$ (*m/e* 69). The latter ion, $C_5H_9^+$, is derived from two separate routes, one of which is directly from the initial complex (Scheme 3). The total yield of secondary ions is less than that for the C_2H_4 system, but unlike ethene the three secondary ions are formed in nearly equal yield. As the pressure



Scheme 3.



Scheme 4. The forward reaction sequence involving even-electron ions derived from $C_3H_6^+$ with C_3H_6.

of propene increases so the yield of the tertiary ion $C_4H_9^+$ (*m/e* 57) increases until at the highest pressures it was the major product ion. The reaction of $C_3H_7^+$ (formed by electron impact on n-butane) with propene was investigated as a separate series of experiments and at relatively high pressures the main product from $C_3H_7^+$ with the starting propene is $C_4H_9^+$ [reaction (9)].

$$\begin{aligned} C_3H_7^+ + C_3H_6 \longrightarrow\ & C_4H_9^+ (66\%) \\ & \text{and} \\ & C_6H_{13}^+ (16\%) \end{aligned} \qquad (9)$$

The formation of the other main tertiary ions was elucidated in a similar series of studies: (i) the reaction of $C_4H_7^+$ (formed by electron impact on methylcyclopentane) with propene yielded $C_7H_{13}^+$ and $C_5H_9^+$ ($+C_2H_4$); (ii) the reaction of $C_5H_9^+$ (formed by electron impact on *trans*-hex-3-ene) with propene yielded $C_8H_{15}^+$ and $C_7H_{13}^+(C_2H_2)$; (iii) C_7H_{13} ions underwent c.i.d. to provide another source of $C_5H_9^+(+C_2H_4)$.

We can now draw Scheme 4 for the principal forward reactions arising from the reaction of $C_3H_6^+$ with C_3H_6.

There are three series of even electron-ions, two of the form C_nH_{n-1} ($C_4H_7^+ \longrightarrow C_7H_{13}^+$ and $C_5H_9^+ \longrightarrow C_8H_{15}^+$) and one of the form C_nH_{2n+1} ($C_3H_7^+ \longrightarrow C_6H_{13}^+ \longrightarrow C_7H_{15}^+$) in contrast to the products with $C_2H_4^+$, where the ions C_nH_{2n-1} form the only series. In the ethene reactions all the predominant ions were even-electron ions, but odd-electron reactions represent important processes in the propene system. Not only is $C_4H_8^{+\cdot}$ an important secondary ion, but $C_5H_{10}^{+\cdot}$ is also a major ion. The concentration dependence of this latter ion shows it to be a tertiary ion.

$$C_3H_6^{+\cdot} + C_3H_6 \longrightarrow [C_6H_{12}]^{*+\cdot} \longrightarrow C_4H_8^{+\cdot}(C_2H_4) \xrightarrow{C_3H_6} C_5H_{10}^{+\cdot}(C_2H_4) \qquad (10)$$

The forward sequence of odd-electron ions derived from $C_3H_6^{+\cdot}$ with C_3H_6.

The most striking feature of the results depicted in Figure 2 is the closeness of the curves of $C_3H_7^+$ and $C_4H_8^{+\cdot}$. There seems no doubt that these ions are derived from a common precursor, and both are associated with the formation of stable species, the allyl radical and the ethene molecule respectively (Scheme 5).

The principal product ions from the interaction of the butenyl radical cations with the corresponding butenes are listed in Table 1. The first feature of this Table is that all the product ions are fragment ions (secondary and tertiary); and no ions with more than seven carbon atoms were detected in appreciable concentration. The secondary ions observed are similar for all three butenes although their structures may differ and the relative proportions of different ions vary considerably. Two separate series of product ions can be distinguished with an even number of electrons (the first series $C_3H_5^+$, $C_4H_7^+$, $C_5H_9^+$, and $C_6H_{11}^+$ and the second series $C_4H_9^+$ and $C_5H_{11}^+$). There is in addition a series of odd-electron ions $C_4H_8^{+\cdot}$, $C_5H_{10}^{+\cdot}$, and $C_6H_{12}^{+\cdot}$. The very different proportions of product ions will be considered in the Discussion section.

Cross-products. (a) C_2H_4 *and* C_3H_6. The reactions between a neutral alkene and a different radical cation can easily be studied in a multiple quadrupole mass spectrometer. The results of the cross reaction between ethenyl cations into propene and propenyl cations with ethene are listed in Table 2. The principal reaction pathways for the interaction of ethene and propene with the corresponding cations can be summarised in Scheme 6. The chief secondary ion in the reaction of an ethene radical cation with a neutral ethene molecule is $C_3H_5^+$ (*m/e* 41), but as the pressure of ethene is raised the yield of the tertiary ion $C_5H_9^+$ (*m/e* 69) increases until at high pressures it becomes the predominant ion. The interaction between the propene radical cation and ethene is endothermic and the extent of reaction is much less, but the predominant secondary ion is $C_4H_7^+$ (*m/e* 55) which at the higher ethene pressure yields $C_6H_{11}^+$ (*m/e* 83) as a tertiary ion. The product ions from the reaction of the propene radical cation with propene are the same as those

Table 1. Principal product ions from the interaction between butenyl radical ions and the corresponding butene: % secondary ion signal at *ca.* 5 × 10^{-3} mbar (3.75 × 10^{-3} Torr)

Olefin	$C_3H_5^+$	$C_4H_7^+$	$C_4H_9^+$	$C_5H_9^+$	$C_5H_{10}^{+\cdot}$	$C_5H_{11}^+$	$C_6H_{11}^+$	$C_6H_{12}^{+\cdot}$
$C_2H_5CH{=}CH_2$	7	8	16	8	12	17	9	10
cis-$CH_3CH{=}CHCH_3$	4	6	8	6	8	5	33	26
$(CH_3)_2C{=}CH_2$	2	1	87	1	2	5	0.5	0.4

Table 2. The principal ions formed in the cross-reactions of ethenyl cations with propene and propenyl cations with ethene at 5 × 10^{-3} mbar (3.73 Torr): % secondary ion signal. *P* = parent ion.

	28	41	42	43	55	56	57	67	69	70	83	111
	$C_2H_4^+$	$C_3H_5^+$	$C_3H_6^+$	$C_3H_7^+$	$C_4H_7^+$	$C_4H_8^{+\cdot}$	$C_4H_9^+$	$C_5H_7^+$	$C_5H_9^+$	$C_5H_{10}^{+\cdot}$	$C_6H_{11}^+$	$C_8H_5^+$
$C_2H_4^{+\cdot} + C_2H_4$	*P*	21			5			11	52		2	
$C_3H_6^{+\cdot} + C_2H_4$		8	*P*		49			2	6	12	16	
$C_2H_4^{+\cdot} + C_3H_6$	*P*	2	5	9	6	9	29	1	14	8	1	1
$C_3H_6^{+\cdot} + C_3H_6$		2	*P*	8	6	8	28	1	14	10	1	3

Table 3. The cross-reactions of ethenyl cations and butenyl cations with ethene and two butenes at 5 × 10^{-3} mbar (3.75 × 10^{-3} Torr): % secondary ion signal. *P* = parent ion.

	41	43	55	56	57	67	69	70	71	82	83	84
	$C_3H_5^+$	$C_3H_7^+$	$C_4H_7^+$	$C_4H_8^{+\cdot}$	$C_4H_9^+$	$C_5H_7^+$	$C_5H_9^+$	$C_5H_{10}^{+\cdot}$	$C_5H_{11}^+$	$C_6H_{10}^{+\cdot}$	$C_6H_{11}^+$	$C_6H_{12}^{+\cdot}$
$C_2H_4^{+\cdot} + C_2H_5CH{=}CH_2$	5	2	9	41	11	1	6	6	7	2	6	4
$C_2H_4^{+\cdot} + CH_3CH{=}CHCH_3$	1	1	2	38	10	1	5	3	3	1	18	16
$C_2H_4^{+\cdot} + CH_2{=}C(CH_3)_2$	2	1	2	8	76		2	2	5	1	1	1
$(C_2H_5CH{=}CH_2)^{+\cdot} + C_2H_4$	18	5	21	*P*		6	29	5	2		10	5
$(CH_3CH{=}CHCH_3)^{+\cdot} + C_2H_4$	15	1	11	*P*		11	37	1	1		3	19
$[CH_2{=}C(CH_3)_2]^{+\cdot} + C_2H_4$	39	4	18	*P*		9	19	2				9

Table 4. The reaction of ethenyl radical cations with ethene molecules expressed as % total secondary ion current

	Ref. 5		Field	Present work			Ref. 3
m/*e*	5 × 10^{-6} Torr	6 × 10^{-5} Torr	2 × 10^{-4} Torr	4.3 × 10^{-4} Torr	2.5 × 10^{-3} Torr	7.8 × 10^{-3} Torr	2 × 10^{-2} Torr
26			0.9	4.5	1.1		0.1
27			7.7	1.8	0.6	0.5	0.2
29	2.3	1.9	19.3		1.7	0.6	0.7
39	0.6	0.7	4.2	2.8	2.3	3.6	5.2
40	0.9	1.1	1.2	2.2	0.7	0.1	0.1
41	84	80	52	77	49	11	5
53		0.2	3	0.5	0.8	1.4	3.1
54	0.4	0.4	0.3	0.3	0.5	0.4	0.2
55	10	9.4	4.2	7.0	7.4	3.7	2.0
56	0.2	0.5	1.5	0.2	0.2	0.7	6.0
57			0.2		0.1	0.4	5.5
67		0.5	0.6	1.5	8.1	12	2.8
69	0.1	3.1	2.1	1.8	27	62	60
79			0.2			0.3	1.2
81			0.01				1.3
83			0.05		0.6	2.7	3.4
97						0.3	1.0

Table 5. The reaction of propenyl radical cations with propene molecules: % of principal secondary ions

m/*e*	Ref. 8	Refs. 12, 13	Ref. 14	Ref. 10	Ref. 9	Present work 7 × 10^{-5}	Present work 4 × 10^{-3}	Ref. 15
$C_3H_7^+$ 43	27	30	27	26	21	24	23	24
$C_4H_7^+$ 55	18	25	21	19	11	20	16	13
$C_4H_8^+$ 56	34	22	29	33	42	33	23	43
$C_5H_9^+$ 69	21	15	23	22	26	23	39	20

Table 6. The reactions of but-1-enyl, but-2-enyl, and 2-methylpropenyl cations with their parent molecules: % principal product ions*

	$C_4H_9^+$	$C_5H_9^+$	$C_5H_{10}^{+\cdot}$	$C_5H_{11}^+$	$C_6H_{11}^+$	$C_6H_{12}^{+\cdot}$	*P*/Torr	Ref.
$CH_3CH_2CH{=}CH_2^{+\cdot} + CH_3CH_2CH{=}CH_2$	25	16	31	6	16	7	5×10^{-6}	13
	14	4	38	3	22	15	5×10^{-5}	8
	22	11	16	24	13	14	4×10^{-3}	
$CH_3CH_2{=}CHCH_3^{+\cdot} + CH_3CH{=}CHCH_3$	55	45					5×10^{-6}	13
	70	4	10		10	6	5×10^{-3}	8
	9	14	9	6	35	28	4×10^{-3}	
$(CH_3)_2C{=}CH_2^{+\cdot} + (CH_3)_2C{=}CH_2$	86	14					5×10^{-6}	13
	93	3	2				5×10^{-3}	8
	90	1	2	6			4×10^{-3}	

* *N.b.* Ref. 8 does not take into account fragment–secondary ions of *m/e* less than that of the primary ion – ions which are seen by both Koyana and ourselves; the figures quoted here are thus expressed as % of the six principal ions used in this Table.

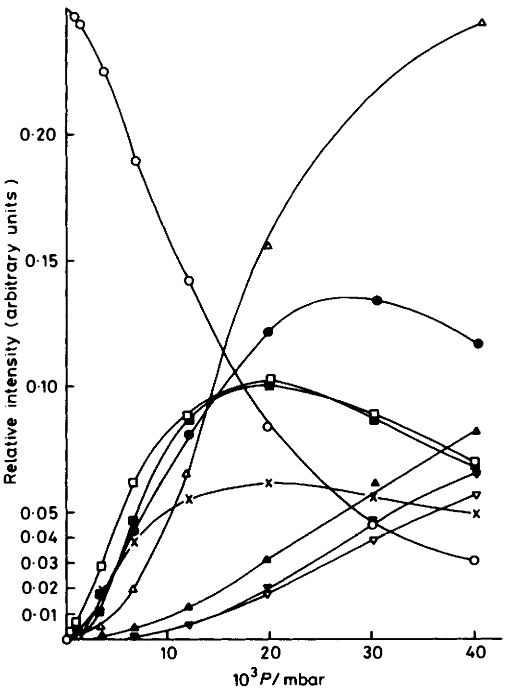
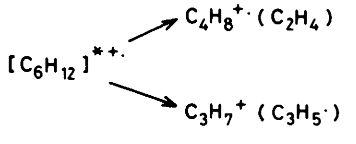
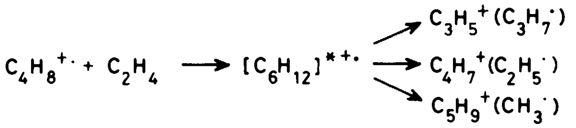


Figure 2. ○, *m/e* 42 × $\frac{1}{4}$; ●, *m/e* 69; □, *m/e* 56; ■, *m/e* 43; △, *m/e* 57; ▲, *m/e* 70; ▽, *m/e* 97; ▼, *m/e* 85; ×, *m/e* 55



Scheme 5. The interaction between butenyl radical cations with but-1-ene, *cis*-but-2-ene, and 2-methylprop-1-ene



Scheme 7.

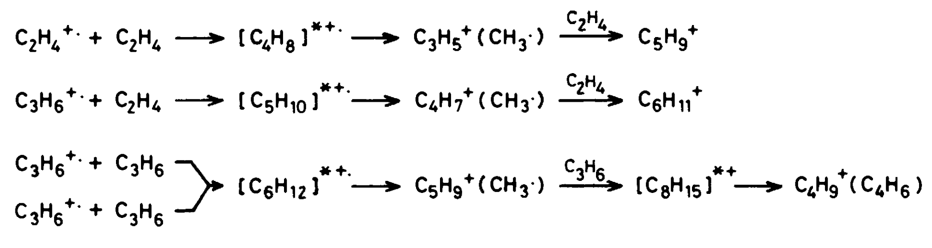
derived from the reaction of the ethene radical cations with propene, and the relative yields are the same. The reason for this is that the principal reaction of the ethene radical cation with propene is charge exchange.

$$C_2H_4^{+\cdot} + C_3H_6 \longrightarrow C_2H_4 + C_3H_6^{+\cdot} \qquad (11)$$

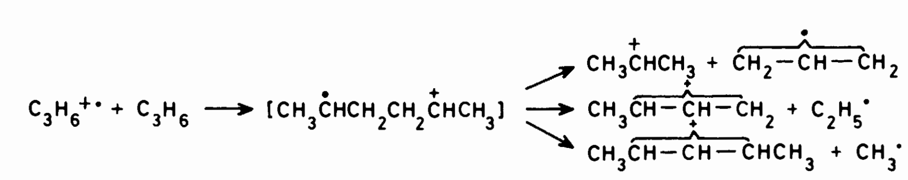
(b) C_2H_4 *and* C_4H_8. Table 3 shows the principal reaction of the ethene radical cation with but-1-ene and but-2-ene is simply charge-exchange. The yields of secondary ions from the reactions of the two butene radical cations with ethene are low as would be expected for an endothermic process. The principal ions are all fragments derived from the simple adduct (Scheme 7). The reactions of the but-1-enyl and but-2-enyl cations, formed by charge exchange with ethenyl ions, are those already observed in the reactions of butenyl cations with the neutral butenes (see Table 1). In particular the high yields of $C_6H_{11}^+$ and $C_6H_{12}^{+\cdot}$ in the reaction of ethenyl cations with but-2-ene should be noted.

Discussion

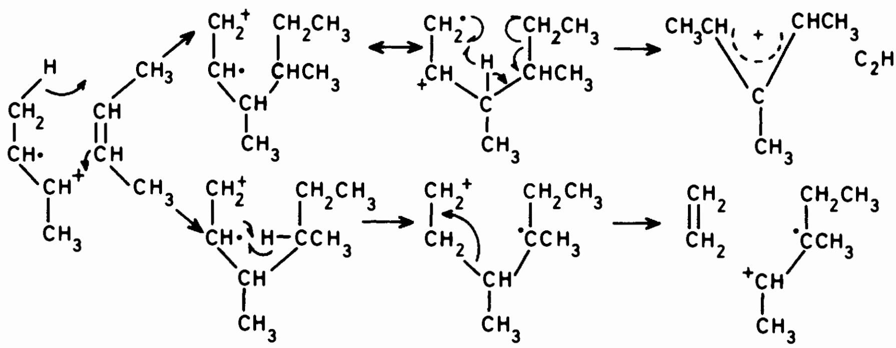
Three studies of the reaction of the ethenyl radical cation with ethene are summarised in Table 4. The most striking feature is the rapid decrease in the yield of the $C_3H_5^+$ (*m/e* 41) ion as the pressure of ethene increases. This decrease in the yield of $C_3H_5^+$ is matched by a dramatic increase in the yield of $C_5H_9^+$ (*m/e* 69). The importance of being able to study the reactions over a



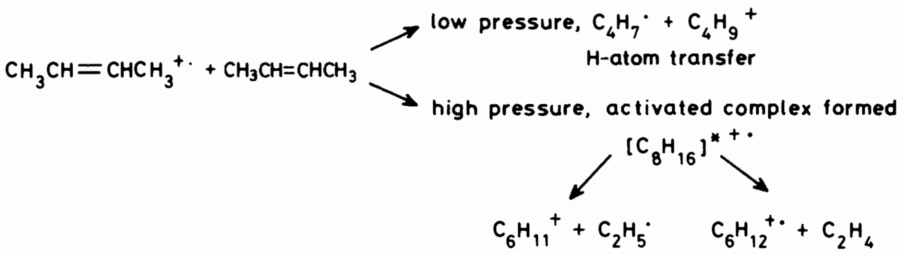
Scheme 6.



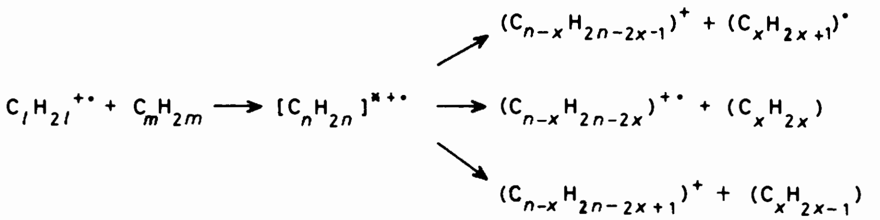
Scheme 8.



Scheme 9.



Scheme 10.



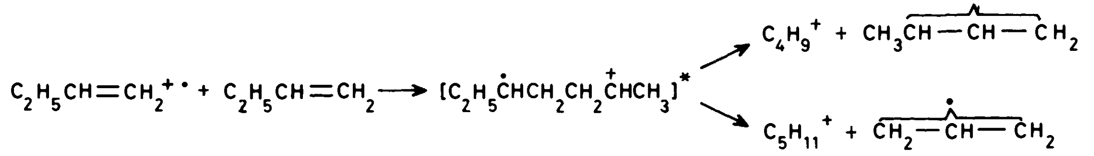
Scheme 11. l = 2,3, ...; m = 2,33, ...; n = (l + m); x = 0,1,2, ...

wide range of pressure illustrates one of the advantages of a multiple quadrupole. The proportion of secondary ions will in general decrease as the pressures rises (*e.g.* $C_2H_5^+$ *m*/*e* 29; $C_3H_5^+$ *m*/*e* 41; $C_4H_7^+$ *m*/*e* 55; $C_3H_3^+$ *m*/*e* 39) while tertiary and higher order ions will increase (*e.g.* $C_4H_5^+$ *m*/*e* 53; $C_5H_7^+$ *m*/*e* 67; $C_5H_9^+$ *m*/*e* 69; $C_6H_{11}^+$ *m*/*e* 83). The present results bridge the data obtained previously. They show that the large cross section for *m*/*e* 29 (see Table 4) reported by Field must have been an artefact and the presence of *m*/*e* 42 reported by Tiernan and Futrell[5] (not included in Table 4) was also probably an instrumental error. On the whole, however, now that the present results are available to cover the important intermediate pressure range, a very concordant picture is obtained.

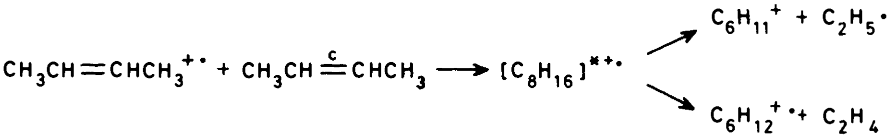
The four principal secondary ions from the reaction of the propenyl radical cation with propene molecules are listed in Table 5. The agreement between the different techniques is satisfactory especially as they represent studies at very different pressures. Steric factors suggest that the intermediate adduct ion was the result of a linear transition state. We can depict the formation of the even-electron ions by Scheme 8.

$C_5H_9^+$ May have the alternative linear structure $C_2H_5\text{-}\overbrace{\text{CH-CH-CH}_2}^{+}$. There is also the odd-electron butene radical cation $CH_3\overset{+}{C}H\text{-}\dot{C}HCH_3$. The major tertiary ion is $C_4H_9^+$ derived from two sources ($C_6H_{13}^{+*} \longrightarrow C_4H_9^+ + C_2H_4$ and $C_8H_{15}^{+*} \longrightarrow C_4H_9^+ + C_4H_6$). Unlike the secondary ions it is probably branched and its relative lack of reactivity, as instanced by its accumulation at higher pressures, suggest that it is either the 2-methylpropyl cation $(CH_3)CHCH_2^+$ or more likely the t-butyl cation $(CH_3)_3C^+$.

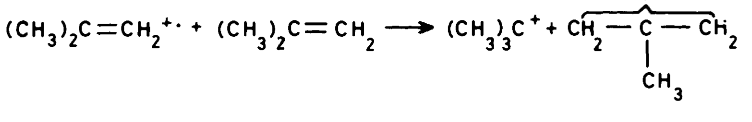
$$C_4H_8^{+\cdot} + C_4H_8 \longrightarrow C_4H_9^+ + C_4H_7^\cdot \qquad (12)$$



$$C_2H_5CH{=}CH_2^{+\cdot} + C_2H_5CH{=}CH_2 \longrightarrow [C_2H_5\dot{C}HCH_2CH_2\overset{+}{C}HCH_3]^* \longrightarrow C_4H_9^+ + CH_3\dot{C}H{-}CH{-}CH_2 \;\text{or}\; C_5H_{11}^+ + \dot{C}H_2{-}CH{-}\dot{C}H_2 \qquad (13)$$



$$CH_3CH{=}CHCH_3^{+\cdot} + CH_3CH\overset{c}{=}CHCH_3 \longrightarrow [C_8H_{16}]^{*+\cdot} \longrightarrow C_6H_{11}^+ + C_2H_5^\cdot \;\text{or}\; C_6H_{12}^{+\cdot} + C_2H_4 \qquad (14)$$



$$(CH_3)_2C{=}CH_2^{+\cdot} + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+ + \dot{C}H_2{-}\underset{CH_3}{\underset{|}{C}}{-}\dot{C}H_2 \qquad (15)$$

The principal reaction of all three butenes was hydrogen transfer (12) but the carbon skeleton of these products probably varied from butene to butene. With but-1-ene and but-2-ene the butyl cation is unlikely to be the 1-methylpropyl ion $CH_3\overset{+}{C}HCH_2CH_3$ but with 2-methylpropene the product cation is almost certainly the t-butyl cation $(CH_3)_3C^+$. With but-1-ene at high pressures the principal product ions are likely to be linear $C_4H_9^+$ and $C_5H_{11}^+$ [reaction (13)]. The principal ions derived from *cis*-but-2-ene at high pressure are $C_6H_{11}^+$ and $C_6H_{12}^{+\cdot}$ [reaction (14)]. The difference between the high-pressure reactions of but-1-ene and but-2-ene can be attributed to steric effects which prevents a linear transition state with the latter and hence leads to a cyclic transition state (Scheme 9). The large difference between the low- and high-pressure reactions of but-2-ene can be attributed to a change in mechanism. At low pressure hydrogen-atom transfer through space is the major pathway whereas at high pressure the principal reactions involve actual collision (Scheme 10). A similar change in mechanism is not observed with but-1-ene because there is no appreciable steric hindrance in the formation of the linear activated complex.

2-Methylpropene behaves very differently, yielding almost only one product $C_4H_9^+$ which is undoubtedly the t-butyl cation [reaction (15)].

Conclusions.—The interaction of an alkenyl radical cation with an alkene of the same or lower ionisation energy results in the formation of an excited adduct which fragments to yield new cations, radicals, and alkenes. Reactions of this kind were extensively studied in the late 1960s using tandem magnetic mass spectrometers and latterly ion cyclotron resonance was developed. Both these techniques involved studies of ion–molecule reactions at 'low pressure' (*i.e.* 10^{-6}—10^{-5} Torr) when the mean free path was much greater than the reaction chamber. Studies were also made using a 'high pressure' (*i.e.* 10^{-2}) source. The triple quadrupole instrument can be used in the intermediate range (10^{-5}—10^{-2} Torr). This is important because many of the reaction pathways change with changing pressure. Thus we have already cited the low-pressure reaction of $C_2H_4^{+\cdot}$ with the neutral C_2H_4 to give $C_3H_5^+$ (*m/e* 41), but at high pressure this secondary ion reacts as fast as it is formed to yield $C_5H_9^+$ (*m/e* 69) (Table 4). Other examples of the effect of changing pressure are illustrated in the reactions of the $C_4H_8^{+\cdot}$ radical ions with the corresponding alkenes (Table 6).

References

1 A. L. Mitchell and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1984, 667.
2 C. E. Melton and P. S. Rudoph, *J. Chem. Phys.*, 1960, **32**, 1128.
3 S. Wexler and R. Marshall, *J. Am. Chem. Soc.*, 1964, **86**, 781.
4 J. J. Myher and A. G. Harrison, *Can. J. Chem.*, 1968, **46**, 101.
5 T. D. Tiernan and J. H. Futrell, *J. Phys. Chem.*, 1968, **72**, 3080.
6 M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 1968, **72**, 3599.
7 F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, 1968, **72**, 1826.
8 F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, 1968, **72**, 1994.
9 A. A. Herod and A. G. Harrison, *J. Phys. Chem.*, 1969, **73**, 3189.
10 A. MacKenzie-Peers, *J. Phys. Chem.*, 1969, **73**, 4141.
11 A. A. Herod, A. G. Harrison, R. M. O'Malley, A. J. Ferrier-Correia, and K. R. Jennings, *J. Phys. Chem.*, 1970, **74**, 2720.
12 I. Koyano, I. Omura, and J. Tanaka, *J. Chem. Phys.*, 1966, **44**, 3850.
13 I. Koyano, *J. Chem. Phys.*, 1966, **45**, 706.
14 A. G. Harrison, *Can. J. Chem.*, 1962, **41**, 236.
15 M. T. Bowers, D. H. Aue, and D. D. Elleman, *J. Am. Chem. Soc.*, 1972, **94**, 4255.

Received 18*th June* 1985; *Paper* 5/1053