The Study of Ion–Molecule Reactions in the Gas Phase using a Triple Quadrupole Mass Spectrometer. Part 1. The Reactions of CH_3^+, CD_3^+, and $C_2H_5^+$ with Simple Olefins

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A triple quadrupole mass spectrometer has been used to study the reactions of simple carbocations with low molecular weight olefins in the gas phase at relatively high pressures (10^{-3}—10^{-4} Torr). In each case a high energy 'addition complex' is formed which fragments spontaneously to give daughter ions, the extent of fragmentation depending to some extent on the pressure and on the translational energy of the primary ions. Also formed are 'second generation' ions due to reactions of the predominant daughter ions with the olefin. Ions with the same mass as the high energy 'addition complexes' have been fragmented by collision (C.I.D.) with inert molecules (N_2) to yield similar daughter ions to those found from the 'addition complexes'. In the reactions, involving CD_3^+ ions, deuterium is widely, but not completely randomly, distributed among the daughter ions.

Ion–molecule reactions, including the reactions of alkyl cations with olefins have been studied intermittently for more than twenty years.[1] Early work involved high pressure mass spectrometry.[2] Later techniques include tandem mass spectometry [3] and more recently ion cyclotron resonance (i.c.r.).[4] The most complete studies of the reactions of methyl and ethyl cations with ethylene are those of Kim *et al.*,[4c] and the earlier study of Herod and Harrison.[4b] So far as we are aware no attempt has been made to study reactions of this kind with a triple qudrupole mass spectrometer. The present work involved the use of a triple quadrupole based on the design of Yost, Enke, McGilvery, and Morrison.[1] The experiments were caried out in the pressure rangel 0^{-4} to 10^{-3} mbar, *i.e.* between the very low pressures of the i.c.r. experiments and the relatively high pressure of the early mass spectrometry work.

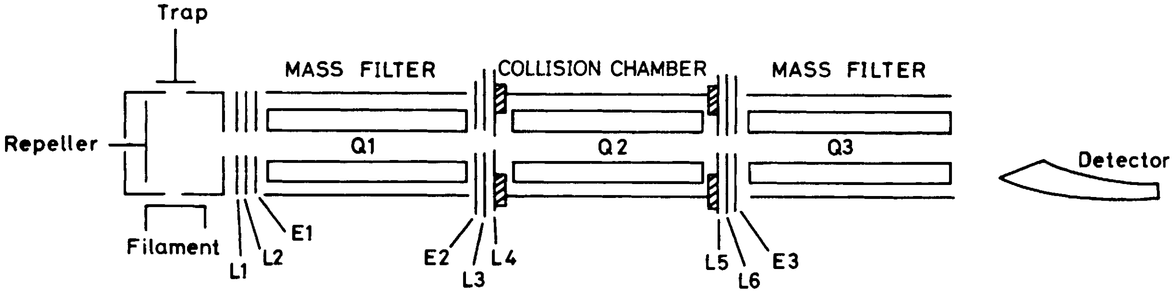


Figure 1.

Experimental

The apparatus shown in schematic form in Figure 1 was broadly similar to units previously described in the literature.[1] Primary ions were generated in a differentially-pumped electron impact source. The energy of the electrons was 70 V. The three quadrupoles, Q1, Q2, and Q3, were VG QXK300 units, with rods of length 125 mm and diameter 6.32 mm. The radiofrequency supply was 0 to 1 320 V, 2 MHz giving a total mass range of 300 a.m.u. The ions were focused into Q1, and between the quadrupole sections, by the apertures L1 to L6, to which adjustable focus potentials were applied, and by apertures E1 to E3, which were earthed.

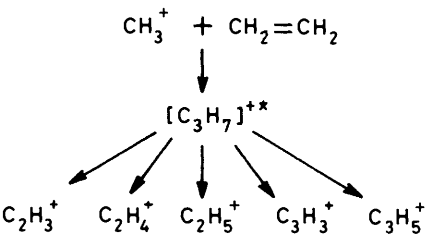
Ions of the required mass-to-charge ratio were selected in Q1 and were injected into Q2 which was pressurised with the collision gas. Ion–molecule reactions occurred, yielding daughter ions (which represented 5% of the total ion current). These ions continued along the axis, constrained by the focussing action of Q2, which operated in the 'total ion' mode, with only RF potentials appearing between the individual rods. An adjustable bias potential was applied to all four rods of Q2, allowing the incident ions to be accelerated or decelerated, thus altering the collision energy. The mass spectrum of ions leaving Q2 was studied by means of Q3.

The collision gas was introduced *via* a side tube and escaped *via* the ion entrance and exit apertures. The pressure inside the cell could be measured directly *via* a second tube, a capacitance manometer being the preferred sensor. The pressure could also be inferred from that indicated by an ionisation gauge (VG VIG23) in the main vacuum chamber. The differential pumping factor was 100, based on comparison with a capacitance manometer (MKS Baratron). Typical collision pressures were in the range 10^{-4} to 10^{-3} mbar.

The system was pumped by an Edwards E04 oil vapour diffusion pump, fitted with a VG NCT4 cold trap, and backed by an Edwards E2M8 rotary pump.

Discussion

$CH_3^+ + CH_2{=}CH_2$.—The simplest system studied was the interaction of CH_3^+ with ethylene. Five secondary ions were observed when a beam of methyl cations was led into molecular ethylene. The effect of the translational energy imparted to the primary ions by the potential difference between the second quadrupole and the source is shown in Table 1.



Scheme 1. The ions formed in the reaction of CH_3^+ with CH_2=CH^2

The first feature to notice about Table 1 is that there is still an appreciable yield of secondary ions even though the bias voltage (*i.e.* the potential difference between source and the second quadrupole) is positive. The relative voltage has to exceed 2.5 V (positive) before all ions are cut off. This is probably due to the build up of positive charge in the centre of the source. Neglecting the experiment in which the energy of the primary ions exceeds 10 eV, the relative proportion of $C_2H_3^+$ ions decreases as the translational energy of the primary ion decreases, while the proportion of $C_2H_5^+$ ions increases; the change is small but it suggests that the two may be connected.

Table 1. The effect of primary-ion energy on the reaction of CH_3^+ with C_2H_4 [a]

Bias voltage/ eV	Relative proportion of secondary ions					Total secondary ion current
	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$	$C_3H_3^+$	$C_3H_5^+$	
−11	0.55	0.15		0.26	0.04	
−2	0.61	0.05	0.06	0.11	0.18	1
−0.5	0.60	0.04	0.09	0.08	0.18	0.7
+1	0.56	0.04	0.12	0.08	0.20	0.3

[a] Total pressure 3 × 10^{-4} Torr.

Table 2 shows the effect of ethylene pressure on the proportions of secondary ions when methyl cations formed by electron impact on methyl chloride were the primary ions. The most striking feature of Table 2 is the increase in the proportion of $C_2H_5^+$ ions and the decrease in the relative proportion of $C_2H_3^+$ ions as the ethylene pressure increases.

This conclusion with that drawn from Table 1 confirms that there is an inverse relationship between $C_2H_3^+$ and $C_2H_5^+$ ions. In Table 2 there is also some evidence of an inverse relationship between the proportion of $C_3H_5^+$ ions and $C_3H_3^+$ ions. There is a very small difference in the ratio of these two ions in Tables 1 and 2 which may be due to a difference in the internal energy of CH_3^+ depending on whether it is prepared by electron impact on acetone (Table 1) or on methyl chloride (Table 2). The two different sources of CH_3^+ were used to detect possible differences of this kind. The effect if present is too small to be outside possible experimental error.

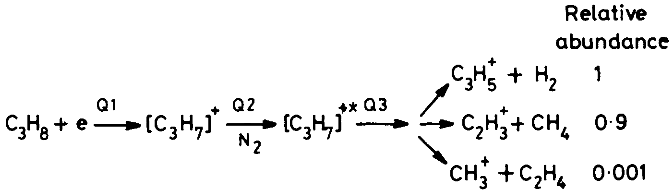
The inverse relationship of the proportions of $C_2H_3^+$ ions and $C_2H_5^+$ ions strongly suggests that there is a direct chemical connection. $C_2H_3^+$ ions were therefore isolated from the total electron impact spectrum of propane using the first quadrupole as mass filter, and passed into the second quadrupole which contained ethylene at a pressure similar to that used in the methyl cation experiments. Three significant secondary ions were detected; the predominant one by nearly one order of magnitude was $C_2H_5^+$. The other two secondary ions of note, $C_3H_3^+$ and $C_4H_5^+$, were only present in very small proportion. The very large relative cross-section for the formation of $C_2H_5^+$ ions confirms that in the reaction of CH_3^+ with ethylene, they are second generation ions formed by the interaction of the daughter ions ($C_2H_3^+$) with the neutral ethylene molecules.

Table 2. The effect of ethylene pressure on the interaction of CH_3^+ ions [a]

Pressure/ 10^4 Torr	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$	$C_3H_3^+$	$C_3H_5^+$
0.3	0.62	0.10	0.02	0.16	0.10
2	0.56	0.11	0.06	0.15	0.12
8	0.42	0.08	0.16	0.13	0.21

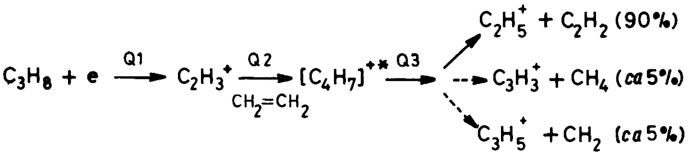
[a] Bias voltage 2 V.

The reaction sequence of CH_3^+ ions with ethylene can be confirmed by studying the collision induced decomposition (C.I.D.) of ions with the same mass as the addition complex formed between the methyl cation and ethylene. The first ion whose C.I.D. spectrum was investigated was $C_3H_7^+$ (*i.e.* the supposed initial addition complex) which was prepared by electron impact on propane and isolated in the first quadrupole and then collided with molecular nitrogen in the second quadrupole. The two predominant ions formed in the C.I.D. spectrum of $C_3H_7^+$ were indeed the two predominant ions in the reaction of methyl cations with ethylene. An exactly similar experiment was carried out using electron impact on n-butane (in place of propane) to generate the $C_3H_7^+$ ions. The secondary ions were the same; the $C_3H_5^+$: $C_2H_3^+$ ratio was slightly larger.

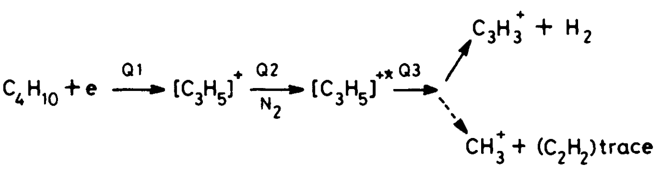


The C.I.D. spectrum of $C_3H_7^+$ ions

No $C_3H_3^+$ ions were detected in the C.I.D. spectrum of $C_3H_7^+$ colliding with molecular nitrogen, so that under our conditions it appears that those ions are not important first generation ions. However when the C.I.D. spectrum of $C_3H_5^+$ ions (formed by electron impact in butane) with nitrogen was investigated, mass 39 a.m.u. was found to be very strong. It thus appears that in our apparatus some, at least, of the $C_3H_3^+$ ions are second generation ions.

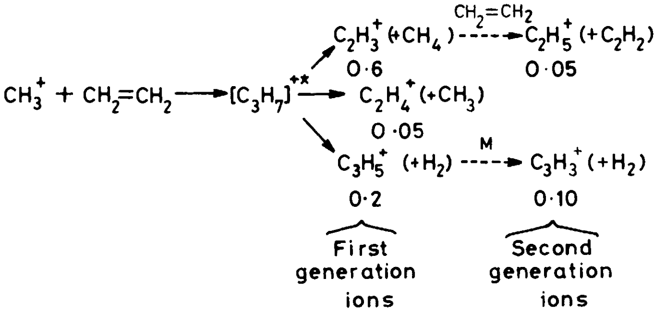


The formation of second generation $C_2H_5^+$ ions



The formation of $C_3H_3^+$ ions

The principal interaction of methyl cations and molecular ethylene can be summarised as follows.



The methyl cation and ethylene (10^{-4} Torr)

$C_2H_5^+ + CH_2{=}CH_2$ *and* $CH_3^+ + CH_2{=}CHCH_3$.—The initial ' addition complex ' $[C_4H_9]^{+*}$ ions formed in the reaction of ethyl cations and ethylene and the ' complex ' $[C_4H_9]^{+*}$ formed by the reaction of methyl cations and propylene have the same mass, but not the same internal energy. In practice the two reactions yield almost the same fragmentation ions, but the ratio of these secondary ions is different.

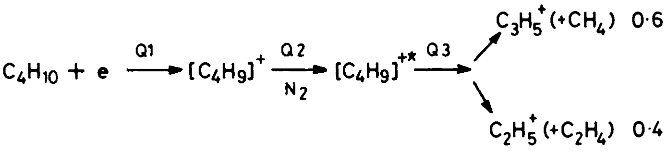
Table 3. Fragmentation of the ' addition complexes ' $C_4H_9^+$ formed by the reactions $CH_3^+ + CH_2{=}CHCH_3$ and $C_2H_5^+ + CH_2{=}CH_2$

$R^+ + \text{Olefin} \longrightarrow [C_4H_9]^{+*} \longrightarrow \text{Fragments}$

	Relative abundance (%)	
Fragment ions	$CH_3^+ + C_3H_6$	$C_2H_5^+ + C_2H_4$
$C_2H_3^+ (+C_2H_6)$	4	22
$C_2H_4^+ (+C_2H_5)$		17[a]
$C_2H_5^+ (+C_2H_4)$	15	
$C_3H_3^+ (+CH_4 + H_2)$	4	1
$C_3H_5^+ (+CH_4)$	21	43
$C_3H_6^+ (+CH_3)$	33[a]	11
$C_3H_7^+ (+CH_2)$	10	0
$C_4H_7^+ (+H_2)$	5	4

[a] These reactions ($C_2H_5^+ + C_2H_4$) and ($CH_3^+ + C_3H_6$) include simple charge exchange processes.

The C.I.D. spectrum of $[C_4H_9]^+$ ions colliding with molecular nitrogen shows two principal fragmentation routes.



The C.I.D. spectrum of $[C_4H_9]^+$ ions

Table 3 shows that both ' addition complexes ' $[C_4H_9]^{+*}$ fragment to yield $C_3H_5^+$ (and $C_2H_5^+$ in the methyl cation–propane system). In addition there were ions due to charge exchange ($C_2H_4^+$, $C_3H_6^+$) and, in the ethyl cation–ethylene system, an additional major fragment $C_2H_3^+$ was also present.

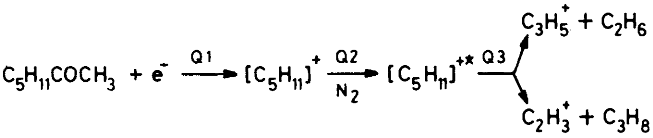
$C_2H_3^+$ ions are important fragments of the ethyl cation–ethylene reaction system ($C_2H_5^+ + C_2H_4$), while they are relatively unimportant ions in the methyl cation–propene reaction system ($CH_3^+ + C_3H_6$). This is consistent with the gross structures of the interacting species, since in the former reaction the formation of $C_2H_3^+$ ions only requires hydrogen atom exchange, while in the latter system the breaking and making of carbon–carbon bonds is involved.

In the reaction of ethyl cations ($C_2H_5^+$) with ethylene, an increase of ethylene pressure in the second quadrupole increased the proportion of the $C_3H_5^+$ ions relative to the $C_2H_3^+$ ions. Previously in the methyl cation–ethylene system it was found that first generation $C_2H_3^+$ ions react rapidly with ethylène and undoubtedly the same situation applies in the ethyl cation–ethylene system.

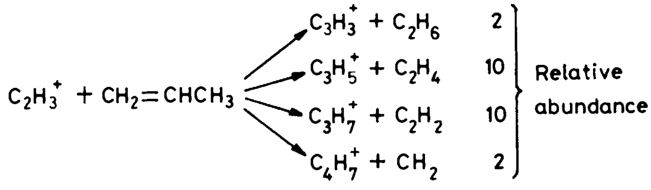
The reactions of methyl cations with propene and ethyl cations with ethylene at low pressures in the gas phase both involve transient ' addition complexes,' $C_4H_9^+$, which fragment to yield the same fragments, but not in the same proportions. This is to be expected since although both ' addition complexes ' are thermally excited the degree of thermal excitation is not the same in the two cases.

$CH_3^+ + CH_2{=}CHC_2H_5$, $CH_3^+ + CH_2{=}C(CH_3)_2$, $C_2H_5^+ + CH_2{=}CHCH_3$, *and* $C_3H_7^+ + CH_2{=}CH_2$.—These four reaction systems proceed *via* ' addition complexes ' $[C_5H_{11}]^{+*}$ which fragment to yield the same daughter ions, but not in the same proportion.

The C.I.D. spectrum of the $C_5H_{11}^+$ ion, prepared by electron impact on heptan-2-one, and collided with molecular nitrogen, had two principal fragmentation routes. The two daughter ions have very different reactivity; $C_2H_3^+$ interacts with ethylene by disproportionation in a reaction which has a very large relative crosss ection (see p. 1264) whereas $C_3H_5^+$ ions barely react with ethylene at all. The $C_2H_3^+$ ions also react with propene.



C.I.D. spectrum of $[C_5H_{11}]^+$ ions



The reactions of $C_2H_3^+$ ions with propene

It is interesting that, in addition to the major fragmentation reactions depicted above, $C_2H_3^+$ ions also react with ethylene in a minor process to yield methylene CH_2 ($C_2H_3^+ + C_3H_6 \longrightarrow C_4H_9^+ + CH_2$). Similarly in the interaction of $C_2H_3^+$ ions with ethylene there is a minor pathway also leading to methylene ($C_2H_3^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_2$) (see p. 1264).

Table 4. The fragmentation of the ' addition complexes ' $C_5H_{11}^+$ formed by the reactions $CH_3^+ + CH_2{=}CHC_2H_5$, $CH_3^+ + CH_2{=}C(CH_3)_2$, $C_2H_5^+ + CH_2CHCH_3$, and $C_3H_7^+ + CH_2{=}CH_2$

$$R^+ + \text{Olefins} \longrightarrow [C_5H_{11}]^{+*} \longrightarrow \text{Fragments}$$

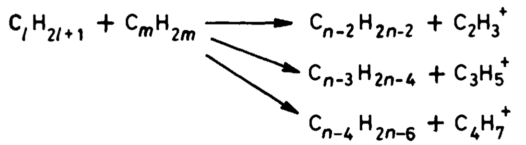
Fragments ions	$CH_3^+ + CH_2{=}CHC_2H_5$[a] [a]	$CH_3^+ + CH_2{=}C(CH_3)_2$[b] [b]	$C_2H_5^+ + CH_2{=}CHCH_3$[c] [c]	$C_3H_7^+ + CH_2{=}CH_2$[d] [d]
$C_2H_3^+ (+C_3H_8)$	6	24	21	16
$C_2H_5^+ (+C_3H_6)$	18	15		17
$C_3H_3^+ (+C_2H_6 + H_2)$	2	7	1	0
$C_3H_5^+ (+C_2H_6)$	11	11	23	63
$C_3H_7^+ (+C_2H_4)$	2	3	44	
$C_4H_7 (+CH_4)$	14	9	5	1

In addition there were charge exchange ions, respectively, [a] $C_4H_8^+$ (47%), [b] $C_4H_8^+$ (31%), [c] $C_3H_6^+$ (6%), and [d] $C_2H_4^+$ (3%).

Table 5. The reaction of CD_3^+ with $CH_2{=}CH_2$ [a]

Bias Voltage/V	$C_2H_3^+$ [27]	$C_2H_4^+$ $C_2H_2D^+$ [28]	$C_2H_5^+$ $C_2H_3D^+$ $C_2HD_2^+$ [29]	$C_2H_4D^+$ $C_2H_2D_2^+$ $C_2D_3^+$ [30]	$C_3H_3^+$ [39]	$C_3H_2D^+$ [40]	$C_3H_5^+$ $C_3HD_2^+$ [41]	$C_3H_4D^+$ $C_3D_3^+$ [42]	$C_3H_3D_2^+$ [43]	$C_3H_2D_3^+$ [44]
5	0.22	0.21	0.22	0.06	0.02	0.05	0.13	0.03	0.03	0.01
2	0.18	0.19	0.25	0.07	0.01	0.04	0.12	0.04	0.06	0.03
0	0.16	0.19	0.27	0.08	0.01	0.03	0.13	0.05	0.06	0.03

[a] Pressure 6 × 10^{-4} Torr.



Scheme 2.

The primary ions in this work have all been of the general formula C_lH_{2l+1} and the olefins have been of the general formula C_mH_{2m}. Their principal fragmentation pathway can be summarised as shown in Scheme 2 (where $n = l + m$; $l = 1, 2, 3 \ldots, m = 2, 3 \ldots$).

The most important feature of the present results is that although the four reactions go through an excited ' addition complex ' with the same mass $[C_5H_{11}]^+$, the degree of excitation varies and the relative proportion of the resultant fragments are different. Table 4 provides evidence that there is a resistance to fragmentation of the carbon chain. However deuterium labelling clearly shows that hydrogen atoms are very extensively scrambled.

$CD_3^+ + CH_2{=}CH_2$.—Table 5 shows that hydrogen atom scrambling is a very extensive process. The positions of the deuterium atoms are not completely random but very nearly so. The concentration of $C_2X_5^+$ ions and $C_2X_3^+$ ions shows the same inverse relationship noted in Table 1. The mass 29 peak and the mass 41 peak can only include $C_2H_5^+$ and $C_3H_5^+$ as second generation ions. Since charge exchange is a minor process in the methyl cation–ethylene reaction the mass 28 peak must be predominantly $C_2H_2D^+$. This is consistent with Table 1 when the predominant peak is 27 (*ca.* 60%), while in Table 5 the sum of the peaks 27, 28, and 29 is proportionally similar (*ca.* 65%).

The reaction of CD_3 with propene was also briefly investigated. The principal ions detected were m/z 27 (0.14), 28 (0.04), 29 (0.07), 30 (0.05), 31 (0.04), 32 (0.04), 39 (0.06), 40 (0.06), 41 (0.23), 42 (0.16), 43 (0.07), 44 (0.03), 45 (0.01). Again the results show extensive, but by no means completely random, scrambling.

Conclusions

The present results demonstrate that the triple quadrupole mass spectrometer is an ideal apparatus for studying ion molecule reactions in the gas phase, in the pressure range 10^{-5} to 10^{-3} Torr. The apparatus is extremely robust and simple to use. Individual steps in a proposed reaction sequence can be verified extremely easily, and the ability to investigate the collision induced decomposition of ions again facilitates the interpretation of secondary and tertiary ion formation. No attempt has been made to measure absolute, as distinct from relative, rates. Absolute rates could be obtained by comparing the rate of a known reaction with an unknown reaction under identical conditions. For many purposes relative rates are sufficient, as in the present work.

The present results on the interaction of simple radicals with olefins are in very good agreement with earlier work using completely different experimental techniques. The reaction of simple carbocations with short-chain olefins clearly involves a high energy ' addition complex ' which fragments to yield a variety of daughter ions. The fragmentation pathways are similar for different ions and different olefins but the relative importance of a particular pathway varies. The initial reactions are mostly very exothermic so that fragmentation and rearrangement are facilitated. The fragmentation is also affected by the translational energy of the ions. In the present work there is surprisingly little change in the fragmentation when the primary ion's translational energy varies from 0.5 to 5 eV. If the translational energy of the primary ion exceeds 10 eV then the fragmentation completely changes. The actual kinetic energy of a primary ion is hard to compute; first there is its oscillatory motion down the second quadrupole and secondly there is the apparent build up of charge in the ion source, which enables primary ions to escape, even though the second quadrupole is slightly more positive than the source. However the very good agreement between the present results and those obtained using very different techniques suggests that these uncertainties do not affect the pattern of the results.

Acknowledgements

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