The Study of Ion–Molecule Reactions in the Gas Phase using a Triple Quadrupole Mass Spectrometer. Part 2.[1] The Reaction of CH_3^+ and $CH_4^{+\cdot}$ with Linear, Branched, and Cyclic Alkanes

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The reactions of CH_3^+ and $CH_4^{+\cdot}$ ions with linear, branched, and cyclic alkanes have been studied in the gas phase using a triple quadrupole mass spectrometer. The reactions with CH_3^+ involve an initial hydride abstraction followed by fragmentation of the resulting carbocation. The initial reaction with $CH_4^{+\cdot}$ is charge exchange, but the resulting cation-radical can fragment in two different ways, one involving the formation of a carbocation and a radical, and the other leading to the formation of a shorter chain alkane and a new cation-radical.

Unlike the reactions of alkenyl cations with alkenes, for which there is an enormous literature (*cf.* Part 3 of this series), there is surprisingly little published work on the reactions of alkyl cations with alkanes. Much attention has been paid to chemical ionisation using methane as the reagent gas at high pressures[2] and the reactions of CH_5^+ with alkanes have been thoroughly investigated.[3] However, the reaction of CH_3^+ with alkanes has only received cursory examination.[4] The present studies represent a preliminary attempt to fill this gap and at the same time contrast the chemistry of CH_3^+ with that of $CH_4^{+\cdot}$. The latter ion has been found to be an important intermediate in many chemical and field ionisation studies,[3,5] although the chemistry of this ion in isolation is not so well studied. There are very few previous studies of the reaction of CH_3^+ with branched chain or cyclic alkanes.

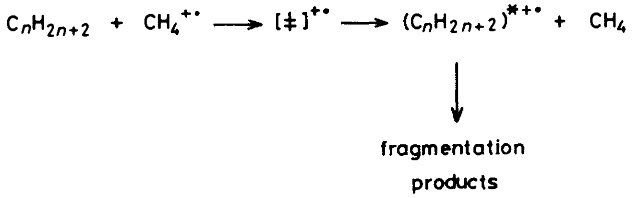
Experimental

The apparatus has been described in a previous paper.[1] The alkanes were all commercial products (99% pure or better). $CH_4^{+\cdot}$ and CH_3^+ were prepared by electron impact on methane; $CD_4^{+\cdot}$ and CD_3^+ were prepared similarly from CD_4. The primary gases CH_4, CD_4, SO_2, and N_2O were all taken directly from commercial cylinders without purification. The primary ions were isolated in the first quadrupole so that the presence of trace impurities in the primary gases was unimportant.

Discussion

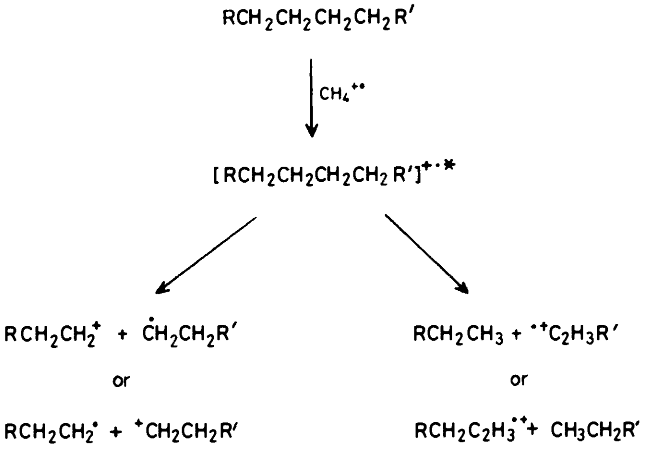
The initial reaction of $CH_4^{+\cdot}$ with neutral linear alkanes C_nH_{2n+2} is electron transfer yielding methane and an excited alkane radical cation which fragments to yield a wide variety of products (Scheme 1).

The fragmentation patterns we have obtained when $CH_4^{+\cdot}$ reacts with normal alkanes are similar, but not identical to the 'cracking patterns' reported in electron impact studies.[6] The unpaired electron of the initial secondary ion $(C_nH_{2n+2})^{*+\cdot}$ is not likely to be centred at one of the terminal methyl groups. Typical secondary ion fragmentation can therefore be depicted as in Scheme 2. The carbocations $RCH_2CH_2^+$ or $R'CH_2CH_2^+$ formed can undergo further fragmentation. The total spectrum (Figure 1) shows evidence of step-wise degradation of the alkyl cations yielding ethylene and a new carbocation of 28 mass units less (Scheme 3). This fragmentation will terminate either in $C_{2l}H_{2l+1}^+$ (*e.g.* $C_2H_5^+$ or $C_3H_7^+$; CH_3^+ and H^+ are less likely). There is a second fragmentation pathway, also initiated by charge exchange and this involves the formation of short chain alkanes C_lH_{2l+2} and the simultaneous formation of radical ions of the general formula $C_mH_{2m}^{+\cdot}$ (where $l + m = n$). Table 1 shows the fragmentation patterns obtained when $SO_2^{+\cdot}$ (ionisation potential 12.3 eV) and $N_2O^{+\cdot}$ (12.9 eV) are compared with the cracking pattern when $CH_4^{+\cdot}$ (12.7 eV) was the primary ion and n-decane was the neutral species in each case.[†] As expected the three charge-exchange mass spectra are very similar but not identical.



$$C_nH_{2n+2} + CH_4^{+\cdot} \longrightarrow [\ddagger]^{+\cdot} \longrightarrow (C_nH_{2n+2})^{*+\cdot} + CH_4$$

Scheme 1.



Scheme 2.

$$R-CH_2-CH_2^+ \longrightarrow R^+ + CH_2{=}CH_2$$

Scheme 3.

The initial reaction of CH_3^+ with the linear alkanes C_nH_{2n+2} is hydride transfer to yield an excited carbocation and

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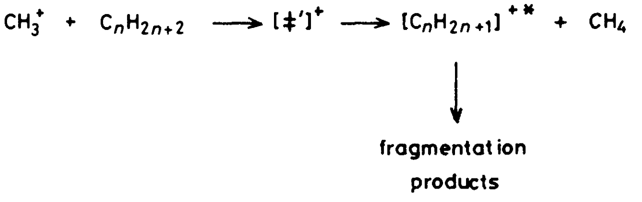
[†] The electron recombination potential is not likely to differ from the ionisation potential.

Table 1. Ions formed in the reaction of $SO_2^{+\cdot}$ (IP = 12.3 eV), $CH_4^{+\cdot}$ (IP = 12.7 eV), and N_2O^+ (IP = 12.9 eV) with n-decane

	29 $C_2H_5^+$	41 $C_3H_5^+$	42 $C_3H_6^+$	43 $C_3H_7^+$	55 $C_4H_7^+$	56 $C_4H_8^+$	57 $C_4H_9^+$	58 $C_4H_{10}^+$	69 $C_5H_9^+$	70 $C_5H_{10}^+$
$SO_2^{+\cdot}$										
Relative abundance		tr.	2	17	1	7	40		1	5
$CH_4^{+\cdot}$										
Relative abundance	tr.	tr.	1	9	tr.	4	34	1	1	4
N_2O^+										
Relative abundance	1	1	3	35	2	5	35	tr.	1	2

	71 $C_5H_{11}^+$	83 $C_6H_{11}^+$	84 $C_6H_{12}^+$	85 $C_6H_{13}^+$	86 $C_6H_{14}^+$	98 $C_7H_{14}^+$	99 $C_7H_{15}^+$	113 $C_8H_{17}^+$	142 $C_{10}H_{22}^+$
$SO_2^{+\cdot}$									
Relative abundance	17	tr.	1	6	tr.	1	1		
$CH_4^{+\cdot}$									
Relative abundance	17	tr.	5	11	tr.	2	3	2	2
N_2O^+									
Relative abundance	11			2		tr.	tr.		

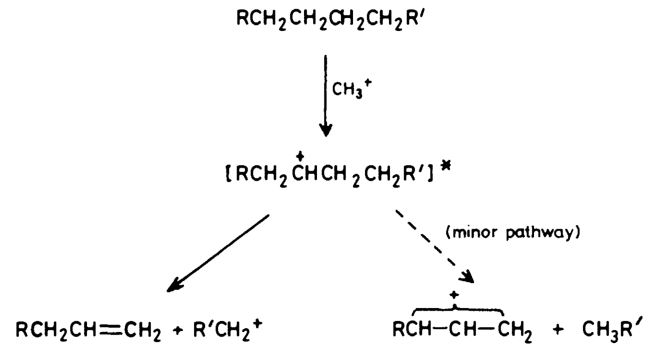
tr. = trace.



Scheme 4.

a methane molecule (Scheme 4). Examination of Figure 1 shows that the fragmentation of the $[C_nH_{2n+1}]^+$ ion is much simpler than the fragmentation of the $[C_nH_{2n+2}]^{+\cdot}$ radical cation (Scheme 5). The principal fragmentation pathway involves the formation of an olefin C_lH_{2l} and a simple carbocation $[C_mH_{2m+1}]^+$ (where $l + m = n$). The carbocation can undergo stepwise degradation (*i.e.* loss of successive C_2H_4 fragments) giving the same series of daughter ions as in the $CH_4^{+\cdot}$ reactions. There is some evidence for an additional minor fragmentation pathway yielding allyl cations $[\overbrace{RCHCHCH_2}^{+}]$ and an alkane.

Tables 2 and 3 depict the fragmentation patterns formed when $CH_4^{+\cdot}$ and CH_3^+ react with the branch chain alkanes isobutane (2-methylpropane) and isopentane (2-methylbutane). Tables 2 and 3 show that the fragment ions for the reactions of $CH_4^{+\cdot}$ and CH_3^+ with n-butane and with isobutane (or with n-pentane and with isopentane) are the same. However, the relative proportions of the secondary ions derived from the linear alkanes are different from those derived from branched chain alkanes when $CH_4^{+\cdot}$ is the primary ion but are almost identical when CH_3^+ is the primary ion. The initial secondary cations in the reaction of



Scheme 5.

straight chain or branched chain alkanes with CH_3^+ have the composition $(C_nH_{2n+1})^+$. Such carbonium ions can rearrange to give a more stable structure. In other words the carbonium ion formed by hydride abstraction from a straight chain ion will rearrange to a branched chain ion, *i.e.* similar to the ions formed by hydride abstraction from the corresponding branched chain alkane. In contrast the radical cation $[C_nH_{2n+2}]^{+\cdot}$, formed by electron transfer, rearranges as it fragments so that the cracking patterns from the straight chain alkane radical ions are different from the cracking patterns from the branched chain radical ions. These conclusions are consistent both with the rearrangements reported by Gaumann [6] and by Wolkoff and his co-workers.[7]

Figure 2 depicts the fragmentation patterns formed when $CH_4^{+\cdot}$ and CH_3^+ react with simple cycloalkanes. Neither series of mass spectra shown in Figure 2 consist of stepwise fragmentation characteristic of the corresponding fragmentations of the linear alkanes described above. The parent ions

Table 2. Ions formed in the reaction of $CH_4^{+\cdot}$ and CH_3^+ with n-butane and 2-methylpropane (%) *

	m/e	27	38	29	41	42	43	55	56	57	58
$CH_4^{+\cdot}$	n-C_4		3	5	1	8	53		2	6	21
	iso-C_4				1	32	51		2	6	8
CH_3^+	n-C_4	5		21	27		13	1		39	0
	iso-C_4	1		26	25	1	18	1		29	1

* Figures rounded off to nearest whole number.

Table 3. Ions formed in the reaction of $CH_4^{+\cdot}$ and CH_3^+ with n-pentane and 2-methylbutane (%) *

	m/e	27	29	41	42	43	55	56	57	70	71	72
$CH_4^{+\cdot}$	n-C_5		1	1	32	37		2	7	5	3	12
	iso-C_5		1	1	31	18		13	16	4	6	10
CH_3^+	n-C_5	1	6	3	1	70	1		2		14	1
	iso-C_5	1	4	2	1	67	2	1	6		15	1

* Figures rounded off to nearest whole number.

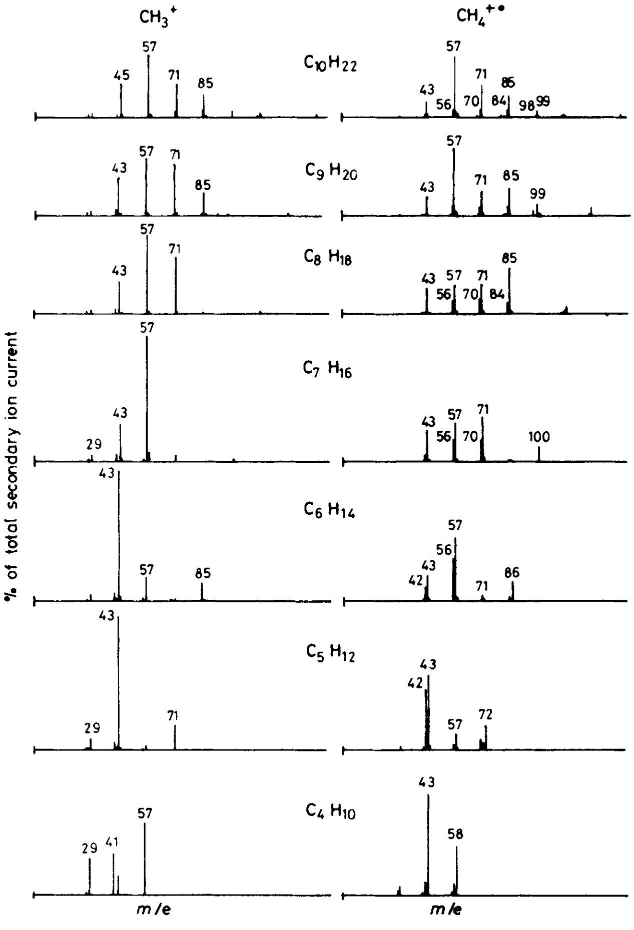


Figure 1. Fragmentation patterns from the reaction of CH_3^+ and $CH_4^{+\cdot}$ ions with normal alkanes

Table 4. % Fragmentation of *m/e* 57 formed from different alkanes

$$RH + CH_4^+ \longrightarrow$$

$C_4H_9^+$(*m/e* 57) $\xrightarrow[\text{c.i.d.}]{N_2}$	$C_3H_6^+$ (42)	$C_3H_6^+$ (41)	$C_2H_5^+$ (29)
R = C_6H_{13}		79	21
C_7H_{15}		83	17
C_8H_{17}	1	24	75
C_9H_{19}		87	13

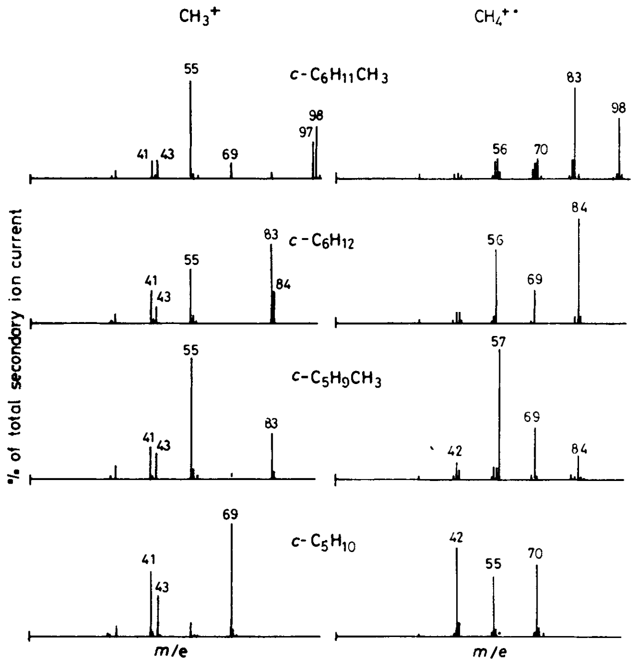


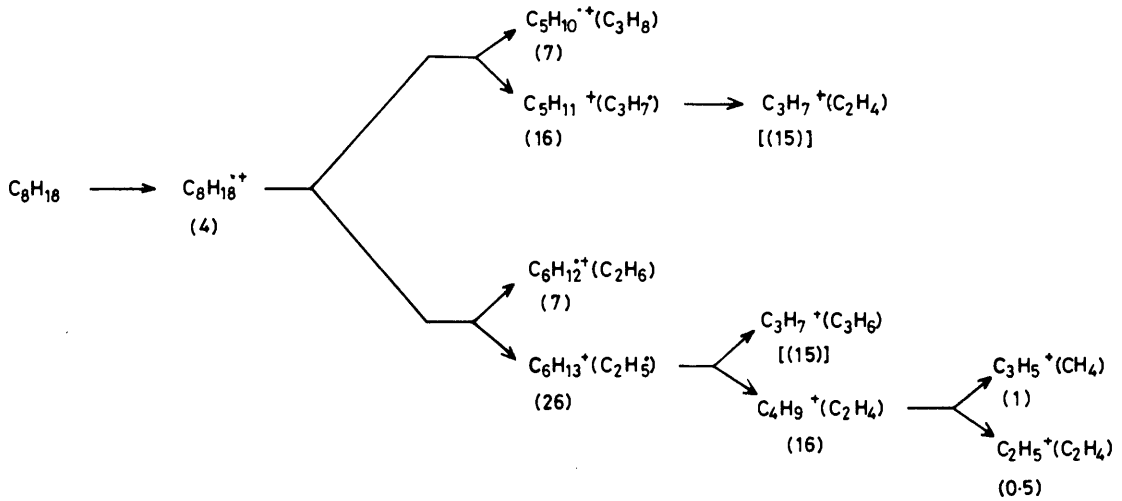
Figure 2. Fragmentation patterns from the reaction of CH_3^+ and $CH_4^{+\cdot}$ ions with cycloalkanes

(from the $CH_4^{+\cdot}$ series) or the parent less one mass unit (from the CH_3^+ series) are relatively much more important than in the spectra of the linear alkanes. In the spectra derived from the CH_3^+ primary ions with methylcyclopentane and methylcyclohexane, the secondary ion $C_4H_7^+$ (*m/e* 55) is the major charged fragment. The ion $C_3H_5^+$ (*m/e* 41), possibly the allyl cation, is also an important ion in all the CH_3^+-initiated reactions.

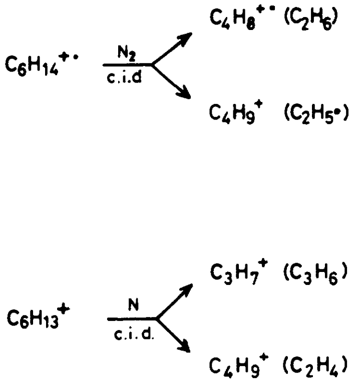
The fragmentation patterns observed for the linear alkanes are consistent with a step-wise loss of C_2H_4 from the initially formed radical cation ($C_nH_{2n+2}^{+\cdot}$ from $CH_4^{+\cdot}$) or carbocation ($C_nH_{2n+1}^+$ from CH_3^+). However there are other possible

Table 5. Ions formed by the reaction of $CH_4^{+\cdot}$ with n-heptane (a) in the triple quadrupole and (b) in the tandem mass spectrometers

m/e	43($C_3H_7^+$)	56($C_4H_8^+$)	57($C_4H_9^+$)	70($C_5H_{10}^+$)	71($C_5H_{11}^+$)	100(P^+)
Triple quadrupole	16	11	20	13	24	9
Tandem	14	7	24	12	15	28



Scheme 6. The successive c.i.d. spectra (nitrogen the collision gas) of the ionic fragments occurring in the reaction between $CH_4^{+\cdot}$ and C_8H_{18} (relative abundance)



Scheme 7. The principal fragment ions formed in collision with nitrogen

fragmentation pathways and for each sequence the observed secondary ions have been formed in the ion source, isolated in the first quadrupole and there subjected to collision-induced decomposition (c.i.d.) using nitrogen as the inert molecule. A degradation scheme of this kind for $C_8H_{18}^{+\cdot}$ is shown in Scheme 6. (Similar schemes have been worked out for all the other linear radical cations.) The particular fragmentation pathway will be partly determined by the neutral species produced. Thus the formation of $C_3H_5^+$ in the fragmentation of $C_8H_{18}^{+\cdot}$ (Scheme 6) is associated with the production of CH_4 and the production of $C_2H_5^+$ with the coproduction of $C_2H_4^{\cdot}$. The principal ions produced by the c.i.d. of $C_6H_{14}^{+\cdot}$ and $C_6H_{13}^+$ are compared in Scheme 7.

The relative proportion of daughter ions derived from a particular fragment ion formed from different neutral molecules can be compared. Thus $C_4H_9^+$, on collision with nitrogen, fragments to $C_3H_6^+$, $C_3H_5^+$, and $C_2H_5^+$ and their relative proportions from different precursors are shown in Table 4. Similar schemes can be drawn for the fragmentation of $C_6H_{13}^+$ and $C_5H_{11}^+$.

The fragmentation pattern observed when $CD_4^{+\cdot}$ replaces $CH_4^{+\cdot}$ as primary ion differed little, but there were additional peaks in the fragmentation pattern observed when CD_3^+ replaced CH_3^+. New ions observed (in addition to those in the ions induced by CH_3^+) in the reaction of CD_3^+ with n-octane included *m/e* 30, 31, 32, 34, 46, 48, 56, 73, 74, 84, 86, 88, 98, and 100. The majority of these additional ions were present in low concentrations and while they are evidence for hydrogen atom scrambling, it was not a major process.

The reaction of $CH_4^{+\cdot}$ with n-heptane was also investigated using the tandem mass spectrometer described in earlier papers.[8] The primary ions $(CH_4)^{+\cdot}$ were injected into the collision chamber with *ca.* 8 V. The predominant secondary ion was the parent (*m/e* 100). The increase in the proportion of the parent ion (*m/e* 100) in the tandem mass spectrometer illustrates the different discrimination of the two instruments (Table 5). The tandem mass spectrometer preferentially selects ions formed by 'long range' transfer since ions formed by actual collision will tend to move out of the extraction zone.

The present results with the triple quadrupole were all taken when the difference in potential between the ion source and the first quadrupole was 0.3 V. However, very little difference in the relative proportions of the various fragmentation ions was observed when the potential difference between the source and the first quadrupole was varied from 0 to 2 V (see also Part 1).

Conclusions.—Although the reactions of the alkyl radical ions ($C_nH_{2n+2}^{+\cdot}$) with alkanes has received considerable study, there has been remarkably little reported about the chemistry of isolated $CH_4^{+\cdot}$ and still less about the reactions of CH_3^+ with alkanes. The present work is an attempt to rectify this omission. The results obtained with the triple quadrupole mass spectrometer are completely consistent with the earlier chemical ionisation studies. The principal fragmentation pathways of $C_nH_{2n+2}^{+\cdot}$ and $C_nH_{2n+1}^{+}$ are very different and even more striking are the differences of cyclo-$C_nH_{2n}^{+\cdot}$ and cyclo-$C_nH_{2n-1}^{+}$. The important feature of the present study is that the fragmentation pathways of alkyl radical cations and carbocations have been clearly identified. This information is essential if the ion–molecule chemistry involving ions and molecules containing heteroatoms attached to alkyl chains is to be understood.

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