Structure and Reactivity of $C_4H_8^+$ Ions Formed in the Radiolysis of Cycloalkanes in the Gas Phase[1]

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Abstract: The structure and reactivity of the $C_4H_8^+$ formed in the fragmentation of cyclohexane and methylcyclopentane parent ions has been examined ($[C_6H_{12}^+]^* \rightarrow C_2H_4 + C_4H_8^+$). It is noted that $C_4H_8^+$ consists of 1-$C_4H_8^+$, *i*-$C_4H_8^+$, and 2-$C_4H_8^+$. The relative abundances of these isomer ions depend on the energy content of the cycloalkane ion. According to the mass spectral cracking pattern of cyclohexane-1,1,2,2,3,3-d_6 the high energy parent ion splits out $C_4H_8^+$ without extensive prior rearrangement. The $C_4H_8^+$ so formed is analogous to the $C_4H_8^+$ ion produced in the photoionization or radiolysis of cyclobutane. The various $C_4H_8^+$ isomers react with the cycloalkanes by acceptance of an H_2^- entity: $C_4H_8^+ + C_6H_{12} \rightarrow C_4H_{10} + C_6H_{10}^+$. The relative reaction rates, which are determined by means of isotopic labeling experiments, differ widely with a change in the structure of both the reactant ion and the reactant molecule, with the rate of reaction being generally higher for the more exothermic process.

In a study of the radiolysis and photoionization of cyclobutane,[2] it was suggested that the parent $C_4H_8^+$ ion undergoes ring opening to isomerize mainly to the 2-$C_4H_8^+$ structure. This was based on an examination of the structures of the butenes formed in charge transfer reactions such as

$$C_4H_8^+ + A \longrightarrow C_4H_8 + A^+ \tag{1}$$

where A is an additive having an ionization potential lower than those of the butenes.

It was noted that the relative abundances of the butenes formed were similar to those observed earlier in a study of the radiolysis of ethylene[3] in the presence of charge acceptors. It has been demonstrated[3] that in ethylene, butene ions result from the reaction

$$C_2H_4^+ + C_2H_4 \longrightarrow C_4H_8^+ \tag{2}$$

Ions of the formula $C_4H_8^+$ are also formed in abundance in the fragmentation of larger cycloalkanes. For instance, according to the 70-eV mass spectral cracking patterns of cyclohexane and methylcyclopentane, $C_4H_8^+$ ions formed by process 3 account for

$$C_6H_{12}^+ \longrightarrow C_4H_8^+ + C_2H_4 \tag{3}$$

more than 20% of the ion fragmentation. Although the reactions of the $C_4H_8^+$ ions formed in cyclohexane have been studied in the mass spectrometer,[4] their structures are not exactly known. The present study represents an attempt to apply the charge acceptor techniques used in the study of $C_4H_8^+$ ions in cyclobutane[2] and ethylene[3] to the determination of the structure of the $C_4H_8^+$ fragment ions in cyclohexane and methylcyclopentane.

In addition, information about the structure and reactivity of the $C_4H_8^+$ ions may be obtained by examining the butane formed in the H_2^- transfer reactions[5] with alkanes or cycloalkanes

$$C_4H_8^+ + C_mH_{m'} \longrightarrow C_4H_{10} + C_mH_{m'-2}^+ \tag{4}$$

where $C_mH_{m'}$ is an alkane or cycloalkane. For example, if a deuterated $C_4D_8^+$ ion is formed in the presence of a nondeuterated alkane or cycloalkane with which it will undergo reaction 4, the isotopic structure of the product butane reveals the structure of the reacting ion.

$$1\text{-}C_4D_8^+ + C_mH_{m'} \longrightarrow CD_2HCDHCD_2CD_3 + C_mH_{m'-2}^+ \tag{5}$$

$$2\text{-}C_4D_8^+ + C_mH_{m'} \longrightarrow CD_3CDHCDHCD_3 + C_mH_{m'-2}^+ \tag{6}$$

$$i\text{-}C_4D_8^+ + C_mH_{m'} \longrightarrow (CD_3)_2CHCD_2H + C_mH_{m'-2}^+ \tag{7}$$

Experimental Section

The irradiation and analytical procedures are the same as described in earlier publications from this laboratory.[6] Quantitative analyses were carried out by injecting aliquots of the irradiated samples onto the columns of two gas chromatographs equipped with flame ionization detectors; one instrument utilized an alumina column, and the other, a squalane column. The *c*-C_6H_{12} and *c*-$C_5H_9(CH_3)$ were standard samples obtained from the American Petroleum Institute. The impurity in the cyclohexane was stated to be 0.007 ± 0.004%, and that in the methylcyclopentane was 0.02 ± 0.01%. *c*-C_6D_{12} contained 11.7% $C_6D_{11}H$, and *c*-C_5D_9-(CD_3) contained 3.5% $C_6D_{11}H$.

Results

All isotopic distributions of reaction products given in the tables have been corrected for the presence of the isotopic impurities in the starting materials.

In addition to the results given in the figures and tables, the following information should be reported.

(1) The partial 70-eV mass spectral cracking patterns which were used to calculate the relative abundances of the two *n*-butane-d_8 products were

m/e	Relative intensity	
	$CD_2HCDHCD_2CD_3$	$CD_3CDHCDHCD_3$
48	88.0	100.0
49	100.0	3.3
66	14.6	7.7

(The complete cracking pattern is not given; the analyses were based on these three peaks.) An examination of the patterns reveals that they are entirely reasonable. The only fragment ion contributing to masses 48 and 49 in these molecules is the propyl ion. Assuming that any rearrangement processes in the

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[1] This research was supported by the Atomic Energy Commission.

[2] (a) R. Doepker and P. Ausloos, *J. Chem. Phys.*, **43**, 3814 (1965); (b) *ibid.*, **44**, 1641 (1966).

[3] G. G. Meisels, *ibid.*, **42**, 3237 (1965).

[4] F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, **71**, 3237 (1965).

[5] (a) R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **44**, 1951 (1966); (b) P. Ausloos and S. G. Lias, *ibid.*, **43**, 127 (1965).

[6] S. G. Lias and P. Ausloos, *ibid.*, **43**, 2743 (1965).

dissociating parent ion were minor, for $CD_2HCDHCD_2$-CD_3, the propyl ions may have two isotopic structures, $C_3D_5H_2^+$ (mass 48) or $C_3D_6H^+$ (mass 49); it might be expected that these two ions should occur with approximately equal intensity. On the other hand, only one propyl ion, $C_3D_5H_2^+$ (mass 48), can be formed from the fragmentation of $CD_3CDHCDHCD_3^+$.

(2) The partial cracking patterns used to analyze the $C_4H_8D_2$ butanes were

	Relative intensity	
m/e	$CH_2DCHDCH_2CH_3$	$CH_3CHDCHDCH_3$
44	91.0	16.1
45	100.0	100.0
59	4.2	1.8
60	18.0	9.4

The $CH_2DCHDCH_2CH_3^+$ ion can fragment to give two propyl ions, $C_3D_2H_5^+$ (mass 45) and $C_3DH_6^+$ (mass 44), while the $CH_3CHDCHDCH_3^+$ should predominantly give a $C_3H_5D_2^+$ (mass 45) propyl ion. Here, the propylene ion, $C_3H_4D_2^+$ (mass 44), may make a minor contribution (3–6% of the total propyl ion) in each case.

(3) In the 10-eV (1236-Å) photolysis of a $2\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$–O_2 mixture (1:1:0.02, total pressure 10 Torr) the mass spectrum of the *n*-butane product showed no peaks which could not be attributed to $C_4H_8D_2$. The observed spectrum of this product was

m/e	Relative intensity
44	15.8
45	100
59	1.8
60	9.5

(4) In the 10-eV photolysis of (A) a $1\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$–O_2 mixture (1:1:0.2, pressure 10 Torr), (B) a Ne–$1\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$–O_2 (100:1:1:0.15, pressure 36 Torr), and (C) a Ne–$1\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$–O_2 (800:1:10:1, pressure 560 Torr), the observed mass spectra of the butane products showed no peaks which could not be attributed to $n\text{-}C_4H_8D_2$ or $n\text{-}C_4H_{10}$. The observed spectra were

	Relative intensities		
m/e	A	B	C
44	85	93	91
45	100	100	100
59	4.2	5.2	4.0
60	17.2	17.8	17.2

(5) In the radiolysis of a $c\text{-}C_6D_{12}$–$c\text{-}C_6H_{12}$–O_2 (1:1:0.1) mixture, the isotopic distribution of the isobutane product is C_4D_{10}, 1.00; C_4D_9H, 0.05; $C_4D_8H_2$, 1.73; $C_4H_8D_2$, 2.03; C_4H_9D, 0.15; C_4H_{10}, 4.9.

(6) In the radiolysis of a $c\text{-}C_5D_9(CD_3)$–$c\text{-}C_5H_9(CH_3)$–O_2 (1:1:0.1) mixture, the isotopic distribution of the isobutane product is C_4D_{10}, 1.00; C_4D_9H, 0.27; $C_4D_8H_2$, 1.03; $C_4H_8D_2$, 0.96; C_4H_9D, 0.25; C_4H_{10}, 1.19.

(7) The product distributions observed in the xenon- and krypton-sensitized radiolyses of cyclohexane in the presence of O_2 and NO are

Rare gas	Additive	C_2H_4	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$1\text{-}C_4H_8$ + $i\text{-}C_4H_8$	Total $2\text{-}C_4H_8$
Xe	O_2	100	18.6	1.0	Nd	5.5
Xe	NO	100	14.1	Nd	1.7	23.8
Kr	O_2	100	5.1	1.9	4.6	10.2
Kr	NO	100	4.2	1.2	6.8	42.8

The ratio of *cis*- to *trans*-2-butene was 0.5 in both oxygen-scavenged experiments, and 0.7 in both NO-scavenged experiments.

(8) The product distributions observed in the xenon- and krypton-sensitized radiolyses of methylcyclopentane in the presence of O_2 as a radical scavenger are

Rare gas	C_2H_4	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$
Xe	100	46.9	2.8
Kr	100	51.6	3.4

Discussion

In the discussion which follows we shall consider several H_2^- (or D_2^-) transfer reactions involving 1- and 2-butene ions formed in the fragmentation of cyclohexane and methylcyclopentane ions. Before proceeding with this discussion, it is useful to side track briefly in order to demonstrate that the 1- and 2-butene ions specifically undergo reactions 5 and 6 (and the analogous reversed deuteration reactions), respectively. That is, there is little or no isomerization of the 1- to the 2-butene ion, or the 2- to the 1-butene ion before or during reaction. In order to demonstrate this, $1\text{-}C_4H_8$ (IP 9.58 eV) and $2\text{-}C_4H_8$ (IP 9.13 eV) were each photolyzed with 10-eV photons in the presence of methylcyclopentane-d_{12}, and O_2 as a radical scavenger (see Results). At this energy, the 1- and 2-butenes will undergo ionization (reactions 8 and 9), with quantum yields of 0.27 and 0.25, respectively,[7] and the ions,

$$1\text{-}C_4H_8 + h\nu\ (10.0\ \text{eV}) \longrightarrow 1\text{-}C_4H_8^+ + e \qquad (8)$$

$$2\text{-}C_4H_8 + h\nu\ (10.0\ \text{eV}) \longrightarrow 2\text{-}C_4H_8^+ + e \qquad (9)$$

in the presence of methylcyclopentane-d_{12} will react[7] (reaction 10) to form butane-d_2. The methylcyclopentane is not ionized at this energy, and, therefore, the D_2 transfer reaction

$$C_4H_8^+ + c\text{-}C_5D_9(CD_3) \longrightarrow C_4H_8D_2 + C_6D_{10}^+ \qquad (10)$$

$$C_4H_8 + c\text{-}C_5D_9(CD_3)^+ \longrightarrow C_4H_8D_2 + C_6D_{10}^+ \qquad (11)$$

cannot contribute to the formation of butane-d_2. It was found that the butane formed in the $2\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$–O_2 mixture consisted entirely of CH_3-$CHDCHDCH_3$ (see Results), indicating that the D_2^- species was transferred cleanly across a double bond in the 2 position.

$$2\text{-}C_4H_8^+ + c\text{-}C_5D_9(CD_3) \longrightarrow CH_3CHDCHDCH_3 + C_6H_{10}^+ \qquad (12)$$

In the $1\text{-}C_4H_8$–$c\text{-}C_5D_9(CD_3)$ mixture, at least 96% of the butane consisted of $CH_2DCHDCH_2CH_3$ formed in the reaction

$$1\text{-}C_4H_8^+ + c\text{-}C_5D_9(CD_3) \longrightarrow CH_2DCHDCH_2CH_3 + C_6D_{10}^+ \qquad (13)$$

On the basis of the mass spectrometric evidence (see Results), in this experiment the presence of a small amount of $CH_3CHDCHDCH_3$ could not, within experimental error, be excluded. However, when 300 Torr of neon was added to the reaction mixture as a deactivator there was no significant change in the mass spectrum of the butane product. Similarly, when the relative concentration of methylcyclopentane-d_{12} was increased by a factor of 10 and 500 Torr of neon was added as a deactivator, no change was seen in the

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(7) J. Herman, K. Herman, and P. Ausloos, *J. Chem. Phys.*, **52**, 281 (1970).

Table I. The Radiolysis of *c*-C_6D_{12}–*c*-C_6H_{12} (1:1) Mixtures. Isotopic Distribution of *n*-Butane[o]

Additive	C_4D_{10}	C_4D_9H	CD_2HCDH–CD_2CD_3	CD_3CDH–$CDHCD_3$	CH_2DCHD–CH_2CH_3	CH_3CHD–$CHDCH_3$	C_4H_{10}
4.8% O_2	1.00	0.00	1.08	0.33	0.91	0.15	1.17
3.6% NO	1.00	0.00	1.31	0.00	1.11	0.00	1.49
200 Torr Xe + 1 Torr O_2	1.00	0.06	1.07	0.11	3.17	~0.4	4.00

[o] Total pressure of cyclohexane 40 Torr.

butane. From these results, we conclude that the isomerization of 1-butene ion to 2-butene ion is very unimportant, if it occurs at all.

It has been similarly demonstrated[7] that the isobutene ion maintains its structure during reaction 7. That is, photoionization of *i*-C_4D_8 in the presence of protonated alkanes yields exclusively $(CD_3)_2CHCD_2H$ as a product.

Cyclohexane

When a *c*-C_6D_{12}–*c*-C_6H_{12} (1:1) mixture is irradiated in the presence of about 5% O_2, added to scavenge free radicals, 90% of the *n*-butanes consists of C_4D_{10}, $C_4D_8H_2$, $C_4H_8D_2$, and C_4H_{10}, indicating that the butane was very probably formed in an H_2^- (or D_2^-) transfer reaction involving butene ions

$$\text{1-}C_4H_8^+ + c\text{-}C_6H_{12} \longrightarrow C_4H_{10} + C_6H_{10}^+ \quad (14)$$

or

$$\text{2-}C_4H_8^+ + c\text{-}C_6H_{12} \longrightarrow C_4H_{10} + C_6H_{10}^+ \quad (15)$$

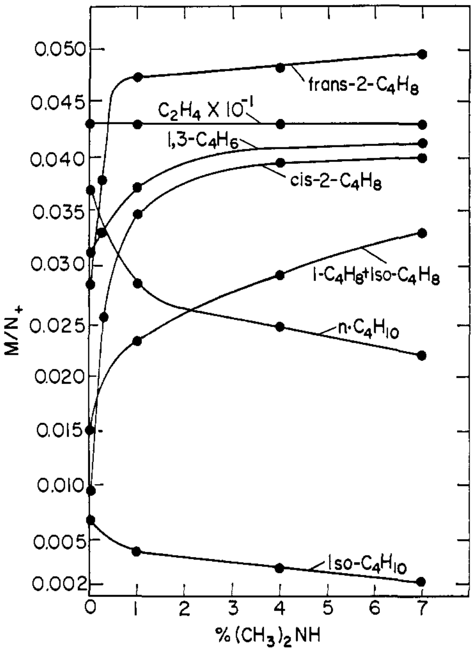

Figure 1. Effect of increasing dimethylamine concentration on the yields of products formed in the gas-phase radiolysis of cyclohexane.

A closer examination of the structure of the $C_4D_8H_2$ (Table I) reveals that it consists of $CD_2HCDHCD_2CD_3$ and $CD_3CDHCDHCD_3$ formed in a ratio of about 3:1. The first of these $C_4D_8H_2$ compounds is formed in a reaction in which the H_2^- species is transferred across a double bond in the 1 position

$$\text{1-}C_4D_8^+ + c\text{-}C_6H_{12} \longrightarrow CD_2HCDHCD_2CD_3 + C_6H_{10}^+ \quad (16)$$

while the second is formed in the reaction of the 2-butene ion

$$\text{2-}C_4D_8^+ + c\text{-}C_6H_{12} \longrightarrow CD_3CDHCDHCD_3 + C_6H_{10}^+ \quad (17)$$

However, when the *c*-C_6D_{12}–*c*-C_6H_{12} mixture is irradiated in the presence of 3.6% NO, the $CD_3CDHCDHCD_3$ product entirely disappears (Table I), although the yield of $CD_2HCDHCD_2CD_3$ is diminished by only about 5%. It has recently been demonstrated in a tandem mass spectrometer[4] that the 2-$C_4H_8^+$ ions undergo an H_2^- transfer reaction with cyclohexane (reaction 15) with a cross section which is not more than 0.5% of the cross section for the analogous reaction of 1-$C_4H_8^+$ ions (reaction 14). The butene ions are known to react with NO through charge transfer

$$C_4H_8^+ + NO \longrightarrow C_4H_8 + NO^+ \quad (18)$$

or condensation

$$C_4H_8^+ + NO \longrightarrow C_4H_8NO^+ \quad (19)$$

The fact that as little as 3.6% NO effectively prevents the occurrence of reaction 17 confirms that 2-$C_4H_8^+$ ions react extremely slowly with cyclohexane, since the rate of reaction 18 as measured in the mass spectrometer[8] for 2-$C_4H_8^+$ ions is only 10^{-11} cc/molecule sec. Therefore, the yield of $CD_3CDHCDHCD_3$ measured in the oxygen-scavenged experiment does not necessarily represent the total yield of the precursor 2-butene ion (even though there are no other exothermic reactions which this ion can undergo with cyclohexane), since neutralization or reaction with impurities or product molecules may compete for removal of the 2-butene ions.

In order to estimate the yield of the 2-butene ions formed in the irradiation of cyclohexane, one can add to the system a molecule with which the butene ions will undergo an efficient charge transfer reaction (reaction 1). The ionization potentials of the butenes are: 1-C_4H_8, 9.58; 2-C_4H_8, 9.13; *i*-C_4H_8, 9.23 eV. Suitable charge-acceptor molecules, therefore, include $(CH_3)_2NH$ (IP 8.24 eV) and $(CH_3)_3N$ (IP 7.82 eV). Furthermore, it has been demonstrated[9] in the mass spectrometer that charge transfer is the only major reaction path between these molecules and the butene ions.

$$\text{1-}C_4H_8^+ + (CH_3)_2NH \longrightarrow \text{1-}C_4H_8 + (CH_3)_2NH^+ \quad (20)$$

$$\text{2-}C_4H_8^+ + (CH_3)_2NH \longrightarrow \text{2-}C_4H_8 + (CH_3)_2NH^+ \quad (21)$$

Figure 1 shows the yields of the butanes and butenes formed in the radiolysis of *c*-C_6H_{12}–O_2 mixtures to which increasing amounts of $(CH_3)_2NH$ have been added as a charge acceptor. In the presence of 1% or less $(CH_3)_2NH$, the yields of *cis*- and *trans*-2-butene are increased drastically to values which remain essen-

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(8) L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, 48, 1409 (1968).

(9) L. W. Sieck, S. Searles, and P. Ausloos, *J. Amer. Chem. Soc.*, 91, 7627 (1969).

tially constant with further increases in $(CH_3)_2NH$ concentration. The yield which one attributes to the 2-butene ion from these experiments is larger, by a factor of approximately 10, than the yield of 2-butene ions which react with cyclohexane in the absence of charge acceptor. The results given in Figure 1 show that in the presence of 0.27% dimethylamine, about 50% of the 2-butene ions have been intercepted. This would indicate that reaction with the amine is at least 250 times faster than the unknown alternate reaction which the 2-butene ion undergoes in the absence of additives.

Figure 1 also shows a gradual diminution in the yields of *n*-butane and isobutane with increasing amine concentration, and a simultaneous increase in the yields of $1\text{-}C_4H_8 + i\text{-}C_4H_8$. (The yields of the latter butenes could not be measured separately under the experimental conditions used in this study.) As discussed above, in the presence of charge acceptor, the *n*-butane can be essentially entirely ascribed to reaction 14 of the 1-butene ion.

An isotopic analysis of the isobutane formed in a $c\text{-}C_6D_{12}\text{-}c\text{-}C_6H_{12}\text{-}O_2$ (1:1:0.10) mixture (see Results) indicates that this product is formed in an H_2^- transfer reaction involving the isobutylene ion

$$i\text{-}C_4D_8^+ + c\text{-}C_6H_{12} \longrightarrow (CD_3)_2CHCD_2H + C_6H_{10}^+ \qquad (22)$$

The presence of isobutylene ions indicates the occurrence of a fragmentation process involving considerable rearrangement. The formation of this ion will be discussed further below.

Thus, the results given in Figure 1 demonstrate that in the presence of 1–7% $(CH_3)_2NH$, there is a competition between reaction of the isobutylene and 1-butene ions with cyclohexane (reactions 22 and 14) and charge-transfer reactions 23 and 20.

$$i\text{-}C_4H_8^+ + (CH_3)_2NH \longrightarrow i\text{-}C_4H_8 + (CH_3)_2NH^+ \qquad (23)$$

Before attempting to obtain quantitative information from the butane and butene yields measured in these experiments, we should first mention that butene ions having 0.4-eV kinetic energy have been observed[4] to undergo an alternate reaction with cyclohexane in the mass spectrometer, namely a hydride transfer reaction to form a butyl radical

$$C_4H_8^+ + c\text{-}C_6H_{12} \longrightarrow C_4H_9 + C_6H_{11}^+ \qquad (24)$$

However, a computation of the heat of reaction 24 for thermal, ground state $1\text{-}C_4H_8^+$, $i\text{-}C_4H_8^+$, and $2\text{-}C_4H_8^+$ ions (using heats of formation for these ions from the literature[10]) shows that reaction 24 is endothermic by 6, 12, and 22 kcal/mol for the three respective ions. It is, therefore, unlikely that reaction 24 occurs to any measurable extent in our system. This has been confirmed by examining the reaction between butene ions and cyclohexane in a quadropole mass spectrometer[9] in which the reacting ions (which are formed by photoionization of the corresponding butene with 10-eV photons) have no excess kinetic energy; in these experiments, less than 5% of the 1-butene ions or 2-butene ions underwent reaction 24.

Thus, we can now equate the yield of the 1-butene ion to the yield of butane formed in reaction 14 in the absence of any charge acceptor; similarly, the yield of isobutylene ion is equal to the yield of isobutane formed in that experiment. From the measured yields of these products (Figure 1) and the isotopic analysis of the butane formed in the radiolysis of a $c\text{-}C_6D_{12}\text{-}c\text{-}C_6H_{12}\text{-}O_2$ mixture (see above discussion and Table I), we can estimate the ion-pair yield of 1-butene ion as approximately 0.03 and that of isobutylene ion as about 0.007, at a total cyclohexane pressure of 40 Torr. Within experimental error, the increment in the yield which can be attributed to 1-butene + isobutylene is in agreement with the depletion of the yields of the corresponding butanes as charge acceptor is added (see Figure 1).

Applying the steady state treatment to the reaction mechanism of the 1-butene ion represented by reactions 14 and 20, we obtain the expression

$$\frac{[n\text{-butane}_0]}{[n\text{-butane}]} = 1 + \frac{k_{20}}{k_{14}}\frac{[(CH_3)_2NH]}{[\text{cyclohexane}]} \qquad (I)$$

where $[n\text{-butane}_0]$ represents the yield of *n*-butane formed by reaction 14 in the absence of $(CH_3)_2NH$. Applying eq I to the data plotted in Figure 1 (remembering that at 0% $(CH_3)_2NH$, the butane formed in reaction 14 is 80% of the total butane yield), we derive the rate of reaction of the $1\text{-}C_4H_8^+$ ion with amine relative to the rate of reaction with cyclohexane

$$k_{20}/k_{14} = 4.8$$

In a completely analogous fashion, we derive

$$\frac{[\text{isobutane}_0]}{[\text{isobutane}]} = 1 + \frac{k_{23}}{k_{22}}\frac{[(CH_3)_2NH]}{[\text{cyclohexane}]} \qquad (II)$$

and calculate a value of ~54 for k_{23}/k_{22}.

Finally, it should be mentioned that in the isotopic distributions of the butanes (Table I) the yield of $C_4D_8H_2$ exceeds that of C_4D_{10} and the yield of C_4H_{10} exceeds that of $C_4H_8D_2$ by a factor of ~1.3 in both cases, indicating the existence of an isotope effect of this magnitude favoring reaction of the 1-butene ion with the undeuterated cyclohexane analog.

The increments in the yields of the 2-butenes when a charge acceptor is added can be approximately correlated to the yield of 2-butene ion. On this basis, $M(2\text{-}C_4H_8^+)/N_+$ is ~0.05. It is true that the added amine may interfere with the formation of the butene product not originating from butene ion reactions 20 and 21. This butene ($M(2\text{-}C_4H_8)/N_+ = 0.038$, in the absence of $(CH_3)_2NH$) probably originates from the $C_4H_7^+$ ion, which is observed in the mass spectrum of cyclohexane, $M(C_4H_7^+)/N_+ = 0.079$. This ion can undergo a hydride transfer reaction with cyclohexane

$$C_4H_7^+ + c\text{-}C_6H_{12} \longrightarrow C_4H_8 + C_6H_{11}^+ \qquad (25)$$

The $C_4H_7^+$ ion might be expected to transfer a proton to $(CH_3)_2NH$ (reaction 26) to form butadiene. In

$$C_4H_7^+ + (CH_3)_2NH \longrightarrow C_4H_6 + (CH_3)_2NH_2^+ \qquad (26)$$

fact, an increase in the yield of butadiene with increasing amine concentration is observed (Figure 1). However, since reaction 25 should be relatively fast,

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(10) Heats of reaction are based on thermodynamic data presented in the following publications: (a) S. W. Benson, "Thermodynamic Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968; (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRD-NBS publication, U. S. Government Printing Office, Washington, D. C., 1969.

Table II. The Radiolysis of $c\text{-}C_5D_9(CD_3)\text{–}c\text{-}C_5H_9(CH_3)\text{–}O_2$ (1:1:0.1) Mixtures. Isotopic Distribution of *n*-Butane[a]

Additive	C_4H_{10}	C_4D_9H	$CD_2HCDH\text{–}CD_2CD_3$	$CD_3CDH\text{–}CDHCD_3$	$CH_2DCHD\text{–}CH_2CH_3$	$CH_3CHD\text{–}CHDCH_3$	C_5H_{10}
None	1.00	0.020	0.54	0.95	0.57	0.84	~1.79
4% $(CH_3)_2NH$	1.00	0.032	0.62	0.66			
8% $(CH_3)_2NH$	1.00	0.010	0.71	0.51	0.87	0.23	~1.88
16% $(CH_3)_2NH$	1.00	0.008	1.09	0.26	1.45	0.37	Nd
430 Torr Xe	1.00	0.075	0.91	0.48	1.05	0.51	~1.80
740 Torr Kr	1.00	0.019	0.28	1.18			

[a] Total pressure methylcyclopentane 40 Torr.

the depletion of this butene product should be relatively slight at the low amine concentrations used here, and the increment in the butene product may indeed be taken as a measure of the $2\text{-}C_4H_8^+$ ion yield.

Methylcyclopentane

Let us now, in a similar fashion, look at the butene ions formed in the radiolysis of methylcyclopentane. The isotopic distribution of butanes formed in the radiolysis of a methylcyclopentane-h_{12}–methylcyclopentane-d_{12}–O_2 mixture is given in Table II. We see the formation of $CD_3CDHCDHCD_3$ and $CD_2HCDHCD_2CD_3$, as well as $CH_3CHDCHDCH_3$ and $CH_2DCHDCH_2CH_3$, indicating the occurrence of the H_2^- transfer reactions

$$1\text{-}C_4H_8^+ + c\text{-}C_5H_9(CH_3) \longrightarrow n\text{-}C_4H_{10} + C_6H_{10}^+ \quad (27)$$

$$2\text{-}C_4H_8^+ + c\text{-}C_5H_9(CH_3) \longrightarrow n\text{-}C_4H_{10} + C_6H_{10}^+ \quad (28)$$

In addition, a small amount of isobutane is formed in these experiments. An isotopic analysis of the isobutane formed in a $c\text{-}C_5D_9(CD_3)\text{–}c\text{-}C_5H_9(CH_3)\text{–}O_2$ mixture (see Results) indicates that this product is mainly formed in an H_2^- transfer reaction involving the isobutylene ion

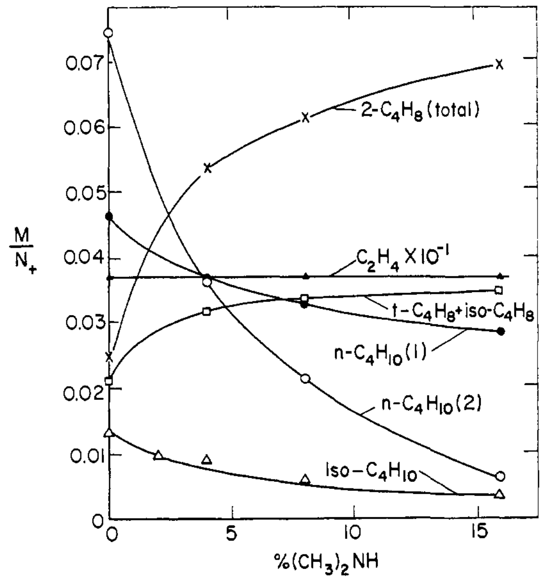

Figure 2. Effect of dimethylamine on the yields of products formed in the gas-phase radiolysis of methylcyclopentane. $n\text{-}C_4H_{10}$ (1) and $n\text{-}C_4H_{10}$ (2) denote the butanes formed by reaction of the 1-butene and 2-butene ions, respectively.

$$i\text{-}C_4H_8^+ + c\text{-}C_5H_9(CH_3) \longrightarrow i\text{-}C_4H_{10} + C_6H_{10}^+ \quad (29)$$

According to a recent mass spectrometric investigation[9] the H^- transfer reaction 30 competing with 27, 28, or 29 is only of importance when $C_4H_8^+$ has the $1\text{-}C_4H_8^+$ ion structure. In this case k_{27}/k_{30} was found to be 30.

$$C_4H_8^+ + c\text{-}C_5H_9(CH_3) \longrightarrow C_4H_9 + C_6H_{11}^+ \quad (30)$$

The yields of the butanes and butenes formed in the presence of varying amounts of $(CH_3)_2NH$ are given in Figure 2. For clarity of presentation, the yields of *cis*- and *trans*-2-butene have been added together. The ratio of *cis*-2-butene to *trans*-2-butene is 0.69 in all experiments. Here, as in the case of cyclohexane, we see an increase in the yields of the butenes and a simultaneous decrease in the butanes with increase in dimethylamine concentration. The yields of the butanes originating from reaction of the 1- and 2-butene ions have been derived from the total measured yields of *n*-butane and the isotopic distributions of the butanes formed in the radiolysis of a $c\text{-}C_5D_9(CD_3)\text{–}c\text{-}C_5H_9(CH_3)\text{–}O_2$ (1:1:0.1) mixture in the presence of varying amounts of charge acceptor (Table II). The results given in Figure 2 show that while the yield of butane resulting from reaction of the 1-butene ion has dropped to about 60% of its original value in the presence of 16% dimethylamine, the yield of butane resulting from reaction of the 2-butene ion has decreased to less than 10% of its original value, indicating that reaction of the 2-butene ion with methylcyclopentane (as with cyclohexane) is much slower than the reaction of the 1-butene ion. However, in this case (unlike the reactions in the cyclohexane system discussed above) in the absence of charge acceptor, all the 2-butene ions apparently do react to form *n*-butane, since the increase in the butene yield observed when dimethylamine is added approximately parallels the depletion of the corresponding butane. From the butane yields given in Figure 2, we can derive that for the 1-butene ion, reaction with the dimethylamine (k_{20}) is faster than reaction with methylcyclopentane by a factor of 4.6; for the 2-butene ion, reaction with dimethylamine is faster than reaction with methylcyclopentane by a factor of 26; for the isobutylene ion, reaction with the charge acceptor is faster than reaction with methylcyclopentane by a factor of 15. Because charge transfer to dimethylamine occurs probably at every collision it follows that reaction of the $1\text{-}C_4H_8^+$ and $i\text{-}C_4H_8^+$ ions with methylcyclopentane are faster than reaction of the $2\text{-}C_4H_8^+$ ion by factors of 6 and 3, respectively.

It is not possible to obtain exact quantitative information from the increments in the yields of the butenes since we do not know to what extent the dimethylamine interferes with the formation of the butene products which are, as in the case of cyclohexane, produced in the hydride transfer reaction

$$C_4H_7^+ + c\text{-}C_5H_9(CH_3) \longrightarrow C_4H_8 + C_6H_{11}^+ \quad (31)$$

Some depletion of this butene product might be expected in the presence of $(CH_3)_2NH$ because of the occurrence of reaction 26. If one tentatively ignores reaction 26, the increments in the 2-butene yields (Figure 2) yield a value of 40 for k_{21}/k_{28}. A value closer to the value of 26, which we obtained above from a consideration of the depletion of the butane, would be obtained if reaction 26 is taken into account. The relative rates of reaction of the $C_4H_8^+$ ions just derived are given in Table III.

Table III. Relative Rates of Reaction of $C_4H_8^+$ Ions

	1-$C_4H_8^+$	2-$C_4H_8^+$	*i*-$C_4H_8^+$
c-C_6H_{12}	0.21	$<10^{-4}$	0.018
c-C_6D_{12}	0.16		
c-$C_5H_9(CH_3)$	0.22	0.038	0.067
c-$C_5D_9(CD_3)$	0.19		
$(CH_3)_2NH$	1.00	1.00	1.00

Relative Rates of Reaction with Different Hydrocarbons

Comparing the relative rates just derived from reaction of the 1-butene ion with methylcyclopentane and with dimethylamine ($k_{20}/k_{27} \approx 4.6$), we see that the 1-butene ion reacts approximately at the same rate with methylcyclopentane as with cyclohexane ($k_{20}/k_{14} = 4.8$). Similarly, we see that the isobutylene ion reacts faster with methylcyclopentane by a factor of ~3.6 than with cyclohexane. These results are confirmed in several experiments in which mixtures of cyclohexane and methylcyclopentane, in which one or the other hydrocarbon was deuterated, were irradiated in the presence of oxygen as a free radical scavenger. The isotopic distributions of the butanes formed are given in Table IV. In such mixtures, all the 2-butene ions will react with the methylcyclopentane rather than with cyclohexane to form the appropriate butane. In the case in which methylcyclopentane is the deuterated component (and the reaction of 2-$C_4D_8^+$ ions will contribute to the formation of *n*-C_4D_{10}) we assume that the ratio of 1- to 2-butene ions originating from methylcyclopentane is the same as that observed for the pure methylcyclopentane system (Table II). Thus, from the results given in Table IV, we calculate in a straightforward manner relative rates of reaction for the 1-butene ion ($C_4D_8^+$ or $C_4H_8^+$) with *c*-C_6D_{12}, *c*-$C_5D_9(CD_3)$, *c*-C_6H_{12}, or *c*-$C_5H_9(CH_3)$, of 1.0, 0.9, 1.3, and 1.1. These relative rates are in reasonably good agreement with those derived above from a kinetic analysis of the depletion of the butane yields in the presence of charge acceptor, and indicate an isotope effect favoring reaction with the undeuterated compounds. These relative rates have also been included in Table III.

Table IV. The Radiolysis of Cyclohexane–Methylcyclopentane–O_2 (1:1:0.1) Mixtures. Isotopic Distribution of *n*-Butane[a]

C_6D_{12}	C_6H_{12}	Additive	C_4D_{10}	$CD_2HCDH-CD_3CD_3$	$CD_3CDH-CDHCD_3$	$CH_3CHD-CH_2CH_3$	$CH_3CHD-CHDCH_3$	C_4H_{10}
Cyclohexane	Methylcyclopentane	None	1.00	0.12	1.12	4.46	1.75	~8.6
		250 Torr Xe	1.00	0.098	1.11	7.49		
		340 Torr Kr	1.00	0.086	3.50	24.5		
Methylcyclopentane	Cyclohexane	None	1.00	0.019	0.20	0.025	0.38	

[a] Total pressure of hydrocarbon 40 Torr.

In order to determine the effect of the structure of the reacting molecule on the relative rate of the H_2^- reaction of the 1-butene ion, *c*-C_6D_{12} was irradiated in the presence of various other hydrocarbons. In such mixtures, the 1-butene ion will undergo reaction with cyclohexane

$$1\text{-}C_4D_8^+ + c\text{-}C_6D_{12} \longrightarrow n\text{-}C_4D_{10} + C_6D_{10}^+ \qquad (32)$$

to form *n*-C_4D_{10}, and reaction with the undeuterated hydrocarbon AH_2

$$1\text{-}C_4D_8^+ + AH_2 \longrightarrow CD_2HCDHCD_2CD_3 + A^+ \qquad (33)$$

In some cases, the 2-$C_4D_8^+$ ion will be able to react with AH_2, to form $CD_3CDHCDHCD_3$, but as reaction of this ion with *c*-C_6D_{12} to form C_4D_{10} can be ignored, its presence will not interfere with the determination of the relative rates of reaction of the 1-butene ion. Since all the mixtures are equimolar in *c*-C_6D_{12}–AH_2, these relative rates are simply given by the ratio $CD_2HCDHCD_2CD_3/C_4D_{10}$ where the C_4D_{10} has been corrected for the minor contributions from butyl ion reactions. The results of these experiments are given in Table V. It can be seen that reaction becomes faster with larger members of a homologous series (compare *n*-pentane with *n*-hexane, cyclopentane with cyclohexane), and the presence of a tertiary hydrogen atom causes an increase in the reaction rate. The results given in Table V also strikingly demonstrate that $CD_3CDHCDHCD_3$ only appears as a product when AH_2 has a tertiary H atom. As anticipated, reaction 34 only occurs in those cases where ΔH of the

$$2\text{-}C_4D_8^+ + AH_2 \longrightarrow CD_3CDHCDHCD_3 + A^+ \qquad (34)$$

reaction is clearly exothermic for ground state 2-$C_4D_8^+$ ions. It follows that internally excited 2-$C_4D_8^+$ are either not formed or that, if formed, they cannot effectively overcome the energy requirements of reaction 34.

Modes of Formation of the $C_4H_8^+$ Ions

Some insight concerning the modes of formation of $C_4H_8^+$ can be gained by a consideration of the changes in the relative importances of the butene ion forming reactions when the energy of the dissociating parent ion is changed. This is accomplished by irradiating the hydrocarbon in the presence of a large excess of rare gas, so that parent hydrocarbon ions are formed nearly exclusively through the charge-transfer reaction

$$X^+ + C_6H_{12} \longrightarrow X + C_6H_{12}^+ \qquad (35)$$

where X is a rare gas atom, and C_6H_{12} is methylcyclopentane or cyclohexane.

Table V. Radiolysis of $c\text{-}C_6D_{12}\text{–}AH_2\text{–}O_2$ (1:1:0.1) Mixtures in the Gas Phase[a]

Additive	C_4D_{10}	C_4D_9H	$CD_2HCDH\text{-}CD_2CD_3$	$CD_3CDH\text{-}CDHCD_3$	k_{33}/k_{32}[b]	ΔH, eV reaction 33	ΔH, eV reaction 34
$c\text{-}C_5H_{12}$	1.00	0.074	0.82	0.00	0.9	−0.74	−0.20
$n\text{-}C_5H_{12}$	1.00	0.047	0.84	0.00	0.9	−0.61	−0.091
$n\text{-}C_6H_{14}$	1.00	0.058	1.19	0.00	1.3	−0.61	−0.095
$i\text{-}C_5H_{12}$	1.00	0.054	0.95	2.5	1.0	−1.08	−0.056
$c\text{-}C_5H_9(CH_3)$	1.00	0.12	1.12	4.5	1.3		
$CH_3CH(CH_3)CH(CH_3)CH_3$	1.00	0.010	1.52	4.2	1.5	−1.47	−0.95

[a] Total pressure 40 Torr. [b] Rate of H_2^- transfer reaction between $1\text{-}C_4D_8^+$ ion and additive relative to rate of analogous reaction with $c\text{-}C_6D_{12}$.

Table VI. The Formation of Butene Ions in the Radiolysis of Cyclohexane and Methylcyclopentane

	Cyclohexane, %			Methylcyclopentane, %		
	$1\text{-}C_4H_8^+$	$2\text{-}C_4H_8^+$	$i\text{-}C_4H_8^+$	$1\text{-}C_4H_8^+$	$2\text{-}C_4H_8^+$	$i\text{-}C_4H_8^+$
Direct radiolysis	34	58	7.8	34	56	10
Xenon-sensitized radiolysis	48	48	3.2	64	31	5.6
Krypton-sensitized radiolysis	12	83	5.0	19	73	8.6

The distribution of butene ions formed in the direct irradiation of methylcyclopentane and cyclohexane, as well as in the xenon- and krypton-sensitized irradiations, are given in Table VI. These distributions are obtained from consideration of the isotopic structure of the butanes formed in the irradiation of $C_6H_{12}\text{–}C_6D_{12}$ mixtures (Tables I and II), as well as of the relative yields of the butenes formed in the presence of a charge acceptor (see Results), according to the reasoning followed in the above discussion.

The most striking aspect of the results given in Table VI is the pronounced change in the abundances of the butene ions caused by a change in rare gas. A second important feature is the general similarity between the distribution of the three $C_4H_8^+$ ions in cyclohexane and in methylcyclopentane. The second feature is perhaps not so surprising in view of the similarities between the 70-eV mass spectral cracking patterns of these two compounds.

Further information on the modes of formation of these ions in cyclohexane was obtained by examining the mass spectrum of cyclohexane-1,1,2,2,3,3-d_6 ionized by 13- and 70-eV electrons. The observed distribution of the $C_4D_2H_6^+$, $C_4D_3H_5^+$, $C_4D_4H_4^+$, $C_4D_5H_3^+$, and $C_4D_6H_2^+$ ions obtained at 13 eV and at 70 eV (where the analogs of the $C_4H_7^+$ ion contribute to the observed ion currents) are given in Table VII. The table also gives the distribution one would obtain if the H and D atoms were completely statistically distributed in the butene ions. A striking similarity can be seen between the calculated statistical distribution and the spectrum of butene ion analogs obtained at low ionizing energy.

Table VII. The Formation of Butene Ions in the Mass Spectrum of Cyclohexane-1,1,2,2,3,3-d_6

Ion	Relative intensity 70 eV[a]	Relative intensity 13 eV	Calculated statistical distribution
$C_4D_2H_6^+$	90	38	7
$C_4D_3H_5^+$	56	65	53
$C_4D_4H_4^+$	100	100	100
$C_4D_5H_3^+$	34	55	53
$C_4D_6H_2^+$	48	25	7

[a] Ion currents include contributions from isotopic analogs of $C_4H_7^+$. In the 70-eV spectrum of $c\text{-}C_6H_{12}$, $C_4H_7^+/C_4H_8^+ = 0.35$.

This result apparently means that in the dissociation of $C_6D_6H_6^+$, formed at low energy, the H and D atoms are statistically distributed in the parent ion prior to its dissociation. Most likely the butene ion is eliminated by a concerted mechanism involving a relatively long-lived parent ion.

On the other hand, in the 70-eV mass spectrum of this compound, we see an alternating pattern in this mass range, with the mass 58, 60, and 62 ion currents high and the intermediate 59 and 61 ion currents lower. Since the contributions of the butene ions to these masses should be far more important than the contributions of the $C_4H_7^+$ analogs (in the mass spectrum of $c\text{-}C_6H_{12}$, the $C_4H_7^+$ ion is only 35% of the intensity of the $C_4H_8^+$ ion), this pattern suggests that in the high energy dissociation of the cyclohexane-1,1,2,2,3,3-d_6 parent ion, the ions of interest are largely formed by the simple cleavage mechanisms

$$c\text{-}C_6D_6H_6^+ \longrightarrow C_4D_2H_6^+ + C_2D_4 \quad (36)$$

$$\longrightarrow C_4D_4H_4^+ + C_2D_2H_2 \quad (37)$$

$$\longrightarrow C_4D_6H_2^+ + C_2H_4 \quad (38)$$

One would expect the radiolysis, as well as the krypton-sensitized radiolysis, to conform more to the processes observed in the high energy mass spectrum.

We can picture the high energy dissociation process as a clean split-out of an ethylene molecule, followed by rearrangement of the excited $C_4H_8^+$ entity to form $1\text{-}C_4H_8^+$, $2\text{-}C_4H_8^+$, or $i\text{-}C_4H_8^+$. Because the ion formed in reactions 36–38 may momentarily have a tetramethylene configuration, it is of interest to reexamine the structures of the butene ions formed from cyclobutane where ring opening in the parent ion would lead directly to the tetramethylene configuration. Recent experiments[9] have demonstrated that this ion rearranges to form the thermodynamically favored 2-butene ion and the isobutylene ion only

$$c\text{-}C_4H_8 \longrightarrow [C_4H_8^+]^* + e \longrightarrow 2\text{-}C_4H_8^+ + e \quad (39)$$

$$\longrightarrow i\text{-}C_4H_8^+ + e \quad (40)$$

If we assume that a similar $[C_4H_8^+]$ precursor is formed in the radiolysis of cyclohexane, we can rationalize the variations in the butene ion distributions with energy (Table VI) by assuming that the high energy excited state of the parent ion (whose decomposition is exemplified by reactions 36, 37, and 38) leads to the excited $C_4H_8^+$ species which undergoes reactions 39 and 40. Thus, we see that the formation of the 2-butene and isobutylene ions are especially important in the krypton-sensitized radiolysis. On the other hand, in the xenon-sensitized radiolysis, the long-lived, low energy state of the $C_6H_{12}^+$ ion yields mainly the 1-$C_4H_8^+$ ion by a concerted unimolecular mechanism even though the heat of formation of the 1-butene ion is greater than that of the 2-butene ion.

In view of the energy dependence on the distribution of the butene ion isomers, it may be anticipated that the relative abundances will also be dependent on the pressure of the system. In accordance with the above interpretation, photoionization experiments which will be reported at a later date[11] show that the yields of both the isobutylene ion and 2-butene ion diminish relative to the 1-butene ion yield with an increase in pressure of either the cycloalkane or a rare gas additive.

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(11) P. Ausloos, submitted for publication.

Analysis of the Ion–Molecule Reactions in Hydrogen–Methane Mixtures Using Ion Cyclotron Resonance[1]

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Abstract: The kinetics and energetics of the principal ion–molecule reactions in hydrogen–methane mixtures are reported. The emphasis is on the reactions of H_3^+ with neutral methane. The pressure dependence of the $CD_4H^+/\Sigma C(H,D)_3^+$ ratio as a function of H_2 pressure in a CD_4–H_2 mixture is presented. In order to explain the details of the pressure dependence, reactions of both excited $[H_3^+]^*$ and collisionally deactivated H_3^+ with CD_4 are postulated. $[H_3^+]^*$ forms CD_3^+ and CD_2H^+ primarily *via* a direct mechanism, while H_3^+ first forms $[CD_4H^+]^*$, which is subsequently collisionally stabilized or decomposes to CD_3^+ or CD_2H^+. Pulsed-ion-ejection double resonance studies support this interpretation and indicate both hydride ion abstraction and some sort of displacement mechanism are simultaneously at play in the direct formation of CD_3^+ and CD_2H^+. The lifetime of the $[CD_4H^+]$ ion was determined to be approximately 2×10^{-4} sec, nearly two orders of magnitude longer than previously estimated by Aquilanti and Volpi.

Ion cyclotron resonance (icr) spectroscopy is rapidly becoming established as a prime tool for studying a wide variety of gas phase ion-molecule processes.[2–5] Of particular interest in these laboratories is the use of icr to determine quantitative kinetic data[5–8] and detailed mechanistic information[6–8] on simple systems of atmospheric importance. Investigations to date have dealt with H_2,[6] $H_2 + N_2$ mixtures,[7,8] and $H_2 + Ar$ mixtures.[8] In this report these studies are extended to include the various ion-molecule reactions in H_2–CH_4 mixtures, a system of considerable importance in the study of the Jovian atmosphere,[9] and possibly crucial to the understanding of the evolution of the earth's primitive reducing atmosphere.

The hydrogen–methane system has been studied by several authors,[10–12] the most recent work being by Aquilanti and Volpi[12] using a high-pressure mass spectrometer with a tritium ionization source. The experiments of Aquilanti and Volpi[12] were restricted to measuring the rate of reaction of H_3^+ with CH_4 and to observing the resulting CH_5^+/CH_3^+ ratio as a function of H_2 pressure. The ratio data of this labotatory agree qualitatively with theirs at high H_2 partial pressures. At lower pressures, however, our data conclusively show curvature and a nonzero intercept while they[12] assume the linear decrease in CH_5^+/CH_3^+ continues to a value of zero at zero H_2 pressure. Aquilanti and Volpi[12] interpret their ratio data by assuming collisional stabilization of excited $[CH_5^+]^*$ by H_2. Our additional

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