

# Kinetic Mass Spectrometric Investigation of the Ion-Molecule Reactions Occurring in C<sub>4</sub> and C<sub>5</sub> Alkanes Following Photoionization at 106.7 and 104.8 nm \*

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The photoionization of C<sub>4</sub> and C<sub>5</sub> alkanes has been investigated at 106.7 and 104.8 nm in a mass spectrometer specifically designed for the investigation of ion-molecule reactions occurring at thermal kinetic energies. Absolute rate constants are reported for the reactions of various fragment ions with the corresponding parent molecule.

The rate constants found for reactions of *sec*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions with *i*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *i*-C<sub>5</sub>H<sub>12</sub>, and *n*-C<sub>5</sub>H<sub>12</sub> were found to be 3.3, 4.4, 4.7, and 5.2 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-second respectively. The C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions were also found to be highly reactive, exhibiting rate constants of 3.6 and 3.8 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-second in reactions with *i*-C<sub>5</sub>H<sub>12</sub> and *n*-C<sub>5</sub>H<sub>12</sub>. The rate constants for reaction of C<sub>3</sub>H<sub>6</sub><sup>+</sup> with *i*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *i*-C<sub>5</sub>H<sub>12</sub>, and *n*-C<sub>5</sub>H<sub>12</sub> were found to be 4.9, 4.9, 7.6, and 7.9 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-second, respectively. Butene ions are less reactive by an order of magnitude. The results are compared with complementary data derived from electron impact experiments, and the relationship between the structure and reactivity of the various ions is discussed.

Key words: gas phase; hydrocarbons; ion-molecule reactions; mass spectrometry; photoionization; rate constants.

## 1. Introduction

Recent publications from this laboratory [1] have illustrated that a photoionization mass spectrometer is advantageous for studying the reactions of parent hydrocarbon ions. In some cases selective ionization of hydrocarbons in the presence of organic or inorganic additives may be achieved by proper utilization of the line emission (123.6, 116.4, or 106.7 nm) of rare gas resonance lamps. Furthermore, when ionization is induced by photoabsorption at energies only slightly above the ionization threshold, it is possible to investigate the reactions of parent ions with parent molecules in the absence of those complicating reactions associated with those fragment ions which would be produced at higher energies. The fact that parent ion-parent molecule reactions could be investigated at thermal kinetic energies in such an instrument at room temperature over a considerable pressure range was instrumental in the elucidation of the kinetics of formation and reaction of alkane dimer ions (C<sub>n</sub>H<sub>2n+2</sub>)<sub>2</sub><sup>+</sup> [1e, 1f].

The present photoionization study differs from those mentioned above in that C<sub>4</sub>–C<sub>5</sub> alkanes were irra-

diated with photons of sufficient energy to induce unimolecular fragmentation of the parent ion. The reactivities of the resultant fragment ions towards the alkanes were derived from the variation of the composite mass spectrum of a particular system as a function of pressure. The ion-molecule chemistry occurring in some of these alkanes (*n*-C<sub>4</sub>H<sub>10</sub>, *i*-C<sub>4</sub>H<sub>10</sub>, and *neo*-C<sub>5</sub>H<sub>12</sub>) has been investigated previously by kinetic mass spectrometry using high energy electrons [2]. In those studies, however, the temperature of the ion source was approximately 500 K and the electron energy was well above that of the photons used in this investigation. Consequently, a considerable variety of fragment ions were produced and it was difficult in some instances to determine which of the many fragment ions were responsible for the formation of ionic products.

It was also considered of interest to compare rate data obtained from this study with that derived from analysis of the neutral products of ion-molecule reactions occurring in alkane systems [3]. Such a comparison is of particular importance since end product analysis has recently revealed the formation of alkyl and olefinic ions with more than one structure in the unimolecular decomposition of *n*-alkane and cycloalkane parent ions [4]. Since isomeric ions are known to exhibit different reactivities, one might expect to de-

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rive additional information from the contour of the ion decay plots obtained from the mass spectrometer.

## 2. Experimental and Results

The high-pressure photoionization mass spectrometer used in the present study has been described elsewhere in detail [1a, b]. In all experiments the reaction chamber (ion source) was operated at  $300 \pm 2$  K in the absence of any internal electric or magnetic fields.

All materials were purified by gas chromatography and subsequently distilled at low temperatures in order to remove traces of water. The techniques used for the evaluation of absolute rate constants for bimolecular reactions have been described in detail elsewhere [1a, b]. Experimentally, the method involves a determination of the composite mass spectrum, including all reactant and product ions, as a function of sample pressure in the photoionization chamber. The logarithm of the percentage composition of the mass spectrum is then plotted versus pressure in the manner displayed in figures 1-6. The thermal bimolecular rate constant is then determined from the slope of the resultant decay curves found for primary

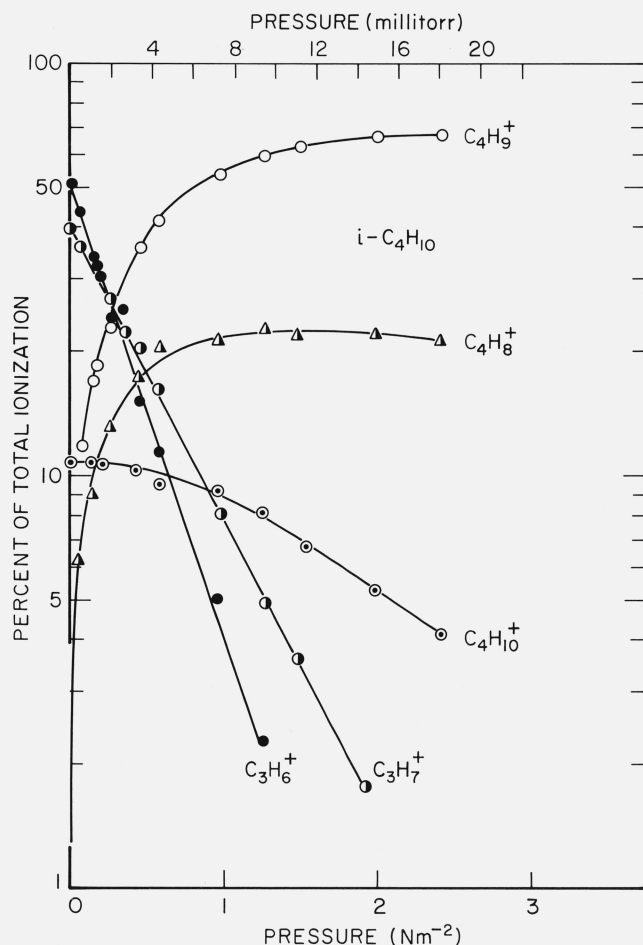


FIGURE 1. Composite mass spectrum obtained from the photoionization (106.7-104.8 nm) of *i*-C<sub>4</sub>H<sub>10</sub> versus pressure of *i*-C<sub>4</sub>H<sub>10</sub>.

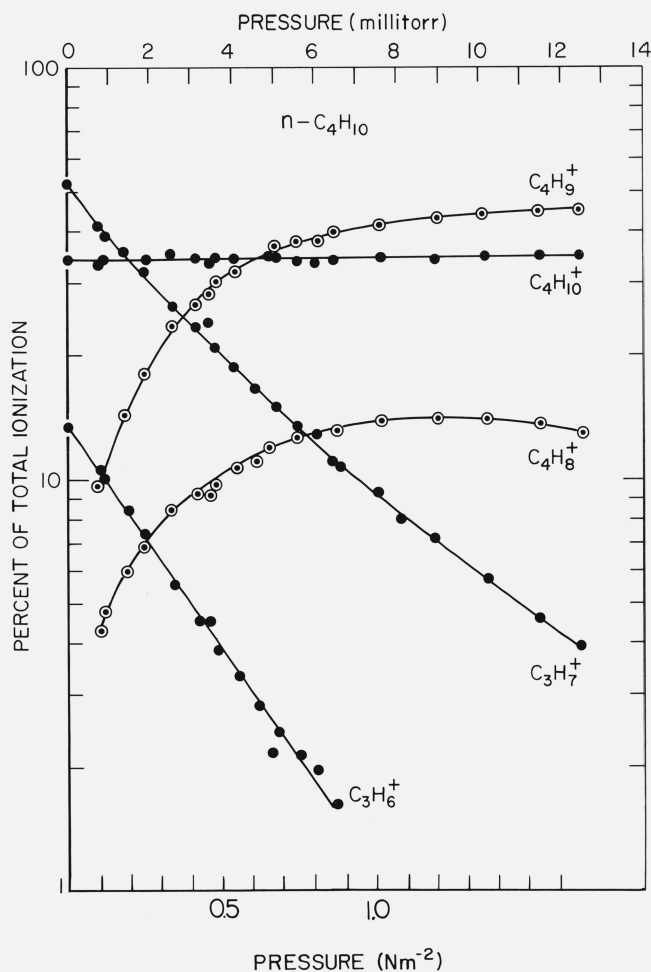


FIGURE 2. Composite mass spectrum obtained from the photoionization (106.7-104.8 nm) of *n*-C<sub>4</sub>H<sub>10</sub> versus pressure of *n*-C<sub>4</sub>H<sub>10</sub>.

ions, which are straight lines for a single reactive species, and the calculated ionic residence time in the photoionization chamber. Rate constants are always derived from initial slopes since the ionic residence time may increase at higher pressures due to non-reactive scattering of ions exhibiting low overall reactivities. This latter condition will yield decay curves which exhibit an increased slope at higher pressures and are concave downward. Alternatively, a decay curve which is concave upwards at low pressures indicates that two or more empirically equivalent ions are present at this particular mass-to-charge ratio, each of which exhibits a different overall reactivity.

## 3. Discussion

### 3.1. Unimolecular Fragmentation

The primary mass spectrum resulting from photoionization of the C<sub>4</sub>-C<sub>5</sub> alkanes by 11.6-11.8 eV photons may be obtained by extrapolating the parent and fragment ion curves given in figures 1 through 6 to

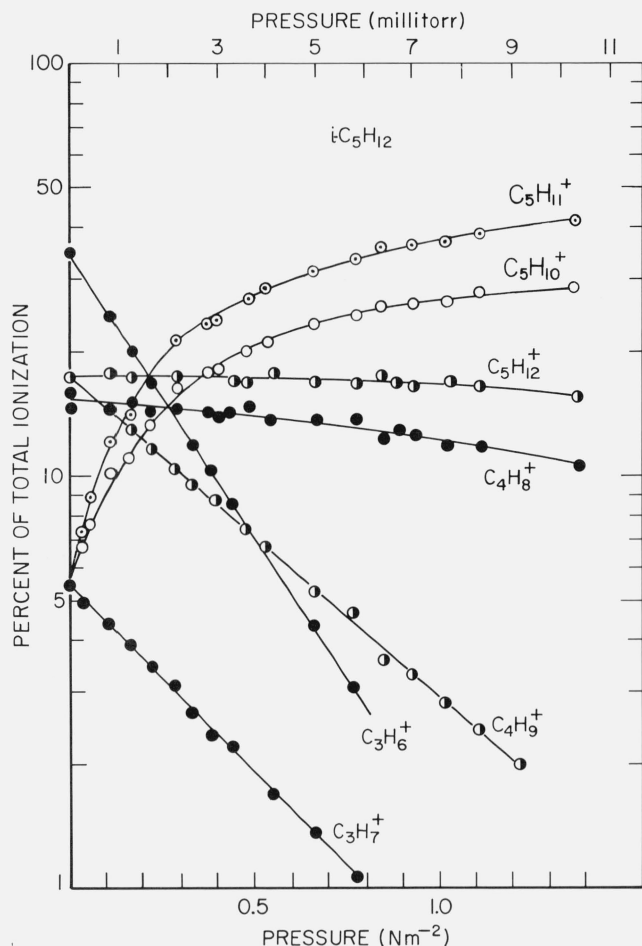


FIGURE 3. Composite mass spectrum obtained from the photoionization (106.7–104.8 nm) of  $i\text{-C}_5\text{H}_{12}$  versus pressure of  $i\text{-C}_5\text{H}_{12}$ .

“zero” pressure. Because the “parent minus one” and “parent minus two” ions in each system are also the products of fast ion-molecule reactions, it was not possible to obtain an accurate estimate of their abundance in the primary mass spectrum. However, it is apparent (figs. 1 to 15) that the primary yields of these ions approach low values at low pressure. For  $n\text{-C}_5\text{H}_{12}$  and  $i\text{-C}_5\text{H}_{12}$ , the  $\Sigma(\text{C}_5\text{H}_{10}^+ + \text{C}_5\text{H}_{11}^+)$  comprise approximately 2 and 10 percent of the primary mass spectra, respectively. As indicated by the summary in table 1, all of the major fragment ions have appearance potentials less than 11.2 eV at 300 K [5]. Ions such as  $\text{C}_2\text{H}_4^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_2\text{H}_3^+$ , etc., were not observed since the threshold energy requirements for formation of these species from  $\text{C}_4$ – $\text{C}_5$  alkanes are either very close to or in excess of [6, 7] the energies of the photons used in this study. The ions listed in table 1 are also the major species observed in a previous study of the photoionization of alkanes at energies approaching 11.5 eV [5]. For comparison, the relative abundances measured in the latter study at 11.25 eV are also included in table 1. As expected, for all compounds listed, the relative abundance of the parent ion is reduced at 11.6–11.8 eV. The other major difference be-

TABLE 1. Abundances of fragment and parent ions at 300 K

	AP eV*	11.26 eV*	11.6–11.8 eV**
		Photon Energy	
$n\text{-C}_4\text{H}_{10}$	$\text{C}_4\text{H}_{10}^+$	0.63	0.34
	$\text{C}_3\text{H}_7^+$	11.11	.20
	$\text{C}_3\text{H}_6^+$	11.09	.13
$i\text{-C}_4\text{H}_{10}$	$\text{C}_4\text{H}_{10}^+$	0.21	0.10
	$\text{C}_3\text{H}_7^+$	11.15	.11
	$\text{C}_3\text{H}_6^+$	10.89	.68
$n\text{-C}_5\text{H}_{12}$	$\text{C}_5\text{H}_{12}^+$	0.43	0.32
	$\text{C}_4\text{H}_9^+$	10.95	.041
	$\text{C}_4\text{H}_8^+$	10.84	.031
	$\text{C}_3\text{H}_7^+$	11.04	.064
	$\text{C}_3\text{H}_6^+$	10.89	.42
$i\text{-C}_5\text{H}_{12}$	$\text{C}_5\text{H}_{12}^+$	0.24	0.18
	$\text{C}_4\text{H}_9^+$	10.97	.066
	$\text{C}_4\text{H}_8^+$	10.68	.20
	$\text{C}_3\text{H}_7^+$	11.14	.017
	$\text{C}_3\text{H}_6^+$	10.74	.47
$neo\text{-C}_5\text{H}_{12}$	$\text{C}_5\text{H}_{12}^+$	0.0006	
	$\text{C}_4\text{H}_9^+$	10.55	.86
	$\text{C}_4\text{H}_8^+$	10.37	.14

\*Reference [5].

\*\*This work.

tween the mass spectral patterns is reflected in the greater probability for C–C scissions over four center olefin ion elimination processes when the energy is increased from 11.25 to 11.6–11.7 eV. In view of the slight differences in energy requirements for these two processes, this observation can largely be ascribed to the lower frequency factor associated with rearrangement reactions [8]. In the discussion which follows, the structures of the reacting ions will be considered.

### 3.2. Bimolecular Reactions

#### a. Alkene Ions

The fractional intensities of the  $\text{C}_3\text{H}_6^+$  ions produced in the photoionization of  $i\text{-C}_4\text{H}_{10}$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $n\text{-C}_5\text{H}_{12}$ , and  $i\text{-C}_5\text{H}_{12}$  decrease linearly as a function of pressure. Therefore, we may assume that this ion has only one structure,  $\text{CH}_3\text{CHCH}_2^+$ , at the time of reaction. The total rate constants for reaction of  $\text{C}_3\text{H}_6^+$  with the various alkanes given in table 2 agree well with those obtained for reaction of  $\text{C}_3\text{D}_6^+$  formed by photoionization of propylene- $d_6$  with 10 eV photons [1b] in the presence of  $\text{C}_4$  and  $\text{C}_5$  alkanes. In the case of  $i$ -butane, for which two reaction channels are possible:



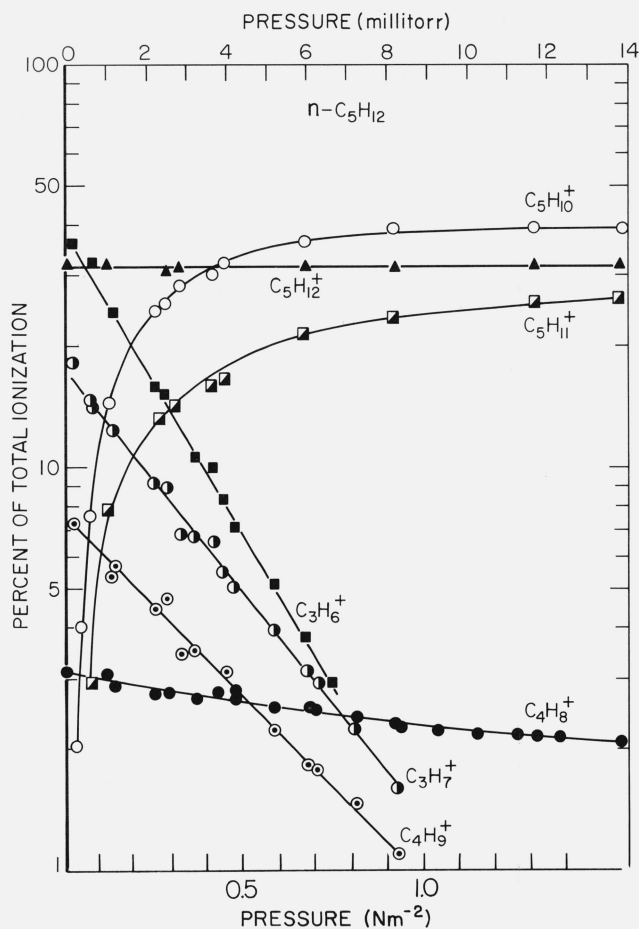


FIGURE 4. Composite mass spectrum obtained from the photoionization (106.7–104.8 nm) of  $n\text{-C}_5\text{H}_{12}$  versus pressure of  $n\text{-C}_5\text{H}_{12}$ .

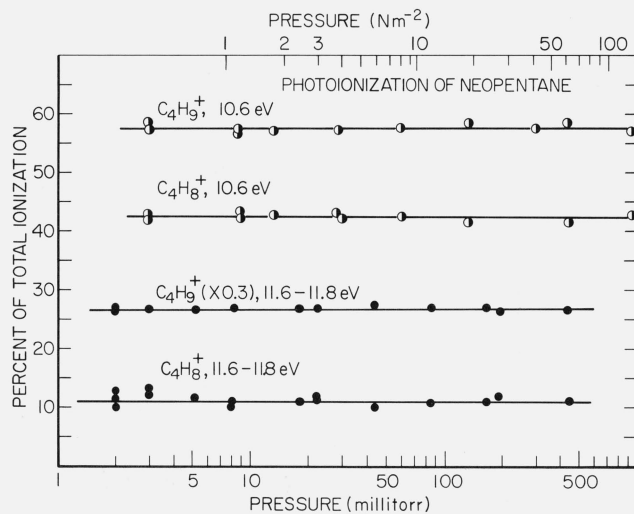


FIGURE 5. Composite mass spectrum obtained from the photoionization of neopentane at 116.5 nm and at 106.7–104.8 nm versus pressure.

TABLE 2. Rate constants ( $\text{cm}^3/\text{molecule}\text{-second} \times 10^{10}$ )

		Mass spectrometric		Neutral product analysis
		Photoionization*	Electron impact**	Electron impact***
<i>i</i> - $\text{C}_4\text{H}_{10}$	<i>sec</i> - $\text{C}_3\text{H}_7^+$	3.3	4.0	3.1
	$\text{C}_3\text{H}_6^+$	4.9	6.7	.....
<i>n</i> - $\text{C}_4\text{H}_{10}$	<i>sec</i> - $\text{C}_3\text{H}_7^+$	4.4	3.9	4.1
	<i>cyclo</i> - $\text{C}_3\text{H}_7^+$	.....	.....	0.9
	$\text{C}_3\text{H}_6^+$	4.9	5.1	.....
<i>i</i> - $\text{C}_5\text{H}_{12}$	<i>sec</i> - $\text{C}_3\text{H}_7^+$	4.7	.....	5.5
	$\text{C}_3\text{H}_6^+$	7.6	.....	.....
	<i>sec</i> - $\text{C}_4\text{H}_9^+$	3.8	.....	2.9
	<i>t</i> - $\text{C}_4\text{H}_9^+$	.....	.....	0.46
	$\text{C}_4\text{H}_8^+$ (2 or more structures)	< 0.5	.....	.....
<i>n</i> - $\text{C}_5\text{H}_{12}$	<i>sec</i> - $\text{C}_3\text{H}_7^+$	5.2	.....	7.3
	<i>cyclo</i> - $\text{C}_3\text{H}_7^+$	.....	.....	1.7
	$\text{C}_3\text{H}_6^+$	7.9	.....	.....
	<i>sec</i> - $\text{C}_4\text{H}_9^+$	3.7	.....	4.1
	<i>t</i> - $\text{C}_4\text{H}_9^+$	.....	.....	< 0.007
	$\text{C}_4\text{H}_8^+$ (2 or more structures)	0.4	.....	.....

\*This work. \*\*Reference [2]. \*\*\*Reference [3].

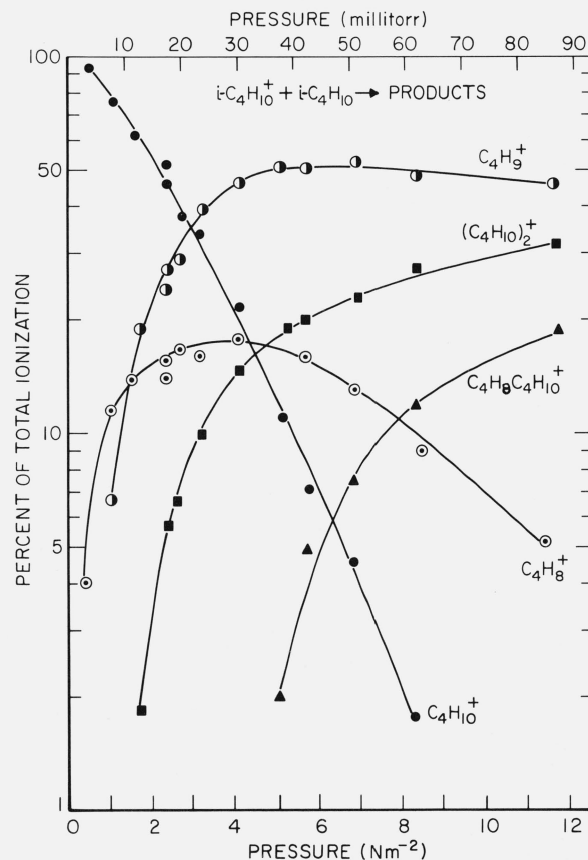


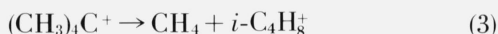
FIGURE 6. Composite mass spectrum obtained from the photoionization of *i*- $\text{C}_4\text{H}_{10}$  at 116.5 nm versus pressure.

the ratio  $k(\text{H}^-)/k(\text{H}_2^-)$  was found to be 1.26 in the present study, and 1.30 in the previous investigation involving  $\text{C}_3\text{D}_6^+$ . Assuming that  $k_1/k_2$  is dependent on the internal energy of the propylene ion (a dependence on kinetic energy has been established [9]) this agreement would indicate that the internal energy content of the propylene ion resulting from the unimolecular decomposition of butane does not differ appreciably from that formed in the photoionization of propylene at 123.6 nm.

Rate constants for reaction of  $\text{C}_3\text{H}_6^+$  with the butane isomers were also obtained in a previous study [2b] in which  $\text{C}_3\text{H}_6^+$  was formed by dissociation of butane following impact with high energy electrons (800 eV). It is apparent from table 2 that the values obtained in that investigation also agree well with those obtained in the present experiments.

The overall reactivity of the  $\text{C}_4\text{H}_8^+$  ions resulting from the fragmentation of  $i\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_5\text{H}_{12}$  is more than an order of magnitude less than that found for  $\text{C}_3\text{H}_6^+$ . No reaction was found between  $\text{C}_4\text{H}_8^+$  and neopentane at pressures as high as  $\sim 1$  torr, indicating an upper limit of  $10^{-14}$  cm<sup>3</sup>/molecule-second for the rate constant. Previous studies have also shown that propylene ions are equally unreactive towards neopentane.

While the majority of the  $\text{C}_4\text{H}_8^+$  ions formed in the fragmentation of neopentane



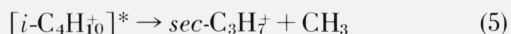
have a branched structure [4], it may be expected that the majority of the butene ions formed in the decomposition of  $i\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_5\text{H}_{12}$  are linear. Radiolysis experiments have shown [4] that  $1\text{-C}_4\text{H}_8^+$  ions are more reactive towards  $n\text{-C}_5\text{H}_{12}$  than the  $2\text{-C}_4\text{H}_8^+$  ions, which were, in fact, not found to react in a static system. The negligible slope in the  $\text{C}_4\text{H}_8^+$  yield curve versus pressure of  $n\text{-C}_5\text{H}_{12}$  above 10 millitorr (fig. 4) may well be due to a nonreactive  $2\text{-C}_4\text{H}_8^+$  component among the butene ions.

#### b. Alkyl ions

It is well established [10] that a reactive collision between an alkyl ion and an alkane molecule results exclusively in the transfer of a hydride ion. This overall process may be represented as:



$\text{C}_3\text{H}_7^+$ . At 11.6–11.8 eV,  $\text{C}_3\text{H}_7^+$  ions are formed in the fragmentation of  $i\text{-C}_4\text{H}_{10}$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_5\text{H}_{12}$ , and  $n\text{-C}_5\text{H}_{12}$ . However, one would anticipate [4] exclusive formation of  $\text{C}_3\text{H}_7^+$  with the secondary structure only in the dissociation of the two branched alkane ions (reactions 5 and 6):



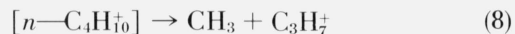
The production of  $\text{C}_3\text{H}_7^+$  with a well-defined structure

in isobutane is supported by the fact that the  $\text{C}_3\text{H}_7^+$  decay curve in figure 3 is linear over the pressure range where 95 percent of these ions have reacted. Also, the rate constants for reaction of  $\text{sec-C}_3\text{H}_7^+$  ions with  $i\text{-C}_4\text{H}_{10}$  and  $i\text{-C}_5\text{H}_{12}$  as determined in the photoionization mass spectrometer are in good agreement with those derived from an analysis of the  $\text{CD}_3\text{CDHCD}_3$  product in radiolysis experiments in which the  $\text{sec-C}_3\text{D}_7^+$  ions were produced by irradiating  $i\text{-C}_4\text{D}_{10}$  in the presence of various alkanes (reaction 7):



Finally, the rate constant obtained for reaction of  $\text{sec-C}_3\text{H}_7^+$  with  $i\text{-C}_4\text{H}_{10}$  in an electron impact mass spectrometer agrees well with that obtained in the present study, even though the electron impact value is based on  $\text{C}_3\text{H}_7^+$  ion currents at pressures above 200 millitorr and our value is derived from measurements at pressures below 10 millitorr (fig. 1). In the former study pronounced curvature was noted in the  $\text{C}_3\text{H}_7^+$  plot, indicating that  $\text{C}_3\text{H}_7^+$  was formed as well as consumed by ionic reactions in butane. No curvature could be detected in our study in the photoionization of either  $n\text{-butane}$  or  $i\text{-butane}$ . Therefore, it must be concluded that if  $\text{C}_3\text{H}_7^+$  is indeed a product of a reaction between a fragment ion and the neutral butane molecule, then the precursor must be among those ions which are only formed at energies above 11.8 eV.

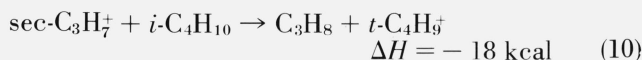
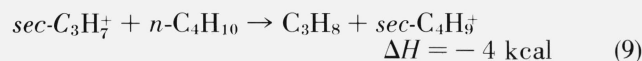
It was recently shown that dissociation of  $n\text{-alkane}$  [3, 4] ions may yield two or more isomeric forms of  $\text{C}_3\text{H}_7^+$ . For example, the  $\text{C}_3\text{H}_7^+$  ions resulting from the unimolecular dissociation



were shown to acquire the  $\text{sec-propyl}$  and protonated cyclopropane structures prior to reaction. It was further demonstrated that the relative abundance of the two isomers varies with the internal energy content of the  $\text{C}_3\text{H}_7^+$  ion. Because the two isomer ions seem to react at rates which differ by nearly a factor of four ( $\text{sec-C}_3\text{H}_7^+$  being the more reactive isomer), it is not surprising that a distinct curvature is observed in the decay of  $\text{C}_3\text{H}_7^+$  in  $n\text{-butane}$  (fig. 2). The reactivity indicated by the initial slope corresponds most closely to that found for the  $\text{sec-C}_3\text{H}_7^+$  ion. In  $n\text{-C}_4\text{H}_{10}$ , the best straight line drawn through the points obtained up to a pressure of 5 millitorr yields a rate constant of  $4.4 \times 10^{-10}$  cm<sup>3</sup>/molecule second, which is in good agreement with value obtained in previous studies (see table 2). The agreement with the electron impact mass spectrometric investigation is somewhat fortuitous since as mentioned above,  $\text{C}_3\text{H}_7^+$  ions of an undetermined structure were also formed as a result of an ion-molecule collision in those experiments.

The variations in the reactivity found for  $\text{sec-C}_3\text{H}_7^+$  with various isomeric alkanes, which are consistent with those observed in earlier radiolysis experiments, can be rationalized in terms of the  $\Delta H$  of reaction [6] as well as statistical and steric considerations. For example, the increase in the rate constant associated

with an increase in molecular weight in an homologous series may be largely, although not exclusively, ascribed to increased exothermicity. On the other hand, the higher rate constant for reaction of  $sec\text{-C}_3\text{H}_7^+$  with  $n\text{-C}_4\text{H}_{10}$  when compared to isobutane must be accounted for by other factors. It is well established that  $sec\text{-C}_3\text{H}_7^+$  reacts to remove a hydride ion exclusively from the secondary and tertiary position in  $n$ -butane and isobutane, respectively. These hydride transfer reactions may be written as follows:



The observation that the more exothermic process (reaction 10) exhibits a lower rate constant than reaction 9 is reasonable since four secondary  $H$  atoms are available in  $n\text{-C}_4\text{H}_{10}$  while only a single tertiary  $H$  atom in  $i\text{-C}_4\text{H}_{10}$  is available for transfer to  $sec\text{-C}_3\text{H}_7^+$  via reaction 10. In addition, the four reactive sites in  $n\text{-C}_4\text{H}_{10}$  are sterically more accessible than in the single reactive site in  $i\text{-C}_4\text{H}_{10}$ , i.e., reaction 10 would be expected to exhibit a lower entropy of activation.

$\text{C}_4\text{H}_9^+$ . It has been demonstrated [4] that the  $\text{C}_4\text{H}_9^+$  ions resulting from the fragmentation of normal alkanes may have either the  $sec\text{-C}_4\text{H}_9^+$  structure or the thermodynamically more stable  $t\text{-C}_4\text{H}_9^+$  configuration. However, although initial C—C cleavage in  $n$ -alkanes will result in a linear structure, there is an energy barrier estimated at 0.67 eV [11] for isomerization to the branched configuration. Because the maximum energy available from the argon resonance lines is only 0.85 eV above the appearance potential of the  $\text{C}_4\text{H}_9^+$  ion, which Semeluk and Lossing [12] have shown to have the  $sec\text{-C}_4\text{H}_9^+$  ion structure, the fraction of  $t\text{-C}_4\text{H}_9^+$  ions should be quite low in photoionized  $n\text{-C}_5\text{H}_{12}$ .

Recent appearance potential measurements [12], as well as mass spectral cracking patterns of deuterium labeled isopentanes, have revealed that the  $\text{C}_4\text{H}_9^+$  ion is formed through a simple C-C cleavage process chiefly with the secondary structure at low energies.

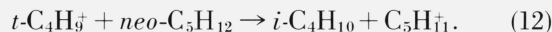
The linear decay curves for the  $\text{C}_4\text{H}_9^+$  ions derived from  $n$ - and  $i\text{-C}_5\text{H}_{12}$  substantiate our view that the majority of the  $\text{C}_4\text{H}_9^+$  ions are of the secondary structure. Participation of  $t\text{-C}_4\text{H}_9^+$  can be ruled out on the basis of the rate constants given in table 2. Comparison of these data indicates that the rate constants found for the reaction of  $\text{C}_4\text{H}_9^+$  in the present study are in reasonable agreement with those obtained by consideration of the  $\text{CD}_3\text{CDHCD}_3\text{CD}_3$  product formed in radiolysis experiments [3] via the well-defined reaction:



Neutral end-product analysis has confirmed that  $t\text{-C}_4\text{H}_9^+$  is much less reactive than  $sec\text{-C}_4\text{H}_9^+$  (table 2) and the presence of such ions would yield a pronounced curvature in the  $\text{C}_4\text{H}_9^+$  plots of figures 3 and 4.

The  $\text{C}_4\text{H}_9^+$  ions resulting from the decomposition of neopentane are exclusively of the  $t\text{-C}_4\text{H}_9^+$  configuration.

The yield of these exhibits no variation with pressure up to the maximum values of 500 to 1000 millitorr covered in the present study (fig. 5). From this result an upper limit of  $10^{-14}$  cm<sup>3</sup>/molecule-second may be estimated for the rate constant of the endothermic reaction:



#### c. Parent Ions

In previous studies we have shown [1] that thermal  $\text{C}_2\text{H}_6^+$  and  $\text{C}_3\text{H}_8^+$  ions react with  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ , respectively, to form the corresponding dimer ions [1e, 1f]. Experiments were carried out to determine if dimeric ions were also formed in the butanes and pentanes. The reactions of the isomeric butane and pentane molecular ions with their parent molecules were investigated using 10.6 eV photons from a krypton resonance lamp. This energy is insufficient to induce fragmentation of the parent ion; consequently, reactions of the parent ions may be studied unambiguously. The photoionization of  $i\text{-C}_4\text{H}_{10}$  as a function of pressure at 10.6 eV is shown in figure 6. At low pressures (< 20 millitorr) the  $\text{C}_4\text{H}_{10}^+$  ions react slowly with  $i\text{-C}_4\text{H}_{10}$  to yield  $\text{C}_4\text{H}_8^+$ . The rate constant for this slow bimolecular reaction is  $\leq 5 \times 10^{-11}$  cm<sup>3</sup>/molecule-second. As the total pressure is increased further,  $\text{C}_4\text{H}_8^+$  ions appear to react slowly with  $i\text{-C}_4\text{H}_{10}$  via a  $\text{H}^-$  transfer reaction to yield  $\text{C}_4\text{H}_9^+$ :



The analogous reaction has been reported for the  $\text{C}_3\text{H}_6^+ - \text{C}_3\text{H}_8$  reaction pair [4]. At pressures greater than approximately 15 millitorr the formation of the dimeric ion  $(\text{C}_4\text{H}_{10})_2^+$  was also detected. At the highest pressure (~ 90 millitorr) this ion constituted approximately 30 percent of the composite mass spectrum in photoionized  $i\text{-C}_4\text{H}_{10}$ . The  $\text{C}_4\text{H}_8 - \text{C}_4\text{H}_{10}^+$  collision complex also appeared to be stabilized to some extent at higher densities.

Although a careful search was made for dimeric ions in  $n\text{-C}_4\text{H}_{10}$  and the pentanes at pressures up to approximately 0.5 torr, the formation of species analogous to  $(\text{C}_4\text{H}_{10})_2^+$  in  $i\text{-C}_4\text{H}_{10}$  was not detected. The only reaction found in any other system was the formation of  $\text{C}_5\text{H}_{10}^+$  in  $i\text{-C}_5\text{H}_{12}$  with a rate constant  $\leq 2 \times 10^{-12}$  cm<sup>3</sup>/molecule-second. The  $n\text{-C}_4\text{H}_{10}^+$  and  $n\text{-C}_5\text{H}_{12}^+$  ions were found to be unreactive towards their parent molecules.

## 4. References

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