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Photoionization of $C_4H_8^+$ Isomers. Unimolecular and Bimolecular Reactions of the $C_4H_8^+$ Ions[1]

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1-Butene, *cis*-2-butene, isobutene and methylcyclopropane have been photoionized with the resonance lines of krypton (10.0–10.6 eV) and argon (11.6–11.8 eV). We have determined that the internally excited 1-$C_4H_8^+$ ion and, to a much lesser extent, the *i*-$C_4H_8^+$ ion isomerizes to the 2-$C_4H_8^+$ structure. In both cases the extent of isomerization increases, approximately by a factor of ten when the photon energy is increased from 10 to 11.7 eV. An inert gas, neon, quenches the isomerization of the *i*-$C_4H_8^+$ ion and, to a much lesser rextent, that of the 1-$C_4H_8^+$ ion.

The unimolecular fragmentation of the $C_4H_8^+$ isomeric ions has been examined at 11.6–11.8 eV. In this energy range the dissociative lifetime of *i*-$C_4H_8^+$ was found to be at least 5×10^{-6} s, and collisional quenching of the dissociative process is already noticeable at pressures in the 10^{-3} torr range.

The rate coefficients for the reaction $C_4H_8^+$ (thermal) $+ C_4H_8 \rightarrow (C_8H_{16}^+)^*$ occurring in the isomeric C_4H_8 systems have been determined under conditions where the structure of the reacting $C_4H_8^+$ ion is established. The values in cm³/molecule · second are 1-C_4H_8—$6.0 \pm 0.5 \times 10^{-10}$, *cis*-2-$C_4H_8$—$0.37 \pm 0.1 \times 10^{-10}$, *i*-$C_4H_8$—$5.4 \pm 0.4 \times 10^{-10}$. At pressure below 10^{-3} torr, the internally excited $(C_8H_{16}^+)^*$ produced in the reaction dissociates along various channels with relative probabilities depending upon the structure of both the ionic and neutral reactant. Above 10^{-3} torr collisional quenching of $(C_8H_{16}^+)^*$ is noted.

Key words: C_4H_8 isomers; collisional stabilization; isomerization; photoionization; rate constants; vapor phase.

1. Introduction

The reactions of $C_4H_8^+$ ions have been examined in several laboratories. In most cases, the $C_4H_8^+$ ions were produced in the ion source of a mass spectrometer using electrons [1], and in some instances photons [2], as ionization sources. Several investigations have also involved the fate of $C_4H_8^+$ ions formed in the gamma radiolysis or vacuum ultraviolet photolysis of various compounds [3]. In many of these investigations, the structures of the $C_4H_8^+$ ions were not precisely established.

In a recent study [3d] the isomerization processes of the $C_4H_8^+$ ions formed in the irradiation of cyclobutane, methylcyclopropane, and in ethylene via the reaction

$$C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$$

were explored and it was concluded that these relatively high energy $C_4H_8^+$ isomers rearrange to the thermodynamically more stable 2-$C_4H_8^+$, *i*-$C_4H_8^+$, and 1-$C_4H_8^+$ configurations. Furthermore, the extent of isomerization as well as the relative distributions of the final isomerization products were found to depend on the internal energy content of the rearranging species; i.e., the isomerization processes were dependent on the mode of ion formation (the initial energy content of the ion) as well as on the collision frequency.

In this related study, the isomerization processes of the lower energy isomeric $C_4H_8^+$, 1-$C_4H_8^+$, 2-$C_4H_8^+$, and *i*-$C_4H_8^+$ ions are examined, and the unimolecular fragmentation processes of the excited primary $(C_4H_8^+)^*$ ions are considered. Since the results of the earlier study would lead us to expect—and indeed this expectation is confirmed in the results reported here—that the structure of $C_4H_8^+$ ions observed in a given system will vary depending on the mode of formation of the ion, we have reexamined the often studied [1,2] reaction:

$$C_4H_8^+ + C_4H_8 \rightarrow (C_8H_{16}^+)^* \rightarrow \text{products} \tag{2}$$

in systems where we know the structure(s) of the reacting ions.

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2. Experimental Procedure

The ion-molecule reactions and fragmentation processes associated with the photoionization of the C_4H_8 isomers at various pressures were investigated with the NBS high pressure mass spectrometer. This instrument, which has been described in detail elsewhere [2b, 4], provides information concerning the reactivity of *thermal* ions at pressures up to approximately 1 torr. The detailed experimental techniques involved in deriving absolute rate parameters have also been discussed previously [2b, 4].

Isomerization reactions were examined by means of static system photolysis experiments, which were performed in the same manner as described in a previous publication [3d]. Some of the krypton resonance photolysis experiments were carried out with a light source emitting both the 123.6 and 116.5 nm (10.0 and 10.6 eV) resonance lines. A krypton lamp emitting only the 123.6 nm (10 eV) line was used in all mass spectrometric and some of the static system photoionization experiments. The argon resonance lamps emitted the 104.8 and 106.7 nm (11.6 and 11.8 eV) lines with about equal intensity. The construction of the light sources has been described [5]. In the static system experiments the yield of a product, X, in tables 1 and 2, is given in terms of the number of molecules (M(X)) produced per positive ion (N_+). This is designated as the ion pair yield ($M(X)/N_+$) of product X.

TABLE 1. *Yields of C_4H_8 Products formed in the photolysis of 1-butene*

	Pressure, torr			M/N_+	
	$1\text{-}C_4H_8$	DMA†	Ne	*trans*-$2\text{-}C_4H_8$	*cis*-$2\text{-}C_4H_8$
10.0–10.6 eV	0.75	0.70	....	0.065	0.057
11.6–11.8 eV	1.0	.25	....	.53	.35
	1.0	.58	....	.54	.36
	0.5	.5	....	.55	.38
	.5	.5	60.	.52	.37
	.5	.5	180.	.46	.34

† Dimethylamine.
All experiments are carried out in the presence of 5 percent oxygen added as a radical scavenger.

TABLE 2. *Yields of C_4H_8 products formed in the photolysis of isobutene*

	Pressure, torr			M/N_+	
	$i\text{-}C_4H_8$	DMA†	Ne	*trans*-$2\text{-}C_4H_8$	*cis*-$2\text{-}C_4H_8$
10.0–10.6 eV	1.0	....	....	0.007	0.005
	1.0	0.5	....	.007	.005
11.6–11.8 eV	0.3	....	....	.071	.053
	1.0	....	....	.073	.056
	2.0	....	....	.072	.056
	2.2	....	40	.036	.030
	2.1	....	266	.0105	.009
	1.1	.2	....	.072	.055
	1.1	.5	....	.071	.053

† Dimethylamine.
All experiments are carried out in the presence of 5 percent oxygen added as a radical scavenger.

3. Results and Discussion

3.1. Isomerization of $C_4H_8^+$ Ions

a. $1\text{-}C_4H_8^+$

In the earlier study [3d] results were obtained from which it was inferred that the high energy $C_4H_8^+$ ions formed in ethylene, cyclobutane, and methylcyclopropane rearranged to a $1\text{-}C_4H_8^+$ structure which, unless deenergized by collisions, would rearrange further to the $2\text{-}C_4H_8^+$ structure (and possibly also to the $i\text{-}C_4H_8^+$ structure). Therefore, it might be expected that sufficiently energetic $C_4H_8^+$ ions formed in the photoionization of 1-butene would undergo the exothermic ($\Delta H = -0.55$ eV) rearrangement:

$$(1\text{-}C_4H_8^+)^* \rightarrow (2\text{-}C_4H_8^+)^* \tag{3}$$

which requires the displacement of only one hydrogen atom. When 1-butene is photolyzed in the presence of dimethylamine, any $2\text{-}C_4H_8^+$ ions formed in isomerization process (3) would be expected [3] to undergo exothermic ($\Delta H = -0.27$ eV) charge transfer:

$$2\text{-}C_4H_8^+ + (CH_3)_2NH \rightarrow 2\text{-}C_4H_8 + (CH_3)_2NH^+ \tag{4}$$

to form neutral 2-butene as a product. The results given in table 1 show the yields of *cis*- and *trans*-$2\text{-}C_4H_8$ formed in mixtures of 1-butene and dimethylamine irradiated with 10.0 and 11.6–11.8 eV photons. It is evident that the yield of 2-butene formed in reaction sequence (3)–(4) increases as the energy of the photon is increased. In the 10.0–10.6 eV photolysis, only about 10 percent of the $1\text{-}C_4H_8^+$ ions isomerize to the $2\text{-}C_4H_8^+$ structure, but at 11.6–11.8 eV, ~ 90 percent of the ions undergo this rearrangement. (Isomerization to the $i\text{-}C_4H_8^+$ structure can not be detected in this kind of experiment, since the analytical techniques used here do not distinguish between $1\text{-}C_4H_8$ and $i\text{-}C_4H_8$.)

These conclusions are qualitatively confirmed in experiments in which the $C_4H_8^+$ ions abstract D_2^- from added methylcyclopentane-d_{12} to form butanes:

$$C_4H_8^+ + C_6D_{12} \rightarrow C_4H_8D_2 + C_6D_{10}^+ \tag{5}$$

The D_2^- species is transferred across the unsaturated site in the $C_4H_8^+$ ion, so the isotopic structure of the partially deuterated butane product indicates the structure of the precursor $C_4H_8^+$ ion. When 1-butene-methylcyclopentane-d_{12} mixtures were irradiated with 10.0 eV photons in the presence of oxygen added to scavenge free radicals, 95 percent of the *n*-butane product had the structure, $CH_2DCHDCH_2CH_3$, indicating again that isomerization is relatively unimportant at this energy. The concentration of added methylcyclopentane in these experiments was varied from 10 to 80 mole percent, in order to confirm that the majority of the $C_4H_8^+$ ions were indeed intercepted. The fact that somewhat less isomerization was observed in this set of experiments than in the corresponding experiments with added dimethylamine may be ascribed to the fact that the 10.6 eV krypton resonance line was filtered out by a calcium fluoride window in the methylcyclopentane experiments, so the ions may have had a slightly lower energy distribution. However, an exact quantitative treatment of the data in these experiments is difficult because of competition from the reaction of the $C_4H_8^+$ ions with the parent butene molecules.

As was found in the dimethylamine additive experiments, isomerization is more important when the photon energy is increased to 11.6–11.8 eV (in the methylcyclopentane-d_{12} experiments at this energy, 40–70 percent of the n-$C_4H_8D_2$ product consisted of $CH_3CHDCHDCH_3$). It should be mentioned that at this energy, a small amount of isobutane was also formed in reaction (5), but the yield was so small that it could not be accurately determined. We can conclude that isomerization of the 1-$C_4H_8^+$ ion to the i-$C_4H_8^+$ structure is unimportant at 11.6–11.8 eV. At 11.6–11.8 eV, the results are not quantitative because at these energies methylcyclopentane is ionized and the methylcyclopentane-d_{12} parent ions are known [6] to react with neutral 1-C_4H_8 molecules as follows:

$$C_6D_{12}^+ + 1\text{-}C_4H_8 \rightarrow CH_2DCHDCH_2CH_3 + C_6D_{10}^+ \qquad (6)$$

The results given in table 1 show that when as much as 180 torr of neon are added to 1 torr of a 1-$C_4H_8^+$–$(CH_3)_2NH$ (1:1) mixture, the importance of isomerization to the 2-$C_4H_8^+$ structure is decreased by only 15 percent. The absence of a major effect indicates that the isomerization is relatively fast at this energy.

2-Butene is also produced in the absence of a charge acceptor, but its formation is entirely quenched upon addition of 400 torr of neon. It would seem therefore that a reaction mechanism involving internally excited 2-$C_4H_8^+$ ions would account for this observation.

b. i-$C_4H_8^+$

The results obtained in the photolysis of isobutene at 10.0 and at 11.6–11.8 eV, indicate that the isomerization of the i-$C_4H_8^+$ ion is unimportant at these energies. For example, experiments carried out in the presence of added dimethylamine as a charge acceptor (table 2) indicate that not more than 1.2 percent of the $C_4H_8^+$ ions isomerize as follows:

$$(i-C_4H_8^+)^* \rightarrow (2-C_4H_8^+)^* \qquad (7)$$

followed by charge transfer reaction (4) at these two energies. However, it should be noted that at both energies, the yield of 2-C_4H_8 is nearly the same in the absence as in the presence of a charge acceptor. Since these products are not formed in the photolysis i-C_4H_8 below its ionization energy, we may infer that they do have $C_4H_8^+$ as precursors. Accepting that these products are formed by a process analogous to that described above for the 2-C_4H_8 products formed in the photolysis of 1-C_4H_8 in the absence of additives, the results given in table 2 indicate that the bulk of the 2-$C_4H_8^+$ ions formed in reaction (8) can transfer their charge to i-C_4H_8:

$$(2\text{-}C_4H_8^+)^* + i\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + i\text{-}C_4H_8^+$$

$$\Delta H = 0.1\ \text{eV} \qquad (8)$$

and yield i-$C_4H_8^+$ ions containing less excess energy than those formed in the primary photoionization process.

Because it is difficult to analyze small quantities of 1-C_4H_8 in i-C_4H_8 using our analytical techniques, isomerization to the 1-$C_4H_8^+$ structure would not be detected in the charge transfer experiments given in table 2. However, when methylcyclopentane-d_{12} was added to isobutene at a total pressure of 2 torr, experiments at both energies failed to reveal the formation of any $CH_2DCHDCH_2CH_3$, which is the partially deuterated butane product that would be formed in reaction (5) if 1-$C_4H_8^+$ ions were present.

At 11.6–11.8 eV, an increase in the pressure of i-C_4H_8 from 0.3 to 2.0 torr has no obvious effect on the extent of isomerization. Addition of neon, however, strongly quenches the ion pair yield of 2-C_4H_8. An interpretation of this observation can be based on the occurrence of a stepwise deactivation of the $(i\text{-}C_4H_8^+)^*$ ions formed in the primary photoionization process by neon. The energy barrier for process (7), which requires carbon skeletal rearrangement, must be substantially higher than for process (3).

c. cis-2-$C_4H_8^+$

Photoionization of cis-2-C_4H_8 (in the presence of O_2 as free radical scavenger) at 10.0 eV and 11.6–11.8 eV results in the formation of $trans$-2-C_4H_8, with ion pair yields of 0.57 and 0.59 respectively. However, $trans$-2-C_4H_8 was also found (quantum yield = 0.05) when cis-2-C_4H_8 was photolyzed at 8.4 eV, which is below the energy threshold for ionization of 2-C_4H_8. A fraction of the $trans$-2-C_4H_8 product observed at 10 and 11.6–11.8 eV may therefore be produced in an unimolecular or bimolecular reaction which does not involve ions. If one assumes that the quantum yield of the neutral process is invariant with the photon energy, the ion pair yield of $trans$-2-C_4H_8, which may be ascribed to the reaction:

$$cis\text{-}2\text{-}C_4H_8^+ \rightarrow trans\text{-}2\text{-}C_4H_8^+ \qquad (9)$$

is approximately equal to 0.4 for the ionizing wavelength regions.

When 38 mole percent methylcyclopentane-d_{12} is added to cis-2-butene at a total pressure of 2 torr, the butane formed in reaction (5) consists of at least 90 percent $CH_3CHDCHDCH_3$ at both 10.0 and 11.6–11.8 eV. Therefore, it may be concluded that the isomerization of cis-2-$C_4H_8^+$ to stable 1-$C_4H_8^+$ ions is unimportant. A small amount of isobutane-d_{12} ($M/N_+ = 0.01$) produced in the same experiment at 11.6–11.8 eV indicates that a minor fraction (< 5%) of the excited 2-$C_4H_8^+$ ions isomerize to the branched structure.

The addition of SF_6 as an electron scavenger in the photoionization of *cis*-2-C_4H_8 raises the ion pair yield of *trans*-2-C_4H_8 at least a hundredfold. A drastic effect of SF_6 was also noted by Hummel [7] in the radiolysis of C_4H_8-SF_6 mixtures and was ascribed to a perturbation of the π-bond in 2-C_4H_8 upon collision with SF_6^-:

$$cis\text{-2-}C_4H_8 + SF_6^- \rightarrow trans\text{-2-}C_4H_8 + SF_6^- \qquad (10)$$

3.2. Fragmentation Patterns of the $C_4H_8^+$ Isomers at 11.6–11.8 eV

Photoionization of the C_4H_8 isomers at 10.0 eV yields only parent ions since the appearance potentials of the possible fragment ions are higher than 11 eV [8]. At 11.6–11.8 eV, however, fragmentation of the $C_4H_8^+$ ions was observed in every case. The fragmentation patterns obtained at these energies are summarized in table 3. Also included are the ΔH_f values for the parent ions. The major dissociative processes found were:

$$(C_4H_8^+)^* \rightarrow C_4H_7^+ + H \qquad (11)$$

$$\rightarrow C_3H_5^+ + CH_3 \qquad (12)$$

The minor dissociation:

$$C_4H_8^{+*} \rightarrow C_3H_4^+ + CH_4 \qquad (13)$$

was also observed for every isomer, and the fragment $C_2H_4^+$ ion was observed from *c*-C_4H_8.

It has been suggested [1f] that the proportion of $C_4H_8^+$ ions capable of dissociation increases with the heat of formation of the ground state parent ion. This trend is not confirmed by the results given in table 3. For instance, 1-$C_4H_8^+$ ($\Delta H_f = 9.6$ eV), 2-$C_4H_8^+$ ($\Delta H_f = 9.05$ eV), and *i*-$C_4H_8^+$ ($\Delta H_f = 9.05$ eV) all show more extensive fragmentation than the methylcyclopropane ion ($\Delta H_f = 10.18$ eV). Actually even the 70 eV mass spectral cracking patterns of the C_4H_8 isomers [1f] do not show a correlation between $\Delta H(C_4H_8^+)$ and the degree of fragmentation of the $C_4H_8^+$ ion. The results given in table 3 do indicate, however, that such a relation may hold when the cyclic $C_4H_8^+$ isomers and the open ring $C_4H_8^+$ isomers are considered separately. Partial retainment of the cyclic structure because of an activation energy requirement for ring opening might account for the higher relative stability of the methylcyclopropane and cyclobutane ions. Static system experiments [3d] have shown that in the case of cyclobutane, ring opening does occur effectively prior to or during reaction. A multitude of factors including bond strengths, Franck-Condon factors, rates of isomerization in the parent ions, etc., will influence the fragmentation patterns. For example only 12 percent of the parent ions from *i*-C_4D_8 fragment at 11.6–11.8 eV compared with approximately 29 percent of those derived from *i*-C_4H_8. Isotope effects of this magnitude in the isomerization and fragmentation processes are not surprising in these experiments since the average photon energy, and therefore the maximum available energy, is only slightly in excess of the threshold energies for the dissociation processes.

TABLE 3. *Fragmentation patterns of C_4H_8 isomers obtained at 106.7–104.8 nm*

	$\Delta H_f(C_4H_8^+)$	Percent distribution			
		$C_4H_8^+$	$C_4H_7^+$	$C_3H_5^+$	$C_3H_4^+$
Cyclobutane	[a] 10.57	48.5	12.7	32.3	5.2
Methylcyclopropane	[b] 10.18	77.3	8.9	11.9	1.9
1-butene	[c] 9.60	48.6	14.4	31.6	5.4
cis-2-butene	[c] 9.05	67.5	16.5	13.4	2.6
Isobutene	[c] 9.05	70.9	12.1	13.3	3.7

[a] Based on 10.3 eV for IP($C_4H_8^+$) see Ref. 1d.

[b] Based on 9.9 eV for IP($C_4H_8^+$) see Ref. 3d.

[c] K. Watanabe, T. Nakayama, and J. Mottel, J. Quant. Spectros. Radiative Transfer, **2**, 369 (1962).

3.3. Collisional Stabilization of the ($C_4H_8^+$) Ions Produced at 11.6–11.8 eV

a. 2-$C_4H_8^+$

Figure 1 presents the decay curves of $C_4H_8^+$ ions formed in the photoionization of *cis*-2-C_4H_8 at 10.0 and 11.6–11.8 eV. The obvious feature at the higher energy is the initial increase in the fractional yield of $C_4H_8^+$ as the total pressure is increased. Since none of the three fragment ions listed in table 3 can produce $C_4H_8^+$ by charge exchange (as verified experimentally by Abramson and Futrell [1b] in a tandem instrument) the increase in the fractional yield can only be ascribed to collisional quenching of the fragmentation processes which produce $C_3H_5^+$ and/or $C_4H_7^+$ (processes 11 and 12). It is of interest that competition between unimolecular dissociation and bimolecular reaction has also been observed in an electron impact mass spectrometric study [1g] of *cis*-2-C_4H_8, even though in that study the mean energy to the butene molecule was considerably higher than in the present investigation.

b. i-$C_4H_8^+$

The decay curves found for the major ions obtained

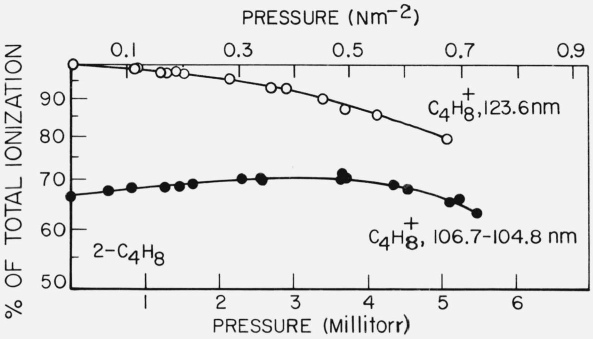

FIGURE 1. *Decay curves for $C_4H_8^+$ from* cis-2-*butene as a function of pressure at 123.6 and 106.7–104.8 nm.*

from the photoionization of $i\text{-}C_4H_8$ at 11.6–11.8 eV are given in figure 2. The decay curve for $C_4H_8^+$ found at 10.0 eV is also included for comparison. As was observed in $2\text{-}C_4H_8$, the fractional yield curve for $C_4H_8^+$ at 11.6–11.8 eV exhibits pronounced curvature although the yield of this ion never exceeds the "zero pressure" value in this particular case. If the assumption is made that the differences in the contours of the decay curves at the two energies are due entirely to quenching of potentially dissociative $(C_4H_8^+)^*$ ions, it is possible to calculate an average half-life (lifetime) for the dissociation processes from the experimental data. As shown later in the discussion, isomerization of $i\text{-}C_4H_8^+$ to $2\text{-}C_4H_8^+$ would result in a decreased reaction rate and therefore a reduced slope in figure 2. However the relatively small degree of isomerization which was shown to occur in this system (see sec. 3.1) would not have a noticeable effect on the $C_4H_8^+$ contour given in figure 2. If we assume that every collision deactivates the $C_4H_8^+$ ion to an energy level from which it can no longer dissociate, then the rate constant for deactivation may be taken as 2×10^{-9} cm^3/molecule · s. and the lifetime of the $(C_4H_8^+)^*$ ions which dissociate prior to collision is approximately 5×10^{-6} s. This value for the deactivation rate constant is approximately equivalent to that expected for the charge-exchange reaction between $i\text{-}C_4H_8^+$ and $i\text{-}C_4H_8$, and exceeds the theoretical ion induced dipole rate constant for complex formation by a factor of two. If deactivation is less efficient than that assumed above the calculated lifetime would increase correspondingly. It is appropriate to compare this estimated lifetime with other lifetimes of more energetic $C_4H_8^+$ species which have been reported. Tiernan and Futrell [9] reported a unimolecular rate constant for dissociation of $C_4H_8^+$ ions formed in reaction (1) (ethylene ion + ethylene) which corresponded to a lifetime of 3×10^{-9} s. In these particular experiments the $C_4H_8^+$ ions were produced in a tendem mass spectrometer in which ionization of ethylene was induced by 100 eV electron impact. As a result these $C_4H_8^+$ ions most likely contained more internal energy than those characteristic of the other experiments we are comparing. It has recently been shown [3d] that $C_4H_8^+$ ions formed in reaction (1) contain more internal energy when ethylene is ionized by highly energetic electrons than when ionization is induced by absorption of 11.6–11.8 eV photons. Gorden and Ausloos [10] estimated an average dissociative lifetime of 5×10^{-8} s. for the $C_4H_8^+$ ion formed in the 11.6–11.8 eV photoionization of ethylene, and Meisels [11] estimated a lifetime of at least 2×10^{-8} s. for the $C_4H_8^+$ ion formed in the radiolysis of ethylene. It appears that the lifetime of the $i\text{-}C_4H_8^+$ ion formed when isobutene is ionized by 11.6–11.8 eV photons is approximately two orders of magnitude greater than that of the $C_4H_8^+$ ion formed in ethylene.

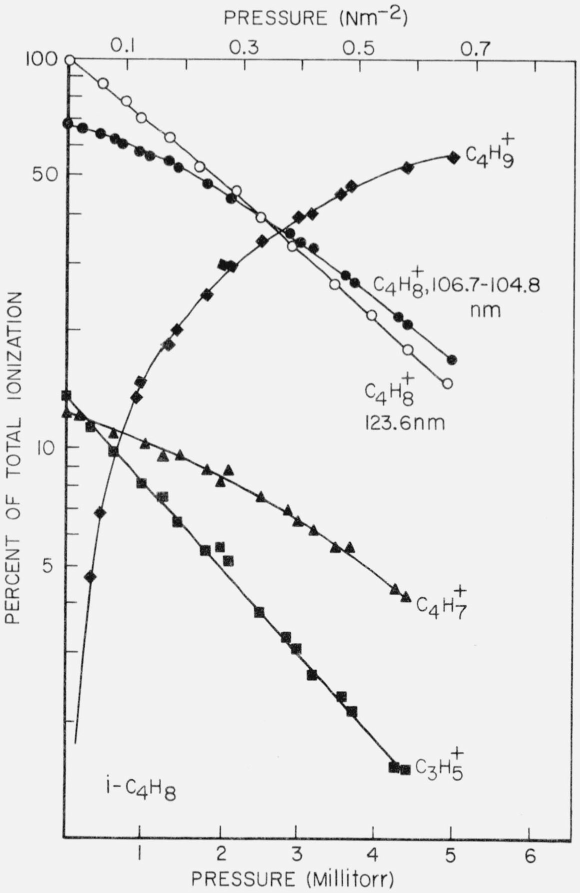

FIGURE 2. *Decay curves for major ions from photoionized* $i\text{-}C_4H_8$ *at 106.7–104.8 nm as a function of pressure.*

Also included (o) is the decay curve for $C_4H_8^+$ from $i\text{-}C_4H_8$ obtained at 123.6 nm.

c. $1\text{-}C_4H_8^+$

In the 11.6–11.8 eV photoionization of $1\text{-}C_4H_8$ (fig. 3) the initial slope of the decay curve is considerably lower than that obtained with 10.0 eV photons. The fact that the difference in slope is much more pronounced for this compound than for $i\text{-}C_4H_8$ (fig. 2) may be due to a longer dissociative lifetime of the $(1\text{-}C_4H_8^+)^*$ ion. However, in view of the results presented in section 3.1 which indicate that the structure of the reactant ion in $1\text{-}C_4H_8$ at 11.6–11.8 eV is mainly $2\text{-}C_4H_8^+$, the lower rate of reaction of this ion as compared to its precursor $(1\text{-}C_4H_8^+)$ probably also contributes to the reduction in slope seen in figure 3.

3.4. Absolute Rate Coefficients of Reaction of $C_4H_8^+$ Ions

Rate coefficients for bimolecular reactions of primary $C_4H_8^+$ ions with their parent molecules were determined from the slopes of the semilogarithmic decay plots of the type displayed in figure 4. Only the 10.0 eV data, were considered, in view of the fact that at this energy fragmentation does not compete with the bimolecular reaction, and isomerization of the butene ions is relatively unimportant (see sec. 3.1). The decay curves are linear in the low pressure range for reactant ions of a single structure when the rate coefficient does not vary with the internal energy distribution of the

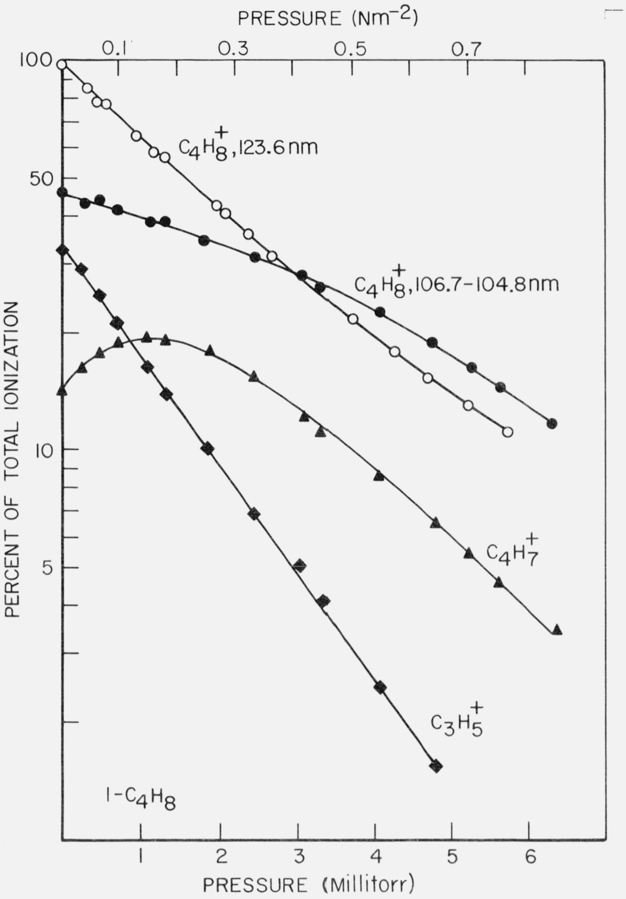

FIGURE 3. *Decay curves for major ions from photoionized* 1-C_4H_8 *at 106.7–104.8 nm as a function of pressure.*

Also included is the decay curve for $C_4H_8^+$ from 1-C_4H_8 obtained at 123.6 nm.

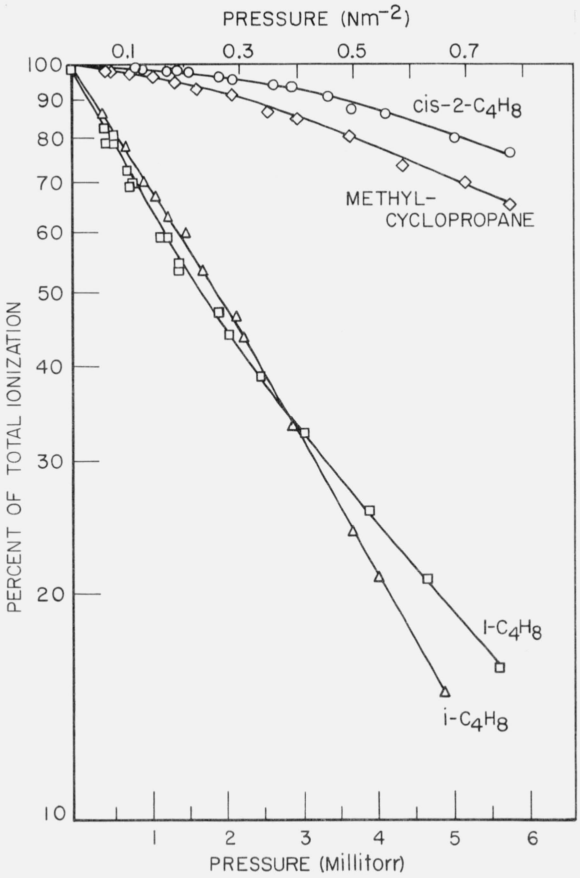

FIGURE 4. *Decay curves for* $C_4H_8^+$ *obtained from the photoionization of* cis-2-C_4H_8, *methylcyclopropane,* 1-C_4H_8, *and* i-C_4H_8 *at 123.6 nm as a function of pressure.*

reactant ion. Most experimental semilogarithmic decay curves will exhibit some downward curvature at higher pressures due to nonreactive scattering of ions, especially if the rate coefficient is relatively low. Alternatively, a decay curve which is concave upwards at higher pressures indicates that two or more ions of the same mass are reacting, and each exhibits a different overall reactivity. The experimental decay curves found for the $C_4H_8^+$ ions obtained from the photoionization of 1-C_4H_8, *i*-C_4H_6, methylcyclopropane, and 2-C_4H_8 at 10.0 eV as a function of pressure are given in figure 4. With the exception of 1-C_4H_8, all of the isomeric systems exhibit an increased slope at higher pressures due to nonreactive scattering of primary ions or other changes in the reaction mechanism. The contour of the experimental decay curve for $C_4H_8^+$ from 1-C_4H_8 indicates one or more minor $C_4H_8^+$ components in the composite signal which exhibit a reduced reactivity when compared to the bulk of the $C_4H_8^+$ ions. This is not unexpected because as shown earlier in the discussion, approximately 10 percent of the 1-$C_4H_8^+$ ions isomerize to the 2-$C_4H_8^+$ structure at 10.0 eV, and it is known [1e] that the latter ions react more slowly with 1-C_4H_8 than the 1-$C_4H_8^+$ ions. Due to the indeterminate effect of nonreactive scattering at higher pressures, however, no attempt was made to resolve the experimental curve into components. Absolute rate coefficients for the various isomers were derived from initial slopes using a best straight line fit through the low pressure points. A summary of these coefficients is given in table 4.

In agreement with earlier observations [1d, 2b, d] the $C_4H_8^+$ ion formed in the photoionization of cyclobutane was unreactive towards cyclobutane. At the pressures at which our experiments were carried out the *c*-$C_4H_8^+$ ion isomerizes to the 2-$C_4H_8^+$, *i*-$C_4H_8^+$, and *c*-$C_3H_5(CH_3)^+$ ion structures [2d].

The relative reaction rates are also given in table 4 and can be compared with those obtained by other investigators. Good agreement is seen between the rate data derived from ion cyclotron resonance experiments [1e] and those obtained in this study. Because the $C_4H_8^+$ ions in the cyclotron experiments were produced by impact with low energy electrons, it may be assumed that the structures of the reactant ions were not very different from those produced in the present 10.0 eV photoionization experiments. Agreement with the relative rate constants obtained

TABLE 4. *Absolute rate coefficients for the reaction:* $C_4H_8^+ + C_4H_8 \rightarrow$ *Products other than* $C_4H_8^+$

	Rate coefficient (cm³/molecule·second)	Relative Rates		
		This work	[a] Ref. 1b	[b] Ref. 1e
cis-2-butene	$0.37 \pm 0.1 \times 10^{-10}$	1	1	1
Methylcyclopropane	$0.60 \pm 0.1 \times 10^{-10}$	1.6	....	....
Isobutene	$5.4 \pm 0.4 \times 10^{-10}$	14.5	5	....
Isobutene-d_8	$5.4 \pm 0.4 \times 10^{-10}$	14.5	....	....
1-butene	$6.0 \pm 0.5 \times 10^{-10}$	16.2	2.5	14.0

[a] Tandem mass spectrometer. Kinetic energy 0.3 ± 0.3 eV, reactant ions produced by 100 eV electron beam.

[b] Ion cyclotron resonance mass spectrometer. Kinetic energy 0–0.1 eV. Ions produced by electrons whose energy is just above the threshold for ionization.

in the tandem mass spectrometer [1b] is, however, poor. The relatively low rate of reaction of the $C_4H_8^+$ produced from 1-C_4H_8 can in part be ascribed to the extensive isomerization to the 2-$C_4H_8^+$ structure which may be expected to occur when an 100 eV electron beam is used to produce $C_4H_8^+$ ions. The excess kinetic energy given to the ions in the tandem mass spectrometer will also tend to bring the rate coefficients closer together.

As shown in figure 2, the photoionization of i-C_4H_8 at 11.6–11.8 eV leads to the formation of $C_4H_9^+$ as the major ion at pressures above $4\text{–}5 \times 10^{-3}$ torr. This indicates the occurrence of the well-known reaction:

$$i\text{-}C_4H_8^+ + i\text{-}C_4H_8 \rightarrow C_4H_9^+ + C_4H_7 \qquad (14)$$

We have investigated the stereospecificity of this overall process via photoionization of $(CD_3)_2C=CH_2$ at both 10.0 eV and 11.6–11.8 eV. At each of these energies, the overall reaction gave 87 percent $C_4D_7H_2^+$ and 13 percent $C_4D_6H_3^+$. The invariance of this result with energy is not surprising in view of the fact that isomerization of the isobutene ion is unimportant in these energy regions (see Part 3.1). Exchange processes such as:

$$C_4D_7H_2^+ + (CD_3)_2C=CH_2 \rightarrow C_4D_8H^+ + C_4D_5H_3 \qquad (15)$$

were also observed under pressure conditions where consecutive reactions occur to a significant extent (that is, at pressures above $3\text{–}4 \times 10^{-3}$ torr).

3.5. Modes of Dissociation of the $(C_8H_{16}^+)^*$ Ions

The $C_4H_8^+$ ions have available to them as at least one possible reaction path, condensation with their parent C_4H_8 compounds:

$$C_4H_8^+ + C_4H_8 \rightarrow (C_8H_{16}^+)^* \qquad (16)$$

(The one exception to this is cyclobutane, which, as noted above, does not react with $C_4H_8^+$ ions.) The condensation ion $(C_8H_{16}^+)^*$, may be collisionally stabilized or undergo one of several possible dissociation processes, including regeneration of the original reactant partners. The major fragmentation channels observed to a greater or lesser extent at low pressures in the mass spectrometer reaction chamber for all of the isomers except cyclobutane, are:

$$C_8H_{16}^+ \rightarrow C_4H_9^+ + C_4H_7 \qquad (17)$$

$$\rightarrow C_5H_9^+ + C_3H_7 \qquad (18)$$

$$\rightarrow C_5H_{10}^+ + C_3H_6 \qquad (19)$$

$$\rightarrow C_5H_{11}^+ + C_3H_5 \qquad (20)$$

$$\rightarrow C_6H_{11}^+ + C_2H_5 \qquad (21)$$

$$\rightarrow C_6H_{12}^+ + C_2H_4 \qquad (22)$$

$$\rightarrow C_7H_{13}^+ + CH_3 \qquad (23)$$

It should be pointed out that proton (or H-atom) transfer reactions such as that shown in reaction (14) occur to some extent in all these systems (see table 5); this is an independent reaction channel of the $C_4H_8^+$-C_4H_8 reaction pairs, and not a mode of dissociation of the $C_8H_{16}^+$ ions. This will be discussed in more detail below.

Typical behavior is shown graphically in figure 5 which reproduces the data obtained as a function of pressure when 1-C_4H_8 was photoionized at 10.0 eV. Although only major ions are displayed, it is apparent that the ionic reaction mechanism is quite complex. The relative probabilities for production of $C_4H_9^+$, $C_5H_{10}^+$ etc., via unimolecular fragmentation of $(C_8H_{16}^+)^*$ may be obtained from such data by determining the relative rates of production of the various secondary ions as a function of pressure. The values for the relative rates were extrapolated to "zero pressure" and the intercepts were taken as the relative probabilities that the condensation ion as initially formed will dissociate via process (17) through (23). It was necessary to derive the zero pressure intercepts in every case since the C_4–C_7 product ions were also found to react further in each isomer. For example, it is evident from figure 5 that the relative rate of production of $C_5H_{10}^+$ decreases rapidly as the pressure of 1-C_4H_8 is increased in the reaction chamber. This behavior is indicative of further reaction of $C_5H_{10}^+$, presumably to produce C_7^+ ions. However, the exact

TABLE 5. *Distribution of product ions obtained from the overall reaction* $C_4H_8^+ + C_4H_8 \rightarrow$ *Products*

	Present work	Henis Ref. 1e	A and F Ref. 1b	Koyano Ref. 2a		Present work	Henis Ref. 1e	A and F Ref. 1b	Koyano Ref. 2a
		cis-2-butene					Isobutene		
$C_4H_9^+$	3.3	9.1	70	[a] 56	$C_4H_9^+$	91.7	n.d.	93	86
$C_5H_{10}^+$	5.8	12.4	4	n.d.	$\Sigma\ C_5^+$	4.5	n.d.	7	14
$C_5H_{11}^+$	3.5	6.2	10	n.d.	$\Sigma\ C_6^+$	3.4	n.d.	n.d.	n.d.
$C_6H_{11}^+$	42.3	31.0	10	n.d.	$\Sigma\ C_7^+$	0.4	n.d.	n.d.	n.d.
$C_6H_{12}^+$	45.1	41.3	6	n.d.					
		Methylcyclopropane					1-butene		
$C_4H_9^+$	< 1.0				$C_4H_9^+$	8.3	15.5	14	24.7
$C_5H_9^+$	8.8				$C_5H_9^+$	4.3	4.7	4	16.1
$C_5H_{10}^+$	69.0				$C_5H_{10}^+$	38.8	31.5	38	30.5
$C_6H_{11}^+$	8.0				$C_5H_{11}^+$	4.2	2.2	3	5.5
$C_6H_{12}^+$	7.6				$C_6H_{11}^+$	26.3	24.0	22	16.1
$C_7H_{13}^+$	6.3				$C_6H_{12}^+$	16.1	18.3	15	7.2
					$C_7H_{13}^+$	2.0	3.8	2	n.d.

[a] Koyano also observed 44 percent $C_5H_9^+$, which is a minor ion in all other studies.

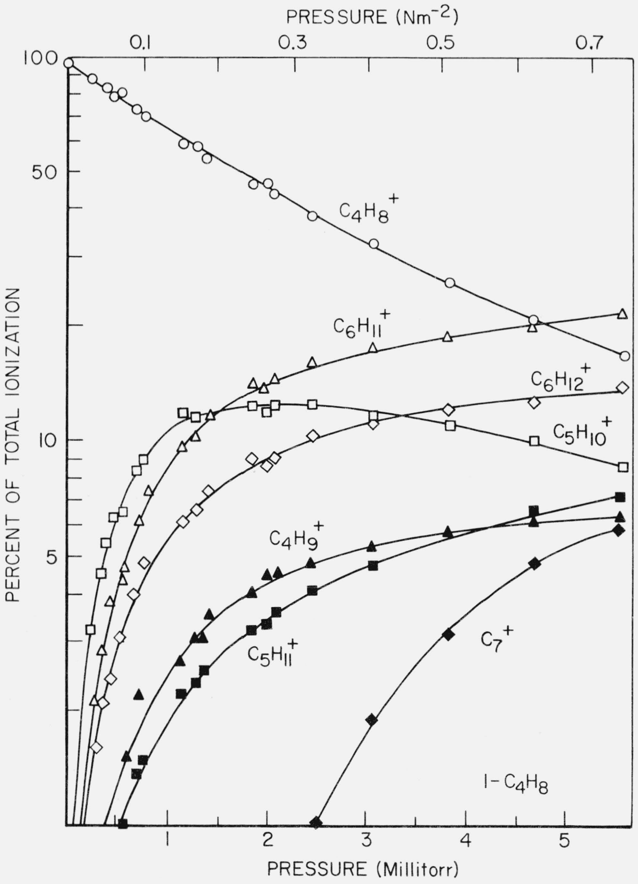

FIGURE 5. *Composite mass spectrum obtained following photoionization of* 1-C_4H_8 *as a function of pressure at 123.6 nm.*

mechanisms leading to consecutive reaction products could not be evaluated due to the complexity of the composite mass spectrum at higher pressures.

In kinetic mass spectrometry, there is a potential source of error in the use of "zero pressure" intercepts for the determination of unimolecular fragmentation patterns of condensation ions which are formed in slow reactions, especially if the precursor reactant ion ($C_4H_8^+$ in this case) isomerizes to a more or less reactive structure to any significant extent. That is, those condensation ions which are formed at very low pressures may result only from the interaction of those ions which for energetic and structural reasons were found to react quickly, and the fragmentation pattern obtained does not necessarily give the modes of dissociation of a condensation ion formed from the bulk of the ions in the system. In the experiments reported here, this effect was minimized by using 10.0 eV photons to generate the $C_4H_8^+$ ions. As indicated previously, isomerization is relatively unimportant at this energy. Included for comparison in table 5 are analogous data obtained by Henis [1e] using ICR techniques with ions at kinetic energies at or near kT, and by Abramson and Futrell [1b] using the ion-injection technique at any impacting energy of approximately 0.3 eV. Additional data obtained by Koyano [2a] using photoionization at 10.2 eV (Lyman α) at kinetic energies in excess of 0.5 eV are also tabulated.

In general our results agree best with those obtained by Henis, which is not unexpected in view of the fact that the ions have low internal and kinetic energies in both studies. However we do find a significantly lower probability for production of $C_4H_9^+$ in both 2-C_4H_8 and 1-C_4H_8 than that seen in the other studies. Abramson and Futrell [1b] have reported that this H^+ or H transfer process in olefins proceeds via a mechanism which does not involve the formation of C−C bonds in the collision complex. Herod and Harrison have actually found that the probability for the formation of the $C_3H_7^+$ ion in the $C_3H_6^+$-C_3H_6 reaction pair increases substantially with the kinetic energy of the $C_3H_6^+$ ion at the expense of the formation of condensation ions (reaction 16). It would seem therefore that the higher

$C_4H_9^+$ yield obtained in the other studies can mainly be ascribed to excess kinetic energy. The effect is particularly evident when comparing the results for 2-C_4H_8 in which Abramson and Futrell, and Koyano, observed 50–70 percent proton transfer.

It is seen (table 5) that for thermal $C_4H_8^+$ ions, the unimolecular fragmentation pattern of $C_8H_{16}^+$ varies considerably from one system to another. The structure of the reactant $C_4H_8^+$ ion and of the neutral molecule, as well as the internal energy content, will determine the fragmentation pattern of the $C_8H_{16}^+$. Henis [1e] has discussed some of these factors for a number of olefinic systems. Some of the main differences noted here can be rationalized in terms of the differences in structure of the $(C_8H_{16}^+)^*$ ions. For instance the much lower abundance of the $C_5H_{10}^+$ product ion in 2-C_4H_8 as compared to 1-C_4H_8 is due to the fact that the $C_8H_{16}^+$ ion resulting from a 2-$C_4H_8^+$-2-C_4H_8 encounter will be highly branched. The 70 eV mass spectral cracking patterns of linear and branched octenes show that process (19) is especially important only in those octenes which exhibit a linear portion of at least three carbon atoms.

The unusually high abundance of the $C_5H_{10}^+$ ion in the methylcyclopropane case would therefore indicate that the $C_4H_8^+$ ion (which as noted before exhibits mainly the 2-$C_4H_8^+$ structure under these conditions) reacts with the neutral methylcyclopropane molecule with ring opening in the 1–2 position.

3.6. Collisional Stabilization of $C_8H_{16}^{+*}$

Although stable $C_8H_{16}^+$ was not detected in any of the various perprotonated C_4H_8 isomers at pressures around 10^{-4} torr, the formation of $C_8D_{16}^+$ was observed in both 2-C_4D_8 and *i*-C_4D_8 in this pressure range. The relative probabilities for production of $C_8D_{16}^+$ at 10^{-4} torr were found to be 0.06 in *i*-C_4D_8 and 0.2 in 2-C_4D_8 when compared with the total probability for production of all other reaction product ions in these systems. The fact that formation of $C_8D_{16}^+$ ions was observed at lower pressures than the $C_8H_{16}^+$ ions is attributed to the theory that the dissociative lifetime of an internally excited deuterated molecule is higher than the protonated counterpart possessing the same amount of energy.

At higher pressures the relative yield of $C_8D_{16}^+$ product ions will increase because of collisional stabilization of the $(C_8D_{16}^+)^*$ condensation ions:

$$(C_8D_{16}^+)^* + M \rightarrow C_8D_{16}^+ + M \qquad (24)$$

which would otherwise dissociate. Experiments were carried out in which 2-C_4D_8 was photoionized in the presence of large excesses of several added gases which are not ionized at 10.0 eV; namely, C_3H_8, Xe, and Ne. The results of these experiments are displayed in figure 6 and were derived in the following manner. A mixture of approximately 2 percent 2-C_4D_8 in, for example, propane was photolyzed at various total chamber pressures in the range 0.001 to approximately 0.5 torr. The extent of stabilization of $C_8D_{16}^+$ in such an experiment is assumed to be represented by the sum of the fractional contributions of $C_8D_{16}^+$, $C_{12}D_{24}^+$, and $C_{16}D_{32}^+$ to the composite mass spectrum ($C_8D_{16}^+$ reacts further with 2-C_4D_8 at higher total pressures to form $C_{12}D_{24}^+$, etc.). The extent of dissociation of $C_8D_{16}^{+*}$ into carbon-containing ions other than $C_4D_8^+$ is reflected mainly (> 90 percent) by the sum of the fractional contributions of the C_6^+, C_{10}^+, and C_{14}^+ ions. In figure 6 the sum of the fractional intensities $(C_8^+ + C_{12}^+ + C_{16}^+)$ is represented by *S* (stabilization) while the parameter *D* represents $C_6^+ + C_{10}^+ + C_{14}^+$. The ratio *S*/*D* is a measure of the stabilization efficiency of the particular additive gas at a particular total pressure, and a plot of *S*/*D* versus total pressure yields the types of curves displayed in figure 6. Relative stabilization efficiencies were derived from the initial slopes found in pure 2-C_4D_8 and mixtures of 2-C_4D_8 with C_3H_8, Xe, and Ne. The relative efficiencies found were as follows: 2-C_4D_8, 1.0; C_3H_8, 0.56±0.06; Xe, 0.20±0.04; and Ne, 0.12±0.03. The drop in the deactivating efficiencies from C_4D_8 to Ne cannot be entirely accounted for by a decrease in the collision rate (as calculated on the basis of the ion-induced dipole formulation). This is not unexpected since removal of internal energy by atoms may require several collisions.

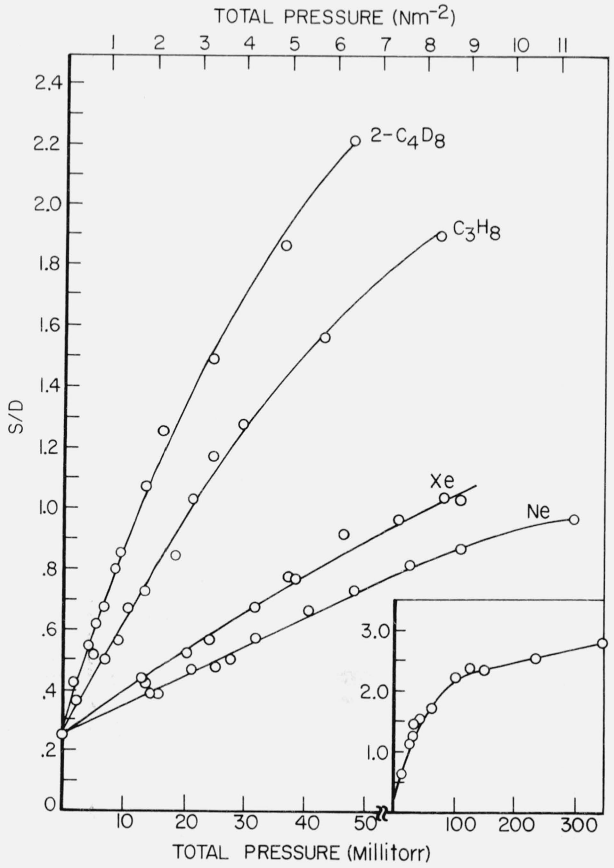

FIGURE 6. *Stabilization to decomposition ratio found for photoionized* 2-C_4D_8 *and mixtures of* 2-C_4H_8 *with* C_3H_8, Xe, *and* Ne *at 123.6 nm as a function of pressure.*

Insert shows ratio for pure 2-C_4D_8 on expanded pressure scale.

3.7. Reaction of $C_8H_{16}^+$ with C_4H_8

Photoionization of i-C_4H_8 and i-C_4D_8 was also carried out at 10.0 eV at pressures up to 50 millitorr in order to investigate higher order processes. Representative results are given in figure 7, which reproduces the fractional intensities of major product ions as a function of pressure for i-C_4H_8. In agreement with previous mass spectrometric investigations of this system we observe the stepwise polymerization of $C_4H_9^+$, which is the major low pressure reaction product (see table 5), to yield $C_4H_9^+$ (C_4H_8) and, at higher pressures, $C_4H_9^+$ $(C_4H_8)_2$. In addition to these processes, however, we also observed the formation of stable $C_8H_{16}^+$ ions:

$$C_4H_8^+ + i\text{-}C_4H_8 \xrightarrow{i\text{-}C_4H_8} C_8H_{16}^+ + C_4H_8 \qquad (25)$$

At pressures greater than approximately 5 millitorr the dimer ion reacts further with i-C_4H_8 via an H_2 transfer reaction to yield $C_8H_{14}^+$ and i-C_4H_{10}

$$C_8H_{16}^+ + i\text{-}C_4H_8 \rightarrow C_8H_{14}^+ + i\text{-}C_4H_{10} \qquad (26)$$

At a pressure of 50 millitorr the sum of the fractional intensities of $C_8H_{16}^+$ and $C_8H_{14}^+$ is 0.31, and appears to be asymptotically approaching a constant value. Quantitative experiments could not be carried out at higher pressures due to the complexity of the composite mass spectrum under those conditions. Analogous experiments with i-C_4D_8 gave the same overall result [12], although the sum of $C_8D_{16}^+$ and $C_8D_{14}^+$ was approximately 0.5 at 50 millitorr. The observation of this reaction sequence accounts for the large ionic yields of isobutane obtained previously in the photoionization and radiolysis of isobutene-O_2 mixtures in closed systems. The analogous reaction scheme has been found in propylene, although the rate of dimer formation and its subsequent reaction was approximately a factor of four slower than found in isobutene. These results have recently been discussed [13].

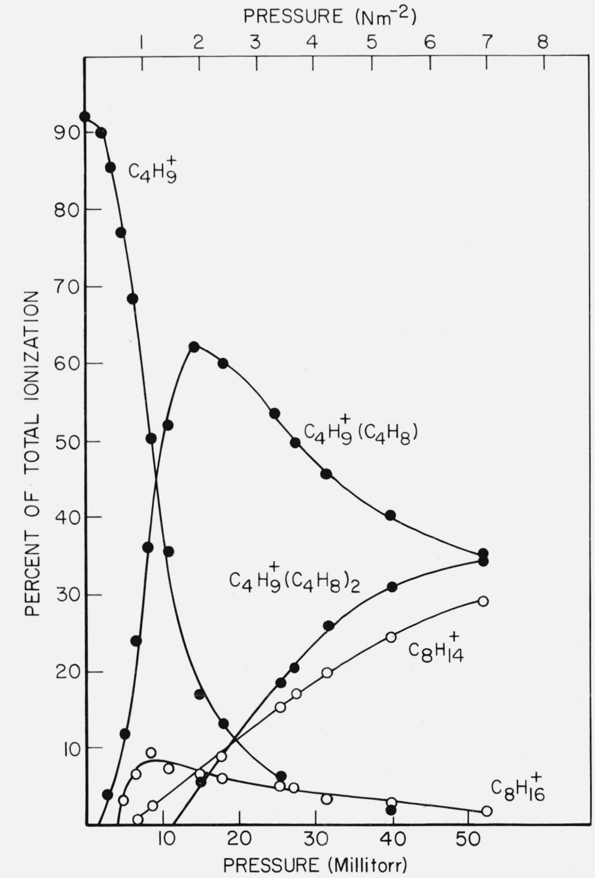

FIGURE 7. *Percentage composition of the product ion mass spectrum (major ions only) obtained from the photoionization of* i-C_4H_8 *at 123.6 nm as a function of pressure.*

The formation of stable dimeric ions and their subsequent reactions has not been considered previously when interpreting the radiation-induced polymerization of isobutene, but the present data indicate that this mechanism will contribute significantly to the chemical end-products. The failure of other mass spectrometric investigators to uncover this sequence is probably either due to the fact that ions were accelerated prior to reaction, the temperatures of the reaction chambers were excessively high, or the total pressures were too low, or some combination of these conditions.

4. References

Some of the more recent papers include:

[1a] Aquilanti, V., Galli, A., Giardini-Guidoni, A., and Volpi, G. G., Trans. Faraday Soc. **63**, 926 (1967).

[1b] Abramson, F. P., and Futrell, J. H., J. Phys. Chem. **72**, 1944 (1968).

[1c] Sieck, L. W., and Futrell, J. H., J. Chem. Phys. **48**, 1409 (1968).

[1d] Hughes, B. M., and Tiernan, T. O., J. Chem. Phys. **51**, 4373 (1969).

[1e] Henis, J. M. S., J. Chem. Phys. **52**, 282 (1970); Ibid. **52**, 292 (1970).

[1f] Meisels, G. G., Park, J. Y., and Giessner, B. G., J. Am. Chem. Soc. **92**, 254 (1970).

[1g] Wisniewsky, S. J., Clow, R. P., and Futrell, J. H., J. Phys. Chem. **74**, 2234 (1970).

[1h] Irie, M., et al., Bull. Chem. Soc. Japan **44**, 2261 (1971).

[2a] Koyano, I., J. Chem. Phys. **45**, 706 (1966).

[2b] Sieck, L. W., Searles, S. K., and Ausloos, P., J. Am. Chem. Soc. **91**, 7627 (1969).

[3a] Lias, S. G., and Ausloos, P., J. Am. Chem. Soc. **92**, 1840 (1970).

[3b] Herman, J., Herman, K., and Ausloos, P., J. Chem. Phys. **52**, 28 (1970).

[3c] Gill, P. S., Inel, Y., and Meisels, G. G., J. Chem. Phys. **54**, 2811 (1971).

[3d] Lias, S. G., and Ausloos, P., Nat. Bur. Stand. (U.S.), J. Res. **75A**, No. 6 589 (1971).

[4] Searles, S. K., and Sieck, L. W., J. Am. Chem. Soc. **92**, 2937 (1970).

[5] Gorden, R., Jr., Rebbert, R. E., and Ausloos, P., Nat. Bur. Stand. (U.S.), Tech. Note 496 55 pages (1969).

[6] Ausloos, P., Progress in Reaction Kinetics, Chapter 3, 113–179, Ed. G. Porter (Pergamon Press Ltd., London, 1970).

[7] Hummel, R. W., Nature **218**, 1050 (1968).

[8] Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., and Field, F. H., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), NSRDS–26, 289 pages (June 1969).

[9] Tiernan, T. O., and Futrell, J. H., J. Phys. Chem. **72**, 3080 (1968).

[10] Gorden, R., Jr., and Ausloos, P., Nat. Bur. Stand. (U.S.), J. Res. **75A**, No. 3, 141 (1971).

[11] Meisels, G. G., Advan. in Chem. **58**, 243 (1966).

[12] Sieck, L. W., and Ausloos, P., J. Chem. Phys. (To be published).

[13] Sieck, L. W., and Ausloos, P., Nat. Bur. Stand. (U.S.), J. Res. 76A, No. 3, (May-June 1972).

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