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Isomerization Processes in Ions of the Empirical Formula $C_4H_8^{+}$*

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Ions of the formula $C_4H_8^+$ have been generated with different initial energies by ionizing ethylene ($C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$, where the $C_4H_8^+$ ion is formed with an initial energy of > 11.51 eV), cyclobutane (initial energy of $C_4H_8^+$, > 10.84 eV), methylcyclopropane (> 10.15 eV), 1-C_4H_8 (> 9.58 eV), and i-C_4H_8 (> 9.06 eV) with 11.6–11.8 eV photons, and in some cases also with 10 eV photons and with gamma radiation. The structures of the ions have been determined from the structures of the C_4H_8 products formed in charge transfer reaction between the ions and charge acceptors such as dimethylamine and nitric oxide, as well as from the structures of the butanes formed in D_2^- transfer reactions with methylcyclopentane-d_{12} ($C_4H_8^+ + C_6D_{12} \rightarrow C_4H_8D_2 + C_6D_{10}^+$).

At low pressures the $C_4H_8^+$ ions initially formed in ethylene, cyclobutane, and methylcyclopropane isomerize to the thermodynamically most stable configurations, i-$C_4H_8^+$ and 2-$C_4H_8^+$. The 2-$C_4H_8^+$ structure predominates in all the experiments. As the pressure is raised, the i-$C_4H_8^+$ ion yield diminishes as that of 2-$C_4H_8^+$ increases, indicating that when the precursor of the i-$C_4H_8^+$ ion is collisionally deactivated, it ends up as 2-$C_4H_8^+$. At high pressures, 1-$C_4H_8^+$ ions are intercepted; their yield increases with increasing pressure, indicating that 1-$C_4H_8^+$ is an intermediate which isomerizes further unless it is collisionally deactivated. The 1-$C_4H_8^+$ ion formed in methylcyclopropane (initial energy > 10.15 eV) is more easily deactivated than that formed in cyclobutane (initial energy > 10.84 eV). That the isomerization of the 1-$C_4H_8^+$ ion to lower energy structures such as i-$C_4H_8^+$ and 2-$C_4H_8^+$ requires excess internal energy is demonstrated by the fact that in the photolysis with 10 eV photons, a negligible amount of isomerization is observed, but with 11.6–11.8 eV photons, more than half of the 1-$C_4H_8^+$ ions isomerize to the 2-$C_4H_8^+$ structure at a pressure of 2 torr. Isomerization of the low energy i-$C_4H_8^+$ ions formed in the photolysis of i-C_4H_8 to other structures is relatively unimportant at 11.6–11.8 eV.

Taking the ratio i-$C_4H_8^+$/2-$C_4H_8^+$ as an indicator of the amount of energy removed by collisions from the intermediate $C_4H_8^+$ species under conditions where only i- and 2-$C_4H_8^+$ ions are intercepted, it is shown that the efficiency of energy transfer from the ions to helium, hydrogen, neon, krypton, xenon, nitrogen, and carbon dioxide is related to the polarizability of the added deactivator.

Key words: Butene; cyclobutane; ion structure; isomerization; methylcyclopropane; photoionization; photolysis; radiolysis.

1. Introduction

Determinations of the structures of organic ions have been the subject of a great deal of interest in the literature recently [1].[1] In particular, n.m.r. spectra of organic ions formed in very strong acids are now being recorded [2]. More classical studies, using analysis of the products formed from ionic reactions in thermal organic systems in the liquid phase [3], or from ions generated by high energy radiation in the gas phase [4], have recently elucidated isomerization mechanisms of the $C_3H_7^+$ and $C_4H_9^+$ carbonium ions. Indirect evidence bearing on ionic structures has been inferred from mass spectrometric results; in particular, many studies recently have attempted to derive information about ionic structures from

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[1] Figures in brackets indicate the literature references at the end of this paper.

the modes and rates of reaction of ions as observed in ion cyclotron resonance mass spectrometry [5].

This investigation is devoted to a detailed examination of the structures and isomerization reactions of the ions having the empirical formula, $C_4H_8^+$. These ions are not known to be formed in thermal chemical reactions, and to our knowledge have not been studied except in systems where they are generated by high-energy radiation. Several years ago, it was reported [6] that when ethylene was irradiated in the presence of a compound having an ionization energy lower than or equal to 9.54 eV, the $C_4H_8^+$ ion formed in the reaction:

$$C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+ \tag{1}$$

would transfer its charge to the additive, A, to form neutral butene molecules:

$$C_4H_8^+ + A \rightarrow C_4H_8 + A^+ \tag{2}$$

whose structures were assumed to correspond to the structures of the precursor $C_4H_8^+$ ions. Using the same technique, it was then demonstrated that the $C_4H_8^+$ ions formed in the radiolysis [7] or photoionization [8] of cyclobutane

$$c\text{-}C_4H_8 \xrightarrow{\text{radiation}} C_4H_8^+ + e \tag{3}$$

acquired the same butene structures as those seen for the $C_4H_8^+$ ions in the ethylene system. In those early studies it was reported that the $C_4H_8^+$ ions formed in ethylene and cyclobutane acquired the 2-$C_4H_8^+$ and 1-$C_4H_8^+$ structures. A mass spectrometric study compared the rate of charge transfer to NO from the $C_4H_8^+$ ions in cyclobutane with the rates of the same reaction for the 1-$C_4H_8^+$, 2-$C_4H_8^+$, and i-$C_4H_8^+$ ions, and seemingly corroborated these results [9]. However, more recently it was noted [10] that when the $C_4H_8^+$ ions formed in the photoionization of cyclobutane at a pressure of 20 torr were allowed to undergo D_2^- transfer reactions with methylcyclopentane-d_{12}, the butane products consisted of $CH_3CHDCHDCH_3$ from the 2-$C_4H_8^+$ reaction:

$$2\text{-}C_4H_8^+ + C_6D_{12} \rightarrow CH_3CHDCHDCH_3 + C_6D_{10}^+ \tag{4}$$

and i-$C_4H_8D_2$, which could only result from a reaction of the i-$C_4H_8^+$ ion:

$$i\text{-}C_4H_8^+ + C_6D_{12} \rightarrow (CH_3)_2CDCH_2D + C_6D_{10}^+. \tag{5}$$

A reexamination of the butenes formed in the charge exchange experiments indicated that the product originally identified as 1-butene was indeed actually isobutene, reconfirming the formation of i-$C_4H_8^+$ ions in cyclobutane. It was later noted that the i-$C_4H_8^+$, rather than the 1-$C_4H_8^+$, ion is also formed in irradiated ethylene [11]. (The original misassignment came about because 1-C_4H_8 and i-C_4H_8 have nearly identical retention times on the gas chromatographic columns used for analysis in these studies.)

The structures of the $C_4H_8^+$ ions formed in the dissociation of cyclohexane and methylcyclopentane parent ions were recently determined by an examination of the structures of the butanes formed in D_2^- transfer reactions, (such as 4 and 5), as well as by the structures of the butenes formed in charge transfer reactions [12]. This study was carried out at a single pressure, so pressure effects on the distribution of the isomeric $C_4H_8^+$ ions could not be observed; because in the 10 eV photolysis of 1-C_4H_8 and 2-C_4H_8 in the presence of methylcyclopentane-d_{12}, no evidence was seen [12] for isomerization of 1-$C_4H_8^+$ to the 2-$C_4H_8^+$ structure, or 2-$C_4H_8^+$ to the 1-$C_4H_8^+$ structure, isomerizations between the different C_4H_8 structures were not considered.

More recently, a study has appeared [11] in which $C_4H_8^+$ ions generated in the photoionization of ethylene (reaction 1) are intercepted by charge exchange with dimethylamine, or toluene. Because the yield which could be attributed to the i-$C_4H_8^+$ ion was seen to increase relative to the 2-$C_4H_8^+$ yield as the concentration of charge acceptor was increased, the results were interpreted in terms of a $C_4H_8^+$ entity which would undergo a rapid equilibrium between the 2-$C_4H_8^+$ and i-$C_4H_8^+$ structures:

$$2\text{-}C_4H_8^+ \rightleftarrows i\text{-}C_4H_8^+. \tag{6}$$

It was suggested that the equilibrium position is affected by the internal energy of the ion, which is gradually diminished as the entity undergoes successive collisions.

Because such a rapid equilibrium between two skeletally different isomers has not been seen for carbonium ions [1], and because detailed information about isomerization process in $C_nH_{2n}^+$ ions is generally lacking, it was considered worthwhile to undertake a study of isomerization processes in these ions. In particular, it was felt that since $C_4H_8^+$ ions formed in ethylene can undergo further reaction with the parent molecule:

$$C_4H_8^+ + C_2H_4 \rightarrow C_6H_{12}^+ \tag{7}$$

it would be of interest to observe the charge transfer and D_2^- transfer products of $C_4H_8^+$ ions in cyclobutane, where such competing processes are absent; $C_4H_8^+$ ions do not react with cyclobutane [10]:

$$C_4H_8^+ + c\text{-}C_4H_8 \not\rightarrow \text{no reaction}. \tag{8}$$

Further, an examination of pressure effects on the structures of $C_4H_8^+$ ions over a wide pressure range seemed warranted.

In the results reported here, $C_4H_8^+$ ions are generated in cyclobutane, ethylene, methylcyclopropane and the butenes, through photoionization with 11.6–11.8 eV photons as well as through γ-radiolysis. The $C_4H_8^+$ (or $C_4D_8^+$) ions are intercepted both by charge transfer and by D_2^- transfer reactions with added alkanes. The pressure of these systems is varied from about 0.1 torr to 1 atm, and in some systems, unreactive deactivator gases are added. As will be seen below, the composite picture which emerges from these various results not only indicates that isomerization process in the $C_4H_8^+$ ions are relatively slow in the energy range accessible for these experiments and can be collisionally quenched, but demonstrates that the isomerization reactions involve several different C_4H_8 structures, not just the 2-$C_4H_8^+$ and *i*-$C_4H_8^+$ configurations.

2. Experimental Procedure

All the hydrocarbons used in this study were rigorously purified by gas chromatography, and low temperature distillation. The irradiation and analytical procedures were the same as those described in earlier publications from this laboratory [13]. The argon resonance lamps, equipped with 0.35 mm thick LiF windows, were fabricated according to the procedure described recently [14]. The 104.8 and 106.7 nm lines emanating from the lamp were of equal intensity, within 10 percent. Impurity lines constituted less than 1 percent of the radiation. After approximately 20 experiments, the transmission of the window was reduced by 50 percent from its initial value because of *F*-center formation. Bleaching of the window with a mercury lamp restored the output of the lamp to its original intensity. Impurity lines did not appear even after extensive usage. The intensity at which most of the experiments were carried out was 10^{13} quanta per second.

The radiolysis experiments were carried out in the NBS cobalt-60 gamma source, which, at the time these experiments were performed, provided 1.7×10^{17} eV/s per gram of hydrocarbon.

Quantitative analyses were carried out by injecting aliquots of the irradiated samples onto a 40 ft squalane column operated at 20 °C in a gas chromatograph equipped with a flame ionization detector. This column did separate 1,3-butadiene from 1-butene and isobutene, but did not separate 1-butene from isobutene. In some experiments, the combined peak of these two butenes was trapped out at liquid nitrogen temperature at the exit of the column and analyzed on a mass spectrometer. The methylcyclopropane was only partially separated from the *cis*-2-butene, but fairly good estimates of the yield of methylcyclopropane could be obtained, especially in experiments in which *cis*-2-butene is a minor product. The identity of the methylcyclopropane product was also confirmed by mass spectrometric analysis, and by injection of several of the samples on an alumina and on a sulfolane column, which separated the methylcyclopropane from the butenes.

All photolysis and radiolysis experiments were carried out in the presence of 3–5 percent oxygen, which effectively scavenges free radicals and prevents their forming hydrocarbon products.

The NBS high pressure photoionization mass spectrometer [10] was used to determine the modes of decomposition of cyclobutane ions, the modes of reaction of the fragment ions with cyclobutane, and the rates of certain reactions of importance to the interpretation of the results reported here.

Product yields are given in ion pair yield units, that is, in molecules (M) of product formed per positive ion (N_+) generated by the radiation in the *parent compound*. In the case of the photolysis experiments, ion pair yield determinations were made using the techniques discussed before [15]. The ion pair yield of a given product (X), is related to its quantum yield and the quantum yield of ionization in the parent compound:

$$\Phi(X)/\Phi_+ = M(X)/N_+.$$

The quantum yield of ionization at 11.6–11.8 eV of ethylene [6c] is 0.20, of cyclobutane [16] is 0.52, and of methylcyclopropane [16], 0.44.

In the case of cyclobutane, it was found that the quantum yield of ethylene plus acetylene was 0.91, independent of pressure from 0.2 to 1 torr. When the intensity of the lamp was kept constant, and 5 percent of dimethylamine was added to the cyclobutane, neither the ratio of ethylene to acetylene nor the absolute yields of these two products changed. Therefore, in photolysis experiments in the presence of larger amounts of dimethylamine, the combined yields of these two products were taken as the base for calculation of the product yields; in this way the fact that dimethylamine absorbed some of the energy was automatically corrected for. The same procedure was followed for experiments in which methylcyclopentane was the additive. In that case, the hydrocarbon additive did contribute to the formation of ethylene; however, because the methylcyclopentane was deuterated, a mass spectrometric analysis of the ethylene formed in the photolysis of c-$C_4H_8$$-$$c$-$C_5D_9(CD_3)$ mixtures verified that the yield of ethylene plus acetylene originating from cyclobutane did indeed remain constant.

It should be pointed out that this yield of ethylene plus acetylene is much lower than that reported in the earlier study [8] of the photolysis of cyclobutane. At the time that study was carried out, it was not realized that ion current measurements made at high sample pressures are generally not valid [15b]; therefore, all the absolute yields reported in that study are too high.

2.1. Ion Interception Techniques

In the discussion which follows, the yields of $C_4H_8^+$ ions of different structures (i.e. *i*-$C_4H_8^+$, 2-$C_4H_8^+$, 1-$C_4H_8^+$, etc.) will be followed under various conditions. In all cases, these yields have been derived from experiments in which (a) it is assumed that the C_4H_8 product formed in a charge transfer reaction

(reaction 2) has a structure which corresponds to the structure of the precursor $C_4H_8^+$ ion, or (b) the yields of the butanes formed in H_2^- or D_2^- reactions (such as 4 and 5) have been related to the yields of precursor ions.

Charge acceptors used in this study are dimethylamine and, in a few ethylene experiments, nitric oxide. In the case of NO, it has been reported [10] that at a pressure of ~ 0.1 torr, only 15–20 percent of the $C_4H_8^+$ ions from cyclobutane undergo charge transfer with NO, the remainder reacting to form an adduct $C_4H_8NO^+$ ion. Adduct formation may possibly also occur with dimethylamine; adduct formation has been reported for the $C_4H_8^+$-trimethylamine reaction pair in one study [9], but was not confirmed in a study from this laboratory [10] (and trimethylamine has been reported to react with $C_4H_8^+$ ions in exactly the same way as dimethylamine [11]). Because the results obtained with NO are in fair agreement with those in which dimethylamine was added, and because the results of the charge transfer experiments in general are, within experimental error, in agreement with what is seen in the H_2^- (or D_2^-) transfer experiments, adduct formation between $C_4H_8^+$ ions and the charge acceptor apparently does not materially alter the relative amounts of the different C_4H_8 isomers which are observed. Also, at pressures below about 100 torr, in cyclobutane the overall yields of products formed in charge exchange reactions with dimethylamine are in good agreement with the yields of products from H_2^- (or D_2^-) transfer reactions in methylcyclopentane additive experiments. However, because of possible complications from adduct formation, as well as the fact that the unambiguous analysis of all the C_4H_8 isomers is difficult with the analytical techniques used here, the results from the charge exchange experiments will generally be considered mainly as corroborative evidence for conclusions drawn from the H_2^- (D_2^-) transfer experiments.

The experiments in which the C_4H^+ ions were trapped by H_2^- (or D_2^-) transfer reactions were mainly carried out with methylcyclopentane-d_{12} as the reactive additive. As was noted before, it has been demonstrated conclusively [12] that the product $CH_3CHDCHDCH_3$ results only from a reaction of a 2-$C_4H_8^+$ ion with c-$C_5D_9(CD_3)$ (reaction 4) while $(CH_3)_2CDCH_2D$ results from reaction of an i-$C_4H_8^+$ ion (reaction 5). Furthermore, 1-$C_4H_8^+$ ions react with c-$C_5D_9(CD_3)$ to give $CH_2DCHDCH_2CH_3$:

$$\text{1-}C_4H_8^+ + C_6D_{12} \rightarrow CH_2DCHDCH_2CH_3 + C_6D_{10}^+ \qquad (9)$$

which is easily distinguishable by mass spectrometry [12] from the n-$C_4H_8D_2$ product formed in reaction 4 of the 2-$C_4H_8^+$ ion. It has been demonstrated in the mass spectrometer [10, 17] that the only reactions between the $C_4H_8^+$ ions and methylcyclopentane are H_2^- transfer reactions (analogous to the D_2^- transfer reactions 4, 5, and 9) and H^- transfer reactions:

$$C_4H_8^+ + C_6H_{12} \rightarrow C_4H_9 + C_6H_{11}^+. \qquad (10)$$

The H^- (or D^-) transfer reactions 10 lead to the formation of butyl radicals, which in our experiments will be scavenged by added oxygen; however, because of the occurrence of reaction 10, the yields of butane products formed in the H_2^- (D_2^-) transfer reactions must be corrected upwards to obtain the correct $C_4H_8^+$ ion yields. Such corrections have been made for all the results presented below. The ratios of H^- transfer to H_2^- transfer (or D^-/D_2^-) for the C_4H^+ (or $C_4D_8^+$) isomeric ions with methylcyclopentane are [10, 16]: 1-$C_4H_8^+$ –0.23; 2-$C_4H_8^+$–only H_2^- transfer; i-$C_4H_8^+$–0.14.

In certain experiments, cyclohexane has been added as an interceptor of $C_4H_8^+$ ions. It has been shown [12] that 2-$C_4H_8^+$ ions do not react with cyclohexane, while 1-$C_4H_8^+$ ions do undergo reaction 9 at a rate about one-fifth of the collision rate when C_6D_{12} is cyclohexane. (i-$C_4H_8^+$ ions react with cyclohexane to form isobutane, but at a very low rate.) Thus, the formation of n-butane in an experiment with cyclohexane additive demonstrates the presence of 1-$C_4H_8^+$ ions. (This has been confirmed by isotopic analyses of butane produced in reaction with c-C_6D_{12} in the experiments discussed below.) The ratio [10, 17] of H^-/H_2^- transfer reactions for the 1-$C_4H_8^+$-c-C_6H_{12} reaction pair is 0.06.

In the following discussion, no distinction will be made between *cis*- and *trans*-2-$C_4H_8^+$. When *cis*- and *trans*-2-C_4H_8 are photolyzed individually in the presence of dimethylamine, it is seen that isomerization between the two structures occurs readily.

2.2. Results and Discussion: Effect of Interceptor Concentration

Figure 1 shows the yields of the i-$C_4H_8^+$ and 2-$C_4H_8^+$ ions formed in the radiolysis of c-C_4H_8 at a pressure of 22 torr, as determined by varying amounts of added methylcyclopentane-d_{12}, which intercepts the ions according to reactions 4, 5 and to a minor extent, 10

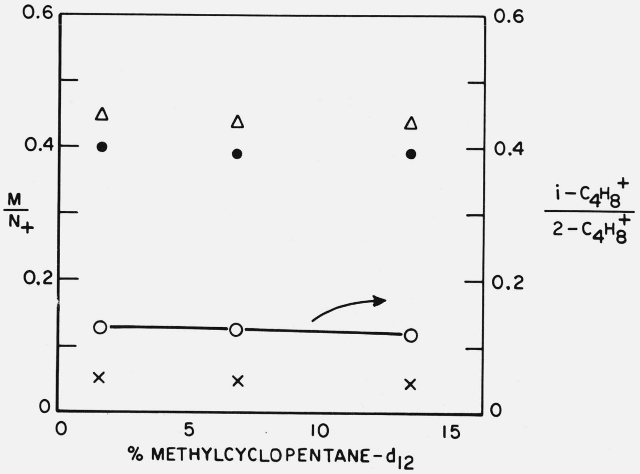

FIGURE 1. *The radiolysis of* c-C_4H_8-c-$C_5D_9(CD_3)$-O_2 *mixtures at a total pressure of 22 torr.*

The effect of methylcyclopentane concentration on the yields of intercepted i-$C_4H_8^+$ (X), 2-$C_4H_8^+$ (•), total $C_4H_8^+$ (△), and the ratio i-$C_4H_8^+$/2-$C_4H_8^+$ (○).

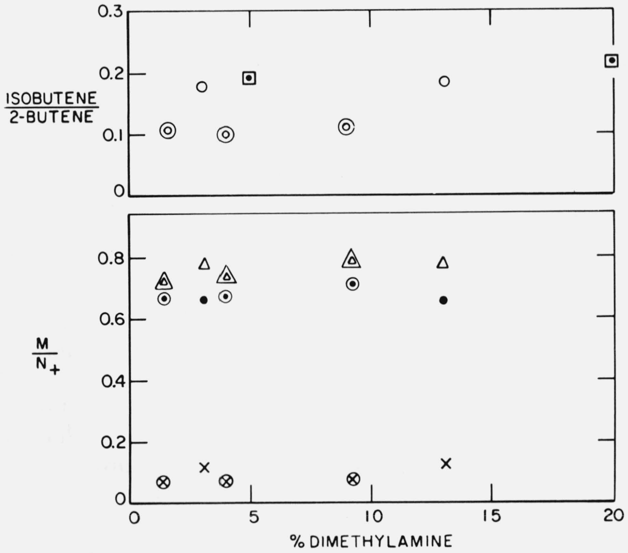

FIGURE 2. *The 11.6–11.8 eV photolysis of cyclobutane-dimethylamine mixtures in the presence of oxygen*

The effect of dimethylamine concentration on the yields of intercepted i-$C_4H_8^+$ ions (X), 2-$C_4H_8^+$ ions (•), and total $C_4H_8^+$ ions (△) in c-$C_4H_8^+$, as well as the yields of i-$C_4H_8^+$ (⊗), 2-$C_4D_8^+$ (⊙), and total $C_4D_8^+$ (◬) in c-C_4D_8. The ratios of isobutene ion to 2-butene ion are also shown: c-C_4H_8 experiments at 9 torr (○), c-C_4D_8 experiments at 4 torr (◎), and c-C_4H_8 experiments at 0.5 torr (⊡). (In the latter two experiments, absolute product yields were not measured.)

as mentioned above. It is seen that the yields of the two isomeric ions do not vary at all as a function of the concentration of interceptor. This result was verified in the 11.6–11.8 eV photolysis of c-C_4H_8 (at 9 torr and at 0.5 torr) and c-C_4D_8 (at 4 torr) in the presence of varying amounts of dimethylamine (fig. 2) which intercepts the ions through reaction 2 to form butene products. The invariance with interceptor concentration of the total yields which can be attributed to the isobutene and 2-butene ions in the cyclobutane systems demonstrates that in this system, where the ions can only react with the added reactive compound, the $C_4H_8^+$ ($C_4D_8^+$) ions are effectively intercepted.

This is in marked contrast to the result reported earlier and discussed in the Introduction, that the ratio of i-C_4H_8 to 2-C_4H_8 observed in ethylene varies as a function of the concentration of added dimethylamine at low dimethylamine concentration; the results of a similar series of experiments, in which ethylene at a pressure of 11 torr was photolyzed at 11.6–11.8 eV in the presence of varying amounts of dimethylamine, are given in figure 3. In the ethylene system, the fact that the total yields of $C_4H_8^+$ ions intercepted (fig. 3 and reference [11]) increase as a function of interceptor concentration (in the same low concentration range where the change in the i- to 2-$C_4H_8^+$ ratio is seen) suggests that the effect observed can be explained if ethylene competes for interception of the i- and 2-$C_4H_8^+$ ions when the concentration of additive is low (reaction 7). It has been reported [18] that reaction 7 between i-$C_4H_8^+$ ions and ethylene is faster than the analogous reaction of 2-$C_4H_8^+$ ions. Thus, one would predict, qualitatively, that at low concentrations of added interceptor, the ethylene would compete more effectively for the i-$C_4H_8^+$ ions than for the 2-$C_4H_8^+$ ions, producing concentration effects like those which are actually observed. Actually, the results given in the earlier study [11] and in figure 3 are what would be predicted if the rate constant of reaction 7 is $\sim 0.3 \times 10^{-10}$ cm³/molecule · s for i-$C_4H_8^+$ ions and $\sim 0.03 \times 10^{-10}$ cm³/molecule · s for 2-$C_4H_8^+$ ions[2] (assuming that the rate constant for reaction 2 with dimethylamine is 1.3×10^{-9} cm³/molecule · s [18b]). These rate constants are higher by about an order of magnitude than the rate constant which can be derived for these reactions from earlier measurements in a tandem mass spectrometer [18a]; however, the results of recent studies of reactions of thermal ions carried out in the NBS photoionization mass spectrometer [10, 17] indicate that the rate constants of the reactions of the energetic ions formed in a tandem instrument often vary widely from those observed for ions at thermal energies. In order to verify that the rate constant for reaction 7 involving thermal i-$C_4H_8^+$ ions is actually higher than the earlier literature value would indicate, i-$C_4H_8^+$ ions were generated by 10 eV photons in the NBS high pressure photoionization mass spectrometer in the presence of bulk C_2D_4 (which is not ionized at this energy). Although the results were too complex to be interpreted in detail, it was observed that both the condensation reaction

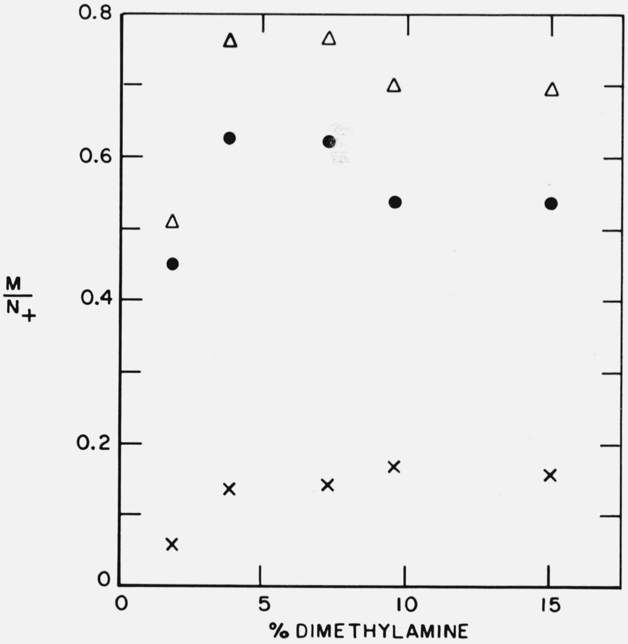

FIGURE 3a. *The 11.6–11.8 eV photolysis of ethylene-dimethylamine mixtures in the presence of oxygen at a pressure of 11 torr.*

The effect of dimethylamine concentration on the yields of intercepted i-$C_4H_8^+$ ions (X), 2-$C_4H_8^+$ ions (•), and total $C_4H_8^+$ ions (△).

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[2] Since this paper was submitted for publication, a value of 0.37×10^{-10} cm³/molecule · s has been determined for the rate constant of the reaction (2-$C_4H_8^+$ + 2-C_4H_8) by L. W. Sieck of this laboratory. Taking this value, and the relative rate constants for these reactions determined by J. M. S. Henis (J. Chem. Phys. **52,** 282 (1970)), one obtains a value of 0.026×10^{-10} for the rate constant of Reaction 7 involving 2-$C_4H_8^+$ ions.

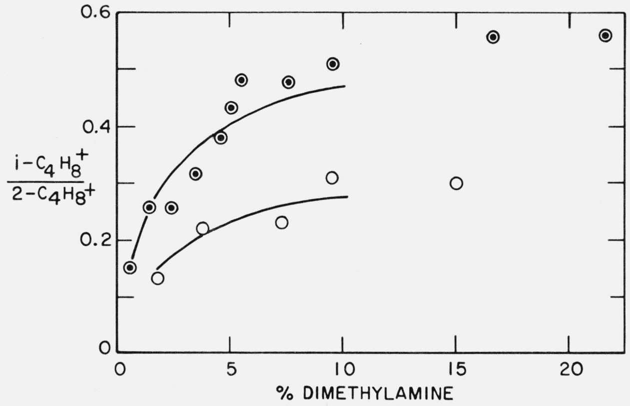

FIGURE 3b. *The ratio of* i-$C_4H_8^+$/2-$C_4H_8^+$ *intercepted in the 11.6–11.8 eV photolysis of ethylene by varying concentrations of dimethylamine as measured in this study* (○) *at a pressure of 11 torr, and in reference* [11] (⊙) *at a pressure of 2.8 torr.*

The solid lines show the ratios calculated on the assumption that the rate constant of reaction 7 is $0.3 + 10^{-10}$ cm³/molecule · s for *i*-$C_4H_8^+$ ions and $0.03 + 10^{-10}$ cm³/molecule · s for 2-$C_4H_8^+$ ions.

(reaction 7) and various D or D^+ exchange reactions—some of which led to the re-formation of butene ions—occurred; the overall rate constant of interaction between these partners was 2.7×10^{-10} cm³/molecule · s at pressures up to 0.05 torr. Although our calculated rate constant of 0.3×10^{-10} for reaction 7 involving *i*-$C_4H_8^+$ ions was not verified, the results obtained would indicate that this rate constant may be entirely feasible for the condensation reaction in the pressure region used for the photolysis and radiolysis experiments.

3. Effect of Pressure

3.1. A. Fragmentation of the $C_4H_8^+$ Ions

Figure 4 shows the effect of pressure on the yields of the *i*-$C_4H_8^+$ ($C_4D_8^+$) and 2-$C_4H_8^+$ ($C_4D_8^+$) ions as determined by the yields of the butane products in the 11.6–11.8eV photolysis of cyclobutane—methylcyclopentane mixtures. It is seen that over the pressure range from 0.1 to 10 torr, the total yield of $C_4H_8^+$ ($C_4D_8^+$) ions intercepted increases greatly; this suggests that a low pressures, some of the $C_4H_8^+$ ions undergo decomposition, but are collisionally deactivated as the pressure is raised. As has been noted before [8, 9], when cyclobutane is irradiated with 11.25 eV photons in a mass spectrometer at a pressure of approximately 10^{-5} torr, about 30 percent of the $C_4H_8^+$ ions undergo fragmentation to form $C_4H_7^+$:

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

or $C_3H_5^+$:

$$C_4H_8^+ \rightarrow C_3H_5^+ + CH_3. \qquad (12)$$

In order to check on the fragmentation mechanisms occurring in cyclobutane at the argon resonance lines, 11.6–11.8 eV, as well as the fates of the fragment ions, cyclobutane was irradiated at this energy in the NBS high pressure photoionization mass spectrometer. The results, given in figure 5, show the fragmentation and ion-molecule reaction mechanisms in pure cyclobutane. The allyl ion formed in process 12 disappears because of a rapid reaction with cyclobutane to form propene [18a]:

$$C_3H_5^+ + C_4H_8 \Rightarrow C_3H_6 + C_4H_7^+. \qquad (13)$$

The $C_4H_7^+$ ions formed in reaction 13 and fragmentation process 11 do not undergo any rapid reactions with cyclobutane; the gradual drop in the yield of $C_4H_7^+$ as the pressure is raised (fig. 5) can probably be traced to collisional quenching of the parent ion decomposition processes 11 and 12.

Returning now to the photolysis results shown in figure 4, one should see a compensating diminution in the yield of propene (from reaction 13) over the pressure range from 0.1 to 10 torr if indeed the observed increase in the total yield of $C_4H_8^+$ ($C_4D_8^+$) ions intercepted is due to a collisional quenching of dissociation process 12; this is seen, as shown in the figure.

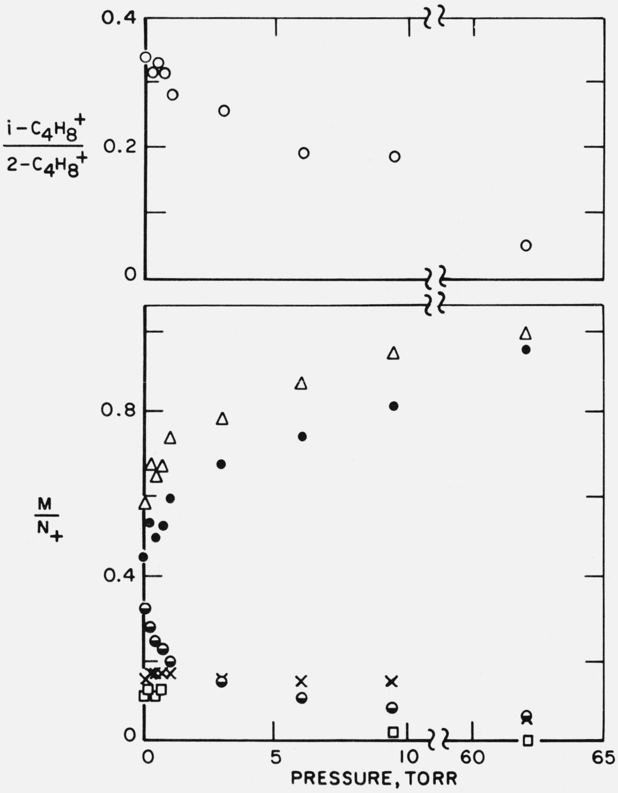

FIGURE 4a. *The 11.6–11.8 eV photolysis of a* c-C_4H_8-c-$C_5D_9(CD_3)$ *(1:0.20) mixture in the presence of oxygen*

The effect of pressure on the yield of intercepted *i*-$C_4H_8^+$ (X) and 2-$C_4H_8^+$ (•) and total $C_4H_8^+$ (△) ions, as well as the yields of propylene (◒) and methylcyclopropane (□). The ratios of isobutene ion to 2-butene ion are also shown (○).

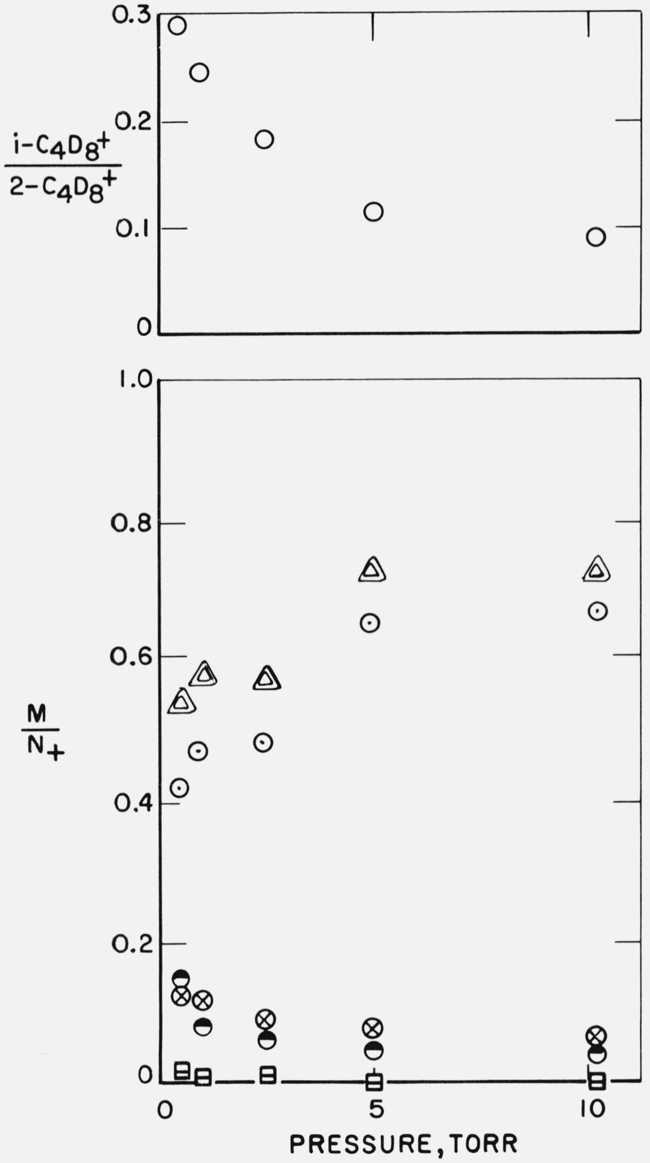

FIGURE 4b. *The 11.6–11.8 eV photolysis of a* $c\text{-}C_4D_8\text{-}c\text{-}C_5D_9(CD_3)$ *(1:0.05) mixture in the presence of oxygen.*

The effect of pressure on the yield of intercepted $i\text{-}C_4D_8^+$ (⊗), $2\text{-}C_4D_8^+$ (⊙), and total $C_4D_8^+$ (△) ions as well as the yields of propylene (◓), and methylcyclopropane (⊟). The ratios of isobutene ion to 2-butene ion are also shown (○).

In these experiments, in which methylcyclopentane is the added interceptor, the $C_4H_7^+$ ($C_4D_7^+$) ions formed by reaction 11 or 13 may undergo a hydride transfer reaction to form C_4H_7D (C_4D_8) products; they will not contribute to the formation of butane products.

In low pressure experiments in which the $C_4H_8^+$ ($C_4D_8^+$) ions are intercepted by dimethylamine, the $C_4H_7^+$ ($C_4D_7^+$) ions formed in reactions 11 and 13 might be expected to react to form butadienes. Small amounts of 1,3-butadiene ($M/N_+ \approx 0.046$ in $c\text{-}C_4H_8$ photolysis) and 1,2-butadiene ($M/N_+ \approx 0.0026$ in $c\text{-}C_4H_8$ photolysis) are observed in such experiments, but the yields do not differ significantly from the yields of these products observed in methylcyclopentane additive experiments (where the 1,3-butadiene yield is ≈ 0.055 and that of 1,2-butadiene ≈ 0.0020 under similar conditions). At any rate, the $C_4H_7^+$ ($C_4D_7^+$) ions formed at low pressures in the presence of dimethylamine do not apparently contribute appreciably to the formation of the butene products; this is shown by the results given in figure 6, which gives the yields of the $i\text{-}C_4D_8$ and $2\text{-}C_4D_8$ products (see reaction 2) formed in the 11.6–11.8 eV photolysis of a $c\text{-}C_4D_8\text{-}(CH_3)_2NH$ mixture over the 0.1–10 torr pressure range. The yields which are attributed to the *i*- and $2\text{-}C_4D_8^+$ ions intercepted in these experiments are in close agreement with the yields which were attributed to these same ions in the D_2^- transfer experiments shown in figure 4b. This agreement also demonstrates that apparently both compounds intercept the $C_4D_8^+$ ions quantitatively under these conditions.

In the photolysis of ethylene over this pressure region, from 0.1 to 10 torr, it was shown some time ago [6c] that the overall yields of $C_4H_8^+$ ions intercepted by NO increase drastically as a function of pressure up to about 10 torr, indicating that the $C_4H_8^+$ ions formed in reaction 1 undergo dissociation at low pressure and are collisionally stabilized as the pressure is increased. This result is confirmed here in experiments in which the $C_4H_8^+$ ions in ethylene were intercepted by dimethylamine and by methylcyclopentane, both shown in figure 7. The $C_4H_8^+$ ions formed in ethylene have more internal energy than the cyclobutane parent ions (table 1), and it is to be expected that they also should dissociate in this pressure region.

It is significant that the yields, as well as the ratios, of ions intercepted in these ethylene experiments by

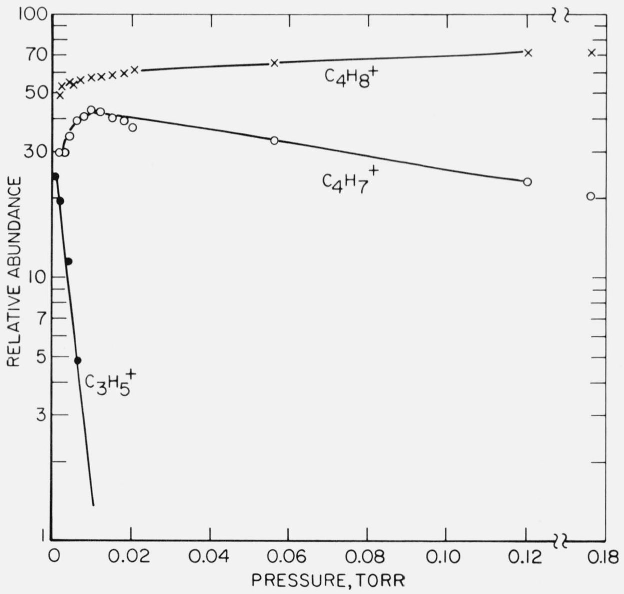

FIGURE 5. *The relative abundance of ions observed as a function of pressure in* $c\text{-}C_4H_8$ *irradiated with 11.6–11.8 eV photons in the NBS high pressure photoionization mass spectrometer.*

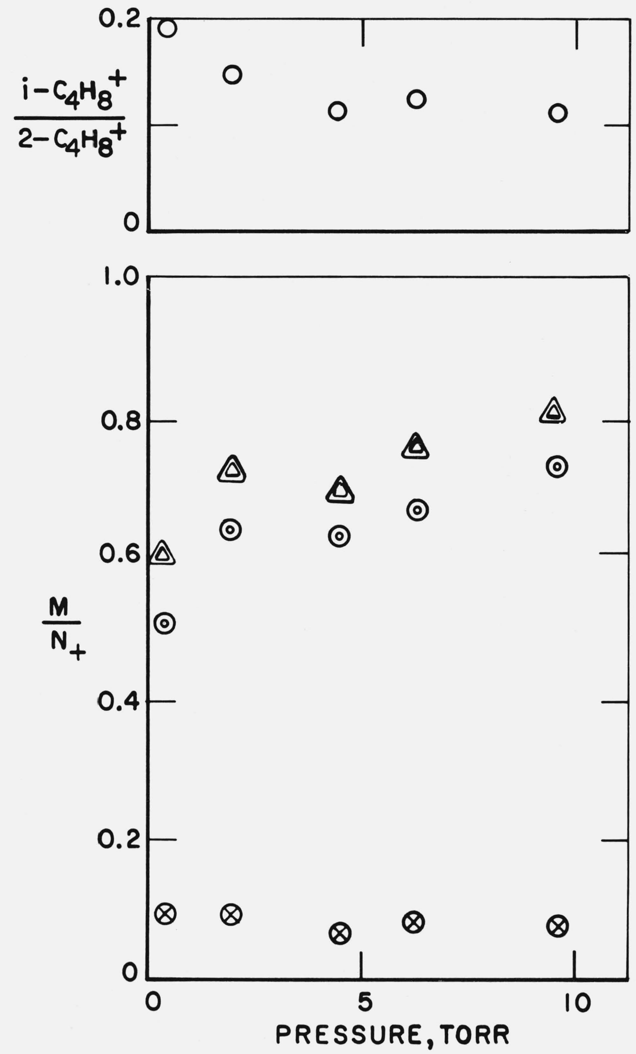

FIGURE 6. *The 11.6–11.8 eV photolysis of a* c-C_4D_8-$(CH_3)_2NH$ *mixture (1:0.09) in the presence of oxygen.*

The effect of pressure on the yields of intercepted *i*-$C_4D_8^+$ (⊗), 2-$C_4D_8^+$ (⊙), total $C_4D_8^+$ (△) and the ratio *i*-$C_4D_8^+$/2-$C_4D_8^+$ (○).

methylcyclopentane are greatly different from those observed in the dimethylamine additive experiments (both shown in fig. 7) in contrast to the agreement seen between these two kinds of experiments in cyclobutane (figs. 4b and 6). Because the $C_4H_8^+$ ions react only about 3–6 percent as fast with methylcyclopentane as with dimethylamine [12], one would predict that the ethylene would compete much more effectively for the $C_4H_8^+$ ions (through reaction 7) in the methylcyclopentane additive experiments. In fact, assuming that the rate constants for reaction 7 are (as estimated above from the dimethylamine results given in fig. 3) 0.3×10^{-10} cm³/molecule · s for *i*-$C_4H_8^+$ ions and 0.03×10^{-10} cm³/molecule · s for 2-$C_4H_8^+$ ions, and taking the measured rate constants [17] for the D_2^- transfer reactions between these ions and methylcyclopentane-d_{12} (and estimating from the results given in reference [11] that the total ion pair yields of the *i*- and 2-$C_4H_8^+$ ions at a pressure of 2.8 torr are 0.20 and 0.38, respectively), one can calculate the yields of ions which would be intercepted by 10 percent methylcyclopentane-d_{12} at 2.8 torr; as shown by the encircled points in figure 7, these calculated yields are in good agreement with the measured butane yields in this pressure region.

3.2. Yields of the Isomeric $C_4H_8^+$ Ions

The relative yields of the *i*-$C_4H_8^+$ ($C_4D_8^+$) and 2-$C_4H_8^+$ ($C_4D_8^+$) ions depend on the pressure of the system, even when the overall pressure is high enough that fragmentation of the $C_4H_8^+$ ($C_4D_8^+$) ions is effectively quenched. This can be readily seen in figure 4a, by comparing the 9.5 torr experiment (M/N_+ of total $C_4H_8^+ = 0.95$) with the 62 torr experiment (M/N_+ of total $C_4H_8^+ = 1.0$); the yield of intercepted *i*-$C_4H_8^+$ drops drastically, and the drop is compensated by an increase in the yield of 2-$C_4H_8^+$. There is also a significant diminution in the ratio *i*-$C_4H_8^+$/2-$C_4H_8^+$ with increasing pressure for ions generated in ethylene, even in the pressure range where all fragmentation has been inhibited, as shown by the results given in figure 8 for the radiolysis and

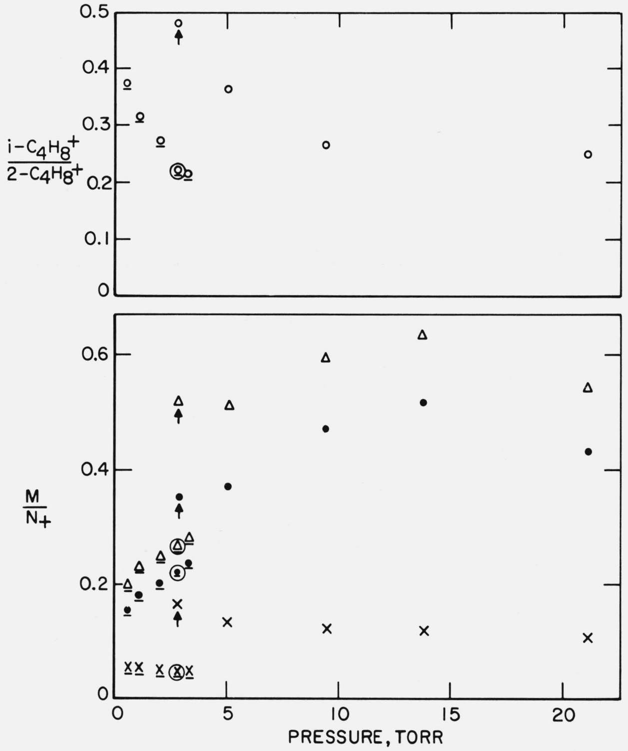

FIGURE 7. *The effect of pressure on the yields of* i-$C_4H_8^+$ (X), 2-$C_4H_8^+$ (●), *total* $C_4H_8^+$ (△), *and the ratio* i-$C_4H_8^+$/2-$C_4H_8^+$ (○) *intercepted in the 11.6–11.8 eV photolysis of ethylene by 10 percent methylcyclopentane*-d_{12} *(underlined points) or by 7 percent dimethylamine.*

Arrows designate experimental points for 7.6 percent dimethylamine experiment from Reference 11. Encircled points are yields one would predict for a methylcyclopentane additive experiment, assuming the estimated rate constants for reaction 7 given in the discussion.

TABLE 1. *Heats of formation of* $C_4H_8^+$ *isomers*

$C_4H_8^+$ Isomer	ΔH_f eV
$C_2H_4^+ + C_2H_4$	11.51
c-$C_4H_8^+$	10.84
c-$C_3H_5(CH_3)^+$ [a]	10.15
1-$C_4H_8^+$	9.58
i-$C_4H_8^+$	9.06
cis-2-$C_4H_8^+$	9.06
tr-2-$C_4H_8^+$	9.02

All values, except c-$C_3H_5(CH_3)^+$, from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, National Standard Reference Data System—NBS, **26,** U.S. Govt. Printing Office (1969).

[a] The heat of formation of the methylcyclopropane ion is calculated assuming that the ionization potential of the neutral molecule is 9.9 eV (F. H. Field, footnote in J. L. Franklin, J. Chem. Phys. **22,** 1304 (1954)). This value, which was chosen because we observed ionization of pure methycyclopropane irradiated with 10.0 eV photons ($\Phi_+ = 0.13$ [16]). is within the limits of error of the more recent value of 10.1 ± 0.02 eV (G. G. Meisels, J. Y. Park, and B. G. Geissner, J. Am. Chem. Soc. **92,** 254 (1970)).

photolysis of ethylene in the presence of charge acceptor.

In order to examine the effect of pressure over a much wider pressure range, a series of radiolysis experiments were performed on a c-C_4H_8-c-$C_5D_9(CD_3)$ (1:0.050) mixture (fig. 9). An isotopic analysis of the n-butane formed at higher pressures revealed that these butanes consisted of a mixture of $CH_3CHDCHDCH_3$ formed in reaction 4 of the 2-$C_4H_8^+$ ion, and $CH_2DCHDCH_2CH_3$ formed in reaction 9 of the 1-$C_4H_8^+$ ion. The presence of 1-$C_4H_8^+$ ions was confirmed by the results of two other series of experiments. First, (fig. 10), when a c-C_4D_8-$(CH_3)_2NH$ (1:0.08) mixture was irradiated at different pressures ranging from 7 torr to 418 torr, the combined yield of intercepted (i-$C_4D_8^+$ + 1-$C_4D_8^+$) increased. Mass spectrometric analysis confirmed that the increase could be attributed to 1-butene. The presence of 1-$C_4H_8^+$ ions was also confirmed by the observation of n-butane [20] in irradiated c-C_4H_8 in the presence of 5 percent cyclohexane; as mentioned above, cyclohexane will intercept 1-$C_4H_8^+$ ions through a $H_2^-(D_2^-)$ transfer reaction, but is unreactive toward 2-$C_4H_8^+$ ions [10, 12, 17]. The yield of 1-$C_4H_8^+$ ions, as determined in both the methylcyclopentane and cyclohexane additive experiments (fig. 9) increased as a function of pressure, while the yield of intercepted i-$C_4H_8^+$ ions dropped off rapidly.

In the high pressure experiments given in figures 9 and 10, the total yield of products which can be attributed to $C_4H_8^+$ ion precursors diminishes with pressure. There are two possible explanations for this: collisional stabilization of adduct ions formed in the $C_4H_8^+$-interceptor encounter, or collisional stabilization of the parent c-$C_4H_8^+$ ions. It should be pointed out that in the liquid [21] and solid [22] phase radiolysis of ethylene, as well as in the solid phase photolysis [22] at 11.6–11.8 eV, cyclobutane is observed as an important product. (In the solid phase photolysis at 8.4 eV, where ionization of ethylene is unimportant, cyclobutane is not observed, so it may be inferred that it has an ionic precursor.) Cyclobutane grows in as a product in the radiolysis of ethylene at very high pressures [23] (> 1 atm). It is tempting to postulate that the $C_4H_8^+$ ion formed in reaction 1 is stabilized in the cyclobutane structure and somehow ends up as neutral cyclobutane. However, it must be pointed out that the mode of formation of the cyclobutane product in ethylene may be plausibly explained in other ways [22].

4. Isomerization Mechanisms of $C_4H_8^+$ Ions

From the results discussed above, it is now possible to derive certain information about the isomerization mechanisms operative in $C_4H_8^+$ ions. These results suggest a mechanism in which the initially formed $C_4H_8^+$ ions rearrange to lower energy structures (see table 1) at a rate which is approximately of the same order of magnitude as the collision rate (10^7–10^{10} s^{-1}). As the pressure is increased, some of the processes which require longer times to occur (i.e. rearrangement to the i-$C_4H_8^+$ structure, for example)

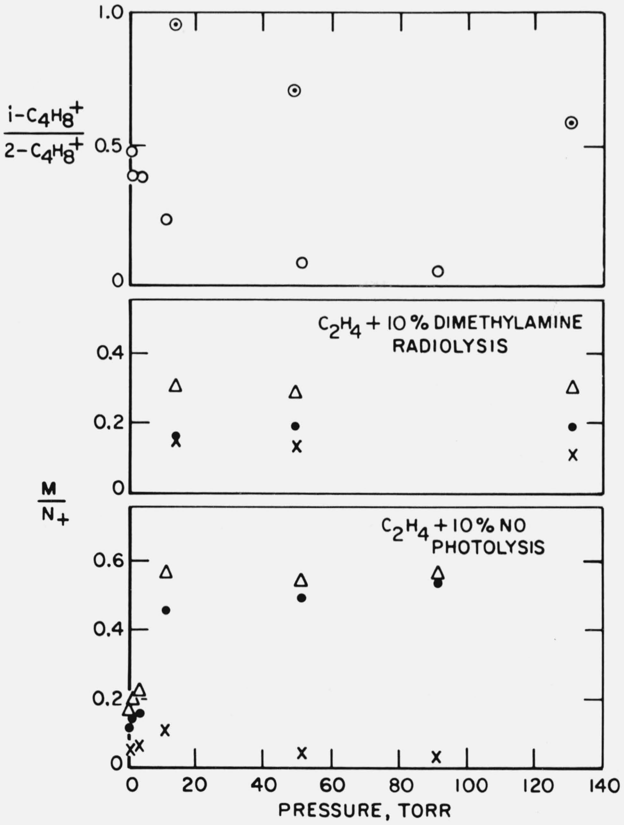

FIGURE 8. *The effect of pressure on the yields of intercepted* i-$C_4H_8^+$ (X), *and* 2-$C_4H_8^+$ (●) *and* ***total*** $C_4H_8^+$ (△) *ions in the 11.6–11.8 eV photolysis and the radiolysis of ethylene-charge acceptor mixtures in the presence of oxygen.*

The i-$C_4H_8^+$/2-$C_4H_8^+$ ratio in the photolysis (○) and radiolysis (○) is also shown.

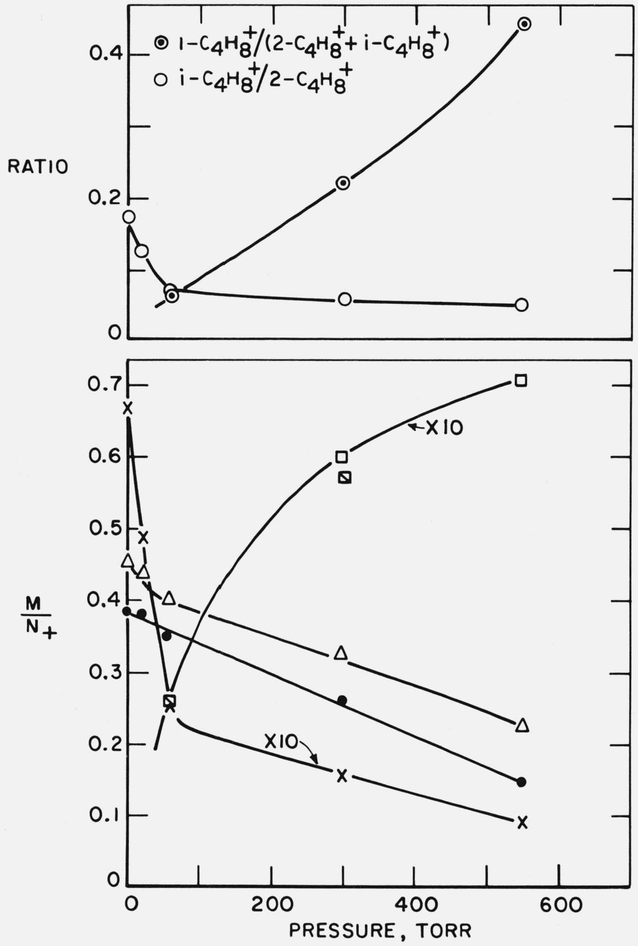

FIGURE 9. *The effect of pressure on the yields of intercepted* i-$C_4H_8^+$ (X), 2-$C_4H_8^+$ (●), 1-$C_4H_8^+$ (□), *and total* $C_4H_8^+$ (△) *in the radiolysis of a* c-C_4H_8-c-C_5D_9 (CD_3) *(1:0.05) mixture in the presence of 3 percent oxygen, as well as the ratios,* i-$C_4H_8^+$/2-$C_4H_8^+$ (○) *and* 1-$C_4H_8^+$/(2-$C_4H_8^+$ + i-$C_4H_8^+$) (⊙).

Also shown are the yields of 1-$C_4H_8^+$ (⧅) as determined from the *n*-butane yields in the radiolysis of a *c*-C_4H_8-*c*-C_6H_{12} mixture, in the presence of 3 percent oxygen.

may be quenched, while some of the higher energy ions (i.e., 1-$C_4H_8^+$) are deactivated or intercepted before having time to isomerize further. The unimolecular rate constants for isomerizations increase with energy. At high enough energies, however, dissociation of the ions will occur (that is, in cyclobutane, the onset of fragmentation is about 0.7 eV above the ionization potential). This means that very fast (i.e., very high energy) isomerization processes may not be observed in experiments such as those reported here.

It is not surprising that the rate of isomerization is the same order of magnitude as the rate of collision. For the $C_4H_8^+$ ion formed in cyclobutane by absorption of 11.6–11.8 eV photons, the main fragmentation process (fig. 5) is the loss of a methyl radical (process 12). Clearly, this fragmentation must involve a rearranged $C_4H_8^+$ structure, and one may therefore assume that the isomerization is at least as fast as the dissociation, which the data given in figure 5 indicate occurs with a rate of the order of 10^6–10^7 s^{-1}. At higher energies, where the rate of fragmentation will be faster, rearrangement becomes much less important, as indicated by the fact that the $C_2H_4^+$ ion is a much more important ion in the 70 eV mass spectral cracking pattern of cyclobutane [18c] (this ion comprises only 1.5 percent of the total ionization in the 11.6–11.8 eV experiments given in fig. 5) than in any of the other isomeric C_4H_8 compounds. It has been noted before that the cyclohexane ion undergoes rearrangement before undergoing low energy fragmentation processes, but maintains the parent structure in high energy dissociations [12].

This mechanism, of course, assumes that 1-$C_4H_8^+$ ions can isomerize to other structures, contrary to the observation reported earlier that when 1-$C_4H_8^+$ ions are formed by photolyzing 1-C_4H_8 with 10 eV photons, isomerization processes are not observed [12]. In order to check on this, 1-C_4H_8 was photolyzed in the presence of dimethylamine with 10 eV and with 11.6–11.8 eV photons; the yields of the 2-$C_4H_8^+$ ions intercepted (reaction 2) are given in table 2. (Analysis of *i*-C_4H_8

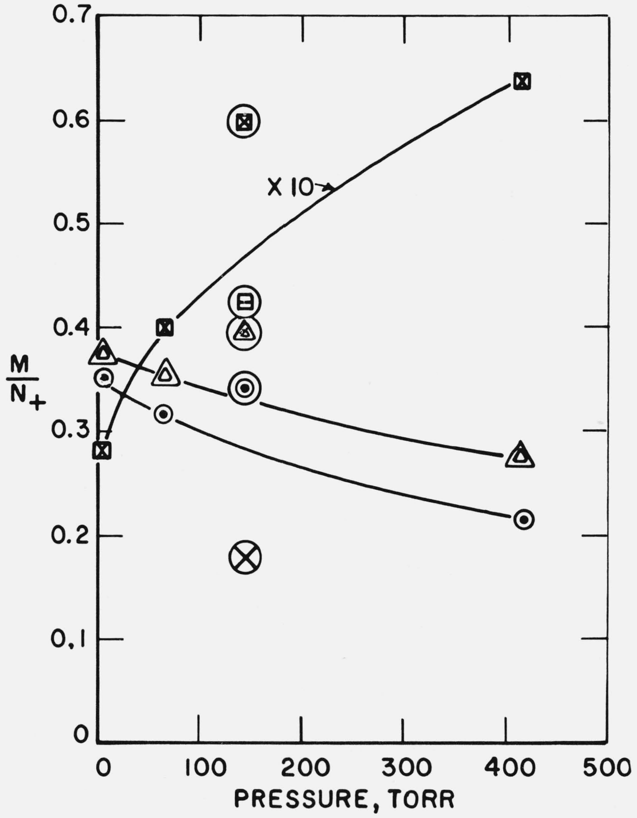

FIGURE 10. *The effect of pressure on the yields of intercepted* (i-$C_4D_8^+$ + 1-$C_4D_8^+$) *ions* (☒), 2-$C_4D_8^+$ *ions* (⊙), *and total* $C_4D_8^+$ *ions* (▲) *in the radiolysis of a* c-C_4D_8-$(CH_3)_2$NH (1:0.08) *mixture in the presence of oxygen.*

Encircled points show, for comparison, the yields of i-$C_4D_8^+$ (X), 1-$C_4D_8^+$ (⊟), 2-$C_4D_8^+$, total $C_4D_8^+$, and the sum (i-$C_4D_8^+$ + 1-$C_4D_8^+$) intercepted by 5 percent methylcyclopentane in the radiolysis of c-C_4D_8.

TABLE 2. *The photolysis of butene-dimethylamine (1:1) mixtures at a pressure of 2 torr; the interception of* $2\text{-}C_4H_8^+$ *ions*

	$M/N_+(2\text{-}C_4H_8^+)$	
	10.0 eV	11.6–11.8 eV
$1\text{-}C_4H_8$	0.05	0.63
$1\text{-}C_4H_8+180$ torr Ne		.52
$i\text{-}C_4H_8$	.002	.050
$i\text{-}C_4H_8+130$ torr Ne		.025

could not be carried out.) It is seen that, indeed, when the ions are formed by absorption of 10 eV photons, isomerization to the $2\text{-}C_4H_8^+$ structure is unimportant, but when the photon energy is raised to 11.6–11.8 eV, at a pressure of 2 torr more than half the ions do rearrange to the $2\text{-}C_4H_8^+$ structure. Furthermore, the importance of this isomerization can be diminished by increasing the pressure, as was demonstrated by photolyzing the $1\text{-}C_4H_8\text{-}(CH_3)_2NH$ mixture in the presence of added neon (table 2). Thus, the isomerization of the $1\text{-}C_4H_8^+$ ion to the $2\text{-}C_4H_8^+$ structure requires that the ions have excess energy; removal of energy by collisions diminishes the probability that the isomerization will occur. The $C_4H_8^+$ ions formed in ethylene and in cyclobutane will have at least 1.93 and 0.67 eV excess energy above the energy of the $1\text{-}C_4H_8^+$ ion (table 1). It is easy to visualize plausible pathways by which such ions could rearrange to the $1\text{-}C_4H_8^+$ structure; for instance:

$$c\text{-}C_4H_8^+ \rightarrow [+CH_2CH_2CH_2CH_2\cdot]^*$$

$$\rightarrow [CH_3\overset{+}{C}HCH_2CH_2\cdot]^*$$

$$\rightarrow CH_3CH_2CH^+=CH_2. \qquad (14)$$

Once the ion has attained the $1\text{-}C_4H_8^+$ structure, the results indicate that it will continue to rearrange to the $2\text{-}C_4H_8^+$ (and probably also to the $i\text{-}C_4H_8^+$) structure, unless sufficient energy is removed by collisions before these rearrangements occur, or unless the excited ion is intercepted before rearrangements occur. In order to distinguish between these two possible interpretations of the observed increase in the yield of $1\text{-}C_4H_8^+$ ions intercepted as the pressure is increased, a series of radiolysis experiments was performed in which the concentration of dimethylamine added to $c\text{-}C_4H_8$ was varied at a pressure of 300 torr, where, as shown above (fig. 9) a significant yield of $1\text{-}C_4H^+_8$ ions can be intercepted. If at high pressures, we are simply intercepting excited $1\text{-}C_4H_8^+$ ions before they have time to isomerize, we should see the yield of intercepted ions increase as the concentration of dimethylamine is increased (i.e. as the time before interception is decreased), but if the ions are collisionally deactivated before interception, there should be little effect of interceptor concentration. The results (fig. 11) indicate that a change in interceptor concentration has, at most, only a slight effect on the ratio of $1\text{-}C_4H_8^+$ to $2\text{-}C_4H_8^+$ ions intercepted. The ratio $1\text{-}C_4H_8^+/2\text{-}C_4H_8^+$ at 2 percent dimethylamine (where 1 collision in 49 is with interceptor) is only about 10 percent lower than at 16 percent dimethylamine (where 1 collision in 5 is with interceptor). We can conclude, then, that most of the $1\text{-}C_4H_8^+$ ions intercepted have been collisionally deactivated.

If the isomerization mechanism proposed here is valid, then it would be expected that if one could form $C_4H_8^+$ ions having a somewhat lower initial energy than those generated in cyclobutane and ethylene, then the intermediate $1\text{-}C_4H_8^+$ ion should be more easily deactivated. The methylcyclopropane ion is such an ion (table 1). Therefore, a methylcyclopropane-methylcyclopentane-d_{12} mixture was photolyzed with 11.6–11.8 eV photons in the presence of varying amounts of xenon (fig. 12). The methylcyclopropane ion apparently isomerizes through the same pathway(s) followed by the $C_4H_8^+$ ion generated in ethylene and by the cyclobutane parent ion. That is, at low pressures, all ions intercepted are in the $i\text{-}C_4H_8^+$ and $2\text{-}C_4H_8^+$ configurations, with the latter predominating. As the pressure is increased the importance of the $i\text{-}C_4H_8^+$ ion diminishes relative to that of the $2\text{-}C_4H_8^+$ ion, and eventually, the $1\text{-}C_4H_8^+$ ion grows in at the expense of the *i*- and $2\text{-}C_4H_8^+$ ions. Because the yields of ions intercepted were strongly dependent on the concentration of interceptor, suggesting that the ions react with the parent methylcyclopropane molecule, methyl-

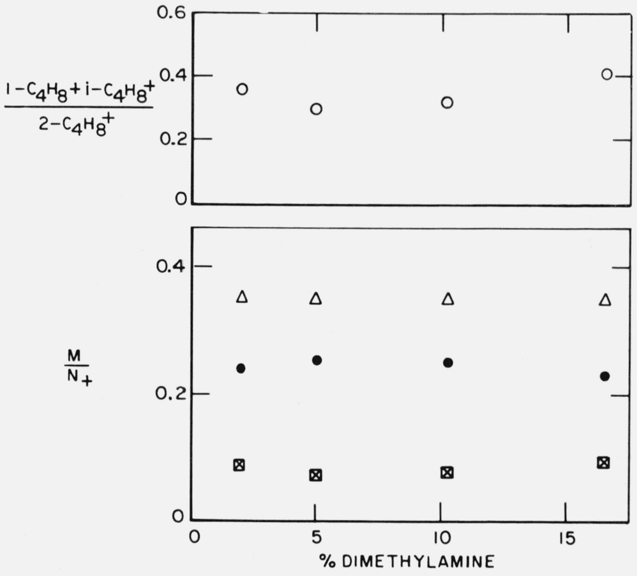

FIGURE 11. *The effect of dimethylamine concentration on the yields of intercepted* $2\text{-}C_4H_8^+$ (●), $1\text{-}C_4H_8^+ + i\text{-}C_4H_8^+$ (☒), *and total* $C_4H_8^+$ (△), *as well as the ratio* $(1\text{-}C_4H_8^+ + i\text{-}C_4H_8^+)/2\text{-}C_4H_8^+$, *in the radiolysis of* $c\text{-}C_4H_8^+\text{-}(CH_3)_2NH$ *mixtures in the presence of oxygen at a total pressure of 300 torr.*

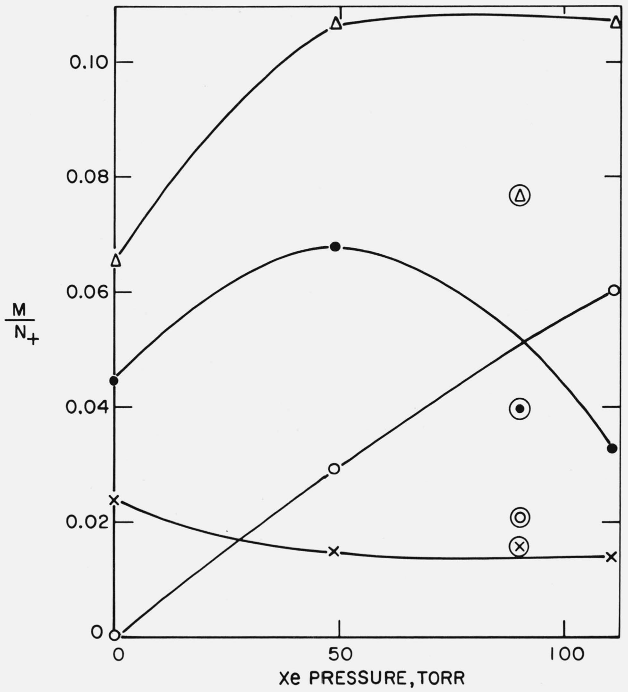

FIGURE 12. *The 11.6–11.8 eV photolysis of 2 torr of a methylcyclopropane-methylcyclopentane-*d_{12} *(1:0.12) mixture (in the presence of 3 percent oxygen), in the presence of added xenon.*

Points show the yields of i-$C_4H_8^+$ (X), 2-$C_4H_8^+$ (●), 1-$C_4H_8^+$ (○), and total $C_4H_8^+$ (△), derived from the yields of the appropriate butane products. Encircled points indicate an experiment performed in the presence of added helium.

cyclopropane was ionized with 11.6–11.8 eV photons in the NBS high pressure photoionization mass spectrometer. The $C_4H_8^+$ ion was seen to react with the parent molecules with a rate constant of 6×10^{-11} cm³/molecule · s; product ions were $C_5H_{10}^+$ (69%), $C_5H_9^+$ (8.8%), $C_6H_{11}^+$ (8.0)%, $C_6H_{12}^+$ (7.6%), and $C_7H_{13}^+$ (6.6%). Because of the occurrence of these reactions, the actual yields of intercepted ions shown in figure 12 have little significance. It is important, however, that when 110 torr of xenon have been added, 56 percent of all $C_4H_8^+$ ions intercepted are in the 1-$C_4H_8^+$ configuration. By contrast, in the 11.6–11.8 eV irradiation of a similar cyclobutane-methylcyclopentane mixture in the presence of 150 torr of xenon, only 2 percent of the $C_4H_8^+$ ions intercepted are in the 1-$C_4H_8^+$ configuration.

The question may be raised of whether or not the $C_4H_8^+$ ions initially formed in ethylene and cyclobutane isomerize to the methylcyclopropane structure. Methylcyclopropane was not observed as a product in the photolysis or radiolysis of cyclobutane in the presence of charge acceptor. However, in the photolysis of cyclobutane at relatively low pressures (0.1–10 torr) in the presence of methylcyclopentane as an interceptor (fig. 4), methylcyclopropane was seen as a product. This product was not seen in the photolysis of a similar mixture below the ionization potential (i.e., at 10 eV), so it may be inferred that it has an ionic precursor. It is feasible that excited methylcyclopropane ions may undergo charge transfer with methylcyclopentane [24], but undergo ring opening when colliding with polar molecules such as dimethylamine. At any rate, the yield of the methylcyclopropane product (fig. 4) is strongly diminished by an increase in pressure, and has essentially vanished at a pressure of 10 torr; if this product does reflect the yield of methylcyclopropane ions in the system, one must conclude that ring closure in the excited $C_4H_8^+$ ions is a slow process which is readily quenched by collisions.

No methylcyclopropane was formed in any ethylene experiment, either in pure ethylene or in the presence of dimethylamine or of methylcyclopentane. A recent paper [25] reports that methylcyclopropane is formed in the 10.2 eV photolysis of ethylene through a reaction of an excited C_2H_4 species with ethylene. A careful examination of the products formed in the 10.0 eV photolysis of ethylene failed to confirm the presence of this product. The quantum yield of this product must be less than 2×10^{-4}.

The results given above demonstrate that at low pressures most of the $C_4H_8^+$ ions formed in ethylene and cyclobutane end up in the i- and 2-$C_4H_8^+$ structures, and that the isomerization to the i-$C_4H_8^+$ structure occurs from some excited entity which, after undergoing collisions, has a lowered probability of rearranging to the i-$C_4H_8^+$ structure and an increased probability of ending up in the 2-$C_4H_8^+$ structure. This excited precursor of the i-$C_4H_8^+$ ion is most likely the 1-$C_4H_8^+$ ion, but we can not exclude the possibility that some of the i-$C_4H_8^+$ may have the 2-$C_4H_8^+$ ion as precursor although this is probably unlikely. Taking the ratio i-$C_4H_8^+$/2-$C_4H_8^+$ as an approximate measure of the energy of the ions under given conditions, we see from the results given in table 3 that, as one would expect, at a given pressure the internal energy content of an ion is lower for ions with a lower initial energy. It is interesting that for $C_4H_8^+$ ions formed in ethylene, the average energy of the ion at a given pressure is much greater in the radiolysis than in the photolysis experiments. This probably reflects the fact that in the photolysis, these ions can be formed with, at most 1 eV excess energy, while in the

TABLE 3. *The ratio of intercepted isobutene to 2-butene ions as a function of the energy with which the ion is initially formed*

Ion Source	Ion minimum initial energy	i-$C_4H_8^+$/2–$C_4H_8^+$ (or i-$C_4D_8^+$/2–$C_4D_8^+$) 10 torr	50 torr
C_2H_4 Radiolysis	11.51 eV	[a] 0.5–1.0	[a] 0.3 ~ 0.7
C_2H_4 Photolysis		~.26	.08
c-C_4H_8 Radiolysis	10.84 eV	.13	.07
c-C_4H_8 Photolysis		~.13	~.07
c-C_4D_8 Photolysis		.09	...

[a] Nitric oxide additive experiments give the low values, and dimethylamine additive experiments give the high values.

radiolysis much higher energy ethylene ions may be formed and undergo reaction 1; the ethylene ion does not fragment unless it has 2.9 eV excess energy). In the cyclobutane experiments on the other hand, the results given in table 3 indicate that the ions are formed with about the same energy in the photolysis and radiolysis. This is not surprising, since in cyclobutane the onset of fragmentation is only about 0.7 eV above the ionization potential, so there is less likelihood for very energetic ions to survive as $C_4H_8^+$ species.

Further corroborative evidence for the mechanism proposed here is given by the isotope effects observed in some of the experiments reported above. for instance, in figure 2, it is seen that the yield, relative or absolute, of the isobutene ion intercepted in c-C_4D_8 is lower than that intercepted in c-C_4H_8, even though the pressure of the C_4D_8 experiments is less than half that of the C_4H_8 experiments. The results shown in figure 4 demonstrate that the pressure effect on the relative yield of the isobutene ion is indeed much more pronounced for the deuterated cyclobutane molecule than for the nondeuterated. It is to be expected that the deuterated ion would lose energy through collisions more readily than the nondeuterated ion, because of a closer spacing of vibrational levels in the excited deuterated species.

Finally, one must ask whether the i-$C_4H_8^+$ and 2-$C_4H_8^+$ ions, once formed, undergo any further rearrangements. In order to obtain a partial answer to this question, i-C_4H_8 was photolyzed with 10 eV and with 11.6–11.8 eV photons in the presence of dimethylamine; the results are given in table 2. It was seen that in the 10 eV photolysis, isomerization of the i-$C_4H_8^+$ ion to the 2-$C_4H_8^+$ structure is negligible, as reported before. When the energy of the photons was raised, 5 percent of the i-$C_4H_8^+$ ions were seen to isomerize to the 2-$C_4H_8^+$ structure. This rearrangement was, however, quenched by the addition of neon. A more detailed discussion of the isomerization reactions and pressure effects of $C_4H_8^+$ ions generated in butenes will be presented elsewhere [26].

5. Collisional Deactivation of Intermediate $C_4H_8^+$ Ions by Added Gases

It is of interest, to examine the relative efficiencies of various gases in removing energy from the excited intermediate ion(s). Therefore, a c-C_4H_8-c-$C_5D_9(CD_3)$ (1:0.05) mixture, with 3 percent oxygen added as a radical scavenger, was irradiated with 11.6–11.8 eV photons in the presence of varying amounts of helium, hydrogen, neon, nitrogen, krypton, xenon, and carbon dioxide. (As mentioned above, 1-$C_4H_8^+$ ions are not observed to any significant extent in these experiments; in the presence of 150 torr of xenon, only 2 percent of the $C_4H_8^+$ ions intercepted are in the 1-$C_4H_8^+$ structure.) The overall product yields observed in the nitrogen and neon additive experiments are given in table 4. As above, the ratio i-$C_4H_8^+$/2-$C_4H_8^+$ was taken as an approximate measure of the deactivation of the ions. It was noted that the extent of lowering of the ratio at a given pressure seemed to depend approximately on the polarizability of the deactivating gas but was not apparently related to any other parameter (such as the rate of collision, the mass of the neutral species, etc.); this is shown in figure 13 for experiments in which 8 torr, 20 torr, and 50 torr of deactivator have been added to 0.2 torr of the hydrocarbon mixture. Thus, from these results we can conclude that the effectiveness of energy transfer from the excited ion to the collision partner depends on the polarizability of the added gas. This is not surprising, since it might be expected that a collision with a more polarizable species would be more "sticky" and that such "sticky" collisions would facilitate energy transfer.

A quantitative treatment of the data for these experiments is not actually feasible at the present time. That is, the relevant detailed mechanisms and unimolecular

TABLE 4. *The 11.6–11.8 eV photolysis of 0.2 torr of a cyclobutane-methylcyclopentane*-d_{12}-O_2 *(1:0.05:0.04) mixture in the presence of added unreactive gases*

Additive	Relative polarizability	Pressure torr	Quantum yields							i-C_4H_{10}/n-C_4H_{10}
			Ethylene	Acetylene	i-C_4H_{10}	n-C_4H_{10}	c-C_3H_5 (CH_3)	i-C_4H_8 + 1-C_4H_8	2-C_4H_8	
None	....	0.2	0.56	0.35	0.094	0.30	0.046	0.017	0.031	0.313
Neon	0.392	20.	.57	.34	.068	.33	.028	.014	.016	.206
		105.	.58	.33	.059	.41	.018	.018	.024	.143
		398.	.59	.32	.045	.44	.0058	.023	.028	.102
Nitrogen	1.730	8.	.57	.34	.073	.35	.029	.014	.0082	.209
		20.	.56	.35	.068	.35	.013	.011	.013	.194
		105.	.58	.33	.051	.41	.0086	.028	.024	.124
		345.	.61	.30	.020	.28	.000	.029	.015	.072

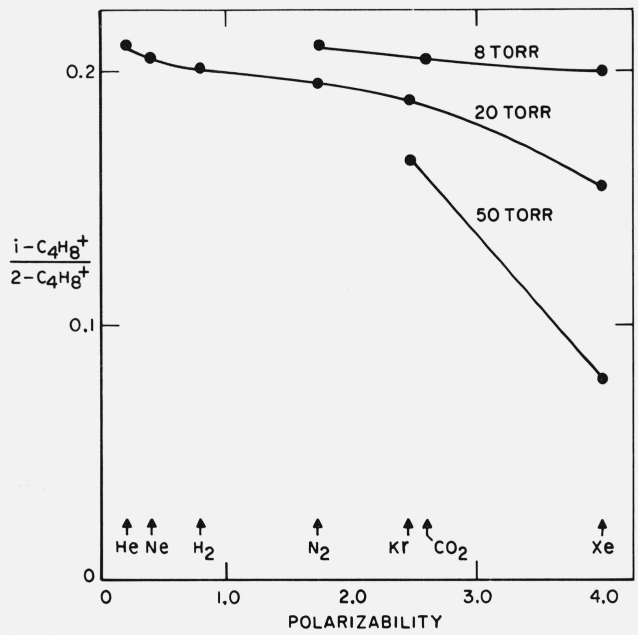

FIGURE 13. *The ratio of* i-$C_4H_8^+$/2-$C_4H_8^+$ *intercepted by 5 percent methylcyclopentane*-d_{12} *in* c-C_4H_8 *irradiated with 11.6–11.8 eV photons at a pressure of 0.2 torr in the presence of 8, 20, or 50 torr of added foreign gas plotted as a function of the polarizabilities of the added compounds.*

rate constants for the isomerization reactions to form *i*-$C_4H_8^+$ and 2-$C_4H_8^+$ are not only unknown, but dependent on the internal energy of the rearranging species. It is not possible now to estimate the energy or the energy distribution of these excited entities.

Similar experiments examining the deactivation of the $C_4H_8^+$ ions formed in the ethylene system would be quite difficult to interpret, since the precursor $C_2H_4^+$ ions would also be deactivated by the added gases, thus shifting the energy distribution of the product $C_4H_8^+$ ions toward lower energies. Therefore, any effects observed would be composites of the deactivation of the $C_2H_4^+$ ions and the $C_4H_8^+$ ions. Ethylene ions formed at 11.6–11.8 eV do have excess internal energy which is retained in the product $C_4H_8^+$ ions. Indeed, it has been seen [18b] that the relative importance of dissociation processes 11 and 12 differs for $C_4H_8^+$ ions formed in ethylene irradiated with 10.0 and with 11.6–11.8 eV photons.

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6. References and Notes

[1] Ausloos, P., in Ion Molecule Reactions, J. L. Franklin, Ed., (Plenum Press, New York, N.Y., 1970).

[2] Olah, G. A., and von R. Schleyer, P., Carbonium Ions, Vol. **II**, (Interscience, New York, N.Y., 1970).

[3a] Karabatsos, G. J., Orzech, C. E., Jr., Fry, J. L., and Meyerson, S., J. Am. Chem. Soc. **92**, 606 (1970).

[3b] Karabatsos, G. J., Fry, J. L., and Meyerson, S., ibid. **92**, 614 (1970).

[3c] Karabatsos, G. J., Hsi, N., and Meyerson, S., ibid. **92**, 621 (1970).

[3d] Karabatsos, G. J., Mount, R. A., Rickter, D. O., and Meyerson, S., ibid. **92**, 1248 (1970).

[4] Lias, S. G., Rebbert, R. E., and Ausloos, P., ibid. **92**, 6430 (1970).

[5a] Eadon, G., Diekman, J., and Djerassi, C., ibid. **92**, 6205 (1970).

[5b] Wilkins, C. L., and Gross, M. L., ibid. **93**, 895 (1971), and references cited therein.

[6a] Meisels, G. G., J. Chem. Phys. **42**, 3237 (1965).

[6b] Meisels, G. G., Adv. in Chem. **58**, 243 (1966).

[6c] Gorden, R., Jr., and Ausloos, P., J. Chem. Phys. **47**, 1799 (1967).

[7] Doepker, R. D., and Ausloos, P., ibid., **44**, 1641 (1966).

[8] Doepker, R. D., and Ausloos, P., ibid., **43**, 3814 (1965).

[9] Hughes, B. M., and Tiernan, J. O., ibid., **51**, 4373 (1969).

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

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

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

[13] Lias, S. G., and Ausloos, P., J. Chem. Phys. **43**, 2748 (1965).

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

[15a] Ausloos, P., Rebbert, R. E., and Lias, S. G., J. Phys. Chem. **72**, 3904 (1968).

[15b] Ausloos, P., and Lias, S. G., Rad. Res. Rev. **1**, 75 (1968).

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

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

[18a] Tiernan, T. O., and Futrell, J., J. Phys. Chem. **72**, 3080 (1968).

[18b] Sieck, L. W., private communication.

[18c] Meisels, G. G., Park, J. Y., and Geissner, B. G., J. Am. Chem. Soc. **92**, 254 (1970).

[19] Natalis, P., Steiner, B., and Inghram, M. G., private communication.

[20] That this *n*-butane product does originate largely from reaction of the 1-$C_4H_8^+$ ion with cyclohexane was confirmed in an experiment in which *c*-C_4D_8 was irradiated in the presence of *c*-C_6H_{12} at a pressure of 300 torr, and the *n*-butane product was analyzed isotopically. The *n*-butane indeed consisted mainly of $CD_2HCDHCD_2CD_3$ from a reaction analogous to 9 but with the deuteration reversed. A small amount of *n*-C_4D_{10} was also observed. The yield of this product ($M/N_+ \approx 0.004$) corresponded approximately to the yields of *n*-butane which are observed in all cyclobutane experiments in which the butane-forming H_2^- (D_2^-) transfer reactions are absent. The mode of formation of the *n*-C_4D_{10} is unknown, but its yield is so small that it constitutes only a small fraction of the *n*-butane formed through H_2^- (D_2^-) transfer reactions in the presence of methylcyclopentane or cyclohexane.

[21] Holroyd, R. A., and Fessenden, R. W., J. Phys. Chem. **67**, 2743 (1963).

[22] Gorden, R., Jr. and Ausloos, P., J. Res. Nat. Bur. Stand. (U.S.), **75A** (Phys. and Chem.), No. 3, 141–146 (May-June 1971).

[23] Lias, S., Ph.D. Thesis, American University (1971).

[24] The enthalpy of this charge transfer reaction can not be calculated exactly since the heat of formation of the methylcyclopentane ion is unknown. However, from the observation made during the course of this study that methylcyclopentane is not ionized by 10.0 eV photons, we can assign a minimum value of 8.85 eV to its heat of formation. Therefore, the postulated charge transfer with methylcyclopropane ions is endothermic by at least 0.1 eV. If the

reaction does occur in the experiments reported here, it must involve excited methylcyclopropane ions.

[25] Inel, Y., Siddiqi, A., and Meisels, G. G., J. Phys. Chem. **75,** 1317 (1971).

[26] Ausloos, P., Lias, S. G., and Sieck, L. W., NBS J. Res., to be published.

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