High-Pressure Photoionization Mass Spectrometry. I. Unimolecular and Bimolecular Reactions of $C_4H_8^+$ from Cyclobutane[1a]

L. Wayne Sieck, Stuart K. Searles,[1b] and P. Ausloos

Contribution from the National Bureau of Standards, Washington, D. C. 20234. *Received June 2, 1969*

Abstract: Various mixtures of cyclobutane with cyclohexane, methylcyclopentane, 2-methylpentane, and cyclopentane have been selectively photolyzed at either 1236 Å (10.0 eV) or 11.65 Å (10.6 eV) in a mass spectrometer designed to provide specific information concerning thermal ion–molecule reactions occurring in the gas phase. The modes of reaction as well as the total reactivity found for $C_4H_8^+$ from cyclobutane in mixtures with the various hydrocarbons have been compared with those determined for 1-$C_4H_8^+$, *i*-$C_4H_8^+$, and 2-$C_4H_8^+$ ions produced by photoionization of the appropriate butene at 10.0 eV. Evaluation of these data, including the charge exchange pattern for $C_4H_8^+$ established by the addition of compounds with various ionization potentials (NO, trimethylamine, cyclohexane, etc.), indicate that the $C_4H_8^+$ ion from cyclobutane is noncyclic and that two or more different open-ring structures may coexist. The reaction $c\text{-}C_6H_{12}^+ + c\text{-}C_4H_8 \rightarrow C_6H_{12} + C_4H_8^+$, where $c\text{-}C_6H_{12}^+$ is produced by photoionization of cyclohexane at 10.0 eV, has also been found. The interesting feature of this process is that charge exchange is exothermic on the basis of current ΔH_f values only if $C_4H_8^+$ acquires a butene ion structure during the lifetime of the collision complex.

Gas-phase radiolysis[2a] and photoionization[2b] experiments conducted in static systems indicate that the $C_4H_8^+$ ion derived from cyclobutane isomerizes to a noncyclic structure prior to or during charge exchange with molecules having ionization energies ≤ 9.54 eV. In such experiments, which require analysis of chemical end-products, the product of the charge exchange reaction appears as a mixture of several isomeric butenes. Recently a photoionization mass spectrometer has been constructed in this laboratory for the purpose of directly investigating thermal ion–molecule reactions occurring in the pressure range 0–20 Torr. This instrument has several inherent advantages when compared with other designs, including an ion source which is operated at room temperature in the absence of electric or magnetic fields. This article describes the ion–molecule chemistry observed when various cyclobutane–additive mixtures were photolyzed with 10.6-eV photons (1165 Å) in this instrument (ionization threshold of cyclobutane ~10.3 eV[3,4]). No ionic fragmentation occurs at this wavelength, and all of the ion chemistry found can be related to the interactions of $C_4H_8^+$. A particularly attractive feature of this system is the fact that $C_4H_8^+$ is not known to participate in ion–molecule reactions with cyclobutane itself;[2a,4] consequently, the structure and properties of $C_4H_8^+$ may be inferred from a variety of experiments involving trace organic and inorganic additives in which the spectrum is not complicated by any reaction involving the bulk component (cyclobutane). For the purpose of comparison with $c\text{-}C_4H_8$–hydrocarbon mixtures, other sources of $C_4H_8^+$ (the isomeric butenes) have been selectively ionized in mixtures with the same hydrocarbons at 1236 Å (10.0 eV).

In principle, the objectives reached in this study could also be satisfied by using a low-energy monoenergetic electron beam. However, in the latter case it would be difficult to obtain comparable intensities because (a) the ionization cross sections for electron impact do not approximate a step function (as in photoionization), and (b) experiments must be carried out at relatively lower pressures. Studies conducted in a tandem mass spectrometer, in which a mass-selected ion initially produced by electron impact is injected into a collision chamber, could also approximate conditions peculiar to our instrument. However, the ion-injection technique requires impacting kinetic energies at least slightly in excess of thermal values, and the range of gas pressures which may be used in the collision chamber is restricted. Tandem instruments, of course, provide a unique advantage in that the reactions of fragment ions may be individually studied and the effect of kinetic energy on the various reaction channels may be determined unambiguously.[5] A study of the reactions of cyclobutane ions has, in fact, been reported using this technique.[4]

Experimental Section

The complete instrument consisted of three operationally separable components: (1) a reaction chamber associated with a gas-handling and pressure-control system, (2) a source of monochromatic photons, and (3) a mass analysis and detection section (see Figure 1).

1. **Reaction Chamber.** The reaction chamber consisted of a stainless steel box equipped with two LiF windows (0.3 mm × 10.0 mm). A circular ion sampling orifice (0.12-mm diameter) was electrolytically prepared in the center of a stainless steel plate which had been fabricated in such a way that the thickness of the plate was <0.02 mm at the edge of the orifice. The perpendicular distance from the orifice to the center line drawn between the two windows was approximately 5 mm, and the sole gas exit channel from the reaction chamber was through the ion-sampling orifice.

---

[1] (a) This research was supported in part by the Atomic Energy Commission; (b) National Research Council–National Bureau of Standards Research Associate, 1968–1969.

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

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

[4] B. M. Hughes, W. L. Hunter, and T. O. Tiernan, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract S-248.

[5] J. Futrell and T. O. Tiernan in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968.

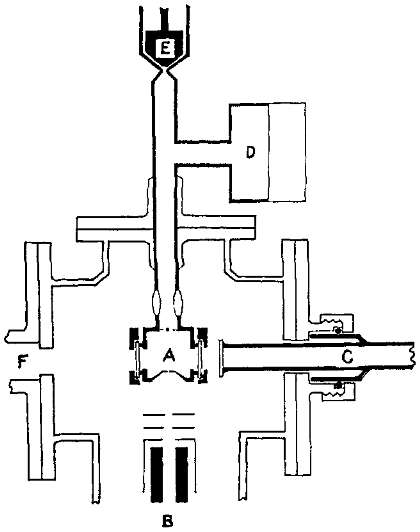

Figure 1. Schematic diagrams of the photoionization mass spectrometer: (A) reaction chamber with pinhole assembly and LiF windows, (B) quadrupole mass filter with ion lens system, (C) krypton resonance lamp equipped with CaF$_2$ window (1236 Å only), (D) capacitance manometer, (E) automatic leak assembly for sample introduction, (F) exit port for monochromator (1236 or 1165 Å).

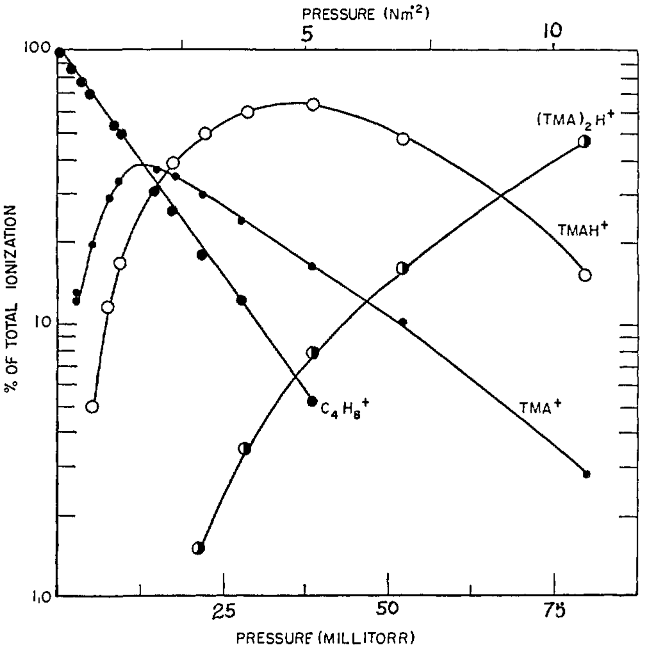

Figure 2. Photoionization of cyclobutane at 1165 Å in the presence of 5 mole % trimethylamine.

There were no electric or magnetic fields in the source itself, and the entire apparatus, although bakable to 150°, was operated at room temperature (25°) during the course of experiments.

Gas samples were admitted to the reaction chamber at selected pressures in the 1–10-Torr range *via* an automatic pressure controller associated with a capacitance manometer directly attached to the source inlet tube (0.5-in. diameter stainless steel). A conventional metal gas-handling system and vacuum system containing ballast reservoirs, etc., was used in sample preparation and routing to the automatic control unit.

2. **Photon Sources.** The design features and general characteristics of the krypton resonance lamps used in this study have been discussed in detail elsewhere.[6] The two wavelengths provided by these lamps (1236 Å, 10.0 eV and 1165 Å, 10.8 eV) were used independently. In order to selectively photolyze the samples at 1165 Å, a Seya-Namioka type vacuum uv monochromator was interposed between a lamp equipped with a LiF window and the reaction chamber (see Figure 1). Radiation at 1236 Å was provided either by an auxiliary krypton lamp equipped with a CaF$_2$ window (which filters out 1165-Å photons) or by using the monochromator. The decrease in intensity when the monochromator was used at 1236 Å was approximately two orders of magnitude. Circular collimating apertures were used to ensure that the light entering the reaction chamber through the LiF windows was essentially parallel.

3. **Ion Detection System.** The ion optical system is shown schematically in Figure 1. Ions freely diffusing from the reaction chamber through the ion exit orifice were accelerated through a potential of 11 V. This potential existed between the source (+12 V) and the first aperture (+1.0 V) of an Einzel lens system. Although this low accelerating voltage results in a somewhat diminished ion current, it was found that endothermic charge exchange processes occurred to some extent in the exit gas stream at elevated pressures when the potential difference was greater than 20–25 V. Such reactions were found to be of negligible importance, however, at accelerating voltages in the range 1–15 V.

The quadrupole mass filter and controls were very similar in design to those provided in the EAI Model 250 residual gas analyzer. Under our conditions of operation the resolution of the mass filter was approximately 250 on a 10% valley basis. Ions were detected by an electron multiplier operating at a gain of ~10^6. The multiplier output was amplified by a high-speed picoammeter and the resulting signal displayed on a strip chart recorder. The output current of the multiplier was in the range 10^{-8}–10^{-11} A. All ion intensities were corrected for (i) the slight mass-dependent decrease in the transmission coefficient associated with the quadrupole filter system as the resolving power is increased and (ii) the mass-dependent gain characteristics of the multiplier.

Differential evacuation of the mass spectrometer system was achieved at three points using 800 l./sec diffusion pumps. At a source pressure of 10 Torr the ambient pressure was approximately 10^{-5} Torr in the source and mass analysis region and 5 × 10^{-7} Torr in the monochromator.

4. **Materials and Sample Preparation.** All hydrocarbons used in the present study were judiciously purified by gas chromatography and selective fractionation *in vacuo*. Nitric oxide was used without further purification except for outgassing at −196° and storage over activated alumina.

Results

1. **Photolysis of Pure Cyclobutane.** In agreement with previous investigators[2,4] no ion–molecule reactions were found when cyclobutane was photolyzed at 1236 and 1165 Å at any pressure up to 7.0 Torr (maximum pressure at which data were recorded). In addition, no fragment ions were found at either wavelength.

2. **Photolysis of Cyclobutane in the Presence of Inorganic Compounds. (a) Cyclobutane–Trimethylamine Mixtures.** The behavior of a 5% trimethylamine (TMA) mixture in cyclobutane at 1165 Å is shown in Figure 2. In such mixtures the only reaction channel found for $C_4H_8^+$ was charge exchange with TMA. At higher pressures the resulting TMA$^+$ ions were rapidly converted to TMAH$^+$ and, as the pressure was increased further, TMAH$^+$ was quickly solvated to give (TMA)$_2$H$^+$, (TMA)$_3$H$^+$, etc. No evidence was found either for a proton-transfer reaction involving $C_4H_8^+$ and TMA or adduct formation (TMAC$_4$H$_8^+$) up to a pressure of 0.5 Torr (where the contribution from $C_4H_8^+$ was reduced to <0.1% of the composite spectrum in a 5% mixture).

(b) Cyclobutane–Nitric Oxide Mixtures. The effect of total pressure on the mass spectrum of several cyclobutane–NO mixtures photolyzed at 1165 Å is shown in Figure 3. The total contribution from NO$^+$ to the composite mass spectrum increases from an initial

---

(6) P. Ausloos and S. G. Lias, *Radiation Res. Rev.*, 1, 79 (1968).

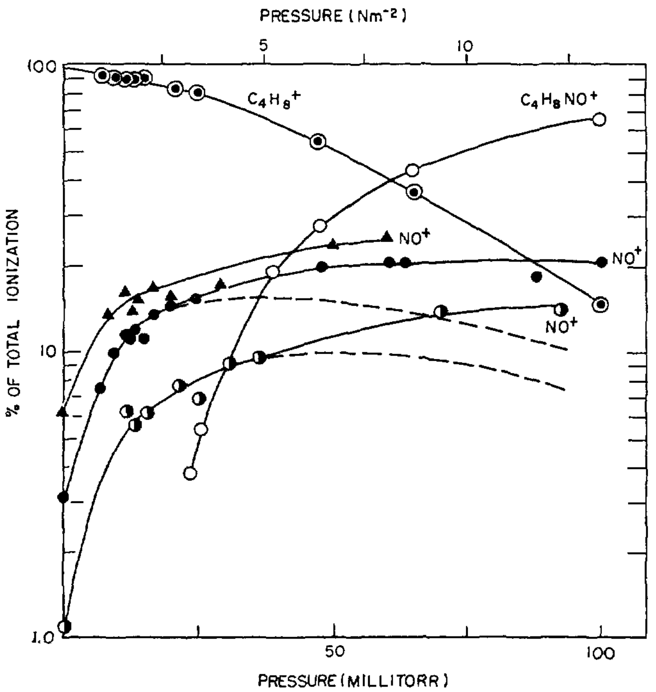

Figure 3. Photoionization of cyclobutane at 1165 Å in the presence of added nitric oxide: (⊙) $C_4H_8^+$, 100 c-C_4H_8:10 NO; (◑) NO^+, 100 c-C_4H_8:3.5 NO; (●) NO^+, 100 c-C_4H_8:10 NO; (▲) NO^+, 100 c-C_4H_8:20 NO; (○) $C_4H_8NO^+$, 100 c-C_4H_8:10 NO.

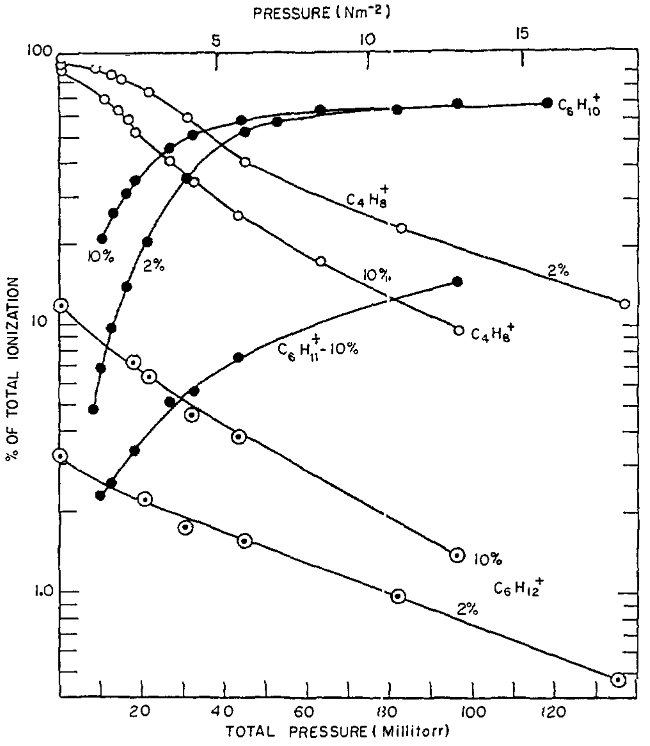

Figure 4. Photoionization of cyclobutane at 1165 Å in the presence of added methylcyclopentane. Percentage given indicates mole per cent of added MCP.

value reflecting direct ionization of NO and approaches an asymptotic level at higher pressures. The net increase comprises approximately 15–20% of the total ion current. It should be pointed out, however, that the measured contribution from *m/e* 30 does not approach the asymptotic values indicated in Figure 3, but in fact reaches a maximum value between 50 and 100 mTorr and decreases at higher pressures (indicated by broken curves). The decrease is due to a reaction between NO^+ and cyclobutane and, in those experiments where the sample was not carefully dried, with water vapor. These secondary reactions of NO^+ were established unambiguously by photolyzing the same mixtures shown in Figure 3 at 1236 Å, where the ionization quantum yield of cyclobutane is ±0.002[7] and ~60% of the primary mass spectrum is due to NO^+ in a 20% mixture in NO in cyclobutane. At this wavelength (as well as at 1165 Å) NO^+ reacts slowly with cyclobutane to yield *m/e* 55, which may be assigned to either $C_4H_7^+$, $C_3H_3O^+$, or $C_3H_5N^+$. Substituting $N^{15}O$ (98%) for $N^{14}O$ at both wavelengths gives the same yield of *m/e* 55 under equivalent conditions, indicating that formation of $C_3H_5N^+$ does not occur. Although analogous experiments were not carried out with NO^{18}, we believe that formation of $C_3H_3O^+$ is untenable on energetic grounds and that *m/e* 55 results from an H^--transfer reaction between NO^+ and cyclobutane. The asymptotic curves displayed in Figure 3 consequently represent the sum of the contributions from *m/e* 30, 55, and, where necessary, 48 (NOH_2O^+). The latter contribution was appreciable only at pressures above 300 mTorr and was always less than 10% of the sum of $C_4H_7^+$ and NO^+ in relatively dry samples.

3. Photolysis of Cyclobutane in the Presence of Other Hydrocarbons. Various mixtures or cyclobutane containing 0.5 to 10.0 mole % methylcyclopentane, 2-methylpentane, or cyclohexane were photolyzed at 1165 Å. No evidence was found for charge exchange between $C_4H_8^+$ and any of these molecules.

(a) Cyclobutane–Methylcyclopentane Mixtures. Representative data obtained with added methylcyclopentane (MCP) are shown in Figure 4. The only reactions found involving $C_4H_8^+$ and MCP were the H_2^-- and H^--transfer processes which yield $C_6H_{10}^+$ and $C_6H_{11}^+$ products. In such mixtures there is a significant contribution from MCP molecular ions to the primary mass spectrum [IP of MCP = 10.45 eV[8]]. Reference to Figure 4 indicates that this contribution decreased with increasing pressure. This behavior is reflected in the unusual contour exhibited by $C_4H_8^+$ in the low-pressure range and apparently indicates a relatively inefficient charge exchange reaction which yields $C_4H_8^+$ as a second-order ion.

Although it is not obvious from Figure 4, the ratio of $C_6H_{10}^+/C_6H_{11}^+$ varies as the total pressure is increased. Figure 5 gives a plot of this ratio for several mixtures over the pressure range covered by Figure 4.

(b) Cyclobutane–2-Methylpentane Mixtures. The $C_4H_8^+$ ion from cyclobutane also reacts quickly with 2-methylpentane to give $C_6H_{13}^+$ and $C_6H_{12}^+$ as secondary ions. Again, a plot of the ratio of $C_6H_{12}^+/C_6H_{13}^+$ as a function of pressure exhibits the same contour as that found for MCP (see Figure 5); *i.e.*, the ratio increases to a maximum value at approximately 0.03 Torr and decreases at higher pressures. In addition, the values found for the ratios in the various mixtures

---

[7] J. Herman, K. Herman, and P. Ausloos, *J. Chem. Phys.*, in press.

[8] A. G. Harrison, R. F. Pottie, and F. P. Lossing, *J. Am. Chem. Soc.*, 83, 3204 (1961).

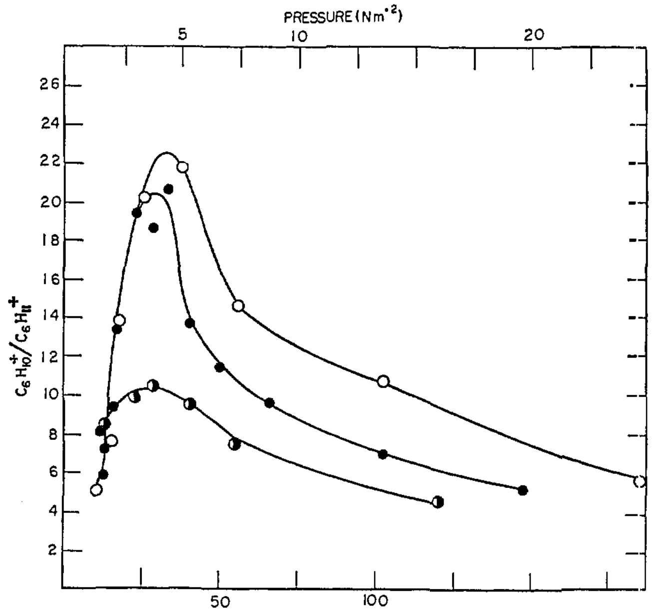

Figure 5. Photoionization of cyclobutane in the presence of added methylcyclopentane. Ratio of $C_6H_{10}^+/C_6H_{11}^+$ *vs.* pressure: (○) 100 c-C_4H_8:2.5 MCP; (●) 100 c-C_4H_8:5 MCP; (◑) 100 c-C_4H_8:10 MCP.

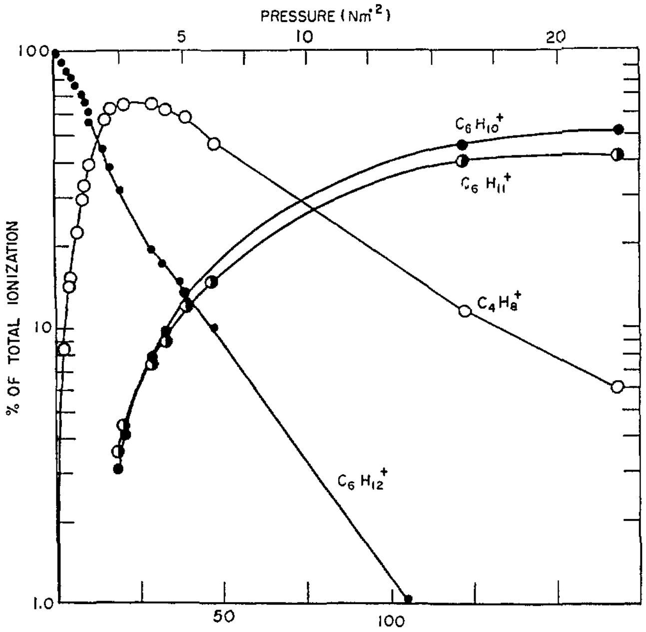

Figure 6. Photoionization of cyclohexane at 1236 Å in the presence of 7 mole % cyclobutane.

with 2-methylpentane were essentially equal to those found in equivalent mixtures of MCP in cyclobutane.

(c) Cyclobutane–Cyclohexane Mixtures. The total reactivity for $C_4H_8^+$ found when dilute mixtures of cyclohexane in cyclobutane were photolyzed at 1165 Å was quite low when compared to equivalent mixtures with MCP and 2-methylpentane. Again the only secondary ions found were $C_6H_{10}^+$ (H_2^- transfer) and $C_6H_{11}^+$ (H^- transfer). However, the ratio $C_6H_{10}^+/C_6H_{11}^+$ is approximately 15:1 in cyclohexane and is essentially independent of pressure. An interesting feature of the 1165-Å photolysis was the extremely rapid decay found for $C_6H_{12}^+$ as the pressure was raised. This result was somewhat unexpected in view of the reported ionization potential for cyclohexane [IP = 9.88[9]]. In an attempt to explore this behavior further, various cyclobutane–cyclohexane mixtures were photolyzed at 1236 Å. At this wavelength the ionization quantum yield of cyclohexane is 0.045[10] and that of cyclobutane is ≤ 0.002. Representative data are given in Figure 6, and it is evident from these curves that $C_6H_{12}^+$ is extremely effective in donating charge to cyclobutane. At higher pressures, the $C_4H_8^+$ ions generated by charge exchange react with cyclohexane to yield $C_6H_{10}^+$ and $C_6H_{11}^+$. However, the ratio $C_6H_{10}^+/C_6H_{11}^+$ is much lower at this wavelenght when compared to the value of 15 obtained at 1165 Å (where $C_4H_8^+$ is produced by photoionization), although it again is essentially independent of the total pressure in any given mixture. A plot of $C_6H_{10}^+/C_6H_{11}^+$ as a function of composition at 1236 Å is given in Figure 7. These data indicate that the probability for H_2^- transfer is favored relative to H^- transfer as the partial pressure of cyclobutane is increased in the mixture at the same total pressure (points taken at a total pressure of 0.1 Torr).

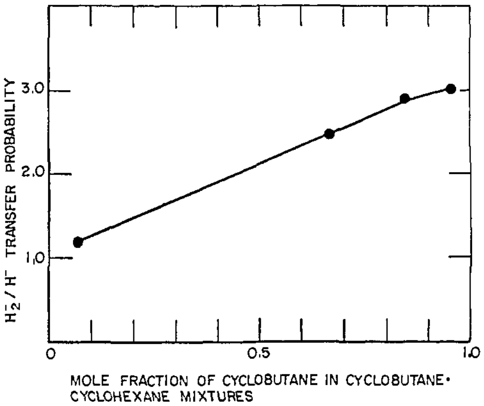

Figure 7. Ratio of $C_6H_{10}^+/C_6H_{11}^+$ (relative probabilities for H_2^- and H^- transfer from cyclohexane to $C_4H_8^+$) found in the 1236-Å photoionization of various cyclohexane–cyclobutane mixtures. Points taken at a total pressure of 0.5 Torr.

We have also determined that the $C_4H_8^+$ ion produced by charge exchange quantitatively transfers charge to NO. The results obtained in a cyclohexane–cyclobutane–NO (100:200:10) mixture photolyzed at 1236 Å is shown in Figure 8. No adducts of the type $C_4H_8NO^+$ were detected and $C_6H_{10}^+$, which is the major reaction product of $C_4H_8^+$ with cyclohexane (see Figure 8), was also not formed when NO was present. At higher pressures the NO^+ produced by charge exchange participates in an H^--transfer reaction with cyclohexane ($NO^+ + c\text{-}C_6H_{12} \rightarrow HNO + C_6H_{11}^+$), and the resultant $C_6H_{11}^+$ ions dimerize with NO (C_6H_{11}-NO^+). The composite growth curve for $C_6H_{11}^+$ + $C_6H_{11}NO^+$ is shown in Figure 8.

When the partial pressure of cyclohexane is increased in the 1165-Å photolysis of cyclohexane–cyclobutane

---

[9] Adiabatic ionization potentials, referred to as "IP," are taken from K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962). Ionization thresholds (IE), not necessarily adiabatic, are taken either from ref 4 or Watanabe, *et al.*

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

mixtures, the ratio $C_6H_{10}^+/C_6H_{11}^+$ is approximately 1.2. As indicated above, the $C_4H_8^+$ produced from the direct photolysis of cyclobutane gives $C_6H_{10}^+/C_6H_{11}^+ \geq 15$.

In addition to the preceding data, the following information was also recorded; when c-C_6D_{12} is substituted for c-C_6H_{12} in mixtures with c-C_4H_8 photolyzed at 1236 Å, $C_4D_8^+$ does not appear in the composite mass spectrum at any pressure. The charge exchange reaction $C_6D_{12}^+ + c\text{-}C_4H_8 \rightarrow C_4H_8^+ + C_6D_{12}$ proceeds at a rate equal (within experimental error) to that found for perprotonated cyclohexane ions.

Cyclohexane ions were found to be unreactive toward methylcyclopentane (IP = 10.45 eV) and cyclopentane (IP = 10.5 eV) in mixtures photolyzed at 1236 Å.

Cyclohexane ions were found to react with cyclopropane (IP = 10.02 eV) exclusively *via* an H or H_2 neutral transfer mechanism to give $C_6H_{11}^+$ and $C_6H_{10}^+$ as products. The charge exchange reaction $c\text{-}C_6H_{12}^+ + c\text{-}C_3H_6 \rightarrow C_6H_{12} + C_3H_6^+$ was not observed. These particular results will be discussed in detail in a forthcoming publication.

The ratio of the probabilities for H_2^- and H^- transfer (H_2^-/H^-) from cyclopentane to the $C_4H_8^+$ derived from the photoionization of cyclobutane at 1165 Å is $\geq$ 15:1. No other reactions were found.

Charge exchange occurs between the $C_8H_{16}^+$ (parent) ion from cyclooctane (IP $\lesssim$ 9.8 eV) and neutral cyclobutane in mixtures photolyzed at 1236 Å. The rate of this reaction is comparable to that found for the c-$C_6H_{12}^+$–cyclobutane reaction pair.

4. Photolysis of Butene in the Presence of Other Hydrocarbons. The reactions of $C_4H_8^+$ resulting from the photoionization of isobutylene and 1- and 2-butene with cyclohexane, cyclopentane, or MCP were also investigated at 1236 Å. In each system the only secondary ions found corresponded to H_2^- and H^- transfer from the additive to $C_4H_8^+$. Data are given in Table I.

Table I. Reactions of $C_4H_8^+$ from 1- and 2-Butene with Cycloalkanes under Thermal Conditions

Source of $C_4H_8^+$	Neutral	H_2^-/H^- transfer probability
1-Butene	Cyclohexane	>15:1
	Cyclopentane	>15:1
	Methylcyclopentane	4.4:1
2-Butene	Cyclopentane	No reaction observed[a]
	Methylcyclopentane	Only H_2^- transfer
Isobutylene	Methylcyclopentane	6.5:1

[a] $k < 10^{-12}$ cc/(molecule sec).

In order to minimize interaction between the butene ions and the neutral butene component in the various mxitures, all experiments were conducted with samples which were relatively dilute (<3 %) in the butene component. Absolute rate constants (see the following section) were determined only for the reactions of isobutylene and 2-butene ions with methylcyclopentane. Because of its higher reactivity it was not possible to determine the analogous value for 1-butene ions in such dilute mixtures.

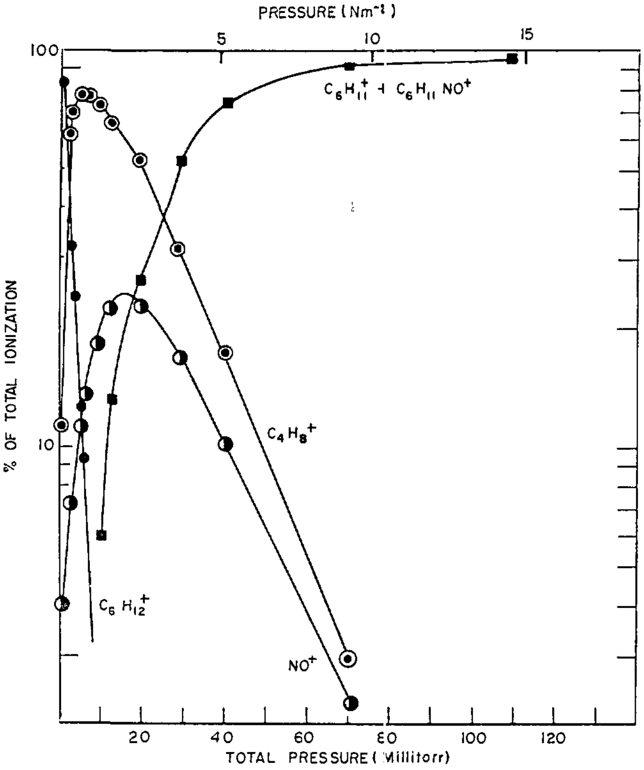

Figure 8. Composite mass spectrum resulting from the photolysis of a cyclohexane–cyclobutane–NO (105:200:10) mixture at 1236 Å as a function of total pressure.

It was also determined that the total reactivity for 1-butene ions is 1.3 times faster with perprotonated MCP when compared with the perdeuterated analog although the relative tranfer probabilities (H_2^-/H^- and D_2^-/D^-) remain essentially equivalent (4.4:1). Butene-2 ions were found to react 1.6 times faster with the perprotonated analog, and in each case exclusively by either H_2^- or D_2^- abstraction (see Table I).

Rate Constants

Absolute cross sections and rate constants may be calculated from the rates of disappearance found for primary ions (as displayed in Figures 2–4 and 6) provided both the reaction path length and reaction time are known. At low pressures, where a potentially reactive ion suffers less than one collision (on the average) during its residence time, the reaction path length is equal to the geometrical distance between the point at which the ion is formed and the point at which the ion passes out of the reaction chamber. Consequently, the average reaction path length will be equal to the perpendicular distance between the center of the photolyzed volume and the sampling orifice (0.5 cm). This distance (0.50 cm) was verified by placing a semicircular slit (0.55 cm o.d., 0.45 cm i.d.) over one of the LiF windows such that the pinhole lay on the center axis of the semicylindrical solid volume exposed to the incident photon beam passing through the slit assembly. Several primary ion disappearance curves were remeasured, and the corresponding rate constants were found to be in excellent agreement with those determined previously with the slit assembly removed. Consequently, at low pressures (<0.1 Torr) the residence time may be calculated accurately from the average reaction path length (0.5

Table II. Rate Measurements

	σ[a]	k[b]
A. $C_4H_8^+$ from Photoionization of Cyclobutane at 1165 Å		
$C_4H_8^+ + MCP \rightarrow$ products	165	6.3
$C_4H_8^+ + 2\text{-}MCP \rightarrow$ products	96	3.6
$C_4H_8^+ + TMA \rightarrow C_4H_8 + TMA^+$	900	32
$C_4H_8^+ + NO \rightarrow C_4H_8 + NO^+$	290	10.7
$C_4H_8^+ + NO \xrightarrow{M} C_4H_8NO^+ + M$		2.5×10^{-25} [c]
B. Photolysis of Cyclobutane–Cyclohexane Mixtures at 1236 Å		
$C_6H_{12}^+$ + cyclobutane $\rightarrow C_6H_{12} + C_4H_8^+$	245	7.7
$C_4H_8^+$ (CE)[d] + cyclohexane $\rightarrow$ products	18	0.7
$C_4H_8^+$ (CE)[d] $+ NO \rightarrow NO^+ + C_4H_8$	~400	~10
C. Photolysis of Isobutylene and 2-Butene in the Presence of MCP at 1236 Å		
$i\text{-}C_4H_8^+ + MCP \rightarrow$ products	265	10
$2\text{-}C_4H_8^+ + MCP \rightarrow$ products	131	5

[a] σ = cross section × 10^{16} cm^2. [b] k = rate constant × 10^{10} cm^3/(molecule sec). [c] Termolecular rate constant, units cm^6/(molecule^2 sec). [d] $C_4H_8^+$ produced by charge exchange.

cm) and the mean thermal velocity of the reactant ion.

At higher chamber pressures the residence time may be influenced by alterations in the ion-transport mechanism, variations in the sampling efficiency, and the consequences of Beer's law. The ion-transport mechanism will be affected chiefly by a transition from molecular to diffusive flow, since in the diffusive flow region the ion residence time increases approximately linearly with pressure. Since diffusion coefficients are not available for our systems, it is not possible to calculate exactly the point at which this transition occurs. However, we estimate that diffusion may begin to affect the ion residence times for higher molecular weight samples at pressures as low as 0.1–0.2 Torr. The effect of bulk gas flow on the ion residence time is negligible if the radius of the sampled volume is greater than *ca.* 0.1 cm. In general, the sampled volume will be limited only by ion–electron recombination occurring within the reaction chamber. We have determined that recombination losses are negligible in our instrument since the total ion current is directly proportional to the photon flux when the latter is varied over three orders of magnitude. Furthermore, the composition of the mass spectrum at any pressure is not dependent upon the lamp intensity. At elevated pressures the average residence time will increase as a consequence of Beer's law since the region of photon absorption is moved closer to the LiF window and the primary ions are generated further from the sampling orifice. With our geometry, however, this effect is negligible at pressures up to approximately 0.4 Torr for a sample exhibiting an extinction coefficient of 1000 atm^{-1} cm^{-1}. The fact that the experimentally determined ion disappearance curves show little curvature at higher pressures indicates that the average residence times do not increase substantially at pressures up to 0.5 Torr in our instrument. However, in order to minimize errors due to these various effects, the rate constants were always calculated from data obtained at the lowest possible pressures.

The rate constants and cross sections so derived are listed in Table II. As indicated above, these rate measurements are applicable to that component of the $C_4H_8^+$ spectrum which exhibits the highest reactivity. In situations where the total reactivity was quite low, as in the photoionization of cyclobutane in the presence of small quantities of cyclohexane at 1165 Å, it was not possible to resolve the $C_4H_8^+$ decay curves into discreet components, and an average reactivity (which includes $C_4H_8^+$ produced by charge exchange from $C_6H_{12}^+$) was calculated. The bulk rate constant obtained for the reaction $C_4H_8^+$ + cyclohexane → products at 1165 Å was $k = 0.3 \pm 0.1 \times 10^{-10}$ cc/(molecule sec).

Discussion

Charge Exchange Pattern for $C_4H_8^+$. The $C_4H_8^+$ ion from cyclobutane (IP ~ 10.3 eV) produced *via* photoionization at 1165 Å does not participate in a charge exchange reaction with any of the following molecules: cyclopentane (IP = 10.5 eV), methylcyclopentane (IP = 10.45 eV), 2-methylpentane (IP = 10.28 eV), and cyclohexane (IP = 9.88 eV). Although it may be argued that charge exchange cannot compete with the H^-- and H_2^--transfer reactions found in these systems, the low total reactivity found for $C_4H_8^+$ in cyclobutane–cyclohexane mixtures (when $C_4H_8^+$ is produced by photoionization of cyclobutane) indicates that the charge-transfer reaction

$$C_4H_8^+ + c\text{-}C_6H_{12} \longrightarrow C_4H_8 + c\text{-}C_6H_{12}^+ \qquad (1)$$

must be energetically unfavorable. Consequently, the recombination energy of the $C_4H_8^+$ ion is less than the ionization potential of cyclobutane, and it may be concluded that the $C_4H_8^+$ ion formed by photoionization does not have the cyclobutane ion structure.

In order to obtain additional information concerning the structure and reactivity of the $C_4H_8^+$ ion, compounds exhibiting still lower ionization potentials were added to cyclobutane. For example, correlation of the rapid decay of $C_4H_8^+$ with the corresponding growth curve for TMA^+ in cyclobutane–TMA mixtures (see Figure 2) indicates that the cross section for charge exchange from $C_4H_8^+$ to TMA is extremely high (Table II). This result is not surprising since all of the isomeric butenes, as well as methylcyclopropane and cyclobutane, exhibit ionization potentials in excess of 8.32 eV (IP of TMA).

These observations confirm the charge-transfer reaction

$$C_4H_8^+ + TMA \longrightarrow C_4H_8 + TMA^+ \qquad (2)$$

which has been suggested to occur in the radiolysis of cyclobutane–$(CH_3)_3N$–O_2 mixtures. Although the radiolysis study was carried out at a considerably higher pressure (20 Torr) than the present mass spectrometric investigation, there is no evidence for any additional reaction channel which competes with charge exchange at pressures up to 500 mTorr. The appearance of $TMAH^+$ and of $(TMA)_2H^+$ at higher pressures can be accounted for by the further reaction of TMA^+ formed in the charge-exchange reaction

$$TMA^+ + TMA \longrightarrow TMAH^+ + C_3H_8N \qquad (3a)$$

$$TMAH^+ + TMA \longrightarrow (TMA)_2H^+, \text{etc.} \qquad (3b)$$

In contrast with the TMA, NO (IP = 9.24 eV) participates in charge-transfer reactions with only 15–20% of the $C_4H_8^+$ ions (see Figure 3).

$$C_4H_8^+ + NO \longrightarrow C_4H_8 + NO^+ \qquad (4)$$

The remainder of the $C_4H_8^+$ ions associate with NO to form $C_4H_8NO^+$ *via* a termolecular (three-body) mechanism.

$$C_4H_8^+ + NO + M \longrightarrow C_4H_8NO^+ + M \quad (5)$$

In order to determine whether or not $C_4H_8NO^+$ could also be accounted for by the analogous reaction

$$C_4H_8 + NO^+ + M \longrightarrow C_4H_8NO^+ + M \quad (6)$$

various cyclobutane–NO mixtures were photolyzed at 1236 Å (10 eV). At this wavelength, where the ionization efficiency of cyclobutane is quite low [<0.002][7] and the major component of the primary mass spectrum is NO^+, the contribution from $C_4H_8NO^+$ to the total mass spectrum was proportional only to the extent of ionization in cyclobutane. The only reaction between NO^+ and cyclobutane seems to be the hydride-transfer reaction

$$NO^+ + c\text{-}C_4H_8 \longrightarrow HNO + C_4H_7^+ \quad (7)$$

The analogous reaction was also found in NO^+–cyclohexane mixtures (see Results). Consequently, $C_4H_8NO^+$ is indeed exclusively formed *via* process 5. Adduct formation ($C_4H_8NO^+$) has also been found in a high-pressure mass spectrometric study of C_2H_4–NO mixtures[11] and more recently[4] in a time-of-flight mass spectrometric investigation of a cyclobutane–NO mixture.

In order to account for the two independent reactions 4 and 5, we propose that ~80–85% of the $C_4H_8^+$ ions formed by photoionization are $2\text{-}C_4H_8^+$ ions with little or no internal energy. This interpretation is based on the fact that $2\text{-}C_4H_8^+$ ions (IP = 9.13 eV) transfer their charge very slowly, if at all, to NO,[11,12] and would very likely be removed only *via* the termolecular association reaction. We have, in fact, produced 2-butene ions at 1236 Å in the presence of NO and a chemically inert third body (*n*-butane) and observed only $C_4H_8NO^+$ formation in the mass spectrometer. In the absence of additional information, those $C_4H_8^+$ ions which disappear *via* reaction 4 at pressures up to 0.2 Torr may be assigned to either $1\text{-}C_4H_8^+$, $i\text{-}C_4H_8^+$, or internally excited species $[C_4H_8^+]^*$ of undefined structure. However, the fact that the butenes found in the radiolysis[13] of cyclobutane–NO and cyclobutane–TMA mixtures are isobutylene (~20%) and $2\text{-}C_4H_8$ (~80%) suggests that any $[C_4H_8^+]^*$ species involved in reaction 4 rearranges to the thermodynamically stable $i\text{-}C_4H_8^+$ configuration prior to or during reaction. In addition to the charge exchange data, conclusive evidence proving that the cyclobutane ion does not acquire the $1\text{-}C_4H_8^+$ structure will be given at a later point in the discussion. Unfortunately, the mass spectrum resulting from the 1165-Å photolysis of cyclobutane–NO mixtures was exceedingly complex at pressures greater than 0.2 Torr, and it was not possible to determine whether or not adduct formation competes with the charge exchange reaction which removes $C_4H_8^+$ ions at lower pressures. If, at higher collision frequencies, those species which do charge exchange with NO are effectively removed *via* the termolecular association reaction, then $C_4H_8^+$ would disappear exclusively through adduct formation in radiolysis experiments conducted at elevated pressures.[2a] Since the relative yields of the butenes are essentially equivalent both in the radiolysis of cyclobutane–NO and cyclobutane–TMA mixtures, we tentatively conclude that the $C_4H_8NO^+$ adduct [or higher $C_4H_8(NO)_n^+$ aggregates[11]] are loosely bound complexes with the positive charge localized on the NO group. Neutralization of such adducts may be expected to yield the same butenes as would be obtained in the charge-transfer reaction (process 4).

Reactions of $C_4H_8^+$ with Other Hydrocarbons. As indicated under Results, $C_4H_8^+$ from cyclobutane disappears *via* the H^-- and H_2^--transfer reactions

$$C_4H_8^+ + RH_2 \longrightarrow C_4H_9 + RH^+ \quad (8)$$

$$\longrightarrow C_4H_{10} + R^+ \quad (9)$$

where RH_2 is an alkane or cycloalkane. Such reactions have been shown to occur for butene ions (Table I), and, in view of the preceding discussion, it is not surprising that they also take place when $C_4H_8^+$ originates from cyclobutane. That butane is indeed the neutral product accompanying the formation of R^+ in reaction 9 was confirmed by analysis of the end-products resulting from the photoionization of $c\text{-}C_4H_8$–$c\text{-}C_5D_9CD_3$–O_2 (1:0.03:0.05) mixtures in a static system at a pressure of 20 Torr. Butane, which was the only alkane observed as a product in these experiments, was found to consist entirely of $C_4H_8D_2$. It is apparent that this product can only be formed by the D_2-transfer reaction

$$C_4H_8^+ + C_6D_{12} \longrightarrow C_4H_8D_2 + C_6D_{10}^+ \quad (10)$$

Furthermore, the $C_4H_8D_2$ fraction consisted of ~80% *n*-butane-d_2 and ~20% isobutane-d_2. The fact that the isobutane-d_2 was $CH_2DCD(CH_3)_2$ indicates that approximately 20% of the $C_4H_8^+$ species which react *via* process 16 have the $i\text{-}C_4H_8^+$ structure. On the other hand, the *n*-butane-d_2 fraction consisted entirely of $CH_3CDHCDHCH_3$, which can only be correlated with a $2\text{-}C_4H_8^+$ precursor.[14] These findings are in agreement with the conclusions reached earlier in the discussion of charge exchange.

In any $C_4H_8^+$–RH_2 reaction pair, the H_2^--transfer reaction is always thermodynamically favored. Actually if one accepts the ΔH_f values available in the literature, the H^--transfer reaction is endothermic when RH_2 is cyclopentane or cyclohexane and $C_4H_8^+$ is a $1\text{-}C_4H_8^+$ or $2\text{-}C_4H_8^+$ ion in the ground state. Consequently, it is not surprising that 1-butene ions formed by photoionization of $1\text{-}C_4H_8$ react with cyclopentane and cyclohexane nearly exclusively *via* reaction 9 (see Table I). The fact that $C_4H_8^+$ formed by photoionization of cyclobutane reacts almost exclusively *via* an H_2^--transfer mechanism with cyclohexane is also consistent, of course, with the proposed open-ring structure for the $C_4H_8^+$ ion. However, when RH_2 has a tertiary hydrogen atom, as in methylcyclopentane or 2-methylpentane, reaction 14 is energetically more favorable and does occur when $C_4H_8^+$ has either the

---

[11] P. Kebarle, R. M. Haynes, and S. Searles, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 210.

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

[13] In earlier studies[1,2] it was stated that $2\text{-}C_4H_8$ and, to a minor extent, $1\text{-}C_4H_8$ were the only C_4H_8 isomers produced in the gas-phase radiolysis of cyclobutane. In the course of a recent reinvestigation it was noted that $i\text{-}C_4H_8$ rather than $1\text{-}C_4H_8$ is the minor butene isomer formed in the radiolysis as well as in the photoionization. The nearly identical retention times of $i\text{-}C_4H_8$ and $1\text{-}C_4H_8$ led to the misassignment.

[14] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, in press.

i-$C_4H_8^+$ or 1-$C_4H_8^+$ structure (Table I). If we now return to the 10.6-eV photoionization of cyclobutane containing small quantities of MCP (Figures 4 and 5), we note that the ratio R^+/RH^+ increases rapidly at higher total pressure and reaches a maximum value at approximately 25–50 mTorr (see Figure 5). We interpret the initial sharp increase in R^+/RH^+ at low pressures as indicating a $C_4H_8^+$ component which exhibits a high probability for reaction 8 and a total reactivity greater than that associated with the majority of the $C_4H_8^+$ species. This behavior is again consistent with the presence of two or more distinguishable $C_4H_8^+$ ions. The rapid dissappearance of $C_4H_8^+$ can be ascribed to either $[C_4H_8^+]^*$ or i-$C_4H_8^+$ since, as pointed out under Results, these ions exhibit a higher reactivity than 2-$C_4H_8^+$ and also exhibit a high probability for participation in an H^--transfer reaction with MCP. The decrease in R^+/RH^+ at pressures >150 mTorr probably reflects secondary H^--transfer reactions involving R^+ and RH_2

$$R^+ + RH_2 \longrightarrow RH + RH^+ \tag{11}$$

and is not associated with a change in the relative probabilities for processes 8 and 9. If reactions of this type (process 11), which have been reported previously in other systems,[15] do occur in cyclohexane or cyclopentane, then the rate constants are $<10^{-12}$ cm^3/(molecule sec).

Production of $C_4H_8^+$ by Charge Exchange. Based on current values for the ionization potential of cyclobutane (IP $\geq$ 10.3 eV),[3,4] the charge exchange reaction

$$RH_2^+ + c\text{-}C_4H_8 \longrightarrow RH_2 + C_4H_8^+ \tag{12}$$

is endothermic by at least 0.3 eV when RH_2^+ is the cyclohexane or cyclooctane ion produced by photoionization at 1236 Å (10.0 eV). Furthermore, the calculated energy deficit (0.3 eV) represents a lower limit for the apparent endothermicity when one considers that the ejected electron may carry away additional energy during the photoionization process. Assuming the validity of the literature values, we are forced to conclude that ring opening occurs during the lifetime of the [RH_2–cyclobutane]$^+$ complex ion and that the $C_4H_8^+$ produced by charge exchange has a noncyclic structure. The over-all reaction involving c-$C_6H_{12}^+$ and cyclobutane is quite exothermic[16] for ground-state reactants.

$$c\text{-}C_6H_{12}^+ + c\text{-}C_4H_8 \longrightarrow C_6H_{12} + i\text{-}C_4H_8^+ \quad \Delta H = -11.3 \tag{13}$$

$$c\text{-}C_6H_{12}^+ + c\text{-}C_4H_8 \longrightarrow C_6H_{12} + cis\text{-}2\text{-}C_4H_8^+ \quad \Delta H = -23 \tag{14}$$

$$c\text{-}C_6H_{12}^+ + c\text{-}C_4H_8 \longrightarrow C_6H_{12} + trans\text{-}2\text{-}C_4H_8^+ \quad \Delta H = -24 \tag{15}$$

$$c\text{-}C_6H_{12}^+ + c\text{-}C_4H_8 \longrightarrow C_6H_{12} + i\text{-}C_4H_8^+ \quad \Delta H = -23 \tag{16}$$

The observation (see Results) that the charge exchange reaction involving cyclohexane ions and cyclopentane (IE = 10.5 eV) does not occur is not unexpected in view of the energetics of the over-all reaction. Even if ring opening were to occur during the charge exchange process, the over-all reaction c-$C_6H_{12}^+$ + c-C_5H_{10} → C_6H_{12} + $C_5H_{10}^+$ would be exothermic for ground-state reactants only when the resultant $C_5H_{10}^+$ species has either the *cis*- or *trans*-2-pentene ion structure, and then only by 4.5 or 6.5 kcal/mole for the respective products. As indicated under Results, cyclohexane ions also react with cyclopropane (IE = 10.02 eV) although the charge exchange product is not observed. However, in this system reaction occurs *via* a neutral transfer mechanism in which ring opening must occur during the lifetime of the collision complex.[17]

The $C_4H_8^+$ species generated in the charge exchange reaction (process 12) exhibits a very high relative cross section for process 8 when compared with the $C_4H_8^+$ formed in the photoionization of cyclobutane at 1165 Å. Furthermore, we have determined (see Figure 8) that it quantitatively transfers its charge to NO, indicating a recombination energy in excess of 9.24 eV (IP of NO). Although the structure of this ion cannot be ascertained from the present results, it appears that it is a highly excited species similar to the more reactive $[C_4H_8^+]^*$ ion derived from the direct photoionization of cyclobutane at 1165 Å. This intermediate is also not easily affected by collision with cyclobutane since the probability for H^- transfer from cyclohexane is quite high even in mixtures which are very dilute in cyclohexane.

Acknowledgment. We are deeply indebted to the Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, for the loan of certain items associated with the quadrupole mass analyzer. We would also like to acknowledge the help provided by Mr. Joseph Ball of the Photochemistry Section of the National Bureau of Standards who provided the krypton lamps and assisted in the design and construction of the instrument.

---

(15) L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, 45, 560 (1966).

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

(17) P. Ausloos and S. G. Lias, *J. Chem. Phys.*, 43, 127 (1965).