High-Pressure Photoionization Mass Spectrometry. II. A Study of Thermal H^- (H^0) and H_2^- (H_2^0) Transfer Reactions Occurring in Alkane–Olefin Mixtures[1a]

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Abstract: Following photoionization of the C_nH_{2n} (olefin) or RH_2 (alkane or cycloalkane) component in RH_2–C_nH_{2n} mixtures with either 1236-Å (10.0 eV) or 1165-Å (10.6 eV) radiation, the following two classes of reactions have been investigated: (I) $C_nH_{2n}^+ + RH_2 \rightarrow C_nH_{2n+1} + RH^+$ (H^- transfer) or $C_nH_{2n+2} + R^+$ (H_2^- transfer); (II) $RH_2^+ + C_nH_{2n} \rightarrow C_nH_{2n+1} + RH^+$ (H transfer) or $C_nH_{2n+2} + R^+$ (H_2 transfer). Although these processes have been subjected to considerable scrutiny, the relative rate constants $k(H^-)/k(H_2^-)$ or $k(H^0)/k(H_2^0)$ found previously by kinetic mass spectrometry for any given reaction pair have always been considerably higher than those derived from photoionization and radiolysis experiments conducted in static systems. However, the values derived in our instrument, which reflect the interactions of ions at thermal energy, are in excellent agreement with the relative transfer efficiencies and other rate parameters derived from static experiments and suggest that kinetic and/or internal energy effects may have been important in previous experiments carried out in mass spectrometers. Rate constants and relative transfer efficiencies found for a number of reaction pairs are reported, and the nature of the collision complex is discussed.

Several years ago a new class of ion–molecule reactions was uncovered as the result of gas-phase radiolysis and photoionization experiments carried out in a static system.[2-5] These processes, which involve the transfer of H^0 and/or H_2^0 from an alkane parent ion to a lower molecular weight olefin, may be represented as follows

$$RH_2^+ + C_nH_{2n} \longrightarrow RH^+ + C_nH_{2n+1} \qquad (1)$$

and

$$RH_2^+ + C_nH_{2n} \longrightarrow R^+ + C_nH_{2n+2} \qquad (2)$$

where RH_2 denotes a saturated hydrocarbon and C_nH_{2n} represents an olefin with a lower carbon number than RH_2. The analogous H^- and H_2^- transfer reactions, which occur when the charge is reversed on the reactants, have also been investigated in detail for a number of RH_2–C_nH_{2n} combinations

$$RH_2 + C_nH_{2n}^+ \longrightarrow RH^+ + C_nH_{2n+1} \qquad (3)$$

and

$$RH_2 + C_nH_{2n}^+ \longrightarrow R^+ + C_nH_{2n+2} \qquad (4)$$

Two experimental approaches have been used to characterize these particle transfer processes: (a) high-pressure kinetic mass spectrometry,[6-9] which affords direct observation of the reaction products R^+ and RH^+, and (b) chemical analysis of the stable end products formed in radiolysis and photoionization experiments conducted in static systems at higher pressures. Although the results obtained by the two methods are in qualitative agreement, experiments carried out previously in mass spectrometers have indicated a greater efficiency for H^0 or H^- transfer than is found at higher pressures in a closed system. This discrepancy has been attributed[10,11] in part to the fact that the reactant ions in the mass spectrometer may have kinetic energies in excess of thermal values. We have recently constructed[12] a photoionization mass spectrometer specifically designed to investigate thermal ion–molecule reactions occurring at room temperature in the pressure range 0–2 Torr. This instrument is well suited for investigating processes 3 and 4 since, in many cases, a wavelength may be chosen which selectively ionizes only the C_nH_{2n} (olefinic) component in an RH_2–C_nH_{2n} mixture. Conversely, the primary mass spectrum obtained at shorter wavelengths in a dilute mixture of C_nH_{2n} in RH_2 will consist almost entirely of RH_2^+ as long as the photon energy is insufficient to cause fragmentation of the RH_2^+ molecular ion. Since it is known[10] that RH_2^+ ions react extremely slowly, if at all, with RH_2, all of the ion–molecule chemistry will involve only the C_nH_{2n} component (processes 1 and 2).

The present study was undertaken in order to derive thermal rate constants for processes 1–4 for a number of reaction pairs and to determine whether or not a real discrepancy exists between the relative transfer probabilities (H^0/H_2^0 or H^-/H_2^-) obtained in static systems and in a mass spectrometer operating under thermal conditions.

Methods and Results

(1) Instrumentation and Materials

The high-pressure photoionization mass spectrometer used in the present study has been described elsewhere in detail.[12] In all experiments the reaction chamber (ion source) was operated at room temperature in the

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[1] (a) This research was supported in part by the Atomic Energy Commission; (b) NRC-NBS Research Associate, 1968–1970.

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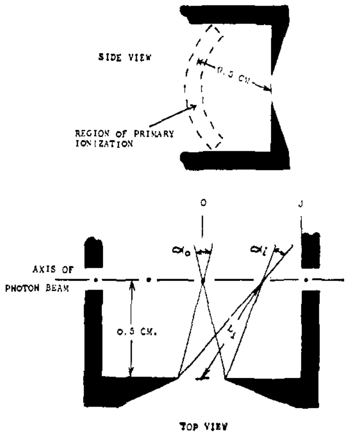

Figure 1. Schematic of ion source: side view, cutaway of chamber at point 0 as viewed from lamp; top view, cutaway identifying various parameters used in path length determination.

absence of any internal electric or magnetic fields. Two wavelengths were used independently for selective ionization in mixtures: 1236 Å (10.03 eV) and 1165 Å (10.64 eV). Radiation at 1236 Å was provided by a krypton resonance lamp equipped with a CaF_2 window, while 1165-Å photons were provided by an auxiliary krypton resonance lamp (LiF window) in conjunction with a Seya-Type 0.3-m vacuum uv monochromator.

All materials were purified by gas chromatography followed by selective fraction *in vacuo*.

(2) Determination of Rate Constants

Rate constants were determined from the slopes of the decay curves obtained from semilog plots of fractional ion intensities *vs.* pressure. The magnitude of the rate constant calculated from such data depends critically on the ion residence time, which we have derived from the average reaction path length and an average ion velocity corresponding to a kinetic energy of kT at 295°K. The residence time (τ) is defined by the expression $\tau = \bar{L}/\bar{C}$, where $\bar{L}$ is the average reaction path length and $\bar{C}$ is the average velocity of an ion mass M as derived from the expression $\bar{C} = [8kT/\pi M]^{1/2}$.

As described in the earlier manuscript, we defined our average reaction path length as ~0.5 cm by placing a semicircular slit (0.55-cm o.d., 0.45-cm i.d.) over the LiF window such that the ion exit pinhole lay on the center axis of the semicircular solid volume subtended by the collimated photon beam (see Figure 1). However, even under such conditions the average reaction path is slightly in excess of 0.5 cm since only those primary ions produced directly over the pinhole and moving perpendicular to the plane of the photon beam in the direction of the ion exit orifice will move 0.5 cm before leaving the reaction chamber. Ions produced at other points along the ionization sheath defined by the slit assembly will necessarily exhibit longer reaction path lengths but will be collected with a reduced efficiency. Under such conditions the average reaction path length ($\bar{L}$) is defined by the expression

$$\bar{L} = \frac{1}{n}\sum_{i=1}^{n}\frac{L_i\alpha_1}{\alpha_0}$$

where L_i is the distance between a point i where the primary ion is formed and the center of the ion exit orifice, α_i is the angle defined by lines drawn from each of the two edges of the ion exit orifice and point i, and α_0 is the corresponding angle defined in a similar manner for those ions produced directly over the ion exit orifice at a distance of 0.5 cm (see Figure 1). The summation is over all values of i placed between p (directly over the pinhole) and j, the point at which photons enter the reaction chamber. The maximum value of L_i in our apparatus is 0.95 cm. Both the three-dimensional and two-dimensional solutions are equivalent owing to the semicircular collimating slits defining the path of the photon beam. Solution of the expression for $\bar{L}$ in our geometry gives an average reaction path length of 0.61 cm in the reaction chamber under conditions of molecular flow (<20 mTorr). Average residence times for the various reactant primary ions were calculated using this value, and the rate constants given in the earlier manuscript were revised in proof to take into account the corrected path length.

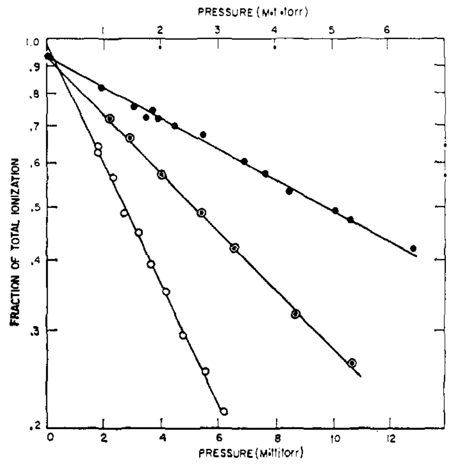

Figure 2. Typical data from which rate constants were derived; fractional intensity of reactant ions *vs.* pressure: ●, decay curve for $C_6H_{12}^+$ obtained when a 100 cyclohexane:2.9 C_3D_6 mixture is photolyzed at 1165 Å; ⊙, decay curve for $C_6H_{12}^+$ obtained in the 1236-Å photolysis of a 100 cyclohexane:13.5 C_2H_4 mixture; ○, decay curve for $C_3D_6^+$ obtained when propylene-d_6 is photoionized at 1236 Å (upper scale).

Typical data from which rate constants were derived are given in Figure 2 for two cyclohexane–C_nH_{2n} combinations and the reaction of $C_3D_6^+$ with C_3D_6. The fact that these plots exhibit no curvature suggests that the average residence time does not increase due to nonreactive scattering in the low-pressure range.

A comparison was made between the thermal rate constant derived in our instrument for the reaction $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ (which occurs when NH_3 is photoionized at 1165 Å) and literature values for this reaction obtained under thermal conditions. The rate constant found for $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ was $1.4 \pm 0.1 \times 10^{-9}$ cm^3/(molecule sec), which compares favorably with the value of 1.6×10^{-9} cm^3/(molecule sec) reported recently.[13]

(3) Photolysis of Propylene–RH_2 Mixtures

(A) Photoionization at 1236 Å. When mixtures of propylene (IP = 9.73 eV) with normal butane (IP = 10.63 eV), isobutane (IP = 10.57 eV), cyclopentane (IP = 10.53 eV), *n*-pentane (IP = 10.35 eV), and iso-

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Table I. Rate Data for H_2^- (D_2^-) and H^- (D^-) Transfer Reactions

Eq no.	λ, Å	$C_nH_{2n}^+$	RH_2	$k(H^-)$[a]	$k(H_2^-)$[a]	Total rate constant	$k(H^-)/k(H_2^-)$	$k(H^-)/k(H_2^-)$[b] (other studies)
5	1165	$C_2H_4^+$	C_3H_8	Nd	Nd	Nd	1.15	2.3 (MS)[c]
6	1165	$C_2H_4^+$	C_3D_8	Nd	Nd	Nd	0.80	0.90 (SS)[d]
7	1165	$C_2H_4^+$	$CD_3CH_2CD_3$	Nd	Nd	Nd	1.10 (H^-/HD^-)[e]	
8	1236	$C_3D_6^+$	i-C_4H_{10}	−2.4	1.8	4.2	1.3	2.2 (MS)[f]
9	1236	$C_3H_6^+$	i-C_4D_{10}	1.8	2.8	4.6	0.66	2.05 (MS)[f]
10	1236	$C_3D_6^+$	n-C_4D_{10}	<0.03	4.4	4.4	0.01	0.11 (MS)[f]
11	1236	$C_3D_6^+$	c-C_5H_{10}	~0.3	8.8	9.1	<0.03	
12	1236	$C_3D_6^+$	i-C_5H_{12}	3.1	4.8	7.9	0.55	
13	1236	$C_3D_6^+$	n-C_5H_{12}	~0.3	7.9	8.2	<0.1	
14	1236	i-$C_4H_8^+$	MCP	0.9	7.9	7.9	0.14	
15	1236	1-$C_4H_8^+$	c-C_5H_{10}	Nd	Nd	Nd	0.05	
16	1236	1-$C_4H_8^+$	c-C_6H_{12}	Nd	Nd	Nd	0.06	0.15 ± 0.02 (MS)[g]
17	1236	1-$C_4H_8^+$	MCP	Nd	Nd	Nd	0.23	
18	1236	2-$C_4H_8^+$	MCP	<0.04	3.9	3.9	<0.01	
19	1236	2-$C_4H_8^+$	c-C_5H_{10}	<0.04	<0.04	<0.04	Nd	

[a] In units of 10^{-10} cm^3/(molecule sec). [b] (MS) denotes a value derived from mass spectrometry and (SS) indicates a value from experiments carried out in a static system. [c] Reference 15. [d] Reference 17. [e] $D^-/H^- < 0.05$, $D_2^-/HD^- < 0.02$. [f] Reference 6. [g] Reference 7.

Table II. Rate Data for H^0 and H_2^0 Transfer Reactions

Eq no.	λ, Å	RH_2^+	C_nH_{2n}	Total rate[a] constants	$k(H^0)/k(H_2^0)$	$k(H^0)/k(H_2^0)$	(Other studies)[b]
20	1236	c-$C_6H_{12}^+$	C_2H_4	10	2.0		11.0 (MS)[c]
21	1236	c-$C_6H_{12}^+$	c-C_3H_6	12	~5.0	5.5 (SS)[d]	23 (MS)[c]
22	1165	c-$C_6H_{12}^+$	C_3D_6	27	0.11	<0.1 (SS)[e]	2.4 (MS)[c]
23	1236	c-$C_6H_{12}^+$	1-C_4H_8	21	≤0.05	<0.02 (SS)[d]	1.2 (MS)[c]
24	1236	c-$C_6H_{12}^+$	C_2D_2	8.4	[f]	14 (MS)[c]	
25	1165	MCP$^+$	1-C_4H_8	12	0.21		
26	1165	n-$C_5H_{12}^+$	C_3D_6	15 ± 2	<0.01		
27	1165	i-$C_5H_{12}^+$	C_3F_6	19 ± 2	1 ± 0.4	<1.0 (SS)[g]	
28	1165	i-$C_5H_{12}^+$	c-C_3H_6	6.0	8.5		

[a] Same as Table I. [b] Same as Table I. [c] Reference 8. [d] Reference 19. [e] Reference 18. [f] Relative H_2^0 transfer efficiency equals 0.15 (present study) and 0.12 (SS), ref 19. [g] Reference 20.

pentane (IP = 10.32 eV) were photolyzed at 1236 Å, all of the ionic reactions which followed could be traced to $C_3H_6^+$ precursors because of the higher ionization thresholds of the saturated hydrocarbons. In such mixtures $C_3H_6^+$ reacts both with propylene and the RH_2 component. When RH_2 is a C_4 or C_5 hydrocarbon, the products of the $C_3H_6^+$–RH_2 and $C_3H_6^+$–C_3H_6 reaction pairs may not be separable since the reaction of $C_3H_6^+$ with C_3H_6 produces both $C_4H_8^+$ and $C_5H_9^+$.[14] In order to avoid mass overlap the completely deuterated analog of either C_3H_6 or RH_2 was used in all experiments. Furthermore, the C_3, C_4, or C_5 ions produced by the reaction of $C_3H_6^+$ with C_3H_6 (or $C_3D_6^+$ with C_3D_6) also react with RH_2 at higher pressures to yield R^+ and RH^+ as tertiary ions. Complications of this type were minimized by taking data from mixtures which were relatively dilute ($\leq$10 mol %) in propylene.

The relative probabilities for H^- (D^-) and H_2^- (D_2^-) transfer to propylene molecular ions from several hydrocarbons, as well as the total rate constants, are listed in Table I. The relative transfer probabilities $k(H^-)/k(H_2^-)$ were found to be essentially independent of pressure throughout the range where data were taken (~0.001 to ~0.2 Torr for most systems). In mixtures with isobutane the $C_4H_8^+$ species resulting from H_2^- transfer was found to react rather effectively with neutral propylene to give a complex spectrum of C_4, C_5, and C_6 ions. Additional secondary reactions involving R^+ and RH^+ were also found at higher pressures in other propylene–RH_2 combinations (see section 6). Consequently, the $k(H^-)/k(H_2^-)$ values reported (Table I) reflect the low-pressure intercept. The values of k derived for [$C_3D_6^+ + RH_2 \rightarrow$ products] were cross-checked in mixtures more concentrated in propylene by comparing the rates of formation of R^+ and RH^+ with the rates of production of the C_4 ions resulting from the reaction of $C_3D_6^+$ with the C_3D_6 component in the mixture. The absolute rate constant for the production of $C_4D_8^+$ (in pure C_3D_6 in the 0–0.010-Torr pressure range) was determined in separate experiments. The rate constants for the $C_3D_6^+$–RH_2 reactions obtained by the relative rate technique were within ±5% of the values derived from the composite decay curves found for C_3D_6 in such mixtures. The total rate constant found for $C_3D_6^+ + C_3D_6 \rightarrow$ products was $0.76 \pm 0.05 \times 10^{-9}$ cm^3/(molecule sec) when propylene-d_6 was photoionized at 1236 Å.

(B) Photoionization at 1165 Å. When dilute mixtures of propylene in i-C_5H_{12}, n-C_5H_{12}, and c-C_6H_{12} (IP = 9.88 eV) are photolyzed at 1165 Å (10.64 eV) essentially all of the primary ionization occurs in the RH_2 component. Accordingly, the neutral transfer reactions (processes 1 and 2) may be studied at this wavelength. The rate constants found for these systems are given in Table II.

(4) Butene–RH_2 Mixtures

At 1236 Å, where the primary ionization in butene–RH_2 mixtures occurs in the butene component, the only reactions found between $C_4H_8^+$ and RH_2 were the H^-

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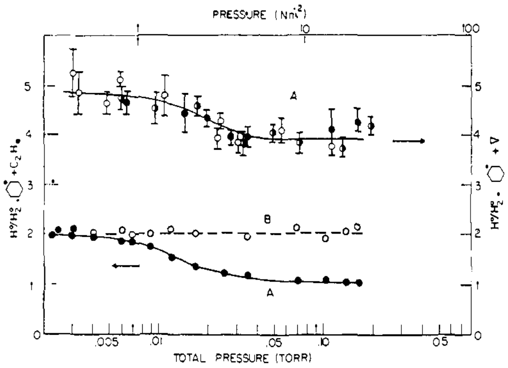

Figure 3. Ratio of $C_6H_{11}^+/C_6H_{10}^+$ *vs.* pressure for the c-$C_6H_{12}^+$–cyclopropane and c-$C_6H_{12}^+$–C_2H_4 reaction pairs. The upper curve (right ordinate) indicates data obtained from c-C_6H_{12}–cyclopropane mixtures containing 3.0 (●), 7.5 (◑), and 11.2 (○) mol % cyclopropane. The left ordinate indicates results obtained for a 10% mixture of C_2H_4 in cyclohexane. Curve A (●) indicates the experimentally determined ratio of $C_6H_{11}^+/C_6H_{10}^+$, while curve B (○) gives $\Sigma C_6H_{11}^+ + [C_6H_{11}C_2H_4]^+/C_6H_{10}^+$ *vs.* pressure.

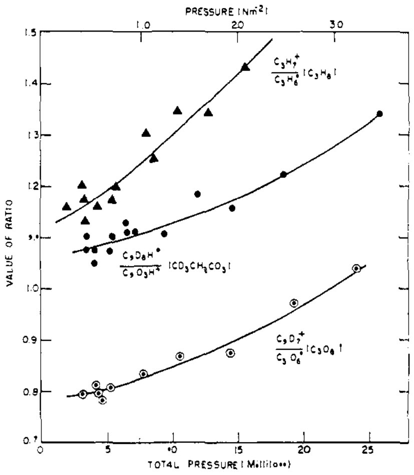

Figure 4. Photolysis of C_2H_4–propane mixtures at 1165 Å. Ratios of $C_3H_7^+/C_3H_6^+$ from C_3H_8, $C_3D_6H^+/C_3D_5H^+$ from $CD_3CH_2CD_3$, and $C_3D_7^+/C_3D_6^+$ from C_3D_8 *vs.* total pressure.

and/or H_2^- transfer processes. The relative transfer probabilities (H^-/H_2^-) were found to be independent of total pressure up to ~0.2 Torr within experimental error. Rate data are given in Table I. Dilute mixtures of 1-butene in methylcyclopentane were also photolyzed at 1165 Å to determine the H and H_2 transfer rates from $C_6H_{12}^+$ to 1-C_4H_8.

(5) Other RH_2–C_nH_{2n} Combinations

(A) Cyclohexane–C_nH_{2n} Mixtures. Mixtures of c-C_6H_{12} with C_2H_4 (IP = 10.51 eV), c-C_3H_6 (IP = 10.06 eV), 1-C_4H_8 (IP = 9.58 eV), and C_2H_2 (IP = 11.41 eV) were photolyzed at 1236 and/or 1165 Å in order to characterize the neutral transfer reactions. Results are given in Table II. Figure 3 gives plots of the relative transfer probabilities found for the c-$C_6H_{12}^+$–C_2H_4 and c-$C_6H_{12}^+$–c-C_3H_6 reaction pairs for several mixtures as a function of total pressure. It was not possible to investigate the reverse reactions (H^- and H_2^-) involving c-$C_3H_6^+$, $C_2H_4^+$, or $C_2H_2^+$ and cyclohexane, since these ions cannot be produced in the absence of $C_6H_{12}^+$ due to their higher ionization potentials.

Cyclohexane ions were found to participate in a charge exchange reaction with neutral methylcyclopropane in mixtures photolyzed at 10.0 and 10.6 eV. No evidence was found for a neutral transfer reaction throughout the pressure range 0–0.2 Torr. The rate constant found for the charge exchange reaction was $1.8 \pm 0.5 \times 10^{-9}$ cm^3/(molecule sec).

In addition to transferring H and H_2, cyclohexane ions also transferred H_3 to acetylene. The relative transfer efficiencies found were H = 0.6, H_2 = 0.15, and H_3 = 0.25. No evidence was found for transfer of H_4^0.

(B) Ethylene–Propane Mixtures. Dilute mixtures of C_2H_4 in C_3H_8 (IP = 11.07 eV), C_3D_8, and $CD_3CH_2CD_3$ were photolyzed at 1165 Å. The relative intensities $C_3H_7^+/C_3H_6^+$, $C_3D_7^+/C_3D_6^+$, and $CD_3CHCD_3^+/CD_2CHCD_3$ found for the respective propanes as a function of total pressure are presented in Figure 4. The apparent increase in the relative probability for hydride transfer to $C_2H_4^+$ at higher pressures is due to the relatively slow reaction $C_3H_6^+ + C_3H_8 \rightarrow C_3H_7^+ + C_3H_7$ reported previously.[6] By analogy with other systems (where the transfer ratios were found to be generally invariant with density) we have taken the zero-pressure intercepts (Figure 4) as representing the true relative transfer probabilities for comparison with other reaction pairs.

Propane was the only molecule in which the reaction $R^+ + RH_2 \rightarrow RH + RH^+$ was detected. A slow exchange reaction $CD_3CHCD_2^+ + CD_3CH_2CD_3 \rightarrow C_3D_4H_2^+ + C_3D_7H$ (where $CD_3CHCD_2^+$ results from HD^- transfer from $CD_3CH_2CD_3$ to $C_2H_4^+$) was also found at higher pressures in C_2H_4–$CD_3CH_2CD_3$ mixtures. The plot of $C_3D_6H^+/C_3D_5H^+$ *vs.* pressure (Figure 4) has been corrected for this process.

(6) Reactions Occurring at Higher Total Pressures

At pressures above 0.02 Torr secondary reactions were observed involving the R^+ and RH^+ species and the C_nH_{2n} component in the mixture for every RH_2–C_nH_{2n} combination except for mixtures of cyclopropane in cyclohexane and isopentane. These reactions were of two general types: (1) adduct formation forming $[RHC_nH_{2n}]^+$ and $[RC_nH_{2n}]^+$ and (2) neutral transfer reactions involving R^+ ions from cycloalkanes and C_nH_{2n}. In mixtures of propylene and butene with cyclopentane, cyclohexane, and methylcyclopentane both adduct formation (involving both R^+ and RH^+) and the neutral transfer process involving the respective R^+ ions were found in samples which were more concentrated in the olefin component. For example, c-$C_5H_8^+$ resulting from H_2^- transfer from cyclopentane to $C_3D_6^+$ exhibited a neutral transfer ratio (H/H_2) of 0.2 in the reaction with the C_3D_6 additive. Similarly, $C_6H_{10}^+$ (from methylcyclopentane) exhibited ratios of 0.4 and 0.13, respectively, in the reaction with neutral 1-C_4H_8 and i-C_4H_8, and cyclohexene ions were found to transfer only H_2 to propylene and 1-C_4H_8. No reactions other than adduct formation were found for the RH^+ ions from any of the cycloalkanes.

An illustration of the effect of secondary reactions on the measured ratio of R^+/RH^+ as a function of pressure is given in Figure 3 for the c-$C_6H_{12}^+$–C_2H_4 reaction pair. In a mixture containing 10 mol % C_2H_4 the ratio $C_6H_{11}^+/C_6H_{10}^+$ decreases at higher total pressures and appears to approach a more or less asymptotic value (curve A). However, when the contributions to the

Table III. Comparison of Relative Rate Data

RH_2	Relative rates of the reaction $C_3D_6^+ + RH_2 \rightarrow C_3D_6H_2 + R^+$: Photoionization[a] of C_3D_6	Radiolysis of[b] c-C_5D_{10}	Present data	Ratio of rate constants for $C_3D_6^+ + RH_2 \rightarrow C_3D_6H_2 + R^+$ / $C_3D_6^+ + C_3D_6 \rightarrow$ products: Photoionization[a] of C_3D_6	Present data
Cyclopentane	1.0	1.0	1.0	1.45	1.21 ± 0.02
n-Butane	0.51	0.65	0.51	0.69 ± 0.04	0.62 ± 0.01
Isobutane	0.21	0.23	0.21	0.33 ± 0.02	0.25 ± 0.02
Neopentane	0.00	0.00	0.00		
Isopentane	0.46	0.45	0.50		
n-Pentane	0.96	1.12	0.90		

[a] Reference 5. [b] Reference 4.

composite mass spectrum from the adducts $[C_6H_{11}\text{-}C_2H_4]^+$ and $[C_6H_{10}\text{-}C_2H_4]^+$ (very small) are added to $C_6H_{11}^+$ and $C_6H_{10}^+$, respectively, a constant value is obtained for the H^0/H_2^0 transfer ratio throughout the experimental range of pressures (curve B). No secondary neutral transfer processes involving $C_6H_{10}^+$ and C_2H_4 were found to occur in this particular system c-C_6H_{12}–C_2H_4).

Also included for illustration is the composite mass spectrum obtained as a function of pressure when a mixture of 3% 1-C_4H_8 in cyclohexane is photolyzed at 1165 Å (Figure 5). The initial reaction is the H_2 transfer process involving $C_6H_{12}^+$ and 1-C_4H_8. As the pressure is increased the cyclohexene ions produced *via* the H_2 transfer process react further with the 1-C_4H_8 additive to yield either $C_{10}H_{18}^+$ or $C_6H_8^+$ + *n*-C_4H_{10} (H_2 transfer). At even higher total pressures (>60 mTorr) $C_{10}H_{18}^+$ complexes with 1-C_4H_8 and, although it may not be evident from Figure 5, the probability for H_2 transfer from cyclohexene ions to 1-C_4H_8 decreases relative to the probability for production of $C_{10}H_{18}^+$. In those RH_2–C_nH_{2n} combinations where adduct formation and/or the secondary neutral transfer processes were relatively efficient reaction channels the H^-/H_2^- (or H/H_2) transfer probabilities (processes 1–4) reported in the tables were derived from experiments in which the sample was dilute (<1%) in the C_nH_{2n} component. Under such conditions secondary reactions did not contribute significantly to the composite mass spectrum and the ratios of R^+/RH^+ obtained reflected only the relative probabilities obtained for the $[RH_2\text{-}C_nH_{2n}]^+$ reaction pair.

Discussion

Comparison of Total Rates. Since the rate data obtained from our instrument reflect the interactions of thermal ions (KE ≤ 0.04 eV) in an environment which is at room temperature (295° K), the results should be directly comparable with the analogous rate data derived from experiments conducted in static systems. Correlations of this type may be effected in two ways: (1) by comparison of total rate constants (reactivities) exhibited by different reaction pairs and (2) by comparison of the relative probabilities found for competing reaction channels in any given reaction pair. For example, the relative rate constants for the reaction

$$C_3D_6^+ + RH_2 \longrightarrow C_3D_6H_2 + R^+ \quad (29)$$

have been reported[4,5] for several alkanes and cycloalkanes (RH_2). In those experiments, which were carried out in a static system at pressures of 3–20 Torr, $C_3D_6^+$ was produced both by the photoionization of C_3D_6 at 1236 Å and *via* the radiolysis of cyclopentane-d_{10}. The relative values, normalized to an arbitrary rate constant of 1.0 for the reaction $C_3D_6^+$ + cyclopentane $\rightarrow C_3D_6H_2 + C_5H_8^+$, are listed in Table III.

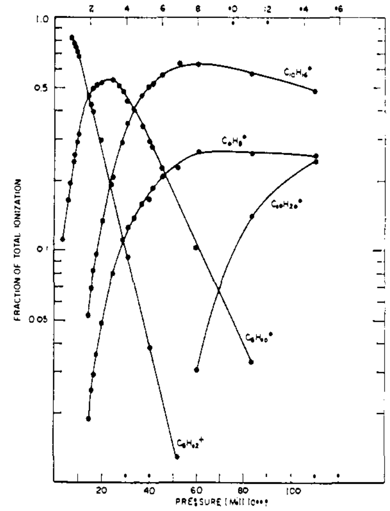

Figure 5. Composite mass spectrum obtained from photoionization of a 3% mixture of 1-C_4H_8 in cyclohexane at 1165 Å as a function of total pressure.

In Table II are given the relative rate constants found in the present study for the same reaction pairs, which may be calculated directly from the absolute values given in Table I for the H_2^- (D_2^-) transfer processes involving propylene molecular ions. Gorden, *et al.*,[5] also reported relative rate constants (k_{29}/k_{30}) found in the photoionization of C_3D_6–RH_2 mixtures at 1236 Å. Those data, as well as the relative rate constants found in the present study, are listed in columns 4 and 5 of Table III. It is evident that the results obtained by the two methods are in excellent agreement.

$$C_3D_6^+ + C_3D_6 \longrightarrow \text{products} \quad (30)$$

Comparison of the total rate constants listed in Table I for the reactions of propylene ions with the isomeric butanes and pentanes indicates that an increase in the molecular weight of the donor molecule results in a corresponding increase in the total reaction rate constant. This result is consistent with the general trends found[11] for the reactivity of carbonium ions with RH_2 molecules falling within a homologous series. The near equivalency of the rate constants found for structural isomers (iso- and *n*-butane or iso- and *n*-pentane) is also in agreement with earlier findings.[11]

Comparison of (H^-/H_2^-) and (H/H_2) Transfer Ratios. Of perhaps more interest are the relative rates found for various competing reaction channels in a given reaction pair (relative H^-/H_2^- or H/H_2 transfer probabilities). As indicated earlier, two types of experimental approaches have been used previously to investigate H^-, H_2^- H, and H_2 transfer reactions. One method, which affords direct observation of the reaction products RH^+ and R^+, has been the use of modified mass spectrometers both of the single-stage[6,9] and tandem geometry.[7,14,15] These experiments have usually been conducted at relatively low sample pressures (generally <0.02 Torr) and higher temperatures (generally $>150°$). Furthermore, the kinetic energies of the reactant ions are not precisely known but usually fall within the range $0 < E < 0.3$–0.4 eV for the lowest energy situation. Comparison of the present results with literature values (see Tables I and II) indicates that the H^-/H_2^- and H/H_2 transfer ratios obtained by the ion injection technique are consistently higher than the thermal values derived in this study. This discrepancy is probably related to kinetic energy effects, since it has been demonstrated in a tandem instrument[14] that an increase in the kinetic energy of the impacting ion greatly increases the relative probability for H (and H^-) transfer. There is also evidence that the transfer ratio is temperature dependent.[16] It should be emphasized that our neutral transfer experiments are carried out in a considerable excess of the RH_2 (alkane) component. Under such conditions RH_2^+ may suffer many collisions with RH_2 (as well as unreactive collisions with the olefin additive) prior to a chemically reactive collision with the C_nH_{2n} component, and the probability is high that any internal energy originally contained in RH_2^+ will be dissipated. In a tandem mass spectrometer, on the other hand, a spectrum of internally excited primary ions produced by high-energy electron impact is injected into a collision chamber containing only the neutral C_nH_{2n} reactant. Consequently the neutral transfer ratios obtained in such experiments may reflect the interactions of ions which have, on the average, a higher energy content.

Although a considerable quantity of data concerning the rates of H_2^- and H_2 transfer has been obtained from radiolysis and photoionization experiments in static systems,[17-20] it is more difficult to derive the analogous data for the H^- and H transfer reactions since a molecular product is not directly produced *via* process 1 or 3. Recently, an extensive study of neutral transfer reactions occurring in static systems has been completed by Ausloos and coworkers.[19] Those transfer ratios, as well as other available literature values, are given in Tables I and II. Again, the agreement with our results is quite satisfactory.

With respect to the H^-/H_2^- transfer ratios found for the various reactions pairs, it is no surprise that H^- transfer occurs efficiently only in those cases where production of RH^+ represents a reasonably exothermic reaction channel for ground state reactants (processes 5–9, 12, 14, and 17). For all of the other reaction pairs cited, where $H^-/H_2^- < 0.1$, transfer of H^- to $C_nH_{2n}^+$ is either thermoneutral or endothermic based on current heats of formation (there are no references in the literature concerning $\Delta H_f°$ for the R^+ and RH^+ species from MCP).[21] Transfer of H_2^- is always favored thermodynamically in any $C_nH_{2n}^+ + RH_2$ combination, which accounts for the observation that $k(H^-)/k(H_2^-)$ is usually <1.0 even when hydride transfer is highly exothermic.

Comments on the Mechanism of H^-, H, H_2^-, and H_2 Transfer. The H_2^- transfer reaction has been described[11] as an extremely rapid stereospecific process in which H^- is first transferred from the most reactive site on RH_2 to the energetically favored position on the attacking olefin ion. Transfer of an H atom within the complex then occurs either simultaneously with this process or follows very quickly, and usually involves a skeletal site on RH^+ adjacent to the original point of H^- loss. Since no D^- transfer is observed from $CD_3CH_2CD_3$ (see Table I), it is reasonable to conclude that only the center carbon atom is involved in the initial hydride transfer to $C_2H_4^+$. If the subsequent transfer of the neutral atom within the complex were a slow process, one would expect a difference in the transfer ratios from C_3H_8 and $CD_3CH_2CD_3$ due to a kinetic isotop eeffect, since a D atom would be transferred in the second step in the latter situation. However, since $k(H^-)/k(H_2^-)$ from C_3H_8 is approximately equal to $k(H^-)/k(HD^-)$ from $CD_3CH_2CD_3$ (Table I), a distinct two-step mechanism can be ruled out in this particular reaction pair.

As indicated in the Methods and Results, we have observed charge exchange in c-$C_6H_{12}^+$–methylcyclopropane and c-$C_6H_{12}^+$–cyclobutane (reported previously[12]) mixtures but have not found any evidence for neutral transfer reactions within our experimental pressure range ($P \leq 0.2$ Torr). However, it has been verified in static systems[19] that c-$C_6H_{12}^+$ ions do disappear *via* H and H_2 transfer mechanisms in such mixtures at higher pressures. Apparently under our conditions of low collision frequency the $[c\text{-}C_6H_{12}\text{–}C_nH_{2n}]^+$ complex (where C_nH_{2n} denotes methylcyclopropane or cyclobutane) dissociates into C_6H_{12} and $C_nH_{2n}^+$ prior to the particle transfer step, while at higher pressures the lifetime of the complex is increased by collision.

The effect of increased density on the product distribution obtained in certain reaction pairs may also be demonstrated by considering the behavior found in c-C_6H_{12}–1-butene mixtures (see the Methods and Results section and Figure 5). In this particular case the initial reaction is

$$c\text{-}C_6H_{12}^+ + 1\text{-}C_4H_8 \longrightarrow C_6H_{10}^+ + n\text{-}C_4H_{10} \qquad (31)$$

which is followed by

$$C_6H_{10}^+ + 1\text{-}C_4H_8 \longrightarrow C_{10}H_{18}^+ \qquad (32)$$

and

$$C_6H_{10}^+ + 1\text{-}C_4H_8 \longrightarrow C_6H_8^+ + n\text{-}C_4H_{10} \qquad (33)$$

at higher total pressures. The net result of this overall sequence is an ion-pair yield for n-C_4H_{10} formation

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which is greater than the yield of $c\text{-}C_6H_{12}^+$ ions due to the additional $n\text{-}C_4H_{10}$ generated *via* process 33. However, in static systems at higher total pressures the ion-pair yield for $n\text{-}C_4H_{10}$ is 1.00,[19] indicating that the $[C_6H_{10}\text{-}C_4H_8]^+$ complex, which dissociates into $C_6H_8^+$ and C_4H_{10} under our conditions, is quantitatively stabilized at much higher collision frequencies.

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The Kinetics and Mechanism of Aquation of Carbonato Complexes of Cobalt(III). III. The Acid-Catalyzed Aquation of Some Carbonatobis(diamine)cobalt(III) Complexes

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Abstract: This study has comprised examination of the aquation of the complex ions $CoN_4CO_3^+$, where $N_4 \equiv$ $(en)_2$, $(pn)_2$, or $(tn)_2$ (en $\equiv$ ethylenediamine, pn $\equiv$ propylenediamine, and tn $\equiv$ trimethylenediamine). The kinetics and mechanism appear to be identical over the range $1 < pH < 5$ with those of the tetraammine analog ($N_4 \equiv (NH_3)_4$), for which the experimental rate constant is given by $k = k_0 + k_1[H^+]$, as previously reported. The values of the rate parameters for the water-catalyzed part of the process are the same within the inescapably large experimental error for all four complexes, with $k_0 \cong 1 \times 10^{-4}$ sec^{-1}, $\Delta H_0^{\ddagger} \cong 16$ kcal/mol, and $\Delta S_0^{\ddagger} \cong -20$ eu. The acid-catalyzed reactions show some small but significant differences such that k_1 is a little smaller at 25° for the $(en)_2$ and $(pn)_2$ species ($0.5\,M^{-1}$ sec^{-1}) than for $(tn)_2$ ($0.8\,M^{-1}$ sec^{-1}), and only about one-third as large as for the tetraammine ($1.5\,M^{-1}$ sec^{-1}), though the other rate parameters are not far apart. Deuterium solvent isotope effect studies confirm the earlier conclusion that these aquations involve a rate-determining proton transfer rather than a proton-preequilibration mechanism.

Our most recent paper in this series[2] reported a study of the acid-catalyzed aquation of carbonatotetraamminecobalt(III) ion over the acidity range $1 < pH < 5$. A combination of spectrophotometric and acidometric rate studies substantiated a stepwise concept for the reaction, with the rate-determining processes being ring opening of the chelated carbonato ligand by the parallel reactions ($N_4 = (NH_3)_4$)

$$CoN_4CO_3^+ + H_2O \xrightarrow{k_0} cis\text{-}CoN_4(OH)(CO_3H)^+ \quad (1)$$

$$CoN_4CO_3^+ + H_3O^+ \xrightarrow{k_1} cis\text{-}CoN_4(OH_2)(CO_3H)^{2+} \quad (2)$$

The other reactions involved, all much more rapid than (1) and (2), consist of two acid–base equilibria and the decarboxylation of the product of reaction 2, *viz.*

$$cis\text{-}CoN_4(OH_2)(CO_3H)^{2+} + H_2O \rightleftharpoons cis\text{-}CoN_4(OH)(CO_3H)^+ + H_3O^+ \quad K_1 \quad (3)$$

$$cis\text{-}CoN_4(OH_2)_2^{3+} + H_2O \rightleftharpoons cis\text{-}CoN_4(OH)(OH_2)^{2+} + H_3O^+ \quad K_2 \quad (4)$$

$$cis\text{-}CoN_4(OH_2)(CO_3H)^{2+} \longrightarrow cis\text{-}CoN_4(OH_2)(OH)^{2+} + CO_2 \quad k_2 \quad (5)$$

The rate law based on this mechanism takes the form

$$k_{\text{obsd}} = k_0 + k_1[H^+] \quad (6)$$

and was shown in the previous study[2] to interpret the data very well.

In a preliminary report,[3] we briefly discussed similar data obtained for the analogous species in which $N_4 \equiv (en)_2$ (en $\equiv NH_2CH_2CH_2NH_2$), utilizing a slightly more complex reaction scheme. We have now reexamined these data in the light of our extensive experiments with the tetraammine complex, and find the mechanism of reactions 1–5 above to be entirely satisfactory for the $(en)_2$ case. Furthermore, results obtained with the closely related complexes in which $N_4 \equiv (pn)_2$ or $(tn)_2$ (pn $\equiv NH_2CH(CH_3)CH_2NH_2$; tn $\equiv NH_2(CH_2)_3NH_2$) also fit well into the proposed general scheme. An added significant feature of this work is a deuterium solvent isotope effect study, which provides additional confirmation of the mechanistic interpretation presented.

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(1) Work done by V. S. Sastri as part of the Ph.D. requirement of the State University of New York at Buffalo, June 1966. Complete dissertation available from University Microfilms, Ann Arbor, Mich.

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