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Isotope Exchange vs Abstraction for H+DCl*

Gerry Odell Wood
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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Rates of isotope exchange reactions in deuterium chloride–hydrogen mixtures photolyzed at 1849 Å have been measured by mass spectroscopy. Under conditions where reactions of product molecules were negligible quantum yields of HD and D_2 were calculated using DCl for actinometry. Large HD quantum yields indicate that chain reactions occur. The ratio of HD to D_2 formed in these chain reactions is shown to be equal to the ratio k_2/k_3 of rate coefficients for the abstraction (2), $H+DCl \rightarrow HD+Cl$, and the exchange (3), $H+DCl \rightarrow HCl+D$. From quantum yields at 27-225°C this ratio is calculated to be $k_2/k_3=(850\pm 200)\exp[-(2220\pm 180)/RT]$. A quantum yield of D_2 independent of chain lengths and with little temperature dependence is attributed to the reaction $D^*+DCl \rightarrow D_2+Cl$ of hot atoms from DCl photodissociation.

INTRODUCTION

The reaction

$$Cl+H_2 \xrightarrow{f} HCl+H$$

and its reverse

$$H+HCl \xrightarrow{r} H_2+Cl$$

are among the most thoroughly studied elementary reactions. Arrhenius parameters for the rate coefficients of the former and for its hydrogen isotope effects have been well established experimentally.[1–3] An Arrhenius expression has been reported for the rate coefficient of the second reaction in good agreement with previous measurements.[3] It would seem therefore that the experimental information needed for a thorough understanding of the H–H–Cl system is available. However, as it has been reported and discussed recently,[3–5] the observed rate coefficients k_f and k_r for $Cl+H_2 \rightleftarrows HCl+H$ do not obey the relation $k_f/k_r=K$, where K is the equilibrium constant. Several possible explanations have been proposed for this observation which yet remain to be confirmed by experimental or theoretical evidence.

Over the past 40 years the systems $DCl–H_2$ and $HCl–D_2$ have been subject to several investigations,[6–10] thermal and photochemical, to determine mechanisms and rates of the isotope-exchange reactions occurring. As better methods for analyzing H_2, HD, D_2 mixtures have developed, the amount of information from these studies has increased. However, there are still some significant differences between the conclusions of the earlier thermal experiments and the more recent photochemical experiments which leave doubts as to the mechanisms important in both. For example, Steiner and Rideal[8] have concluded from thermal studies of D_2–HCl mixtures at 900°K that $k_b/k_c \gg 1$ and $k_a/k_b \ll 1$ for the following reactions:

$$H+D_2 \rightarrow HD+D, \tag{a}$$

$$H+HCl \rightarrow H_2+Cl, \tag{b}$$

$$D+HCl \rightarrow DCl+H, \tag{c}$$

$$D+HCl \rightarrow HD+Cl, \tag{d}$$

while de Vries and Klein[10] have concluded from photochemical experiments at 295°K that $k_d/k_c=0.0\pm 0.9$ and $k_a/k_b=14\pm 4$. Therefore, it was decided to reinvestigate the photochemically induced reactions in the $DCl–H_2$ system in order to obtain the H+DCl exchange/abstraction ratio.

I. EXPERIMENTAL

Prepared mixtures of DCl and H_2 were photolyzed at 1849 A and at 27–225°C. The products D_2 and HD were then determined as a function of time by mass spectrometry.

TABLE I. Quantum yields and rate coefficient ratios.

Exptl	Temp (°C)	Φ_{D_2}	Φ_{HD}	k_2/k_3
1	28	0.53	3.67	20.4
2	27	0.68	6.01	18.2
3	29	0.78	8.71	20.2
4	29	0.59	4.93	20.5
5	30	0.55	3.73	18.6
6	28	0.80	8.42	18.7
7	121	0.67	14.69	56.5
8	125	0.69	13.13	46.9
9	125	0.88	19.18	40.8
10	125	2.00	80.17	50.4
11	125	1.09	44.46	65.4
12	125	1.07	45.23	68.5
13	125	1.03	37.12	59.9
14	125	0.98	35.36	62.0
15	75	0.77	15.89	40.7
16	75	0.98	26.14	43.6
17	225	1.86	98.85	70.1
18	175	1.50	65.94	61.6
19	175	1.21	39.38	50.5
20	75	0.97	19.00	32.2
21	125	1.19	36.69	47.0
22	125	1.71	75.55	58.1
23	125	1.42	59.05	58.5
24	125	1.53	54.94	49.1
25	125	0.86	27.08	60.2

A. Reagents

Deuterium chloride was obtained from Stohler Isotope Chemicals with a deuterium isotope purity of 99%. Hydrogen (99.9%) was purified immediately before use by passing it through a heated palladium thimble. Xenon (99.995%) was obtained from the Linde Division of Union Carbide Corporation.

B. Apparatus and Procedure

The experimental apparatus consisted of a mercury-free high-vacuum line for the preparation of reaction mixtures; two cylindrical quartz photolysis cells (15 cm×5 cm diam), one wrapped with asbestos insulation containing heating tapes and thermocouples; a Hanovia SC2537 low-pressure mercury arc lamp with a Suprasil window for transmitting 1849-Å radiation; and a CEC 21-201 mass spectrometer for analyses of H_2, HD, D_2 product mixtures. Pressures of the reactants introduced into the cells were measured with a Texas Instruments, Inc., quartz-spiral gauge with an estimated precision of ±0.05 torr. Three points of contact fixed with respect to the lamp allowed reproducible positioning of the photolysis cells with approximately a 2-cm separation for a shutter. The source emitted strongly at 1849 and 2537 A but the DCl absorption spectrum is such that only the 1849-A radiation is absorbed. A Sola constant voltage transformer and a Variac were used to adjust and maintain a constant lamp intensity. For the analysis of H_2, HD, D_2 product mixtures a stainless-steel capillary tube led into the mass spectrometer ionization chamber from a capillary stopcock attached to the photolysis cell.

Except for one window and a Teflon stopcock the second quartz cell was wrapped with asbestos containing three copper–constantan thermocouples and three separate sections of heating tape. The thermocouples were placed in contact with the cell wall near the front window (nearest the lamp), near the center of the cell body, and on the rear window. Each of the heating tape sections covered approximately one-third of the wrapped cell surface and was connected to a separate variable voltage transformer. By observing and controlling the temperatures of the three cell sections variations from the nominal reaction temperatures were kept within 1°C during the periods of photolysis.

Quantities of H_2 and DCl were added in succession to a photolysis cell at 302 ± 4°K and the total pressure measured after each addition. The cell was then positioned in front of the lamp with the shutter closed and attached to the mass spectrometer capillary leak. Upon evacuation of the capillary leak through the mass spectrometer an isotopic analysis of hydrogen was made as follows: The cell was rotated away from the lamp, cooled to room temperature, and the front window submerged in liquid nitrogen to condense to negligible pressures all gases but H_2, HD, and D_2. The capillary stopcock to the mass spectrometer leak was then opened and masses 3 and 4 scanned at least twice. After an analysis the cell was warmed again to the reaction temperature. After each period of photolysis (60 ± 1 to 600 ± 2 sec) the analysis was repeated.

II. EXPERIMENTAL RESULTS

The experimental data are summarized in Table I. For each experiment with an initial mixture of 20.0 torr each of DCl and H_2 the data were obtained as a series of mass spectrometer signals at masses 3 and 4 and the corresponding total photolysis times. Plots of these signals vs photolysis time were always linear which is attributed to the very small extents of reaction (<0.6% DCl decomposition) for which reactions of products were negligible. Least-square fits of these plots were made to obtain rates of signal increases. The mass spectrometer was calibrated with prepared mixtures of D_2 and HD under experimental conditions. No thermal isotope exchange was observed up to 225°C in the absence of exposure to lamp output.

For actinometry measurements of the lamp output at 1849 Å frequent photolyses of 20.0 torr DCl were done. The initial quantum yield of D_2 formation in such photolyses is unity.[11] Quantum yields Φ_{HD} and Φ_{D_2} were calculated by dividing rates of HD and D_2 increases in photolyzed mixtures containing 20.0 torr each of H_2 and DCl by the rate of D_2 increase in a sample containing 20.0 torr of DCl only. For Φ_{HD} suitable corrections were made for the ratio of mass spectrometer sensitivities for HD and D_2.

The experimental quantum yields from photolyzing 25 mixtures of 20.0 torr each of DCl and H_2 at 27–225°C are listed in Table I. Experiments were done in the order listed. Experiments 2, 3, and 4 had 299.3, 154.2, and 20.6 torr of Xe added, respectively.

III. INTERPRETATION OF RESULTS

The photodissociation of DCl gives D atoms and Cl atoms which initiate the reactions which occur. The observation that quantum yields $\Phi_{HD}>1$ for all experiments can only mean that HD was mostly formed by a chain reaction. The steps most likely to be involved in this chain at small extents of reaction are

$$\mathrm{Cl+H_2\rightarrow HCl+H}, \tag{1}$$

$$\mathrm{H+DCl\rightarrow HD+Cl}, \tag{2}$$

$$\mathrm{H+DCl\rightarrow HCl+D}, \tag{3}$$

$$\mathrm{D+H_2\rightarrow HD+H}, \tag{4}$$

$$\mathrm{D+DCl\rightarrow D_2+Cl}. \tag{5}$$

The reaction $\mathrm{Cl+DCl\rightarrow Cl_2+D}$ is omitted since it is quite endothermic and, therefore, much less likely to occur relative to Reaction (1) which is nearly thermoneutral. Assuming that a steady state concentration of [D] is established by the chain reaction the following expression can be derived:

$$\frac{\Phi_{D_2}}{\Phi_{HD}}=\frac{d[D_2]/dt}{d[HD]/dt}=\left[\frac{k_4[H_2]}{k_4[H_2]+k_5[DCl]}+\frac{k_2}{k_3}\right]^{-1}. \tag{6}$$

For a constant temperature and $[H_2]=[DCl]$ a plot of Φ_{D_2} vs Φ_{HD} should be linear with a slope of $[k_4/(k_4+k_5)+k_2/k_3]^{-1}$. In Fig. 1 are plotted the quantum yields from six experiments at 27–30°C and 12 at 125°C. Linear least squares fits yield slopes of 0.052 ± 0.004 for the former and 0.0180 ± 0.0016 for the latter.

However, the intercepts of these plots are not zero as predicted by the mechanism above, but are $\Phi_{D_2}{}^0=0.35\pm0.02$ and 0.41 ± 0.08, respectively. These nonzero intercepts indicate a source of D_2 independent of the chain reactions. One possibility is the reaction of deuterium atoms formed by dissociation of DCl, i.e.,

$$\mathrm{D^*+DCl\rightarrow D_2+Cl}. \tag{7}$$

The asterisk indicates a hot atom reaction since the D* atoms are formed with an excess energy of about 2 eV upon photodissociation of DCl with 1849-Å light.[11] These hot atoms can also react with the H_2 present[12]

$$\mathrm{D^*+H_2\rightarrow HD+H}. \tag{8}$$

The quantum yields of D_2 and HD from Reactions (7) and (8) must be less than unity and equal to the fraction of these hot deuterium atoms reacting with DCl and H_2, respectively. Furthermore, these quantum yields would be independent of the quantum yields from the chain reaction and would have little temperature dependence. The linearity of the plots of Fig. 1 and the agreement of the intercepts of the data at 27–30°C and 125°C within experimental uncertainty suggest that the nonzero intercepts are due to Reaction (7).

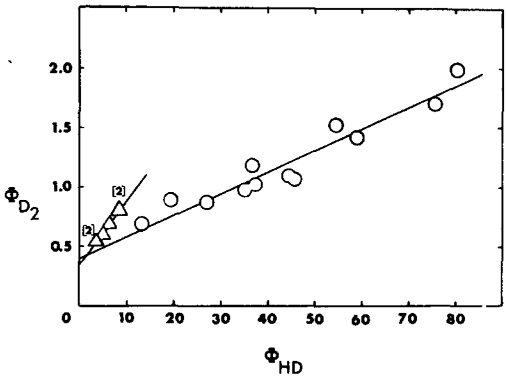

FIG. 1. Quantum yields of D_2 and HD at 27–30°C, △, and at 125°C, ○.

A second possibility as a source of the D_2 formed independent of the chain reaction is the termination step

$$\mathrm{D+D+M\rightarrow D_2+M} \tag{9}$$

by a three-body encounter in the gas phase or at the wall. Reaction (9) would compete with other termination reactions such as

$$\mathrm{H+D+M\rightarrow HD+M}. \tag{10}$$

Neglecting isotope effect factors the relative rate of Reactions (9) and (10) would be

$$R_9/R_{10}\approx[D]/[H]=k_3[DCl]/(k_4[H_2]+k_5[DCl])$$
$$=k_3/(k_4+k_5)\approx(k_3/k_2)[k_5/(k_4+k_5)]. \tag{11}$$

This atom concentration ratio is obtained from steady-state considerations of the chain reaction, from $[DCl]=[H_2]$, and from $k_2\approx k_5$. Using the ratios k_2/k_3 and k_4/k_5 derived below, $R_9/R_{10}\approx0.05$ at 27–30°C and 0.02 at 125°C. This means that the quantum yield of D_2 from Reaction (9) was ≤0.05, i.e., too small to account for the intercepts of Fig. 1. Very likely other atom recombination reactions occurred which would decrease this upper limit even further. Thus the hot D atom reaction (7) appears to be the major contributor to the intercept of Fig. 1.

Xenon was added in Expts. 2, 3, and 4 to change the chain length. Addition of 20.6 and 154.2 torr of xenon in Expts. 4 and 3 increased the chain length by inhibiting atom diffusion to the walls. Further increase of xenon to 299.3 torr in Expt. 2 further inhibited atom diffusion to the walls, but chain lengths (quantum yields) decreased due to the enhancement of three-body gas-phase atom recombinations. In order to extend the

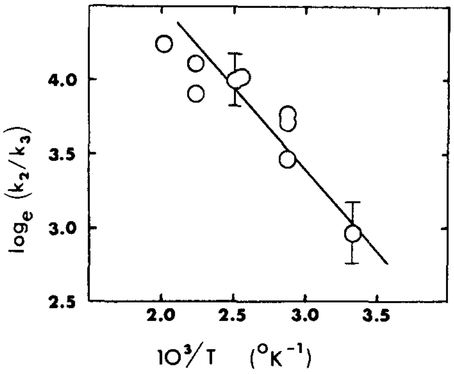

FIG. 2. Arrhenius plot for the H+DCl abstraction/exchange rate coefficient ratio.

range of quantum yields further it would have been necessary to make the cell walls more inefficient for atom recombination by a special treatment or coating. The addition of xenon did not significantly affect the intercept of Fig. 1, i.e., the fractions of hot atoms reacting with DCl and H_2. This is in agreement with the report that Xe affects hot D* atom distributions much, much less than comparable amounts of a diatomic gas such as DCl.[11]

In order to calculate the ratios k_2/k_3 from the slopes of Fig. 1 it is necessary to know k_4/k_5. Westenberg and deHaas have reported measurements of the rate coefficient of Reaction (b), $H+HCl \rightarrow H_2+Cl$, in the range 251–456°K by a fast flow technique and ESR spectroscopy.[3] The Arrhenius expression which they reported, $k_b = 2.3 \times 10^{13} \exp(-3500/RT)$ cm^3 $mole^{-1} \cdot sec^{-1}$, was found to agree well with values of k_b reported previously, including those from the thermal experiments of Steiner and Rideal at higher temperatures.[13,8] No rate coefficients have been reported for the analogous Reaction (5), $D+DCl \rightarrow D_2+Cl$. Therefore, transition-state theory has been used to calculate k_5 from k_b and the potential energy surface reported by Westenberg and deHaas[3]: $k_5 = 6.4 \times 10^{12} \exp(-3804/RT)$ cm^3 $mole^{-1} \cdot sec^{-1}$. By the same experimental technique Westenberg and deHaas have obtained $k_4 = 4.4 \times 10^{13} \exp[-7610/RT]$ cm^3 $mole^{-1} \cdot sec^{-1}$ for Reaction (4), $D+H_2 \rightarrow HD+H$, over the range 250–750°K.[14] Again, these k_4 values were in good agreement with previous measurements.[15] The ratio of these rate coefficients is $k_4/k_5 = 6.86 \exp(-3806/RT)$, giving $k_4/k_5 = 0.012$ at 27–30°C, 0.056 at 125°C, and 0.147 at 225°C, the highest experimental temperature. From Slope $= [k_4/(k_4+k_5) + k_2/k_3]^{-1}$ it is then calculated that $k_2/k_3 = 19.2 \pm 4.4$ at 27–30°C and $k_2/k_3 = 55.5 \pm 6.2$ at 125°C. The uncertainties for these values include one standard deviation in the least-square fits and uncertainties in the mass spectrometer calibration.

To compare all 25 experiments on the same basis it has been assumed that the small difference in intercepts of Fig. 1 is real and corresponds to a small activation energy for Reaction (7) relative to Reaction (8). This yields intercepts ranging from 0.38 at 75°C to 0.45 at 225°C. From these values and quantum yields for all experiments the abstraction/exchange ratios k_2/k_3 given in Table I were calculated.

In Fig. 2 an Arrhenius plot has been made for these ratios of rate coefficients. The error bars include one standard deviation from the averages for the sets of experiments at 27–30°C and 125°C and the uncertainty in mass spectrometer calibration. A least-squares fit of this plot gives the Arrhenius expression for the H+DCl abstraction/exchange ratio:

$$k_2/k_3 = (850 \pm 200) \exp[-(2220 \pm 180)/RT]. \quad (12)$$

IV. DISCUSSION

The ratio of rate coefficients for abstraction (2), $H+DCl \rightarrow HD+Cl$, and exchange (3), $H+DCl \rightarrow HCl+D$, has been found to be $k_2/k_3 = 19 \pm 4$ at 27–30°C. In terms of the mechanism of isotope exchange in the H_2–DCl photochemical system this result indicates that for an average of about every 19 molecules of HD formed by the chain of reactions, $Cl+H_2 \rightarrow HCl+H$ and $H+DCl \rightarrow HD+Cl$, one molecule of D_2 is formed by an alternate chain, $H+DCl \rightarrow HCl+D$, $D+DCl \rightarrow D_2+Cl$, and $Cl+H_2 \rightarrow HCl+H$. In comparison with other H+DX reactions the ratio $k_3/k_2 = 0.05 \pm 0.01$ is of the same magnitude as exchange/abstraction rate coefficient ratios 0.09 ± 0.03 and 0.05 ± 0.03 for H+DBr and H+DI, respectively, near 300°K.[16] The results reported here are also in agreement with the conclusions of Steiner and Rideal that for thermal isotope exchange reactions in D_2, HCl, and H_2, DCl mixtures at 900°K the abstraction reactions predominate over the exchange reactions.[8] However, these results are in disagreement with deVries and Klein who have reported from photochemical experiments that the exchange predominates.[10]

The temperature dependence of k_2/k_3 in the Arrhenius expression (12) shows that the large abstraction/exchange ratios are due entirely to a large pre-exponential factor ratio $A_2/A_3 = 850$; the activation energy for abstraction is actually 2.22 kcal/mole greater than the activation energy for exchange. Since identical reactants are involved the pre-exponential factor ratio can also be considered a steric factor ratio. Combining this with a reported[13] steric factor of 0.025 for $H+HCl \rightarrow H_2+Cl$ gives 3×10^{-5} as the steric factor for exchange.

The 2.2-kcal/mole activation energy difference suggests that no common intermediate such as a bent H–Cl–D complex occurs in both reactions. When this $E_2 - E_3$ is combined with the 3.5 kcal/mole activation energy of $H+HCl \rightarrow H_2+Cl$,[3] the activation energy for exchange is found to be approximately 1.3 ± 0.4 kcal/mole. This value is close to the 1.0 ± 1.3 kcal/mole reported by deVries and Klein.[10]

In a recent review of hydrogen–halogen potential energy surfaces Parr and Truhlar[17] have examined the semiempirical surfaces which have been proposed for HHCl.[2,3,8] This review will not be repeated here but some major features of these surfaces are listed in Table II. For a real H+HCl collision in three dimensions the same potential energy function should describe the exchange as well as the abstraction. Thus a test of these surfaces is to construct linear HClH surfaces with the same potential energy functions and to compare predicted exchange activation energies with the experimental value of 1.3 kcal/mole. The HClH configuration has been calculated[8,17] with the results given in Table II.

The general feature of a symmetrical well for all three surfaces predicts a bound linear HClH complex. Nelson and Pimentel[18] have observed the infrared spectrum of ClHCl in a rare gas matrix, but no such evidence for the existence of HClH has been reported. This negative evidence alone is insufficient to challenge the qualitative form of these HClH surfaces. The LEPS and extended LEPS surfaces do not have barriers from which activation energies can be calculated by transition-state theory and compared with the 1.3 kcal/mole reported in this paper. The LEP surface has a 5-kcal/mole barrier much too high and also a well probably much too deep (since HClH has not been observed). One method for obtaining activation energies for both the exchange and abstraction is a three-dimensional trajectory calculation. Such studies are now in progress for several surfaces.

Once a potential energy function is found which predicts the correct activation energies for both the H+HCl abstraction and exchange, the large pre-exponential factor of k_2/k_3 can be used as a further test of the surface. From the LEP surface Steiner and Rideal concluded that the predominance of abstraction over exchange is due to a low transmission coefficient for exchange. In absolute rate theory this transmission coefficient is one factor in the pre-exponential term of k_2/k_3. Other factors which may be significant are quantum mechanical tunneling corrections or long-range interactions. However, before such possibilities can be examined it is first necessary to have a potential energy function which adequately gives the experimental activation energies and pre-exponential factors for $k(\mathrm{H}+\mathrm{HCl}\rightarrow\mathrm{H_2}+\mathrm{Cl})$ and for k_2/k_3 as well as the isotope effects for $\mathrm{Cl}+\mathrm{H_2}$.

TABLE II. A comparison of potential energy surfaces.

		Surface features (kcal/mole)		
Ref.	Type	HHCl barrier[a]	HClH barrier[a]	HClH well[a]
8	LEP	10	5	−18
2, 3	LEPS	4–5	None	−5
2	Extended LEPS	5	None	−9

[a] Relative to H+HCl.

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