# Hot-Atom Reactions in the Photolysis of Deuterium Chloride at 1849 Å*

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(Received 19 May 1969)

The importance of hot deuterium atoms in photolyses of DCl–Cl₂ mixtures at 1849 Å has been demonstrated, and the kinetics of this system have been described. Photodecomposition of DCl was followed by mass-spectrometric analysis of the D_2 formed after successive intervals of time. The observed decreases in the initial rate of D_2 formation upon addition of Cl_2 and inert gases CO_2, Xe, and CF_4 may be readily interpreted in terms of a hot-atom mechanism but cannot be made compatible with a completely thermal mechanism. Rate coefficient ratios for the hot-atom reactions,

$$D^*+DCl \xrightarrow{2} D_2+Cl,$$
$$D^*+M \xrightarrow{3} D+M,$$
$$D^*+Cl_2 \xrightarrow{6} DCl+Cl,$$
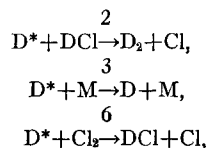
were found to be $k_6/k_2 \approx 6.5$, $k_3^{DCl}/k_2 = 0.65$, $k_3^{CO_2}/k_2 = 1.15$, $k_3^{CF_4}/k_2 \approx 1.15$, and $k_3^{Xe}/k_2 < 0.1$. The ratio k_6/k_2 increased from 6.5 in the absence of inert gas to 9.2 when $[CO_2]/[DCl] = 1.87$. This ratio increases to ≈ 300 for a thermal atom distribution at 300°K. Comparisons of thermalizing efficiencies for several molecules suggest that inelastic collisions are important in thermalizing hot atoms produced photochemically at 2.1 eV.

INTRODUCTION

The hydrogen halides HI and HBr and their isotopic analogs have been widely used in recent years as photochemical sources of high-energy hydrogen atoms.[1–5] These "hot" atoms produced following absorption of an ultraviolet photon either undergo chemical reactions while possessing relatively high translational energies or relax to a thermal energy distribution via elastic and inelastic collisions and are then removed by thermal reactions. The reactive and nonreactive processes which occur in these systems are of interest because they involve higher average energies than those readily accessible in thermal systems at ordinary temperatures. Experimental data from studies of photochemically produced hot-atom systems contain information about the reactive and nonreactive cross sections involved at relative energies up to about 3 eV in experiments reported in the literature. In principle, the hot-atom experimental data together with thermal data may be compared with numerical computations[6–8] to provide a more sensitive test of the applicability of various model cross sections than can be obtained using thermal data alone.

The reactions of hydrogen atoms with HI and I₂ in the gas-phase photolysis of HI have been the subject of two recent papers[9,10] in which the effect of thermalization by inert gases was studied. Rate constant ratios for thermal H atoms reacting with I₂ and HI were extracted and found to agree at least qualitatively with Sullivan's[11] estimates of these same ratios. The hot-atom rate-constant ratio corresponding to the thermal ratio mentioned above has been obtained by Ogg and Williams.[12]

We report here our work on the analogous DCl–Cl₂ system. The purpose of this work was: (1) to study the significant hot-atom effects in the photolysis at 1849 Å of DCl–Cl₂ mixtures, (2) to study the influence of various inert thermalizing agents, and (3) to compare hot-atom results with thermal data. Deuterium chloride was chosen instead of HCl because the product D_2 could be measured much more accurately than H_2 on the mass spectrometer. Background signals at $m/e = 2$ introduced considerable error since they were often comparable to the net product signal. Background signals at $m/e = 4$ were negligible.

EXPERIMENTAL

The experiments described in this paper consisted essentially of photolyzing at 1849 Å a known mixture of DCl, Cl_2, and an inert thermalizing species followed by mass-spectrometric analysis of the D_2 produced.

Reagents

Deuterium chloride was obtained in 1-liter Pyrex bulbs from Merck, Sharpe and Dohme of Canada, Limited, with a deuterium isotope purity of 99% but partially decomposed (<1%) into Cl_2 and D_2. The deuterium was removed by pumping after freezing with liquid nitrogen. Chlorine was removed by multiple distillations from a 2-methylbutane slush bath (−160°C) to a liquid-nitrogen bath (−196°C). Chlorine (99.5%) was obtained from The Matheson Company, Incorporated, in lecture bottles. Carbon dioxide (99.99%), deuterium (99.5%), and xenon (99.995%) were purchased from the J. T. Baker Company. Chlorine was further purified by multiple distillations from a dry-ice–acetone bath (−78.5°C) to a liquid-nitrogen bath and by pumping on the chlorine frozen in a 2-methylbutane
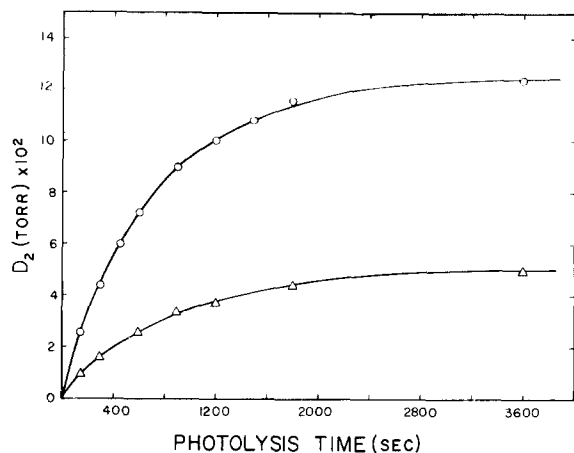
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FIG. 1. Variation of D_2 with time. O, 99 torr of DCl; △, 99 torr of DCl and 15 torr of Cl_2.

slush bath to remove HCl. Distillations of DCl and Cl_2 were carried out as soon before use as practical. The CO_2 and Xe were used as supplied.

Apparatus and Procedure

The experimental apparatus consisted of a mercury-free vacuum line for preparing the reaction mixtures, a cylindrical quartz photolysis cell (15.1-cm×5-cm diam) with Suprasil quartz windows, a Hanovia SC2537 low-pressure mercury arc lamp with a Suprasil window for transmitting 1849-Å radiation, and a modified Varian Partial Pressure Gauge Model 974–0036 with recorder for measuring the amount of deuterium in the cell. The vacuum line and cell were prepared initially by evacuation to 10^{-6} torr, filling with about 50 torr of DCl for at least 24 h, and re-evacuation. Initial pressures of reactants were measured by a null-indicating Pace pressure transducer separating the vacuum line from a manifold containing a mercury manometer. The vacuum line was also used for multiple distillations of deuterium chloride and chlorine. The lamp and cell were permanently fixed in position with approximately 1 cm separating the two windows to allow room for a shutter. The source emits strongly at 1849 and 2537 Å but the DCl spectrum is such that only the 1849-Å radiation is absorbed. A Sola constant voltage transformer and a Variac were used to adjust and maintain a constant lamp current of 120 mA. For the analysis of D_2 product a stainless-steel capillary tube (inner diameter 0.15 mm; length 50 cm) led into the partial pressure gauge analyzer tube from a capillary stopcock attached to the photolysis cell. With a deuterium pressure of 1.00 torr in the photolysis cell and the cell under experimental conditions the deuterium partial pressure reading in the analyzer tube was nominally $(7.0\pm0.3)\times 10^{-9}$ torr. During the course of the experiments the cali-

bration was checked at intervals and the analyzer tube reading was found to be always linear with pressure up to 5 torr of D_2. The pressure decrease in the photolysis cell during an analysis was undetectable.

The procedure for all the experiments was the same. After evacuating the cell and closing the capillary stopcock quantities of distilled DCl, Cl_2, and/or inert gas were added in succession and the total pressure measured after each addition. The initial temperature of the reactants was $303\pm2°K$. Photolysis was begun by removing a shutter while starting an electric timer manually; photolysis was concluded by the opposite procedure. The resulting uncertainty in the photolysis time was ±2 sec. Immediately liquid nitrogen was placed around the photolysis cell such that the main body of the cell (excluding the stopcocks) was completely submerged. Within a few seconds all gases except deuterium condensed and had negligible partial pressures. The deuterium pressure in the cell was then measured by opening the capillary stopcock to the partial-pressure gauge and scanning the mass-3 and mass-4 peaks at least twice. During the analysis the liquid-nitrogen vessel was kept filled. After analysis the capillary stopcock was closed, the liquid-nitrogen bath was removed, and the cell was warmed up to the initial temperature with a distilled water bath and dried. Complete remixing of all gases occurred in the 15 min required to rewarm the cell. The photolysis of the same sample was then continued with intermittent stops and analyses as described above until sufficient data for the variation of $[D_2]$ with time had been obtained.

As soon as possible following each photolysis of DCl (or DCl and inert gas) several photolyses were done at nearly the same initial $[DCl]$ and $[M]$ but with added Cl_2. The results of these experiments were compared only with the results of the preceding photolysis of the same pressure of DCl in the absence of Cl_2. This was
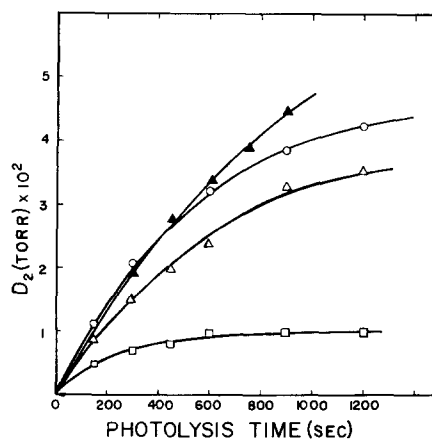

FIG. 2. Variation of D_2 with time. O, 99 torr DCl, 5.4 torr Cl_2; ▲, 99 torr DCl, 4.5 torr Cl_2, 350 torr Xe; △, 99 torr DCl, 4.4 torr Cl_2, 90 torr CO_2; □, 99 torr DCl, 5.0 torr Cl_2, 195 torr CO_2.

necessary since the lamp intensity varied over long intervals of time.
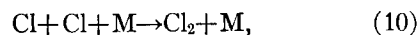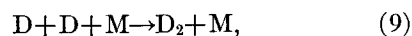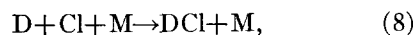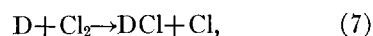
EXPERIMENTAL RESULTS

For each experiment with an initially prepared mixture of DCl, Cl_2, and inert gas the data were obtained as a series of partial pressure gauge peak heights and the corresponding total photolysis times. From calibrations of the apparatus with known deuterium pressures the peak heights can be converted to pressures of deuterium product in the photolysis cell at room temperature. The deuterium product concentration $[D_2]$ is then obtained from known cell volume and temperature. Figure 1 shows typical examples of the experimentally determined variation of deuterium pressure with time in the presence and absence of Cl_2. The results are characterized by a monotonic increase in deuterium pressure to some nearly asymptotic value. The pronounced effect of adding Cl_2 is clearly demonstrated.

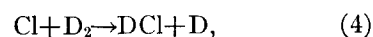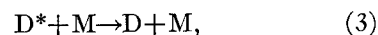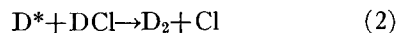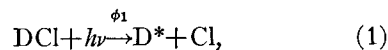Figure 2 illustrates the effect of adding the inert gases CO_2 and Xe to a DCl–Cl_2 mixture. The addition of CO_2 retards the initial rate of formation of D_2 as well as lowering its asymptotic value. Xenon, on the other hand, has very little effect on the initial rate of D_2 formation but the asymptotic value of $[D_2]$ is larger than in the absence of xenon. These effects are interpreted below in terms of the effective thermalization of "hot" D atoms by CO_2, the ineffective thermalization by Xe, and the influence of three-body recombination reactions. All the photolysis experiments are summarized in Table I including those using CF_4 as the inert thermalizing species. Blank experiments performed in the absence of irradiation showed no decomposition. Attempts to use thermalizing species which are not condensible at 77°K were unsuccessful because of difficulties in calibrating the partial pressure gauge.

MECHANISM

Upon absorption of 1849-Å light by DCl, photodissociation occurs with the excess energy (2.22 eV) above that required to break the bond (4.48 eV) going into the product atoms. The only accessible excited electronic state of the product atoms is $Cl(^2P_{1/2})$ which lies 0.11 eV above the ground state.[13] Therefore, at least 2.11 eV must end up as translational energy of the product atoms, distributed between them to conserve momentum. The D atom then has a kinetic energy of $E_D = (M_{Cl}/M_{DCl})E_T = (35/37)$ (2.11 or 2.22 eV) = $(37/39)(2.11$ or 2.22 eV) = 2.00 or 2.10 eV, for either chlorine isotope. The average kinetic energy of a particle which is part of a thermal Boltzmann distribution at 298°K is $E = (3/2)kT = 0.038$ eV. Therefore, D atoms formed by the photochemical process described above will have initial kinetic energies considerably greater than average thermal molecules and atoms in the photolysis system. Such high-energy atoms are expected to be more reactive and are called "hot atoms."

Assuming the production of a steady-state nonthermal reactant distribution arising from photodissociation of DCl and subsequent collisions of D atoms, the following reactions must be considered in the mechanism for systems containing DCl, Cl_2, inert gas, and D_2:

$$DCl + h\nu \xrightarrow{\phi_1} D^* + Cl, \tag{1}$$

$$D^* + DCl \rightarrow D_2 + Cl \tag{2}$$

$$D^* + M \rightarrow D + M, \tag{3}$$

$$Cl + D_2 \rightarrow DCl + D, \tag{4}$$

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

$$D^* + Cl_2 \rightarrow DCl + Cl, \tag{6}$$

$$D + Cl_2 \rightarrow DCl + Cl, \tag{7}$$

$$D + Cl + M \rightarrow DCl + M, \tag{8}$$

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

$$Cl + Cl + M \rightarrow Cl_2 + M, \tag{10}$$
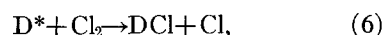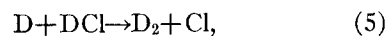
where ϕ_1 is the rate at which DCl is photodissociated. In these reactions D^* denotes deuterium atoms whose energy distribution is nonthermal while D denotes deuterium atoms possessing a thermal energy distribution characteristic of the macroscopic reaction vessel temperature. The distribution of D^* energies is determined by Reactions (1)–(3) and (6). The reaction $Cl + DCl \rightarrow Cl_2 + D$ is strongly endothermic ($\Delta E_0° = 46$ kcal/mole) and therefore may be neglected at ordinary temperatures in comparison to other chlorine-atom reactions.[14] This eliminates the possibility of a chain reaction for D_2 formation in this system. Molecule–molecule reactions are also neglected due to large activation energies.[15] In Reactions (8)–(10) M represents all bodies which act as third bodies in the recombination reactions. The M in Reaction (3) represents all bodies which act to transform the hot-atom energy distribution into a thermal distribution by means of nonreactive collisions. The rate coefficients for reactions of D^* with DCl and Cl_2 molecules are expected to be significantly larger than for the analogous reactions of D atoms with energies corresponding to a room-temperature thermal distribution.

Making the steady-state approximation for $[D^*]$ and $[D]$ and assuming that the rates of three-body recombinations of D atoms are much smaller than the rates of other reactions of D atoms, i.e., that

$$k_5[D][DCl] \gg 2k_9[D]^2[M] + k_8[D][Cl][M], \tag{11}$$

the rate of formation of deuterium is given by

$$\frac{d[D_2]}{dt} = \left(\frac{\phi_1}{1+(k_6[Cl_2]/k_2[DCl])+(k_3[M]/k_2[DCl])}\right)\left(1+\frac{(k_3[M]/k_2[DCl])}{1+(k_7[Cl_2]/k_5[DCl])}\right)$$
$$-\left(\frac{k_4(k_7[Cl_2]/k_5[DCl])[Cl][D_2]}{1+(k_7[Cl_2]/k_5[DCl])}\right). \quad (12)$$

Taking our experimental conditions, reasonable estimates for the rate constants k_5, k_8, and k_9, and the experimental value of ϕ_1, the assumption (11) requires the D-atom pressure to be less than 10 torr, a requirement met by all our experiments. The concentration of chlorine atoms [Cl] is not eliminated from Eq. (12) and subsequent equations since the chlorine-atom recombination mechanism is uncertain and since it is only necessary to assume a steady-state concentration of Cl to perform the calculations involved in the analysis of these experiments.

The first two limiting cases of the differential equation (12) may now be examined. For $k_7[Cl_2]/k_5[DCl]\ll1$ and $k_6[Cl_2]/k_2[DCl]\ll1$, Eq. (12) simplifies to

$$d[D_2]/dt\cong\phi_1-(k_7[Cl_2]/k_5[DCl])k_4[Cl][D_2]. \quad (13)$$

These conditions are expected to be valid only in the

initial stages of the photolysis of pure DCl or DCl–M mixtures. The rate constant ratio k_7'/k_5' for the isotopically analogous reactions of H atoms with Cl_2 and HCl, respectively, is about 90 at 25°C and decreases to smaller values at higher temperatures.[16] For thermal D atoms reacting with Cl_2 and DCl, respectively, the ratio k_7/k_5 is estimated from k_7'/k_5' and transition-state theory to be 310 at 25°C (see discussion below). In the photolysis of DCl alone the maximum decomposition was approximately 0.5% implying $k_7[Cl_2]/k_5[DCl]\lesssim0.8$ when the reactions were terminated. Hence, Eq. (13) is not valid except at the beginning of a photolysis of pure DCl or of a DCl–M mixture. In such a photolysis the initial slope of $[D_2]$ vs time is ϕ_1, the rate of photodissociation and the rate of absorption of light.

The second limiting case is $k_7[Cl_2]/k_5[DCl]\gg1$, for which

$$\frac{d[D_2]}{dt}\cong\left(\frac{\phi_1}{1+(k_6[Cl_2]/k_2[DCl])+(k_3[M]/k_2[DCl])}\right)\left(\frac{1+(k_7[Cl_2]/k_5[DCl])+(k_3[M]/k_2[DCl])}{1+k_7[Cl_2]/k_5[DCl]}\right)$$
$$-k_4[Cl][D_2]. \quad (14)$$

For photolyses of mixtures of DCl and Cl_2 with

$$[Cl_2]/[DCl]>0.1$$

this rate expression should be valid since

$$k_7[Cl_2]/k_5[DCl]\gtrsim31.$$

The initial rate of deuterium formation is less than ϕ_1

when Cl_2 is added due to the competition of Reactions (6) and (3) with Reaction (2) for D* atoms. The ratio of initial slopes of plots of $[D_2]$ vs time for two photolyses, one without added Cl_2 and one with added Cl_2, is the ratio of the first terms on the right-hand side of Eqs. (13) and (14), respectively. If the lamp intensity and [DCl] are fixed from experiment to experiment, ϕ_1 is then fixed and this ratio becomes

$$R = \left(1+\frac{k_6}{k_2}\frac{[Cl_2]}{[DCl]}+\frac{k_3}{k_2}\frac{[M]}{[DCl]}\right)\left(\frac{1+(k_7[Cl_2]/k_5[DCl])}{1+(k_7[Cl_2]/k_5[DCl])+(k_3[M]/k_2[DCl])}\right). \quad (15)$$

This equation relates experimentally measured quantities to the rate coefficients of reactions involved in the mechanism and is used below to analyze the data.

If hot atoms are not present in the system a thermal mechanism, neglecting Reactions (2), (3), and (6), should describe the experimental results. For such a mechanism,

$$\frac{d[D_2]}{dt} = \left(\frac{\phi_1}{1+(k_7[Cl_2]/k_5[DCl])}\right)-\left(\frac{k_4(k_7[Cl_2]/k_5[DCl])[Cl][D_2]}{1+k_7[Cl_2]/k_5[DCl]}\right) \quad (16)$$

and

$$R = 1 + (k_7[Cl_2]/k_5[DCl]). \qquad (17)$$

The addition of inert gases will have no effect on this ratio provided conditions are chosen such that the assumption (11) is valid.

DATA ANALYSIS

To obtain experimental values of R it is necessary to determine the initial slopes of graphs of $[D_2]$ vs time. These initial slopes could not be obtained graphically by linear extrapolation since the second term of the rate law equation (12) causes curvature in the $[D_2]$-vs-time graphs beginning below the limits of reliable $[D_2]$ measurability. In order to obtain initial slopes, the data for each experiment were fit to an equation of the form $d[D_2]/dt = A - B[D_2]$ or

$$[D_2] = (A/B)[1 - \exp(-Bt)].$$

This functional form is obtained from Eq. (14) for cases where $[Cl_2]$ was initially present by assuming a steady-state chlorine-atom concentration and noting that the product of the two factors making up the first term of the right-hand side of Eq. (14) is nearly constant if the fractional decomposition of DCl is small. The maximum fractional decomposition in our experiments was 0.005. Empirically, we found the data from experiments in which Cl_2 was initially absent to be well described by an equation of the same form. Equation (13), for the reason discussed above, furnished a much poorer representation of the data, especially late in the photolysis.

In the fitting procedure, the constants A and B were adjusted until the standard deviation of the experimental D_2 pressures from the calculated values were minimized. The lines drawn through the experimental points in Figs. 1 and 2 are the calculated curves. At large times (>3600 sec) the experimental slope becomes very small but does not go to zero as predicted by the mechanism. For example, after photolyzing 100 torr of DCl for 6 h the D_2 product pressure increased at the rate of 0.001 torr/h while in the first 1800 sec of photolysis the rate was 0.22 torr/h. This effect is attributed to a small contribution by Reaction (9), the recombination of deuterium atoms. To minimize the effect of this reaction (which was neglected in deriving the rate equations) only experimental data for times less than 1800 sec were used to calculate initial slopes.

The results of the fitting procedure are given in Table I. The standard deviations σ listed provide a measure of the scatter of experimental points from the calculated curves for D_2 pressure vs time. The last column shows the ratio R of initial rate in the absence of Cl_2 to the initial rate when Cl_2 is added to the re-
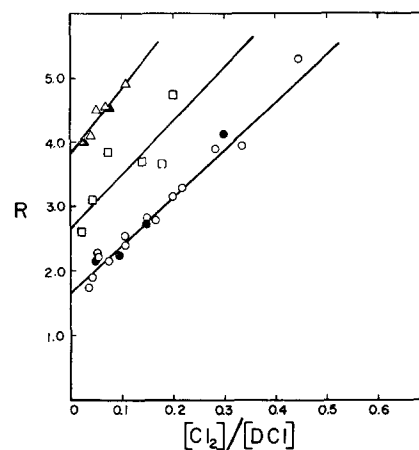

FIG. 3. Variation of ratio of initial rates with $[Cl_2]/[DCl]$. $\bigcirc$, DCl; $\bullet$, DCl, Xe; $\square$, $[CO_2]/[DCl]=0.9$; $\triangle$, $[CO_2]/[DCl]=1.9$; $\blacktriangle$, $[CF_4]/[DCl]=1.8$.

actants. Figure 3 shows a plot of these ratios against the ratios of initial concentrations $[Cl_2]/[DCl]$. The open circles refer to experiments in which no inert gas was present. The result is a linear relationship between R and $[Cl_2]/[DCl]$, with an intercept of 1.65 ± 0.07 and a slope of 7.48 ± 0.38. The uncertainties are standard deviations from a linear least-squares fit. The addition of xenon did not affect the value of R when $[Xe]/[DCl]=3.5$ as shown in Fig. 3. The addition of CO_2, however, gave rise to a pronounced change in the intercept and an apparent small change in the slope. Figure 3 shows these results graphically and Table II summarizes the slopes and intercepts. Table I also shows that in experiments involving a constant DCl pressure and no Cl_2, the initial rates with and without added CO_2 are within experimental uncertainty, the same. This result confirms that CO_2 is chemically inert in this system even though the 23.5-kcal/mole activation energy of the reaction of hydrogen atoms with CO_2 is less than the 47.3 kcal/mole with which D* atoms are formed.[17,18]

INTERPRETATION

The experimental results presented above may be readily interpreted in terms of the proposed hot-atom mechanism but cannot be made compatible with a completely thermal mechanism because the extrapolated intercepts shown in Fig. 3 are greater than unity and vary with the addition of CO_2 which is itself chemically inert. We therefore interpret our results in terms of Eq. (15).

In the absence of an inert thermalizing species Eq. (15) reduces to

$$R = \left[1 + \frac{k_3^{DCl}}{k_2} + \left(\frac{k_6}{k_2} + \frac{k_3^{Cl_2}}{k_2} \right) \frac{[Cl_2]}{[DCl]} \right] \left[\frac{1 + (k_7[Cl_2]/k_5[DCl])}{1 + (k_3^{DCl}/k_2) + [k_7/k_5 + (k_3^{Cl_2}/k_2)]([Cl_2]/[DCl])} \right], \qquad (18)$$

TABLE I. Initial rates of deuterium formation.

Reactant pressures			Inert gas L	$[Cl_2]/[DCl]$	$[L]/[DCl]$	Initial rates $A \times 10^4$ (torr/sec)	Standard deviation σ (torr)	Ratio R
P_{DCl} (torr)	P_{Cl_2} (torr)	P_L (torr)						
74.7	...	...	...	...	...	2.55	0.226	1.00
74.4	21.2	...	...	0.284	...	0.656	0.050	3.88
73.8	...	...	...	...	...	1.73	0.051	1.00
73.5	12.3	...	...	0.168	...	0.630	0.048	2.76
135.4	...	...	...	...	...	1.75	0.145	1.00
135.0	14.7	...	...	0.109	...	0.734	0.108	2.38
134.5	...	...	...	...	...	1.82	0.043	1.00
134.1	6.0	...	...	0.444	...	0.969	0.107	1.88
134.0	26.8	...	...	0.200	...	0.579	0.055	3.15
99.3	...	...	...	...	...	1.90	0.115	1.00
99.0	14.9	...	...	0.150	...	0.679	0.078	2.80
99.4	5.4	...	...	0.054	...	0.843	0.042	2.26
99.3	21.8	...	...	0.219	...	0.582	0.067	3.26
73.6	...	...	...	...	...	1.62	0.048	1.00
73.4	4.1	...	...	0.056	...	0.727	0.031	2.23
73.3	7.7	...	...	0.106	...	0.637	0.004	2.54
225.	...	...	...	...	...	2.02	0.081	1.00
224.	8.3	...	...	0.037	...	1.16	0.238	1.73
224.	17.2	...	...	0.077	...	0.936	0.090	2.15
224.	74.8	...	...	0.334	...	0.512	0.069	3.93
169.	...	...	...	...	...	2.23	0.557	1.00
100.6	...	...	...	...	...	2.06	0.246	1.00
36.4	...	...	...	...	...	1.33	0.021	1.00
99.4	...	178.	CO_2	...	1.80	1.92	0.057	1.00
99.3	4.1	178.	CO_2	0.042	1.80	0.469	0.037	4.09
99.2	10.9	178.	CO_2	0.109	1.80	0.391	0.042	4.90
99.9	5.0	194.	CO_2	0.050	1.95	0.427	0.026	4.49
99.9	6.8	194.	CO_2	0.068	1.95	0.423	0.050	4.53
73.4	...	132.	CO_2	...	1.80	1.74	0.070	1.00
132.3	...	235.	CO_2	...	1.78	1.81	0.226	1.00
99.7	...	90.4	CO_2	...	0.91	1.96	0.030	1.00
99.4	4.4	90.4	CO_2	0.044	0.91	0.633	0.082	3.09
99.4	13.9	90.4	CO_2	0.140	0.91	0.533	0.053	3.68
99.9	20.0	89.6	CO_2	0.201	0.90	0.414	0.020	4.73
99.4	2.4	88.8	CO_2	0.024	0.89	0.759	0.041	2.58
99.3	7.5	88.8	CO_2	0.075	0.89	0.512	0.040	3.83
99.2	17.7	88.8	CO_2	0.179	0.90	0.539	0.113	3.64
100.1	...	180.1	CF_4	...	1.80	1.54	0.239	1.00
99.9	2.9	180.1	CF_4	0.029	1.80	0.383	0.043	4.00
99.8	7.9	180.1	CF_4	0.079	1.81	0.338	0.053	4.54
99.1	5.1	31.6	Xe	0.052	0.32	0.872	0.039	2.18
99.0	9.4	31.6	Xe	0.095	0.32	0.856	0.039	2.22
99.1	15.0	349.8	Xe	0.151	3.53	0.694	0.065	2.74
99.0	29.6	349.8	Xe	0.299	3.53	0.461	0.007	4.12

where k_3^{DCl} and $k_3^{Cl_2}$ represent thermalization by DCl and Cl_2, respectively. From Fig. 3 we note that R is linear over the range $0.04 \leq [Cl_2]/[DCl] \leq 0.5$. For this to be the case either $k_7/k_5 \cong k_6/k_2$ or $k_7[Cl_2]/k_5[DCl] \gg k_3^{DCl}/k_2 + k_3^{Cl_2}[Cl_2]/k_2[DCl]$. The former would, contrary to our results, imply little or no detectable difference rate of D_2 formation as inert gas is added to a DCl–Cl_2 mixture while the latter is a reasonable approximation. With the latter, Eq. (18) becomes

$$R \cong 1 + (k_3^{DCl}/k_2)$$

$$+ [(k_6/k_2) + (k_3^{Cl_2}/k_2)]([Cl_2]/[DCl]). \quad (19)$$

From this relation and the experimental results, $k_3^{DCl}/k_2 = 0.65 \pm 0.07$ and $(k_6 + k_3^{Cl_2})/k_2 = 7.48 \pm 0.38$.

Similar arguments may be used in the analysis of the Xe, CO_2, and CF_4 thermalization experiments resulting

in the following relation for R:

$$R \cong 1 + \frac{k_3^{DCl}}{k_2} + \frac{k_3^L}{k_2} \frac{[L]}{[DCl]} + \left(\frac{k_6}{k_2} + \frac{k_3^{Cl_2}}{k_2}\right) \frac{[Cl_2]}{[DCl]}, \quad (20)$$

where $[L]$ is the concentration of the inert species. With this relation and the intercepts from Fig. 3 and Table II, $k_3^{CO_2}/k_2 = 1.14$ when $[CO_2]/[DCl] = 0.90$, $k_3^{CO_2}/k_2 = 1.16$ when $[CO_2]/[DCl] = 1.87$; taken together these results furnish $k_3^{CO_2}/k_2 = 1.15$ with good agreement between the two sets of data.

The slopes of Fig. 3 increase as CO_2 is added suggesting that the coefficient of $[Cl_2]/[DCl]$ in Eq. (21) is not independent of $[L]$. While the experimental uncertainty in these slopes makes treatment of them somewhat uncertain, we may nevertheless note that an increase in slope is not surprising. The method we have used in the analysis of these experiments partitions the

TABLE II. Effect of CO_2 thermalization.

M	[M]/[DCl]	Intercept I	ΔI	$\dfrac{\Delta I}{[CO_2]/[DCl]}$	Slope S
None	0	1.65 ± 0.07	0	0	7.48 ± 0.38
CO_2	0.90 ± 0.01	2.68 ± 0.28	1.03	1.14	8.26 ± 2.3
CO_2	1.87 ± 0.08	3.82 ± 0.22	2.17	1.16	10.2 ± 3.1

bimolecular collisions into two groups, hot and thermal, each of which is characterized by a single rate coefficient independent of the concentrations of the species present. This method must be regarded as only a first approximation to a rigorous description in terms of reactive and nonreactive cross sections, which, in principle, accounts for variations of the non-Boltzmann reactant (hot-atom) distribution function with concentration. Changes in this distribution function lead to variations in rate coefficients for hot-atom reactions whose ratios in general will then change.

With regard to the experimentally observed changes in slope we may argue that as CO_2 increases, the average energy of the non-Boltzmann distribution decreases. As a result k_6 and k_2 decrease while $k_3^{Cl_2}$ increases. A similar argument applied to the intercepts suggests that k_3^{DCl} and $k_3^{CO_2}$ should increase as CO_2 is added while k_2 should decrease. The experimental results however are consistent with the interpretation that k_3^{DCl}/k_2 and $k_3^{CO_2}/k_2$ do not vary significantly under the conditions of our experiments, in turn this suggests that $k_3^{Cl_2}/k_2$ may also be considered approximately constant. If this is indeed the case then k_6/k_2 must increase quite rapidly as inert gas is added to lower the average energy of the reactive encounters. In the limit of infinite dilution in inert gas, k_6/k_2 must approach the value of its thermal counterpart $k_7/k_5 \approx 300$ at 300°K as estimated below. In the absence of rare gas we have $k_6/k_2 \leq 7.48$ indicating that significant changes in k_6/k_2 may be expected as inert gas is added. While these arguments are qualitative they do suggest that it is not unreasonable to expect the observed changes in slope.

The results shown in Figs. 2 and 3 indicate that thermalization by Xe is minimal and that $k_3^{DCl} \gg 3.5 k_3^{Xe}$. The ineffectiveness of Xe may be attributed both to its large mass compared to D and to its lack of internal degrees of freedom. Taking account of the experimental uncertainties we estimate $k_3^{Xe}/k_2 < 0.1$.

Figure 3 also shows that CF_4 is a very effective thermalizing agent and appears equivalent to CO_2 so that we may estimate $k_3^{CF_4}/k_2 \cong 1.15$. If we assume that Cl_2 is approximately as effective as DCl, CO_2, and CF_4 in thermalizing hot D atoms we obtain $k_3^{Cl_2}/k_2 \sim 1$ and $k_6/k_2 \sim 6.5$ as reasonable estimates for the photolysis of DCl–Cl_2 mixtures alone. Assuming $k_3^{Cl_2}/k_2$ is con-

stant, then k_6/k_2 increases to 7.3 when

$$[CO_2]/[DCl] = 0.90$$

and to 9.2 when $[CO_2]/[DCl] = 1.87$.

That three-body atom recombinations of D atoms are not significant in the kinetics is confirmed experimentally by the absence of effects on initial rates of (1) added CO_2 in DCl photolyses and (2) added Xe in DCl–Cl_2 photolyses.

It is apparent from Fig. 2 that added Xe enhances the amount of D_2 present at long photolysis times. This may be accounted for by two effects: first, Xe will enhance the three-body recombination rate of D atoms and second, Xe will also enhance the three-body recombination rate of Cl atoms thus lowering the steady state [Cl] and making smaller the contribution of the second term in Eq. (12) which arises as a result of Reaction (4). The latter effect of added Xe is by far the most significant.

DISCUSSION

We conclude from the evidence presented that the hot deuterium atoms produced by the photolysis of DCl are readily distinguishable from their thermal counterparts in systems containing DCl and Cl_2. First note that Fig. 3 cannot be explained by a completely thermal mechanism as has been pointed out above. Second, note that $k_6/k_2 \simeq 6.5$ as compared to the thermal counterpart $k_7/k_5 \simeq 300$ (as discussed below) indicating the rate coefficients of reactions (6) and/or (2) are strongly energy dependent. Further, addition of CO_2 and CF_4 leads to results which suggest that k_6/k_2 increases as the distribution of reactant energies shifts to lower values. The variation of thermalizing efficiency with the molecule used as a thermalizing species also suggests the importance of hot-atom kinetics. For example, xenon was observed to have no detectable effect on the experimental results. This is easily explained by elastic collisions occurring between D* and the heavy, atomic Xe with a hard-sphere fractional energy loss per collision of

$$\langle f \rangle = 2(m_1 m_2)/(m_1 + m_2)^2 = 0.030.$$

TABLE III. Comparison of thermalization probabilities.

M	$p_3{}^M/p_2$	$\langle f \rangle_{D*-M}$	ν_M (cm^{-1})	$I(10^{-40}$ g-cm$^2)$
DCl	0.65 ± 0.07	0.096	2091	5.14
CO$_2$	1.01 ± 0.12	0.083	668 [2], 1320, 2350	65.67
Xe	0.00 ± 0.06	0.030	$\cdots$	$\cdots$

The molecules CO$_2$, Cl$_2$, CF$_4$, and DCl are lighter making $\langle f \rangle$ larger and in addition have vibrational and rotational degrees of freedom which may participate in energy-transfer processes. These molecules were quite effective thermalizing agents.

Another objective of this study was to compare the hot-atom ratio k_6/k_2 with its thermal counterpart k_7/k_5. The ratio k_7'/k_5' for the isotopically analogous reactions

$$H+HCl\rightarrow H_2+Cl, \qquad (5')$$

$$H+Cl_2\rightarrow HCl+Cl, \qquad (7')$$
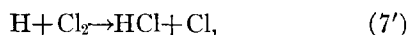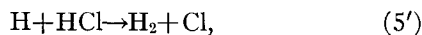
as a function of temperature has been obtained recently by Klein and Wolfsberg[16] from the photolysis of Cl$_2$ in mixtures of H$_2$ and TCl. The results of these experiments can be expressed as

$$k_7'/k_5' = (7.1\pm1.6)\ \exp[(1540\pm130)/RT]$$

for temperatures 273–335°K with the activation energy difference in calories/mole. From the reactions of thermalized hydrogen atoms in x- and γ-irradiated HCl and Cl$_2$ mixtures at 196, 274, and 296°K, Davidow, Lee, and Armstrong[19] have obtained values of k_7'/k_5' which agree well with the results of Klein and Wolfsberg. Morris and Pease[20] have indirectly deduced the lower limit $k_7'/k_5' = 10 \exp(>1400/RT)$ from the experimental data available up to 1935 on the inhibition of the H$_2$–Cl$_2$ photochemical reaction by HCl. This conclusion compares well with the above-mentioned results. From the same kind of inhibition experiments Bodenstein[21] has reported

$$k_7'/k_5' = 4.1 \exp[(2440\pm180)/RT].$$

Since no values for k_7/k_5 have been reported, we have used Klein and Wolfsberg's data together with a linear transition-state model[22] to estimate it. Parameters for the reactant molecules are readily available[23] and those for the activated complexes were taken from Wilkins[24] and, where required, appropriately adjusted for isotope effects. The resulting expression for k_7/k_5 is

$$k_7/k_5 = (12.9\pm2.9)\ \exp[(1887\pm160)/RT]. \qquad (21)$$

The uncertainties given in Eq. (21) are taken to be the same percentage as those obtained by Klein and Wolfsberg for k_7'/k_5'. For $T=298$°K the above expression predicts $k_7/k_5 = 310\pm40$ which is to be compared with

the hot-atom value of $k_6/k_2\sim6.5$. The change in this ratio by a factor of 50, suggests that the HCl–Cl$_2$ system should be very sensitive to hot-atom effects.

For the experiments reported here relative thermalization rate constants can be calculated and compared. Experimental results have been analyzed in a manner similar to Biordi, Rousseau, and Mains' treatment of their HI–hydrocarbon flash-photolysis results.[25] The thermalization rate coefficient for a particular compound M is defined as the rate coefficient for reducing a hot atom to energies below the energy threshold of a given reaction (R) by collisions with M, including all elastic and inelastic processes and averaged over the energy distribution of collisions occurring above this threshold. In the case of these experiments the thermalizing compounds are Cl$_2$, DCl, CF$_4$, Xe, or CO$_2$. The hot atom is D* formed at about 2.1 eV; the reaction observed is D*+DCl→D$_2$+Cl with an Arrhenius activation energy of 3500 cal/mole.[26] The alternate reaction for thermalized D atoms is the reaction with Cl$_2$ which has a rate constant about 300 times larger than that of the reaction with DCl at thermal energies corresponding to the cell temperature.

First consider the experiments in which no inert gas was present and the ratio $k_3{}^{DCl}/k_2 = 0.65\pm0.07$. The average probabilities per D*–DCl collision of reaction (2) and thermalization (3) are $p_2 = k_2/Z_{D*DCl}$ and $p_3{}^{DCl} = k_3{}^{DCl}/Z_{D*DCl}$, where Z_{D*DCl} is the average collision rate coefficient. One other type of collision must be considered, a nonreactive, nonthermalizing collision in which the D* energy is reduced by an elastic or inelastic process to an energy still above the reaction threshold. Because the rate coefficient for this process is not available from these experimental results, the ratio $p_3{}^{DCl}/p_2 = 0.65\pm0.07$ can be calculated, but not the probabilities per collision $p_3{}^{DCl}$ and p_2. When considering total probabilities P_2 and $P_3{}^{DCl}$ obtained by summing over all collisions, this third type of collision does not remove hot atoms, so that $P_2+P_3{}^{DCl} = 1$ and $P_3{}^{DCl}/P_2 = 0.65\pm0.07$ which gives $P_2 = 0.61\pm0.03$ and $P_3{}^{DCl} = 0.39\pm0.06$. These total probabilities are equivalent to the F_{hot} and F_{mod} calculated by Biordi et al. from their HI–hydrocarbon photolyses. Their values of P_3 were larger, averaging about 0.9, which is reasonable because the abstraction by H atoms of an H from saturated hydrocarbons proceeds with a larger activation energy than the abstraction of H from hydrogen halides.[26-28]

Next consider the experiments in which the inert gas CO$_2$ was added and the ratio $k_3{}^{CO_2}/k_2 = 1.15\pm0.14$ was obtained, where $k_3{}^{CO_2}$ is the rate constant for thermalization by CO$_2$. Taking $k_3{}^{DCl}/k_2 = 0.65\pm0.07$ as described above, the total probability $P_2+P_3{}^{DCl}+P_3{}^{CO_2} = 1$ and the ratio $P_3{}^{CO_2}/P_2 = k_3{}^{CO_2}[CO_2]/k_2[DCl]$ imply

$$P_2 = \{(1.65)+(1.15)([CO_2]/[DCl])\}^{-1},$$

$$P_3{}^{DCl} = 0.65P_2, \qquad P_3{}^{CO_2} = 1-1.65P_2. \qquad (22)$$

Average probabilities per collision are related by

$$p_3^{CO_2}/p_2 = k_3^{CO_2} Z_{D*DCl}/k_2 Z_{D*CO_2}.$$

Collision diameters from viscosity data[29] ($\sigma_D \approx \sigma_{He} = 2.58$ Å, $\sigma_{DCl} \approx \sigma_{HCl} = 3.30$ Å, and $\sigma_{CO_2} = 3.90$ Å) allow the calculation of the ratio of collision rate constants

$$\frac{Z_{D*DCl}}{Z_{D*CO_2}} = \left(\frac{\sigma_{D*DCl}}{\sigma_{D*CO_2}}\right)^2 \left(\frac{\mu_{D*CO_2}}{\mu_{D*DCl}}\right)^{1/2} = 0.83, \qquad (23)$$

which gives $p_3^{CO_2}/p_2 = 1.01 \pm 0.12$.

For the experiments with added xenon no effect was observed within experimental uncertainty so that $k_3^{Xe}/k_2 = 0.00 \pm 0.07$ and $p_3^{Xe}/p_2 = 0.00 \pm 0.06$. Table III summarizes the thermalization results. Average fractional energy losses per elastic hard-sphere collision, vibrational frequencies with their degeneracies, and moments of inertia are also listed. If only elastic collisions were responsible for thermalizing hot atoms p_3^M would be proportional to $\langle f \rangle_{D*M}$. That this is not the case is readily seen in Table III. For a $D*$–M collision involving 2.1 eV there are, including degeneracies, 8, 6, and 0 vibrational levels and 55, 194, and 0 rotational levels energetically accessible to DCl, CO_2, and Xe, respectively. Table III indicates that for DCl, CO_2, and Xe the ratio P_3^M/P_2 is quite sensitive to the number of internal energy levels which are accessible. Since only semiquantitative data were obtained for CF_4 and Cl_2, they are not included in Table III.

It appears therefore that inelastic collisions are important in thermalizing hot atoms produced photochemically at 2.1 eV when the thermalizing molecule can be excited vibrationally or rotationally. This is in contrast with Penzhorn and Darwent's[10] conclusion that deactivation of 2.0 and 0.8 eV hot H atoms by CO_2 may be interpreted with reasonable accuracy in terms of simple elastic collisions. Studies of the reactions of nuclear recoil hot tritium atoms with hydrocarbons in the region 2–10 eV have shown that collisions which do not result in reaction in this region may be quite inelastic with a highly efficient transfer of energy from translational to internal modes.[30,31] The results reported in this paper indicate that this can also be the case at 2.1 eV and below.

It should be kept clearly in mind that we have assumed that the k_3^M/k_2 hot-atom rate constant ratios do not change with addition of various amounts of inert gas or with the $[Cl_2]/[DCl]$ ratio. Although, rigorously, these ratios do change, the method used here is the only tractable one at present. The variation of the k_3^M/k_2 ratio with $[Cl_2]/[DCl]$ would result in nonlinear plots in Fig. 3, which are not observed within the uncertainty of calculated values. Also, the addition of CO_2 changed the ratio k_6/k_2 (slope of Fig. 3) by less than 50%, indicating that the hot-atom energy distribution was shifted to only slightly lower energies. The $k_3^{CO_2}/k_2$ results for two different $[CO_2]/[DCl]$ ratios agree within the uncertainty of the experiments. Therefore, the assumption of constant ratios k_3^M/k_2 is acceptable, considering the uncertainties of calculated values.

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