Deactivation of HCl (v = 1) and DCl (v = 1) by H and D Atoms at T = 295 K

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1 June 1976

Interim Report

ADA025252

Prepared for

AIR FORCE WEAPONS LABORATORY
Kirtland Air Force Base, N. Mex 07117

SPACE AND MISSILE SYSTEMS ORGANIZATION
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract F04701-75-C-0076 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lt. Ronald C. Lawson was the project officer.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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FOR THE COMMANDER

Ronald C. Lawson, 1st Lt., USAF
Research Applications Directorate
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REPORT DOCUMENTATION PAGE

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REPORT NUMBER

SAMSO-TR-76-109

TITLE (and Subtitle)

DEACTIVATION OF HCl(v = 1) AND DCl(v = 1)
BY H AND D ATOMS AT T = 295 K.

6. PERFORMING ORG. REPORT NUMBER

6(6603)-1

Jerry F. Bott and Richard F. Heidner, III

8. CONTRACT OR GRANT NUMBER(s)

F04701-75-C-0076

9. PERFORMING ORGANIZATION NAME AND ADDRESS

The Aerospace Corporation
El Segundo, Calif. 90245

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

Air Force Weapons Laboratory
Kirtland AFB, N. Mex. 87117

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

Space and Missile Systems Organization
Air Force Systems Command
Los Angeles, Calif. 90009

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemical kinetics
Hydrogen chloride
Isotope kinetic effects

Vibrational relaxation
Hydrogen atoms
Laser-induced fluorescence

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The techniques of isothermal calorimetry (for H atoms) and laser-induced fluorescence [for HCl(1)] were combined to yield absolute rate coefficients for H and D atom removal of HCl(1) and DCl(1). At T = 295 K. the rate coefficients for H + HCl(1), D + HCl(1), H + DCl(1), and D + DCl(1) are $(4.6 \pm 1.4) \times 10^{12}$, $(6.5 \pm 2.0) \times 10^{12}$, $(1.15 \pm 0.3) \times 10^{12}$, and $(1.2 \pm 0.4) \times 10^{12}$ cm^3/mol-sec, respectively.

X × 10 + the 12th power

X + a =

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CONTENTS

TABLES

FIGURES

I. INTRODUCTION

The HCl chemical laser[1,2] was the first system reported in which a population inversion was produced by a bimolecular reaction, in this case,

$$H + Cl_2 \longrightarrow HCl + Cl^\dagger \tag{1}$$

Corneil and Kasper[3] suggested that deactivation of $HCl^\dagger$ by atomic species, in particular Cl atoms, is a limiting factor in the laser performance subsequently, several independent groups supported that hypothesis by measuring the rate of

$$Cl + HCl(1) \longrightarrow Cl + HCl(0) \tag{2}$$
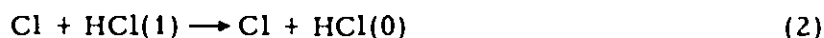
to be $\sim 5.1 \times 10^{12}$ cm^3/mol-sec at room temperature.[4] Even though Cl atoms are in higher concentration than H atoms in the H_2-Cl_2 chain laser, under some experimental conditions and for other HCl laser systems, the rate of H-atom quenching of $HCl^\dagger$ may also be significant. The measurements reported here provide a basis for such a comparison. The results are discussed in the context of previous experimental and theoretical studies on the H_2Cl system.

II. EXPERIMENTAL

The apparatus has been discussed in some detail in a previous study[5] of the kinetics of H + HF(v = 1). In general, only the modifications to that system will be presented.

Hydrogen or deuterium atoms are generated by a microwave discharge through a mixture of $H_2(D_2)$ and He. The mixture of H, H_2, and He flows through a 20-cm-long section of 1-cm i.d. quartz coated with halocarbon wax prior to entering the similarly coated 2.2-cm i.d. pyrex fluorescence cell. All experiments were conducted with He diluent at total pressures of 1.6 to 2.5 Torr with partial pressures of H_2 or D_2 between 0.1 and 1.2 Torr. The H(D) atom concentration ranged between 0.005 and 0.05 Torr (between 2.7×10^{-10} and 2.7×10^{-9} mol/cm^3). HCl injected into a flow of H atoms is subject to removal by H-atom abstraction and, in the case of a D-atom flow, by Cl-atom abstraction. To minimize these effects, a 3-mm-diam teflon tube was used to inject the HCl(DCl) into the main gas flow only 2 cm upstream of the fluorescence window. At the average flow velocity of 300 cm/sec, the time for reaction was 7 msec before the HCl reached the center of the fluorescence window. Despite the use of this procedure, substantial removal of the HCl(0) or DCl(0) was observed. For example, the [HCl(0)] was reduced by a factor of 2 at a $[D] \approx 1.2 \times 10^{-9}$ mol/cm^3. The fraction of HCl removed at the fluorescence window was estimated from the intensity reduction of the laser-induced fluorescence signal since that signal is proportional to the [HCl(0)] at the low concentration, one can obtain reasonably accurate estimates of the absolute rates for H and D atom removal of HCl(0) and DCl(0).[6]

-5-

In addition to reducing the fluorescence signal, the "prereactions" cited above introduce Cl atoms, HD, and DCl as vibrational deactivators and remove HCl, D_2, and D as deactivators. The concentration of HCl was reduced to ~0.001 Torr to avoid these complications. At these small HCl concentrations, it was necessary to employ digital signal averaging techniqes. Results obtained for H + HCl(v = 1) deactivation at high HCl concentrations[5] (~0.05 Torr) agreed with the data taken at the low HCl concentrations. Experiments with the other isotopic combinations were performed only at the low HCl(DCl) concentrations.

The fluorescence was detected with an InSb infrared detector operated at 77 K; the resulting signal was amplified by a Perry Model 050 amplifier and recorded with a Biomation 805 transient recorder. The recorded signals were transferred to a Nicolet Model 1072 signal averager, where 32 to 128 experiments were stored and averaged before being displayed on an X-Y recorder.

The gases used included H_2 (Matheson Co., 99.95%), D_2 (Oak Ridge, > 98%), He (Air Products, 99.99%), HCl (Matheson Co., 99.99% in liquid phase), and DCl (ICN, > 98%). The bottle of DCl was cooled to 195 K, but otherwise was not purified. The He (at 16 psia) flowed through a Linde 5A molecular sieve trap at 77 K before entering the flow tube. The remaining gases were used without further purification.

Results obtained with the H_2 and D_2 passing through a trap at 77 K were indistinguishable from data obtained without the cold trap. No power change on the probe was measured when the microwave discharge was struck in He

with the $H_2(D_2)$ completely shut off, which indicated that there was no discharge-induced heating effect on the probe and that no impurities in the He contributed to the atom measurement.

III. RESULTS

The time history of the HCl(v = 1) fluorescence intensity subsequent to the laser excitation was recorded with no atoms present (the microwave discharge turned off) as well as with the H atoms present. A sample set of fluorescence traces is shown in Fig. 1. Semilogarithmic plots of the fluorescence intensity gave straight lines from which exponential decay times were determined. A set of data that includes the decay times in the absence (τ_{off}) and presence (τ_{on}) of the microwave discharge is listed in Table I. These data were obtained at a total pressure of ~ 2.5 Torr and an HCl partial pressure of 0.05 Torr. The change in the decay rate $\Delta(1/\tau) = \tau_{on}^{-1} - \tau_{off}^{-1}$ can be directly related to the H-atom concentration by[5]

$$\Delta(1/\tau) = (k_{HCl-H} - 1/2 \, k_{HCl-H_2})[H] \qquad (3)$$

where k_{HCl-H} and k_{HCl-H_2} are rate coefficients for HCl(v = 1) deactivation by H and H_2, respectively. Other effects, such as gas heating and changes in impurity deactivation were negligible contributions and, thus, were neglected in Eq. (3). Figures 2 through 5 are plots of $\Delta(1/\tau)$ versus [H] and [D] for the relaxation of HCl(v = 1) and DCl(v = 1).

In the D + HCl(v = 1) experiments, HCl(0) injected into the stream of D, D_2, and He can react with D atoms by one of two channels
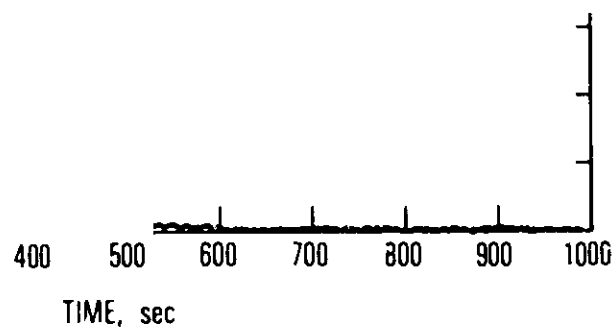
$$D + HCl(0) \overset{k_4}{\rightleftharpoons} DH + Cl \qquad (4)$$

-9-

Fig. 1. Fluorescence signals from HCl(v = 1) obtained with
and without H atoms. Average of 32 traces;
$[H] = 1.1 \times 10^{-9}$ mol/cm^3; $[H_2] = 2.1 \times 10^{-8}$ mol/cm^3;
$[HCl] \approx 5 \times 10^{-11}$ mol/cm^3; total pressure = 1.84 Torr.

TABLE 1. Removal Rate of HCl(v = 1) in the Presence of H Atoms

Run	P_{total}, Torr	$[H] \times 10^9$, mol/cm^3	$[H_2] \times 10^9$, mol/cm^3	τ_{on}, μsec	τ_{off}, μsec	$\Delta(1/\tau)$, sec^{-1}	$k_{HCl-H} \times 10^{-12}$, cm^3/mol-sec
1			64	158	740	5000 ± 30	5.20 ± 0.33
2			64	177	740	4300 ± 260	5.34 ± 0.32
3			64	150	740	5300 ± 360	5.32 ± 0.35
4			64	177	740	4300 ± 260	6.42 ± 0.39
5			64	82	340	9300 ± 790	3.95 ± 0.33
6			64	55	505	16200 ± 1000	5.35 ± 0.33
7			64	82	505	10200 ± 750	5.12 ± 0.38
8			73	68	662	13200 ± 870	5.29 ± 0.35
9			73	90	662	9600 ± 620	5.57 ± 0.37
10			73	121	662	6750 ± 480	4.77 ± 0.35
11			72	145	662	5390 ± 390	4.28 ± 0.31
12			59	123	955	7080 ± 470	4.48 ± 0.31

$\Delta (1/\tau) \times 10^3$, sec^{-1}

$[H] \times 10^9$, mol/cm^3

Fig. 2. Removal rate of HCl(v = 1) by H atoms. H-atom concentration uncorrected for probe position; circles are for HCl ≈ 0.05 Torr; triangles are for HCl ≈ 0.001 Torr.

$\Delta (1/\tau) \times 10^3, \text{sec}^{-1}$

$[D], \times 10^9 \text{mol/cm}^3$

Fig. 3. Removal rate of HCl(v = 1) by D atoms. D-atom
concentration uncorrected for probe position. Four
sets of data are shown.

-13-

$\Delta(1/\tau) \times 10^3$, $\sec^{-1}$

$[H]$, $\times 10^9$ mol/cm^3

Fig. 4. Removal rate of DCl($v = 1$) by H atoms. H-atom concentration uncorrected for probe position.

$\Delta(1/\tau) \times 10^3$, sec^{-1}

$[D], \times 10^9$ mol/cm^3

Fig. 5. Removal rate of DCl(v = 1) by D atoms. D-atom concentration uncorrected for probe position.

and

$$D + HCl(0) \underset{k_5}{\rightleftarrows} DCl + H \qquad (5)$$

At large concentrations of D atoms (~ 0.02 Torr), the peak intensity of the laser-pumped HCl(v = 1) fluorescence was reduced to less than half the intensity that was observed without any D atoms present. The removal of HCl was kinetically controlled since the large concentration of D atoms relative to HCl would have removed a much larger fraction of the HCl if equilibrium had been reached. Above ~ 0.04 Torr of D atoms, the decay rate $\Delta(1/\tau)$ did not increase in proportion to increases in the D atom concentration, but rather reached a plateau. The phenomenon was not caused by the response time of the detection system but appeared to be correlated with the large fraction of HCl removed by Reactions (4) and (5). The interpretation of these observations is unclear, and we have calculated the rate coefficient from the data for the lower pressures of D atoms.

The two sets of data plotted in Fig. 2 were obtained with ~ 0.05 Torr of HCl for the open circles and ~ 0.001 Torr of HCl for the closed circles; they were taken one year apart. The reproducibility of the D + HCl measurement was not as good; four sets of data are shown in Fig. 3, three of which agree and one of which has a slower rate by a factor of 0.75. We have reported the rate indicated by the three agreeing sets of data.

For most of the experiments, the isothermal probe was positioned ~ 3.5 cm downstream from the point at which fluorescence from the laser-excited HCl(v = 1) was monitored. Probe measurements with and without HCl indicated

that the H-atom concentration decreased along the flow direction such that the actual H-atom concentration in the fluorescence volume was $\sim 20 \pm 10\%$ larger than that measured by the probe at its usual downstream position. Measurements of the fluorescence decay rates combined with atom measurements obtained with the probe at several positions also indicated the $20 \pm 10\%$ effect on the rates for each of the isotopic combinations. Therefore, the rates calculated from the data in Figs. 2 through 5 have been reduced by a factor of 1.2 to reflect this probe position correction. The corrected rate coefficients are listed in Table II. A value of 1×10^{11} cm^3/mol-sec for k_{HCl-D_2} was taken from Refs. 7 and 8. The other molecular deactivation rates[9,10] are negligible contributions to Eq. (3).

We have assigned uncertainties to the results in Table II on the basis of $\pm 10\%$ for the standard deviation calculated for each set of data and $\pm 20\%$ for systematic error. The latter comes primarily from the H-atom measurement and represents possible errors in the H-atom mass flow rate (calorimetric probe), He mass flow rate (flow meter), and total pressure. The relative rates for the several isotopic combinations have smaller uncertainties than the absolute rates since the systematic errors are largely the same in each case.

TABLE II. Removal Rate of HCl(v = 1) and DCl(v = 1) in the Presence of H and D Atoms

Excited Molecule	Collision Partner	Removal Rate Coefficients (This Work)		Arnoldi and Wolfrum[9] (Experiment), cm^3/mol-sec	Wilkins[10] (Calculation), cm^3/mol-sec
		$(\mu sec-Torr)^{-1}$	cm^3/mol-sec		
HCl(v = 1)	H	0.25 ± 0.08	$(4.6 \pm 1.4) \times 10^{12}$	$(3.9 \pm 1.3) \times 10^{12}$	3.1×10^{13}
HCl(v = 1)	D	0.36 ± 0.10	$(6.5 \pm 2.0) \times 10^{12}$		
DCl(v = 1)	H	0.058 ± 0.017	$(1.15 \pm 0.3) \times 10^{12}$		
DCl(v = 1)	D	0.067 ± 0.020	$(1.2 \pm 0.4) \times 10^{12}$		

IV. DISCUSSION

The results of the four isotopic experiments involving H- and D-atom removal of HCl(v = 1) and DCl(v = 1) are given in Table II along with the results of a previous experiment[11] and a trajectory calculation[12] for H + HCl(v = 1). Although three classical trajectory calculations have been reported for this system,[12-14] only that of Wilkins[12] is directly comparable to the experiments. This calculation disagrees sharply in magnitude with experiment, but there is agreement[11, 12] that for the two distinguishable reactions

$$H + HCl(1) \xrightarrow{k_6} H_2 + Cl \tag{6}$$

and

$$H + ClH(1) \xrightarrow{k_7} H + ClH(0) \tag{7}$$
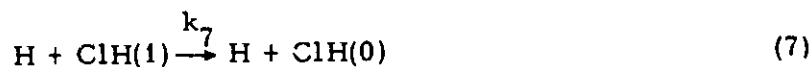
$k_7 \gg k_6$.

In an extensive review article on three-atom systems involving hydrogen and halogens, Parr and Truhlar[15] described the sensitivity of semiempirical potential energy hypersurfaces to the exact method of their calculation. Often, such surfaces are calibrated with experimental data of only one type, e.g., an Arrhenius equation over a limited temperature range. Trajectory calculations on the surface are then used to refine the surface to the experimental data. Smith[16] has emphasized that agreement between theory and experiment is illusory in these situations unless the same surface can predict other kinetic properties, e.g., isotope effects.

In this context, the H_2Cl system is extremely valuable because of the wealth of experimental data that is available. Rate coefficients have been determined for

$$H + HCl(0) \underset{k_8}{\overset{k_8}{\rightleftarrows}} H_2 + Cl \qquad (8)$$

in both directions, [17,18] although a discrepancy persists with regard to the ratio of the forward and backward rate coefficients. [19] In addition, a considerable amount of relative rate data has been obtained for Reactions (4) and (5) and the analogous reactions involving H and DCl; however, some of these data are contradictory. De Vries and Klein[20] determined that $k_4/k_5 = 0.0 \pm 0.9$ at $T = 295$ K, whereas Wood[21] concluded from similar room-temperature experiments that for H + DCl, D-atom abstraction was 20 times more likely than Cl-atom abstraction. It is unlikely that both of these results are correct. Arnoldi and Wolfrum[11] observed that H-atom abstraction is relatively slow even for HCl(v = 1) and that the removal of HCl(v = 1) by H-atoms proceeds predominantly by other channels. They could not distinguish between inelastic collisions with no atom exchange and reactive collisions involving Cl-atom exchange. These data, along with the isotopic results presented here provide a very useful test of future semiempirical surfaces. Clearly, further experiments are needed that differentiate between Reactions (4) and (5). Temperature dependent data, even for the overall removal rate of HCl(v = 1) by H, would provide valuable information about the potential energy surface when combined with the Arrhenius equation for the ground state reaction k_8.

Recent quantum mechanical calculations for the H-F-H[22] surface have brought into question the validity of the semiempirical approximations to that surface that are generated from experimental data on $F + H_2$. The present quantum mechanical calculations on the H_2Cl surface[23] are considerably less sophisticated than those for H_2F. More precise calculations could better define the minimum basis set of experimental data required to construct a semi-empirical surface with good predictive power.

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