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Hydrogen Atom Reactions with Molecular Halogens: The Rate Constants for $H + F_2$ and $H + Cl_2$ at 298 K[†]

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The rate constants for H atom reactions with Cl_2 and F_2 have been measured by monitoring the loss rate of hydrogen atoms in the presence of excess $[Cl_2]$ and $[F_2]$ via time-resolved, laser-induced Lyman-α fluorescence. The rate constants for $H + F_2$ and $H + Cl_2$ were found to be $2.4 \pm 0.4\ (2\sigma) \times 10^{-12}$ and $2.52 \pm 0.18\ (2\sigma) \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, respectively. The result for $H + F_2$ is consistent with the recommendation of Baulch et al. [*J. Phys. Chem. Ref. Data* **1981**, *10* (Suppl. 1)], and our $k(H + Cl_2)$ value is consistent with the majority of previous measurements.

I. Introduction

In the HF chemical laser, vibrationally excited HF is generated primarily by the F atom reaction with molecular hydrogen

$$F + H_2 \rightarrow HF(v = 0-3) + H \tag{1}$$

or via the secondary reaction

$$H + F_2 \rightarrow HF(v = 0-9) + F \tag{2}$$

The rate constant[1,2] and nascent HF(v) distribution[3,4] for reaction 1 are well established, $k_1(T) = 1.1 \pm 0.1 \times 10^{-10} \exp(-(450 \pm 50)/T)\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ and 0.0:0.15:0.55:0.30 for $P_0{:}P_1{:}P_2{:}P_3$. The detailed dynamics of reaction 1 have been exhaustively studied, both theoretically[5,6] and experimentally[7−12] by numerous investigators.

Surprisingly, the same cannot be said for reaction 2. The 1981 kinetics review by Baulch et al.[13] lists only eight previous measurements of the rate constant (compared to 22 for reaction 1) and recommends $k_2(T) = 1.46 \times 10^{-10} \exp(-1210/T)\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ and $k_2(298\ \mathrm{K}) = 2.5 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. A 1983 review by Cohen & Westberg[14] evaluated the same ensemble of measurements and selected $k_2(T) = 4.8 \times 10^{-15} T^{1.4} \exp(-667/T)\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ and $k_2(298\ \mathrm{K}) = 1.5 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. The five room-temperature rate constants reported for reaction 2 range from 1.0×10^{-12} to $4.2 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$.

The reaction of H with Cl_2

$$H + Cl_2 \rightarrow HCl(v = 0-4) + Cl \tag{3}$$

is an important source of HCl(v) in the HCl chemical laser system and has been used as a reference for competitive H atom reaction studies.[15,16] Dobis and Benson[17] recently applied their very low-pressure reactor (VLPR) technique to this reaction and measured $k_3(298\ \mathrm{K}) = 0.96 \pm 0.04 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. This result is a factor of 2 smaller than the generally accepted value[13]

Our intention in the present study was to reduce the uncertainty of the room-temperature $H + X_2$ rate constants by applying a novel experimental approach. With the exception of the work reported in ref 17, previous investigations of these reactions have used molecular hydrogen as the H atom source. In some cases, a discharge was applied to H_2 directly, whereas in others, a discharge based F atom source and $F + H_2$ prereactor were used to generate a known flow of H atoms. As H_2 reacts rapidly with atomic fluorine or chlorine to regenerate H atoms, the presence of undissociated H_2 in these systems complicated the analysis and tied the accuracy of the measurements to assumptions about the rate constants for the secondary reactions.

Here we report direct measurements of the rate constants for the reaction of H atoms with molecular fluorine and chlorine. Low concentrations of H atoms were produced by photolysis of H_2S, thereby avoiding complications stemming from the presence of H_2. The H atoms were generated in the presence of a large excess of F_2 or Cl_2 and monitored via laser induced fluorescence of the Lyman-α transition. Typically, the initial pool of H atoms was monitored for 100−200 microseconds or less, so that complications related to secondary reactions and wall losses could be avoided.

II. Experimental Methods

To observe the reaction of H atoms with F_2 or Cl_2, the H_2S was present as a minor constituent of F_2/He or Cl_2/Ar mixtures. Partial pressures of the halogen/rare gas mixtures were 0.5−6.0 Torr of 5% Cl_2 in Ar (Matheson) or 0.5−1.75 Torr of 10% F_2 in He (Matheson). The flow of H_2S was adjusted to provide a partial pressure of approximately 5 mTorr. The main carrier gas was Ar, and the total reactor pressure was typically 100 Torr. The flow rates of H_2S and Ar were controlled by needle valves, whereas a mass flow controller was used for F_2/He or Cl_2/Ar addition.

Hydrogen sulfide was photolyzed at 193 nm by a Lumonics TE-860-4 excimer laser operating at 10 Hz. The laser emission

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(~60 mJ/pulse) was focused by a 50 cm focal length lens, providing a power density (150 MW cm^{-2}) that was sufficient to dissociate all of the H_2S in the focal region. Photodissociation at 193 nm produces translationally hot H and SH fragments.[18,19] The high pressure of Ar buffer gas was used to thermalize the H atoms and limit their diffusion out of the detection region. Both F_2 and Cl_2 have very weak absorption cross-sections at 193 nm and were not photodissociated to any significant degree.

LIF detection of H atoms was accomplished by two-photon excitation of the 2s−1s transition of atomic hydrogen. Collisions rapidly quench the 2s state to 2p, which then emits Lyman-α radiation as it relaxes back to the ground state.[20] A tunable dye laser (Lambda-Physik EMG-203/FL3002 system) was used to generate 486 nm light. This was frequency doubled using a BBO crystal. A short (20 cm) focal length lens was used to focus the UV in the center of the photolysis cell. The photolysis and LIF lasers were arranged in an overlapping, counter-propagating configuration. The delays between the photolysis and probe laser pulses were controlled with a precision pulse delay generator (SRS model DG535). A solar blind photomultiplier tube (Hammamatsu R6835), and narrow band interference filter (121 nm, 10 nm fwhm) combination was used to detect the vacuum ultraviolet fluorescence while discriminating against scattered UV light from the photolysis and probe lasers. The probe laser was scanned across the Lyman-α line to characterize the line shape. The Gaussian profile exhibited a line width of 1.2 cm^{-1}, which demonstrated that the translational energy distribution had been relaxed to the ambient temperature by collisions with the buffer gas.

Some difficulty was encountered in finding appropriate conditions for the H + F_2 reaction. It was found that H_2S and F_2 could not be mixed too far upstream of the photolysis region because of a slow prereaction ($k \leq 6.4 \times 10^{-16}$ cm^3 s^{-1}).[21] This problem was manifested by a total loss of the H atom LIF signal at high [F_2]. To limit the consumption of [H_2S], the reaction time was minimized by mixing the reagents just prior to their injection into the photolysis reactor. A second and more troublesome complication for the collection of reliable H + F_2 data was then discovered. For moderate to high [F_2] and long delays between the photolysis and probe laser pulses, the LIF signal deviated significantly from single exponential decay. Vibrationally excited HF is produced by H + F_2. The bond strength of HF is 136.3 kcal mol^{-1}, and a single 243 nm photon can photolyze HF($v \geq 2$). The deviation from single exponential decay was associated with the regeneration of H atoms from probe laser photolysis of vibrationally excited HF. This problem was minimized by considering only the first 50−100 μs of the decay curve and keeping [F_2] relatively low.

Measurements for the H+Cl_2 system were straightforward. We did not see any evidence of a prereaction between H_2S and Cl_2, and the H atom decay curves were single exponentials for all of the conditions investigated.

III. Results and Discussion

A. H + F_2. A pair of representative H atom decay curves are shown in the upper panel of Figure 1. For our conditions, the slow decay in the absence of added F_2 (Γ~2700 s^{-1}) was dominated by diffusion out of the small volume sampled by the probe laser. The addition of [F_2] = 2.5 × 10^{15} cm^{-3} clearly increased the H atom loss rate. Within the 0−100 μs range, the decay curves were single exponential and the rate constant was extracted by fitting the data to the expression

$$y = y_0 + Ae^{-bt} \tag{4}$$

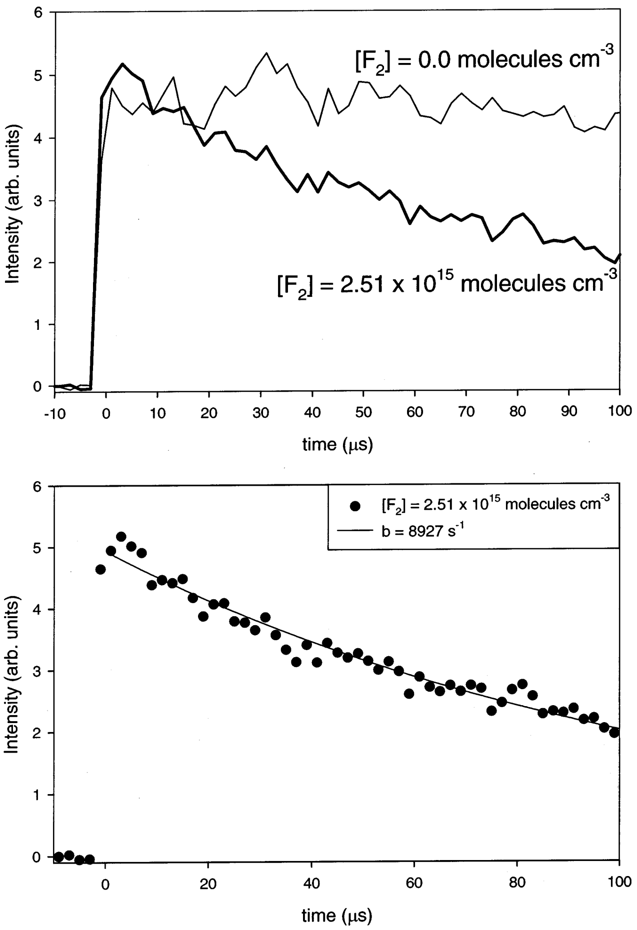

Figure 1. Representative H + F_2 data are shown. The slow decay in the absence of F_2 in the upper panel is attributed to diffusion and H atom loss via reactions with photoproducts. The lower panel demonstrates the quality of the fit to a single-exponential decay. The best least-squares fit gives b = 8927 s^{-1}.

TABLE 1: Conditions and Results for H + F_2 Measurements

[F_2] 10^{15} cm^{-3}	H atom decay rate[a] 10^5 s^{-1}	[F_2] 10^{15} cm^{-3}	H atom decay rate 10^5 s^{-1}
1.063	0.044	3.928	0.114
1.578	0.070	3.928	0.117
1.578	0.038	3.928	0.119
2.318	0.067	4.540	0.141
2.415	0.088	4.991	0.164
2.512	0.074	5.120	0.189
2.512	0.089	5.152	0.150
3.252	0.092	5.571	0.145
3.928	0.084		

[a] These are the raw observed decay rates, uncorrected for the decay rate (Γ) in the absence of F_2. The initial concentration of H_2S for these measurements was 1.6 × 10^{14} cm^{-3}. Photolysis caused complete dissociation, giving $[H]_0 = [SH]_0 = 1.6 \times 10^{14}$ cm^{-3}.

where

$$b = k_2[F_2] + \Gamma \tag{5}$$

and Γ is the loss rate when [F_2] is not present. The baseline intensity, y_0, was determined from the pre-photolysis signal level. For the faster decay shown in Figure 1, an exponential fit gave b = 8927 s^{-1}. The decay rate vs [F_2] data are summarized in Table 1 and plotted in Figure 2. The slope of Figure 2 gives the rate constant, $k_2 = 2.4 \pm 0.4\ (2\sigma) \times 10^{-12}$ cm^3 s^{-1}.

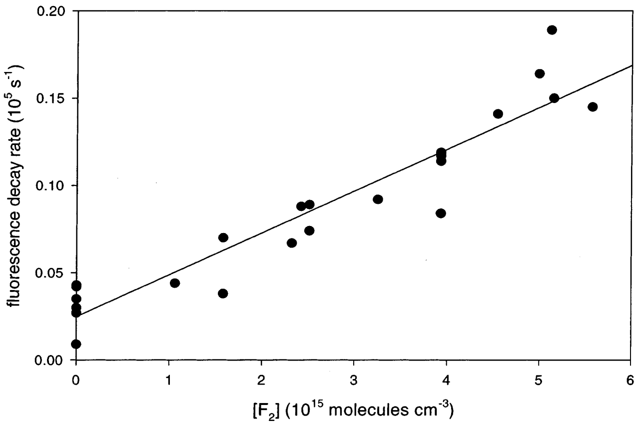

Figure 2. H atom decay rate vs [F_2]. The rate constant for reaction 2 is given by the slope, $k_2 = 2.4 \pm 0.4$ (2σ) $\times$ 10^{-12} cm^3 s^{-1}.

TABLE 2: Comparison of Measured Rate Constants for H + F_2 at 298 K

ref	k_2(298 K) ($\times 10^{-12}$ cm^3 s^{-1})
experiments	
Homann, et al.[23]	1.6 ± 0.4
Albright, et al. [22,26]	3.0 ± 0.4
Sung, et al.[15]	1.0[a]
Levy & Copeland [24]	1.0 ± 0.15[b]
Rabideau, et al. [25]	4.2 ± 0.3
this work	2.4 ± 0.4
Reviews	
Cohen & Westberg[14]	1.5[c]
Baulch, et al.[13]	2.5[c]

[a] Authors reported $k_2/k_3 = 0.053$, absolute value calculated using $k_3 = 1.9 \times 10^{-11}$ from ref 13. [b] Authors reported k_2/k(H + O_2 + M)[M] = 4.6 ± 0.7, absolute value calculated using k(H + O_2 + M)[M] from ref 13. [c] Recommendation based on literature review.

Photolysis of H_2S also yields SH radicals, but it is unlikely that the present results are significantly influenced by the reactions of this fragment. As F_2 is the most abundant reactant available, it is most pertinent to consider the reaction of SH with F_2. This reaction does not appear to have been studied previously, but the possible products are HSF + F and S + HF + F. As far as the present measurements are concerned, the only deleterious effect these reactions can have is to reduce the concentration of F_2. An upper bound for the error that this would introduce can be estimated by examining the measurement with the lowest F_2 concentration ([F_2] = 1.6×10^{15} cm^{-3}). Assuming a rate constant of 2.4×10^{-12} cm^3 s^{-1} for reaction 2, this process would reduce the F_2 concentration by 5×10^{13} cm^{-3} within the first 100 μs. If the reaction of SH with F_2 goes to completion within this time, a further reduction of F_2 by 1.6×10^{14} cm^{-3} will occur. Modeling of this limiting situation shows that the rate constant derived from the H atom decay under the assumption of first-order removal would be underestimated by 12%. This error decreases to 5% for measurements made with the highest pressure of F_2.

Table 2 summarizes the results from the five previous reports of k_2 measured at room temperature. Our result compares well with the recommended value of Baulch et al.[13] and the experimental results of Dodonov et al.[22] The agreement with Homann et al.[23] is marginal (just inside the combined error bars), and we are in poor agreement with Sung et al.,[15] Levy and Copeland,[24] and Rabideau et al.[25] Interestingly, Baulch et al.[13] chose a k_2 value that lies halfway between the results of Homann et al.[23] (k_2(298 K) = 1.6 ± 0.4 $\times 10^{-12}$ cm^3 s^{-1}) and Dodonov et al.[22,26] (k_2(298 K) = 3.0 ± 0.4 $\times 10^{-12}$ cm^3 s^{-1}). Although Dodonov et al.'s method has been criticized for its poor definition of the reaction time and the unknown role of mixing,[23] the results appear to be accurate not only for the H + F_2 reaction but also for H + Cl_2, (see Table 4 and the discussion below).

TABLE 3: Conditions and Results for H + Cl_2 Measurements[a]

[Cl_2] 10^{15} cm^{-3}	H atom decay rate[a] 10^5 s^{-1}	[Cl_2] 10^{15} cm^{-3}	H atom decay rate[a] 10^5 s^{-1}
0.74	0.32	4.81	1.27
1.66	0.40	5.02	1.11
1.66	0.50	5.23	1.56
1.98	0.56	5.47	1.53
2.11	0.60	5.55	1.67
2.11	0.64	5.59	1.50
2.13	0.59	6.44	1.83
2.29	0.79	6.50	1.77
2.83	0.71	7.12	2.06
2.83	0.88	7.28	1.74
3.22	0.90	7.53	1.56
3.27	0.89	7.63	1.98
3.75	0.64	8.60	2.47
4.06	1.28	8.63	2.22
4.31	1.32	9.05	2.34
4.35	1.15	10.55	2.79
4.73	0.87		

[a] These are the raw observed decay rates, uncorrected for the decay rate (Γ) in the absence of Cl_2. The initial concentration of H_2S for these measurements was 1.6×10^{14} cm^{-3}. Photolysis caused complete dissociation, giving $[H]_0 = [SH]_0 = 1.6 \times 10^{14}$ cm^{-3}.

TABLE 4: Comparison of Measured Rate Constants for H + Cl_2 at 298 K

ref	k_3(298 K) (10^{-11} cm^3 s^{-1})
Klein & Wolfsberg[27]	0.46 ± 0.19[a,b]
Davidow, Lee, & Armstrong[29]	0.49 ± 0.03[b,c]
Jardine, Ballash, & Armstrong[28]	0.43 ± 0.04[b,d]
Ambidge, Bradley, & Whytock[30]	0.70 ± 0.14
Dobis & Benson[17]	0.96 ± 0.04
Dodonov, et al.[22,26]	2.97 ± 0.89
Stedman, Steffenson, and Niki[39]	3.5 ± 1.2
Wagner, Welzbacher and Zellner[33]	1.91 ± 0.25
Bemand & Clyne[32]	2.19 ± 0.32
Michael & Lee[40]	1.6 ± 0.1
Jaffe and Clyne[41]	2.13 ± 0.78
Kita and Stedman[42]	1.7 ± 0.26
Seeley, Jayne, and Molina[43]	1.8 ± 0.5[e]
this work	2.52 ± 0.18

[a] Authors reported $k_6/k_3 = 0.143 \pm 0.033 \exp(-(1540 \pm 130)/RT)$. [b] k_3(298 K) calculated from k_6(298 K)[13] = 4.25×10^{-14} cm^3 s^{-1}. [c] Authors reported $k_6/k_3 = 0.0088 \pm 0.0005$ at 298 K. [d] Authors reported $k_6/k_3 = 0.01 \pm 0.001$ at 298 K. [e] Authors do not give a numerical result, but the value in the table is estimated from Figure 16 of ref 43.

B. H + Cl_2. We tested the reliability of our method by applying it to the well-studied H + Cl_2 reaction. As the rate constant for H atom removal by Cl_2 is large, this system should be less sensitive to variations in Γ, the baseline decay rate. Representative temporal profiles of the [H] dependent VUV fluorescence signal with and without added Cl_2 are shown in the upper panel of Figure 3. The addition of [Cl_2] (~50 mTorr) dramatically increased the H atom decay rate, and the entire time history was consistent with a single-exponential decay. Clearly, no detectable amounts of reaction products underwent photolysis to yield H atoms.

The lower panel of Figure 3 shows an example of a single-exponential fit to the H atom decay data. Figure 4 and Table 3 summarize the conditions and results for reaction 3. The slope of the plot in Figure 4 gives $k_3 = 2.52 \pm 0.18$ (2σ) $\times$ 10^{-11}

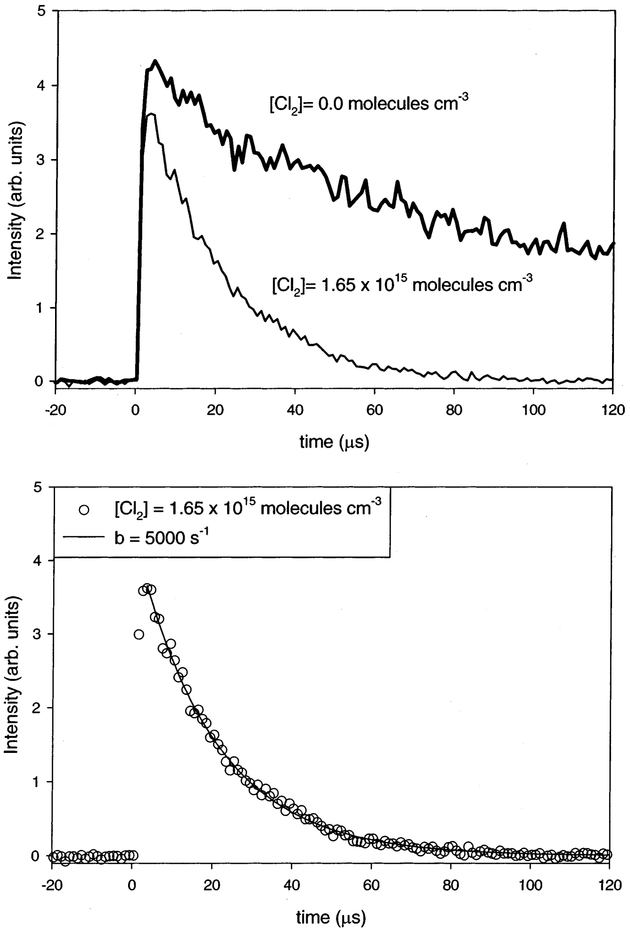

Figure 3. Representative H + Cl_2 data are shown. The slow decay in the absence of Cl_2 in the upper panel is attributed mainly to diffusion out of the observation zone with a minor amount of H atom loss via reactions with photoproducts. The lower panel demonstrates the quality of the fit to a single-exponential decay. The corresponding decay rate is 5000 s^{-1}.

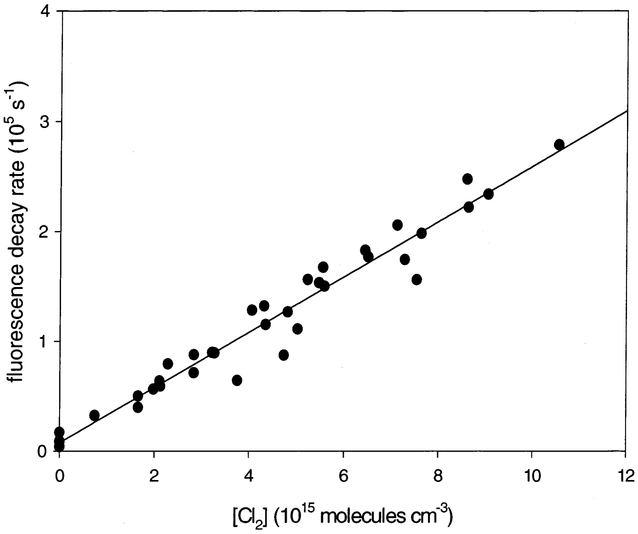

Figure 4. H atom decay rate vs [Cl_2]. The rate constant for reaction 3 is given by the slope, $k_3 = 2.52 \pm 0.18\ (2\sigma) \times 10^{-11}$ $cm^3\ s^{-1}$.

$cm^3\ s^{-1}$, and the intercept is consistent with the measured decay rate in the absence of Cl_2.

Our result is in good agreement (i.e., within the combined error bars) with the recommended value of Baulch et al.[13] and other previous measurements, see Table 4. The difference between Dobis and Benson's[17] value and ours is outside of the combined uncertainty.

Table 4 shows that the results from previous measurements of k_3 can be roughly separated into two groups. A majority of the previous studies report $k_3 = 2 \pm 1 \times 10^{-11}$ $cm^3\ s^{-1}$, whereas a smaller number give $k_3 \leq 1 \times 10^{-11}$ $cm^3\ s^{-1}$. A more detailed examination of this second group of experiments shows that nearly all were performed under conditions where secondary reactions were important, and the primary data must be carefully processed to extract k_3. For example, the experiments of Klein and Wolfsberg[27] and Armstrong and co-workers[28,29] provided estimates for the ratio of the rate constants for reactions 3 and 6

$$\mathrm{H} + \mathrm{HCl} \rightarrow \mathrm{Cl} + \mathrm{H_2} \qquad (6)$$

by measuring the yield of H_2 following long-term irradiation (i.e., many minutes of reaction time) of a variety of gaseous mixtures containing HCl. Their results[27,29] range from $k_4/k_3 = 1.07 \pm 0.15 \times 10^{-2}$ to $8.8 \pm 0.5 \times 10^{-3}$. If the Baulch et al.[13] recommendation for k_6 is adopted ($k_6(298\ \mathrm{K}) = 4.25 \times 10^{-14}$ $cm^3\ s^{-1}$), then k_3 ranges from $4.1 \pm 0.6 \times 10^{-12}$ to $4.8 \pm 0.3 \times 10^{-12}$ $cm^3\ s^{-1}$. Because of the long reaction times and the chemical complexity of the system, a complicated mechanism must be deconvoluted to extract the ratio k_6/k_3. In addition, the role of wall reactions could not be determined, and considerable error can occur if the model is not complete.

The present result is also in disagreement with the k_3 value reported by Whytock and co-workers[30,31] ($k_3(298) = 0.7 \pm 0.22 \times 10^{-11}$ $cm^3\ s^{-1}$). The accuracy of this result has been questioned on several occasions.[17,32,33] The measurements of Whytock and co-workers[30,31] did not correspond to pseudo-first-order conditions, and they were working in an extremely difficult H atom regime for detection by electron spin resonance.

Dobis and Benson[17] used a phosphoric acid coated discharge tube to create a small concentration of H atoms ($\sim 10^{10}$ cm^{-3}) to which Cl_2 was added. Mass spectrometry was used to monitor [Cl_2], [Cl], and [HCl] as a function of $[Cl_2]_0$ under steady-state flow conditions. Dobis and Benson[17] attribute the difference between their result and the larger k_3 values listed in Table 4 to unaccounted-for wall reactions that remove H atoms. The difference between our result, which is unaffected by wall effects, and Dobis and Benson's[17] is not clear. We note that Dobis and Benson's[34,35] application of their VLPR apparatus to the Cl + HBr reaction also resulted in a rate constant that was a factor of 2 smaller than the majority of previous results.[36–38]

IV. Summary

The H + F_2 and H + Cl_2 reactions were examined under pseudo-first-order conditions. Pulsed photolysis of low concentrations of H_2S was used to generate H atoms. The subsequent removal of H atoms was monitored by two-photon laser induced fluorescence. For H + Cl_2, simple exponential decay curves were observed, and a rate constant of $2.52 \pm 0.18\ (2\sigma) \times 10^{-11}$ $cm^3\ s^{-1}$ was obtained. This value was in good agreement with several earlier determinations.

Study of the reaction H + F_2 was complicated by the production of vibrationally excited HF, which could be photodissociated by the probe laser. Measurements were made under conditions that minimized the influence of this secondary process. The initial H atom decay rate as a function of [F_2] defined a rate constant of $2.4 \pm 0.4\ (2\sigma) \times 10^{-12}$ $cm^3\ s^{-1}$. This result is in good agreement with the value obtained by Baulch et al.[13] from a critical review of previous determinations. We recommend continued use of the Baulch et al.[13] Arrhenius parameters in computational models of HF chemical lasers.

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