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THE HOMOGENEOUS RATE CONSTANT FOR THE RECOMBINATION OF FLUORINE ATOMS WITH F₂ AS THE THIRD BODY

WILLARD H. BEATTIE and GLENN A. LAGUNA

Los Alamos National Laboratory, Chemistry Division, P. O. Box 1663
Los Alamos, NM 87545 (U.S.A.)

SUMMARY

The rate constant for the homogeneous recombination of F-atoms with F₂ as the third body was found to be $(3.6 \pm 1.4) \times 10^{14} \text{ cm}^6/\text{mol}^2\text{s}$ at 300 to 320 K. The corresponding rate constants with He and Ar as third bodies were also measured.

INTRODUCTION

The homogeneous recombination rate of F-atoms for the reaction



has been reviewed by Baulch *et al.* [1]. Several measurements of the rate constant, k_1 , at ambient room temperature have been reported with values ranging from 2.18×10^{14} to $\leq 1.5 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for M = He, and a value of $2.9 \times 10^{13} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for M = Ar. Due to the scarcity and wide variation of the data, Baulch *et al.* [1] made no recommendation of the value of the rate constant at temperatures <1400 K. Ultee [2] estimated that the value of k_1 varied with M in the order $k_1 (\text{M} = \text{F}_2) > k_1 (\text{M} = \text{He}) > k_1 (\text{M} = \text{Ar})$.

In this paper we report the first measurement of the rate constant of Eq. (1) for M = F₂. F-atoms were produced by passing low pressure F₂ gas (with or without an inert carrier gas) through a microwave discharge. The F-atoms were allowed to partially recombine while passing through a 1-m long Teflon tube, and finally were detected in a flow-through absorption cell.

The F-atom concentrations were measured in the presence of F_2 by laser diode absorption spectroscopy of the magnetic dipole $^2P_{3/2} - ^2P_{1/2}$ transition of atomic fluorine [3,4] in the 25- μm region. F-atom concentrations were determined from the peak absorbance at 404.116 cm^{-1} , using the cross section of $(1.25 \pm 0.20) \times 10^{-18}\text{ cm}^2$ obtained from Stanton and Kolb's data [3].

EXPERIMENTAL

Standard commercial sources were used for argon (99.995% pure), helium (99.995% pure), and fluorine (98% pure). The commercial fluorine was passed through a sodium bifluoride trap to remove HF impurity. Ultrapure fluorine (>99.7% pure) was prepared by formation and decomposition of a Ni(IV) complex [5] and used in some runs.

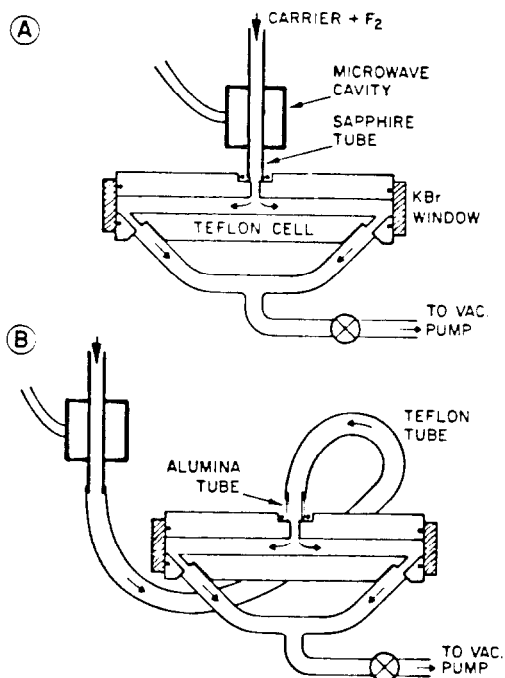


Fig. 1. Schematic of experimental apparatus. In configuration A, the initial F-atom concentration was measured; in configuration B, the F-atom concentration was measured after the additional time delay required to traverse the Teflon tube.

The experimental apparatus is shown in Fig. 1. A stream of F_2 passing through a 1.27-cm o.d. sapphire tube is dissociated with a microwave discharge at 2450 MHz using an Evenson cavity and 100-W Opthos Instrument power generator. In configuration A, the dissociated fluorine flows into a 30-cm long absorption cell with Teflon walls and KBr windows. In configuration B, the dissociated fluorine passes through a 1.4-m long \times 1.27-cm i.d. Teflon tube before entering the absorption cell. The gas residence time in the Teflon tube was varied between 0.3 and 5.4 s by varying the pressure and flow rate.

The flow rates of fluorine and inert carrier gas were regulated and measured with a flow regulator and pressure transducer (MKS Baratron, Model 170) and mass flowmeter (Hastings-Raydist).

The gas streams were mixed upstream of the microwave cavity. The pressure in the experimental apparatus was measured with another pressure transducer, and regulated downstream of the experimental apparatus with two throttling valves connected in parallel. The vacuum pump was preceded by a soda lime trap to absorb F_2 .

Diode laser absorption measurements were made as previously described [6], and the F-atom partial pressure was obtained from the relationship, $P(\text{torr}) = -(0.83 \pm 0.11) \ln T$, where T is transmittance through the 30.0-cm-long cell, and the constant is derived from Stanton and Kolb's cross section measurements.

In any given run, a series of experimental measurements were made in configuration B (Fig. 1) holding the total pressure and fluorine fraction constant while measuring transmittances as a function of flow rate. From this we obtained P_F^B as a function of t_B , the calculated travel time from the microwave discharge to a point midway through the absorption cell. The process was then repeated in configuration A at identical pressure, fluorine fraction, and flow rates, from which P_F^A as a function of t_A was derived.

DATA ANALYSIS

It was necessary to make corrections for the heterogeneous F-atom recombination on the Teflon tube walls. This recombination may be described by an absorption step followed by a surface recombination step,



where F_w is an F-atom adsorbed on the vessel walls. It is assumed that Reaction 2 is rate determining, so that the kinetics of heterogeneous recombination follows a first-order rate law. Under our conditions, the wall reaction and homogeneous reactions proceed simultaneously, and the total rate equation for the F-atom recombinations is given by

$$-\frac{dP_F}{dt} = k_w P_F + k_g P_F^2 P_M \quad (4)$$

where P_F and P_M are respectively partial pressures of F-atoms and third bodies M, and k_w and k_g are rate constants for the wall reaction and the homogeneous gas phase reactions, respectively.

In preliminary experiments, the wall recombination rate was measured under conditions of low concentrations of F_2 in He carrier gas, where

$$P_{F_2} \ll P_{He}, \text{ so that } P_M \approx P_{He}.$$

The integrated form of Eq. (4), with $M = He$ and $k_g = k_{He}$, is

$$\ln \left(1 + \frac{k_w}{k_{He} P_{He} P_F^B} \right) - \ln \left(1 + \frac{k_w}{k_{He} P_{He} P_F^A} \right) = k_w (t_B - t_A) \quad (5)$$

where P_F^A and P_F^B are the partial pressures of F-atoms in the absorption cell, and t_A and t_B are transit times from the microwave discharge to the cell, under configurations A and B, respectively.

Under conditions of low P_{He} , i.e., $P_F < 2$ torr and $F_2 < 3\%$ of carrier gas, Eq. (5) reduces to

$$\ln \left(\frac{P_F^A}{P_F^B} \right) \approx k_w (t_B - t_A) \quad (6)$$

which gives a simple first-order plot from which k_w may be determined. At relatively high total pressure or fluorine concentration, first-order plots exhibit downward curvatures at high values of $(t_B - t_A)$.

Under contrasting conditions of relatively high pressures of He carrier gas, the second terms in the ln functions of Eq. (5) are small, and an expansion of the ln functions reduces to the simple form,

$$\frac{1}{P_F^B} - \frac{1}{P_F^A} \approx k_{He} P_{He} (t_B - t_A) \quad (7)$$

in which case, k_{He} may be determined from a second-order plot.

In the runs made in pure F_2 without a carrier gas, the homogeneous recombination rate was measured with only F_2 and F-atoms as third bodies. In this case, the combined wall plus three-body recombination rate is given by

$$-\frac{dP_F}{dt} = k_w P_F + k_{F_2} P_F^2 + k_F P_F^3 \quad (8)$$

where k_{F_2} and k_F are the rate constants for $M = F_2$ and $M = F$, respectively.

The integrated form of Eq. (8) is given by

$$\ln \left[\frac{Z^2(\alpha + \beta + \gamma)}{\alpha + \beta Z + \gamma Z^2} \right] - \frac{\beta}{q} \ln \left[\frac{2\gamma Z + \beta - q}{2\gamma + \beta - q} \cdot \frac{2\gamma + \beta + q}{2\gamma Z + \beta + q} \right] = -2k_w(t - t_0) \quad (9)$$

where

$$\alpha = \frac{2k_w}{P_F^{\circ 2} k_{F_2}}, \quad \beta = \frac{2P_{F_2}^{\circ} + P_F^{\circ}}{P_F^{\circ}}, \quad \gamma = \frac{2k_F}{k_{F_2}} - 1, \quad q = \sqrt{4\alpha\gamma - \beta^2}, \quad Z = P_F/P_F^{\circ}$$

and P_F° and $P_{F_2}^{\circ}$ are the respective partial pressures of F and F_2 at t_0 .

Note that $P_{F_2} = P_{F_2}^{\circ} + \frac{1}{2}(P_F - P_F^{\circ})$.

In our experiments P_F° and $P_{F_2}^{\circ}$ at time, t_0 , are unknown; however, P_F^A , $P_{F_2}^A$ and t_A measured in configuration A are respectively substituted into Eq. (9) and P_F , P_{F_2} and t are understood to refer to P_F^B , $P_{F_2}^B$ and t_B , measured in configuration B. Equation (9) was evaluated by an iterative program to compute $P_F^A - P_F^B$ from experimental values of $t_B - t_A$, using k_w and k_{F_2}/k_F as parameters to obtain agreement with the experimental values of $P_F^B - P_F^A$.

RESULTS AND DISCUSSION

The value of the wall recombination rate, k_w , was obtained from preliminary runs at low pressures where $k_w \gg k_{He} P_{He} P_F$. Runs were made in configurations A and B at identical flow rates and pressures and k_w was obtained from the slopes of plots of Eq. (6). It was found that the value of k_w varied from run to run depending upon the exposure of the apparatus to air and subsequent passivation with fluorine. A typical run gave a value of $k_w = 0.42 \pm 0.05 \text{ s}^{-1}$.

In that run, the gas introduced contained 1.01% F_2 and the pressure of F_2 was 0.0121 ± 0.0004 torr, based upon the flow ratios and total pressure. We calculated the F-atom pressure at the microwave cavity by extrapolation of experimental values of P_F^A from absorbance measurements to t_o obtaining $P_F^O = 0.028 \pm 0.005$ torr. Most of the uncertainty in P_F^O , ± 0.004 torr, arises from the standard deviation of the F-atom cross section in Stanton and Kolb's data. If we compare the original pressure of F_2 with P_F^O , we may conclude that the dissociation was approximately 100% in this run. By this comparison, it appears that Stanton and Kolb's absorptivities may be slightly low.

k_{He} was obtained from preliminary runs carried out in excess He carrier gas so that $k_{He} P_{He} \gg K_{F_2} P_{F_2}$ and at pressures high enough that $k_{He} P_F P_{He} \gg k_w$. The slopes of plots of Eq. (7) gave an average value of $k_{He} = (2.2 \pm 0.1) \times 10^{14} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for the two best runs.

k_{Ar} was obtained from preliminary runs in a large excess of Ar carrier gas, analogous to those in He carrier gas. Due to insufficient data, the error limits are substantially greater for these runs than for those in He carrier gas. The average from three runs gave $k_{Ar} = (2.1 \pm 0.7) \times 10^{14} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Within experimental error, the values of k_{Ar} and k_{He} were identical. The errors in these preliminary runs were estimated from visual examination of the slopes of the lines and the scatter of the points.

Measurements of the F-atom recombination rate in pure fluorine were made in the same manner as described for those with carrier gas. We found that it was impossible to obtain unambiguous values of both k_{F_2} and k_F from the data of a run because a range of values of the ratio k_{F_2}/k_F could satisfy the equations within experimental error. Therefore, k_F was assumed to be identical to the homogeneous rate constants obtained for the other monatomic gases, He and Ar. In any case, the assumed values of k_F did not have a great effect upon the calculated value of k_{F_2} ; i.e., if k_F was arbitrarily set to zero, the value of k_{F_2} was increased by a factor of less than 2.

The results of the best runs are summarized in Table I. In our computer program, errors in $t_B - t_A$, k_w , and k_F/k_{F_2} accumulate in the computed value of k_{F_2} ; therefore, the standard deviations in Table I are larger than the standard deviations of k_{F_2} alone. The standard deviation of the average value of k_{F_2} is calculated from the values of the individual runs.

TABLE I

Results for runs with pure F₂

Run No.	Total Pressure P(torr)	Range t _B - t _A (s ⁻¹)	k _w (s ⁻¹)	$\frac{k_F}{k_{F_2}}$	k _{F₂} , Std. Dev. (cm ⁶ /mol ² s)
9	1.20	0.36-2.1	0.45	0.58	(3.6 ± 1.0) × 10 ¹⁴
10	2.51	0.70-5.0	0.45	0.58	(5.0 ± 0.2) × 10 ¹⁴
19	1.20	0.34-3.1	0.10	0.58	(2.2 ± 0.5) × 10 ¹⁴
Average					(3.6 ± 1.4) × 10 ¹⁴

In the evaluation of Runs 9 and 10, the parameter k_w, was set at 0.45, which is close to the value obtained in preliminary runs.* In Run 19, a thorough passivation was done prior to the run and the ultrapure F₂ was used, but no preliminary experimental value of k_w was determined. Therefore, k_w was varied as a parameter until consistent values of k_F/k_{F₂} were obtained. The precise value of k_w did not have a great effect upon the value of k_{F₂}; i.e. in Run 19 if k_w was set at 0.2 instead of 0.1, the average value of k_{F₂} would be decreased by 15% and its standard deviation increased by 15%.

A source of random error was instability of the microwave discharge. Small changes in the position of the cavity or its tuning bar affected the energy reflected from the cavity, and probably affected the fractional dissociation of F₂.

Our value of k_{He}, (2.2 ± 0.1) × 10¹⁴ cm⁶ mol⁻² s⁻¹, at an estimated temperature of 300 to 320 K is in agreement with Ultee's [2] value of (2.18 ± 0.4) × 10¹⁴ cm⁶ mol⁻² s⁻¹ at 298 K. However, our value of k_{Ar}, (2.1 ± 0.7) × 10¹⁴ cm⁶ mol⁻² s⁻¹, is substantially greater than Ganguli and Kaufman's [8] value of (2.9 ± 0.2) × 10¹³ cm⁶ mol⁻² s⁻¹ at 295 K. Our value of k_{F₂}, (3.6 ± 1.4) × 10¹⁴ cm⁶ mol⁻² s⁻¹ is approximately 60% greater than our value of k_{He}, indicating that F₂ is only a slightly more efficient third body than He and Ar.

*The theoretical treatment and recombination coefficients for F-atoms on alumina surfaces given by Nordine and LeGrange [7] indicate that diffusional corrections to k_w are negligible in our apparatus at pressures ≤ 100 torr. Therefore the value of k_w should be independent of pressure.

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