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A shock tube study of the reaction of H atoms with DF*

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The reaction rate of H with DF has been measured at temperatures between 2100 and 3900°K in a shock tube study. The measurements indicate that the sum of the two reaction rates for $H+DF \rightarrow HD+F$ (rate k_3) and $H+DF \rightarrow D+HF$ (rate k_4) has an activation energy of 33 700 cal/mol·sec. These data establish upper limits for each of the rate coefficients and should serve as a guide for theoretical calculations.

I. INTRODUCTION

When the first shock tube measurements of HF dissociation rates were performed by Jacobs, Giedt, and Cohen[1] in 1965, there were no data for the rate of HF removal by H atoms in the reaction

$$H + HF \xrightarrow{k_1} H_2 + F, \quad \Delta E = 31\,700 \text{ cal/mol} . \tag{1}$$

H atoms produced by the dissociation of HF can accelerate the removal rate of HF so that Reaction (1) must be considered in the data analysis. They used a best guess of $k_1 = 10^{13} \exp(-35\,000/RT)$ cm^3/mol-sec for the rate coefficient of this reaction in the analysis of their data. The subsequent interest in HF chemical lasers stimulated both experimental[2-7] and theoretical[8,9] investigations of the reverse of Reaction (1):

$$F + H_2 \xrightarrow{k_{-1}} HF + H, \quad \Delta E = -31\,700 \text{ cal/mol} . \tag{-1}$$

The experimental data for Reaction (− 1) have been obtained at temperatures between 173 and 400 °K, and the measured rates range between 10^{12} and $10^{13.6}$ cm^3/mol-sec at 300 °K. Largely on the basis of the data of Homann *et al.*[2] and theoretical calculations of Refs. 8 and 9, Cohen[10] has recommended a rate coefficient of $k_{-1} = 1.6 \times 10^{14} \exp(-1600/RT)$ cm^3/mol-sec, which corresponds to $k_1 = 8.3 \times 10^{13}\, T^{0.111} \exp(-33\,000/RT)$ cm^3/mol-sec. These recommended values are larger than the 1965 estimates of Jacobs *et al.*[1] by a factor of approximately 30 at temperatures between 2000 and 4000 °K.

Trajectory calculations[11] have indicated that the exchange reaction

$$H' + H''F \xrightarrow{k_2} H'' + H'F \tag{2}$$

makes an important contribution to the vibrational deactivation of HF by H atoms and occurs with a small activation energy. On the other hand, Bender *et al.*[12] have performed *a priori* electronic structure calculations and estimated a barrier height of 40 kcal/mol for Reaction (2). In the present study, we have performed experiments to measure rate coefficients for the isotopic variations of Reactions (1) and (2):

$$H + DF \xrightarrow{k_3} DH + F , \tag{3}$$

$$H + DF \xrightarrow{k_4} HF + D . \tag{4}$$

We have measured the sum of the two reaction rate coefficients, k_3 and k_4, in the temperature range of 2000 to 4000 °K. Although the separate values of k_3 and k_4 cannot be extracted unequivocally from the data, the measurements do place upper limits on each of these two rate coefficients. These upper limits are useful for comparison to theoretical calculations, in particular, to trajectory calculations for abstraction reactions such as Reaction (4) or Reaction (2). Such comparisons serve as tests of potential energy surfaces used in the calculations. In turn, the theoretical calculations can serve as a guide in estimating the relative magnitudes of k_3 and k_4.

II. EXPERIMENTAL APPARATUS

The shock tube has a $6\frac{3}{8}$ in. diam, 35 ft long driven section with a 3 in. diam, 10 ft driver section. The driven section is evacuated with a diffusion pump backed up by a mechanical pump. A manifold connects the tube to two mixing tanks made of the same $6\frac{3}{8}$ in. diam tubing (surplus periscope tubing). The pressures are measured with Heise 0–200 psi, Heise 0–400 psi, and Heise 0–800 Torr Class AA test gauges. The stainless steel tubing was passivated with the DF in the test mixture. After filling the tube to the desired pressure, the test mixture was flowed through the driven section to flush out any impurities pushed to the end of the tube by the initial fill. A similar procedure was used successfully for HF (DF) vibrational relaxation studies.[13,14]

The ir emission of DF near 3.6 μm was monitored with a Texas Instrument InSb detector. Interference filters allowed only the fluorescence between 3.6 and 4.5 μm to enter the detector. In a few experiments, the HF fluorescence at 2.0 to 2.5 μm was monitored. The detector output across a 1000 Ω resistor was amplified by a Perry Associates Model 50 amplifier and displayed on Tektronix oscilloscopes equipped with camera attachments. The combined risetime of the detector amplifier combination was 1.4 μsec.

Two sets of experiments were performed. The ir emission was monitored behind the incident shock wave in one set and behind the reflected shock wave in the second set. In both cases, the emission from the center of the shock tube was focused on the detector element with a 2 in. diam, 6 in. focal length CaF$_2$ lens in a $2f$–$2f$ configuration. A 1 in. focal length CaF$_2$ lens placed 1 in. in front of the detector element increased the effective area of the element. Two 0.1 in. ×0.3 in. apertures placed at the shock tube window and in front of the detector (~ 2.5 in. from the detector and ~ 9.5 in. from the lens) restricted the monitored volume of gas

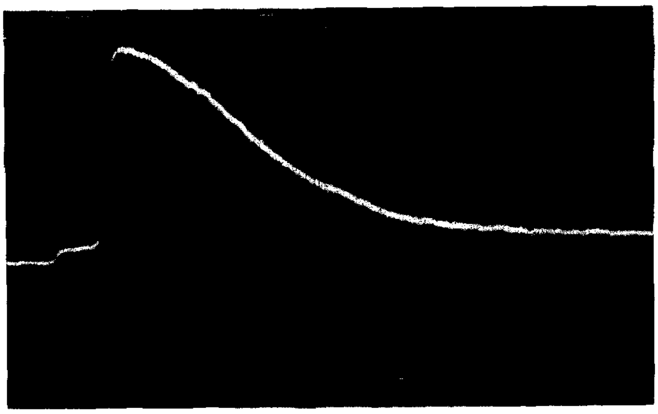

FIG. 1. DF fluorescence behind a reflected shock wave in a mixture of 0.1% DF, 2% H_2, and Ar. $T = 2558$ °K and pressure $= 14.4$ atm. $\tau^2_{1/e} = 2.1 \times 10^4$ (μsec^2). Sweep speed = 50 μsec/cm. Signal shown on two sensitivity settings.

so that the shock wave traversal time was short compared to the chemical reaction time. For the measurements behind the reflected shock wave, the emission was monitored along an axis located 0.5 in. from the end wall. The incident shock measurements were made 6.5 ft from the end of the shock tube.

The shock speeds were measured with thin-film platinum heat gauges and a raster display. The gauges were placed at 1 ft intervals for the incident shock experiments and 6 in. intervals for the reflected shock experiments. The estimated uncertainties in the incident shock velocities were approximately 0.3%. A shock wave attenuation of approximately 1% per meter was observed in the reflected shock experiments and $\leq 0.5\%$ per meter in the incident shock experiments. The shock speed was interpolated for the incident shock experiments and extrapolated to the end wall for the reflected shock experiments.

The gases used included ultrahigh purity H_2 (99.999%) and ultrahigh purity Ar (99.999%) from Matheson Gas Products. Ozark Mahoning 98% DF was distilled by cooling to LN_2 temperature, pumping off any residual gas, and warming to a temperature such that the vapor pressure of DF was approximately 30 Torr.

III. RESULTS

Figure 1 shows an oscilloscope record of the DF emission behind a reflected shock wave in a mixture of 0.1% DF, 2% H_2, and Ar. The conditions behind the shock wave were calculated to be 2558 °K and 14.4 atm. The emission intensity can be described by $(I - I_\infty) = A\exp(-t^2/\tau^2)$ where I_∞ is the final intensity. At the temperatures and pressures of the experiments, the DF emission is optically thin[1] and, therefore, is proportional to the DF concentration. The values of τ^2 were obtained from semilog plots of $(I - I_\infty)$ versus t^2. The results obtained behind incident and reflected shocks are listed in Tables I and II, respectively. The gas mixtures contained 0.1% DF, 2–4% H_2, and the balance Ar in the reflected shock experiments, and 0.5%–1% DF, 5%–10% H_2, and the balance Ar in the incident shock experiments. At low temperatures, the large activation energy for the H_2 dissociation stretched out the reaction zone for pressures obtained behind the incident shock waves. Therefore, low temperature experiments were performed behind reflected shock waves, where higher pressures could be produced.

The dominant reactions that govern the disappearance of DF are the following:

$$H_2 + M \xrightarrow{k_5^M} 2H + M , \qquad (5)$$

$$H + DF \xrightarrow{k_3} HD + F , \qquad (3)$$

$$H + DF \xrightarrow{k_4} HF + D , \qquad (4)$$

$$F + H_2 \xrightarrow{k_{-1}} HF + H , \qquad (-1)$$

$$D + H_2 \xrightarrow{k_6} HD + H . \qquad (6)$$

The four-center reaction, $H_2 + DF \rightarrow HF + HD$, that could compete with this set of reactions at lower temperatures has not been included. Such a reaction would cause the DF fluorescence to decay exponentially with t instead of with the observed t^2. Hydrogen atoms are produced by the dissociation of H_2 described by Reaction (5) with M representing the various collision partners, principally Ar and H_2. The atoms can react with DF by either Reaction (3) or (4). Reactions (−1) and (6) are exother-

TABLE I. Data obtained behind incident shock waves.

Shock velocity (mm/μsec)	$[DF] \times 10^8$, $[H_2] \times 10^7$ (mol/cm^3)	$[Ar] \times 10^6$ (mol/cm^3)	T (°K)	$(\rho_2/\rho_1)^a$	$\tau^2_{1/e}$ lab (μsec)^2	$(k_3 + k_4)^b$ (cm^3/mol·sec)
2.059	0.74	1.39	3785	3.87	223	3.55×10^{12}
1.973	1.03	1.95	3524	3.90	350	2.93×10^{12}
1.966	2.15	1.91	3231	3.96	1290	1.14×10^{12}
1.966	2.15	1.91	3231	3.96	1312	1.12×10^{12}
1.876	1.65	3.13	3191	3.80	925	1.92×10^{12}
1.742	2.54	4.81	2790	3.75	8100	8.76×10^{11}
1.742	2.54	4.81	2790	3.75	9600	7.39×10^{11}
1.643	4.00	7.59	2513	3.69	41500	5.06×10^{11}

[a] Density ratio across shock wave.

[b] $(k_3 + k_4) = \left[k_5[H_2]([Ar] + 4[H_2])\tau^2_{1/e} \text{ lab } (\rho_2/\rho_1)^2\right]^{-1}$.

TABLE II. Data obtained behind reflected shock waves.

Shock velocity (mm/μsec)	$[DF]\times 10^8$ (mol/cm^3)	$[H_2]\times 10^6$ (mol/cm^3)	$[Ar]\times 10^5$ (mol/cm^3)	T (°K)	$\tau^2_{1/e}$ (μsec)^2	$(k_3+k_4)^a$ (cm^3/mol·sec)
1.160	5.8	1.15	5.62	2971	1.00×10^3	7.2×10^{11}
1.110	6.4	1.28	6.25	2732	3.9×10^3	6.5×10^{11}
1.096	6.8	1.35	6.60	2667	8.3×10^3	4.2×10^{11}
1.072	7.0	1.41	6.89	2558	2.1×10^4	3.4×10^{11}
1.045	7.7	1.54	7.53	2438	5.1×10^4	3.1×10^{11}
1.015	8.3	1.66	8.12	2307	2.5×10^5	1.71×10^{11}
1.025	12.3	4.90	11.75	2292	7.2×10^4	1.49×10^{11}
1.0237	8.4	3.37	8.07	2287	1.74×10^5	1.37×10^{11}
0.9852	9.3	1.85	9.04	2182	8.2×10^5	1.47×10^{11}
0.9925	9.4	3.74	8.96	2158	8.1×10^5	9.0×10^{10}
0.9749	14.8	5.91	14.16	2087	8.0×10^5	8.0×10^{10}

[a] $(k_3+k_4)=\left[k_5[H_2]([Ar]+4[H_2])\tau^2_{1/e}\right]^{-1}$.

mic and essentially thermoneutral, respectively. Both are fast compared to Reactions (3) and (4). Therefore, Reaction (3) followed by Reaction (− 1) leads to the same products as Reaction (4) followed by Reaction (6). The removal of a DF molecule by an H atom leads directly to the production of one HF and one HD molecule and a replacement of the H atom. As a consequence, the experiments performed in the present study cannot distinguish between these two parallel reaction paths. The results of the few experiments in which HF was monitored were in complete agreement with those in which DF was monitored.

The DF concentration can be described by

$$\frac{d}{dt}[DF] = -(k_3+k_4)[DF][H]\ . \tag{7}$$

Because of the speed of Reactions (− 1) and (6) and the excess of H_2 over DF, the concentrations of F and D remain small, and the reverse Reactions (− 3) and (− 4) can be neglected in Eq. (7). At times that are short compared to the H_2 dissociation time, the H atom production rate can be approximated by Eq. (8):

$$\frac{d}{dt}[H] = 2k_5^M[H_2]_0[M]\ , \tag{8a}$$

$$[H] = 2k_5^M[H_2]_0[M]t\ , \tag{8b}$$

where $[H_2]_0$ is the initial H_2 concentration. The substitution of Eq. (8b) into Eq. (7) and integration give

$$\frac{[DF]}{[DF]_0} = \exp\{-(k_3+k_4)k_5^M[H_2]_0[M]t^2\}\ . \tag{9}$$

The values of (k_3+k_4) can be calculated from the measured values of $\tau^2_{1/e}$ listed in Tables I and II with

$$k_3+k_4 = \{k_5^M[H_2]_0[M]\tau^2_{1/e}\}^{-1}\ . \tag{10}$$

Equation (10) is valid if DF is removed before a large fraction of the H_2 dissociates. The H_2 dissociation cools the gas so that the temperature-dependent k_5^M decreases. After a large fraction of H_2 has dissociated, the concentration of H atoms is not properly described by Eq. (8b) in which the H_2 concentration is approximated by $[H_2]_0$ and k_5^M is assumed to be constant. The fraction of H_2 dissociated by the time $[DF]/[DF]_0 = e^{-1}$ was largest at the highest temperatures. However, the sensitivity of (k_3+k_4) to the temperature drop is not as great as would be inferred from Eq. (10), since this equation is obtained only after two integrations of Eq. (8a). In a test case, a complete calculation was performed that included the gas-dynamic equations as well as Reactions (1), (3)–(6). The calculated DF concentration decreased from $[DF]_0$ to $[DF]_0/e$ with an average exponential decay rate that agreed within 10% with that predicted by Eq. (10). This is well within the experimental scatter of ± 30%. Two gas dynamic effects tend to offset the temperature drop resulting from the H_2 dissociation. Shock attenuation (estimated to be $\leq 0.5\%$ per meter for the incident shock experiments) and laminar boundary layer growth both cause the temperature to increase behind the shock wave.[15,16] This temperature rise was estimated to be smaller than the temperature decrease from the dissociating H_2. We have included only those incident shock experiments in which the [DF] had decreased to $[DF]_0/e$ before the theoretically predicted transition to a turbulent boundary layer had occurred.

We have chosen for the hydrogen dissociation rate coefficient $k_5^{Ar} = 1.34\times 10^{20}\ T^{-1.44}\exp(-106\,400/RT)$ cm^3/mol · sec, which was calculated from the back reaction rate $k_{-5}^{Ar} = 0.72\times 10^{18}\ T^{-1}$ cm^6/mol^2 · sec. The latter expression is a good fit to the theoretical calculations of Shui, Appleton, and Keck,[17] which in turn agree closely with data at both room temperature and shock tube temperatures. Jacobs *et al.*[18] measured the slightly faster rate of $k_{-5}^{Ar} = 10^{18}\ T^{-1}$ between 2600 and 4800 °K. We have included Ar and H_2 and neglected the other minor species in calculating the H_2 dissociation rates. For the dissociation rate of H_2 by H_2, we have used $k_{-5}^{H_2} = 4\times k_{-5}^{Ar}$, which was determined by Jacobs *et al.*[18] Although they do not directly enter the analysis, the rate coefficients $k_{-1} = 1.6\times 10^{14}\exp(-1600/RT)$ and $k_6 = 10^{13.37}\exp(-6140/RT)$ cm^3/mol · sec were taken from Refs. 10 and 19, respectively. Reactions such as HF (DF) dissociation were too slow to contribute to the DF disappearance; other reactions involved species in such small concentrations that they could be neglected ($F+D_2$, D_2+Ar, $HD+Ar$, $H+HD$).

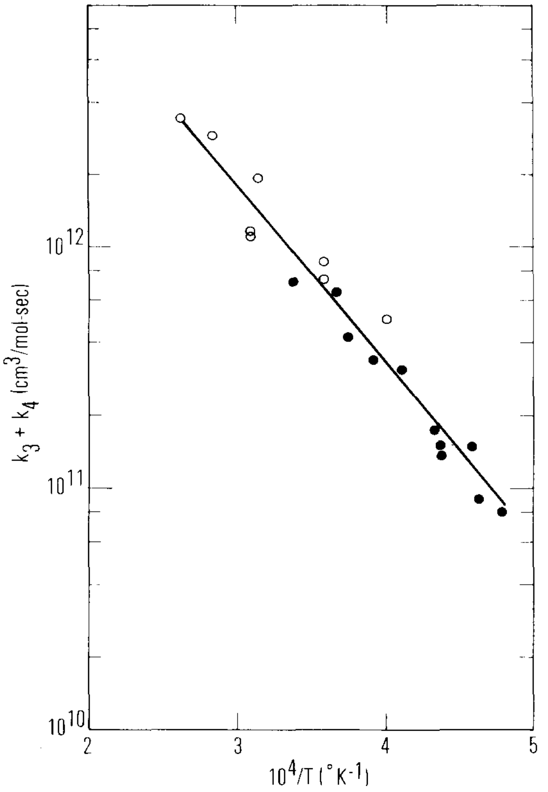

FIG. 2. Experimental data for (k_3+k_4) versus $10^4/T$. ○, incident shock data, ●, reflected shock data.

The deduced values of (k_3+k_4) are listed in Tables I and II and are plotted in Fig. 2. The results of the incident shock measurements are in substantial agreement with those of the reflected shock measurements despite the fact that the concentrations and boundary layer effects differed in the two sets of experiments. The scatter of the data about the solid line in Fig. 2 is approximately ± 30%.

IV. DISCUSSION

The measurements of (k_3+k_4) between 2100 and 3900 °K are plotted in Fig. 2. The data can be described with the Arrhenius expression $(k_3+k_4) = 2.9\times10^{14} \times\exp(-33\,700/RT)$ cm^3/mol · sec. The separate values of k_3 and k_4 cannot be extracted unequivocally from the data, but the measurements do place upper limits on each of these two rate coefficients. Since the trajectory calculations for Reaction (3) and Reaction (4) sample different regions of the potential energy surface, they need to be compared separately to the measured values of (k_3+k_4). These comparisons provide tests of the potential energy surfaces used in the trajectory calculations.

We will consider first the trajectory calculations[8,9,20] for Reaction (− 1) $F+H_2 \rightarrow HF+H$, the isotopic analog of Reaction 3. Since only Wilkins[9,21,22] has calculated the rate coefficients for the various isotopic combinations of H and D in Reaction (− 1) over a full set of temperatures, his calculations will be used for comparisons with the present experimental data. [He used an LEPS surface having a barrier height of 1500 cal/mol[9] that was chosen to give good agreement of the trajectory calculations with experimental data for the overall rate of Reaction (− 1) and the initial vibrational distribution.] The calculated effects of isotopic substitution on the overall reaction rates are in good agreement with room temperature measurements.[23-25] Wilkins' calculated rate coefficients are shown in Fig. 3 along with values for the $F+H_2$ rate coefficients which Cohen[10] recommended on the basis of the experimental evidence. The theoretical and recommended values are in agreement at room temperature and are within a factor of 1.7 at 3000 °K. Semiclassical trajectory calculations that give good results for a reaction can be expected to give good results for the same reaction with isotopic substitution in the high-temperature limit where quantum mechanical effects should be minimal. For comparison with the measured values of (k_3+k_4), the trajectory calculations for k_{-3} and the equilibrium constant for the reaction (calculated from the thermodynamic data[26]) can be used to calculate theoretical values for k_3. These theoretical values of k_3 imply an activation energy of ~ 33 700 cal/mol, the same as the measured values of (k_3+k_4). [The activation energy can be calculated from the equilibrium constant and an activation energy of ~ 1600 cal/mol for the exothermic reaction (− 3).] However, the calculated values are smaller than the measured values by a factor of ~ 6. This comparison would suggest that k_4 is the more significant contribution to the measured sum of k_3+k_4 and that it has an activation energy of ~ 34 000 cal/mol and a pre-exponential factor of $10^{14.4}$.

Even if k_3 is the chief contribution, certain limits can still be placed on k_4. A lower limit to the value of the pre-exponential factor of k_4 can be estimated by the methods outlined by Benson.[27] A value of $A > 10^{12.6}$ cm^3/mol · sec is calculated with the assumption of a bent in-

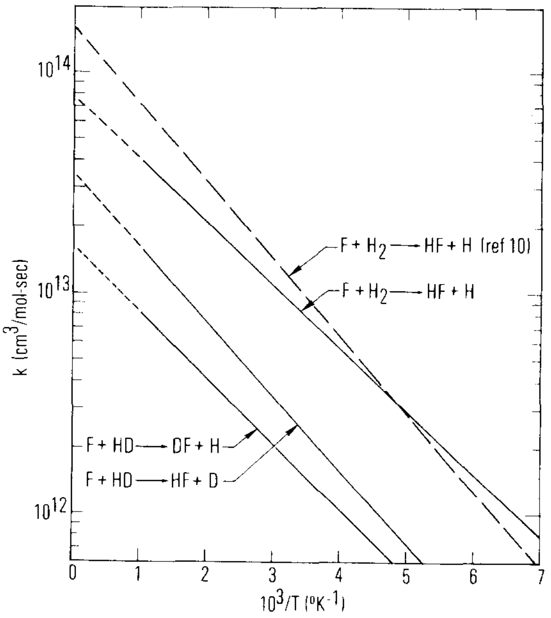

FIG. 3. Rate coefficients for the reactions of F with H_2 and HD: ----, values recommended for $F+H_2$ in Ref. 10; ——, trajectory calculations of Refs. 9 and 22.

termediate similar to the ground state H_2S geometry. The pre-exponential factors for similar metathesis reactions range between $10^{13.4}$ and $10^{14.4}$ $cm^3/mol \cdot sec$[28,29]; thus, this estimate of $10^{12.6}$ for the lower limit seems reasonable. McDonald and Herschbach[29] have found that the pre-exponential factor for Reaction (11),

$$H + DCl \rightleftarrows HCl + D \tag{11}$$

must be $\geq 10^{13}$ $cm^3/mol \cdot sec$. Therefore, halogen abstraction rate coefficients do not appear to have abnormally low pre-exponential factors.[30] For $A \geq 10^{12.6}$ and an activation energy as low as 19 000 cal/mol, k_4 would contribute 50% to the measured sum of $(k_3 + k_4)$ at 2100 °K and would seriously affect the temperature dependence of $(k_3 + k_4)$. The data show no such effect, and we conclude that the activation energy of k_4 must be $> 19\,000$ cal/mol.

We consider next the comparison of the present data to calculations for Reaction 4. Wilkins studied the vibrational deactivation of HF by H atoms with trajectory calculations[11,31] on the same LEPS surface used in the calculations for Reaction (– 1), $F + H_2 \rightarrow HF + H$. In his calculations Reactions (2) contributed significantly to the vibrational deactivation of HF $(v = 1)$ by H atoms. Subsequent calculations[32] on the same LEPS surface for the exchange

$$D + FH(v = 0, J = 2) \xrightarrow{k_{12}} DF(v' = 0) + H \tag{12}$$

resulted in a rate coefficient of $k_{12} = 10^{15.6} T^{-0.84} \times \exp(-2638/RT)$ $cm^3/mol \cdot sec$ between 300 and 1000 °K, which extrapolates roughly to values between 3 and 6 $\times 10^{12}$ at 2000 °K. With the assumption of a weak J dependence, the rate coefficient k_4 can be approximated by k_{-12}. This calculated value, however, is ~ 50 times larger than the total value of $k_3 + k_4$ measured in the present study and has a very weak temperature dependence compared to the large temperature dependence (33 700 cal/mol) of the measurements.

Prior to the present study, Heidner and Bott[33] attempted to measure the rate of Reaction (– 4) at 300 °K in a slow flow discharge tube in which HF was mixed with D atoms. In that experiment, they observed no evidence of Reaction (– 4) within the sensitivity of the laser induced fluorescence monitoring technique. They inferred an upper limit of $10^{8.3}$ $cm^3/mol \cdot sec$ for k_{-4} from their results (this corresponds to an upper limit of $10^{7.5}$ for k_4), a value that is ~ 3 orders of magnitude less than that predicted by the trajectory calculations[32] at $T = 300$ °K. Therefore, the LEPS surface used in the trajectory calculations for Reaction (4) and the vibrational relaxation of HF $(v = 1)$ by H atoms[33] does not appear to reproduce the experimental results even though the surface parameters were calibrated on the $F + H_2$ reaction (– 1).

In a recent paper, Thompson *et al.*[34] described similar discrepancies between experimental data and trajectory calculations for the exchange Reaction (11). They discussed the complications in the several continuous photolysis experiments as possible explanations of the discrepancy as well as the possible failure of the theoretical calculations. Those experimental complications do not occur in the present study of H + DF or in a measurement of the rate of Reaction (11) in this laboratory.[30] We can only conclude that there is a basic problem in adjusting an LEPS surface for a given reaction, and then performing trajectory calculations for a different reaction even though the same three atoms are involved.

The limitation of the LEPS formalism was demonstrated recently when Bender, Garrison, and Schaefer[12] performed *a priori* electronic structure calculations of the H + FH barrier for the exchange reaction (2). They concluded that the barrier is ~ 40 000 cal/mol, rather than the 1500 cal/mol used by Wilkins.[11] Wadt and Winter[35] with similar calculations have found a comparable barrier and evidence of a very "non-LEPS" angular dependence for the surface. Although our data neither prove nor disprove a barrier of 40 000 cal/mol, a barrier of at least 19 000 is required for their reasonable interpretation. If the removal of DF proceeds primarily by Reaction (4), then the measured values of $(k_3 + k_4)$ indicate a barrier of ~ 34 000 cal/mol.

In conclusion, we have measured the sum of the rate coefficients $(k_3 + k_4)$ between 2100 and 3900 °K. These measurements establish upper limits for the exchange rate k_4 that are ~ 50 times smaller than recent trajectory calculations on an LEPS surface and should serve as a test of future theoretical predictions. The data support the existence of a large barrier of H atom abstraction in H + HF collisions.

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