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Chemical Physics Letters 401 (2005) 455–458

CHEMICAL PHYSICS LETTERS

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The rate constants of the two channels of the reaction of F atoms with HD in the temperature range 193–300 K

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Received 14 November 2004; in final form 14 November 2004
Available online 15 December 2004

Abstract

The rate constants for the two channels of the reaction of F atoms with HD, k_{F+HD} and k_{F+DH}, have been determined in the temperature range 193–300 K. The sum of rate constants $k_{F+HD} + k_{F+DH}$ was determined by a competitive method and a discharge-flow-mass spectrometric technique, using the $F + D_2$ reaction as a reference reaction. By combining the results for this sum of rate constants with published results for the rate constant k_{F+D_2} and for the ratio of rate constants k_{F+HD}/k_{F+DH}, values were derived for the individual rate constants k_{F+HD} and k_{F+DH}. The experimental results are compared with published results of quantum mechanical calculations and of quasiclassical calculations on the Stark–Werner potential energy surface.

1. Introduction

The study of the $F + H_2$ reaction is of central importance to the development of theories in chemical dynamics [1,2]. Numerous experimental and theoretical studies of this reaction and of its isotopic variants $F + D_2$ and $F + HD$ have been carried out in recent years. Comparisons between theoretical predictions based on various potential energy surfaces (PESs) and experimental measurements have led to conclusions concerning the accuracy of these surfaces. Among the experimental measurements carried out for this system are the determinations of rate constants as a function of temperature. Quite accurate kinetic results over wide temperature ranges are available for the $F + H_2$ and $F + D_2$ reactions [3–5] (for a critical review of available kinetic data and recommended rate constants see [6]). Quite accurate results are also available for the ratio of rate constants for the two channels of the reaction of F atoms with HD (intramolecular kinetic isotope effect k_{F+HD}/k_{F+DH}) [7]

$$F + HD \rightarrow HF + D \tag{1a}$$

$$F + DH \rightarrow DF + H \tag{1b}$$

However, no experimental results are available concerning the individual rate constants k_{F+HD} and k_{F+DH}.

The ab initio PES developed by Stark and Werner (SW PES) [8] is considered to be the most accurate PES available today [1,2,9]. Nevertheless, there are still some discrepancies between some experimental results and results of quantum mechanical (QM) calculations based on this PES [9–15]. Significant discrepancies exist with respect to the intramolecular kinetic isotope effect k_{F+HD}/k_{F+DH}, especially at low temperatures (see Fig. 7 of [14] and Fig. 7 of [15]). Discrepancies also exist with respect to the rate constants of the $F + H_2$ reaction at low temperatures [16]. In both cases the QM rate constants are significantly higher than the experimental rate constants. It was suggested [12,13] that some of the discrepancies between QM calculations and experimental data indicate that the potential energy barrier of the

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doi:10.1016/j.cplett.2004.11.103

SW PES is too narrow, causing excessive tunneling. The potential energy curve of the SW PES along the entrance channel was calculated in [16] and was presented in Fig. 5 of [16]. This figure shows that the barrier is rather thin, thus permitting significant tunneling.

Quantum mechanical tunneling is of prime importance for the $F + H_2$ system at low temperatures. However, the extent of the tunneling contribution to reaction depends on the isotopic variant. As was discussed by Castillo and Manolopoulos [9], out of the four isotopic variants $F + H_2$, $F + D_2$, F + HD and F + DH, the QM tunneling effect is expected to be least important for F + DH and most important for F + HD, due to the fact that the skewing angle in the potential energy surface is the largest for F + DH and the smallest for F + HD (see Fig. 1 of [9]). Thus, the two channels of the F + HD reaction constitute two extremes with respect to the significance of the tunneling contribution to reaction. This fact finds its expression in the differences between the excitation functions for these two reactions at low collision energies. A combined experimental and QM study of integral cross-sections as a function of collision energy at 50 K for the reaction of F atoms with HD was carried out by Skodje et al. [12,13]. For the F + DH channel, the behavior was found to be essentially classical, with a direct over-the-barrier mechanism. On the other hand, it was found that the F + HD channel, at very low collision energies, is dominated by tunneling through the barrier. Whereas the cross-section increases monotonically with collision energy for the F + DH channel, for the F + HD channel, a resonance peak is observed, both experimentally and theoretically, near a collision energy of 0.5 kcal mol^{-1}. No such peak was observed in quasiclassical calculations on the same PES (the SW PES) [17]. In view of these significant differences in the behavior for the two channels of the reaction of F atoms with HD, it seems rather interesting and important to determine experimentally the individual rate constants k_{F+HD} and k_{F+DH} and to compare the results with available results of QM calculations [14] and of quasiclassical trajectory calculations (QCT) [17] on the SW PES. This was the purpose of the present study.

In this study the sum of rate constants $k_{F+HD} + k_{F+DH}$ was determined experimentally over a wide temperature range by a competitive method, using as a reference reaction the reaction of F atoms with D_2

$$F + D_2 \rightarrow DF + D \qquad (2)$$

From the ratios of rate constants $(k_{F+HD}+k_{F+DH})/k_{F+D_2}$ and available data for k_{F+D_2} [6] and for the ratios of rate constants k_{F+HD}/k_{F+DH} [7], absolute values were calculated for the individual rate constants k_{F+HD} and k_{F+DH}. The experimental results are compared with results of QM [14] and of QCT [17] calculations.

2. Experimental

Experiments to determine the ratio of rate constants $(k_{F+HD} + k_{F+DH})/k_{F+D_2}$ were carried out in the temperature range 193–300 K. The experimental setup and procedure used in this study were similar to those used by us in our earlier studies of the reactions of F atoms with HBr [18], DBr [19], CH_4 [20,21], H_2S [21], CH_3F and CH_2F_2 [22] and C_2H_6 [23]. Therefore they will be described here only briefly.

Experiments were carried out in a fast-flow system with mass spectrometric analysis of the reaction mixture. In the experiments below room temperature the reaction cell was cooled by a stream of cold nitrogen gas. The temperature in the cell was measured by copper-constantan thermocouples at three locations along the axis of the cell. The temperature in the cell was uniform to within ±2 °C in all the experiments.

Fluorine atoms were produced by a microwave discharge in a dilute mixture of CF_4 in Ar and flowed into the reaction cell through one of its inlets. The F atoms reacted with a mixture of HD and D_2, also diluted by Ar, which flowed into the reaction cell through a second inlet. The reaction mixture was continuously sampled through a small orifice and analyzed by a quadrupole mass spectrometer (Balzers Model QMG 511). As in our earlier studies of reactions of F atoms, the walls of the discharge tube and reaction cell, both made of quartz, were treated by a 10% HF solution to minimize the heterogeneous recombination of F atoms. The flow rates of the reagents into the reaction cell were controlled by calibrated capillaries and were of the order of 0.005–0.012 $\mu mol\,s^{-1}$ for HD and D_2, 0.002–0.008 $\mu mol\,s^{-1}$ for CF_4 and around 100 $\mu mol\,s^{-1}$ for Ar. The total pressure in the reaction cell was 1–1.5 Torr.

The concentrations of the reagents were followed, by measuring the appropriate mass spectrometric signals (mass to charge ratios $m/e = 3$ and 4, due to HD and D_2, respectively). The ratio of rate constants for the competing reactions is given by the expression

$$(k_{F+HD} + k_{F+DH})/k_{F+D_2} = \ln([HD]_0/[HD])/\ln([D_2]_0/[D_2]) \qquad (I)$$

where [HD] and $[D_2]$ are the concentrations of these reagents at the end of the reaction cell when the reactions with F atoms take place (microwave discharge turned on) and $[HD]_0$ and $[D_2]_0$ are their concentrations when no F atoms are present (microwave discharge turned off).

3. Results and discussion

The ratio of rate constants $(k_{F+HD} + k_{F+DH})/k_{F+D_2}$ was determined at four temperatures in the temperature range 193–300 K. At each temperature, a set of experiments was carried out in which the extent of reaction was varied over a wide range, by varying the concentration of the F atoms. Plots of $\ln([HD]_0/[HD])$ vs $\ln([D_2]_0/[D_2])$ for the two extreme temperatures, 193 and 300 K, are presented in Fig. 1. The straight lines in this figure were calculated by the least-squares method. As can be seen, no significant scatter of the points around the lines is observed, and the lines have near-zero intercepts. This behavior indicates that the calculated ratios of rate constants are independent of the extent of reaction and proves that secondary reactions are not important under the conditions of our experiments. Plots for the two other temperatures, 219 and 249 K, not shown in Fig. 1, also gave results independent of the extent of reaction.

Ratios of rate constants $(k_{F+HD} + k_{F+DH})/k_{F+D_2}$, calculated from the straight lines shown in Fig. 1, and from similar lines, not shown in this figure, for two other temperatures, are presented in Table 1. These ratios of rate constants were combined with available data for k_{F+D_2} [6] and for the ratio of rate constants k_{F+HD}/k_{F+DH} [7] to calculate the individual rate constants k_{F+HD} and k_{F+DH}. The Arrhenius expressions used for this purpose are ([6,7], respectively)

$$k_{F+D_2} = (1.06 \pm 0.12) \times 10^{-10} \times \exp[-(635 \pm 55)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \mathrm{(II)}$$

and

$$k_{F+HD}/k_{F+DH} = (1.26 \pm 0.02) \times \exp[(35 \pm 3)/T] \quad \mathrm{(III)}$$

The calculated values of k_{F+HD} and k_{F+DH} are presented in the third and fourth columns of Table 1, respectively, and are plotted, on a logarithmic scale, as a function of $1000/T$, in Fig. 2. The Arrhenius expressions corresponding to the experimental straight lines are

$$k_{F+HD} = (5.80 \pm 0.80) \times 10^{-11} \times \exp[-(530 \pm 70)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \mathrm{(IV)}$$

$$k_{F+DH} = (4.60 \pm 0.60) \times 10^{-11} \times \exp[-(565 \pm 70)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \mathrm{(V)}$$

Table 1
Ratios of rate constants $(k_{F+HD} + k_{F+DH})/k_{F+D_2}$ and rate constants k_{F+HD} and k_{F+DH} as a function of temperature

T (K)	$(k_{F+HD} + k_{F+DH})/k_{F+D_2}$[a]	$10^{12}\ k_{F+HD}$[a,b]	$10^{12}\ k_{F+DH}$[a,b]
193	1.53 ± 0.06	3.65 ± 0.35	2.40 ± 0.23
219	1.48 ± 0.04	5.15 ± 0.45	3.50 ± 0.30
249	1.39 ± 0.03	6.80 ± 0.60	4.70 ± 0.42
300	1.31 ± 0.03	9.80 ± 0.90	6.90 ± 0.65

[a] Quated errors are 2σ.
[b] Units: $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

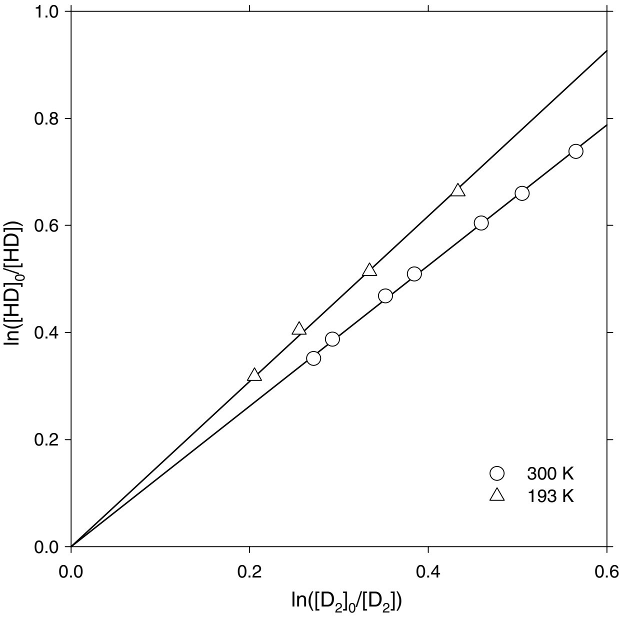

Fig. 1. Plots of $\ln([HD]_0/[HD])$ vs $\ln([D_2]_0/[D_2]$ for the reaction of F atoms with a mixture of HD and D_2 at 193 and 300 K.

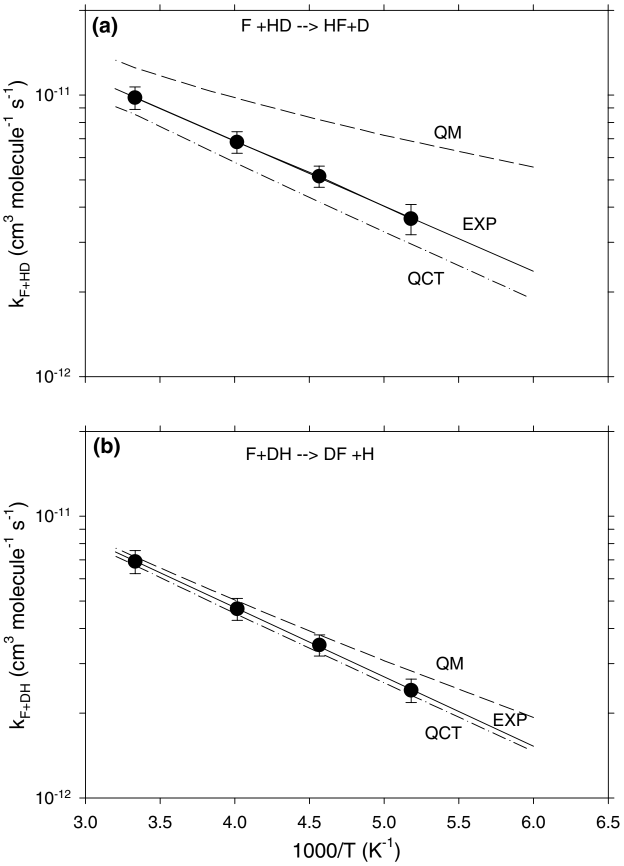

Fig. 2. Semi-logarithmic plots of the rate constants for the two channels of the reaction of F atoms with HD, k_{F+HD} and k_{F+DH}, as a function of $1000/T$. A comparison between the present experimental results (solid lines) and results of quantum mechanical calculations (dashed lines) [14] and of quasiclassical trajectory calculations (dot-dashed lines) [17] on the SW PES.

Fig. 2 includes also the results of QM [14] and of QCT [17] calculations, based on the SW PES. As can be seen from Fig. 2, the experimental results are between the QCT and the QM results. The QCT results are somewhat lower than the experimental results, since they do not include any tunneling contributions. On the other hand, the QM results are higher than the experimental results, probably because of excessive tunneling contributions. The differences in the tunneling contributions for the two channels of the reaction of F atoms with HD are clearly observed by comparing the corresponding figures (Fig. 1a,b). While for the F + DH channel, the QM and QCT results are rather close and do not differ significantly from the experimental results, in the temperature range of this study, significant differences are observed for the F + HD channel and they increase as the temperature is lowered. As pointed up in Section 1, following the discussion in [9], the large differences in the tunneling contributions for the two competing channels F + HD and F + DH are rather expected.

This study clearly indicates that the SW PES predicts too much tunneling for the F + HD channel of the reaction of F atoms with HD. This is consistent with earlier conclusions based on the comparison between QM and experimental cross-sections for this reaction [12,13] and on the comparison between QM and experimental results for the ratios of rate constants k_{F+HD}/k_{F+DH} [14,15]. It seems that some modifications in the SW PES are needed in order to close the gaps between theoretical and experimental results for the F + H_2 system. Recently, Aquilanti et al. [24,25] carried out QM calculations for the F + H_2 reaction using the SW PES, after it was modified in the entrance channel. The barrier for the modified PES is broader than the barrier of the original SW PES, thus reducing the amount of tunneling, while the barrier height is preserved. The QM rate constants obtained by them were found to be in good agreement with the experimental data for the F + H_2 reaction [3–6]. It would be very interesting to find out whether this PES, or any other modified SW PES, reproduces correctly the rate constants reported here for the two channels of the reaction of F atoms with HD.

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