MASTER

MEASUREMENTS OF GAS-PHASE REACTION RATES:

Progress Report

For the Period September 1, 1980 - November 31, 1981

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May, 1981

Prepared for

DEPARTMENT OF ENERGY

UNDER CONTRACT NO. EG-77-S-02-4426

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I. Detailed Balance in Cl+H₂

A. Introduction

During FY1981 we focused our efforts on the reactions of the Cl-H₂ system. These reactions have played a major role in the history of molecular dynamics, and have provided a testing ground for numerous electronic structure and dynamics calculations. The work through 1978 has been reviewed by Weston.¹ Despite the intense effort to understand this elementary system, a number of significant problems have remained. One of these is the observation that the ratio of the forward and reverse rate constants for the reactions

apparently does not equal the known equilibrium constant.² Various explanations have been offered to resolve this paradox. One point of view has been that detailed balance in fact does not hold for the rate constants actually measured for reactions (1) because of disequilibrium effects in one or both directions. For example, Snider³ and Clyne⁴ suggested that the observed k_f could be smaller than anticipated if Cl(²P_{1/2}) is so much more reactive than Cl(²P_{3/2}) that its relative concentration were significantly depleted by the reaction. Alternatively, Westenberg and deHaas² suggested that k_r could be larger than expected if HCl formed in the forward reaction has sufficient excess rotational energy to enhance the reverse reaction rate.

Because of the usefulness of detailed balance in many areas of chemical kinetics, the possibility that it might not hold in this test case would have profound significance. Galante and Gislason⁵ showed, however, that the postulated enhanced reactivities of electronically excited Cl and rotationally excited HCl could not compete with quenching processes under actual experimental conditions. Consequently, an alternate point of view which has been offered by various authors is that the measurements of k_f and/or k_r were erroneous. Since a recent measurement⁶ of k_f using different methods confirmed the earlier results, it appears that the error lies in k_r . Every recent study^{2, 7-9} of $H + HCl$ has invoked stoichiometric factors to correct for secondary reactions of H. All of these studies used flow reactors, in which wall reactions of Cl were present. To account for the secondary reactions of H, various artificial mechanisms were introduced. These mechanisms invoked collisions of product Cl atoms with the flow tube wall resulting in the formation of species such as Cl_2 ,⁸ HCl_2 ,⁸ and vibrationally excited HCl,^{9, 10} and desorption of these species into the reaction mixture. An unambiguous measurement of the $H + HCl$ reaction rate constant has not been reported to date.

Because of the experimental difficulties present in the flow studies, we decided to reexamine the $Cl-H_2$ system with a method that virtually eliminates wall effects. The flash photolysis-resonance fluorescence (FP-RF) technique is ideal for this purpose because the reaction takes place in the center of the cell at a

rate which is typically two orders of magnitude faster than the rate of diffusion to the walls.

B. Experimental Methods

The FP-RF apparatus in its present form is depicted in Fig. 1. Basically, the equipment consists of a variable temperature (200-500K) reaction cell housed in a vacuum chamber with three mutually perpendicular optical ports to accommodate a flash lamp, resonance lamp, and photomultiplier tube. Temperature was measured with a thermocouple in direct contact with the reaction gas, while pressure in the cell was measured with a capacitance manometer.

Atomic reactants were generated with a tungsten flash lamp operating at approximately atmospheric pressure of flowing N_2 . The nominal lamp energy was 100-200 joules/pulse, at a pulse rate of 0.3 to 0.5 Hz. The reaction mixture was flowed through the cell at a rate sufficient to be replenished at least once between flashes. The uv radiation used to monitor hydrogen and chlorine atoms was generated with a conventional microwave powered resonance lamp.

Detection of the fluorescent signal was accomplished by means of a solar blind photomultiplier tube mounted perpendicular to the flash and resonance lamps. Individual photon pulses were amplified, discriminated, counted and stored in a dedicated computer. Further details of the apparatus appear in ref. 11.

Figure 1. Schematic drawing of the flash-photolysis resonance-apparatus. The temperature controlled reaction cell (RC) is located in a vacuum housing (VH). The flash lamp (FL) consists of a tungsten spark gap powered by a high voltage power supply (HVPS) which charges resistor R and charging capacitor HVC. The resonance lamp (RL) is powered by a microwave power supply. The solar blind photomultiplier tube (PM) is perpendicular to both FL and RL. A trigger pulse is supplied by a fiber optic (FO) connected to a photodiode (PD). A gated pulse amplifier, discriminator, and counter (ADC) is interfaced to an on-line LSI-11 computer and an off-line PDP-11/45 computer.

C. Results

Typical experimental data for pseudo-first order decay of Cl atoms in a mixture of H_2 , CF_3Cl and He is shown in Fig. 2. Also shown is the non-reactive diffusion, which was typically 1-10% as fast as the reactive rate.

The measured rate constant k_f for $Cl + H_2$ is plotted in Fig. 3 as a function of temperature. Our results are seen to be in excellent agreement with previous measurements, and in particular with Watson's recommendation.¹²

The reverse reaction was studied under nearly identical conditions, and the results are plotted in Fig. 4. It is evident that our measurements are in conflict with all of the previous studies. The quantity of immediate interest is the ratio of k_f/k_r , which is plotted for all the studies in Fig. 5. Also shown is the equilibrium constant, which is accurately represented by the expression

$$K_{eq} = 1.94 \exp (-1110/RT). \quad (2)$$

In comparison, our data are fitted by the expression

$$k_f/k_r = 2.02 \exp (-1090/RT). \quad (3)$$

It is clear from the figure that the data of Westenberg and de Haas² and of Ambidge et al⁸ could be brought into good agreement by dividing their k_r by a factor of two. This correction can be interpreted as a stoichiometric factor resulting from a secondary reaction of H with wall products. From the present study, where wall

Figure 2. Comparison of the diffusion and reaction rates for a typical H+HCl run. The experimental parameters for the diffusion data were: CH₄ pressure = 0.227 Torr, total pressure = 40 Torr, T = 294.7K, flash energy = 162 joules. For the reaction data the parameters were: HCl pressure = 0.217 Torr, total pressure = 40 Torr, T = 296.3K, flash energy = 162 joules. Data were accumulated for 80 flashes for both diffusion and reaction, with a channel width of 3000 μ sec/channel for diffusion and 400 μ sec/channel for reaction.

Figure 3. Rate constants for the reaction $\text{Cl} + \text{H}_2$. The data points are from the studies of Westenberg and de Haas (WD), Lee et al (LMPS), and the present work (MG). The line is the recommendation of Watson. Error bars are one std. dev.

Figure 4. Rate constants for the reaction $\text{H}+\text{HCl}$. The data points are from Clyne and Stedman (CS), Westenberg and de Haas (WD), Ambidge et al (ABW), and the present study (MG). Error bars are one std. dev.

Figure 5. Ratio of forward to reverse rate constants. Symbols are the same as in Figs. 2 and 3. The solid line is the exact K_{eq} , while the dashed line is $0.5 K_{eq}$. For the data of Clyne and Stedman and Ambidge et al the recommended values of Watson were used for k_f .

reactions were not a problem, we conclude that the ratio of the forward to the reverse rate constant is indeed equal to the equilibrium constant.

II. Isotope Effects in Cl+H₂

A. Introduction

A second study that we carried out during FY1981 is a measurement of the rate constant of the reaction

which may be compared with our previous study of

There were two motivations for this study. First, isotope effects are a very sensitive probe of the features of a potential energy surface. In a series of static bulb studies Klein and coworkers¹³⁻¹⁵ measured as a function of temperature five ratios of the form k_X/k_Y , where X and Y refer to different H'H" isotopes. From their data they determined the saddle point geometry and force constants of the potential energy surface.^{14, 16} This surface has since been used in classical^{17, 19} and quantal^{20, 21} scattering calculations and for generalized transition state theory.^{22, 23} Since none of the rate constants other than k_{H_2} have ever been measured directly, we felt that a direct determination of k_{D_2} would be of interest.

There is a second, more important reason for verifying the photochemical studies of Klein and coworkers. There is at present a major controversy surrounding the branching ratio for abstraction

vs. exchange in the reactions

As our own study of k_H confirmed, the rate constant for the abstraction process is approximately, $3 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ at room temperature, with an activation energy of 3.5 kcal/mole.

The controversy centers on the exchange process, which Thompson, Suzukawa and Raff²⁴ call "a paradox" in chemical kinetics. Using a potential energy surface which gives reliable results for twelve related reactions, they obtained from classically trajectory calculations a value of 1.2×10^{13} for k_e at room temperature, in agreement with the molecular beam studies of McDonald and Herschbach.²⁵ In contrast, Heidner and Bott²⁶ found in a flow experiment with laser fluorescence detection of HCl that $k_e = 2.4 \times 10^{10}$. A similar contradiction exists in photochemical measurements of the branching ratio, k_a/k_e . Klein and Veltman²⁷ obtained a value of 1.64 for $\text{D} + \text{HCl}$ and 0.74 for $\text{H} + \text{DCl}$, whereas Wood²⁸ obtained a value of 19 ± 4 for the latter case. A recent measurement by Endo and Glass,²⁹ using a flow tube with ESR detection, yielded for $\text{D} + \text{HCl}$ a branching ratio of $k_a/k_e = 280 \pm 280$ at 300 K and 40 ± 25 at 1000K.

The problem can perhaps be best appreciated by comparing the studies of Dunning and Klein. Using accurate GVB wave functions, Dunning³⁰ obtained an activation energy for the exchange reaction of 25 kcal/mole. This result should be accurate to within a few

kcal/mole, and similar calculations have been carried out at this level of accuracy for numerous systems. On the other hand, it is hard to fault the photochemical work of Klein and co-workers,^{2,7,31} who find that $k_e \approx k_a$. The present study, while dealing with a somewhat simpler kinetic problem, does provide a test of the consistency of Klein's measurements.

B. Results

The measured rate constants for reactions (4) and (5) are shown in Fig. 6. Above 250K our values of k_{H_2}/k_{D_2} are in fair agreement with the results of Persky and Klein.¹⁴ Our ratio varies from 9.4 to 3.9 as the temperature is increased from 257K to 499K, with a room temperature value of 8.9. In comparison, Persky and Klein obtain a ratio that varies from 14.9 to 7.5 over the temperature range 243-343K, with a room temperature value of 9.9.

Below 250K there is an anomalous departure from Arrhenius behavior in k_{D_2} . Since k_{H_2} and k_{D_2} were measured in the same way, and since k_{H_2} varies normally over the entire temperature range, the only artifact which could explain the anomalous behavior of k_{D_2} is an impurity in the deuterium gas. For example, at 200K 2.4 PPM of ethane would suffice to explain the discrepancy. However, a careful mass spectrographic analysis with a 1 PPM sensitivity did not reveal any reactive contaminants. While we cannot completely rule out the possibility that some highly reactive impurity is responsible for the anomalous temperature dependence, it does appear that the

Figure 6. Rate constants for the reactions $\text{Cl} + \text{H}_2$ and $\text{Cl} + \text{D}_2$.

non-Arrhenius behavior is real. A possible explanation of the data is that long range attractive forces increase the reactive cross section at low kinetic energies. For the faster H_2 this effect would occur only at lower temperatures. We are continuing to consider this matter further.

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IV. Publications

1. Robert J. Gordon, "A Metastable Complex Model for Vibrational Relaxation," J. Chem. Phys. 74, 1676 (1981).
2. Yannis Vlahoyannis and Robert J. Gordon, "Vibrational Relaxation of O₃ by H₂O and D₂O," J. Chem. Phys. 74, 1682 (1981).
3. John C. Miller and Robert J. Gordon, "Kinetics of the Cl-H System. I. Detailed Balance in the Cl+H Reaction," submitted to J. Chem. Phys.
4. John C. Miller and Robert J. Gordon, "Kinetics of the Cl-H System," submitted to the ACS National Meeting, New York City, August, 1981.