A High-Temperature Photochemistry Study of the H + HCl → H_2 + Cl Reaction from 298 to 1192 K

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Rate coefficients for the reaction between ground-state H atoms and HCl have been measured using the HTP (high-temperature photochemistry) technique. The hydrogen atoms were generated by flash photolysis of NH_3, and the relative atom concentrations were monitored by time-resolved resonance fluorescence. The data in the 298–1192 K range are well fitted by the expression $k_1(T) = 2.8 \times 10^{-11} \exp(-2082\ K/T)$ cm^3 molecule^{-1} s^{-1} with 2σ precision limits of ±6% to ±12%, depending upon temperature, and corresponding 2σ accuracy limits of about ±23%. A transition state theory calculation based on a semiempirical London–Eyring–Polanyi–Sato potential energy surface leads to excellent agreement with the experimental results. By combining the present best fit with current equilibrium data, we derive for the reverse reaction $k_{-1}(T) = 4.9 \times 10^{-11} \exp(-2567\ K/T)$ cm^3 molecule^{-1} s^{-1}.

Introduction

Reactions of HCl at elevated temperatures play a role in a number of applications. In flames containing chlorinated compounds they lead to inhibition and as a result soot formation.[1,2] The inhibition results from[3] H atom removal by

$$H + HCl \rightarrow H_2 + Cl \qquad (1)$$

which reduces the rates of the chain-branching flame propagation reaction $H + O_2 \rightarrow OH + O$. In waste incineration, reaction 1 needs to be considered in models for the formation of toxic compounds, such as dibenzodioxins and dibenzofurans.[4] HCl is considered the main agent causing volatilization of hazardous metals in such environments.[5]

ΔH for reaction 1 is -4 kJ mol^{-1}.[6] Baulch et al.[7] have reviewed the $k_1(T)$ data. The original direct measurements by the discharge flow method were too high compared to data calculated from the better studied reverse reaction and thermodynamic equilibrium data. Spencer and Glass[8] attributed this to wall reactions and obtained a new k_1(298 K) rate coefficient which was in agreement with these K_1 and k_{-1} data. Ambidge et al.[9] also found good agreement and extended the measurements to 521 K. Both these groups again used discharge flow reactors but used wall poisons to suppress the wall reaction contribution. Nonetheless, Baulch et al. considered it more reliable to make a recommendation based on the reverse reaction, i.e., $k_1(200\text{–}650\ K) = 1.3 \times 10^{-11} \exp(-1710\ K/T)$ cm^3 molecule^{-1} s^{-1}. This recommendation is in good agreement with the essentially simultaneously published data by Miller and Gordon[10] for k_1 over the 200–500 K temperature range, by the essentially wall-less flash photolysis resonance fluorescence technique. We here report on a reinvestigation of reaction 1 in an environment where wall reactions similarly play no role, i.e., by the HTP (high-temperature photochemistry) technique. We use the results to derive a $k_1(T)$ expression for the 300–1200 K temperature range and to recommend a $k_{-1}(T)$ expression for the reverse reaction for the same temperature range.

Experimental Technique

The experiments were performed in the HTP reactor, shown as reactor B by Mahmud et al.[11] which has previously been used for O atom studies only. This reactor includes a 5-cm-diameter alumina reaction tube surrounded in sequence by 20 alternately stacked SiC heating rods, insulation, and a water-cooled steel vacuum chamber. The NH_3 flows through a movable cooled inlet, to prevent thermal decomposition, while the bath gas Ar and the HCl are introduced at the upstream (bottom) side of the reactor. The reaction zone temperature is measured by a doubly shielded thermocouple placed axially to the reaction tube. A second thermocouple placed just off-axis of the reaction tube serves to check the performance of the first thermocouple. Pressure measurements are made by an MKS baratron pressure transducer located downstream of the reaction zone. Flow rates of gases are determined by precalibrated flow meters and controllers.

H atoms are generated by flash photolysis of NH_3 through a MgF_2 window. The relative concentrations of the H atoms are monitored by resonance fluorescence at 121.6 nm through a MgF_2 window. The source of resonance radiation is a microwave discharge flow lamp through which a 1% mixture of H_2 in He flows at about 3.2 mbar. The H atom fluorescence signals are spectrally isolated by means of a gas filter providing a 2.5 cm path of dry air at atmospheric pressure[12] and are detected by a solar-blind PMT connected to a multichannel scaler.

The gases used are Ar from the liquid, 99.998%, and He (99.991% U.H.P) both supplied by Linde, NH_3, 99.999%, 10.8% HCl (99.3% in Ar (99.999%)), and 1.00% HCl (99.3% in Ar (99.999%)) from Matheson, and 0.103% HCl (99.6% in Ar (99.999%)) from MG Industries.

The current operating and analysis procedures have been described.[12-14] Briefly, the experiments are carried out under pseudo-first-order conditions [H] ≪ [HCl], for which the fluorescence intensity I, proportional to [H], can be written as[11]

$$I = I_0 \exp(-k_{ps1}t) + B \qquad (2)$$

where I_0 is the intensity at time $t = 0$, k_{ps1} the pseudo-first-order rate coefficient, and B the background due to scattered light. The values of k_{ps1} are obtained by fitting[15] observed I vs t profiles to eq 2. In all cases exponential ln I vs t plots were obtained, as verified by a two-stage residual analysis.[14] Typically, five or six k_{ps1} at varying [HCl] are used to obtain k_1 at the temperature and pressure of the experiment.

Results and Discussion

A total of 47 measurements of k_1 were made from 298 to 1192 K. The upper temperature limit was determined by the thermal stability of the NH_3. Temperature variations in the course of a

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TABLE I: Summary of Rate Coefficient Measurements on H + HCl Reaction

T,[a] K	P, mbar	[M], 10^{18} cm^{-3}	[NH_3], 10^{15} cm^{-3}	[HCl], 10^{14} cm^{-3}	z, cm	$\bar{v}$, cm s^{-1}	FE, J	$k \pm \sigma_k$, cm^3 molecule^{-1} s^{-1}
298	243	5.9	21.0	13–24[b]	28[e]	10	18	2.72 ± 0.35 (−14)[f]
298	243	5.9	21.0	13–26[b]	28	10	9	2.98 ± 0.26 (−14)
299	327	7.9	28.9	20–30[b]	28	8	15	3.95 ± 0.13 (−14)
302	317	7.6	49.8	0.0–23[b]	28	5	18	3.51 ± 0.22 (−14)
316	246	5.7	15.3	5.7–10[b]	28	11	18	4.97 ± 0.68 (−14)
319	201	4.6	9.6	6.0–23[b]	28	9	7	4.77 ± 0.54 (−14)
319	367	8.3	9.8	0.0–17[b]	28	10	7	4.69 ± 0.81 (−14)
320	201	4.5	9.6	4.4–24[b]	28	9.1	18	4.27 ± 0.56 (−14)
332	268	5.8	9.1	3.4–13[b]	28	15	12	5.90 ± 0.42 (−14)
337	285	6.1	23.2	5.4–43[b]	28	5	12	5.60 ± 0.19 (−14)
351	495	10.2	14.1	7.2–19[b]	28	13	15	7.00 ± 0.45 (−14)
353	181	3.7	14.7	3.4–12[b]	28	12	15	7.72 ± 0.30 (−14)
356	181	3.7	14.6	6.6–24[b]	28	12	18	9.25 ± 0.30 (−14)
369	207	4.1	22.6	16–34[b]	28	9	18	9.35 ± 0.52 (−14)
369	199	4.1	22.6	16–34[b]	28	9	5	1.00 ± 0.08 (−13)
387	267	5.0	13.7	2.3–15[b]	28	18	18	1.00 ± 0.16 (−13)
391	265	4.9	13.6	2.0–17[b]	28	18	18	1.19 ± 0.30 (−13)
404	133	2.4	19.0	0.21–2.0[b]	28	10	12	2.20 ± 0.41 (−13)
412	140	2.5	25.3	0.39–4.4[b]	28	7	12	2.04 ± 0.28 (−13)
439	738	12.4	30.3	0.48–3.3[b]	28	10	12	1.98 ± 0.16 (−13)
443	399	6.5	33.9	0.89–2.9[b]	28	10	18	2.34 ± 0.27 (−13)
445	444	7.2	11.3	0.5–2.0[b]	28	17	18	2.75 ± 0.28 (−13)
445	444	7.2	11.3	2.7–9.3[b]	28	17	9	2.00 ± 0.30 (−13)
452	742	11.9	29.0	0.70–3.2[c]	28	10	15	2.85 ± 0.16 (−13)
491	745	11.0	27.1	0.68–2.6[b]	28	11	9	3.82 ± 0.33 (−13)
495	443	6.5	15.8	0.44–2.5[b]	28	11	9	4.17 ± 0.41 (−13)
500	443	6.4	16.0	0.61–2.7[c]	28	12	18	3.81 ± 0.16 (−13)
539	208	2.7	14.8	0.0–5.4[c]	28	15	18	7.17 ± 0.56 (−13)
559	212	2.7	15.1	0.0–5.5[b]	28	15	5	6.97 ± 0.11 (−13)
567	453	5.7	15.2	0.0–6.0[c]	28	16	18	5.11 ± 0.23 (−13)
605	900	10.8	18.0	6.0–19[c]	15	10	9	7.66 ± 0.61 (−13)
621	468	5.4	13.9	5.4–19[c]	15	10	9	1.27 ± 0.12 (−13)
624	467	5.4	12.1	1.9–13[c]	15	10	18	1.41 ± 0.05 (−12)
659	272	3.0	9.8	2.5–14[c]	15	12	4	1.45 ± 0.14 (−12)
670	275	3.0	9.8	2.9–11[c]	15	12	15	1.51 ± 0.14 (−12)
820	265	2.4	7.2	0.17–1.1[c]	15	16	12	2.01 ± 0.13(−12)
828	336	3.0	11.3	0.0–0.54[d]	8	16	12	2.12 ± 0.29 (−12)
830	337	2.9	11.1	0.19–0.8[d]	8	16	4	2.18 ± 0.27 (−12)
918	161	1.3	7.4	0.6–2.6[d]	28	45	7	2.59 ± 0.14 (−12)
937	211	1.3	13.1	0.1–0.52[c]	10	14	7	2.68 ± 0.28 (−12)
968	265	2.0	6.7	0.21–0.91[c]	10	18	7	3.74 ± 0.32 (−12)
1033	539	3.8	5.1	0.16–0.65[d]	6	23	7	4.15 ± 0.41 (−12)
1042	287	2.0	4.5	0.15–0.52[d]	6	24	7	4.44 ± 0.42 (−12)
1086	554	3.7	6.2	0.03–0.12[d]	6	26	15	4.95 ± 0.48 (−12)
1153	287	1.8	3.9	0.08–0.39[d]	5	26	7	5.31 ± 1.30 (−12)
1176	364	1.8	4.9	0.0–0.56[d]	3	27	7	5.22 ± 0.49 (−12)
1192	533	3.2	3.2	0.06–0.19[d]	3	22	7	5.12 ± 0.49 (−12)

[a] σ_T/T = 2%. [b] Used 10.8% HCl in Ar. [c] Used 1% HCl in Ar. [d] Used 0.103% HCl in Ar. [e] z = 28 cm corresponds to premixing of reactant and bath gases; the cooled inlet was not used. [f] Read as (2.72 ± 0.35) × 10^{-14}.

rate coefficient measurement were always less than 5 K. From Table I it may be seen that these rate coefficients are independent of variation in the following: total pressure, from 130 to 750 mbar, corresponding to total gas concentrations [M] from 1.2 × 10^{18} to 1.2 × 10^{19} cm^{-3}; average gas velocities from 4 to 45 cm s^{-1}; flash energies from 4 to 18 J; the length of the prereaction zone z from 3 to 28 cm.[16] As a final safeguard, three different cylinders of HCl from two different sources were used. The absence of any effect of these changes on the rate coefficients indicates that any errors arising from interference from reaction products, photofragments, or impurities in the gases are negligible.

The rate coefficient data for reaction 1 are plotted in Arrhenius form in Figure 1. They can be well-fitted by an empirical Arrhenius expression

$$k_1(T) = A \exp(-E\ \mathrm{K}/T) \tag{3}$$

resulting in

$$k_1(298\text{–}1192\ \mathrm{K}) = 2.84 \times 10^{-11} \exp(-2082\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \tag{4}$$

with variances and covariances; $\sigma^2_A = 5.02 \times 10^{-3} A^2$, $\sigma_{AE} = 2.42 \times 10^{-11} A$, and $\sigma^2_E = 1332$. These yield[17] 2σ precision levels of between ±6% and ±12%, depending on temperature. Allowing for possible systematic errors of ±20%, we estimate the accuracy of the rate coefficient measurements to vary from ±21% to ±23% at the 2σ statistical confidence limit. A fit to the three-parameter expression $k_1(T) = A'T^n \exp(-E'\ \mathrm{K}/T)$ leads to $k_1(T) = 5.1 \times 10^{-11}(T/\mathrm{K})^{0.85} \exp(-1600\ \mathrm{K}/T)$ cm^3 molecule^{-1} s^{-1}, with essentially the same uncertainty limits. For the present temperature range there therefore appear no reason to prefer the latter expression.

It is seen in Figure 2 that the present data agree very well with the recommendation of Baulch et al.[7] and the experiments of Spencer and Glass,[8] Ambidge et al.,[9] and Miller and Gordon,[10] as well as the older work by Steiner and Rideal[18] as recalculated by Benson et al.[19] The agreement with the latter measurements is noteworthy, as the static pyrolysis technique used is usually not considered to be the best suited for elementary reaction rate coefficient measurements.

The present results can be compared to those obtainable from calculations based on a semiempirical London–Eyring–Polanyi–Sato (LEPS) potential energy surface.[20–22] A linear transition state complex is assumed, since it gives the lowest barrier height.[23]

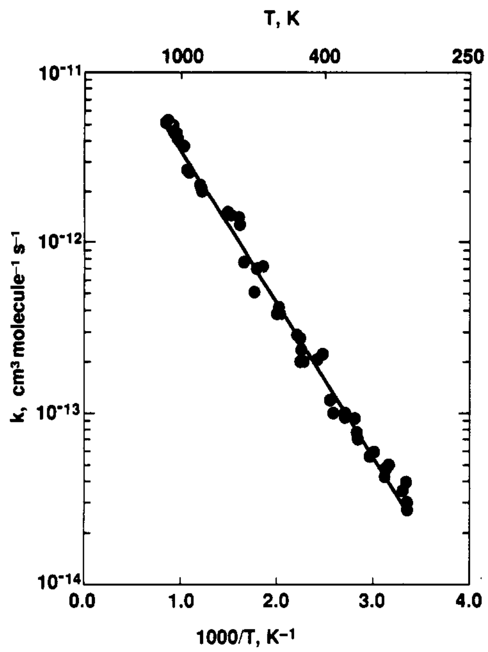

Figure 1. Summary of the present measurements for the H + HCl reaction: (●) present study; (—) best fit to present data, eq 4.

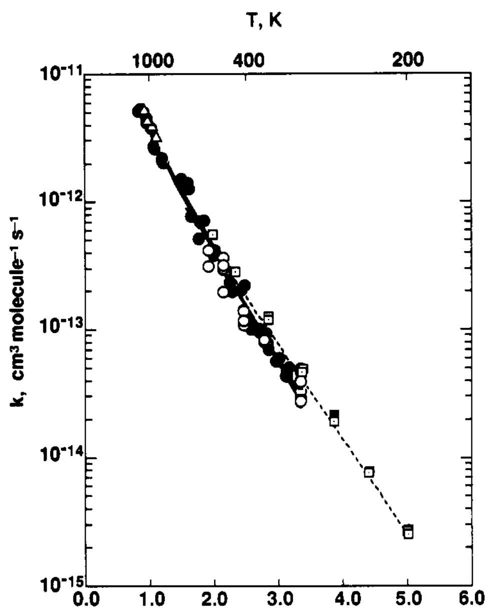

Figure 2. Comparison of rate coefficient measurements for the H + HCl reaction: (●) present study; (O) Ambidge et al. (298–521 K);[9] (⊡) Miller and Gordon (200–500 K);[10] (△) Steiner and Rideal (901–1071 K);[18] (...) Baulch et al. (200–650 K);[7] (—) best fit to present data (298–1192 K), eq 4.

The following equations are used to calculate the potentials:

$$Q_i = {}^1/_4 D_e\{(3 + K) \exp(-2\beta(R_i - R_e) - (2 + 6K) \times \exp(-2\beta(R_i - R_e)\} \quad (5)$$

$$J_i = {}^1/_4 D_e\{(1 + 3K) \exp(-2\beta(R_i - R_e) - (6 + 2K) \times \exp(-2\beta(R_i - R_e)\} \quad (6)$$

$$V_l = Q_1 + Q_2 + Q_3 + \{{}^1/_2[(J_1 - J_2)^2 + (J_2 - J_3)^2 + (J_3 - J_1)^2]\}^{1/2} \quad (7)$$

$$V_s = V_l/(1 + K) \quad (8)$$

Here, Q and J are Coulombic and exchange energies, V_l is the London potential, K is the Sato parameter, and V_s is the Sato potential. The subscript i takes the values 1, 2, and 3. R_1 is the H–H distance, R_2 is the H–Cl distance, and $R_3 = R_1 + R_2$. The Morse parameters[24] for H–H are equilibrium distance R_{e1} = 7.41 nm, classical dissociation energy D_{e1} = 458.39 kJ mol^{-1}, and molecular constant β = 19.44 nm^{-1}. For HCl the corresponding parameters are R_{e2} = 12.75 nm, D_{e2} = 445.66 kJ mol^{-1}, and β = 18.68 nm^{-1}. The Sato parameter K can be adjusted to yield approximately the experimental activation energy. This process results for a K of 0.185 in a classical E_c of 16.77 kJ mol^{-1}, which is corrected[22] to give E_0 = 16.03 kJ mol^{-1}. The symmetric and bending frequencies for the transition state are calculated to be 1312 and 728 cm^{-1}, respectively. Using these frequencies a theoretical A factor in eq 3 is obtained which is combined with E_0 to yield

$$k_1(T)_{calc} = 3.21 \times 10^{-10} T^{-0.5}[1 - \exp(-4159\ K/T)]/[1 - \exp(-1888\ K/T)][1 - \exp(-1047\ K/T)]^2 \times \exp(-1928\ K/T)\ \ cm^3\ molecule^{-1}\ s^{-1} \quad (9)$$

This expression is plotted in Figure 3 where it is compared with the experimental data and may be seen to give as good a fit as that obtained from the experiment-based expression (4).

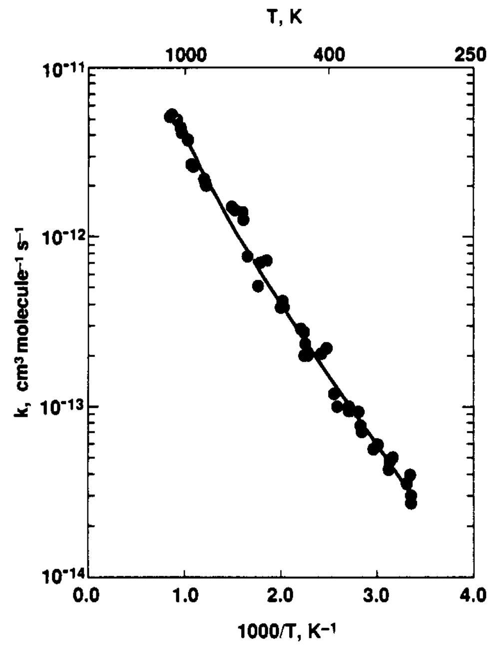

Figure 3. Comparison of the calculated rate coefficients with the experimental results: (●) experimental data; (—) $k_1(T)_{calc}$, eq 9.

Under the conditions of the present experiments, it is expected that changes in populations of molecules among different energy states will be small and negligible. Under these conditions the measured rate coefficients are the same as those at equilibrium and the relation $K = k_1/k_{-1}$ holds. From current thermochemical data,[6] an expression for the equilibrium constant for reaction 1 is derived as

$$K_1(T) = 0.57 \exp(485\ K/T) \quad (10)$$

Combining the present best fit expression (eq 4) with this $K_1(T)$ yields

$$k_{-1}(298\text{–}1192\ K) = 4.98 \times 10^{-11} \exp(-2567\ K/T)\ \ cm^3\ molecule^{-1}\ s^{-1} \quad (11)$$

for the reverse reaction. Baulch et al. recommended k_{-1}(200–650 K) = 2.41 × 10^{-11} exp(−2200 K/T) cm^3 molecule^{-1} s^{-1} and Miller and Gordon k_{-1}(200–500 K) = 3.65 × 10^{-11} exp(−2310 K/T) cm^3 molecule^{-1} s^{-1}. The differences with the present results range for the former from 37% at 298 K to 18% at 650 K and for the latter from 42% at 298 K to 19% at 500 K. As these slight differences increase with decreasing temperature, we do not recommend use of eq 11 outside the temperature range of our measured k_1 values.

In summary, direct measurements of k_1 have been obtained, and a recommendation for $k_1(T)$ is given which more than doubles the range of the previous one. A recommendation for the reverse reaction is also obtained.

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References and Notes

(1) Senkan, S. M.; Robinson, J. M.; Gupta, A. K. *Combust. Flame* **1983**, *49*, 305.

(2) Chang, W. D.; Karra, S. B.; Senkan, S. M. *Combust. Flame* **1987**, *69*, 113.

(3) Hastie, J. W. *High Temperature Vapors. Science and Technology*; Academic Press: New York, 1975; Section 5-V-(A-C).

(4) Lighty, J. S.; Giddings, E. G.; Lindgren, E. R.; Xiao-Xue, D.; Pershing, D.; Winter, R. M.; McClennen, W. H. *Combust. Sci. Technol.* **1990**, *74*, 31.

(5) Chang, W. D.; Senkan, S. M. *Environ. Sci. Technol.* **1989**, *23*, 442.

(6) Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1), 743.

(7) Baulch, D. L.; Duxbury, J.; Grant, S. J.; Montague, D. L. *J. Phys. Chem. Ref. Data* **1981**, *10* (Suppl. 1), 161.

(8) Spencer, J. E.; Glass, G. P. *J. Phys. Chem.* **1975**, *79*, 2329.

(9) Ambidge, P. F.; Bradley, J. N.; Whytock, D. A. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2143.

(10) Miller, J. C.; Gordon, R. J. *J. Chem. Phys.* **1981**, *75*, 5305.

(11) Mahmud, K.; Kim, J.-S.; Fontijn, A. *J. Phys. Chem.* **1990**, *94*, 2994.

(12) Marshall, P.; Ko, T.; Fontijn, A. *J. Phys. Chem.* **1989**, *93*, 1922.

(13) Ko, T.; Marshall, P.; Fontijn, A. *J. Phys. Chem.* **1990**, *94*, 1401.

(14) Ko, T.; Adusei, G. Y.; Fontijn, A. *J. Phys. Chem.* **1991**, *95*, 8745.

(15) Marshall, P. *Comput. Chem.* **1987**, *11*, 219.

(16) $z = 28$ cm corresponds to premixing of reactants and bath gas; the cooled inlet was not used in those experiments.

(17) Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 711.

(18) Steiner, H.; Rideal, E. K. *Proc. R. Soc. London* **1939**, *A173*, 503.

(19) Benson, S. W.; Cruickshank, F. R.; Shaw, R. *Int. J. Chem. Kinet.* **1969**, *1*, 29.

(20) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper Collins Publishers: New York, 1987; pp 68, 69.

(21) Smith, I. W. M. In *Modern Gas Kinetics Theory, Experiments and Application*; Pilling, M. J., Smith, I. W. M., Eds.; Blackwell Scientific Publications: London, 1978; pp 55–58.

(22) Johnston, H. S. *Gas Phase Reaction Rate Theory*; The Ronald Press: New York, 1966; pp 169–179, 333–339.

(23) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill Book Co.: New York, 1941; p 87.

(24) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; pp 250, 286.