Rate Constant for the Reaction of H with H₂O and OH with H₂ by the Flash Photolysis–Shock Tube Technique over the Temperature Range 1246–2297 K

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Rate constants for the reaction of atomic hydrogen with water, reaction 1, were measured by the flash photolysis–shock tube technique utilizing atomic resonance absorption to monitor the change in H atom concentrations with time. Experiments were carried out over the temperature range 1246–2297 K, and the results can be expressed by the Arrhenius equation $k_1(T)$ = $(4.58 \pm 0.61) \times 10^{-10} \exp[(-22966 \pm 482 \text{ cal mol}^{-1})/RT]$ cm³ molecule⁻¹ s⁻¹. The errors are given at the one standard deviation level. By use of the known values of the equilibrium constant, $K_1(T)$, for reaction 1, each experimental $k_1(T)$ measurement was converted to its corresponding value of the rate constant of the reverse reaction, $k_{-1}(T)$. Over the temperature range 1246–2297 K, the $k_{-1}(T)$ results can be expressed by the Arrhenius equation $k_{-1}(T) = (1.05 \pm 0.17) \times 10^{-10} \exp[(-8037 \pm 482 \text{ cal mol}^{-1})/RT]$ cm³ molecule⁻¹ s⁻¹. A composite data base for $k_{-1}(T)$ was constructed for the temperature range 250–2581 K from the present results and selected previously published data. The resulting Arrhenius plot is nonlinear and may be fitted by the three-parameter expression $k_{-1}(T) = 3.59 \times 10^{-16} T^{1.51} \exp(-1726 \text{ K}/T)$ cm³ molecule⁻¹ s⁻¹. These results are compared to earlier experimental measurements and to recently reported theoretical calculations.

Introduction

The reaction of atomic hydrogen with water

$$H + H_2O \rightarrow OH + H_2 \qquad (1)$$
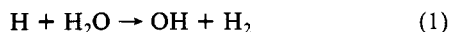
plays an inhibiting role in combustion systems, and it contributes significantly to establishing the well-known pseudoequilibrium in the postcombustion regime.[1,2] The reverse step

$$OH + H_2 \rightarrow H_2O + H \qquad (-1)$$
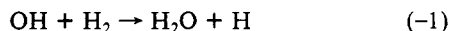
is a critical chain-propagating reaction in H₂ combustion. The importance of these reactions is evident in the large number of investigations that are reported in several critical reviews.[3-11] Baulch et al.,[3] in a review of data published up to 1972, list 39 citations that include 13 earlier reviews for reaction 1 and 128 for reaction –1. Since 1972 there have been at least nine additional reviews[2,4-11] of the kinetic data for these reactions.

In the case of reaction 1, no direct measurements of $k_1(T)$ have been made and only three experimental determinations of $k_1(T)$ by indirect techniques have been reported.[12-14] The most recent study of Madronich and Felder[14] gives

$$k_1(T) = (5.2 \pm 4.5) \times 10^{-10} \exp[-(22056 \pm 2206) \text{ cal mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This expression was derived from the analysis of measured [OH] vs time profiles at three temperatures, 1158, 1274, and 1387 K, following the flash photolysis of H₂O in their high-temperature photochemistry (HTP) apparatus. In the absence of reliable experimental kinetic data,[3] $k_1(T)$ values have been calculated from the well-established equilibrium constant for reaction 1, $K_1(T)$, and the experimental values of $k_{-1}(T)$ from the relationship $k_1(T) = K_1(T) k_{-1}(T)$.

There have been numerous direct experimental measurements of the rate constant for reaction –1 at ambient temperature[15-20] and over the limited low-temperature range of 246–500 K.[21-25] In addition, two studies[26,27] over the extended temperature range of 250–1050 K have been reported. In these investigations a variety of techniques were used: flash photolysis–resonance fluorescence (FP–RF), flash photolysis–ultraviolet absorption, and discharge flow–ESR absorption. A shock tube study over the temperature range 1692–2581 K has been recently reported.[28] The nonlinearity of the Arrhenius plot for reaction (–1), when taken over a large temperature range, is now firmly established, and both Warnatz[11] and Cohen and Westberg[9] have reported

recommended expressions for $k_{-1}(T)$.

In this paper, we report the first direct measurements of the rate constant for reaction 1, $k_1(T)$. They were determined over the temperature range 1246–2297 K by using the Brookhaven flash photolysis–shock tube (FP–ST) apparatus. Also reported are the corresponding values for the reverse reaction, $k_{-1}(T)$, which were obtained from the experimental values of $k_1(T)$ and the values of $K_1(T)$. These new results are compared with previous experimental values and with the results from recent theoretical calculations.[29,30]

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Experimental Section

The FP–ST method[31] and the apparatus and techniques used in this laboratory[32] have been described previously in detail. Therefore, only those techniques that are specific to the present study are given here.

In this study, the reactant molecule, H_2O, also serves as the photolytic source. Hydrogen atoms are produced in the reflected shock regime by the photodissociation of H_2O[33] following absorption of the ultraviolet light emission from a N_2-filled flash lamp. The light output from the lamp passed through a Suprasil lens (focal length 10 cm), and hence the lower wavelength cutoff was about 165 nm. In each experiment, flash energies were adjusted so that the initial concentration of H atoms, $[H]_0$, was not greater than $\sim 2 \times 10^{12}$ atoms cm^{-3}. At this low $[H]_0$, secondary reactions involving H atoms and OH radicals were negligibly slow in the time scale of the [H] decay ($t_{1/2} \sim 0.06$–0.7 ms). The flash energy ranged from 132 to 613 J. With larger concentrations of H_2O, the flash energy required to produce the required signal was lower. The high-temperature limit of the experiments was determined by the need to use a concentration of H_2O that was small enough to give a measurable decay rate and yet large enough to produce a sufficiently large $[H]_0$. The highest temperature achieved was 2297 K with a water concentration of 3×10^{15} molecules cm^{-3}. The lower temperature limit, 1246 K, was dictated by the maximum mole fraction of H_2O (X_{H_2O} = 10^{-2}) that could be tolerated without significantly perturbing the thermodynamic state of the initally shocked gas in the reflected regime from that of pure Ar. This was determined by correcting for the mean heat capacity in the usual way.[34]

Corrections for nonidealities due to boundary layer growth behind the incident shock front were made as described previously.[32b] These correction procedures have been used in three earlier FP–ST studies from this laboratory: $H + NH_3 \rightarrow NH_2 + H_2$;[35] $O + CH_4 \rightarrow OH + CH_3$;[36] and $O + H_2 \rightarrow OH + O$.[37] In each case the measured rate constants agreed within experimental error with those determined by established methods (e.g., flash photolysis–resonance fluorescence, discharge flow–resonance fluorescence, or resonance absorption techniques), and therefore, the correction procedure is now well-established.

In the FP–ST method, atoms are produced by flash photolysis in a time period that is short compared to their decay by chemical reaction. Since there are no secondary reactions removing or re-forming the H atoms at the low initial concentrations used, the rate of decay of the [H] is controlled only by reaction 1. It has been shown previously that Beer's law holds,[32c] (i.e., $(ABS)_t = \sigma l [H]_t$). Hence

$$\ln (ABS)_t = -k_{1st}t + \ln (ABS)_0 \qquad (2)$$

where

$$k_{1st} = k_1 [H_2O] \qquad (3)$$

Loss of H atoms by diffusion has previously been shown to be negligible in this apparatus under the present experimental conditions.[32a]
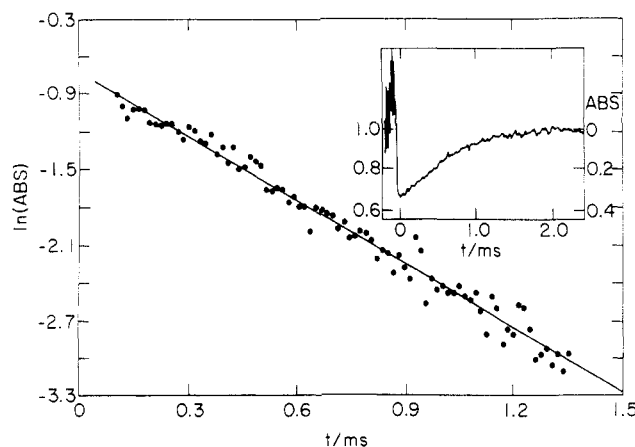
Figure 1. Typical signal observed after flash photolysis in the reflected shock wave regime. $P_1 = 15.71$ Torr, $[H_2O]_0 = 7.315 \times 10^{15}$ cm^{-3}, and $T = 1496$ K. The graph shows the first-order plot from the raw data in the inset. $k_{1st} = 1654 \pm 34$ s^{-1} giving $k_1 = 2.26 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

It was recognized early in this study that adsorption/desorption of water in the shock tube and in the gas handling vacuum system might complicate the measurement of the rate constants. With regard to mixture stability in the shock tube it is estimated, using measured outgassing rates,[38] that a negligible fraction of the H_2O is desorbed from the surface of the present, 6-m-long, stainless steel shock tube during the ~ 15-min pump-down period. Usually, premixed reagents are in contact with the stainless steel wall for only approximately 1 min between the loading and the firing of the shock. When mixtures were allowed to stand in the shock tube for periods of up to 5 min, there was no observable effect on the measured rate constant. Also, it was observed that neither the storage time of the gas mixture (up to 2 weeks) nor the pressure in the storage bulb had any effect on the measurements. Thus, it is concluded that the $[H_2O]$ in the H_2O/Ar mixtures, used in the present investigation, was unperturbed by selective adsorption. This conclusion was verified by the consistent results obtained by using three different total pressures and gas mixtures in which the $[H_2O]$ was varied by about a factor of 7 (Table I). The present conclusions are in agreement with those of Zabarnick et al.,[39] who, in their study of the reactivity of CH with H_2O, also found that mixes containing water were stable.

Argon (Scientific Grade, 99.9999%) was obtained from MG. Industries. Gas mixtures were made with singly distilled water that had been first passed through a Millipore Ultra Pure filtration unit and then bulb-to-bulb distilled in an all-glass vacuum system. The middle fraction was used. Helium, which was used both in the resonance lamp and as the driver gas, was obtained from Linde Division, Union Carbide. It was Ultra-High Purity Grade (99.999%).

Results

Figure 1 shows the kinetic data obtained from a typical FP–ST experiment. The inset is the reduced trace of the change in Lyman-α transmission with time following flash photolysis in the reflected shock regime. The corresponding first-order plot of ln $(ABS)_t$ vs time is also shown, and from the negative slope, $-k_{1st}$, the bimolecular rate constant, k_1, is obtained directly from eq 3. The H_2O concentration in the reflected shock regime was obtained from the measurement of the incident Mach number and the initial values of pressure, temperature and mole fraction of water.[32]

Rate constants were measured over the temperature range 1246–2297 K, and the experimental data are tabulated in Table I. Errors in the Mach number measurement ranged from $\sim 0.5\%$

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TABLE I: Data for the Forward and Reverse Reaction Rate Constants and the Equilibrium Constant of H + H$_2$O $\rightleftharpoons$ H$_2$ + OH

P_1, Torr	$M_s{}^a$	$k_{obsd}{}^b$ s^{-1}	$\rho_5{}^c$	T_5, K	$k_1{}^d$	$K_1{}^e$	$k_{-1}{}^f$	P_1, Torr	$M_s{}^a$	$k_{obsd}{}^b$ s^{-1}	$\rho_5{}^c$	T_5, K	$k_1{}^d$	$K_1{}^e$	$k_{-1}{}^f$
							X_{H_2O} = 0.0100								
10.93	2.358	1618	1.998	1403	0.81	0.0207	0.39	10.39	2.431	3844	1.965	1468	1.96	0.0262	0.75
10.44	2.333	1247	1.877	1387	0.66	0.0194	0.34	10.53	2.514	6854	2.042	1560	3.36	0.0355	0.95
10.46	2.420	3375	1.944	1476	1.74	0.0270	0.65	10.50	2.513	4882	2.028	1564	2.41	0.0359	0.67
10.65	2.383	2177	1.960	1434	1.11	0.0232	0.48	10.31	2.551	7114	2.022	1599	3.52	0.0399	0.88
10.47	2.431	3710	1.960	1483	1.89	0.0276	0.68	10.83	2.321	1146	1.951	1366	0.59	0.0179	0.33
10.52	2.465	3586	2.030	1493	1.77	0.0286	0.62								
							X_{H_2O} = 0.0050								
10.32	2.545	5139	2.000	1606	5.13	0.0407	1.26	10.60	2.621	4624	2.088	1700	4.43	0.0527	0.84
10.48	2.438	2602	1.961	1493	2.65	0.0286	0.93	10.55	2.404	1888	1.937	1467	1.95	0.0261	0.75
10.40	2.549	4344	2.012	1617	4.32	0.0420	1.03	10.40	2.294	768	1.831	1356	0.84	0.0172	0.49
10.90	2.496	2038	2.074	1559	1.97	0.0354	0.56	10.54	2.521	4553	2.014	1591	4.52	0.0390	1.16
							X_{H_2O} = 0.00250								
10.73	2.620	2138	2.113	1699	4.05	0.0526	0.77	10.37	2.889	9045	2.174	2019	16.6	0.1060	1.57
10.86	2.667	2823	2.166	1751	5.21	0.0600	0.87	10.84	2.720	5072	2.185	1818	9.29	0.0702	1.32
10.73	2.714	3455	2.167	1806	6.38	0.0683	0.93	10.53	2.779	6499	2.161	1881	12.0	0.0807	1.49
10.49	2.776	5357	2.144	1884	10.0	0.0812	1.23								
							X_{H_2O} = 0.0025								
15.37	2.680	5241	3.066	1743	6.84	0.0588	1.16	15.43	2.706	5968	3.078	1784	7.76	0.0649	1.20
15.83	2.663	4849	3.143	1724	6.17	0.0561	1.10	15.55	2.583	2296	3.009	1641	3.05	0.0450	0.68
15.57	2.751	10030	3.162	1823	12.7	0.0711	1.79	15.66	2.657	5183	3.094	1722	6.70	0.0558	1.20
15.38	2.636	4171	3.012	1706	5.54	0.0536	1.03								
							X_{H_2O} = 0.00125								
15.54	2.583	1145	2.982	1655	3.07	0.0468	0.66	15.56	2.819	2747	3.205	1905	6.86	0.0848	0.81
15.65	2.665	2366	3.083	1740	6.14	0.0584	1.05	15.70	2.903	5826	3.281	2015	14.2	0.1052	1.35
15.47	2.693	2575	3.070	1772	6.71	0.0631	1.06	15.49	2.710	2346	3.087	1791	6.08	0.0660	0.92
15.38	2.717	2959	3.060	1805	7.73	0.0682	1.13	15.33	2.866	4155	3.190	1960	10.4	0.0948	1.10
15.46	2.724	2849	3.072	1820	7.42	0.0706	1.05	15.34	2.840	3314	3.174	1930	8.35	0.0893	0.94
15.42	3.086	8036	3.339	2290	19.3	0.1647	1.17	15.75	2.722	2360	3.159	1798	5.98	0.0671	0.89
15.70	2.759	3673	3.136	1866	9.37	0.0781	1.20	15.96	2.671	1809	3.160	1741	4.58	0.0585	0.78
15.47	2.751	2997	3.094	1851	7.75	0.0756	1.02	15.54	2.933	6569	3.261	2068	16.1	0.1158	1.39
15.52	2.812	5216	3.138	1928	13.3	0.0889	1.50	15.75	2.828	4001	3.207	1941	9.98	0.0913	1.09
							X_{H_2O} = 0.00100								
15.51	3.102	11602	3.391	2297	34.2	0.1663	2.06	15.70	2.862	3659	3.241	1969	11.3	0.0964	1.17
15.52	2.806	3806	3.164	1903	12.0	0.0845	1.42	15.92	3.094	11823	3.486	2278	33.9	0.1618	2.09
15.34	2.844	3849	3.154	1948	12.2	0.0926	1.32	15.52	2.817	4275	3.172	1916	13.5	0.0868	1.56
15.48	2.688	2353	3.067	1766	7.67	0.0622	1.23	15.91	2.830	4464	3.261	1931	13.7	0.0895	1.53
							X_{H_2O} = 0.0100								
15.50	2.272	1656	2.720	1306	0.61	0.0139	0.44	15.54	2.336	3588	2.772	1383	1.29	0.0191	0.67
15.44	2.249	1636	2.683	1284	0.61	0.0126	0.48	15.45	2.381	3972	2.804	1428	1.42	0.0227	0.62
15.68	2.208	1181	2.666	1249	0.44	0.0107	0.41	15.63	2.444	4217	2.901	1491	1.45	0.0284	0.51
15.72	2.211	1345	2.676	1252	0.50	0.0108	0.46	15.57	2.373	4322	2.817	1420	1.53	0.0221	0.69
15.70	2.295	2341	2.763	1337	0.85	0.0159	0.54								
							X_{H_2O} = 0.0050								
15.85	2.352	1555	2.848	1396	1.09	0.0201	0.54	15.86	2.496	5742	2.998	1544	3.83	0.0337	1.14
15.49	2.394	1311	2.779	1392	0.94	0.0198	0.47	15.89	2.442	3467	2.939	1492	2.36	0.0285	0.83
15.53	2.372	1803	2.783	1430	1.30	0.0229	0.57	15.34	2.422	2644	2.818	1471	1.88	0.0265	0.71
15.53	2.342	1455	2.751	1399	1.06	0.0204	0.52	15.32	2.553	5723	2.938	1610	3.90	0.0412	0.95
15.52	2.472	4083	2.882	1534	2.83	0.0327	0.87	15.24	2.549	6694	2.919	1605	4.59	0.0406	1.13
15.24	2.433	2007	2.830	1474	1.42	0.0268	0.53	15.48	2.377	1992	2.797	1425	1.42	0.0225	0.63
15.92	2.448	3408	3.011	1531	2.26	0.0324	0.70								
							X_{H_2O} = 0.0025								
15.94	2.425	1218	2.943	1469	1.66	0.0263	0.63	15.55	2.569	2854	3.007	1621	3.80	0.0425	0.89
15.71	2.451	1654	2.926	1496	2.26	0.0289	0.78	15.77	2.622	5772	3.096	1678	7.46	0.0498	1.50
15.62	2.581	3365	3.031	1634	4.44	0.0441	1.01	15.67	2.603	3463	3.060	1658	4.53	0.0471	0.96
15.50	2.502	2988	2.936	1549	4.07	0.0343	1.19								
							X_{H_2O} = 0.0050								
30.56	2.308	1722	5.143	1325	0.67	0.0151	0.44	30.44	2.420	2935	5.447	1429	1.08	0.0228	0.47
30.35	2.327	2005	5.171	1340	0.78	0.0161	0.48	30.43	2.321	2794	5.170	1333	1.08	0.0156	0.69
30.73	2.350	2982	5.276	1369	1.13	0.0181	0.62	30.49	2.238	1261	4.994	1246	0.51	0.0105	0.48
30.26	2.395	3703	5.303	1417	1.40	0.0218	0.64								

^{a}The error in measuring the Mach number is typically about ±0.7%, at the one standard deviation level. ^{b}The error in measuring the observed first-order H atom decays is ±1–3%, at the one standard deviation level. ^{c}Units of density are 10^{18} molecules cm^{-3}. ^{d}Units of the experimental forward rate constant, k_1, are 10^{-13} cm^3 molecule^{-1} s^{-1}. ^{e}Equilibrium constant calculated from data in the JANAF (1982) tables at temperature T_5 (see text). ^{f}Units of the calculated reverse rate constant, k_{-1}, are 10^{-11} cm^3 molecule^{-1} s^{-1}.

to 1%, leading to a corresponding error of ±1–2% in the temperature of the reflected regime. Within the experimental error,

no change in the measured values of $k_1(T)$ was observed when the initial pressure was varied by a factor of 3 and the [H$_2$O] by
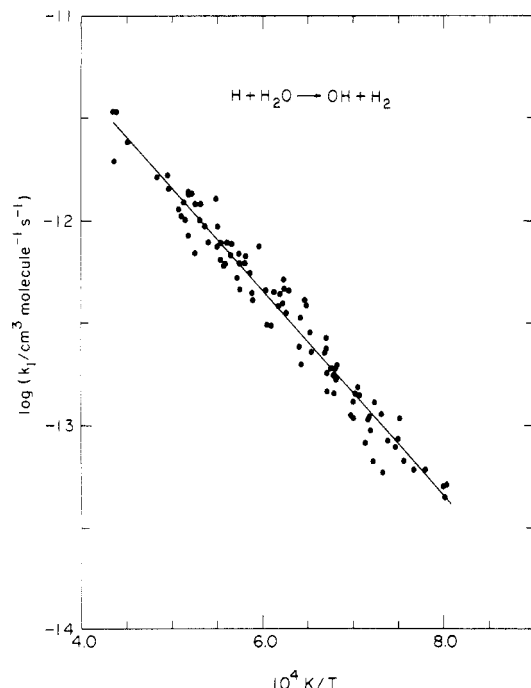
Figure 2. Arrhenius plot of the data from Table I. The solid line is a two-parameter least-squares fit to the data. $k_1(T) = (4.58 \pm 0.61) \times 10^{-10} \exp[(-22966 \pm 482 \text{ cal mol}^{-1}/RT)]$ cm^3 molecule^{-1} s^{-1}.

a factor of 7 (see Table I), clearly confirming the pseudo-first-order kinetic behavior of the system under the present experimental conditions.

Also shown in Table I are the equilibrium constant values which were determined at each experimental temperature from the data listed in the JANAF tables,[40] and the rate constants for the reverse reaction, $k_{-1}(T)$, which were calculated from the appropriate values of $K_1(T)$ and $k_1(T)$ from the relationship $k_{-1}(T) = k_1(T)/K_1(T)$. $K_1(T)$ was calculated at each experimental temperature from the equation

$$K_1(T) = (4.38 \pm 0.04) \exp[(-14929 \pm 30 \text{ cal mol}^{-1})/RT] \tag{4}$$

which was obtained from a linear least-squares fit to the tabulated JANAF data taken over the experimental temperature range 1246–2297 K. Equation 4 reproduces the JANAF values to better than 1%.

The rate constant data for reaction 1 are plotted according to the Arrhenius equation in Figure 2. The linear least-squared fit to the data results in the expression

$$k_1(T) =$$
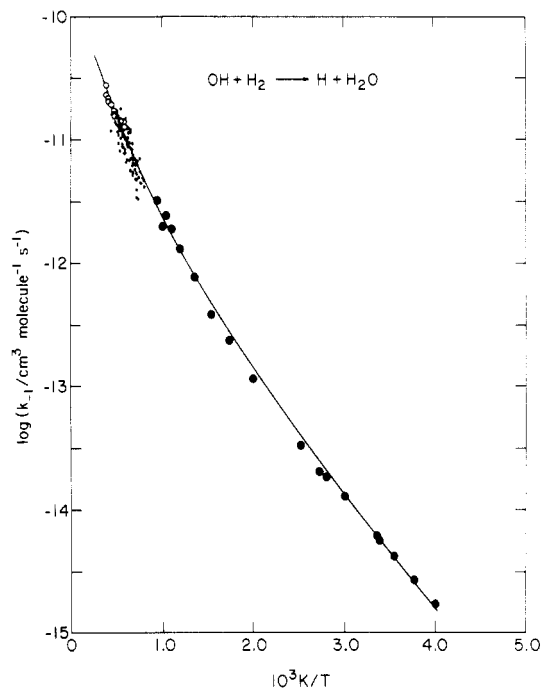$$(4.58 \pm 0.61) \times 10^{-10} \exp[(-22966 \pm 482 \text{ cal mol}^{-1})/RT] \tag{5}$$

The units of $k_1(T)$ are cm^3 molecule^{-1} s^{-1}, and the error is given at the one standard deviation level. The temperature range is 1246–2297 K. A similar treatment of the $k_{-1}(T)$ data resulted in the following equation

$$k_{-1}(T) =$$
$$(1.05 \pm 0.17) \times 10^{-10} \exp[(-8037 \pm 482 \text{ cal mol}^{-1})/RT] \tag{6}$$

Discussion

The present results, as expressed by eq 5, can be compared to those of previous studies. Of the three reported determinations of $k_1(T)$, the one that is most direct is that of Madronich and Felder,[14] who give

$$k_1(T) =$$
$$(5.2 \pm 4.5) \times 10^{-10} \exp[(-22056 \pm 2206 \text{ cal mol}^{-1})/RT] \tag{7}$$

(40) Chase, M. W., Jr.; Curnutt, J. L.; Downey, J. R., Jr.; McDonald, R. A.; Syverud, A. N.; Valenzuela, E. A. *J. Phys. Chem. Ref. Data* **1982**, *11*, 695.

Figure 3. Arrhenius plot of the data from Table I (small solid points) that have been transformed to $k_{-1}(T)$ values by the relationship $k_{-1}(T) = k_1(T)/K_1(T)$. The open circles are data from Frank and Just.[28] The large circles represent the data of Tully, Ravishankara, and co-workers.[26,27] The solid line is a three-parameter least-squares fit to the composite data set comprising the present data, that of Frank and Just,[28] and that of Tully, Ravishankara, and co-workers[26,27] (eq 10 of the text).

for the temperature range 1158–1387 K. For this temperature range, eq 7 results in $k_1(T)$ values that are uniformly higher by about 60% than those calculated from eq 5. This discrepancy is larger than the combined errors of the two data sets. From kinetic analysis of data from flame studies, Fenimore and Jones[12] and Dixon–Lewis et al.[13] give respective values for k_1 of 8×10^{-14} cm^3 molecule^{-1} s^{-1} at 1285 K and 7.1×10^{-15} cm^3 molecule^{-1} s^{-1} at 1072 K. These estimates are high by 30% and low by 25%, respectively, compared to the present results.

In contrast to the few available measurements for $k_1(T)$, the kinetics of rection -1 have been extensively investigated. Since the Baulch et al. review[3] was published in 1972, there have been at least nine direct studies[18-20,22-27] of this rate constant. These, together with the earlier direct studies,[15-17,21] have been reviewed and evaluated by Warnatz[11] and by Cohen and Westberg.[6,9] Two of the most recent investigations are those of Tully and Ravishankara[26] and Ravishankara et al.[27] over the temperature range 250–1050 K. The second evaluation of Cohen and Westberg[9] is strongly influenced by these studies, and it should also be noted that the results from the recent shock tube study of Frank and Just[28] were not available to these evaluators. The calculated values of $k_{-1}(T)$, on which eq 6 is based, are plotted in Arrhenius form in Figure 3. In Figure 3, the shock tube results of Frank and Just,[28] measured over the temperature range of 1692–2581 K, are compared with those obtained from the present FP–ST investigation. As seen in this Figure, the data sets agree with one another within the combined errors in the region of temperature overlap, even though the respective constants in the Arrhenius expressions for the data differ. Frank and Just[28] give

$$k_{-1}(T) =$$
$$(7.87 \pm 1.08) \times 10^{-11} \exp[(-6094 \pm 526 \text{ cal mol}^{-1})/RT] \tag{8}$$

This expression is to be compared to eq 6. This observation further illustrates that, where there is curvature in the Arrhenius plot, it is unwise to extrapolate the simple Arrhenius expressions beyond the experimental temperature limits for which they are valid. For the low-temperature input to the data base, the FP–RF results of Tully and Ravishankara[26] and of Ravishankara et al.,[27] obtained over the temperature range 250–1050 K, were chosen. Their

TABLE II: Comparison of k_{-1} (298 K) ($\times 10^{15}$) Calculated from the Three-Parameter Fit (Eq 10) with the Experimental Results Obtained by Different Techniques at ~298 K

eq 10	exptl	ref
5.97	7.1 ± 1.7	Kaufman and delGreco[15] (1962)
	6.5 ± 0.35	Dixon-Lewis et al.[16] (1966)
	7.9	Greiner[21] (1969)
	7.11 ± 1.06	Stuhl and Niki[18] (1972)
	7.66 ± 0.76	Westenberg and deHaas[22] (1973)
	7.11 ± 1.00	Smith and Zellner[23] (1974)
	6.97 ± 0.70	Atkinson et al.[25] (1975)
	5.97 ± 0.27	Overend et al.[20] (1975)
	6.08 ± 0.37	Ravishankara et al.[27] (1981)

eq 10	review	ref
5.97	6.57 ± 1.99	Wilson, Jr.[4] (1972)
	6.51 ± 1.33	Baulch[3] (1972)
	5.8	Zellner[41] (1979)
	6.3 ± 0.7	Cohen and Westberg[9] (1983)
	5.8	Warnatz[11] (1984)

measurements, which are in good agreement with most earlier direct studies,[9] are expressed by the three-parameter equation

$$k_{-1}(T) = 4.12 \times 10^{-19} T^{2.44} \exp(-1281 \text{ K}/T) \qquad (9)$$

The experimenal data points on which this equation is based, those of Frank and Just,[28] and the results from the present FP–ST study are all shown in Figure 3. For extrapolated temperatures higher than they measured, the large exponent on T, 2.44, reported by Ravishankara et al.[27] results in values of $k_{-1}(T)$ that are much larger than the values from this study and from those of Frank and Just.[28] A composite data base was prepared from the results of Ravishankara et al.,[26,27] the data of Frank and Just,[28] and the results from the present FP–ST study. A three-parameter least-squares fit was then made to this data base for the temperature range 250–2581 K, with equal weight being given to each experimental point. The result is

$$k_{-1}(T) = 3.59 \times 10^{-16} T^{1.51} \exp[-1726 \text{ K}/T] \qquad (10)$$

This equation is shown as the solid line in Figure 3. In Table II the rate constant, k_{-1}(298 K), calculated from eq 10, is compared to the experimental values which have been measured by several authors using a variety of experimental techniques. The agreement is excellent. As for the temperature dependence of $k_{-1}(T)$, it is noted that eq 10 agrees within ±10% with the first evaluation of Cohen and Westberg[6] and also with that of Zellner.[41] There is poorer agreement between eq 10 and the second evaluation of Cohen and Westberg[9] since it appears that the high-temperature results of Tully, Ravishankara, and co-workers[26,27] are weighted more heavily in this later review.

Reactions 1 and −1 have been the subject of several theoretical studies. An ab initio theoretical investigation of the potential energy surface for OH and H$_2$ was carried out by Walch and Dunning,[29] and this surface was used by Schatz and Walch[42] to calculate thermal rate constants for reaction −1 using activated complex theory. Schatz and Elgersma[43] parametrized the ab initio
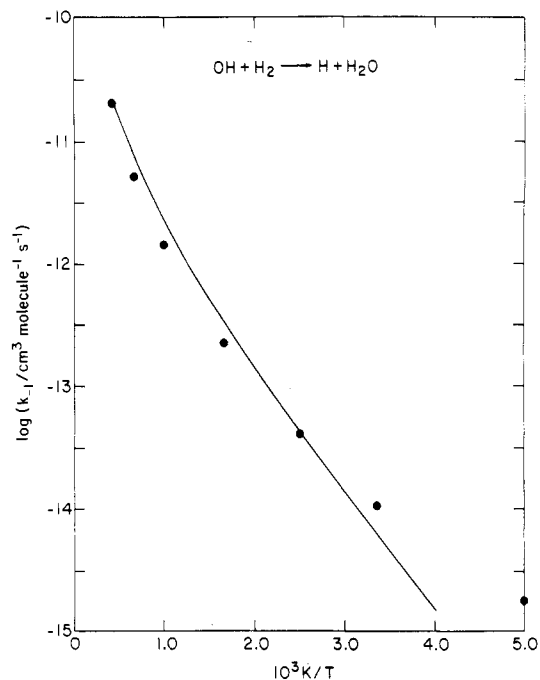
Figure 4. Comparison of theory to experiment. The experimental results for $k_{-1}(T)$ are expressed as the solid line which is the same as that given in the caption to Figure 3 (eq 10 in the text). The theory is shown as the solid points and is the CVT/SCSAG theoretical results of Isaacson and Truhlar.[30]

potential energy results of Walch and Dunning,[29] and this fit was subsequently used by Isaacson and Truhlar[30] in their "best" variational transition-state calculation, CVT/SCSAG. These theoretical results are shown in Figure 4 along with the present experimental result, eq 10. The theoretical results are in reasonably good agreement with eq 10, but more curvature is apparent in the theoretical values, especially at low temperature. This curvature has been attributed largely to tunneling.[30] However, it has been suggested[44,45] that the Schatz and Elgersma[43] fit may not adequately represent certain details in the ab initio surface.[29] Furthermore, the dynamics method employed by Truhlar[45] is known to slightly underestimate tunneling for a given surface; and thus the significant curvature in the theoretical result would indicate that the Walch–Dunning–Schatz–Elgersma surface may have too thin a barrier.[45]

(41) Zellner, R. *J. Phys. Chem.* **1979**, *83*, 18.
(42) Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1980**, *72*, 776.

(43) Schatz, G. C.; Elgersma, H. *Chem. Phys. Lett.* **1980**, *73*, 21.
(44) Dunning, T. H., Jr., private communication.
(45) Truhlar, D. G., private communication.