RATE CONSTANT FOR THE REACTION OF O(³P) WITH H₂ BY THE FLASH PHOTOLYSIS—SHOCK TUBE AND FLASH PHOTOLYSIS—RESONANCE FLUORESCENCE TECHNIQUES; 504K ≤ T ≤ 2495K

J. W. SUTHERLAND, J. V. MICHAEL, A. N. PIRRAGLIA, F. L. NESBITT AND R. B. KLEMM

Brookhaven National Laboratory
Department of Applied Science
Upton, New York 11973

The rate constant for the reaction,

$$O(^3P) + H_2 \rightarrow OH + H, \tag{1}$$

was measured over the temperature range of 504K to 2495 K by two independent experimental methods. The flash photolysis-shock tube (FP-ST) technique, combined with atomic resonance absorption spectroscopy (ARAS), was used over the temperature range 880K to 2495K. The results from the FP-ST work, expressed in simple Arrhenius form, are:

$$k_1(T) = (3.1 \pm 0.2) \times 10^{-10} \exp(-13620 \pm 170/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the units of R in this and succeeding expressions are cal mole^{-1}K^{-1}.

The flash photolysis-resonance fluorescence (FP-RF) technique was utilized to measure rate constants from 504K to 923K. Results from the FP-RF experiments, also expressed in simple Arrhenius form, are:

$$k_1(T) = (7.2 \pm 0.4) \times 10^{-11} \exp(-10430 \pm 70/RT) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

These kinetic results for the reaction of O(³P) with H₂ exhibit non-Arrhenius behavior. This conclusion is confirmed by the recent kinetic data of Presser and Gordon (297K ≤ T ≤ 471K). The combined results from these three data sets are expressed by the three parameter fit:

$$k_1(T) = 8.4 \times 10^{-20} \ T^{2.67} \exp(-6290/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The estimated error in this expression is about ±30% over the entire temperature range, 297K to 2495K. Rate constants for reaction (1) from recent *ab initio* calculations are in excellent agreement with these experimental results.

Introduction

The rate constant for the reaction,

$$O(^3P) + H_2 \rightarrow OH + H, \tag{1}$$

has been the subject of numerous studies.[1-21] Baulch, et al.[22] have reviewed earlier studies up to 1972 and two more up-to-date reviews [23,24] were published in 1983. The recommended rate expressions were given in the form, $k = AT^m \exp(-E/RT)$. In their study, Cohen and Westberg[23] considered a large data base [1-21] that drew mainly on the more direct flow tube studies which were limited to temperatures below 1000K. Hence their recommended expression,

$$k_1(T) = 1.8 \times 10^{-20} T^{2.8} \exp(-5920 \text{ cal mole}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{2}$$

although adequately reproducing the existing low temperature data, was considered to be accurate only to plus or minus a factor of two at temperatures greater than about 1600K.[23] In the other review, Warnatz[24] considered fewer studies,[5,7,8,11,22] and it appears that his recommendation is weighted toward the high temperature shock tube data of Schott, et al.[11] Warnatz's three parameter expression,

$$k_1(T) = 2.49 \times 10^{-17} \ T^{2.0} \exp(-7550 \text{ cal mole}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \tag{3}$$

adequately reproduces the existing high temperature data but agrees less well with the experimental values obtained at lower temperatures. This is evident from a comparison of Eqs. (2) and (3). Over most of the temperature range, the two recommendations disagree by about a factor of two, and the Cohen and Westberg[23] results are always lower.

More recently, since the publication of the later reviews,[23,24] there has been an important additional study at low temperatures, $297K \le T \le 471K$, by Presser and Gordon.[25] The results from this direct flash photolysis-resonance fluorescence (FP-RF) study were higher at all temperatures than those predicted from the recommendation of Cohen and Westberg,[23] Eq. (2). At 297K the recommended value was 0.63 times the experimental value, and at 471K, the value calculated from Eq.(2) was 0.85 times the experimental value. It should be noted further that, even though these reviewers considered the shock tube results of Schott, et al.,[11] Pamidimukkala and Skinner,[9] and Frank and Just,[10] their recommended expression (Eq. (2)) does not reproduce these experimental results accurately.

Because of this lack of agreement in the value of $k_1(T)$, and because reaction (1) is an essential propagation reaction in the combustion of hydrogen, it was important to re-measure its rate constant over as wide a temperature range as possible using two independent experimental techniques. The first technique, flash photolysis-shock tube (FP-ST), combines flash photolysis-resonance absorption with reflected shock wave heating under conditions where secondary reaction complications are unimportant.[26-29] Rate constants were measured over the temperature range, $880 \le T \le 2495K$, with this method. The second technique was that of flash photolysis-resonance fluorescence (FP-RF) [30-32] which was used to measure $k_1(T)$ over the temperature range, $504 \le T \le 923K$. It should be noted that the rate data from these two direct methods overlap in temperature and that the flash photolysis-shock tube technique provides data in an important temperature range that was not previously accessible, i.e. $1000K \le T \le 1400K$.

The present results from this study will be compared to those from earlier experimental work and also to recent *ab initio* calculations[33] of the rate constant for reaction (1).

Experimental

Two experimental techniques were used in this study: A) a Flash Photolysis—Shock Tube apparatus where O-atom analysis is accomplished by atomic resonance absorption spectroscopy[26,27] (ARAS); and B) a Flash Photolysis—Resonance Fluorescence apparatus.

Experiment A

This apparatus has been fully described elsewhere.[26,27] The procedures for the measurement of the rate constants for the reactions of H-atoms[26,28] and O-atoms[29] have already been discussed extensively; thus only a brief description is given here.

Oxygen atoms were produced by the flash photolysis of NO through a sapphire window ($\lambda \ge 145$nm). The concentration of NO was sufficiently large that the $N(^2D)$ or $N(^4S)$ atoms, formed along with $O(^3P)$ in the photo-decomposition, reacted with NO within about 20µs to give another $O(^3P)$ atom.[34] The O-atom concentration, at an initial level of $\sim 2 \times 10^{12}$ atoms cm^{-3}, was then measured in real time by the ARAS technique. The details of this photometer system have been given previously in connection with a study of the O + CH$_4$ reaction.[29] The transient signals from the transducers and the photomultiplier were digitized with a dual channel oscilloscope (Nicolet model 4094). The common time scale was 4 milliseconds, and the time resolution was 0.5µs per point. The photomultiplier (voltage) signal (8000 points) was reduced to 100 points, converted to absorbance $((ABS)_t = \ell n(I_o/I_t))$, and stored and analyzed with a microprocessor (Tektronix 4051 system).[35] A typical signal is shown in the inset in Fig. 1. Since Beer's law is known to hold for the small absorbances used here,[36] $[O]_t$ is proportional to $(ABS)_t$. Diffusion of atoms out of the viewing zone has been shown to be negligible over the test time of the present technique,[26] and hence, the decrease in $[O]_t$ only results from reaction (1), and the rate constant for the loss of O-atoms is given in Eq. (4):

$$\ln(ABS)_t = k_{1st}t + C; \qquad (4)$$

where

$$k_{1st} = k_1[H_2]; \qquad (5)$$

and k_1 is the bimolecular rate constant for reaction (1). Figure 1 also shows a typical first-order plot of the experimental record according to Eq. (4). The [H$_2$] is calculated from the initial mole fraction and shock wave equations. With this [H$_2$], Eq. (5) is used to derive k_1.

Experiment B

The flash photolysis-resonance fluorescence apparatus (FP-RF) and procedures used in this study have also been fully described previ-
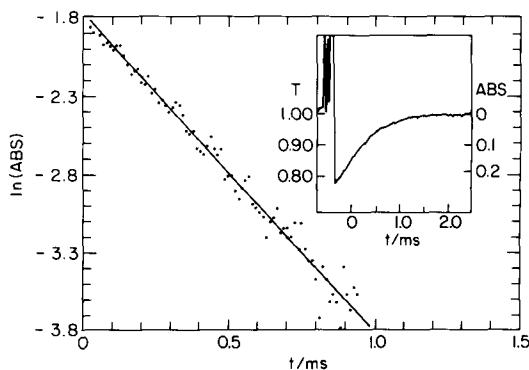
FIG. 1. Typical signal observed after flash photolysis in the reflected shock wave regime. $P_1 = 10.57$ for [H$_2$] = 8.27×10^{15} molecule cm^{-3} and $T = 962$K. The graph shows the first-order plot from the raw data in the inset. $k_{1st} = 2019 \pm 32$ s^{-1}; hence, $k_1 = 2.44 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1}.

ously.[31,32] This apparatus has been used and data have been reported for O-atom reactions in two previous symposia in this series.[37a,b] Thus, only those procedures that are specific to the present investigation will be given here.

The present work was carried out in a high temperature quartz reaction cell.[38] Experiments were readily performed at $T > 900$K to overlap the low temperature limit of the shock tube experiment. In this technique, O-atoms, produced by repetitive photolysis flashes, are monitored via resonance fluorescence. The detected single photon counts are stored in a multichannel analyzer operating in the multiscaling mode. Since $[O]_t$ is proportional to fluorescence counts, the real-time O-atom decays obey Eq. (6):

$$\ell n \text{ (fluorescence counts)} = -K_{exp}t + C, \quad (6)$$

where K_{exp} is the experimentally observed, first-order rate constant. In this case, O-atoms can diffuse out of the reaction viewing zone and they can also react with the NO in a third-order reaction[34,39], thereby giving a finite rate constant even when the reactant, hydrogen, is not present. Therefore, experiments must be performed with constant [NO] and Ar diluent gas both with and without added H$_2$. Designating this O-atom loss term due to diffusion and third-order reaction as K_{diff}, the observed first-orders rate constant, K_{exp}, consists of contributions from K_{diff} and reaction (1), k_1[H$_2$]. Thus,

$$K_{exp} = k_1[\text{H}_2] + K_{diff} \quad (7a)$$
$$k_1 = (K_{exp} - K_{diff})/[\text{H}_2] \quad (7b)$$

Reagents. All of the gases used in this work, except NO, were of the highest purity obtainable and were used directly from cylinders without further purification. The helium, argon and hydrogen were all 99.9999% pure (MG Industries). The nitric oxide (Matheson, 99.0%) was purified by outgassing at 77K and vacuum distilling. In one case the distillation was performed several times from 175K (methanol slush) to 77K with about a 50% yield. In another case, the NO was distilled under vacuum at 90K, with the middle third being retained.

Results and Discussion

The results from Experiment A., the FP-ST apparatus, are given in Table I and are shown in Fig. 2. Table II gives the results from Experiment B., the FP-RF apparatus, and these results are also shown in Fig. 2. The Arrhenius rate constant expressions are:

(A.) $\quad k_1(T) = (3.10 \pm 0.20) \times 10^{-10}$
$\exp(-13619 \pm 167/RT)$, and
(Temperature Range 880K $\leq T \leq$ 2495K)
(B.) $\quad k_1(T) = (7.19 \pm 0.41) \times 10^{-11}$
$\exp(-10428 \pm 72/RT)$,
(Temperature Range 504 $\leq T \leq$ 923K)

where R has units, cal mole^{-1} K^{-1}, k_1 is expressed in cm^3 molecule^{-1}s^{-1} and the errors are given for one standard deviation. These results show two important features. Firstly, the rate constants, obtained by the different techniques, agree with one another to within about $\pm 15\%$ over the common range of overlap in temperature. This error is well within the accuracy of either technique at the two standard deviation level. Secondly, the combined results, as seen clearly in Fig. 2, show non-Arrhenius behavior over the temperature range, $504 \leq T \leq 2495$K. All the results can be accurately expressed by the three parameter, least-squares fit:

$$k_1(T) = 4.97 \times 10^{-18} \, T^{2.15}$$
$$\exp(-7270/RT) \text{ cm}^3 \text{ molecule }^{-1} \text{ s}^{-1}, \quad (8)$$

This expression is shown as the solid line in Fig. 2.

It is important to compare the present data with earlier results. This is done in Table III where the individual two parameter and the combined three parameter, least-squares representations from the present investigation are given along with the expressions from previous work. Although the constants of the three

TABLE I

Rate Constant Data for the Reaction, $O(^3P) + H_2 \rightarrow OH + H$, from the Flash Photolysis—Shock Tube Experiment

P_1/torr	^aM_s	$^ak_{1st}$/s^{-1}	$\rho_5/10^{18}$ molecule cm^{-3}	T_5/K	$k_1/10^{-12}$ cm^3 molecule^{-1} s^{-1}
$^bX_{H2} = 1.800 \times 10^{-4}$					
10.80	2.891 ± 0.021	3449 ± 48	2.228	2024	8.60
10.54	2.905 ± 0.021	3512 ± 55	2.183	2043	8.94
10.62	2.961 ± 0.017	4026 ± 86	2.233	2117	10.02
10.42	3.232 ± 0.014	9085 ± 457	2.331	2495	21.65
10.58	3.128 ± 0.016	6267 ± 116	2.315	2347	15.04
$X_{H2} = 3.775 \times 10^{-4}$					
10.33	2.953 ± 0.026	9965 ± 391	2.167	2106	12.18
10.66	2.983 ± 0.019	10534 ± 391	2.254	2146	12.38
10.94	2.830 ± 0.012	8976 ± 135	2.247	1961	10.58
10.70	2.768 ± 0.006	6378 ± 87	2.167	1887	7.80
10.24	2.728 ± 0.016	5373 ± 68	2.053	1841	6.93
$X_{H2} = 6.250 \times 10^{-4}$					
10.70	2.725 ± 0.012	9916 ± 276	2.144	1836	7.40
10.40	2.641 ± 0.008	5614 ± 94	2.059	1723	4.36
10.22	2.615 ± 0.018	5660 ± 140	2.002	1699	4.52
10.36	2.472 ± 0.012	3868 ± 38	1.942	1542	3.19
10.35	2.567 ± 0.015	5739 ± 65	1.992	1651	4.61
$X_{H2} = 4.038 \times 10^{-3}$					
10.54	1.972 ± 0.007	3330 ± 61	1.571	1057	0.525
10.56	1.896 ± 0.006	2041 ± 43	1.499	991	0.337
10.28	2.047 ± 0.008	4102 ± 61	1.600	1125	0.635
10.31	2.123 ± 0.015	5868 ± 109	1.671	1195	0.870
10.58	2.139 ± 0.010	6574 ± 112	1.729	1210	0.942
10.47	2.221 ± 0.011	8616 ± 278	1.779	1289	1.20
10.25	2.237 ± 0.008	10453 ± 141	1.753	1304	1.48
10.55	1.784 ± 0.007	929 ± 18	1.379	897	0.167
$X_{H2} = 5.573 \times 10^{-3}$					
10.63	2.119 ± 0.009	8280 ± 313	1.715	1194	0.866
10.20	2.043 ± 0.012	6055 ± 145	1.596	1113	0.681
10.57	1.870 ± 0.014	2019 ± 32	1.485	962	0.244
10.34	1.922 ± 0.008	2648 ± 42	1.494	1013	0.318
10.53	1.953 ± 0.005	3950 ± 52	1.553	1040	0.457
10.60	2.176 ± 0.007	8227 ± 235	1.765	1244	0.836
10.79	2.121 ± 0.009	9683 ± 199	1.742	1196	0.997
$X_{H2} = 1.800 \times 10^{-4}$					
15.85	2.857 ± 0.015	6770 ± 77	3.262	1967	11.53
15.84	3.149 ± 0.011	15089 ± 303	3.505	2360	23.91
15.90	3.171 ± 0.024	12712 ± 254	3.524	2400	20.04
15.45	2.897 ± 0.010	6472 ± 81	3.193	2032	11.26
15.22	2.821 ± 0.022	5042 ± 85	3.097	1931	9.04
15.32	3.092 ± 0.017	11373 ± 184	3.336	2289	18.94
15.18	3.036 ± 0.010	10027 ± 103	3.262	2211	17.08
15.31	2.884 ± 0.019	7901 ± 146	3.163	2008	13.88
15.57	2.871 ± 0.052	7232 ± 83	3.206	1992	12.53
15.70	2.730 ± 0.012	4294 ± 73	3.128	1825	7.63

TABLE I (*continued*)
Rate Constant Data for the Reaction, O(^{3}P) + H$_2$ → OH + H, from the Flash Photolysis—Shock Tube Experiment

P_1/torr	^aM_s	$^ak_{1st}$/s^{-1}	$\rho_5/10^{18}$ molecule cm^{-3}	T_5/K	$k_1/10^{-12}$ cm^3 molecule^{-1} s^{-1}
X$_{H2}$ = 3.775 × 10^{-4}					
15.36	2.245 ± 0.008	1866 ± 32	2.607	1307	1.90
15.44	2.308 ± 0.011	1601 ± 19	2.700	1365	1.57
15.64	2.378 ± 0.009	2480 ± 42	2.809	1435	2.34
15.60	2.407 ± 0.008	2821 ± 38	2.832	1466	2.64
15.92	2.485 ± 0.020	5167 ± 62	2.968	1547	4.61
15.48	2.565 ± 0.012	4769 ± 56	2.958	1633	4.27
15.50	2.598 ± 0.018	5553 ± 57	3.001	1664	4.90
15.30	2.755 ± 0.012	9509 ± 200	3.077	1847	8.18
15.53	2.665 ± 0.009	9003 ± 89	3.053	1744	7.82
15.68	2.805 ± 0.009	10153 ± 98	3.202	1899	8.40
X$_{H2}$ = 1.238 × 10^{-3}					
15.80	2.119 ± 0.011	1066 ± 23	2.555	1175	0.667
15.22	2.260 ± 0.013	2628 ± 62	2.618	1312	1.61
15.38	2.292 ± 0.012	2899 ± 46	2.681	1344	1.73
15.17	2.373 ± 0.011	4090 ± 85	2.720	1430	2.41
15.55	2.443 ± 0.006	5799 ± 110	2.878	1493	3.22
15.31	2.509 ± 0.014	5760 ± 116	2.896	1562	3.18
15.38	2.636 ± 0.009	9443 ± 396	3.020	1700	5.00
15.92	2.484 ± 0.012	6309 ± 109	2.977	1541	3.39
15.46	2.567 ± 0.012	7967 ± 220	2.967	1630	4.30
15.44	2.584 ± 0.011	8220 ± 145	2.978	1648	4.42
X$_{H2}$ = 1.238 × 10^{-3}					
15.65	1.922 ± 0.013	940 ± 16	2.238	1009	0.339
15.75	2.005 ± 0.015	1643 ± 33	2.363	1086	0.562
15.45	2.002 ± 0.016	2021 ± 29	2.314	1083	0.706
15.31	2.072 ± 0.017	2212 ± 38	2.392	1143	0.747
15.53	2.128 ± 0.015	3045 ± 62	2.489	1198	0.988
15.20	2.190 ± 0.012	3490 ± 48	2.510	1257	1.12
15.22	2.224 ± 0.008	4534 ± 68	2.553	1290	1.44
15.59	2.314 ± 0.005	5879 ± 156	2.716	1379	1.75
15.55	2.319 ± 0.011	6214 ± 89	2.714	1384	1.85
15.38	2.387 ± 0.011	7668 ± 156	2.755	1453	2.25
15.66	2.398 ± 0.012	8334 ± 101	2.816	1465	2.39
X$_{H2}$ = 4.038 × 10^{-3}					
15.37	2.076 ± 0.013	6001 ± 94	2.410	1144	0.617
15.24	2.144 ± 0.009	10058 ± 268	2.474	1207	1.01
15.55	2.175 ± 0.011	10145 ± 170	2.562	1237	0.980
15.52	2.119 ± 0.010	8295 ± 101	2.497	1180	0.823
15.41	2.082 ± 0.009	7019 ± 116	2.432	1146	0.715
15.20	1.983 ± 0.011	4932 ± 75	2.268	1057	0.539
15.75	1.946 ± 0.009	3764 ± 73	2.297	1025	0.406
15.36	1.920 ± 0.010	3036 ± 50	2.196	1006	0.342
15.51	1.859 ± 0.011	1914 ± 30	2.128	954	0.223
15.78	1.802 ± 0.006	1703 ± 31	2.075	907	0.203
X$_{H2}$ = 5.573 × 10^{-3}					
15.42	1.791 ± 0.006	1814 ± 28	1.994	907	0.163

REACTION KINETICS

TABLE I *(continued)*
Rate Constant Data for the Reaction, $O(^3P) + H_2 \rightarrow OH + H$, from the Flash Photolysis—Shock Tube Experiment

P_1/torr	^aM_s	$^ak_{1st}$/s^{-1}	$\rho_5/10^{18}$ molecule cm^{-3}	T_5/K	$k_1/10^{-12}$ cm^3 molecule^{-1} s^{-1}
15.81	1.847 ± 0.007	2660 ± 48	2.160	941	0.221
15.26	1.773 ± 0.008	1467 ± 22	1.971	880	0.133
15.28	1.866 ± 0.010	2853 ± 59	2.116	957	0.242
15.26	1.918 ± 0.008	3781 ± 60	2.188	1000	0.310
15.08	1.960 ± 0.010	5035 ± 109	2.221	1036	0.407
15.76	1.995 ± 0.012	6424 ± 121	2.371	1067	0.486
15.48	2.038 ± 0.012	8581 ± 145	2.387	1105	0.645
15.71	2.112 ± 0.012	8173 ± 392	2.520	1173	0.582
15.65	2.054 ± 0.020	7996 ± 144	2.435	1120	0.589
$X_{H2} = 1.800 \times 10^{-4}$					
30.58	2.404 ± 0.002	2748 ± 44	5.288	1417	2.89
30.19	2.352 ± 0.008	2356 ± 34	5.142	1362	2.55
30.42	2.272 ± 0.006	2192 ± 49	5.004	1289	2.43
30.70	2.322 ± 0.001	2502 ± 43	5.169	1332	2.69
$X_{H2} = 3.775 \times 10^{-4}$					
30.56	2.196 ± 0.007	2539 ± 37	4.851	1222	1.39
30.28	2.144 ± 0.008	2072 ± 60	4.709	1171	1.17
30.87	2.317 ± 0.011	4033 ± 81	5.189	1328	2.06
30.76	2.258 ± 0.009	2979 ± 41	5.031	1275	1.57
30.18	2.271 ± 0.011	3481 ± 48	4.980	1283	1.85
$X_{H2} = 6.250 \times 10^{-4}$					
30.36	2.397 ± 0.003	7685 ± 207	5.238	1409	2.35
30.36	2.365 ± 0.011	7226 ± 125	5.179	1378	2.23
30.36	2.201 ± 0.009	4349 ± 51	4.831	1226	1.44
30.32	2.228 ± 0.007	4813 ± 79	4.882	1252	1.58
30.30	2.214 ± 0.001	3548 ± 47	4.834	1243	1.17
$X_{H2} = 1.238 \times 10^{-3}$					
30.70	1.930 ± 0.006	1992 ± 28	4.232	988	0.380
30.70	1.982 ± 0.012	2823 ± 57	4.369	1032	0.522
30.33	2.028 ± 0.010	3077 ± 63	4.444	1068	0.559
30.28	2.146 ± 0.004	5336 ± 101	4.714	1171	0.915
30.21	2.161 ± 0.009	5571 ± 77	4.721	1189	0.954
30.74	2.188 ± 0.010	6577 ± 83	4.864	1214	1.09
30.34	2.291 ± 0.008	10791 ± 371	5.000	1315	1.74
30.65	2.220 ± 0.011	6756 ± 168	4.902	1247	1.11

^{a}Error is one standard deviation.
^{b}X is the mole fraction.

parameter expressions are different, these expressions predict rate constants that are in reasonable agreement over the temperature range, 400K to 2500K. Clearly, rather large combined variations in A, n, *and E* can result in nearly the same values of $k_1(T)$ over the range of temperature applicability. For example, the results from the 1972 review of Baulch, et al.[22] agree with the values calculated from the present combined three parameter fit (Eq. 8) to within about ±20% over the range $400 \leq T \leq$ 1400K. At 2000K, the difference is 36%. The Cohen and Westberg[23] expression gives results that are uniformly lower by about 25% from those calculated by Eq. (8). However, the expression from the review of Warnatz[24] gives results uniformly higher by about 50% over most of the temperature range.

TABLE II

Rate Constant Data for the Reaction, O(^{3}P) + H$_2$ → OH + H, from the Flash Photolysis—Resonance Fluorescence Experiment[a]

T (K)	H$_2$ (torr)	NO (mtorr)	Total Pressure (torr)	Flash Energy (J)	K_{exp} (s^{-1})		k_1 (cm^3 molecule^{-1} s^{-1})		
								($\times 10^{15}$)	
504 ± 1	6.228	113.1	50	90	357	± 12	2.20	±	0.13
	6.228	113.1	50	90	353	± 5	2.18	±	0.08
	6.228	113.1	50	90	361	± 8	2.25	±	0.10
	6.228	113.1	50	38	363	± 7	2.27	±	0.09
	6.233	113.1	50	90	384	± 10	2.44	±	0.12
	6.233	113.1	50	90	369	± 9	2.32	±	0.11
	6.233	113.1	50	38	376	± 12	2.37	±	0.13
	—	113.1	50	90-23	93	± 4	—		
	9.342	169.7	75	90	580	± 11	2.31	±	0.08
	9.342	169.7	75	90	553	± 5	2.16	±	0.04
	9.350	169.7	75	38	577	± 41	2.29	±	0.25
	—	169.7	75	90-23	166	± 3	—		

$$k_1 = (2.28 \pm 0.09) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

T (K)	H$_2$ (torr)	NO (mtorr)	Total Pressure (torr)	Flash Energy (J)	K_{exp} (s^{-1})		k_1 (cm^3 molecule^{-1} s^{-1})		
								($\times 10^{15}$)	
558 ± 2	10.206	227.5	100	90	1096	± 46	5.11	±	0.34
	10.206	227.5	100	38	1108	± 27	5.18	±	0.24
	10.206	227.5	100	83	1149	± 70	5.49	±	0.49
	10.206	227.5	100	76	1136	± 46	5.37	±	0.35
	4.885	227.5	100	86	664	± 46	5.61	±	0.72
	4.885	227.5	100	36	655	± 30	5.48	±	0.53
	4.885	227.5	100	94	669	± 23	5.64	±	0.45
	—	225.0	100	86	191	± 15	—		
	2.443	113.8	50	36	307	± 8	5.41	±	0.21
	2.443	113.8	50	90	314	± 17	5.58	±	0.43
	—	112.5	50	90	78	± 1	—		

$$k_1 = (5.43 \pm 0.19) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

T (K)	H$_2$ (torr)	NO (mtorr)	Total Pressure (torr)	Flash Energy (J)	K_{exp} (s^{-1})		k_1 (cm^3 molecule^{-1} s^{-1})		
								($\times 10^{14}$)	
643 ± 4	1.420	228.8	100	90	580	± 42	2.19	±	0.22
	1.420	228.8	100	90	545	± 14	2.01	±	0.09
	1.420	228.8	100	38	571	± 18	2.14	±	0.11
	2.774	228.8	100	90	1074	± 17	2.31	±	0.05
	1.393	228.8	100	38	555	± 16	2.11	±	0.10
	—	228.8	100	90-38	116	± 5	—		
	1.387	114.4	50	90	465	± 14	1.91	±	0.07
	1.387	114.4	50	90	444	± 13	1.81	±	0.07
	—	114.4	50	90	64	± 1	—		

$$k_1 = (2.07 \pm 0.17) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

T (K)	H$_2$ (torr)	NO (mtorr)	Total Pressure (torr)	Flash Energy (J)	K_{exp} (s^{-1})	k_1 (cm^3 molecule^{-1} s^{-1})		
						($\times 10^{14}$)		
741 ± 3	0.641	261.3	100	86	688 ± 33	7.09	±	0.42
	0.641	261.3	100	86	670 ± 20	6.84	±	0.26
	0.641	261.3	100	86	584 ± 10	5.78	±	0.14
	1.280	261.3	100	90	1094 ± 46	5.99	±	0.29
	0.630	262.5	100	38	602 ± 22	6.15	±	0.29
	0.630	262.5	100	38	607 ± 30	6.22	±	0.39
	—	261.3	100	90-38	100 ± 2	—		
	0.320	130.6	50	86	309 ± 12	5.86	±	0.31

REACTION KINETICS

<div align="center">

TABLE II (*continued*)

Rate Constant Data for the Reaction, $O(^3P) + H_2 \rightarrow OH + H$, from the Flash Photolysis—Resonance Fluorescence Experiment[a]

</div>

T (K)	H_2 (torr)	NO (mtorr)	Total Pressure (torr)	Flash Energy (J)	K_{exp} (s^{-1})	k_1 (cm^3 molecule^{-1} s^{-1})		
	0.320	130.6	50	38	317 ± 11	6.05	±	0.29
	0.320	130.6	50	90	318 ± 2	6.08	±	0.07
	0.640	130.6	50	90	551 ± 19	5.84	±	0.24
	--	130.6	50	90-38	63 ± 1	—		
				$k_1 = (6.19 \pm 0.44) \times 10^{-14}$ cm^3 molecule^{-1}s^{-1}				
						(× 10^{13})		
932 ± 2	0.180	275.0	100	90	549 ± 45	2.53	±	0.25
	0.180	275.0	100	90	535 ± 21	2.45	±	0.12
	0.180	275.0	100	90	487 ± 27	2.19	±	0.15
	0.180	275.0	100	90	490 ± 17	2.20	±	0.10
	0.180	275.0	100	38	535 ± 14	2.45	±	0.09
	0.183	275.0	100	38	564 ± 18	2.57	±	0.11
	0.183	275.0	100	38	570 ± 15	2.60	±	0.09
	0.39	275.0	100	90	912 ± 21	2.06	±	0.06
	—	275.0	100	90-38	74 ± 2	—		
	0.091	137.5	50	86	327 ± 5	2.74	±	0.06
	0.091	137.5	50	86	318 ± 16	2.68	±	0.18
	—	137.5	50	90	65 ± 1	—		
				$k_1 = (2.45 \pm 0.23) \times 10^{-13}$ cm^3 molecule^{-1}s^{-1}				

[a]Errors are one standard deviation.

The two parameter Arrhenius expressions listed in Table III show remarkable agreement for shock tube data. The results of Schott et al.[11] and of Pamidimukkala and Skinner[9], are only 24% and 18% higher, respectively, than the present FP-ST results. These uncertainties are well within the combined errors of these studies. It is also of interest that Frank and Just,[40] in their recent study on the $H+O_2$ reaction, suggested that the rate constants of Pamidimukkala and Skinner[9] are 20% too high.

The two parameter expressions from the present FP-RF study and that of Presser and Gordon[25] (Table III) aparently do not agree. However, such lack of agreement does not reflect error in the experimental data but is a consequence of non-Arrhenius behavior in $k_1(T)$. At 500K, where the temperature ranges nearly overlap, the values of k_1 predicted by both expressions agree to within ± 6%. Hence, within experimental error, the two data sets give an accurate representation of $k_1(T)$ from 297K–923K.

Fig. 3 shows the extensive data from the present study together with those of Presser and Gordon.[25] The non-Arrhenius behavior of $k_1(T)$ is clearly apparent over the extensive temperature range of 297K to 2495K. These

data were fitted by the least-squares technique to give the three parameter expression:

$$k_1(T) = 8.44 \times 10^{-20} \, T^{2.67} \, \exp(-6292/RT)$$
$$\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}. \tag{9}$$

This expression is shown as the solid line in Fig. 3 and is listed in Table III. It is valid for the temperature range $300K \le T \le 2500K$ and predicts values of $k_1(T)$ that are generally within ± 20% of those measured experimentally. Also, it should be pointed out that the values of $k_1(T)$ predicted by Eq. (9) agree with the results of Pamidimukkala and Skinner[9] ($1919 \le T \le 2781K$). For example, differences range from only +10% at 1919K to −25% at 2781K. Therefore it is recommended that Eq. (9) be used to calculate rate constants for reaction (1) in the temperature range 300K to 2800K.

The $O(^3P) + H_2$ reaction has probably been the subject of more theoretical work than any other chemical reaction with the exception of the $H + H_2$ exchange reaction. The early work was thoroughly reviewed and evaluated by Schatz, et al.[41] These authors also compared it to their study which was based on the Pol CI-RMOS potential surface[42] for the reaction. Using a minor modification of this potential
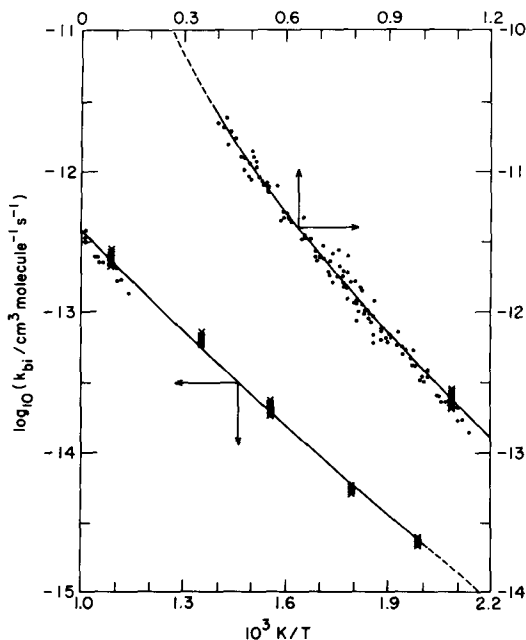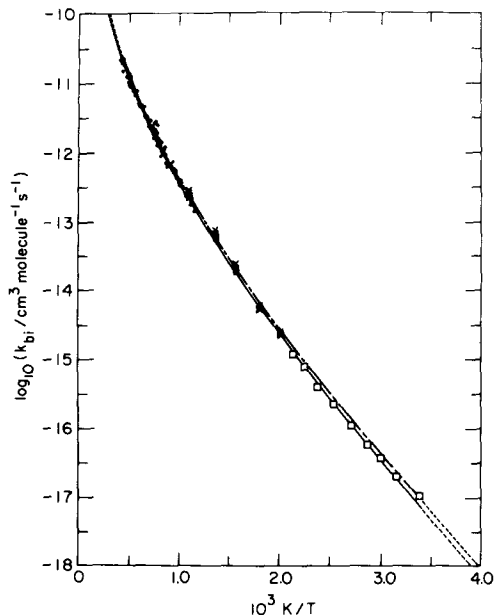
FIG. 2. Three parameter Arrhenius plot for the O(^{3}P) +H$_2$ reaction from the FP-ST and FP-RF data of Tables I and II. The solid line is the three parameter least-squares expression, $k_{bi} = 4.97 \times 10^{-18}$ $T^{2.15}$ exp(-7270/ RT) cm^3 molecule^{-1}s^{-1}. ●-FP-ST; X-FP-RF.

energy surface, the Argonne-IIT group has calculated the rate constant with increasing degrees of sophistication.[41,43-47] The final best calculation,[33(a,b)] which is designated as CEQB/G (Collinear Exact Quantum with an adiabatic incorporation of Bending motion in the Ground bend state), gives theoretical results that can be expressed within 5% at any T by the three parameter expression,

$$k_I^{Th} = 1.77 \times 10^{-20} \ T^{2.89} \ \exp(-5952/RT) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}, \quad (10)$$

over the temperature range 300 ≤ T ≤ 2100K. Results calculated from Eq. (10) are only 18% higher over the entire temperature range of the experiments than those derived from the expression for the combined FP-ST and FP-RF results, Eq.(9) and Table III.

Truhlar and coworkers have also investigated reaction (1) theoretically.[48,49] In their most recent study, [33(a,c)] the Pol CI-RMOS collinear potential surface with global fits to *ab initio* bend potentials are used in an improved canonical variational theory calculation (ICVT) with a least-action ground state transmission coefficient (LAG) evaluation of tunneling. The

FIG. 3. Three parameter Arrhenius plot for the O(^{3}P) + H$_2$ reaction from the FP-ST and FP-RF data of Tables I and II and the data of Presser and Gordon.[25] The solid line is the three parameter least-squares expression, $k_1 = 8.44 \times 10^{-20}$ $T^{2.67}$ exp(-6292/RT) cm^3 molecule^{-1} s^{-1}. The dashed line is the three parameter least-squares fit to the theoretical calculations of ref. 33.
$k_I^{Th} = 5.82 \times 10^{-20}$ $T^{2.73}$ exp(-6201/RT)cm^3 molec^{-1} s^{-1} ●- FP-ST; X- FP-RF; ☐-Presser and Gordon.

results of this study can be expressed to within 8% at any T by the three parameter, least-squares fit,

$$k_I^{Th} = 7.28 \times 10^{-20} \ T^{2.69} \ \exp(-6207/RT) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}, \quad (11)$$

for 300 ≤ T ≤ 2500K. Values of $k_1(T)$ calculated from Eq. (11) are only 9% higher than the experimental values (Eq. (9) and Table III).

Three important points arise from these comparisons. Firstly, both theoretical result agree with experiment within a two standard deviation error of ±24% over the entire temperature range, 300–2500K. Secondly, the potential energy surface in this case contains no significant adjustable parameters. Thirdly, even though the methods for calculating the rate constants (including tunneling effects) are different in the two groups, the final results agree within a few percent over the entire temperature range. The results of both theoretical calculations were therefore combined and then fitted to a three parameter expression, by a least-squares procedure to give,

TABLE III

Rate Parameters for $O(^3P) + H_2 \rightarrow OH + H$ in the form, $k = AT^n \exp(-E/RT)$

A/cm^3 molecule^{-1} s^{-1} K^{-n}	n	E/cal mole^{-1}	Trange/K	Comments
3.0×10^{-14}	1.0	8,902	400–2000	ref. 22; based on ~ 120 references
1.80×10^{-20}	2.8	5,921	400–2400	ref. 23; based on 23 references
2.49×10^{-17}	2.0	7,553	300–2500	ref. 24; based on 5 references
3.65×10^{-10}	0	13,742	1400–1900	ref. 11, shock tube
3.82×10^{-10}	0	13,742	1919–2781	ref. 9, shock tube
$(3.94 \pm 1.01) \times 10^{-12}$	0	$7,682 \pm 169$	297–471	ref. 25, FP-RF
$(3.10 \pm 0.20) \times 10^{-10}$	0	$13,619 \pm 167$	880–2495	present work, FP-ST
$(7.19 \pm 0.41) \times 10^{-11}$	0	$10,428 \pm 72$	504–923	present work, FP-RF
4.97×10^{-18}	2.15	7,270	504–2495	present work, combined FP-ST and FP-RF
8.44×10^{-20}	2.67	6,292	297–2495	present work combined with ref. 25

$$k_1^{Th} = 5.82 \times 10^{-20} \, T^{2.73} \exp(-6201/RT)$$
$$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \tag{12}$$

This combined theoretical result, Eq. (12) is shown as the dashed line in Fig. 3. Rate constants calculated from Eq. (12) are only 12% higher than the experimental values over the entire temperature range, $297K \leq T \leq 2495K$.

Conclusion

New experimental results for the $O(^3P) + H_2$ reaction between 504K and 2495K have been presented. These results were combined with those of Presser and Gordon[25] to give the recommended rate expression:

$$k_1(T) = 8.44 \times 10^{-20} T^{2.67}$$
$$\exp(-6292/RT) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \tag{9}$$

Taking into account how well the predictions from this expression agree with earlier shock tube studies,[9,11] Eq. (9) can be used over the temperature range 300K to 2800K. The accuracy of the values of $k_1(T)$ from Eq. (9) is conservatively estimated to be $\pm 30\%$ over the entire temperature range. Also, recent extensive theoretical calculations on $k_1(T)$ were shown to agree remarkably well within the experimental error with the present experimental results.

Acknowledgement

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COMMENTS

Reinhard Zellner, Inst. f. physikalische Chemie, Univ. Göttingen, 3400 Göttingen FRG. In an experimental study and theoretical evaluation of a reaction like O + H_2 the importance of vibrationally excited H_2 ($v = 1$) must not be overlooked.

1. In an earlier study of O + H_2 (G.C. Light, Aerospace Corporation) it had been concluded that the measured rate coefficient at 300 K is influenced by the presence of H_2 ($v = 1$) formed by energy transfer from N_2 in new discharges. The vibrational rate enhancement k (O + H_2 ($v = 1$) / k (O + H_2 ($v = 0$)) was found to be of the order of 10^3.

2. With this rate enhancement one would expect that at higher temperatures a large fraction of the reactive flux occurs via H_2 ($v = 0$) + M $\longrightarrow$ H_2 ($v = 1$) + M and O + H_2 ($v = 1$) $\longrightarrow$ OH + H, in which case curvature of the Arrhenius graph at T > 1000 K is to be expected (cf. R. Zellner in "Combustion Chemistry" (W.C. Gardiner ed.) Springer 1985). Such effect cannot be dealt with by a TST calculation.

Author's Reply. We agree that vibrationally excited H_2 ($v = 1$) will become an important factor in the O + H_2 reaction at high temperatures. Our measured rate constant represents the total thermal reaction rate of O-atom reacting with hydrogen in a system at equilibrium and thus the reaction with H_2 ($v = 1$) and H_2 ($v = 0$) are included in our result. Although there are no accurate measurements on the temperature dependence for the state selected rate constant for O + H_2 ($v = 1$), we may use the calculated rates of Garrett and Truhlar[1] to estimate that the contribution of H_2 ($v = 1$) to the total, observed rate constant is as follows: at 1000K about 5%; at 1500K about 25%; and at 2000K about 50%. These estimates are very rough, but they are quite consistent with your own conclusions[2] that the reaction of O + H_2 ($v = 1$) will contribute to curvature at high temperatures in the $k_1(T)$ Arrhenius plot. We also agree that a simple TST calculation will not deal with this effect.

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Al Wagner, 200—D—165, Argonne Nat. Laboratory, Argonne IL 60439, USA. I have several comments regarding remarks made by J. Troe and D. Golden. First, in response to J. Troes' question about tunneling, our calculations and those of Truhlar and Garrett show that tunneling is about an 80%–90% effect at room temperature. Furthermore, the strong temperature dependence of the isotope effect, k_{H_2} + o/k_{D_2} + O, also requires tunneling in order to agree with the experiment.

Second, in response to D. Golden, new measurements of the rate at low temperatures could upset this conclusion about tunneling measurements. But the consistent agreement of experiment and theory for a matrix of measurements (thermal rate, all isotope effects (HD,DH,DD) + O) and the vibrationally excited H_2 ($v = 1$) rate) suggests that not just one new measurement but a family of new measurements would be required to change conclusions regarding tunneling.

Author's Reply. We agree with your conclusion regarding the significance of tunneling in the O + H_2 reaction.

We also point out that the empirical TST calculations (as noted by D. Golden at the meeting) provide a poor fit to the low temperature experimental kinetic data for the O + H_2 reaction and that this may be a significant observation. This observation might point to problems with the experiments and ab initio calculations reported and discussed in our paper; or it could suggest limitations in the applicability of such TST calculations. In any case, we still concur with your comment to D. Golden that the now consistent agreement between experiment and theory demand that the burden of proof for any dispute with these results be placed mainly on the new measurements or calculations.

●

P. Marshall and A. Fontijn, Rensselaer Polytechnic Inst., Troy, NY 12180-3590 USA. We are currently studying the reactions O + H_2 and O + D_2 using our high-temperature photochemistry (HTP) method, a higher temperature adaption of FP-RF.

Preliminary analysis of our data for O + H_2 yields the empirical fit k_1 (T) $\approx$ 4.3 × 10^{-32} (T/K)$^{6.4}$ exp (− 1075 K/T) cm^3 molecule^{-1} s^{-1} over the temperature range 365 to 1180 K. This range is being extended up to around 1600 K. Our HTP measurements fall about 30% below Cohen and Westberg's recommendation[1], with this difference decreasing to zero at approximately 1000 K, while your results lie 30% *above* the recommendation. This systematic discrepancy remains despite an extensive variation of our experimental conditions such as argon bath gas pressure, flow velocity, inlet position, type of thermocouple and flash energy. CO_2 is our main photolytic source of atomic O, although we obtained equivalent results with O_2 or NO. Unlike O_2, CO_2 does not lead

to the HO$_2$ chemistry which can cause k_1 to be overestimated, as carefully analyzed by Presser and Gordon[2].

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Author's Reply. You have reported interesting preliminary results from your HTP experiment and we look forward to seeing your final results. We will be most interested in those results that you obtain above ~1200K, and in the uncertainties in your rate measurements at all temperatures. We agree that your present preliminary results represent a systematic discrepancy between the experimental results reported here and those of Presser and Gordon.[1] The cause of this discrepancy is not evident and this is all the more disconcerting since your HTP experiment operates in a manner relatively similar to our flash photolysis-resonance fluorescence experiment. We do note, however, that our recommended expression for $k_1(T)$ (Eq. 9 in the paper) was derived from the independent results obtained in our laboratory and that of Prof. R. J. Gordon, using two completely different methods and three separate apparatuses. Moreover, this recommended expression is in good to excellent agreement, over a very wide temperature range, with the evaluations of Warnatz[2] and Cohen and Westberg[3] as well as with the extensive ab initio calculations of Garrett and Truhlar[4], and Wagner and co-workers.[5]

Finally, we include a relevant comment from Prof. R. J. Gordon and co-workers[6] concerning the question of tunneling in the O + H$_2$ reaction.

"Reported curvature in the Arrhenius plot of the rate constant for the reaction O(^{3}P) + H$_2$ has been interpreted as due to tunneling at low temperatures.[7] Even stronger evidence for tunneling is seen in the branching ratio for the reaction O(^{3}P) + HD. In ongoing experiments we have measured the ratio of OH to OD products, using the method of laser-induced fluorescence to probe the product composition in a flow-discharge apparatus. Both conventional and variational transition state theory without tunneling corrections predict a branching ratio that is insensitive to temperature with [OH]/[OD] ≈ 2 at 370 K. In contrast we observe a strong inverse temperature dependence of this ratio which is in accord with the calculations of Bowman and Wagner[8] and of Garrett and Truhlar[9] only when tunneling is taken into account. At 372 ± 4K we observed a branching ratio of 6.0 ± 1.2 (1 std. dev.). This preliminary result compares favorably with value of 5.6 calculated by Bowman and Wagner using the CEQB method and a value of 5.4 calculated by Truhlar and Garrett using the ICVT/LAG method."

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