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Rate coefficient of the $O + H_2 = OH + H$ reaction determined via shock tube-laser absorption spectroscopy

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Abstract

The rate coefficient for the reaction $O + H_2 = OH + H$ was determined via OH profile measurements in a lean $H_2/O_2/Ar$ mixture behind reflected shock waves. Over the temperature range 1424–2427 K our expression is $k_2 = (1.88 \pm 0.07) \times 10^{14} \exp(-6897 \pm 53 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. We do not support strong curvature in the rate expression for this temperature range.

1. Introduction

The title reaction is an important chain branching reaction in the combustion of hydrogen and hydrocarbon fuels. It has been the subject of numerous experimental [1-8] and theoretical [9,10] studies. When the results of the various experimental studies, covering the temperature range 300-3530 K, are combined there is the appearance of strong upward curvature, i.e. the rate coefficient is described by a non-Arrhenius expression. This is attributed to the participation of vibrationally excited $H_2(v = 1)$ which is increasingly populated at higher temperatures. The ratio k(v = 1)/k(v = 0) is reported to be 2600 at 300 K [11]. However, curvature is normally not present in the k_2 expressions determined in the individual shock tube studies.

Early shock tube studies, Schott et al. (SGS) [1], Pamidimukkala and Skinner (PS) [2], Frank and Just (FJ) [3] and Sutherland et al. (SMPNK) [4], support an Arrhenius expression with a temperature dependence near 6900 K. SMPNK combined their own shock tube and flow reactor measurements with the flow reactor measurements of Presser and Gordon [12] to develop an extended temperature non-Arrhenius expression. Above 1400 K this new expression has an apparent temperature dependence near 9500 K. Subsequent shock tube studies, Natarajan and Roth (NR) [5], Shin et al. (SFG) [6] and Davidson and Hanson (DH) [7], support an Arrhenius expression with temperature dependence near 9500 K. Only NR reports a non-Arrhenius expression based solely upon shock tube data. In the most recent shock tube study, Yang et al. (YSG) [8] combined their data with SFG and obtained an Arrhenius expression with a temperature dependence closer to the lower value.

At 2500 K the lower and upper bounds for k_2 are set by SMPNK and DH respectively. Their expressions differ by 50%, however, their experiments are almost identical. Both use the same calibration independent diagnostic and clean photolytic O-atom source, NO. In both studies k_2 is determined via the pseudo-first-order depletion of O-atoms, a method considered to be free of interference from secondary reaction chemistry. The main difference between the studies is the composition of the test gas. SMPNK worked at higher H_2 concentrations and the DH mixture additionally contained N_2O , used to test the agreement between pyrolytic and photolytic initiation.

There exists disagreement as to the absolute value, temperature dependence and possible curvature of k_2 . To address these issues we performed a series of experiments in a lean $H_2/O_2/Ar$ mixture behind reflected shock waves. The mixture was chosen to have an H_2 concentration intermediate to SMPNK and DH. We followed OH profiles using laser absorption spectroscopy and used two independent methods to determine k_2 from these profiles.

2. Experimental

The experimental apparatus has been described in detail previously [13]. Briefly, a rolled square stainless steel shock tube 63.5 mm in cross-section was pumped below 3×10^{-6} Torr by a Varian V60 turbopump. The shock tube had a combined leak and outgassing rate of 5×10^{-6} Torr min⁻¹. Shocks were initiated by mechanically bursting aluminum diaphragms. Shock properties were computed using standard techniques [14], NASA thermochemical data [15] and measured incident shock velocities extrapolated to the end wall. Temperature and density were corrected for the effect of shock/boundary layer interaction following the methodology of Michael and Sutherland [16], resulting in an average 1.4%

Table 1 Experimental conditions and results ^a. 0.05% H₂, 0.5% O₂, 99.45% Ar ($\phi = 0.05$)

$\overline{T_5}$	P5	A _{max}	NS _{max}	t ₅₀	$k_2^{b}/10^{12}$	$k_2 c/10^{12}$	_
1424	1.801	0.198	4292	797	1.50	1.50	_
1430	1.813	0.190	4552	795	1.55	1.58	
1449	1.837	0.198	4803	756	1.54	1.62	
1528	1.903	0.238	6067	558	2.28	2.14	
1529	1.912	0.238	6084	592	1.96	1.99	
1559	1.967	0.235	6719	505	2.29	2.36	
1564	1.964	0.263	6558	508	2.23	2.30	
1671	1.829	0.259	7683	422	2.94	3.04	
1691	1.844	0.247	8445	382	3.25	3.31	
1715	1.887	0.220	8063	371	3.19	3.19	
1732	1.942	0.257	8785	335	3.58	3.40	
1769	1.898	0.295	8816	322	3.65	3.71	
1898	1.826	0.269	9981	252	5.00	4.70	
1948	1.903	0.280	11642	225	5.26	5.59	
1951	1.900	0.259	11293	219	5.29	5.40	
2093	2.008	0.294	14336	160	7.14	7.36	
2123	1.928	0.305	13245	157	7.40	6.79	
2127	1.935	0.306	13957	157	7.44	7.77	
2285	2.004	0.318	15968	125	9.12	8.83	
2334	1.950	0.299	16341	118	9.90	9.90	
2350	1.964	0.300	16726	114	10.1	9.94	
2370	1.993	0.305	17619	109	10.4	10.8	
2405	2.050	0.297	17976	101	10.9	10.9	
2416	2.041	0.301	17544	98	10.8	10.3	
2427	2.064	0.296	18182	94	11.1	11.3	

^a Units are K for T_5 , atm for P_5 , μ s for t_{50} and cm³ mol⁻¹ s⁻¹ for k_2 .

^b $k_2(t_{50})$.

 $k_2(NS_{max}).$

increase in temperature. Concentration profiles of OH radical were monitored via absorption of the $P_1(5)$ line of the (0, 0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ system at 310.032 nm (air). A cw laser beam was produced by intracavity doubling of a stabilized dye laser (Coherent Model 699-1). The UV laser output was split into three parts: a probe beam that was passed twice through the shock tube; a reference beam used in the double beam scheme for measurement noise reduction; and a wavelength calibration beam that was passed through a burner stabilized CH_4 /air flame to determine OH line center. Test gas mixtures were prepared manometrically and allowed to stand for 48 h before use. The maximum uncertainty of the final reactant concentrations was 0.5% or less. Test gases were used without further purification, stated purities were: H₂, 99.9995% (Linde Research Grade, THC as $CH_4 < 0.3$ ppm); O₂, 99.6% (Linde Zero Grade, THC as $CH_4 < 0.3$ ppm); Ar,

Table 2 Reaction mechanism ^a

99.996% (Linde Zero Grade, THC as $CH_4 < 0.3$ ppm).

3. Results and discussion

A typical hydroxyl radical absorption profile is shown in Fig. 1. The rapid rise of the signal after an induction period follows the essentially exponential growth of OH due to chain branching and propagating reactions. Depending upon experimental conditions the OH concentration reached a partial equilibrium or a maximum. It has been shown previously [17,18] that a small set of carefully chosen observables can embody the full information content of an experiment. We chose A_{max} , the maximum absorption, t_{50} , the time to reach 50% of A_{max} , and NS_{max}, the normalized slope at the point of maximum OH growth, defined as NS_{max} = $-d[(I/I_0)/dt]_{max}/$

	Reaction	A ^b	n	θ	Ref.	
(1)	$H + O_2 = OH + O$	7.13 (+13)	0.0	6957	[13]	_
(2)	$O + H_2 = OH + H$	1.88 (+14)	0.0	6897	this work	
(3)	$OH + H_2 = H_2O + H$	2.14 (+08)	1.52	1736	[21]	
(4)	$O + H_2O = OH + OH$	4.51 (+04)	2.70	7323	[22]	
(5)	$\mathbf{O} + \mathbf{O} + \mathbf{M} = \mathbf{O}_2 + \mathbf{M}$	1.00 (+17)	- 1.0	0	[17]	
	$Ar = 1.0, H_2 = 2.9, O_2 = 1.2, H_2C$) = 18.5				
(6)	$\mathbf{H} + \mathbf{H} + \mathbf{M} = \mathbf{H}_2 + \mathbf{M}$	6.40 (+17)	-1.0	0	[17]	
	$Ar = 1.0, H_2 = 4.0, H_2O = 12.0, H_2O = 1$	I = 26.0				
(7)	$\mathbf{H} + \mathbf{O} + \mathbf{M} = \mathbf{O}\mathbf{H} + \mathbf{M}$	6.17 (+16)	-0.6	0	[20]	
	$Ar = 1.0, H_2O = 5.0$					
(8)	$\mathbf{H} + \mathbf{O}\mathbf{H} + \mathbf{M} = \mathbf{H}_2\mathbf{O} + \mathbf{M}$	8.40 (+21)	-2.0	0	[17]	
	$Ar = 1.0, H_2 = 2.5, H_2O = 16.25$					
(9)	$\mathbf{H} + \mathbf{O}_2 + \mathbf{M} = \mathbf{HO}_2 + \mathbf{M}$	7.00 (+17)	-0.8	0	[17]	
	$Ar = 1.0, H_2 = 3.33, O_2 = 1.33, H$	$_{2}O = 21.3$				
(10)	$HO_2 + H = OH + OH$	2.50 (+13)	0.0	710	[25]	
(11)	$HO_2 + H = H_2 + O_2$	5.00 (+12)	0.0	350	[26]	
(12)	$HO_2 + H = H_2O + O$	2.00 (+13)	0.0	710	[25]	
(13)	$HO_2 + O = O_2 + OH$	2.00 (+13)	0.0	0	[26]	
(14)	$HO_2 + OH = H_2O + O_2$	1.06 (+11)	0.0	0	[26]	
(15)	$\mathrm{HO}_2 + \mathrm{HO}_2 = \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	1.20 (+17)	0.0	- 855	[27]	
(16)	$H_2O_2 + M = OH + OH + M$	2.20 (+14)	0.0	22900	[17]	
	$Ar = 0.67, O_2 = 0.78, H_2O = 6.0$					
(17)	$H_2O_2 + H = HO_2 + H_2$	1.70 (+12)	0.0	190	[26]	
(18)	$H_2O_2 + H \approx H_2O + OH$	1.00 (+13)	0.0	180	[26]	
(19)	$H_2O_2 + O = HO_2 + OH$	2.80 (+13)	0.0	322	[27]	
(20)	$H_2O_2 + OH = H_2O + HO_2$	7.00 (+12)	0.0	720	[26]	

^a Rate coefficients are in the form $k = AT^n \exp(-\theta/T)$. Units are K, cm³, mol, and s.

^b Numbers in parentheses are powers of 10.

 A_{max} . Experimental conditions and results are given in Table 1. Temperature ranged from 1424 to 2427 K and pressures were near 1.9 atm.

Computer simulations were performed using the detailed reaction mechanism in Table 2, which is the mechanism of Yuan et al. [19] with the following changes. The reaction H + O + M was added [20], k_3 was taken from the critical review of Oldenburg et al. [21], k_4 was taken from the critical review of Michael [22] and we used our own recent determination for k_1 [13]. Reverse reaction rate coefficients were computed from the principle of the detailed balancing and the NASA thermochemical data base [15] was used in all calculations. A set of stiff differential equations describing chemical kinetics under constant volume conditions assumed for reflected shock conditions [14] was solved using the LSODE integration package [23].

Local logarithmic response sensitivities calculated for the Fig. 1 condition are shown in Fig. 2. Similar sensitivities are also observed for other reaction conditions. It is not possible to determine k_2 under chemical isolation using our apparatus. For any reasonable set of experimental conditions there is al-



Fig. 1. Typical experimental record of OH absorption, 0.05% H₂, 0.5% O₂, 99.45% Ar, $T_5 = 1898$ K, and $P_5 = 1.83$ atm. Spike at time zero is the schlieren signal due to reflected shock front passage. Smooth line is computed OH absorption profile using the Table 2 mechanism and the OH absorption coefficient determined at A_{max} .



Fig. 2. Sensitivity spectra for the experimental condition in Fig. 1. Sensitivities are for 200% increase to Table 2 values and absorption coefficient. Reaction numbers are listed in Table 2. \blacksquare for NS_{max} sensitivity; shaded blocks for t_{50} sensitivity and blocks filled with dots for A_{max} sensitivity.

ways sensitivity to other reactions. The experimental mixture, 500 ppm H₂ and 5000 ppm O₂ in Ar, possesses certain beneficial features. Sensitivity to k_2 is high for both NS_{max} and t_{50} , uncertainty in the values of k_1 and k_3 are smaller, NS_{max} is insensitive to k_{11} (H + HO₂ = H₂ + O₂, the initiation reaction) and t_{50} is insensitive to k_4 (O + H₂O = OH + OH). Therefore, each of the observables provide independent corroboration of the other and confounding due to the sensitivity of the observables to other reactions is negligible. Both NS_{max} and t_{50} are insensitive to the value of ϵ (OH).

Matching A_{max} results in a self-calibration of the absorption profile. The derived values for k_2 , obtained using NS_{max} and t_{50} , are shown in Fig. 3. There is very good agreement between the values obtained using the two different observables. Combining the data we obtain an Arrhenius expression for k_2 given by

$$k_2 = (1.88 \pm 0.07)$$

 $\times 10^{14} \exp(-6897 \pm 53 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$

A standard propagation-of-error analysis [24] was performed for individual experimental determinations of k_2 . Contributions to uncertainty were estimated using the measurement accuracy of the vari-





Fig. 3. Arrhenius plot of the experimental data for k_2 . \bigcirc are $k_2(NS_{max})$, \Box are $k_2(t_{50})$, the dotted line is the least squares fit to our combined NS_{max} and t_{50} data, the solid line is the SMPNK fit to their shock tube data and the dashed line is the SMPNK extended temperature fit.

10kK/T

ous transducers and oscilloscopes. Maximum uncertainties in the determination of $k_2(NS_{max})$ were 7.5% and $k_2(t_{50})$ were 9.5%. The larger of these values was then used as the error limit instead of the smaller value derived from the scatter of the data about the fitted Arrhenius expression.

A profile computed using the Table 2 mechanism

Table 3 Comparison of rate coefficient expressions ^a

Fig. 4. Comparison of present and	previous	determinations	of	k_2
Abbreviations explained in text.				

is shown in Fig. 1 as the smooth line. The mechanism reproduces the experimental profile quite well. Similar fidelity of match is obtained for the other experimental conditions. Our k_2 expression and those reported in previous studies are given in Table 3 and shown in Fig. 4. We do not support strong curvature in k_2 in our temperature range. The maximum temperature dependence of the pre-exponential factor compatible with our data is 0.36, smaller than the value of 2.7 directly determined by NR and the value

Authors ^b	T range	A	n	θ	Ref.
SGS	1400-1900	2.20×10^{14}	0.00	6916	[1]
PS	1919-2781	2.30×10^{14}	0.00	6916	[2]
FJ	1700-2400	$1.85 imes 10^{14}$	0.00	6976	[3]
SMPNK	880-2495	$(1.87 \pm 0.12) \times 10^{14}$	0.00	685 ± 485	[4]
	504-923	$(4.34 \pm 0.25) \times 10^{13}$	0.00	5249 ± 36	[4]
	297-2495	$5.06 imes 10^{4}$	2.67	3165	[4] ^c
NR	1713-3532	3.72×10^{6}	2.17	4080	[5]
	300-3530	$3.87 imes 10^4$	2.70	3150	[5] ^d
SFG	1790-2250	$7.90 imes 10^{14}$	0.00	9382	[6]
DH	2120-2750	$8.13 imes 10^{14}$	0.00	9540	[7]
YSG	1600-2250	$3.63 imes 10^{14}$	0.00	7818	[8]
RHR	1424-2427	$(1.88 \pm 0.07) imes 10^{14}$	0.00	689 ± 753	this work

^a Rate coefficient expression is in the form of $k_2 = AT^n \exp(-\theta/T)$. Units are K, cm³, mol, and s.

^b Abbreviations explained in text.

^c Extended temperature fit by combining with the low temperature data (277-471 K) of Presser and Gordon [12].

^d Extended temperature fit by combining with the data of SMPNK [4] and low temperature data (277-471 K) of Presser and Gordon [12].

of 2.67 used in the SMPNK extended temperature fit. We support the lower value, near 6900 K, for the temperature dependence in agreement with SGS, PS, FJ and SMPNK. Our k_2 expression is in excellent agreement with the SMPNK expression derived from their shock tube data. However, our expression is $\approx 50\%$ lower than the SMPNK extended temperature fit at 2500 K (as is the SMPNK expression derived from their shock tube data). That fit, based upon data taken in shock tubes and flow reactors, covers eight orders-of-magnitude in k_2 . This disagreement, while small on the scale of the SMPNK fit, is important for combustion modeling.

4. Conclusions

We determined the rate coefficient for k_2 over the temperature range 1424–2427 K. The absolute value and the temperature dependence of our k_2 expression agrees with the shock tube data of SMPNK. We do not support strong upward curvature in the rate coefficient expression.

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