

Shock tube study of the rate coefficient of $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$

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Received 19 September 1994; in final form 25 October 1994

Abstract

The $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ reaction was reexamined by monitoring OH radical concentrations using cw UV laser absorption spectroscopy in $\text{H}_2\text{--O}_2\text{--Ar}$ test gas heated by 1850–3550 K shock waves. The rate coefficient expression $(1.0 \pm 0.1) \times 10^{14} \times \exp(-7690 \pm 250 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived. Fitting the present data together with those of Shin and Michael [J. Chem. Phys. 95 (1991) 262] gave $k_4 = (7.6 \pm 0.7) \times 10^{13} \exp(-7065 \pm 140 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the temperature range 1100–3550 K. The reverse reaction rate coefficient was found to be $(9.3 \pm 0.8) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ independent of temperature from 1850 to 3550 K.

1. Introduction

The reaction between hydrogen atoms and oxygen molecules,



controls the rate of chain branching in the oxidation of hydrocarbon fuels. Many experimental [1–12] and theoretical [13–16] studies of its rate coefficient have been reported. Formerly the most reliable expression for its rate coefficient was considered to be that of Schott [1], which was supported with quasi-classical trajectory calculations by Miller [13]. Frank and Just [3] questioned the negative temperature dependence in Schott's a factor, however, and reported higher rate coefficient values derived from H-atom atomic resonance absorption spectroscopy (ARAS) data. Troe [15] reported semi-empirical statistical adiabatic channel model calculations that supported the Frank and Just result. Since then eight groups have reported experimental measurements of the rate

coefficient of this reaction at high temperatures using shock tube techniques. Four [4,7,8,12] used cw UV dye laser absorption measurements to monitor OH radicals, one [5] added ARAS O-atom concentration measurements to similar OH measurements, another [10] used a tunable laser flash absorption technique to monitor OH concentration, and the last two used conventional [6] or laser [9] flash photolysis to produce H atoms and follow their decay by ARAS. The experimental results agree with one another below about 2000 K. However, the spread in reported values increases to about a factor of 2 at temperature of 2500 K. Measurements of k_4 made at the University of Texas [4] using cw UV dye laser absorption by OH deviate significantly at the high end of the temperature range studied from other results [7,8,12] obtained with the same experimental technique. Suspecting that this deviation may have caused by undetected small air leaks at the observation windows, we undertook a reinvestigation with a different shock tube.

2. Experimental

The experiments were again carried out using cw UV dye laser absorption to monitor OH concentrations. The method and the apparatus have been previously described [4,5], and therefore only a brief description of the system and the features unique to the new experiments will be presented here.

The time history of OH absorption was monitored by absorption of a cw UV dye laser (Coherent model CR-699) beam in reflected shock waves in a 76.2 mm inside diameter Monel shock tube [17]. The wavelength was set as close as possible to the center of the $P_1(5)$ line of the 0–0 band of the $^2\Sigma-^2\Pi$ system of OH (309.941 nm in air). The absorption and reference beam intensities were monitored by high-speed photomultiplier tubes and amplifiers. Signals were recorded with a digital oscilloscope having 8 bit resolution.

Shock parameters were computed from measured incident shock velocities by standard methods using JANAF [18] and NASA [19] thermochemical data under the assumption of steady flow and no wall boundary layer formation. Ar (99.999%, Matheson), H_2 (99.995%, Big Three) and O_2 (99.99%, Matheson) were used without further purification. Test gas mixtures were prepared manometrically and allowed to stand for 48 h before used.

3. Results and discussion

OH concentration measurements were made in reflected shock waves over the temperature range from 1850 to 3550 K at densities from 8.5 to 17.0 mol/m³. The mixture compositions studied were 1.02% H_2 –0.100% O_2 and 3.02% H_2 –0.220% O_2 diluted in Ar.

A representative experimental record of absorption at 309.941 nm is shown in Fig. 1. The extinction coefficient of OH was determined for each experiment from the observed absorption signal at partial equilibrium and the partial equilibrium OH concentration computed by integrating the Table 1 [20–23] mechanism to partial equilibrium. The times at which the absorption signal reached 10%, 20%, ..., 80% and 90% of its peak value were recorded. The eight intervals between these times, $\Delta\tau_i(\text{exp})$, were compared to corresponding intervals $\Delta\tau_i(\text{calc})$ obtained by in-

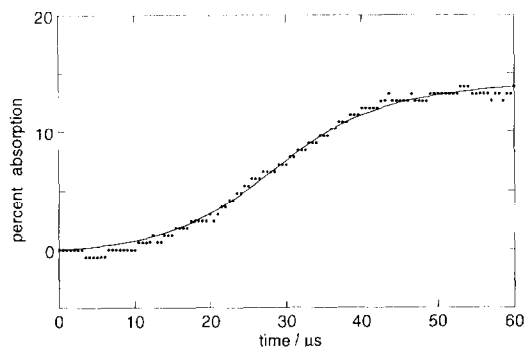


Fig. 1. Typical absorption profile at 309.941 nm. The line was calculated using the Table 1 mechanism; the time zero was adjusted to fit the experimental profile. Shock front conditions $P_0 = 32.6$ Torr, $T_3 = 2903$ K in $H_2/O_2/Ar = 1.02/0.10/98.88$.

tegrating the set of ordinary differential equations describing the Table 1 reaction mechanism as an initial value problem for adiabatic constant density reaction at the starting conditions corresponding to ideal shock reflection. Preliminary calculations had shown that for the conditions of these experiments such calculated differences are very sensitive to the rate coefficient of reaction (4) and relatively insensitive to the rate of chain initiation – which can be strongly affected by impurities as well as by uncertainties in values of rate coefficients of initiation reactions – and the other reactions included in the mechanism. The objective function composed of the eight squared residuals,

$$O(k_4) = \sum [\Delta\tau_i(\text{exp}) - \Delta\tau_i(\text{calc})]^2,$$

was accordingly minimized by trial-and-error variation of the A factor of reaction (4) to obtain the value of k_4 for each experiment. The results are summarized in Table 2.

Rate coefficients of reaction (4) so derived are shown in Fig. 2. Least-squares fitting these data for the temperature range from 1850 to 3550 K gives the expression

$$k_4 = (1.0 \pm 0.1) \times 10^{14} \times \exp(-7690 \pm 250 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

where the errors represent one standard deviation.

Fig. 2 shows that in the region of temperature over-

Table 1
Reaction mechanism ^a

Elementary reaction	log <i>A</i>	<i>n</i>	<i>E_a</i> (kJ)	Ref.
(1) H ₂ + Ar → H + H + Ar	14.73		402	[20]
(2) H ₂ + O ₂ → OH + OH	12.42		163	[21]
(3a) H + HO ₂ → H ₂ + O ₂	13.63		5.9	[20]
(3b) H + HO ₂ → OH + OH	14.23		3.7	[20]
(3c) H + HO ₂ → H ₂ O + O	13.48		7.2	[20]
(4) H + O ₂ → OH + O	14.00		63.9	this work
(5) O + H ₂ → OH + H	14.56		65.0	[22]
(6) OH + H ₂ → H ₂ O + H	8.33	1.51	14.0	[23]
(7) OH + OH → H ₂ O + O	9.18	1.14	0.01	[20]
(8) H + O ₂ + Ar → HO ₂ + Ar	17.79	−0.80	0.0	[20]
(9) H + OH + Ar → H ₂ O + Ar	21.92	−2.0	0.0	[20]

^a Rate coefficient expression is $k = AT^n \exp(-E/RT)$. Units are mol/cm³ and s.

Table 2
Experimental results

<i>P</i> ₁ (Torr)	<i>T</i> _s (K)	<i>ρ</i> _s (mg/cm ³)	<i>P</i> _s (atm)	<i>k_t</i> /10 ¹² (cm ³ mol ^{−1} s ^{−1})	<i>k_r</i> /10 ¹² (cm ³ mol ^{−1} s ^{−1})
45.3	1849	0.604	2.36	1.54	9.18
46.2	1962	0.632	2.62	2.16	10.1
45.7	2025	0.633	2.71	2.31	9.50
41.7	2032	0.579	2.49	2.20	8.90
45.9	2038	0.637	2.69	2.68	10.7
40.2	2052	0.560	2.43	2.43	9.48
41.3	2178	0.590	2.72	2.87	8.99
46.7	2250	0.676	3.22	3.10	8.65
43.6	2389	0.646	3.26	3.55	8.10
40.0	2430	0.596	3.07	3.51	7.59
45.0	2490	0.675	3.49	5.32	10.7
38.2	2623	0.584	3.18	5.53	9.48
39.9	2707	0.616	3.46	6.11	9.56
37.5	2755	0.582	3.33	6.15	9.16
35.6	2844	0.559	3.30	7.30	9.97
32.6	2903	0.515	3.10	6.55	8.47
31.3	2939	0.496	3.02	7.21	9.04
25.3	3108	0.408	2.68	8.99	9.81
26.5	3285	0.428	2.92	9.43	9.03
20.8	3549	0.335	2.46	12.4	10.1

lap the present results are in good agreement with the data of Shin and Michael [9]. We combined our present data with those of Shin and Michael [9] and least-squares fitted all points in the temperature range from 1100 to 3550 K to get the expression

$$k_4 = (7.6 \pm 0.7) \times 10^{13} \\ \times \exp(-7065 \pm 140 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

As shown in Fig. 3, the present result is in good agreement with those reported by Masten et al. [7], Du and Hessler [10], Ryu et al. [12], and Yu et al. [11], who reexamined the Yuan et al. data [8].

The rate coefficients for reaction (4) together with equilibrium constant from the JANAF [18] thermochemical data base were used to compute values of the rate coefficient for the reverse reaction,

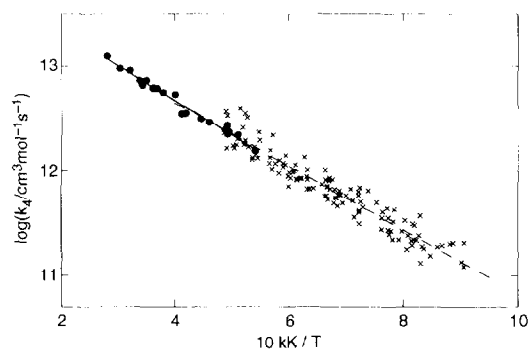


Fig. 2. Rate coefficient for $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. (●) This work; (×) Ref. [9] (LP-ST with H-atom ARAS); (—) the least-squares fit to the present data, (---) the least-squares fit of Ref. [12].

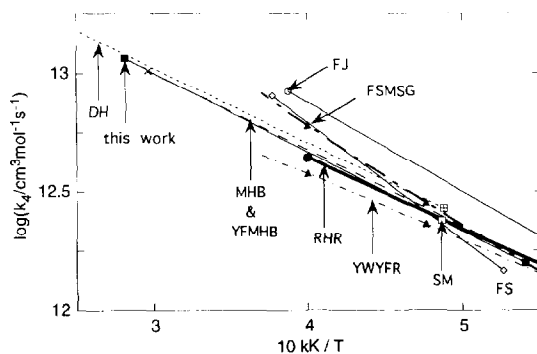
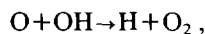


Fig. 3. Comparison of high-temperature rate coefficient expressions for $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. FJ – Frank and Just [3]; FS – Fujii and Shin [4]; FSMG – Fujii et al. [5]; MHB & YFMHB – Masten et al. [7] and Yu et al. [11]; YWYFR – Yuan et al. [8]; SM – Shin and Michael [9]; DN – Du and Hessler [10]; RHR – Ryu et al. [12]. The line labelled 'this work' is a least-squares fit to the combined data of this work and Ref. [9].



shown as open circles in Fig. 4. There is no significant temperature dependence of k_{-4} within the temperature range from 1850 to 3550 K, its average value being

$$k_{-4} = (9.3 \pm 0.8) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

where the errors are given at the one-standard-deviation level. This value is about half of the consensus

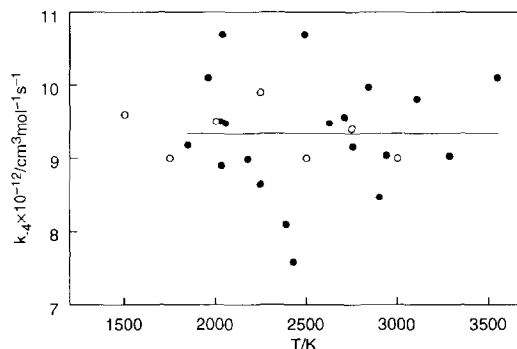


Fig. 4. Rate coefficient for $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$. (●) This work; (○) Ref. [16] (QCT-IEQMT); (—) average of the solid circles.

room temperature value, $2.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and consistent with the negative temperature $1.4 \times 10^{13} \exp(+110 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ found near room temperature [24].

The present result for k_{-4} agrees with the quasi-classical trajectory-internal energy quantum mechanical threshold (QCT-IEQMT) calculation of Varandas et al. [16], who calculated k_{-4} for the temperature range from 150 to 3000 K using the double many-body expansion (DMBE IV) potential energy surface of Pastrana et al. [25]. The Varandas et al. [16] result is in agreement with the experimental room temperature rate coefficient and predicts that above 1500 K k_{-4} practically does not depend on temperature and has a value of $9.34 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, the same as our measurements.

4. Conclusions

Reinvestigation of earlier work from our laboratories showed that the k_4 values reported before were in error. A least-squares fit to our new data from 1850 to 3550 K gave the expression $(1.0 \pm 0.1) \times 10^{14} \exp(-7690 \pm 250 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the rate coefficient of $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, in good agreement with other experimental and theoretical investigations.

Acknowledgement

This research was supported by the Gas Research Institute, the Robert A. Welch Foundation, KOSEF and the Korean Ministry of Education under grant BSRI-94-3419.

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