RATE CONSTANT FOR O+H$_2$→OH+H BY LASER ABSORPTION SPECTROSCOPY OF OH IN SHOCK-HEATED H$_2$–O$_2$–Ar MIXTURES

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The rate constant expression $k = 7.9 \times 10^{14} \exp(-78 \, \text{kJ}/RT)$ cm^3 mol^{-1} s^{-1} for O+H$_2$→OH+H was determined from cw laser absorption spectroscopic measurements of OH radical concentration growth rates in lean H$_2$–O$_2$–Ar mixtures heated to temperatures between 1790 and 2250 K in reflected shock waves.

1. Introduction

The reaction O+H$_2$→OH+H is an important chain reaction in combustion. Many experimental [1–5] and theoretical [6,7] studies of its rate constant have been reported. A review of all investigations up to 1972 was presented by Baulch et al. [8], and Cohen and Westberg [9] and Warnatz [10] reviewed the experimental work up to 1983. More recently, Sutherland et al. [3] measured the rate constant over the temperature range 500 to 2500 K by flash photolysis–shock tube–atomic resonance absorption spectroscopy and flash photolysis–resonance fluorescence techniques. Natarajan and Roth [5] also studied it behind reflected shock waves in the temperature range 1700 to 3500 K using atomic resonance absorption spectroscopy. The differences between the results of the recent experimental studies suggest a need for more experimental high temperature data obtained using a different experimental technique than atomic resonance absorption spectroscopy of O or H atoms.

We report a set of measurements of OH concentration profiles in the shock-initiated reaction of lean ([H$_2$] ≪ [O$_2$]) mixtures. By using a narrow band frequency-doubled cw dye laser as the spectroscopic source and double-beam differential signal acquisition it was possible to attain detection sensitivity approaching that of atomic resonance absorption and hence use high dilutions in Ar. This technique differs essentially from atomic resonance absorption in that it offers direct measurement of OH concentration without resort to any independent sensitivity calibration. The present rate constant results agree with the Natarajan and Roth expression.

2. Experimental

The measurements were made using a rectangular aluminum shock tube of 96×54 mm internal cross section and a frequency-doubled cw dye laser. A detailed description has been given elsewhere [11,12]. During this investigation the test section leak and outgassing rate was less than 1×10^{-4} Torr/min; it was evacuated to less than 2×10^{-4} Torr before each experiment. The state of the test gas behind the reflected shock wave was computed from the incident shock wave velocity, which was measured by four piezoelectric transducers, using conventional procedures [13]. The OH concentration was monitored by measuring the absorption of a beam from a cw UV dye laser passing twice across the 96 mm dimension of the shock tube through sapphire windows located 30 mm from the downstream end. The absorption beam was derived as the second-harmonic output from a LiIO$_3$ doubling crystal inside a ring dye laser pumped by a 15 W argon ion laser (Coherent model CR-699). Kiton-red 620 dye was

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used for this experiment. It was split into reference and absorption beams, each of which was monitored using high-speed photomultiplier tubes (EMI 9924 QB) immediately after leaving the laser housing. The photomultiplier signals were recorded both as absolute and as differential signals on a double-beam digital oscilloscope (Nicolet model 204) and stored on floppy disks for later use. During the final setup of each run 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 (310.123 nm in air) by electronic adjustment of a Brewster plate while monitoring the absorption of a sample split from the reference beam and passed through a premixed natural gas–air flame. Test gas mixtures were prepared manometrically from 99.999% Ar (Matheson), 99.995% H_2 (Big Three) and 99.99% O_2 (Matheson) and allowed to mix for 48 h before use. The test gas used for all experiments reported here had 0.025% H_2 and 0.25% O_2 in Ar. This composition had been determined by preliminary experiments and computer simulations to optimize the sensitivity to the rate constant of $O+H_2$ taking the OH detection limit of the spectroscopic diagnostic into consideration. The starting pressures used, from 22 to 40 Torr, led to reflected shock pressures between 1.5 and 3 bar

3. Results and discussion

A typical absorption profile is shown in fig. 1. The ratio of the heights of the schlieren spikes shows the relative sensitivities of the differential (upper trace) and absolute (lower trace) absorption signals. The
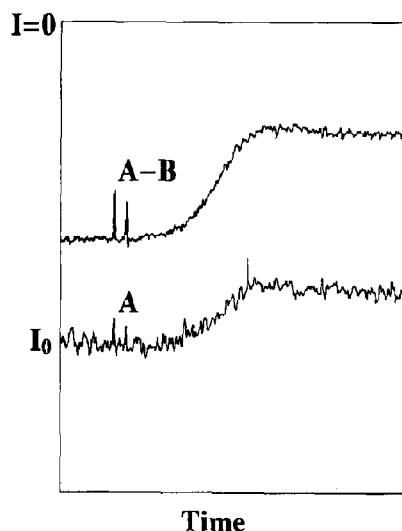

Fig. 1. Sample oscillogram. Zero intensity for the lower trace is at the top; the portion of the sweep shown is 1024 µs wide. The upper and lower traces are the differential and ordinary absorption signals, respectively.

partial equilibrium concentration of OH is computed for this run to be 6×10^{-10} mol cm^{-3}. The maximum formation rate of OH was determined for each experiment by converting the maximum slope of the absorption trace to d[OH]/dt by applying Beer's law using the extinction coefficient expression as a function of temperature

$$\epsilon_{OH} = 1.36\times10^7 \exp(-1260\ \text{K}/T)\ \text{cm}^2\ \text{mol}^{-1},$$

which was calculated from the observed absorption signal at partial equilibrium and the partial equilibrium OH concentration computed by integrating the table 1 mechanism to long reaction times. Fig. 2

Table 1
Reaction mechanism and rate constants [a]

	Elementrary reaction	log A	B	E_a (kJ)	Ref.
(1)	$H_2+Ar\rightarrow H+H+Ar$	14.34	–	402	[10]
(2)	$H_2+O_2\rightarrow OH+OH$	12.40	–	163	[8]
(3)	$H_2+O_2\rightarrow H+HO_2$	13.74	–	242	[8]
(4)	$H+O_2\rightarrow OH+O$	14.78	–	95	[12]
(5)	$O+H_2\rightarrow OH+H$	14.90	–	78	this work
(6)	$OH+H_2\rightarrow H_2O+H$	8.00	1.6	13.8	[10]
(7)	$OH+OH\rightarrow H_2O+O$	9.18	1.14	0	[10]
(8)	$H+O_2+Ar\rightarrow HO_2+Ar$	17.85	−0.8	0	[10]
(9)	$H+OH+Ar\rightarrow H_2O+Ar$	23.15	−2.0	0	[8]

[a] Rate constant expression is $k=AT^B\exp(-E_a/RT)$. Units are mol/cm^3 and s.
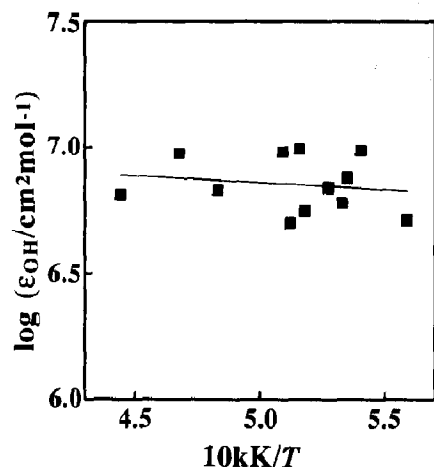
Fig. 2. Arrhenius graph of extinction coefficients of OH at 310.123 nm.

shows an Arrhenius graph of extinction coefficients of OH radical at 310.123 nm. In fig. 3 are shown the results of a sensitivity analysis performed for the middle of the experimental temperature range by doubling and halving the rate constant expressions of the table 1 mechanism. Reactions involving HO_2 and H_2O_2 were omitted because of their very low concentrations. It is seen that the rate coefficient for $O+H_2 \rightarrow OH+H$ has primary significance under these conditions. Three other reactions, $H+O_2 \rightarrow OH+O$, $OH+H_2 \rightarrow H_2O+H$ and $OH+OH \rightarrow$

H_2O+O, also have sensitivities, and thus changes in the rate constants of these reactions would alter the evaluation of rate constant for $O+H_2 \rightarrow OH+H$. Its rate constant expression was adjusted until the best fit shown in fig. 4 was obtained. The fitted line shown corresponds to the expression

$$k = 7.9 \times 10^{14} \exp(-78 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and represents the present data to with a scatter of about $\pm 15\%$ over the temperature range 1790 to 2250 K. Fig. 5 compares this expression with those reported by earlier investigators. The present result is in excellent agreement with the recent expression of Natarajan and Roth,

$$k = 3.22 \times 10^6 (T/K)^{2.17}$$

$$\times \exp(-4080K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The influence of impurities present in the test gas or swept into it from the wall boundary layer was investigated by computer simulations for the test gas mixtures presumed to contain C_2H_6 at ppm levels. A 141-elementary-reaction mechanism [15] capable of simulating the reaction paths of small hydrocarbon oxidation was used. It was found that while the ignition delays change markedly at this assumed contaminant concentration, the maximum OH
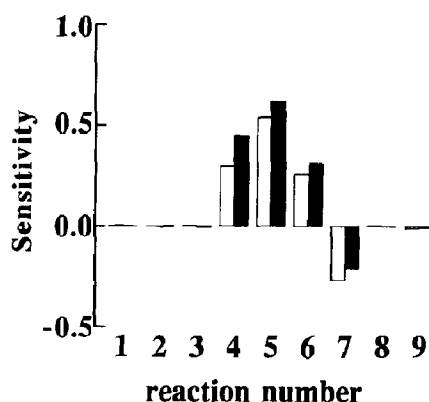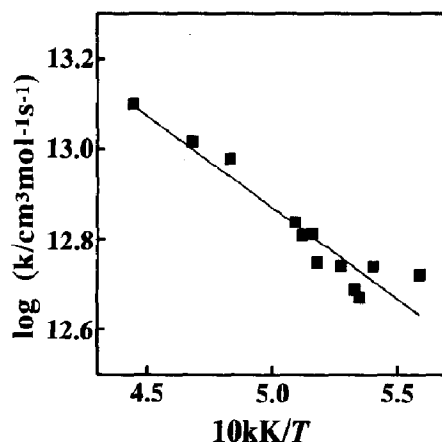

Fig. 3. Logarithmic response sensitivity spectra [14] for the maximum rate of OH absorption change for 0.025% H_2–0.25% O_2 mixtures with $P_1 = 30$ Torr and $T_5 = 2020$ K. The open and filled bars were computed by multiplying and dividing the table 1 rate constant values by 2.

Fig. 4. Arrhenius graph of rate constant data of the reaction $O+H_2 \rightarrow OH+H$. The ratios of experimental to computed values (using the table 1 mechanism and the rate constants) for the derivatives $[d(I/I_0)/dt]_{max}$ were 1.01, 1.03, 1.06, 1.02, 0.98, 1.02, 0.96, 0.98, 0.95, 0.94, 1.05, 1.15 for the data points shown, in order from left to right.
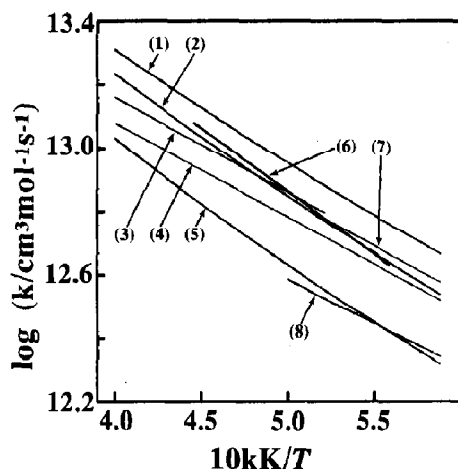
Fig. 5. Comparison of high-temperature rate constant expressions for $O+H_2 \rightarrow OH+H$. (1) Warnatz [10]; (2) Natarajan and Roth [5]; (3) Pamidimukkala and Skinner [2]; (4) Sutherland et al. [3]; (5) Cohen and Westberg [9]; (6) this work; (7) Presser and Gordon [4]; (8) Baulch et al. [8].

growth rates were unaffected. We infer that the conclusions drawn here concerning the rate constant of the $O+H_2$ reaction were not influenced by hydrocarbon contamination of the test gas.

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