

RATE CONSTANT FOR $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ BY LASER ABSORPTION SPECTROSCOPY OF OH IN SHOCK-HEATED $\text{H}_2\text{-O}_2\text{-Ar}$ MIXTURES

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The rate constant expression, $k = 6.0 \times 10^{14} \exp(-95 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ was determined from cw laser absorption spectroscopic measurements of OH radical concentration growth rates in rich $\text{H}_2\text{-O}_2\text{-Ar}$ mixtures heated to temperatures between 1900 and 2650 K in reflected shock waves.

1. Introduction

After many decades of study the mechanism of the $\text{H}_2\text{-O}_2$ reaction seems to be clear, and there is general agreement about the rate constants of each elementary reaction. Reviews have been given by Baulch et al. [1], Schott and Getzinger [2], Dixon-Lewis and Williams [3], Baulch et al. [4], Cohen and Westberg [5] and Warnatz [6] among others. One of those reactions, the $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ reaction, is particularly important, as it is the most sensitive determinant of the rates of flame propagation and ignition in virtually all combustion systems. For many years the expression derived by Schott [7] has appeared to be the most trustworthy description of its high-temperature rate constant, essentially because his measurement technique was more direct than any other, and also because theoretical arguments supporting the unusual temperature dependence of Schott's expression were presented [8]. Nonetheless, it has been repeatedly called into question by the combustion modeling community on the ground that it is difficult to reconcile computed laminar flame speeds with experiments unless one adopts higher values than that provided by Schott's expression for this rate constant. Measurements of atomic resonance absorption spectroscopy of the H and O concentration profiles in the shock-initiated $\text{H}_2\text{-O}_2$

reaction have supported such higher values [9], and the potential surface used for the theoretical investigation has also been questioned [10–12].

We report a set of measurements of the OH concentration profiles in the shock-initiated rich ($[\text{H}_2] \gg [\text{O}_2]$) mixtures. By using a narrow band frequency-doubled cw dye laser as the spectroscopic source and double-beam differential detection it was possible to attain high sensitivity comparable with that of atomic resonance absorption and hence to use dilutions much higher than are possible using other direct diagnostics of reaction progress. The laser absorption measurement of the OH concentration has the advantage over atomic resonance absorption of the H or O concentrations that each experiment can provide calibration of the extinction coefficient pertinent to that run. Reaction conditions were therefore selected so as to permit accurate internal run-by-run calibration of the extinction coefficient and to isolate the sensitivity of the measurement to the rate constant of this elementary reaction. While the results support Schott's expression at the lower end of the temperature range studied (1900 K), higher values, about a factor of 2, are indicated at the higher end (2500 K).

2. Experimental

The experiments were conducted using a rectangular aluminum shock tube of 96×54 mm internal

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cross section. A detailed description has been given elsewhere [13]. During this investigation the leak and outgassing rate of the test section 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 [14].

The time history of the OH concentration was monitored by measuring the absorption of a beam from a cw UV dye laser (Coherent model CR-699, with an angle-tuned intracavity doubling crystal). The absorption beam was double-passed through the 96 mm dimension of the shock tube. Inside the shock tube its diameter was about 1 mm. The laser frequency was initially tuned with a Burleigh WA-10 wavemeter. 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 (310.123 nm in vacuum, 310.032 nm in air) by electronic adjustment of a scanning Brewster plate while monitoring the absorption of a sample split from the reference beam and passed through a premixed natural gas-air flame. (This line offered the best compromise between line strength and temperature independence for the temperature range studied here [15].) The UV beam was split into the reference and absorption beams, each of which was monitored using high-speed photomultiplier tubes, immediately after leaving the laser housing. The photomultiplier anode signals were brought to equal levels by adjusting the dynode supply voltages and recorded as both absolute and differential signals, the latter after analog processing with a video amplifier and both being appropriately impedance-matched with high speed buffers. The signals were recorded on a double-beam digital oscilloscope, at 50 ns/point sampling speed and 8-bit resolution, and stored on floppy disks for later analysis. 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. It was determined from computer simulations and preliminary experiments that O_2 concentrations of 250 ppm and temperatures ranging from about 1900 to 2600 K would offer appropriate compromises between reaction rate, signal level, and isolation of sen-

sitivity to the rate constant of $H + O_2 \rightarrow O + OH$. All experiments reported here had this O_2 concentration and 10- or 20-fold as much H_2 in the test gas. The starting pressures, from 22.5 to 40 Torr, led to reflected shock pressures between 1.5 and 3 bar.

3. Results and discussion

A sample experimental record is shown in fig. 1. 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 inferred 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. All simulations were done assuming a constant density reaction starting from the computed reflected shock conditions [14]; thermochemical properties were computed from polynomial fits to the 1982 JANAF data for all species except for H_2O and HO_2 [16]. The computed partial equilibrium OH concentration for

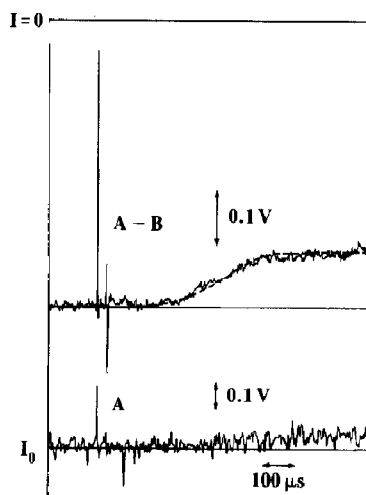


Fig. 1. Sample oscillogram of OH absorption. Zero intensity for the lower trace is at the top; the position of the sweep shown is $1024 \mu s$ wide. The ratio of the heights of the schlieren spikes shows the relative sensitivities of the differential (upper) and ordinary (lower) absorption signals. Dotted line shows kinetically calculated change of OH concentration, where the position of the induction period was adjusted to fit the experimental value (see text).

Table 1
Reaction scheme and rate constants ^{a)}

	Elementary reaction	log A	B	E (kJ)	Ref.
(01)	$\text{H}_2 + \text{Ar} \rightarrow \text{H} + \text{H} + \text{Ar}$	14.34	—	402.0	[6]
(02)	$\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$	13.74	—	242.0	[1]
(1)	$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$	14.78	—	95.0	this work
(2)	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	7.18	2.0	31.6	[6]
(3)	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	8.00	1.6	13.8	[6]
(4)	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	9.18	1.14	0	[6]
(5)	$\text{H} + \text{O}_2 + \text{Ar} \rightarrow \text{HO}_2 + \text{Ar}$	17.85	-0.8	0	[6]
(6)	$\text{H} + \text{OH} + \text{Ar} \rightarrow \text{H}_2\text{O} + \text{Ar}$	23.15	-2.0	0	[1]

^{a)} Rate constant expression is $k = AT^B \exp(-E/RT)$ (units are $\text{mol cm}^{-3} \text{s}^{-1}$).

the run shown in fig. 1 is $6 \times 10^{-11} \text{ mol/cm}^3$. The maximum slope data for the $[\text{H}_2]/[\text{O}_2] = 20/1$ mixture are shown in fig. 2; they are normalized through division by the square value of shock-front O_2 concentration $[\text{O}_2]_0$. Shown for comparison are the results of doubling and halving the rate constant expressions for $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ and $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$, the only reactions of the table 1 mechanism which were found in sensitivity scans to affect the maximum OH growth rates for these conditions. The rate constant expression for $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ was

accordingly adjusted until the fit to both mixtures was optimized (fig. 3). The fitted line shown corresponds to the expression

$$k_1 = (6.0 \pm 3) \times 10^{14} \exp(-95 \pm 5 \text{ kJ}/RT) \\ \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$$

and represents the present data within its scatter of about $\pm 20\%$ over the temperature range 1900 to 2600 K. Also shown on fig. 3 are the lines representing the expression of Baulch et al. [1] and that of Warnatz [6] which reproduces the Schott [7] expression in the temperature range shown. The present data lie up to about a factor of 2 above the latter, and hence the present data support the long-suspected feeling of combustion modelers that there is some difficulty unappreciated so far with the Schott experiments. The present results are compared with the expressions of Baulch et al. [1] and Warnatz [6]

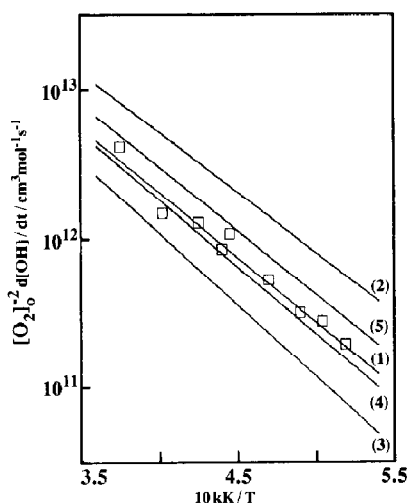


Fig. 2. Comparison of computed (for $p_1 = 30$ Torr) and experimental (squares, for a mixture of $\text{H}_2/\text{O}_2/\text{Ar} = 0.5/0.025/99.475$) maximum OH formation rates. Line (1) was calculated using the rate constant set listed in table 1; lines (2) and (3) were calculated using the same set except for doubling and halving, respectively, the value of k_1 ; lines (4) and (5) were calculated using the same set except for doubling and halving, respectively, the value of k_3 .

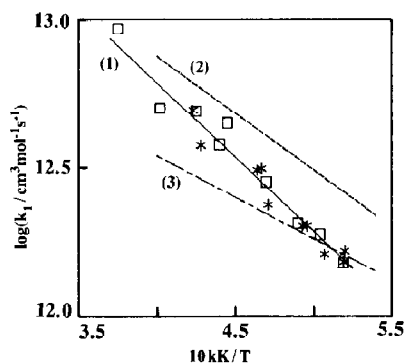


Fig. 3. Rate constants for $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$. Squares: $\text{H}_2/\text{O}_2/\text{Ar} = 0.5/0.025/99.475$. Stars: $\text{H}_2/\text{O}_2/\text{Ar} = 0.25/0.025/99.725$. Line (1): this work, line (2): Baulch et al. [1], line (3): Schott [7].

and with the experimental results of Schott [7] and Chiang and Skinner [17] in fig. 4.

The influence of the impurities present in the test gas or those swept into it from the wall boundary layer has to be considered in any study of ignition. We investigated the possible effects upon the maximum absorption slopes in the following manner. A mechanism with 148 elementary reactions [6] capable of simulating the reaction paths of small hydrocarbon oxidation was run for test gas mixtures which were presumed to contain C_2H_6 at 1 and 5 ppm as contaminants in addition to the H_2 and O_2 components of the test gas used in our experiments. An example of the calculated OH concentration profiles is shown in fig. 5. It can be seen that while the ignition delays change markedly at these assumed contaminant concentrations, the maximum OH growth rates were unaffected. We infer that the conclusions drawn here concerning the rate constant of the $H+O_2$ reaction are not influenced by the hydrocarbon contamination in the test gas. The fact that low contaminant concentrations did show appreciable effects upon the computed ignition delay times led us to refrain from drawing any conclusion from the measured values. A full analysis of laser-absorption OH profiles covering a wide range of composition will be reported elsewhere.

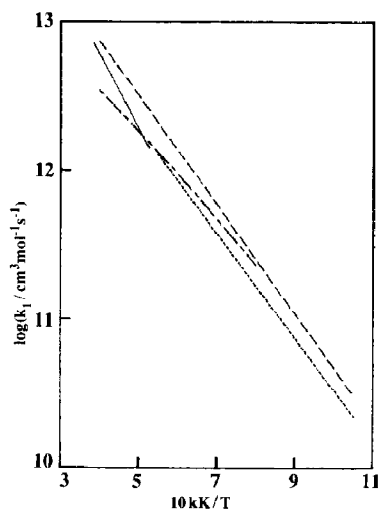


Fig. 4. Comparison of high-temperature rate constant expressions for $H+O_2 \rightarrow O+OH$. — This work, --- Baulch et al. [1], -.-.- Warnatz [6], ... Chiang and Skinner [17].

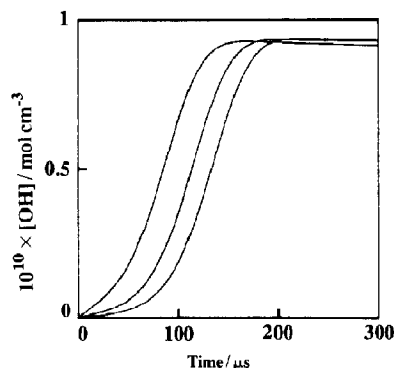


Fig. 5. Effect of C_2H_6 contamination on computed $[OH]$ profiles in a reflected shock wave in $H_2/O_2/Ar=0.25/0.025/99.725$ with $P_1=30$ Torr, $T_5=2000$ K. Left to right: $[C_2H_6]$ in the test gas 5, 1 and 0 ppm.

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