

Rate Coefficient Measurements of the Reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ from 950 K to 1200 K

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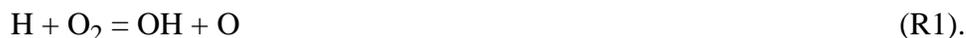
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Rate coefficients of the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ were measured behind reflected shock waves in a series of very lean $\text{H}_2 - \text{O}_2 - \text{Ar}$ mixtures ($\phi = 0.0125 - 0.025$) using OH diagnostics. The rate coefficient expression is $k_{9,0}/[\text{M}] = 7.55 \times 10^{17} T^{-0.8} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ with uncertainty of $\pm 30\%$ in the temperature and density range of 950 - 1200 K and 15 - 51 $\mu\text{mol cm}^{-3}$, respectively. Our results are consistent with the high range of published values.

Introduction

In high temperature $\text{H}_2 - \text{O}_2$ system, reaction characteristics are governed by the chain-branching reaction,



At intermediate temperatures, competition between the chain-branching reaction (R1) and the chain-terminating reaction determines the reaction characteristics.



In classical experiments, explosion limit pressures for stoichiometric $\text{H}_2 - \text{O}_2$ mixture were measured at relatively low temperatures (670 - 840K) in static bulb reactors¹⁻³ and three explosion limits were established. The results were then used in developing a reaction mechanism for the $\text{H}_2 - \text{O}_2$ system. In these studies, it was found that the second explosion limits at given temperatures were determined by rates of the chain-branching and chain-terminating reaction.¹⁻³ Later, with the aid of shock tube or high temperature flow tube techniques, the “extended second explosion limits” were found at higher temperature and density regime in diluted stoichiometric $\text{H}_2 - \text{O}_2 - \text{N}_2$ (or Ar) mixtures.⁴⁻⁷ Ignition delay times from various diagnostics^{4,6,8} have been measured in this regime and incorporated into computer simulations with assumed reaction mechanisms to elucidate whether the reaction characteristics belong to the “strong ignition” or “weak (mild) ignition” regime.^{6,9} Recently species concentration measurements from high temperature flow tube experiments were utilized to establish the extended second explosion limits.⁷

Because of its density (pressure) dependence the chain-terminating reaction (R9) has been recognized as the most important reaction for determining the reaction characteristics in the second and third explosion regimes. Therefore, R9 has been investigated by many authors¹⁰ with various methods but no clear consensus exists as to the rate coefficients which span a range of 4 at 1000 K. This uncertainty motivated us to explore the reaction. All experiments were performed

behind reflected shock waves in very lean $\text{H}_2 - \text{O}_2 - \text{Ar}$ mixtures using OH absorption spectroscopy at ca. 310 nm. Rate coefficients were derived by matching characteristic times obtained from OH absorption profiles.

Experimental

All experiments were performed behind reflected shock waves in a rolled-square stainless steel shock tube with a cross sectional diameter of 63.5 mm. The test section of the shock tube was routinely pumped to 3 μTorr and shocks were initiated within 1 min of admitting the test gas mixture. Incident shock velocities, measured at four axial locations, were fitted to a second-order polynomial in distance. Reflected shock properties were derived from the incident shock velocity extrapolated to the end wall using NASA thermodynamic data and assuming full vibrational relaxation and no chemical reaction at the shock front. The computed ideal shock properties were corrected for the effects of reflected shock—boundary layer interaction in a method similar to Michael and Sutherland.¹¹⁻¹³ The postshock pressure used for the correction for reflected shock—boundary layer interaction was measured using the pressure transducer located axially at the center of the windows 12.7 mm from the end wall. Pressure transducers were calibrated in their mounting assemblies at the NASA Glenn Research Center Calibration Laboratory. Corrected temperatures were always higher than ideal shock temperatures. The percent correction varied from 0.7% to 1.1% depending on mixture composition (γ_{mix}) and initial test gas pressure.

Hydroxyl radical temporal behavior was monitored using 310 nm light ($\text{P}_1(5)$ line of the (0,0) band of the OH $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ transition) from a frequency doubled ring-dye laser operating in a standard double-beam absorption plus frequency reference configuration.^(12,13) Light was detected using three matched THORN EMI 9224QB photomultiplier tubes (PMT) run in a five-dynode configuration to ensure the optimum linearity.

Selection of Experimental Conditions and Computer Simulation.

Extensive simulations were performed in order to determine the mixtures and conditions that would be most sensitive to the title reaction. Either SENKIN¹⁴ or a custom code were used as appropriate. The custom code is based on the LSODE¹⁵ integrator and has built-in features suitable for optimization. Indistinguishable results were obtained from the two codes for a series of calculations with GRI_MECH version 3.0,¹⁶ the $\text{H}_2 - \text{O}_2$ reaction mechanism of Mueller et al.,⁷ and that of GRC, and either NASA thermodynamic data or GRI_thermodynamic data. In computer simulation, the previous GRC $\text{H}_2 - \text{O}_2$ reaction mechanism¹² was modified to accommodate the duplicated feature for $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ reaction. The rate coefficient expressions were taken from the recent review of Baulch et al.¹⁷

A series of modeling study was performed for characteristic times (t_{25} , t_{50} , t_{75}) and the maximum absorption, A_{max} , using the reaction mechanism described above. A quadratic response surface was constructed using a three - level, four parameter full design of 81 individual computer experiments for the 107 experimental runs. The objective function comprising the squared residual sum of this response surface was searched for minima using a brute force method. The observables we have chosen contain sufficient information content in determining the rate coefficients of the title reaction via computer simulation.^{12,13}

Results

Typical 310 nm OH absorption profiles indicated an induction period followed by rapid growth to an absorption maxima followed by a decay to equilibrium OH concentrations. From these absorption profiles, experimental observables were reduced as described above.

Very lean H₂ – O₂ – Ar mixtures ($\phi = 0.0125 - 0.025$) were used in the present study, and so the effect of vibrational relaxation times on the data reduction must be examined. In our experiments, the vibrational relaxation time of O₂ predominates. Computed relaxation time (τ) under our experimental conditions ranged from 8 to 50 μ s. We compared τ with the shortest characteristic time, t_{25} . The ratio, t_{25}/τ ranged from 10 to 110. We, therefore, conclude that vibrational relaxation time of O₂ did not affect our data reduction.

Experiments were performed using four different lean stoichiometries. Low pressure limit conditions were met for all experiments. Characteristic times did not vary linearly with $1/T$ but showed considerable curvature. In computer simulations, A_{\max} was exactly matched by adjusting the absorption coefficients of hydroxyl radical ($\epsilon(\text{OH})$). The $\epsilon(\text{OH})$ values agreed well with those of R₁(5) line(18) that were computed with the measured pressure-broadening factor. The matches between experiments and computer simulations for the characteristic times were excellent over the full range of temperature and density range studied. Optimized rate coefficient values for the title reaction were well fit by the expression:

$$k_{9,0}/[\text{M}] = 7.55 \times 10^{17} T^{-0.8} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

with uncertainty of $\pm 30\%$ in the temperature and density range of 950 - 1200 K and 15 - 51 $\mu\text{mol cm}^{-3}$, respectively. In least-squares fit of the data, because our temperature range is rather narrow, we retained the original T -exponent ($n = -0.8$) and T -dependence ($\Theta = 0$ K) used in $k_{9,0}/[\text{M}]$ expression ($k_{9,0}/[\text{M}] = AT^n \exp(-\Theta/T)$) in our initial reaction mechanism and only Arrhenius A -factor was fitted.

Our results are in good agreement with the rate coefficient expressions given by GRI_MECH version 3.0¹⁶ and Baulch et al¹⁷ and the experimental measurements of Gutman et al¹⁹ and Davidson et al.¹⁰ Our expression is, in the intermediate temperature range, in good agreement with the data of Hsu et al²⁴ and in reasonable agreement with the data of Ashman and Haynes,²⁰ Mueller et al,²⁷ and the rate coefficient expression of Pirraglia et al.²¹ At room temperature, it is in good agreement with the data of Hsu et al,²⁴ Wong and Davis,²² and Carleton et al.²⁴ However, our data does not support the room to intermediate temperature data of Kurylo²³ and the high temperature measurements of Getzinger and Schott.²⁶

Details of the experimental results and data analysis will be discussed. Comparison of our results to previous studies and critical re-evaluation of those studies will be presented.

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