

Rate coefficients for $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ and $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ by kinetic laser absorption spectroscopy in shock waves

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Received 30 September 1992; in final form 9 February 1993

Rate coefficient expressions for $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ (5H) and $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ (5D) over the temperature ranges 1600–2250 and 2370–3390 K, respectively, of $k_{5\text{H}} = 3.7 \times 10^{14} \exp(-65 \text{ kJ}/RT)$ and $k_{5\text{D}} = 4.7 \times 10^{14} \exp(-74 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were derived from laser absorption spectroscopic measurements in shock-heated $\text{H}_2\text{--O}_2\text{--Ar}$, $\text{H}_2\text{--N}_2\text{O--Ar}$ and $\text{D}_2\text{--O}_2\text{--Ar}$ mixtures. The expression $k_{5\text{D}} = 1.2 \times 10^8 T^{1.72} \exp(-4880/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived for the temperature range 340–3390 K by combining our measurements with those of earlier studies. The isotope effect $k_{5\text{H}}/k_{5\text{D}}$ was found to be in agreement with theoretical expectation in the temperature range studied.

1. Introduction

Many experimental [1–5] and theoretical [6,7] studies of the $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ reaction have been reported. A review to 1972 was presented by Baulch et al. [8], and Cohen and Westberg [9] and Warnatz [10] reviewed work up to 1983. Since then its rate coefficient was measured by Sutherland et al. [3] and Natarajan and Roth [5] using atomic resonance absorption spectroscopy (ARAS), by Shin et al. [11] using laser absorption spectroscopy of OH and by Davidson and Hanson [12] using shock tube photolysis and pyrolysis methods. Four high-temperature studies of the rate coefficient of its isotopic counterpart $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ have been reported – by Pamidimukkala and Skinner [2] and Appel and Appleton [13] using ARAS in shock tubes; by Marshall and Fontijn [14] using high-temperature photochemistry; and by Michael [15] using flash photolysis shock tube (FP-ST) and ARAS techniques. Here we report measurements of OH and OD concentration profiles in the shock-initiated reactions of $\text{H}_2\text{--O}_2\text{--Ar}$, $\text{H}_2\text{--N}_2\text{O--Ar}$ and $\text{D}_2\text{--O}_2\text{--Ar}$ mixtures, from which high-temperature rate coefficients

of $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ and $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ are derived.

2. Experimental

Measurements were made using dual-beam, differential detection laser absorption spectroscopy in a rectangular aluminium shock tube [11,16–18]. Test gas mixtures were prepared manometrically from 99.999% Ar (Matheson), 99.995% H_2 (Big Three), 99.5% D_2 (Matheson), 99.99% O_2 (Matheson) and 99.0% N_2O (Matheson) and allowed to mix for 48 h before use. N_2O was purified by trap-to-trap distillation; the other gases were used without further purification. During the final setup of each run the wavelength was set as close as possible to the center of the $\text{P}_1(5)$ line of the 0–0 band of the $^2\Sigma\text{--}^2\Pi$ system of OH (310.032 nm in air) or the $\text{P}_2(8)$ line of the 0–0 band of the $^2\Sigma\text{--}^2\Pi$ system of OD (309.957 nm in air [19]) by electronic adjustment of a Brewster plate. Experiments were done with 250 ppm $\text{H}_2\text{--}2500 \text{ ppm O}_2$ mixtures in Ar over the temperature range 1750–2250 K at 1.4–2.2 bar pressure, 1000 ppm $\text{N}_2\text{O--}500 \text{ ppm H}_2$ mixtures in Ar over the temperature range 1600–2140 K at 1.2–1.9 bar pressure, and a 690 ppm $\text{D}_2\text{--}7260 \text{ ppm O}_2$ mixture in Ar

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over the temperature range 2370–3390 K at 1.3–1.8 bar pressure.

3. Results and discussion

A typical absorption profile of OD radical is shown in fig. 1. The narrow band frequency-doubled cw dye laser as spectroscopic source and double-beam differential signal acquisition provide detection sensitivity approaching that of ARAS. Because partial equilibrium OH or OD concentrations are not sensitive to individual rate coefficients, as confirmed by kinetic modeling, our technique differs essentially from ARAS in that it permits direct measurement of OH and OD concentrations without resort to independent calibrations.

The maximum formation rate of OH or OD was determined for each experiment by converting the maximum slope of the absorption trace to $d[\text{OH}]/dt$ or $d[\text{OD}]/dt$ using Beer's law with the extinction coefficient calculated from the observed absorption signal at partial equilibrium and the partial equilibrium OH or OD concentration computed by integrating the table 1 [20–23] or table 2 [24] mechanism to long reaction time. Rate coefficient values corresponding to the slopes were determined by adjusting the $k_{5\text{H}}$ or $k_{5\text{D}}$ A factors to match maximum slopes of each absorption trace.

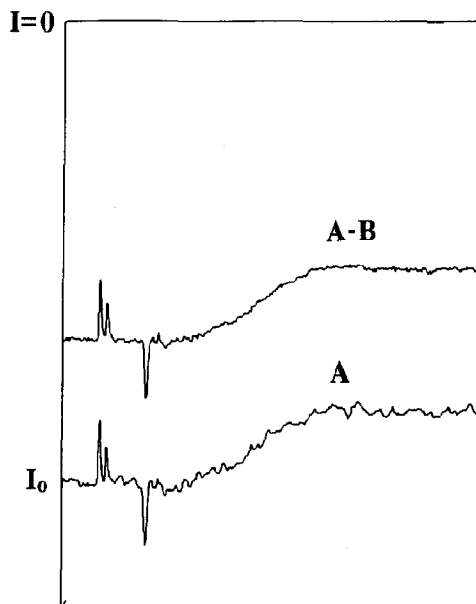


Fig. 1. Typical absorption profile of OD radical. Zero intensity for the lower trace is at the top; the portion of the sweep shown in 256 μs wide. The upper and lower traces are the differential and ordinary absorption signals, respectively. Shock front conditions T_2 2540 K, density 6×10^{-6} mol/cm³; computed partial equilibrium [OD] 2.0 nmol/cm³.

3.1. Reaction mechanism

Rate coefficient expressions for the table 1 and 2

Table 1

Reaction mechanism and rate coefficient parameters used in simulations of the chemistry of the shock-heated $\text{H}_2\text{--O}_2\text{--Ar}$ and $\text{H}_2\text{--N}_2\text{O--Ar}$ mixtures ^{a)}

Elementary reaction	log A	n	E_a (kJ)	Ref.
(b1) $\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$	15.00	–	251	[20]
(b2) $\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$	13.88	–	63	[21]
(b3) $\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}$	13.84	–	111	[21]
(b4) $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$	14.00	–	117	[21]
(b5) $\text{N}_2\text{O} + \text{OH} \rightarrow \text{N}_2 + \text{HO}_2$	11.80	–	42	[21]
(1) $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	14.34	–	402	[10]
(2) $\text{H}_2 + \text{O}_2 \rightarrow \text{OH} + \text{OH}$	12.42	–	163	[8]
(3) $\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$	13.74	–	242	[8]
(4) $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	7.00	2.0	45	[22]
(5) $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	14.56	–	65	this work
(6) $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	8.33	1.51	14	[23]
(7) $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	9.18	1.14	0	[10]
(8) $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	17.85	–0.8	0	[10]
(9) $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	23.15	–2.0	0	[8]

^{a)} Rate coefficient expression is $k = AT^n \exp(-E_a/RT)$. Units are mol/cm³ and s. Eqs. (b1)–(b5) are used for $\text{H}_2\text{--N}_2\text{O--Ar}$ mixture only.

Table 2

Reaction mechanism and rate coefficient parameters used in simulations of the chemistry of the shock-heated D_2 - O_2 -Ar mixture ^{a)}

Elementary reaction	$\log A$	n	E_a (kJ)	Ref.
(1) $D_2 + M \rightarrow D + D + M$	14.63	-	418	[8] ^{b)}
(2) $D_2 + O_2 \rightarrow OD + OD$	12.42	-	163	[8] ^{b)}
(3) $D_2 + O_2 \rightarrow D + DO_2$	13.75	-	206	[8] ^{b)}
(4) $D + O_2 \rightarrow OD + O$	14.57	-	87	[24]
(5) $O + D_2 \rightarrow OD + D$	14.67	-	75	this work
(6) $OD + D_2 \rightarrow D_2O + D$	14.09	-	51	[10] ^{b)}
(7) $OD + OD \rightarrow D_2O + O$	13.45	-	26	[10] ^{b)}
(8) $D + O_2 + M \rightarrow DO_2 + M$	17.85	-0.8	0	[10]
(9) $D + OD + M \rightarrow D_2O + M$	21.88	-2.0	0	[10]

^{a)} Rate coefficient expression is $k = AT^n \exp(-E_a/RT)$. Units are mol/cm³ and s.^{b)} See text.

mechanisms were taken from standard compilations [8,10,21] augmented by a few recent measurements [20,22-24]. Three reactions ((4), (6) and (7)) besides $O + H_2 \rightarrow OH + H$ affect $(d[OH]/dt)_{\max}$ values for the conditions studied. The k_4 expression we used agrees over the temperature range studied to within 20% with the results of more recent studies [25-27], and the rate coefficients of reactions (6) and (7) are not controversial [10,23].

For the higher temperatures used in our $O + D_2 \rightarrow OD + D$ experiments, reactions (1) and (3) also show some sensitivity. For the former we were able to use the Baulch et al. [8] recommendation directly; for the latter we converted the $H_2 + O_2$ expression given by Baulch et al. to a $D_2 + O_2$ expression by calculating the isotope effect using the BEBO method [28]. The rate coefficient expression used for reaction (4) was determined from experiments in rich D_2 - O_2 mixtures that will be reported elsewhere. Rate coefficient expressions for the deuterium reactions (6) and (7) were derived from the Warnatz [10] hydrogen expressions by the same BEBO procedure. The expression so derived for k_6 agrees with the expression derived for the reverse reaction by Fisher and Michael [29] to within a few percent over the 1280-2260 K temperature range studied by them. The insensitive deuterium reactions (2), (8) and (9) were assigned the rate coefficient expressions given by Warnatz [10] for their hydrogen counterparts.

3.2. Sensitivity analysis

In figs. 2a and 2b are shown the results of sensitivity analyses [30] for H_2 - O_2 -Ar and H_2 - N_2O -Ar mixtures performed for the middle of the experimental temperature range by doubling and halving the table 1 rate coefficient expressions. It is seen that the rate coefficient for $O + H_2 \rightarrow OH + H$ has primary significance under both these conditions. In the 250 ppm H_2 -2500 ppm O_2 mixture, 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, while in the 1000 ppm N_2O -500 ppm H_2 mixture three entirely different reactions, $N_2O \rightarrow N_2 + O$, $N_2O + H \rightarrow N_2 + OH$ and $OH + H_2 \rightarrow H_2O + H$, have sensitivities. The two mixtures, with quite different sensitivity spectra, give OH profile results that are shown below to agree very well for the rate coefficient of $O + H_2 \rightarrow OH + H$.

Fig. 2c shows the results of a sensitivity analysis of the maximum slope of OD absorption in the D_2 - O_2 -Ar mixture performed for the middle of the experimental temperature range by doubling the table 2 rate coefficient expressions. The rate coefficient of $O + D_2 \rightarrow OD + D$ has the greatest effect on the maximum slope. The $OD + D_2 \rightarrow D_2O + D$, $D + O_2 \rightarrow OD + O$ and $OD + OD \rightarrow D_2O + O$ reactions also affect the maximum slope of OD profile to a lesser extent.

From this and many similar sensitivity analyses it was estimated that the result reported below for the rate coefficient of $O + D_2 \rightarrow OD + D$ has an uncer-

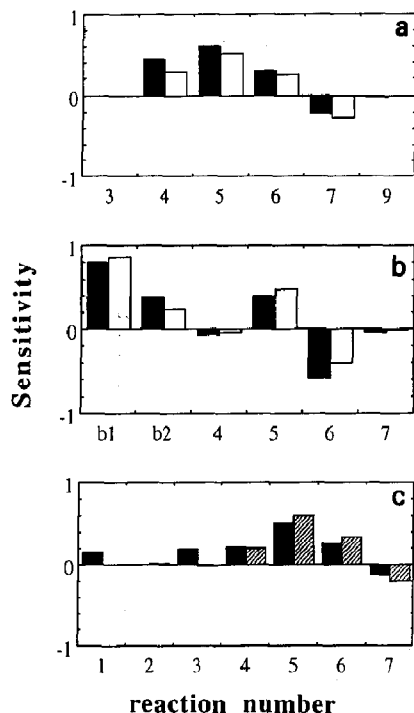


Fig. 2. Logarithmic response sensitivity spectra for maximum rate of OH absorption change. The conditions were 0.025% H_2 -0.25% O_2 mixture, P_1 30 Torr and T_3 2020 K in (a) and 0.05% H_2 -0.1% N_2O mixture, P_1 30 Torr and T_3 1850 K in (b). The filled and open bars were computed by multiplying and dividing the table 1 rate coefficient values by 2. (c) Logarithmic response sensitivity spectra for the maximum rate of OD absorption change. The conditions were 0.0688% D_2 -0.7257% O_2 mixture, P_1 14 Torr and T_3 3390 K for the filled bars and P_1 20 Torr and T_3 2370 K for the striped bars.

tainty of about $\pm 15\%$ from its dependence on the rate coefficients assigned to the other reactions in the mechanism.

3.3. Rate coefficients

Adjustment of the k_5 expression to match the maximum slope values for the 500 ppm H_2 -1000 ppm N_2O and 250 ppm H_2 -2500 ppm O_2 mixtures gave the best fit line (fig. 3) corresponding to the expression

$$k_{5\text{H}} = 3.7 \times 10^{14} \exp(-65 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

which represents the data to within about $\pm 15\%$ from 1600 to 2250 K. This result is in excellent agreement

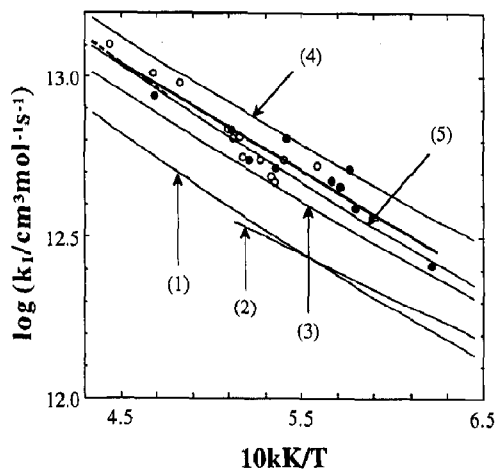


Fig. 3. Comparison of high-temperature rate coefficient expressions for $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$. (\circ) H_2 - O_2 -Ar mixture [11]; (\bullet) N_2O - H_2 -Ar mixture (present study); the bold line is the best fit line to the data for H_2 - O_2 -Ar and N_2O - H_2 -Ar mixtures; (---) ref. [12]; (1) ref. [9]; (2) ref. [8]; (3) ref. [3]; (4) ref. [10]; (5) ref. [5].

with the high-temperature expression of Natarajan and Roth [5] for 1710-3530 K, $3.72 \times 10^{16} T^{-2.17} \exp(-4080/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and for 297-3530 K, $3.87 \times 10^4 T^{2.70} \exp(-3150/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, as well as that of Davidson and Hanson [12] and also agrees well with the rate coefficient of Sutherland et al. [3] within the combined experimental uncertainties.

We were concerned that the $k_{5\text{H}}$ values inferred from our results in the 250 ppm H_2 -2500 ppm O_2 mixture might, despite the conclusions from the initial sensitivity study, be significantly influenced by our choice of $k_{5\text{H}}$ expression, which gives $k_{4\text{H}}$ values the same as the expression of Du and Hessler [27] at 1700 K but becomes about 20% higher at the upper end of the temperature range studied in that mixture. In order to check this possibility we compared computed maximum slope values for the highest temperature experimental profile, with $T_3 = 2134$ K. When the Du and Hessler [27] expression was used instead of that of Fujii et al. [22], the inferred $k_{5\text{H}}$ value was increased about 8%. For lower temperature profiles the $k_{4\text{H}}$ influence became negligible.

Experiments in the D_2 - O_2 -Ar mixture over the temperature range 2370-3390 K were analyzed in the same way. The results for the rate coefficient of

$\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ (fig. 4) [31,32] ^{#1} can be represented by the Arrhenius expression

$$k_{\text{SD}} = 4.7 \times 10^{14} \exp(-74 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

which agrees within an average deviation 6% with the data of Michael [15] in the overlapped temperature range 2300–2500 K. The average deviations between this expression and Pamidimukkala and Skinner's results [2] are 25% at 2300 K and 30% at 2500 K. Combining our 10 data points with 10 calculated from Michael's [15] analytical expression over the temperature range he studied and all seven points of Zhu et al. [32] (see footnote 1) in a non-linear regression gives for the temperature range 340–3390 K

$$k_{\text{SD}} = 1.2 \times 10^8 T^{1.72} \exp(-4880/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

3.4. Kinetic isotope effect

To express the kinetic isotope effect we combine Natarajan and Roth's [5] expression, which represents our k_{SH} data to within 6% maximum deviation in the overlapped temperature range, with the above

k_{SD} expression to get an isotope effect expression for the temperature range 2400–3400 K

$$k_{\text{SH}}/k_{\text{SD}} = 3.1 \times 10^{-2} T^{0.45} \exp(800/T).$$

Our results are compared in fig. 5 to Michael's results over 1500 K, to his equation (eq. (13) in ref. [15]) for the temperature range 350–2500 K,

$$k_{\text{SH}}/k_{\text{SD}} = 3.47 \times 10^{-4} T^{0.97} \exp(1744/T),$$

and to theoretical calculations [6,7,32–36]. While high levels of quantum theory are important for computing the isotope effect correctly at lower temperatures [32–36], in the temperature range of our experiments much simpler approaches lead to the correct result. We computed the isotope effect by the BEBO method [28] using Walch's [37] transition state structure and barrier height, which give the BEBO parameters V^* 12.39 kcal/mol, $r_{\text{H-H}}^*$ 0.9245 Å, $r_{\text{O-H}}^*$ 1.228 Å, H–H–O angle 180°, ω_1 1843 cm⁻¹, ω_2 493 cm⁻¹, and ω_3 1796i cm⁻¹ for OH₂; for OD₂ the vibrational frequencies become ω_1 1345 cm⁻¹, ω_2 350 cm⁻¹ and ω_3 1297i cm⁻¹. The isotope effect expression implied by these parameters,

^{#1} The multiplication factor at the head of column four of table 1 of ref. [32] should be 10¹⁸ rather than 10⁶ [33].

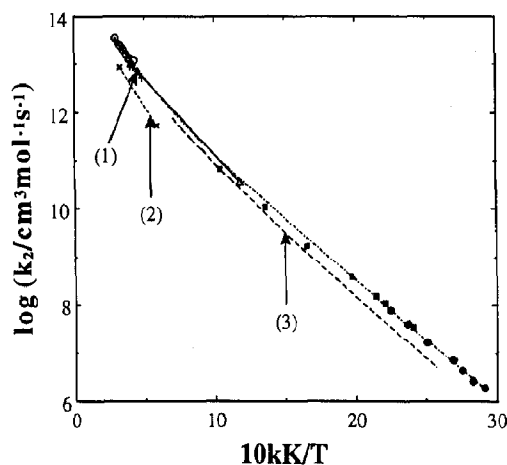


Fig. 4. Comparison of high-temperature rate coefficient expressions for $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$. (O) Present study; (●) ref. [32]; (■) ref. [31]; (–Δ–) ref. [15]; (1) ref. [2]; (2) ref. [13]; (3) ref. [14]; (---) nonlinear least-squares fit of present results together with those of refs. [15,32].

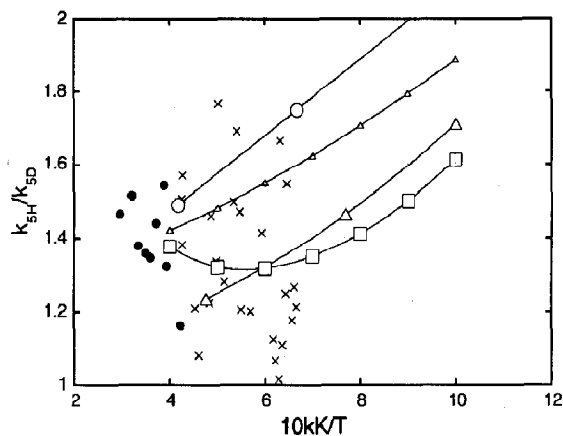


Fig. 5. Isotope effect. (Δ) ref. [6]; (O) ref. [7]; (□) eq. (13) of ref. [15]; (x) k_{SD} data of ref. [15] for temperatures greater than 1500 K, combined with the ref. [3] expression for k_{SH} ; (Δ) BEBO calculation (see text); (●) present results. Several data points from ref. [15] outside the 1.0–2.0 range were omitted for clarity, as was the 2.10 value at 1000 K from ref. [7]. The upward curvature of the eq. (13) line from ref. [15] is an artifact caused by its having been fitted to the modified Arrhenius form to match data spanning all the way out to 28.6 on this x axis scale; it can be seen that the ref. [15] data points themselves are in good agreement with the present results.

$$k_{5H}/k_{5D}(\text{BEBO}) = 0.905 T^{0.04} \exp(563/T),$$

can be seen in fig. 5 to account for the experimentally observed isotope effect in this temperature range just as well as the more ponderous levels of theory. A similar conclusion was reached by Michael [38] on the basis of conventional transition state theory.

Acknowledgement

The authors gratefully acknowledge financial support of this work by the Gas Research Institute, the Robert A. Welch Foundation, and the Korea Science and Engineering Foundation, and an insightful discussion with J.V. Michael.

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