

Rate Constant for $\text{H} + \text{H} + \text{Ar} = \text{H}_2 + \text{Ar}$ from 1300 to 1700 K

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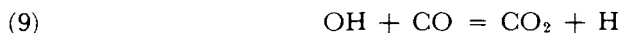
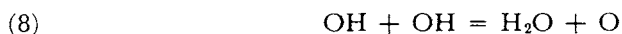
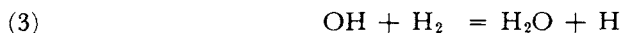
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Abstract

Shock tube experiments on the decay of OH-radical concentration after shock-initiated combustion of $\text{H}_2:\text{O}_2:\text{Ar} = 10:1:89$ mixtures were analyzed to give the rate constant $1 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for the reaction $\text{H} + \text{H} + \text{Ar} = \text{H}_2 + \text{Ar}$ over the temperature range 1300 to 1700 K.

1. Introduction

In a series of shock tube experiments on H_2 and CO combustion it has been found that appropriate parameterization of reaction profiles combined with extensive computer simulations can provide accurate rate constant expressions for individual elementary reactions despite the complexity of the overall reaction mechanisms [1-3]. By utilizing test gas compositions far from stoichiometric, we were able to measure rates for the elementary reactions



In this paper we report the analysis of a set of experiments in "rich" test gas mixtures ($\text{H}_2:\text{O}_2:\text{Ar} = 10:1:89$) to yield a rate constant for the recombination of hydrogen atoms..

The profile studied in these experiments was concentration of OH radicals. For the slow time scale of atom recombination, the OH concentration is closely coupled to the H atom concentration by very fast "shuffling" reactions [4]. It is well known that the behavior of OH in the post-induction period region in combustion of H_2 -rich mixtures is governed almost exclusively by the rate of hydrogen atom recombination. The primary sensitivity of the experimental parameter chosen to characterize the long-term OH profile of our experiments to the specific rate constant for $\text{H} + \text{H} + \text{M}$ was verified by systematically halving and doubling each rate constant in the mechanism. It was found that the experi-

mental parameter was indeed primarily sensitive to the hydrogen atom recombination rate, and to a substantially lesser extent also to the rate constant expressions for two of the shuffling reactions.

2. Experimental

The shock tube and data acquisition procedures have been described in detail elsewhere [1]. Briefly, we used a rectangular aluminum shock tube with 4.0 cm by 10.0 cm cross section. The shock speed was measured with counters triggered by shock arrival at thin-film resistance gauges. The OH concentration was followed by absorption of the 306.7-nm Bi resonance line as monitored by a photomultiplier-narrow-band filter station. The photomultiplier output signal was recorded on a Tektronix 555 oscilloscope with a 1A1 preamplifier. Overall system time response was better than 1 μ s. The test gases had a nominal composition of 10% H₂, 1% O₂, and 89% Ar and deviated from the nominal composition by negligible amounts. The impurity level was < 10 ppm by mass spectrometer analysis. The starting pressure was 2.67 kPa (20 torr) and the shock front temperatures, calculated from the shock velocity, ranged from 1350 to 1670°K.

3. Data Reduction

Sample oscilloscope trace photographs are shown in Figure 1. They show the expected feature of sudden OH appearance, after an induction period, followed by slow decay to the equilibrium OH concentration.

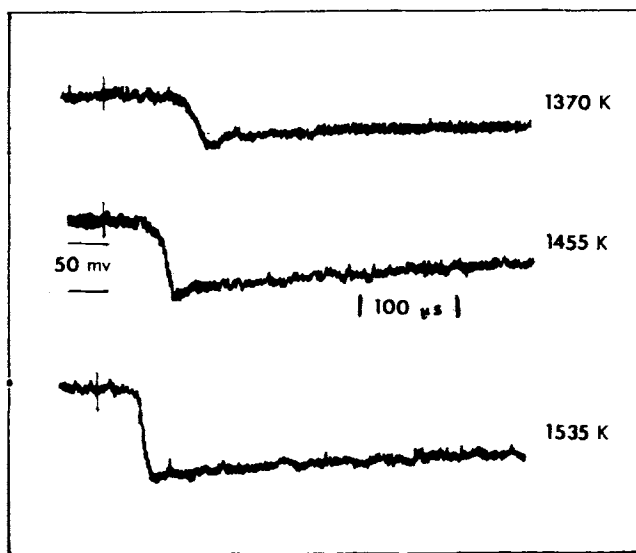


Figure 1. Oscillograms for three experiments. The 1535 K experiment shown is the data point well below the line in Figure 2. Shock arrival is shown by the vertical bars.

The experimental traces were parameterized as follows. The transmitted intensities at the OH maximum, at 100 μs past the maximum, and at 200 μs past the maximum were measured from the photographs. These intensities were substituted into Beer's law and the concentrations thus found were used to calculate a recombination ratio, defined as

$$\text{RATIO} = \frac{[\text{OH}]_{\text{max}+100} - [\text{OH}]_{\text{max}+200}}{[\text{OH}]_{\text{max}}}$$

The experimental RATIO values are plotted against temperature in Figure 2.

The use of ratios of absorbances $[\ln(I_0/I)]$ allows us to get results which do not depend upon knowing the value for the extinction coefficient. In addition we do not require that Beer's law hold exactly. If $\ln(I_0/I) = \epsilon[\text{OH}] - k[\text{OH}]^2$, then

$$\text{absorbance ratio} = \frac{[\text{OH}]_{\text{max}+100} - [\text{OH}]_{\text{max}+200}}{[\text{OH}]_{\text{max}}} \frac{1 + k[\text{OH}]_{\text{max}}/\epsilon}{1 - k[\text{OH}]_{\text{max}}/\epsilon}$$

and the error depends only on the degree to which Beer's law holds and ϵ^{-1} on the exact value of k or ϵ . For our system we have found $\epsilon \sim 1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1}$ and $k \sim 8 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2}$ for 10-cm path length. The largest $[\text{OH}]_{\text{max}}$ is less than $10^{-9} \text{ mole/cm}^3$ so that our error would be $<10\%$ and generally around 3–5%. Since our results have a data scatter of 8–15%, there was no attempt made to refine the absorbance data.

The set of differential equations representing the reaction mechanism, together with the conservation of mass, momentum, and energy, were integrated by a modified Gear-method numerical integration procedure. The flow equations were those of a steady-state boundary layer. In some calculations Mirels' formulas were employed; in others we used the two-dimensional viscous flow model of Ehrhardt [5]. The difference between the two boundary layer formalisms was small, as indicated in Figure 2. The ideal (constant area) flow gave similar results for the RATIO calculations. However, the concentration of hydroxyl radicals was very different in the constant area calculation. The mechanism and set of trial rate constant expressions are given in Table I.

In order to determine the sensitivity of the measurements to the assumed rate constant expressions, we systematically doubled and halved the rate constant of each elementary reaction from the values given in Table I, and recalculated the RATIO values. The results are plotted in Figure 3.

4. Results

It can be seen in Figure 3 that the ratio values are most sensitive to the rate constant expression assumed for the recombination (REC) reaction (Table I), with a lesser sensitivity to the rate constant expressions assumed for reactions (1) and (3). The rate of reaction (1) has been measured in several different investi-

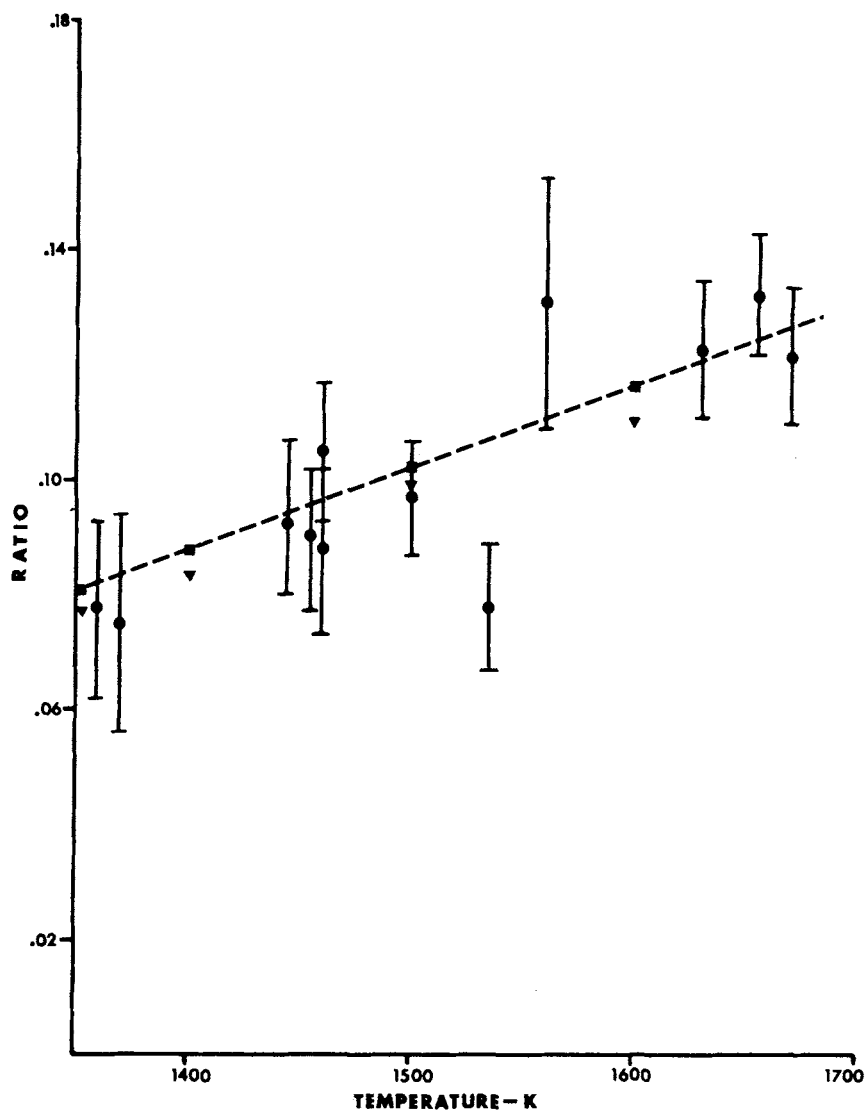


Figure 2. RATIO values as a function of temperature. The error bars represent estimated reading error on each experimental record. Filled squares, dashed line—reference calculations; filled triangles—ratio values calculated using reference set rate constant expressions and Ehrhardt boundary layer. The constant area flow calculations are all within the spread of the triangles. The values for constant area are fractionally lower at the low end of the T range and fractionally higher at the high end of the T range.

TABLE I. Rate constant expressions.^a

REACTION		$k = A T^n \exp(-E_a / RT)$ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ or $\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$		REFERENCE	
		A	n	E_a	
REC	$\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$	1.4×10^{15}	0.	0.	This work
A	$\text{H}_2 + \text{O}_2 = 2 \text{OH}$	1.7×10^{13}	0.	201 kJ (48.15 kcal)	(6)
1	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	1.22×10^{17}	-0.907	69.6 kJ (16.63 kcal)	(7)
2	$\text{O} + \text{H}_2 = \text{OH} + \text{H}$	4.76×10^{17}	-0.907	69.6 kJ (16.63 kcal)	(8)
3	$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	5.2×10^{13}	0.	27 kJ (6.5 kcal)	(1)

^a A complete 16-reaction mechanism was used in all calculations. The other reactions and rate constant expressions are to be found in [1]. The above reactions are the only ones expected and found to play a role in determining the RATIO parameter.

gations, and it is reasonable to assume that it is known to within about 20% in this temperature range [9]. We have recently remeasured the rate of reaction (3), in another study of OH profiles in H_2 -rich mixtures, and our result is in good agreement with other results [1]. The only unknown that affects the ratio values significantly is then the rate of H atom recombination. The rate constant for recombination was systematically varied until calculated and experimental ratio values were in agreement (Fig. 2). Our value for the rate constant of $\text{H} + \text{H} + \text{M}$ is $1.4 \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$, assuming equal efficiency for all M. If we accept the relative third-body efficiencies $\text{H}/\text{Ar} = 20$, $\text{H}_2/\text{Ar} = 2.5$, and $\text{H}_2\text{O}/\text{Ar} = 6$ determined in other work [10–12], we can also analyze the data to get the rate constant of $\text{H} + \text{H} + \text{Ar} = 1 \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$. In both cases our result shows no apparent temperature dependence between 1350 and 1600 K. Figure 3 also shows two other recent determinations of the rate constant of $\text{H} + \text{H} + \text{M}$. Gay and Pratt [12] report $0.33 (+0.32, -0.13) \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$ from 1950 to 2575 K and $0.38 \pm 0.05 \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$ between 1220 and 2370 K. As seen in Figure 2, this rate constant implies ratio values that are much lower than our data. Dixon-Lewis [13] found $4.5 \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$ for all third bodies. Using the ratio $k_{\text{Ar}}/k_{\text{M}}$ assumed in our work, the Dixon-Lewis result for k_{Ar} becomes $3.2 \times 10^{15} \text{ cm}^6 \text{mol}^{-2} \text{s}^{-1}$. Comparing ratio values calculated with this value for recombination to our results (Fig. 3) shows that it yields RATIO values that are far too high.

As a check on the self-consistency of our results, we investigated the time to peak in the OH profile (Fig. 4). The data fall on a straight line on a semilog plot and are reasonably well characterized by the calculations with the reference set of rate constants (Ref.). It is possible to bring this reference line into the data by adjusting the activation energy of k_{A} , but the deviation is so slight that the reference set can be said to find the data. This gives further proof that the k_1

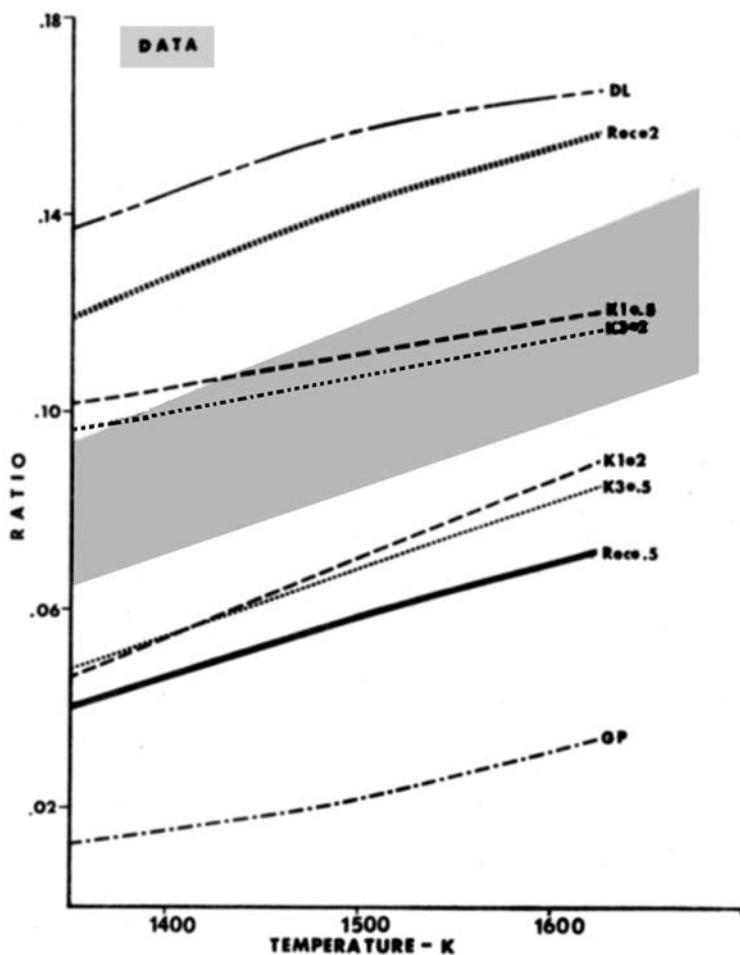


Figure 3. Sensitivity of calculated ratio values to assumed rate constant expressions. The data are represented by gray area. The rates which were doubled or halved are indicated. DL—rate constant of [10]; GP—rate constant of [9].

value would not be more than 15–20% in error. Adjustment of k_1 is therefore not a plausible operation that would move the calculated RATIO line (Fig. 4) out of the data scatter.

Our rate constant for $\text{H} + \text{H} + \text{Ar}$ is compared with previous experimental results in Figure 5. Values extrapolated from higher temperature experiments on H_2 dissociation are also included, as are the theoretical results of Shui and Appleton [21].

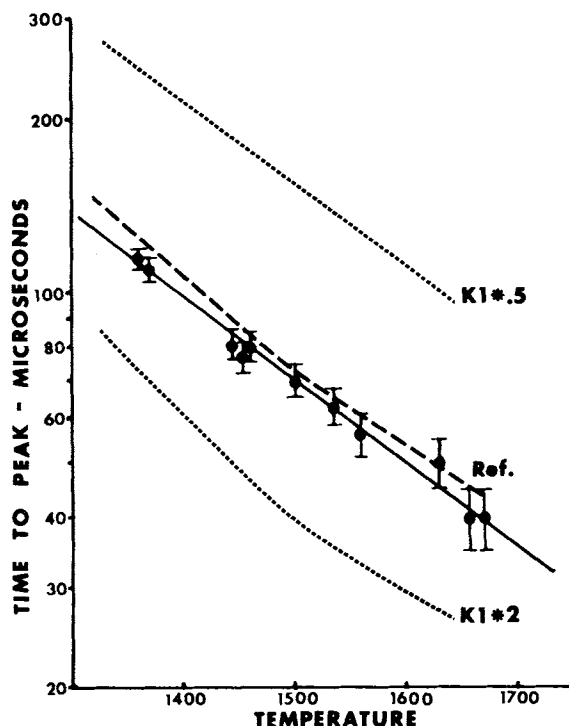


Figure 4. Time to peak values. The halving and doubling of k_A , k_2 , and k_3 fall close to reference line. Of these three, only k_3 has any substantial effect, and it is quite small compared to the effect of k_1 . Solid line—least squares fit through data; dotted line—calculation from reference set of rate constants.

It should be noted in Figure 5 that long extrapolations of experimental rate constant expressions for this reaction are likely to lead to unreasonable values. The agreement between the high-temperature work of Patch [17], Myerson and Watt [20], Breshears and Bird [14], and Sutton [19] breaks down dramatically as their respective expressions are extended beyond their experimental temperature ranges. The difference between the results measured at temperatures below 2000 K reflects the indirect and generally difficult nature of these experiments. None of these experiments measured the H_2 molecule or the H atom concentration. Each of them is subject to assumptions as to the values of k_1 and k_3 , and the shock tube results are also subject to assumptions about the flow conditions. Considering their limitations, we consider the agreement among the various studies to be quite good. A factor-of-two curved band would cover almost all of the 12 studies shown in Figure 5 in their own temperature ranges.

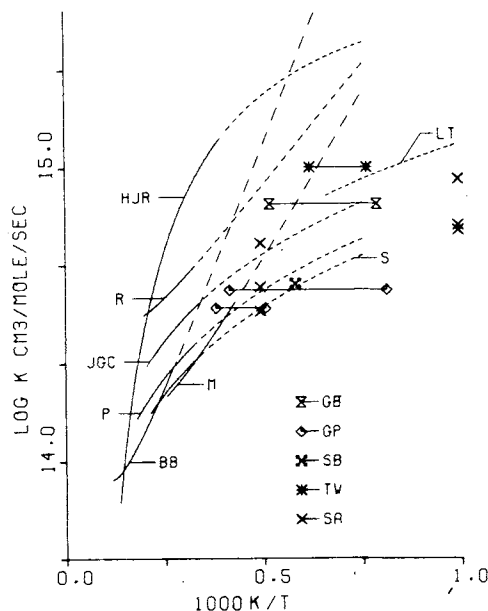


Figure 5. Arrhenius graph for $\text{H} + \text{H} + \text{Ar}$. BB—Reference [14]; HJR—Reference [15]; JGC—Reference [8]; LT—Reference [16]; GB—Reference [7]; GP—Reference [9]; P—Reference [17]; R—Reference [18]; S—Reference [19]; M—Reference [20]; SA—Reference [21]; SB—Reference [4]; TW—this work. Solid lines—reported rate expressions over experimental temperature ranges; dashed lines—extrapolations into other T ranges.

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