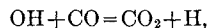
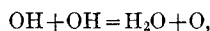
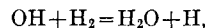


ELEMENTARY REACTION RATES FROM POST-INDUCTION-PERIOD PROFILES IN SHOCK-INITIATED COMBUSTION

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Elementary reaction rates were measured by following the reaction profiles in the transition zone between the exponential growth and recombination zones in the shock-initiated combustion of $\text{H}_2:\text{O}_2:\text{Ar}=10:1:89$, $\text{H}_2:\text{O}_2:\text{Ar}=1:10:89$, $\text{H}_2:\text{O}_2:\text{CO}:\text{Ar}=1:5:3:91$, and $\text{H}_2:\text{O}_2:\text{CO}_2:\text{Ar}=5:1:4:90$ mixtures in the temperature range 1200°–2500°K. Rate-constant expressions for the reactions



were found to be $5.2 \times 10^{13} \exp(-6.5 \text{ kcal}/RT)$, $5.5 \times 10^{13} \exp(-7.0 \text{ kcal}/RT)$, and $4.0 \times 10^{12} \times \exp(-8.0 \text{ kcal}/RT) \text{ cm}^3/\text{mole}/\text{sec}$, respectively. None of these expressions extrapolate linearly on an Arrhenius graph to the room-temperature data. Possible interpretations of nonlinear Arrhenius graphs are discussed.

Introduction

The mechanisms of the high-temperature combustion reactions of small molecules are now generally regarded as quite well known, and over the past decade considerable progress has been made in obtaining rate-constant expressions for many of the important elementary reactions. Shock-tube experiments have contributed most of the recent kinetics data. In these experiments, attention was usually directed either to the exponential growth zone of the explosion,^{1,2} or to the recombination zone³; in the relatively few studies in which a total reaction profile was investigated, mechanistic complexities have usually led to a considerable degree of ambiguity in the assignment of rate constants to specific elementary reactions.⁴

Hamilton and Schott showed, on theoretical grounds, that values for certain rate-constant ratios could be obtained from the analysis of atom or radical profiles in the transition zone between the exponential growth and recombination zones of the shock-initiated combustion of $\text{H}_2\text{--O}_2$ mixtures in which the $\text{H}_2:\text{O}_2$ ratio is far from stoichiometric.⁵ In a subsequent experi-

mental study of lean ($\text{H}_2:\text{O}_2 = 1:10$) mixtures, we used their ideas to derive information about the rates of elementary reactions (2) and (8)⁶ (Table I). Since that time, additional information from exponential growth constant studies has come forth; in particular, values of k_2 well above what seemed reasonable then now appear to be well established. Also, the shock-tube community has become aware that the effects of boundary-layer growth on shock flow have to be taken into account in computer analysis of shock-tube rate data.² Utilizing this information permits a more-sophisticated, and more-successful, analysis of our original data, which is reported here. We have also found that by careful tuning of a Bi (306.7-nm) source lamp it is possible to obtain sufficient signal-to-noise ratio to measure the parameters of the very small OH radical spikes that occur in the shock-initiated combustion of rich ($\text{H}_2:\text{O}_2 = 10:1$) mixtures. These experiments provide a measurement of the rate-constant ratio k_1/k_3 (Table I).

We showed in an earlier paper that the shock-initiated $\text{H}_2\text{--O}_2$ reaction could serve to generate a reactive environment in which slower reactions of H or O atoms or OH radicals could be followed.⁷

TABLE I

Rate-constant expressions

	Reaction		Rate constant (cm ³ mole ⁻¹ sec ⁻¹ or cm ⁶ mole ⁻² sec ⁻¹)	Ref.
01	H ₂ +M=2 H+M	M=Ar, O ₂	$k_{01}=2.23 \times 10^{12} T^{1/2} \exp(-92.6 \text{ kcal}/RT)$	a
		M=H ₂	$k_{01A}=2.5k_{01}$	b
		M=H	$k_{01B}=20k_{01}$	b
		M=H ₂ O	$k_{01C}=6k_{01}$	c
02	O ₂ +M=2 O+M	M=Ar, H ₂	$k_{02}=1.85 \times 10^{11} T^{1/2} \exp(-95.7 \text{ kcal}/RT)$	d
		M=O	$k_{02A}=30k_{02}$	d
		M=O ₂	$k_{02B}=10k_{02}$	d
03	H ₂ +M=H ₂ *+M		$k_{03A}=4.11 \times 10^{12} \exp(-49.6 \text{ kcal}/RT)$	e
	H ₂ *+O ₂ =2 OH		$k_{03B}=5.0 \times 10^{10} T^{1/2}$	e
1	H+O ₂ =OH+O		$k_1=4.01 \times 10^{13} \exp(-12.3 \text{ kcal}/RT)$	f
2	O+H ₂ =OH+H		$k_2=1.6 \times 10^{14} \exp(-13.5 \text{ kcal}/RT)$	see text
3	OH+H ₂ =H ₂ O+H		$k_3=5.2 \times 10^{13} \exp(-6.5 \text{ kcal}/RT)$	see text
4	H+O ₂ +M=HO ₂ +M	M≠H ₂ O	$k_4=2.0 \times 10^{15} \exp(0.87 \text{ kcal}/RT)$	g
		M=H ₂ O	$k_{4A}=25k_4$	g
5	H+OH+M=H ₂ O+M	M≠H ₂ O	$k_5=7.5 \times 10^{23} T^{-2.6}$	h
		M=H ₂ O	$k_{5A}=20k_5$	h
6	HO ₂ +H=2 OH		$k_6=6.0 \times 10^{13}$	i
7	HO ₂ +O=OH+O ₂		$k_7=1.0 \times 10^{13}$	i
8	OH+OH=H ₂ O+O		$k_8=5.5 \times 10^{13} \exp(-7.0 \text{ kcal}/RT)$	see text
9	CO+OH=CO ₂ +H		$k_9=4.0 \times 10^{12} \exp(-8.0 \text{ kcal}/RT)$	see text
10	CO+O ₂ =CO ₂ +O		$k_{10}=3.14 \times 10^{11} \exp(-37.6 \text{ kcal}/RT)$	e
11	H ₂ +HO ₂ =H ₂ O+OH		$k_{11}=2.0 \times 10^{11} \exp(-24 \text{ kcal}/RT)$	j
12	CO+O+M=CO ₂ +M		$k_{12}=3.4 \times 10^{11} \exp(23.4 \text{ kcal}/RT)$	k

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 j. V. V. Voevodsky, *Seventh Symposium (International) on Combustion*, p. 34, Butterworths, 1959.
 k. M. C. Lin and S. H. Bauer, *J. Chem. Phys.* **50**, 3377 (1969).

These experiments have now been subjected to a more-sophisticated data analysis, as well, to derive a rate constant for Reaction (9) (Table I).

The general result of these studies is a demonstration that the drastic changes in reactant concentrations and in reaction stoichiometry at the conclusion of the exponential growth zone of an H₂-O₂ explosion permit an unusual chance to measure rate parameters for elementary reactions, whereby the results are but slightly affected by such uncertainties as may still exist in the pertinent reaction mechanisms. A par-

ticular result of more than passing interest is a demonstration that using the "Arrhenius Law" to extrapolate rate constants from temperatures over 1000°K back to room temperature, or *vice versa*, is invalid, as was suggested recently on theoretical grounds.⁸

Experimental

The experiments were done in incident shock waves using an apparatus described previously.⁷

Gas mixtures were prepared manometrically from the purest gases obtainable commercially. The nominal compositions, starting pressures, and temperature ranges studied were:

"Rich mixture"

$\text{H}_2:\text{O}_2:\text{Ar} = 10:1:89$, $p_0 = 20$ torr,
 $1200 < T < 1600^\circ\text{K}$;

"Lean mixture"

$\text{H}_2:\text{O}_2:\text{Ar} = 1:10:89$, $p_0 = 10$ torr,
 $1200 < T < 2500^\circ\text{K}$;

"Reducing mixture"

$\text{H}_2:\text{O}_2:\text{CO}_2:\text{Ar} = 5:1:4:90$, $p_0 = 10$ torr,
 $1500 < T < 2100^\circ\text{K}$;

"Oxidizing mixture"

$\text{H}_2:\text{O}_2:\text{CO}:\text{Ar} = 1:5:3:91$, $p_0 = 10$ torr,
 $1500 < T < 2100^\circ\text{K}$.

The exact compositions were used to compute shocked-gas properties from the measured shock velocity.

Observations were made of OH-radical profiles by absorption spectroscopy⁶; of CO_2 profiles by monitoring the ν_3 thermal-emission intensity, which was isolated from other emissions by an interference filter at $4.2\ \mu\text{m}$, and calibrated by independent experiments with CO_2 -Ar mixtures; and of $[\text{CO}][\text{O}]$ profiles by monitoring the carbon monoxide flame spectrum emission through a Corning 5-58 filter. Conventional procedures were used to record and reduce the data. Sample records are shown in Fig. 1.

In order to compare theory with experiment it was expedient to characterize the profiles with appropriate parameters. The eight parameters discussed in this paper are defined as follows (see Fig. 1): R_r and R_l , the spike height ratio of the OH profiles in the rich and lean mixtures, respectively, are defined as the OH-concentration maximum divided by the back-extrapolated OH concentration at the time of the maximum; D_r and D_l are the widths of the OH spikes in the rich and lean mixtures, measured at half-height and expressed in laboratory time; S_o is the CO_2 concentration change in the oxidizing mixture corresponding to an IR emission intensity change from one-third the maximum value to two-thirds the maximum value, divided by the laboratory time required for this change; S_r is the CO_2 concentration change in the reducing mixture corresponding to an IR-emission

intensity change from two-thirds the difference between the precombustion value and the equilibrium value to one-third of this difference, divided by the laboratory time required for this intensity change; T_o is the laboratory time of maximum visible emission intensity in the oxidizing mixture minus the laboratory time at half the maximum intensity; T_r is the laboratory time at attainment of two-thirds the maximum visible emission intensity in the reducing mixture minus the laboratory time at one-third the maximum intensity.

The R_r and R_l values are but slightly dependent on the value of the Beer's Law coefficient, since only small concentration changes are involved, and thus afford an almost direct correlation between oscilloscope trace photographs and computed OH profiles. They were used in preference to the D_r and D_l values for data analysis, due to this direct correlation, and also due to the facts that the experimental D_r and D_l values have less accuracy and that computed D_r and D_l values depend on the assumed-flow model. All final results are concordant, however, with the experimental D_r and D_l values. The experimental S_o and S_r values rely upon the calibrations coupling IR-emission intensity to CO_2 concentration and temperature; the computed values depend on the flow model used to provide the laboratory time scale. The computed T_o and T_r values depend on the flow model and also on the validity of the conventional assertion that the intensity of the carbon monoxide flame spectrum is proportional to the concentration product $[\text{CO}][\text{O}]$. The primary data analysis for the rate of Reaction (9) was done with S_o . The parameters S_r , T_o , and T_r are also sensitive to k_9 ; all final results are concordant with the experimental values of all four parameters, as will be described in detail in a later publication.

For comparison with experiment, values for the eight parameters were obtained from numerical integrations of the differential equations describing the chemical kinetics and the shocked-gas flow. The mechanisms assumed were appropriate combinations taken from the over-all list of elementary reactions shown in Table I. All computations were done using Mirels' limiting-flow equations for a laminar boundary layer,⁹ which was found by heat-transfer-gauge observations to exist throughout the flow duration for all experimental conditions discussed here. The substantial effect of the flow model on conclusions drawn from profiles at substantial distances from the shock front has been noted before,¹⁰ and was confirmed in our computer experiments. Large differences in all eight parameters were found between predictions

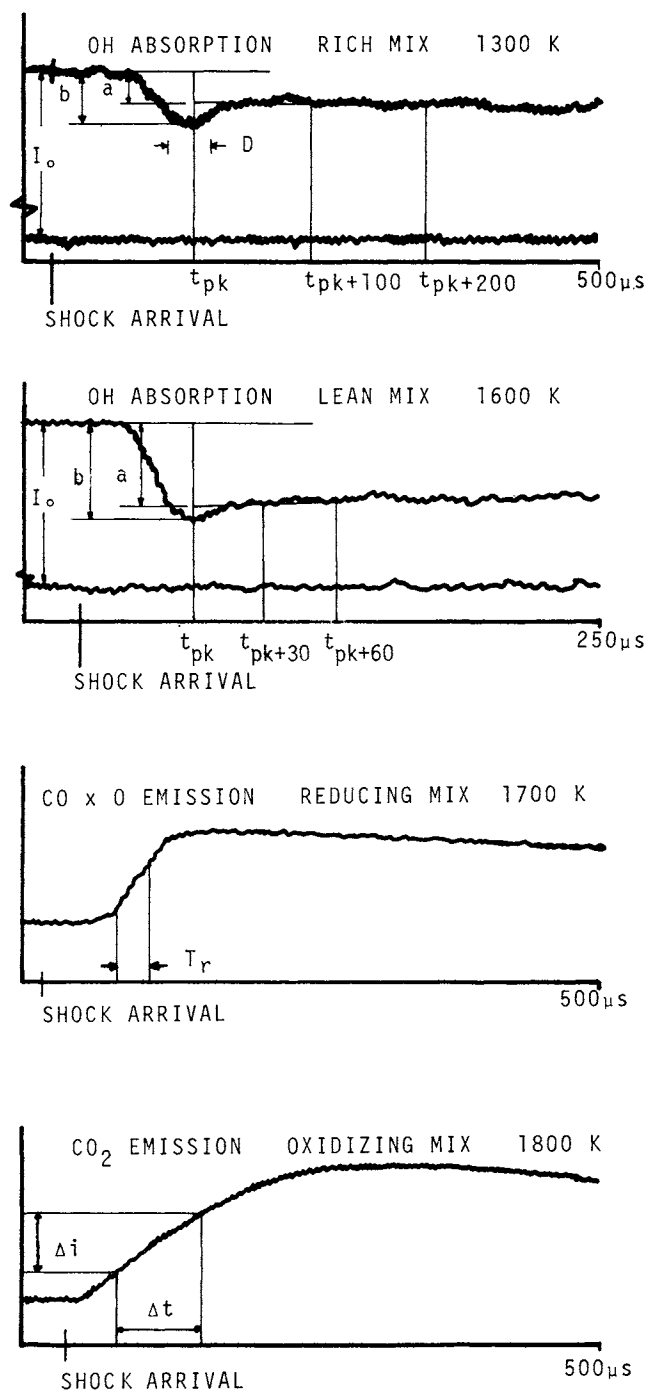


FIG. 1. Sample oscilloscope traces. The R_r and R_i values were calculated from the indicated a and b lengths from $R = \ln [(I_0 - b)/(I_0 - a)]$. The S_o values were calculated from the indicated Δi and Δt values, using results of calibrations runs to convert Δi to ΔC , with the formula $S_o = \Delta C / \Delta t$.

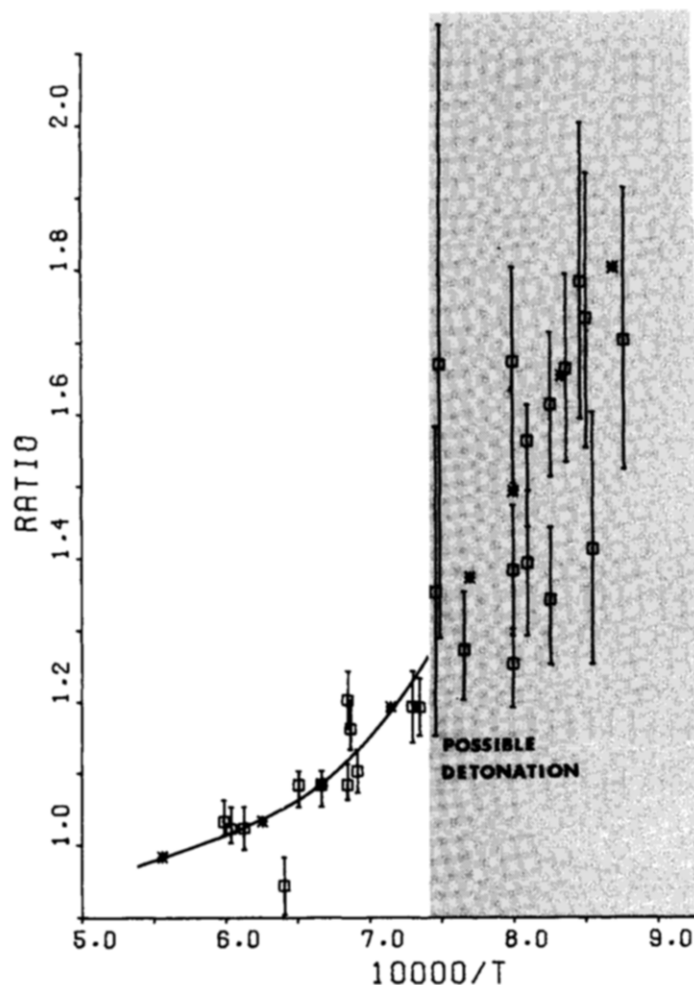


FIG. 2. Spike ratios for the rich mixture. The line was calculated with the set of rate-constant expressions shown in Table I. The error bars were assigned from the maximum excursions of the a and b measurements (Fig. 1) compatible with each experimental record (cf. Ref. 6). The temperature used for reference is the no-reaction shock temperature.

made assuming ideal flow and corresponding ones made taking the effect of boundary-layer growth into account; the differences between the predictions assuming laminar and assuming turbulent flow were, to our surprise, relatively small. The starting points for the rate constants used in the calculations were various literature values, as indicated in the citations for Table I.

Results

We consider first the rich-mixture OH spike ratios R_r , shown in Fig. 2. At the lower end of

the temperature range studied (below 1300°K), they exhibit more scatter than can be accounted for as random temperature errors or oscilloscope trace noise. This scatter may well exhibit the onset of flow instability.¹¹ As noted by Hamilton and Schott,⁵ the small excursion of the R_r values above unity is compensated by the great sensitivity of computed R_r values to the ratio k_1/k_3 .

Communicating our conclusions about the sensitivity of calculated parameters to assumed rate constants in short compass is difficult. In order to convey at least a general impression of the situation as a whole, we display in Table II the effects on the computed parameters of

TABLE II

Sample set of sensitivities of post-induction parameters to assumed rate constants*

	k_1	k_2	k_3	k_8	Recombination	k_9
R_r at 1300°K	1.60 0.77	1.01 0.99	0.78 1.65	1.00 1.00	1.08 0.90	
D_r at 1300°K	0.70 0.80	1.05 1.00	0.60 1.10	1.00 1.00	1.15 0.90	
R_i at 1650°K	1.03 0.95	1.15 0.90	0.97 1.03	0.90 1.15	1.00 1.00	
S_o at 1800°K	0.97 1.01	0.97 1.01	1.01 0.98	1.02 0.99	1.00 1.00	1.90 0.60
T_r at 1600°K	1.05 0.80	0.95 1.15	0.95 1.10	0.95 1.03	1.00 1.00	0.60 1.40

* Each entry denotes the factor change in a parameter when a rate constant is doubled (upper left) or halved (lower right). The reference rate constant set in each case is that of Table I. "Recombination" refers to all termolecular reactions together. The duration D_r is seen to be unsuitable for analysis. All sensitivities change with temperature, as will be detailed in later papers from this laboratory.

doubling and halving each of the rate constants. Reaction conditions in the middle of the temperature range studied in each mixture were chosen for this comparison, using for reference the standard-rate-constant set with parameters shown in Table I. It can be seen that the computed R_r values depend in a substantially reciprocal fashion on k_1 and k_3 , to a small degree on k_2 and the recombination rates, and essentially not at all on the assumed values of other rate constants.

It has been found that exponential growth constants in the shock-initiated combustion of very rich H_2 - O_2 mixtures depend almost entirely on the value of k_1 .^{1,2,12,13} Since the temperature range and other conditions of the studies were about the same as those of the present experiments, a rate-constant expression for k_1 obtained from exponential growth constants can be used to reduce the data analysis for R_r to a one-parameter problem, in order to derive an expression for k_3 . We chose Schott's expression.¹ The parameters of the k_3 expression were then varied until an optimum fit to the R_r data over the temperature range 1200°–1800°K was achieved (Fig. 2). The resulting expression is $k_3 = 5.2 \times 10^{13} \exp(-6.5 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, with an error estimated from the data scatter of $\pm 20\%$. It is compared with other determinations of k_3 in Fig. 3. The corresponding expression for k_1/k_3 is $k_1/k_3 = 0.77 \times \exp(-5.8 \text{ kcal}/RT) \pm 15\%$. If an activation

energy for k_1 greater than Schott's value of 12.3 kcal is preferred, then, by simple algebra, the local value of the activation energy for k_3 would have to be increased by the same amount; however, the limited accuracy and temperature range of our data severely limit the accuracy of our k_3 activation-energy determination.

The lean-mixture spike-height ratios are displayed in Fig. 4. Again, one notes the scatter of the results at lower temperatures, here below 1400°K. As in our previous analysis of lean-mixture OH profiles,⁶ it is found that R_i is sensitive to the assumed values of k_2 and k_8 . There is a small degree of sensitivity to k_1 and k_3 (Table II). We reduced the analysis of the R_i data to a one-variable problem by accepting the k_3 expression from the foregoing rich-mixture experiments, coupling this with Schott's expression for the rate-constant product $k_2 k_8$,¹ and varying the parameters of the k_8 expression to obtain an optimum fit to the R_i data over the temperature range 1500°–2000°K. The resulting expression is $k_8 = 5.5 \times 10^{13} \exp(-7.0 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, with an error estimated from the data scatter of $\pm 25\%$. It is compared with other determinations in Fig. 5.

In contrast to the situation with the rich- and lean-mixture OH-profile parameters, $[CO_2]$ and $[CO][O]$ profile parameters in both the oxidizing and reducing mixtures were found to be sensitive almost entirely to a single rate constant, k_9 (Table II). Of the four sets of parameters, we

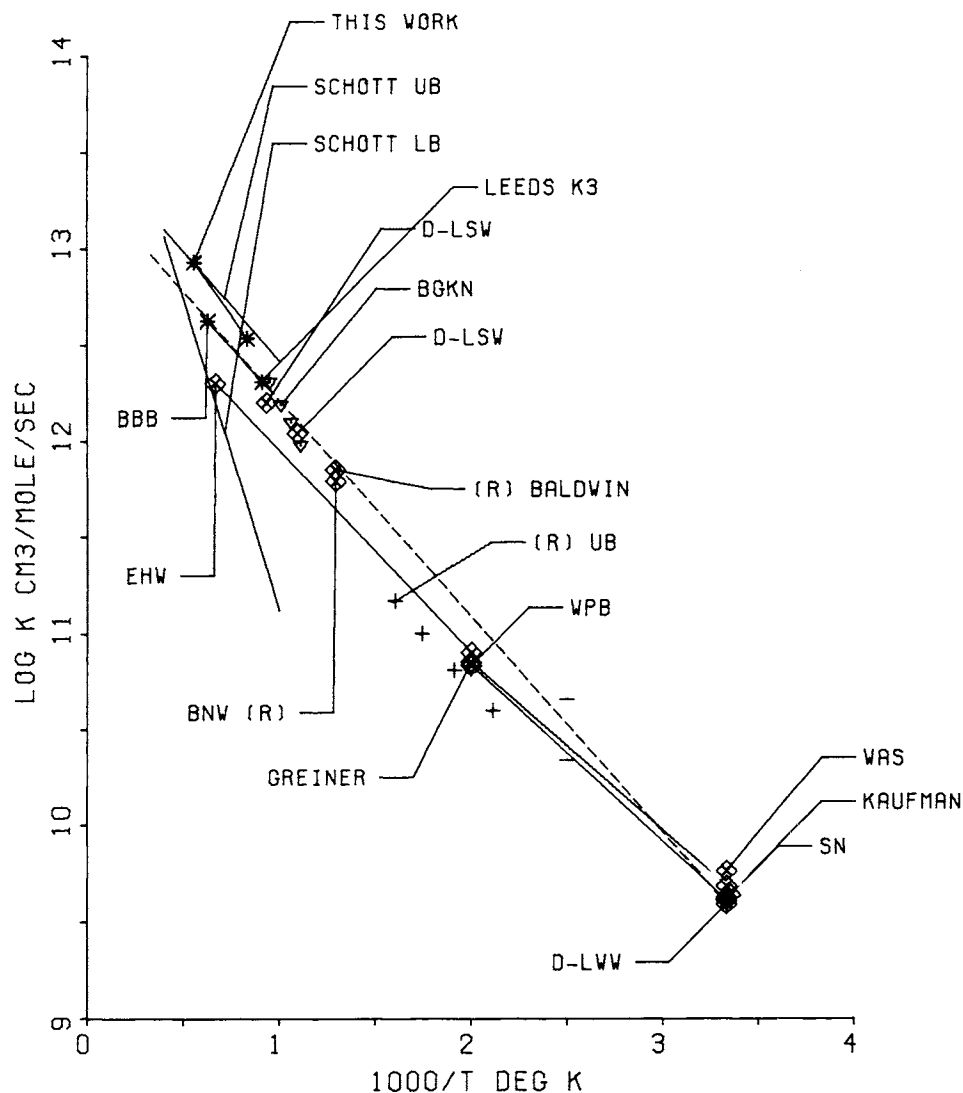


FIG. 3. Arrhenius graph for $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$. The symbols refer to literature data as follows. (R) Baldwin, quoted by G. Dixon-Lewis et al., *J. Chem. Phys.* 44, 2877 (1966); BBB, Ref. 2; BGKN, V. P. Balakhinin, Yu. M. Gershenzon, V. N. Kondratiev, and A. B. Nalbandyan, *Doklady Akad. Nauk (SSSR)* 170, 1117 (1966); BNW (R), R. R. Baldwin, A. C. Norris, and R. W. Walker, *Eleventh Symposium (International) on Combustion*, p. 889, The Combustion Institute, 1967; D-LSW, G. Dixon-Lewis, M. M. Sutton, and A. Williams, *J. Chem. Soc.* 1965, 5724 (upper); *Tenth Symposium (International) on Combustion*, p. 495, The Combustion Institute, 1965 (lower); D-LWW, G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *J. Chem. Phys.* 44, 2877 (1966); EHW, K. H. Eberius, K. Hoyer mann, and H. Gg. Wagner, *Thirteenth Symposium (International) on Combustion*, p. 713, The Combustion Institute, 1971; GREINER, N. R. Greiner, *J. Chem. Phys.* 51, 5049 (1969); KAUFMAN, F. Kaufman, *Ann. Geophys.* 20, 106 (1964); LEEDS, D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, *Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems*, No. 2, p. 9, Leeds University, 1968; SCHOTT LB and SCHOTT UB, lower and upper bounds given by G. L. Schott, Ref. 1; (R) UB, A. Y. M. Ung and R. A. Back, *Can. J. Chem.* 42, 753 (1964); WAS, H. Wise, C. M. Ablow, and K. M. Sancier, *J. Chem. Phys.* 41, 3569 (1964). WPB, E. L. Wong, A. E. Potter, and F. E. Belles, NASA TN D-4162, 1967, and NASA TN D-5707, 1970. The horizontal bars denote the error limits suggested in the Leeds report. The data denoted (R) refer to measurements of the rate-constant ratio k_2/k_3 , converted to k_3 values using our expression for k_3 , connected to the low-temperature data by a smooth curve (cf. Fig. 7). All the data except for the EHW expression would be represented by a single curved line to about $\pm 20\%$, well within the error limits of the cited investigations. The line denoted THIS WORK is referenced to Schott's (Ref. 1) expression for k_1 , and would be shifted as indicated in the text for other k_1 values.

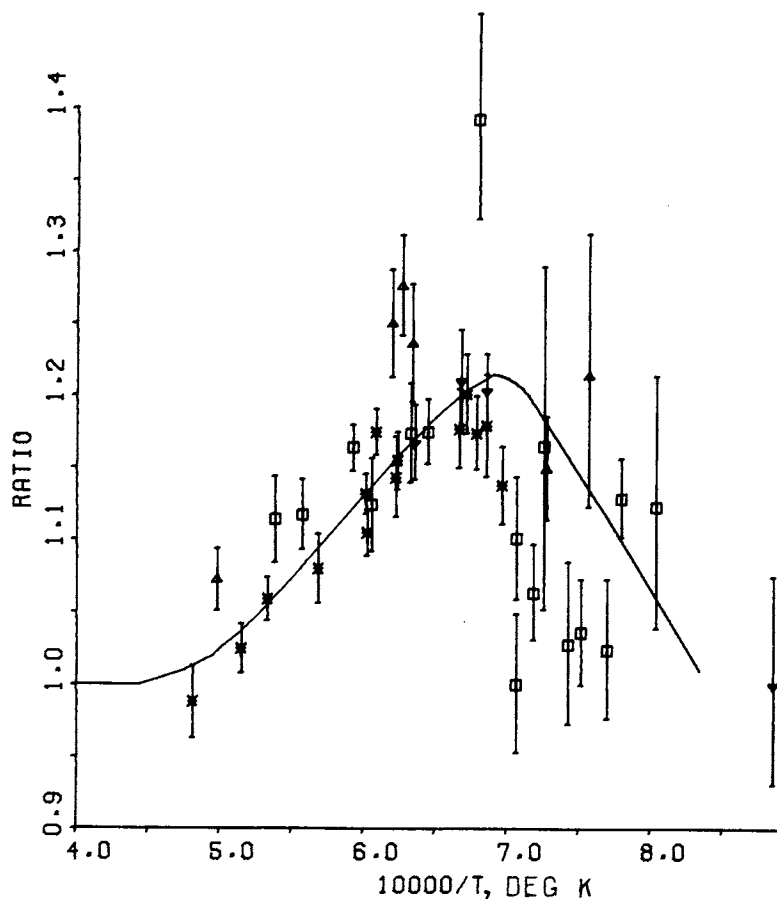


FIG. 4. Peak ratios R_1 for $\text{H}_2:\text{O}_2:\text{diluent}=1:10:89$, starting pressure 10 torr. The data points correspond to mixtures as follows: \square , diluent Ar; *, diluent Ar, experimental gas admitted through a liquid-nitrogen trap; \triangle , diluent He:Kr=17:72; ∇ , diluent He:Kr=24:65. The curve was calculated using the rate-constant set of Table I. The temperature used for reference is the no-reaction shock temperature.

display the most uniquely sensitive data of all, S_o , in Fig. 6. Using the rate-constant expressions for $\text{H}_2\text{-O}_2$ chemistry, derived from the rich- and lean-mixture OH profiles, the k_9 parameters were adjusted until an optimum fit to the S_o data over the temperature range 1500°–2000°K was obtained. The same expression also gives an excellent fit to the S_r , T_o , and T_r data. Our result is $k_9 = 4.0 \times 10^{12} \exp(-8.0 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, with an error estimated from the data scatter of $\pm 25\%$. It is compared with previous results in Fig. 7.

The computer simulations were done, in general, assuming the nominal gas compositions, starting pressures, and limiting laminar boundary layer gas flow. It was found in auxiliary computations that the deviations from these conditions pertaining to the specific experiments were too small to have appreciable effects on the derived rate-constant expressions.

Discussion

High-temperature data for k_3 and k_9 have been available for some time. While the present results are not notably different in magnitude from earlier results, the relative freedom from mechanistic complications afforded by the present experiments lends a substantial additional degree of assurance that the expressions derived here really represent the rates of these two key combustion reactions in the temperature ranges studied. The expression derived for k_3 is the first high-temperature result for this reaction.

It has been noted from time to time, in various contexts, that high-temperature experiments, shock-tube experiments in particular, sometimes yield parameters for the Arrhenius expression $k = A \exp(-E_a/RT)$ that, when extrapolated to temperatures like $300^\circ \pm 200^\circ\text{K}$, appear to indicate serious or even flagrant disagreement

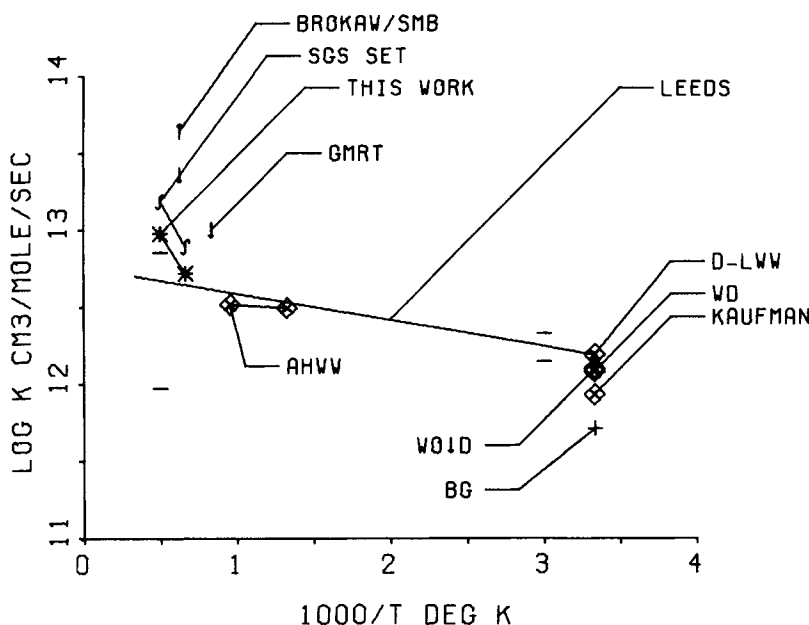


FIG. 5. Arrhenius graph for $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$. The symbols refer to literature data as follows. AHWW, E. A. Albers, K. Hoyer, H. G. Wagner, and J. Wolfrum, *Thirteenth Symposium (International) on Combustion*, p. 81, The Combustion Institute, 1971; BG, J. E. Breen and G. P. Glass, *J. Chem. Phys.* **52**, 1082 (1970); BROKAW/SMB, Approximate range calculated by R. S. Brokaw, *Eleventh Symposium (International) on Combustion*, p. 1063, The Combustion Institute, 1967, from data of B. F. Myers, E. R. Bartle, and K. G. P. Sulzmann, *J. Chem. Phys.* **42**, 3969 (1965); **43**, 1220 (1965); D-LWW, G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966); GMRT, W. C. Gardiner, Jr., K. Morinaga, D. L. Ripley, and T. Takeyama, Ref. 6; KAUFMAN, F. Kaufman, *Ann. Geophys.* **20**, 106 (1964); LEEDS, D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, *Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems*, No. 2, Leeds University, 1968; WD, A. A. Westenberg and N. de Haas, *J. Chem. Phys.* **43**, 1550 (1967); WO'D, W. E. Wilson and J. T. O'Donovan, *J. Chem. Phys.* **43**, 1550 (1965). All the room temperature data is derived from the decay rate of OH radicals generated by titration of H atoms with NO_2 , a system that has been subjected to serious criticism; cf. M. F. R. Mulcahy and R. H. Smith, *J. Chem. Phys.* **54**, 5215 (1971). The AHWW expression was derived from their results on the rate of the reverse reaction. The horizontal bars denote the error limits suggested in the Leeds report.

with rate studies done at these lower temperatures. Usually this disagreement has been ascribed to errors in the shock-tube temperature measurements, incorrect data interpretation, mechanistic uncertainties, or other assumed but unstated flaws in the shock-tube technique. Our Arrhenius parameters for k_3 , which do not yield an extrapolation to the room-temperature data (Fig. 7), seem to us to be so free of experimental or mechanistic complications that criticisms of this kind are completely pointless. The k_3 and k_8 results reported here also support nonlinear Arrhenius behavior, as do the most recent results on k_1 , k_2 , and k_{10} . It appears to be a general fact that straight lines do not connect

rate-constant expressions above 1000°K to low-temperature data.

Traditionally, chemists regard anything but a slight amount of curvature in a graph of $\log k$ versus $1/T$ as heresy, although even Arrhenius himself pointed out that there are no fundamental laws of nature that force such graphs to be straight, or nearly straight, lines.¹⁴ One reason for this viewpoint is the specious textbook argument, traceable to van't Hoff,¹⁵ that rate constants must depend on temperature as do equilibrium constants. The hypothesis introduced by Arrhenius, that at least one of the reactants must be "activated," with expenditure of energy, before reaction can occur, does lead by valid

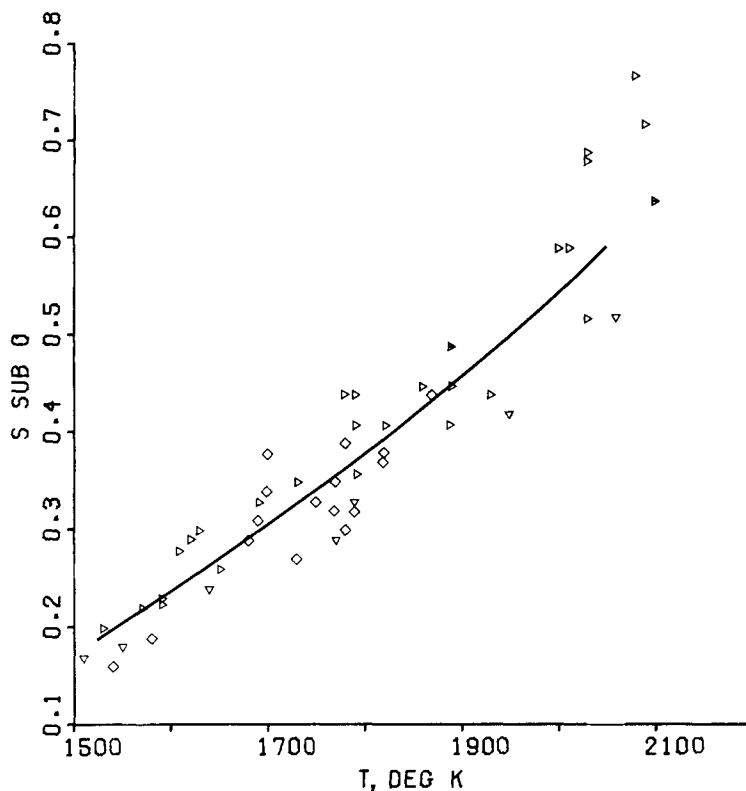


FIG. 6. CO_2 -profile parameter S_0 for $\text{H}_2:\text{O}_2:\text{CO}:\text{Ar}=1:5:3:91$, starting pressure 10 torr. The different data-point symbols are from mixtures with slightly different actual compositions, but with the same nominal composition. The line was calculated using the rate-constant set of Table I. The temperature is the no-reaction shock temperature. The units of S_0 are moles/liter/sec, laboratory time.

thermodynamic or statistical mechanics arguments to the conclusion that the only possible deviation from a straight line in a $\log k$ versus $1/T$ graph for an elementary reaction is that due to the usually rather small temperature dependence of the energy of activation, providing that the "activated" species is unique and is in chemical equilibrium with its unactivated precursor.

It is possible that the nonlinear behavior of the k_9 graph (Fig. 7), and also the k_3 and k_8 graphs (Figs. 3 and 5), may be due to temperature dependence of an energy of activation in this sense. The effect is magnified visually for k_8 and k_9 by the fact that the activation energy measured at low temperatures is almost zero for these reactions. The activated complex theory recently advanced for Reaction (9) does predict the observed behavior essentially on this basis.⁸

An alternative interpretation, based on collision theory, is more attractive to us. At low temperatures, bimolecular reactions may proceed

predominantly through ground vibrational states of the reactant molecules, while at high temperatures the dominant channels are through excited vibrational states of one or both molecules. The greatly enhanced equilibrium populations and vibrational relaxation rates at high temperatures permit, in effect, a mechanism change when the thermal energy and the relaxation rates increase sufficiently. In this interpretation, the reason for the change in apparent activation energy is dynamic rather than energetic in origin.

Such a proposal is not really novel, although previously proposed mechanisms requiring vibrational excitation prior to reaction have been concerned with three-center reactions or with four-center exchange reactions, rather than with four-center atom-transfer reactions, and in addition have assumed that a substantial energy barrier to reaction has to be overcome.^{16,17} These previous studies have also considered the apparent activation energy to be constant. The results of the experiments reported here demon-

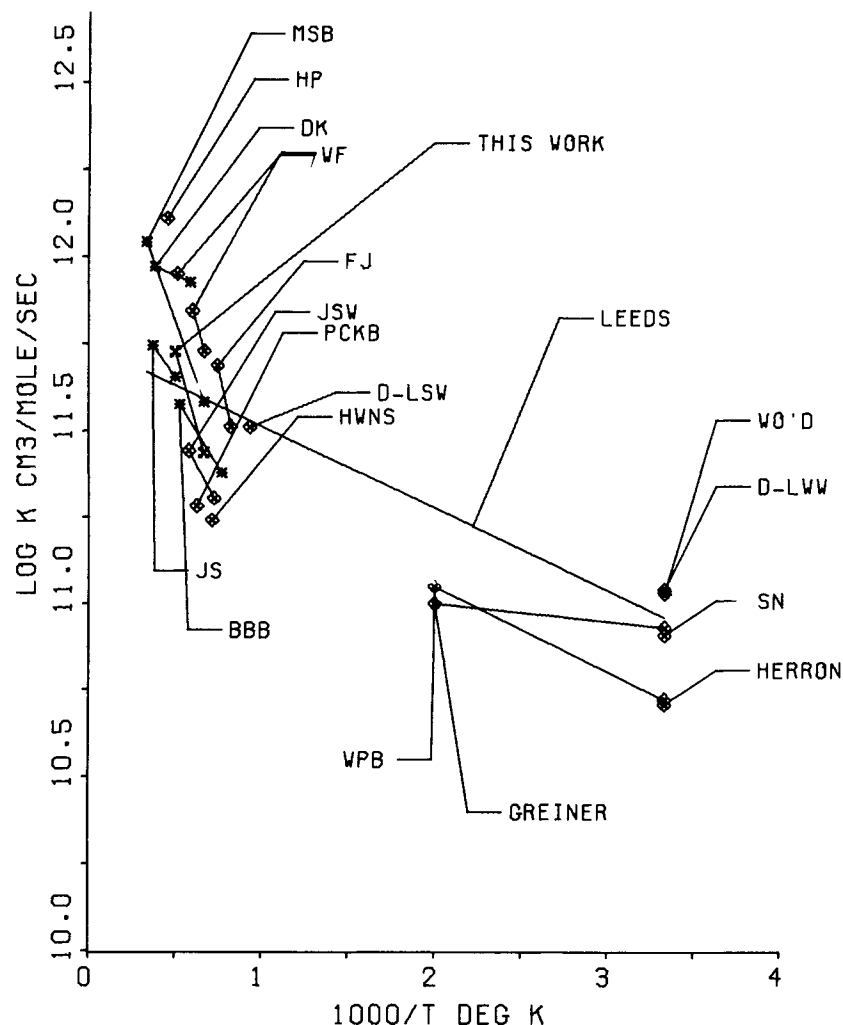


FIG. 7. Arrhenius graph for $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$. The symbols refer to literature data as follows: BBB, Ref. 2; DK, A. M. Dean and G. B. Kistiakowsky, *J. Chem. Phys.* **53**, 830 (1970); D-LSW, G. Dixon-Lewis, M. M. Sutton, and A. Williams, *Trans. Faraday Soc.* **61**, 255 (1965); D-LWW, G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966); FJ, C. P. Fenimore and G. W. Jones, *J. Phys. Chem.* **62**, 1950 (1962); GREINER, N. R. Greiner, *J. Chem. Phys.* **51**, 5049 (1969); HP, G. A. Heath and G. S. Pearson, *Eleventh Symposium (International) on Combustion*, p. 967, The Combustion Institute, 1967; HERRON, J. T. Herron, *J. Chem. Phys.* **45**, 1854, (1966); HWNS, H. C. Hottel, G. C. Williams, N. M. Nerheim, and G. R. Schneider, *Tenth Symposium (International) on Combustion*, p. 111, The Combustion Institute, 1965; JSW, W. Jost, H. Gg. Schecker, and H. Gg. Wagner, *Z. Physik. Chemie N.F.* **45**, 47 (1965); JS, Th. Just and S. Stepanek, *Proceedings of the Seventh Shock Tube Symposium*, University of Toronto, 1969, and S. Stepanek, *Deutsche Luft- und Raumfahrt Forschungsbericht* 69-79, 1969; LEEDS, D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, *Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems*, No. 1, Leeds University, 1968; MSB, B. F. Myers, K. G. P. Sulzmann, and E. R. Bartle, *J. Chem. Phys.* **43**, 1220 (1965); PCKB, R. P. Porter, A. H. Clark, W. E. Kaskan, and W. E. Browne, *Eleventh Symposium (International) on Combustion*, p. 473, The Combustion Institute, 1967; SN, F. Stuhl and H. Niki, unpublished results; WF, A. A. Westenberg and R. M. Fristrom, *J. Phys. Chem.* **65**, 591 (1961), and *Tenth Symposium (International) on Combustion*, p. 473, The Combustion Institute, 1965; WO'D, W. E. Wilson and J. T. O'Donovan, *J. Chem. Phys.* **47**, 5455 (1967); WPB, E. L. Wong, A. E. Potter, and F. E. Belles, NASA TN D-4162, 1967, and NASA TN D-5707, 1970. All shock-tube data is denoted by asterisks.

strate that nonlinear $\log k$ versus $1/T$ graphs may be expected in the high-temperature range associated with flames and explosions. Apparent increases in activation energy should not be expected in general, however, since contrary cases, with decreasing apparent activation energy, are already known.^{1,4} Indeed, it has previously been concluded on theoretical grounds that the near-zero activation energy of Reaction (-1) implies a gradual decrease in its activation energy at high temperatures.¹⁸

Conclusions

Experiments on the transition zones of shock-initiated combustion reactions were analyzed to find rate-constant parameters for the elementary reactions $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$, $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$, and $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$. The Arrhenius graphs derived do not yield linear extrapolations to room-temperature results; the practice of using a single equation of the form $k = A \exp(-E_A/RT)$ to describe the temperature dependence of an elementary reaction rate constant, both at room temperature and at combustion temperature, should be discontinued. The theoretical interpretation of bimolecular rate constants over wide temperature ranges promises to be a fruitful field of investigation.

Acknowledgments

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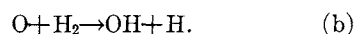
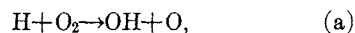
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COMMENTS

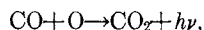
R. W. Getzinger, *Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, N. Mex.* The authors have reported measurements and an interpretation of transient spikes in the OH

concentration during the transition regime of the hydrogen-oxygen reaction. The computations of Hamilton and Schott,¹ cited in this paper, also indicate that oxygen atoms may

exhibit concentration spikes in the same reaction regime for very fuel-rich mixtures over a limited temperature range. The magnitude of these [O] spikes are, to a good approximation, proportional to the rate coefficient ratio k_a/k_b



We have recently completed² a systematic study of oxygen-atom spikes in shock-heated $\text{H}_2\text{-O}_2\text{-CO-CO}_2\text{-Ar}$ mixtures, by following the flame-band emission from the radiative recombination



where the intensity I is given by

$$I = I^0[\text{CO}][\text{O}].$$

Carbon monoxide and carbon dioxide were added in approximately equilibrium proportions to minimize changes in [CO]. With a nearly constant temperature early in the over-all reaction, I was essentially proportional to [O].

Transient emission-intensity maxima, followed by the usual slow recombination-limited approach to final equilibrium, were clearly evident in mixtures with $[\text{H}_2]_0/[\text{O}_2]_0 = 6, 10$, and 16 , but were absent when this ratio was 4 or less.

Calibration between I and [O] was achieved by shocking low-density, $1:1$ mixtures where, in the absence of concentration spikes, the broad intensity maxima could be identified with the calculable condition of partial equilibrium in the absence of any recombination (denoted: p.e.). When applied to experiments exhibiting oxygen-atom spikes the calibration revealed ratios of $[\text{O}]_{\text{max}}$ to $[\text{O}]_{\text{p.e.}}$ of as large as $10\text{--}12$.

Numerical integration of the complete set of differential gasdynamic and reaction-rate equations confirmed significant sensitivity of $[\text{O}]_{\text{max}}$ to only the ratio k_a/k_b , and yielded, by systematic variation of k_a/k_b , a consistent ratio adequately describing all observations in the experimental temperature range $1400^\circ\text{--}1900^\circ\text{K}$. Using the well-known value of k_a at these temperatures, k_b was evaluated with an estimated accuracy of $\pm 25\%$.

Our result over this temperature range is expressed as $k_b = 3.2 \times 10^{14} \exp(-15.0 \text{ kcal}/RT) \text{ cm}^3/\text{mole}\cdot\text{sec}$. This expression is steeper and $2\text{--}3$ times higher than a straight Arrhenius extension of the expression $k_b = 3.2 \times 10^{13} \exp(-10.2 \text{ kcal}/RT) \text{ cm}^3/\text{mole}\cdot\text{sec}$ obtained below 1000°K by Westenberg and de Haas.³ We have succeeded

in correlating these two sets of results with a transition-state theory calculation, using a set of independently determined parameters for a linear O-H-H activated complex.⁴ This calculation was forced to fit the slope and magnitude of the low-temperature expression at 600°K . The calculated values of k_b are about 15% lower than our experimental values at $1400^\circ\text{--}1900^\circ\text{K}$.

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T. C. Clark, University of Toronto, Department of Chemistry, Toronto, Ontario, Canada. Previous investigations have indicated¹ that the rate coefficient for $\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$ at 1350°K was substantially larger than was predicted by extrapolating an Arrhenius line drawn through low-temperature data. It was suggested that the curved Arrhenius plot of rate coefficient calculated by the BEBO transition state method of H. S. Johnston would reduce this discrepancy. It has also been claimed² that the activation energy between $1200^\circ\text{--}1400^\circ\text{K}$ for the reaction was larger than that observed at lower temperatures. These same phenomena were found³ for the reaction $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ at $1270^\circ\text{--}1370^\circ\text{K}$. Again, the BEBO method gives an Arrhenius curve which passes through high- and low-temperature data. In a recent article,⁴ we examined these effects for three hydrocarbon reactions by making BEBO calculations, and conclude that the Arrhenius-plot curvature is more serious for abstraction reactions involving a radical and a molecule. Whether quantum mechanical tunnelling is considered or not, the largest change in activation energy on an Arrhenius plot over the range of $300^\circ\text{--}2000^\circ\text{K}$ will occur above 1000°K . This calculated increase above 1000°K is largely caused by the changing contribution from a term T^x within the BEBO expression. The power x is $3/2$ for an atom abstracting an atom, but is $5/2$ for a radical or diatom abstracting an atom, assuming a linear transition complex. Thus, the larger effect for

abstraction by a radical is to be expected. It is therefore interesting to note that the reactions which you have discussed in your paper all fall into this category.

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Authors' Replies. We doubt that meaningful descriptions of high-temperature Arrhenius-graph curvature can be given by any form of activated complex theory (ACT), due to the large number of adjustable parameters, none of which can be measured experimentally or calculated quantum mechanically, that are embodied in the theory. A demonstration of the sensitivity of ACT calculations to these parameters follows. For the reactions discussed in our paper, the fundamental ACT equation¹

$$k(T) = (kT/h) (q_C^{\ddagger}/q_A^* q_B^*) \exp(-E_b'/kT)$$

becomes, for linear complexes,

$$k = 5.75 \times 10^{-61} \mu^{-1/2} T^{-3/2} (d^2/I_A I_B) (\sigma_A \sigma_B / \sigma_C) \times \prod_{i=1}^6 [1 - \exp(-T_{C_i}^v/T)]^{-1} [1 - \exp(T_A^v/T)] \times [1 - \exp(T_B^v/T)] \exp(-E_b'/kT), \quad (1)$$

in $\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ units. d =inter-c.m. dimension of the activated complex, μ =reduced mass of collision, I =moment of inertia, σ =symmetry number, $T^v = hc\omega_0/k$ =characteristic temperature for vibration. At temperatures well below 1000°K, the ACT value of $k(T)$ can be scaled by adjusting d , while the ACT Arrhenius-graph slope can be changed by adjusting E_b' . At high temperatures, i.e., when T becomes comparable to some of the T^v , the Arrhenius-graph slope becomes very sensitive to the set of T^v assumed for the activated complex.

The ACT equation (1) was evaluated for Reaction (3) at the midpoint of the $1/T$ range of our data, or $T=1543^\circ\text{K}$, for various sets of parameters. At this temperature, the experi-

mental rate constant is $\log k=12.79$, and the experimental activation energy is 6.50 kcal; these compare to the Leeds consensus values of $\log k=12.61$, $E_A=5.15$ kcal. The low-temperature data was matched at 400°K by assuming $d=7.9 \text{ \AA}$, and $E_b'=E_A(\text{Leeds})+(3/2)RT=6.35$ kcal.

Given d and E_b' , $k(1543)$ and $E_A(1543)$ are functions of the set of six vibration frequencies for the activated complex. For all six assumed to be 3000 cm^{-1} , the 1543°K results are $\log k=12.24$, $E_A=4.61$ kcal; for all six assumed to be 2000 cm^{-1} , $\log k=12.52$, $E_A=7.63$ kcal; for all six assumed to be 1000 cm^{-1} , $\log k=13.38$, $E_A=12.47$ kcal; for the set 500, 1000, 1500, 2000, 2500, and 3000 cm^{-1} , $\log k=13.00$, $E_A=9.43$ kcal. A calculation was also done based on a set of frequencies for real molecules assumed to be similar to the activated complex, viz., 1050, 1550, 1550, 3760, 3870, and 3870 cm^{-1} . With d reset to 3.0 \AA to restore agreement at 400°K , this set gives, at 1543°K , $\log k=12.56$, $E_A=6.81$ kcal. A similar degree of flexibility would also be found for a nonlinear activated complex. We conclude from this comparison that, although a plausible parameterization of the activated complex does give a rate-constant temperature dependence in accord with experiment, a wide variety of equally plausible parameterizations would give widely different results. For this reason, we feel that ACT is not likely to serve fruitfully as a framework for understanding high-temperature Arrhenius graph curvature.

There are, of course, amendments to the ACT formalism that remove some of the arbitrariness of ACT itself. The BEBO procedure mentioned by Dr. Clark has already been applied to a large variety of high-temperature reactions involving small numbers of atoms.² Also, the empirical thermochemical procedures described by Golden³ could be systematically applied to reactions in which Arrhenius-graph curvature is observed. The results of these types of ACT calculations might turn out to be reasonably close to the experimentally observed Arrhenius graphs.

The collision theory approach that we favor has the great advantage over ACT in that its parameters, presently just as adjustable as the ACT parameters, are at least conceptually accessible to practical experimental measurements. In view of the current general advance in the technology of measuring inelastic cross sections, excitation functions, and specific rate constants, it will be surprising if the collision-theory parameters are not soon known for at least one of the bimolecular reactions displaying high-temperature Arrhenius-graph curvature.

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3. D. M. Golden, This Symposium.

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Dennis M. Zallen, *Purdue University, W. Lafayette, Ind. 47906*. You mentioned that your leak rate was about 1 micron an hour. Other shock-tube users, reporting at previous symposia, could not get less than 1 micron per minute. Could you comment on your techniques, since impurities have been shown to be extremely important, say, in the CO kinetics.

Authors' Reply. Micron-per-hour shock tubes require careful construction techniques. We found, by RGA analysis, that the residual outgassing in our shock tube consists of air and water vapor, presumably from wall porosity and permeation of O-ring seals, and would not affect the chemistry studied here. A more-subtle danger from impurities in shock-tube experiments originates from pump oil or mercury vapor; unless these are carefully trapped out, they can ruin experiments, even though their partial pressures are well below the micron level.

↓

A. K. Oppenheim, *University of California, Berkeley, Cal.* For a stoichiometric hydrogen-oxygen mixture, with argon dilution of an order 90%, as used by the authors, the exothermic effects of the reaction at a level of 1000°K are significant. In reducing shock-tube data, one must take into account the temperature variation associated with these effects. If it has been established that the reaction zone is propagated at a steady rate, i.e., that it proceeded without any distortion over a sufficient length of the test section in characteristic distances of induction

and exothermic zones, it is reasonable to assume that the change of state is determined by an appropriate Rayleigh Line. My question is whether this has been done in the reduction of experimental data and whether a check was made that the Rayleigh Line terminates at the Hugoniot curve corresponding to an equilibrium composition of products.

Authors' Reply. In the experiments described here, the dilution and temperatures were well above the cited conditions, where heat release has a prominent effect on the course of reaction. With a single observation station, only indirect arguments are available to support the view that the reaction zone is steady. Experiments were done in our apparatus to investigate these indirect arguments.¹ Variations in degree of dilution, starting pressure, driver composition and pressure, and use of an argon pad between reactive gas and the diaphragm, all failed to show any effects that could be attributed to nonsteady ignition kinetics of the H₂-O₂ reaction. According to the CJ criterion, detonations can occur in the "oxidizing mix" for a shock temperature of about 1700°K. It is possible, therefore, that some of the low-temperature scatter in the oxidizing-mix data could be due to unstable flow. The data reduction, of course, assumed steady "Rayleigh Line" flow throughout, except that a variable area flow pattern was used to simulate the effects of boundary-layer formation on free-stream conditions.

It was found that the measured OH and CO₂ concentrations after combustion were in good accord with calculations, and corresponded approximately to partial equilibrium.² Total equilibrium is not achieved within the flow time of these experiments. Even if it were, the pervasive influence of boundary-layer growth upon free-stream conditions at long reaction times would significantly impede interpretation of the profiles in terms of equilibrium conditions.

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