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Shock-Tube Study of Chain Branching during the Induction Period of the Hydrogen-Oxygen Reaction

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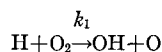
AND

GARRY L. SCHOTT

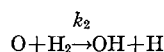
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(Received 12 December 1966)

The growth of "blue continuum" emission has been measured during the induction period of the reaction of H_2 (0.5%, 1.5%, and 5%)– CO (3.3% and 33%)– O_2 (0.5%)– Ar mixtures between 1100° and 1700°K. For sensitivity, the reacting gas behind reflected shock waves was viewed axially through a large end plate window and lens. The observed intensity I , representing the integral of $I'(x)dx$ between reflected shock front and end plate, exhibited 2 to 3 decades of exponential growth, $I = I_0 \exp(\alpha t)$. α is related to the branching chain kinetics of H_2 – O_2 combustion through the proportionality of $I'(x)$ to the product $[\text{CO}][\text{O}]$. α was found to be satisfactorily proportional to density and independent of $[\text{CO}]$, and its dependence upon $[\text{O}_2]$ and $[\text{H}_2]$ was analyzed to yield rate coefficients for



and



between 1290° and 1667°K. These are represented by

$$k_1 = 10^{10.89} \exp(-14.45 \text{ kcal}/RT) \text{ liter mole}^{-1} \cdot \text{sec}^{-1}$$

($\pm 10\%$) over our range, and

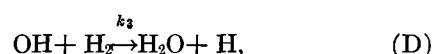
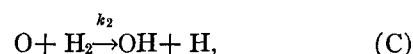
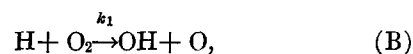
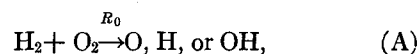
$$k_2 = 10^{10.51} \exp(-10.0 \text{ kcal}/RT) \text{ liter mole}^{-1} \cdot \text{sec}^{-1}$$

from combination of our mean result with literature data at 400°K.

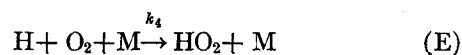
INTRODUCTION

WHEN mixtures of H_2 and O_2 are heated suddenly, a short induction period is observed during which there is negligible depletion of the reactants and exponential rise in the concentrations of the chain carriers at essentially constant temperature and pressure. Theoretical studies have been done on the kinetics of this induction period,¹⁻⁵ and its length has been measured under a variety of conditions.⁵⁻⁹ These

studies have shown that the reactions which are significant during this period are



with the reaction:



also included at high pressures and low temperatures. The experimental results have been used to calculate rate constants for the chain reactions—especially Reaction (B). In making these calculations it has always been necessary to make assumptions as to the role of the initiation Reaction (A) and the absolute radical concentration at the end of the induction period. In the most recent study, Ripley and Gardiner⁴ have shown that the initiation reaction plays an important role in the induction period, and that its rate must be

¹ V. N. Kondratiev, *Kinetika Ximitcheskix Gasovix Reaktsii* (USSR Academy of Sciences, Moscow, 1958), Sec. 38 [English transl.: *Chemical Kinetics of Gas Reactions* (Pergamon Press, Inc., New York, 1964), Sec. 39].

² R. S. Brokaw, Symp. Combust. 10th, University of Cambridge, Cambridge, England, 1964, 269 (1965).

³ F. E. Belles and M. R. Lauver, Symp. Combust. 10th, Univ. of Cambridge, Cambridge, England, 1964, 285 (1965).

⁴ D. L. Ripley and W. C. Gardiner, Jr., *J. Chem. Phys.* **44**, 2285 (1966).

⁵ T. Asaba, W. C. Gardiner, Jr., and R. F. Stubbeman, Symp. Combust. 10th, Univ. of Cambridge, Cambridge, England, 1964, 295 (1965).

⁶ G. L. Schott and J. L. Kinsey, *J. Chem. Phys.* **29**, 1177 (1958).

⁷ S. Fujimoto, *Bull. Chem. Soc. Japan* **36**, 1233 (1963).

⁸ G. B. Skinner and G. H. Ringrose, *J. Chem. Phys.* **42**, 2190 (1965).

⁹ D. R. White and G. E. Moore, Symp. Combust. 10th, Univ. of Cambridge, Cambridge, England, 1964, 785 (1965).

determined before the experimental data can yield accurate rate constants for the chain reactions.

In order to avoid the above complications and still obtain detailed information on the rates of the chain reactions, we undertook to measure the actual exponential growth of the free-radical concentrations *during* the induction period. We were able to obtain these measurements by shock heating $\text{H}_2\text{-O}_2\text{-CO-Ar}$ mixtures and monitoring the chemiluminescent emission of the $\text{O} + \text{CO} \rightarrow \text{CO}_2 + h\nu$ reaction. Since the emission intensity is proportional to $[\text{CO}][\text{O}]$ and since the concentration of CO is constant during the induction period, the emission will exhibit the same exponential growth as the O atoms. To obtain sufficient emission intensity for our induction period measurements, we developed a special "end on" technique in which we studied the reaction behind the reflected shock wave by monitoring the total light emitted axially through a 7.6-cm-diam window in the end flange of the shock tube. Under suitable conditions, the exponential growth constant of the integrated emission observed by this technique is identical to that for the free-radical growth during the induction period. Using the data from experiments done at different $[\text{H}_2]/[\text{O}_2]$ ratios, we were able to calculate values for both k_1 and k_2 .

EXPERIMENTAL

Apparatus and Procedure

The 10-cm-diam shock tube used for this study has been described previously.^{10,11} The piezoelectric sensors used to determine the incident shock-wave velocity were relocated to positions 6.1, 16.1, 26.1, 46.1, and 91.1 cm from the end of the shock tube.

The end flange of the shock tube was fitted with a Pyrex glass disk 10 cm in diameter and 1.25 cm thick, masked on the outside to provide a 7.6-cm-diam axial window. A thin film gauge (1 mm \times 73 mm) was vacuum-deposited across the inside of the window and connected at the ends to leads sealed through the window.¹² This gauge acted as a sensor to detect the shock wave arrival at the end of the tube. A convex glass lens (diameter 7.6 cm, focal length 60 cm) located 2 cm behind the window focused the light which is emitted parallel to the axis of the shock tube onto a telecentric aperture 1.25 cm in diameter located at the focal point. The light intensity was recorded by an R.C.A. 6655-A photomultiplier tube (S-11 response) located behind the aperture. The output voltage of the multiplier was produced across a 100-k Ω anode resistor and was fed directly into a cathode follower. To exclude stray light, the entire optical system from the shock tube end flange to the photomultiplier tube was en-

closed in a brass cylinder painted flat black on the inside.

The output of the cathode follower was directed to two oscilloscopes in order to record the emission signal simultaneously at different sensitivities. A Tektronix 315 oscilloscope was used to record the early rise of the CO-O emission. Typical settings used were 0.2-V/division vertical deflection and 10- μsec /division sweep rate. The other oscilloscope, a Tektronix 545 with CA preamplifier, recorded a larger portion of the emission. Typical settings used on the second scope were 1-V/division vertical sensitivity and 20- μsec /division sweep rate. The signal from the thin film gauge in the end flange of the tube was amplified and strongly differentiated to yield a narrow spike. This signal was added to the emission signal on the 545 oscilloscope through the other half of the CA preamplifier. Both oscilloscopes were triggered to single sweep by a proportional delay circuit which was adjusted to start both sweeps just before the shock wave arrived at the end of the tube. A baseline and timemarks were put on both oscillograms immediately after each experiment. The linearity of the over-all detection system was checked by a technique described by Kiefer and Lutz.¹³

Experimental gas mixtures were prepared manometrically in a thoroughly evacuated glass-lined tank from commercial gases and heated from beneath to promote convective mixing for at least 18 h before use. The CO used was specially purified, and a mass-spectrographic analysis showed that CO_2 (0.06%) was the only detectable impurity. The shock tube was evacuated with a diffusion pump to a pressure below 3×10^{-4} torr before the introduction of the test gas mixture.

The incident shock waves were weak enough that bulk reaction did not occur behind them during the time of the measurements. To eliminate premature burning upon the diaphragm burst, we did find it necessary to introduce the last $\sim 10\%$ of the initial downstream gas, whose inlet port was next to the diaphragm, in the form of pure argon.

In total, 75 experiments were run using gas mixtures with three different $[\text{H}_2]/[\text{O}_2]$ ratios (1:1, 3:1, 10:1). The results are listed in Table I.

Data Reduction

The shock-wave velocity on arrival at the end of the tube was obtained from graphical smoothing and extrapolation of the data from the four piezoelectric sensors located within five tube diameters of the end. Hugoniot calculations for conditions of no chemical reaction behind both incident and reflected shock waves were used to determine the temperature and concentration conditions in each experiment.

The two oscillograms obtained from each experiment (see Fig. 1) were read on an optical comparator and the

¹⁰ G. L. Schott and P. F. Bird, *J. Chem. Phys.* **41**, 2869 (1964).

¹¹ R. W. Getzinger and G. L. Schott, *J. Chem. Phys.* **43**, 3237 (1965).

¹² V. Blackman, *J. Fluid Mech.* **1**, 61 (1956).

¹³ J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.* **44**, 658 (1966).

TABLE I. Experimental results of induction-period emission experiments.

$\alpha \times 10^{-5}$ (sec ⁻¹)	[M] $\times 10^2$ (mole/liter)	$\alpha' \times 10^{-8}$ (liter/mole·sec)	T (°K)	$\alpha \times 10^{-5}$ (sec ⁻¹)	[M] $\times 10^2$ (mole/liter)	$\alpha' \times 10^{-8}$ (liter/mole·sec)	T (°K)
$X_{H_2}=0.0049, X_{O_2}=0.0049, X_{CO}=0.0322, X_{Ar}=0.958$				$X_{H_2}=0.0147, X_{O_2}=0.0049, X_{CO}=0.0328, X_{Ar}=0.9476$ (Cont.)			
0.621	2.90	2.14	1368	1.08	1.90	5.68	1580
0.672	2.90	2.31	1368	1.53	1.85	8.27	1615
0.395	2.79	1.32	1302	1.44	1.82	7.89	1660
0.599	2.88	2.08	1355	1.00	2.14	4.67	1488
1.00	4.44	2.25	1415	1.25	2.06	6.01	1505
0.849	4.37	1.94	1370	1.46	1.83	8.00	1690
0.692	4.24	1.63	1317	1.59	1.78	8.91	1722
0.630	4.18	1.51	1295	1.65	4.48	3.68	1440
0.542	4.14	1.31	1268	1.56	4.46	3.50	1422
1.27	1.98	6.40	1695	1.64	4.52	3.63	1450
1.28	1.97	6.49	1688	1.15	2.96	3.88	1408
1.05	2.08	5.06	1595	1.14	3.02	3.77	1455
0.862	2.05	4.20	1560	1.00	2.99	3.34	1432
1.10	2.09	5.27	1605	1.01	2.52	3.41	1425
0.434	5.34	0.813	1200	0.459	1.47	3.12	1397
0.527	6.71	0.786	1207	0.740	1.53	4.82	1495
0.260	6.46	0.402	1150	0.446	1.48	3.01	1408
0.135	6.29	0.215	1110	1.27	1.63	7.80	1670
0.355	6.50	0.546	1162	1.60	1.68	9.52	1780
0.866	2.04	4.24	1542	$X_{H_2}=0.0151, X_{O_2}=0.0050, X_{CO}=0.3274, X_{Ar}=0.6525$			
0.96	2.06	4.67	1568	1.26	3.99	3.16	1395
0.718	2.08	3.45	1505	1.34	4.01	3.34	1408
0.700	2.12	3.30	1478	2.03	4.20	4.83	1497
0.625	2.16	2.89	1422	0.337	3.54	0.952	1190
0.705	2.24	3.15	1432	0.353	3.53	1.00	1190
$X_{H_2}=0.0147, X_{O_2}=0.0049, X_{CO}=0.0328, X_{Ar}=0.9476$				1.71	4.09	4.18	1449
0.88	2.94	2.99	1383	2.96	4.41	6.71	1608
0.765	4.23	1.81	1295	0.800	3.77	2.12	1295
0.700	4.39	1.60	1250	$X_{H_2}=0.0500, X_{O_2}=0.0050, X_{CO}=0.0328, X_{Ar}=0.9122$			
0.600	4.58	1.31	1215	0.913	4.28	2.13	1278
0.490	4.79	1.02	1190	1.27	4.40	2.90	1335
0.172	4.80	0.358	1110	0.909	4.32	2.10	1290
0.280	6.38	0.439	1122	1.67	4.42	3.78	1375
1.17	4.07	2.87	1370	2.30	4.66	4.93	1480
1.00	4.16	2.40	1338	2.75	4.62	5.95	1532
0.99	4.22	2.34	1332	3.24	4.62	7.00	1538
1.23	3.61	3.40	1412	3.40	4.72	7.20	1598
0.167	5.00	0.334	1088	3.92	4.80	8.2	1648
0.443	6.50	0.681	1157				
1.38	1.79	7.71	1658				

vertical deflection of each was plotted as a function of time on semilog paper. A straight line was hand drawn through the data points and an experimental time constant α (seconds⁻¹) was calculated for each. In the 44 experiments where both oscilloscope traces yielded good exponential growth constants, the value for α reported in Table I is the average of the two. The average difference between the two values obtained in these runs is 6%.

Significance of Experimental α

If every element of gas behind the reflected shock wave is still in the induction period, the total emission observed through the end of the tube will be given by (see Appendix A)

$$I(t) = I_0[e^{\alpha t} - \alpha(1 + \Delta)t - 1] \quad (1)$$

where I_0 and Δ are constants, the latter of the order of unity or smaller.

There are two limiting times which define the region of exponential growth of the recorded emission. For a short time after shock reflection the linear terms in Eq. (1) are significant and the signal (on a semilog plot) rises with negative curvature but with a slope greater than that in the exponential region. As soon as $e^{\alpha t} \gg \alpha t$, the total emission will rise with the characteristic time constant α . In our experiments, the exponential growth constant α was of the order of 1×10^5 sec⁻¹, so that the exponential term exceeded 90% of $I(t)/I_0$ for all times greater than about 45 μ sec. At long times the gas near the end of the shock tube is no longer in the induction zone and the total emission, although continuing to rise, is no longer described by Eq. (1) and also has negative curvature on a semilog plot. In some of our experiments we observed the first behavior on the early part of the oscillograms from the high-sensitivity oscilloscope, and in other experiments we observed the second type of behavior in the late portion of the oscillograms from the low-sensitivity

oscilloscope (see Fig. 1). These nonexponential regions were carefully excluded in evaluation of α .

Considerations Involving the Added CO

The addition of CO to the $\text{H}_2\text{-O}_2$ system introduces several kinetic considerations which are discussed below. The first is the assumption that the emission observed is due solely to the reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$. To obtain semiquantitative intensity measurements to verify this assumption, we monitored the total emission behind the shock wave through a quartz window and collimating slits at the side of the shock tube. Under these experimental conditions the emission profile exhibits a spike. The early part of the front of this spike shows exponential growth and is the end of the induction period.

In the first set of experiments the total emission was monitored behind shock waves in the following mixtures: $\text{CO-O}_2\text{-Ar}$, $\text{CO-H}_2\text{-Ar}$, $\text{H}_2\text{-O}_2\text{-Ar}$, as well as in pure Ar. Except for the $\text{H}_2 + \text{O}_2 + \text{Ar}$ mixture, no emission was observed on the time and amplification scales of the spike. The small signal observed in the $\text{H}_2 + \text{O}_2 + \text{Ar}$ mixture was completely eliminated by placing a uv cutoff filter in front of the first slit. It is possible that this small signal was due to OH chemiluminescence, since the shape of the emission signal was about the same as the OH emission signal reported by Belles and Lauver.¹⁴

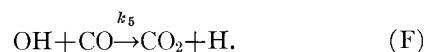
A second set of experiments was performed under closely identical conditions to compare the shape, location and magnitude of the total emission spike with spikes observed where the emission first passed through narrow bandpass filters. Interference filters with approximately 40-Å bandpass with maxima at 4360, 4040, and 4010 Å were successively used, and peak shapes and locations were identical with each other, as well as with those observed when the total emission was

monitored. In addition, the height of all the filtered peaks was the same. Thus, the magnitude and the shape of the emission are the same at three different wavelengths. The unfiltered peak height was 40 times greater than any of the filtered ones. This reduction factor of 40 agrees closely with an estimate by Kaskan¹⁵ of a reduction factor of 194 between the unfiltered emission from 3500 to 6000 Å and a 10-Å band at 4345 Å, which he observed in $\text{CO-H}_2\text{-air}$ flames.¹⁵ The attenuation factor of 40 is also very close to that expected, based on the spectral distribution of the CO-O continuum.¹⁶

From the above tests and from the absence of any evidence of molecular bands or atomic lines in a spectrogram made, without time resolution, through the end plate window, we conclude that the emission recorded by our photomultiplier, with only the glass window and lens as filters, arises from the radiative recombination of O atoms with CO.

The second consideration is the assumption that the emission is proportional to the product $[\text{CO}][\text{O}]$. This proportionality has been tested and verified in flames,¹⁵ shock tubes,¹⁷ and flow systems,¹⁸ under a very wide range of conditions. Therefore we felt it unnecessary to investigate this relationship extensively. We did, however, perform a final set of preliminary experiments in which the total emission was monitored behind shock waves in which the CO concentration was 2 times greater than in previous runs. Within experimental accuracy, the height of the spike was 2 times that of earlier runs at the same temperature and pressure.

The third consideration is whether the added CO affects the kinetics of the $\text{H}_2 + \text{O}_2$ reaction. We believe that during the exponential growth regime the only reaction of CO which need be considered under our experimental conditions is



This reaction does compete with Reaction (D) for OH radical removal, since it has a rate constant between 0.1 and 0.01 of k_3 ¹⁹ at temperatures above 1100°K. In our experiments, however, we confined ourselves to rich mixtures, where Reaction (D) is much faster than Reactions (B) or (C). Hence the rate of OH removal, whether by Reaction (D) alone or by Reactions (D) and (F) together, will not affect the rate of the over-all reaction (see next section). The reaction $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ is too slow²⁰ to affect the branching chain

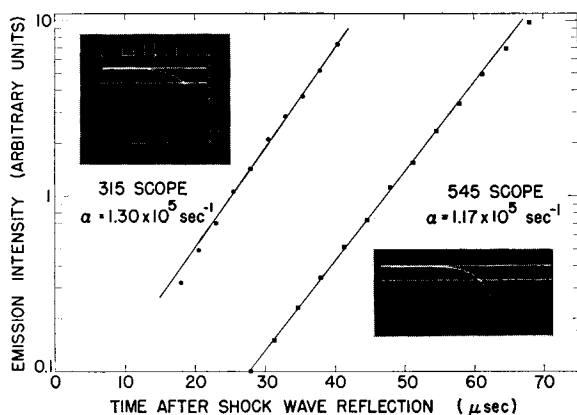


FIG. 1. Oscilloscopes and exponential growth plots from typical experiment. 1.5% H_2 , 0.5% O_2 , 3.3% CO , 94.7% Ar ; $T = 1412^\circ\text{K}$. 315 scope amplification 25 times that of 545 scope. 10-μsec timing marks on oscilloscopes.

¹⁴ F. E. Belles and M. R. Lauver, *J. Chem. Phys.* **40**, 415 (1964).

¹⁵ W. E. Kaskan, *Combust. Flame* **3**, 39 (1959).

¹⁶ A. G. Gaydon, *The Spectroscopy of Flames* (Chapman and Hall Ltd., London, 1957), Chap. 6.

¹⁷ D. R. White, *Phys. Fluids* **4**, 465 (1961).

¹⁸ M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc. (London)* **A269**, 404 (1962).

¹⁹ G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966).

²⁰ B. F. Myers, K. G. P. Sulzmann, and E. R. Bartle, *J. Chem. Phys.* **43**, 1220 (1965).

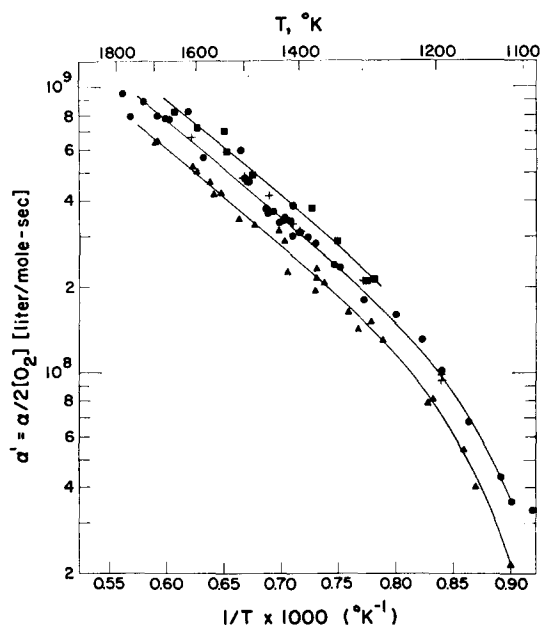


FIG. 2. α' derived from individual experiments (see Table I) plotted to reveal dependence on temperature and $\text{H}_2:\text{O}_2$ ratio. Triangles and lowest curve, $\text{H}_2:\text{O}_2=1.0$; circles, crosses, and middle curve, $\text{H}_2:\text{O}_2=3.0$; squares and uppermost curve, $\text{H}_2:\text{O}_2=10.0$. Solid points, 3.3% CO; crosses, 33% CO. All mixtures, 0.5% O_2 .

kinetics under our conditions, though it may contribute to initiation.

The final consideration is whether the slow vibrational relaxation of CO will affect the kinetic results, since complete relaxation was assumed in the computation of the final temperatures and concentrations. We intentionally used a low percentage of CO (3%) in our experiments to minimize this problem. To test this or other possible effects of the presence of CO, eight runs with an $\text{H}_2/\text{O}_2=3.0$ mixture were performed with 33% CO added (see Table I). The results of these 33% CO runs agree satisfactorily with those done with the same $[\text{H}_2]/[\text{O}_2]$ ratio but with 3% CO. Thus we conclude that the mole fraction of CO is unimportant in this study.

KINETIC TREATMENT

The exponential growth constant α is a function of the rate constants of the chain reactions of the induction period as well as of the concentrations of H_2 and O_2 . We first develop the equations relating α and the rate constants assuming only Reactions (B)–(D) are important because the simple form of the resulting equations gives a clearer picture of how the rate constants are obtained from the data. It also indicates the sensitivity of the calculated rate constants to errors in the determination of α . Later we present a more complete solution, which includes Reaction (E).

The Approximate Solution

Under conditions where Reaction (E) may be neglected, Kondratiev¹ and others have shown that the growth constant α is less than $2K_1$ and is the positive root of the cubic equation

$$\alpha^3 + (K_1 + K_2 + K_3)\alpha^2 + K_2K_3\alpha - 2K_1K_2K_3 = 0 \quad (2)$$

where

$$K_1 = k_1[\text{O}_2], \quad K_2 = k_2[\text{H}_2] \quad \text{and} \quad K_3 = k_3[\text{H}_2] + k_5[\text{CO}].$$

We can obtain a useful approximate relationship between k_1 , k_2 , and α under the conditions of our study (i.e., $[\text{H}_2]/[\text{O}_2] \geq 1$), where $K_3 \gg K_1$, K_2 , by neglecting α^3 and reducing the coefficient of α^2 to K_3 . We thus obtain

$$\alpha^2 + K_2\alpha - 2K_1K_2 = 0. \quad (3)$$

Substituting the definitions for K_1 and K_2 into this equation and defining $\alpha' = \alpha/2[\text{O}_2]$ and $\mathbf{n} = [\text{H}_2]/[\text{O}_2]$ we now obtain

$$2\alpha'^2 + k_2\mathbf{n}\alpha' - k_1k_2\mathbf{n} = 0. \quad (4)$$

The variable α' is only a function of k_1 , k_2 , and \mathbf{n} , and its limit with increasing \mathbf{n} is k_1 . If we determine α' in two separate experiments where the $[\text{H}_2]/[\text{O}_2]$ ratios are different, \mathbf{n}_1 and \mathbf{n}_2 , but the temperatures are the same, we will obtain two α' values, α'_1 and α'_2 . Since the temperature was constant, k_1 and k_2 remained constant and we may write two equations of the form of Eq. (4) which we solve for k_1 and k_2 ²¹:

$$k_1^0 = \alpha'_1\alpha'_2(\alpha'_1\mathbf{n}_2 - \alpha'_2\mathbf{n}_1)/(\alpha_1'^2\mathbf{n}_2 - \alpha_2'^2\mathbf{n}_1), \quad (5)$$

$$k_2^0 = 2(\alpha_1'^2\mathbf{n}_2 - \alpha_2'^2\mathbf{n}_1)/\mathbf{n}_1\mathbf{n}_2(\alpha_2' - \alpha_1'). \quad (6)$$

In actual practice we conducted three series of experiments in which we varied the temperature but kept \mathbf{n} constant. In each experiment we determined α and calculated α' (see Table I). All the α' values were plotted on a semilog plot against $1/T$, and a smooth curve was hand drawn through each series of points (see Fig. 2). These curves show that α' increases regularly with increasing \mathbf{n} at each temperature over the entire range of this study. From each curve we took values of α' at a sequence of $1/T$ points and calculated values of k_1^0 and k_2^0 .

Using an iterative technique, we also solved the two complete equations of the form of Eq. (2) for k_1^0 and k_2^0 using values for k_3 reported by Kaufman and Del Greco.²² These values for k_1^0 and k_2^0 agree with those obtained using Eqs. (5) and (6) to three significant figures. Also we varied k_3 by a factor of 2 in both directions and obtained the same results for k_1^0 and k_2^0 . Therefore, under the conditions of our experiments

²¹ Hereafter the values for k_1 and k_2 obtained by neglecting Reaction (E) are designated k_1^0 and k_2^0 .

²² F. Kaufman and F. P. Del Greco, Symp. Combust. 9th, Cornell Univ., Ithaca, New York, 1962, 659 (1963).

($[\text{H}_2]/[\text{O}_2] \geq 1$), Eqs. (5) and (6) yield accurate calculations for the two constants.

The most notable feature in Eq. (6) is that $(\alpha_2' - \alpha_1')$ appears in the denominator. This makes the calculated k_2^0 very sensitive to the absolute difference between the two α' curves. Since the curves lie close together and the data scatter is of the order of half the differences between adjacent curves, the accuracy of the calculated values of k_2^0 will be less than that of the experimental quantities α_1' and α_2' . Equation (5), which is used to calculate k_1^0 , does not contain the quantity $(\alpha_2' - \alpha_1')$ and therefore the calculated values for k_1^0 are less sensitive to the absolute differences.

Solution Including Reaction (E)

The values of k_1^0 obtained from the $n_1=1, n_2=3$ data for $1000/T \geq 0.80$ do not form a straight $\ln k_1^0$ vs $1/T$ curve with those for the higher temperatures; instead the curves bend downward in the same manner as the α' curves in Fig. 2. This observation leads us to recognize that Reaction (E) may not be neglected over much of the range of conditions of our experiments.

When we include Reaction (E) in the induction-period mechanism, the cubic equation for α becomes²

$$\alpha^3 + (K_1 + K_2 + K_3 + K_4[M])\alpha^2 + (K_2K_3 + K_2K_4[M] + K_3K_4[M])\alpha + (K_2K_3K_4[M] - 2K_1K_2K_3) = 0, \quad (7)$$

where $K_4[M] = k_4[\text{O}_2][M]$. Within the regime $(2k_1 - k_4[M]) > 0$, this equation has the same properties as Eq. (2).¹ Again, a simpler solution for k_1 and k_2 can be obtained by making approximations valid in this study.

When we assume $K_4[M]$ is significant compared to K_1 and K_2 , but is still much smaller than K_3 , then Eq. (7) reduces to²

$$\alpha^2 + (K_2 + K_4[M])\alpha + K_2(K_4[M] - 2K_1) = 0. \quad (8)$$

Again defining $\alpha' = \alpha/2[\text{O}_2]$ and $\mathbf{n} = [\text{H}_2]/[\text{O}_2]$, we obtain two equations of the form of Eq. (4) for two experiments done at the same temperature but with different $[\text{H}_2]/[\text{O}_2]$ ratios. If we further assume that $[M]$ was the same in both experiments, then solving for k_1 and k_2 we obtain

$$k_1 = \frac{(2\alpha_1' + k_4[M])(2\alpha_2' + k_4[M])(\alpha_1'\mathbf{n}_2 - \alpha_2'\mathbf{n}_1)}{4(\alpha_1'^2\mathbf{n}_2 - \alpha_2'^2\mathbf{n}_1) + 2k_4[M](\alpha_1'\mathbf{n}_2 - \alpha_2'\mathbf{n}_1)}, \quad (9)$$

$$k_2 = \frac{2(\alpha_1'^2\mathbf{n}_2 - \alpha_2'^2\mathbf{n}_1) + k_4[M](\alpha_1'\mathbf{n}_2 - \alpha_2'\mathbf{n}_1)}{\mathbf{n}_1\mathbf{n}_2(\alpha_2' - \alpha_1')}. \quad (10)$$

Equations (9) and (10) reduce to Eqs. (5) and (6) when $[M]=0$. In Eq. (9), $k_4[M]$ appears in additive terms in both numerator and denominator, while in Eq. (10) it appears only in the numerator. This has the effect of making the calculated k_1 less sensitive to

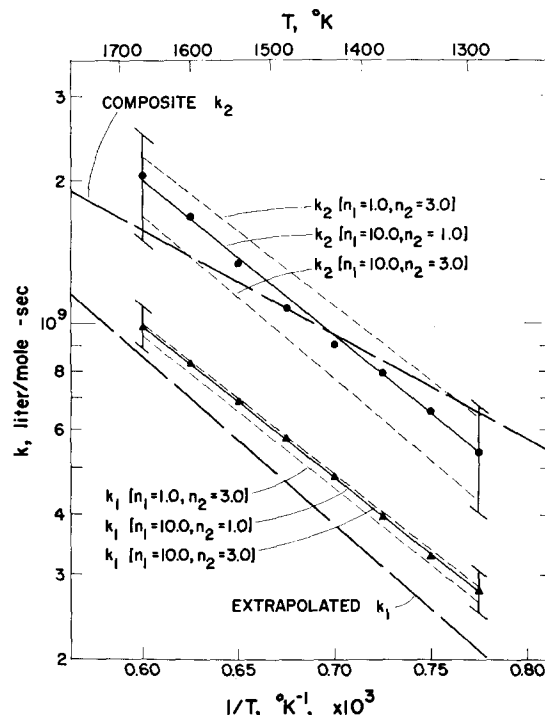


FIG. 3. Rate coefficients from chain branching kinetics. Lower curves, k_1 ; upper curves, k_2 . Truncated curves, expressions from Table II with points (Δ , k_1 ; \bullet , k_2) and estimated uncertainty bars ($\pm 10\%$ for k_1 ; $\pm 25\%$ for k_2) shown for solid ($n_1=10; n_2=1$) curves. Dashed extended curves: $k_1 = 1.09 \times 10^{11} \exp(-16.06 \text{ kcal/RT})$ liter mole⁻¹·sec⁻¹ extrapolated from low-temperature work; $k_2 = 3.22 \times 10^{10} \exp(-10.0 \text{ kcal/RT})$ liter mole⁻¹·sec⁻¹ joining 1481° and 400°K points.

the addition of Reaction (E) than the calculated k_2 . For example, at $T=1250^\circ\text{K}$ and $[M]=5 \times 10^{-2}$ moles/liter the inclusion of Reaction (E) increased the calculated k_1 by 17% and the calculated k_2 by 38%.

CALCULATION OF RATE CONSTANTS

The values for the rate constants k_1 and k_2 obtained from the α' curves are plotted in Fig. 3. As mentioned above, values of α' at various $1/T$ values were obtained from the smooth curves drawn through the experimental points. The k_4 values needed for these calculations were obtained from the expression $k_4^{\text{Ar}} = 8.6 \times 10^{14} \exp(+1280/RT)$ cc²/mole²·sec reported by Getzinger and Schott.¹¹ Mean values of the experimental range of $[M]$ were used at each temperature. In the temperature region where there are experimental points for all three $[\text{H}_2]/[\text{O}_2]$ ratios, three values for both k_1 and k_2 were calculated from the three permutations of the two α' values needed in the equations.

These calculated values of k_1 and k_2 were fit to Arrhenius rate expressions by the method of least squares in the temperature range $1290^\circ\text{--}1667^\circ\text{K}$, where we have α' values for all three values of \mathbf{n} . The parameters are listed in Table II. In one case ($n_1=1, n_2=3$) the data did yield k_1 and k_2 values below 1290°K .

TABLE II. Arrhenius parameters A and E [$k = A \exp(-E/RT)$] for k_1 and k_2 determined for the temperature range 1290°–1667°K using different pairs of α' values.

n_1	n_2	k_1		k_2	
		A (liter/mole·sec)	E (kcal/mole)	A (liter/mole·sec)	E (kcal/mole)
1.00	3.00	$10^{10.88}$	14.55	$10^{11.23}$	14.32
10.00	1.00	$10^{10.89}$	14.45	$10^{11.26}$	14.91
10.00	3.00	$10^{10.88}$	14.34	$10^{11.27}$	15.56

However, below this temperature and at the densities of our study, the production of HO_2 becomes appreciable and further reactions such as $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$ and $\text{HO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{OH}$ must be included in the kinetic scheme.² Once these reactions become important, the calculations for k_1 and k_2 become much more complex and the resulting accuracy depends strongly on the limited knowledge of the rate constants for reactions involving HO_2 . Moreover the increased curvature of the α' curves below 1290°K makes the smoothing of the data less precise. This effect and the smaller range of α' provided by the $n_1=1$ and $n_2=3$ data both diminish the reliability of the calculated rate coefficients.

The sensitivity of the calculated values for k_1 as well as k_2 to possible errors in the α' values used to calculate the constants was examined by the following procedure. k_1 and k_2 values were calculated first using one of the α' values 10% higher than the value on the curve (Fig. 2). Then, the other α' was made 10% higher than the curve value and finally both were raised 10%. It was observed that the least change in the rate constants occurs for the 10:1 and 1:1 α' values. This is because these two curves are the farthest apart, and the results are therefore least sensitive to a change in the difference between them.

k_1

We estimate the error in α' to be less than 5% of the value on the curve. Therefore in calculating k_1 from the 10:1 and 1:1 curves, we would be in error by 15% if the 10:1 α' is 5% low and the 1:1 α' is 5% high. The possible error in the calculated k_1 is greater using the other two permutations of the α' values. However, the three calculated k_1 values are virtually the same at each temperature. Therefore, on the basis of consistency, we estimate the k_1 values to be accurate to within $\pm 10\%$ in the temperature range 1290°–1667°K. An additional 10% uncertainty in k_1 may arise from a systematic inaccuracy of $\sim 2\%$ in the reflected shock temperatures.

The values of k_1 which we have obtained from the direct measurement of α are distinctly lower (by factors between 1.5 and 4) than those previously reported at

similar temperatures and which were based on both induction time measurements^{4,6} and flame profiles.²³

Our results for k_1 fall within the error estimates (a factor of 2) of two of the previous studies^{6,23} and in this sense there is no conflict; the present work simply provides a more accurate determination. Since satisfactory correlations of the previous high-temperature rate constants have been made with lower temperature measurements,^{4,24,25} we have compared our present values of k_1 with the same lower-temperature data. Using a set of values for k_1 compiled by Baldwin and Melvin,²⁴ we deleted the high-temperature points and fit the remaining five values to an Arrhenius expression by least squares. The resulting expression, $k_1 = 10^{11.04} \exp(-16.06 \text{ kcal}/RT)$ liter/mole·sec, when extrapolated to the temperatures of this study, yields values which agree with ours within 20%, and are in fact below ours (see Fig. 3). Thus the values for k_1 reported here are also satisfactorily related to the lower temperature work.

The activation energy determined by this study is below the 16–17 kcal/mole value obtained by the correlations mentioned above. Although our value may be low by 1 kcal/mole, it should be pointed out that a recent absolute rate theory calculation by Kurzius and Boudart²⁶ on Reaction (B) has predicted a temperature dependence of the apparent Arrhenius activation energy. Their calculations yielded values which vary from 16.7 kcal/mole at 300°K to 14.0 kcal/mole at 2000°K.

k_2

The accuracy of the k_2 determination can be assessed as before. Again, it is clear that the least sensitivity to error comes from using the 10:1 and 1:1 α' curves. If the α' uncertainty is again taken as $\pm 5\%$, the resulting possible error in k_2 is $\pm 25\%$. The fact that the other two k_2 curves differ from this one by only 20% when a $\pm 5\%$ error in α' could have displaced them over 100%, indicates that the 5% error estimate is sufficient. Therefore, we accept the k_2 values from the 10:1 and 1:1 α' curves as the most accurate and estimate the error limits at $\pm 25\%$.

Our values for k_2 can be compared directly with values reported by Ripley and Gardiner⁴ based on induction time measurements in shock waves and by Fenimore and Jones based on studies of the $\text{H}_2\text{--O}_2\text{--N}_2\text{--N}_2\text{O}$ flame.²⁷ At 1667°K this study overlaps the other two, and at this temperature our value for k_2 is a factor of 2.6 higher than the induction time value

²³ C. P. Fenimore and G. W. Jones, J. Phys. Chem., **63**, 1154 (1959).

²⁴ R. R. Baldwin and A. Melvin, J. Chem. Soc. **1964**, 1785.

²⁵ A. A. Westenberg and R. M. Fristrom, Symp. Combust. 10th, Univ. of Cambridge, Cambridge, England, 1964, 473 (1965).

²⁶ S. C. Kurzius, Symp. Combust. 10th, Univ. of Cambridge, Cambridge, England, 1964, 385 (1965).

²⁷ C. P. Fenimore and G. W. Jones, J. Phys. Chem., **65**, 993 (1961).

and a factor of 8 higher than the flame study value. Although our determination of k_2 is not as precise as that of k_1 , these two lower values lie far outside our error estimates. We are unable to reconcile these much lower values of k_2 with the value for k_1 and our observed small variation of α' with the $[\text{H}_2]/[\text{O}_2]$ ratio.

We attach no significance to the 14.9 kcal/mole activation energy obtained for k_2 . The slope of the k_2 curve is very sensitive to the location of the α' curves and a slight displacement would change this slope markedly.

We can obtain an Arrhenius expression for k_2 for correlation with low-temperature data by joining a value for k_2 at 400°K where three independent studies report the same value (1.1×10^9 liter/mole·sec)²⁸⁻³⁰ with a value 1.08×10^9 liter/mole·sec at 1481°K taken from the midpoint of our k_2 curve. This Arrhenius line has the expression $k_2 = 3.22 \times 10^{10} \exp(-10.0 \text{ kcal}/RT)$ liter/mole·sec, and is shown in Fig. 3. Within the temperature range of this study, values for k_2 from this line lie within our error limits for this rate constant. This Arrhenius expression agrees closely with that reported by Wong and Potter²⁹

$$[k_2 = 4.3 \times 10^{10} \exp(-10.0/RT) \text{ liter/mole} \cdot \text{sec}]$$

and Westenberg³⁰ whose expressions are derived only from the data in their respective studies. The agreement with Clyne and Thrush's result for k_2 , $1.2 \times 10^{10} \exp(-9.2 \text{ kcal}/RT)$ liter/mole·sec,²⁸ is also moderately good in their temperature range. Azatyan and co-workers³¹ have reported values for k_2 around 900°K based on explosion limit studies of the H_2 - O_2 -CO system. Their values agree with the above Arrhenius line within 15% in their temperature range.

We do not regard the high-temperature value of k_2 as being settled by the present experiments, whose conditions were deliberately more auspicious for the determination of k_1 , and believe that improvement can be made by extending our study to higher temperatures and to $[\text{H}_2]:[\text{O}_2]$ ratios less than 1.

DISCUSSION OF METHOD

Exponential growth of OH chemiluminescence in the reaction of a lean H_2 -air mixture behind shock waves has been reported by Belles and Lauver¹⁴ as part of an investigation of the mechanism of the chemiluminescence, and the growth coefficients were found to be

consistent with the mechanism under study and literature data for k_0 - k_3 . Our approach with CO added to the system is to make use of a luminescent reaction which is already well established by other work. The utility of the H_2 -CO- O_2 system to isolate Reactions (B) and (C) in rate-determining roles and still preserve the essential simplicity of the H_2 - O_2 kinetics has already been demonstrated in the first explosion limit regime by Azatyan, *et al.*³¹ We believe that the present study provides the first straightforward measurements of the chain-branching coefficient in the high temperature, 10^5 sec^{-1} regime and the most direct since Kovalskii's³² classic pressure change measurements of the explosive reaction near the first limit.

The technique of end-on observation of the rapidly reacting gas behind the reflected shock wave was adopted after difficulty was experienced in preliminary work with conventional differential viewing of the reaction behind incident shocks through collimating slits at the side of the tube. We could not view a sufficient volume of gas with adequate solid angle and still maintain adequate discrimination against scattered emission from adjacent, more luminous gas upstream. The geometry of the view through a large aperture window in the tube end affords much greater sensitivity for observing the early rise of emission in the reacting gas at the end, and there is no interference from any more strongly luminous region nearby. The technique is reminiscent of that used for one of the earliest studies of ignition temperatures and delays in shock tubes³³ and for measuring the linear growth of emission from equilibrium gas accumulated behind reflected shock waves.³⁴

Many of the recognized complications of reflected shock waves are avoided in the present system. The observations are made primarily on the gas adjacent to the end wall, and they are terminated when the reaction becomes macroscopically exothermic. Thus aplanarity and velocity variation of the reflected shock, which develop some distance from the wall because of incident shock boundary layer and finite reaction effects, do not enter. We do recognize, but have not assessed quantitatively, the possibility of conductive cooling of the static boundary layer gas at the cold window surface. Also, we recognize the difficulty inherent in determining the reflected shock-wave properties from the incident shock-wave velocity, which must necessarily be determined over a finite distance upstream from the reflection and extrapolated to the end-plate position.

In approaching this problem, we elected to confine our velocity measurements to a few tube diameters of the end plate, in order to make the extrapolation short.

²⁸ M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc. (London)* **A275**, 544 (1963); *Nature* **189**, 135 (1961).

²⁹ E. L. Wong and A. E. Potter, *J. Chem. Phys.* **43**, 3371 (1965).

³⁰ A. A. Westenberg, in discussion in Symp. Combust. 11th, Berkeley, Calif., August 1966 (to be published) reported $k_2 = 4 \times 10^{10} \exp(-10 \text{ kcal}/RT)$ liter/mole·sec, valid below 1000°K, and based on ESR measurements.

³¹ V. V. Azatyan, V. V. Voevodskii, and A. B. Nalbandyan, *Kinetika i Kataliz* **2**, 340 (1961). [English transl.: *Kinetics Catalysis (USSR)* **2**, 315 (1961)].

³² Described in Ref. 1.

³³ M. Steinberg and W. E. Kaskan, *Symp. Combust.* 5th, Pittsburgh, 1954, 664 (1955).

³⁴ R. Watson, *J. Quant. Spectry. Radiative Transfer* **4**, 1 (1964); and related work by S. S. Penner and his co-workers.

With short intervals, we experienced scatter in the apparent velocity rather than uniform attenuation of the incident wave which measurements over a longer base often show. Besides the possible systematic error in reflected shock temperature associated with its derivation from incident-wave velocity measurements, we believe that the lack of regularity in the apparent incident shock speed, of a few tenths of a percent rms, has contributed significantly to the scatter in the exponential growth coefficients which is evident in Fig. 2.

The temperature range of the present study was limited at the lower end by the slowness of the reaction and the smallness of the emission signals. Work at higher temperatures was prevented by the occurrence of luminous burning in the gas far behind the incident shock waves, which interfered with the axial observation by superimposing a noisy, uncertain component upon the exponential growth of the reflected shock light. We believe this interference can be dealt with by the use of a substantial buffer gas section in the shock tube.³³

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APPENDIX: DERIVATION OF TOTAL REFLECTED EMISSION, EQ. (1)

In this derivation we assume that the reflected shock wave is plane and steady, and consider times short enough that negligible depletion of reactants or other change of state occurs anywhere behind the reflected shock wave. Then, from the general solution of the induction period kinetics,^{1,2,4} $[O]$ in a layer of gas shocked at time t_i is given by

$$[O]_i = A \exp[\alpha(t-t_i)] + B \exp[-\beta(t-t_i)] + C \exp[-\gamma(t-t_i)] - (A+B+C), \quad (A1)$$

where $-\beta$ and $-\gamma$ are the negative (possibly complex

conjugate with negative real part) roots of Eq. (7), whose positive root, α , has been considered as a function of the rate parameters K_i in the text. The sum $(A+B+C)$ is equal to

$$[(d[H]/dt) + (d[OH]/dt) + (d[HO_2]/dt)]_0 / 2K_2$$

evaluated from the initiation rates alone. A , B , and C may be evaluated for specific cases from the K 's and an assumed initiation mechanism. For present purposes, we note that both A and $(A+B+C)$ are positive, and that $|\Re(\beta)|$, $|\Re(\gamma)| > \alpha$. If we specifically assume that O atoms are not produced by the initiating reactions and that K_3 is large enough to permit use of Eq. (3), we find that C is negligible and $A/B = -\beta/\alpha > 1$. Thus we conclude that for our circumstances, $(A+B+C)/A$ is positive and of the order of unity. Since the emission is negligible until $\alpha(t-t_i)$ is appreciable, we proceed to formulate $[O]_i$ as

$$[O]_i = A \{ \exp[\alpha(t-t_i)] - 1 - \Delta \}, \quad (A2)$$

where Δ represents the residual constants, $(B+C)/A$, which are subsidiary though not negligible compared to unity.

Application of the considerations of the emission mechanism explored by Davies³⁵ to the present case of constant $[CO]$ and exponentially growing $[O]_i$ shows that the times which concern us are long compared to the mean lifetime for collisional destruction of the radiating state of CO_2 , and the emission is accurately proportional to the product $[CO][O]$. This leads to the differential emission intensity of layer i given by

$$dI_i(t_i) = I_0' \{ \exp[\alpha(t-t_i)] - 1 - \Delta \} dx. \quad (A3)$$

The shock wave is reflected from $x=0$ at $t=0$ and has velocity v_{rs} , so that $t_i = x/v_{rs}$. Since the telecentric stop excludes rays more than $\pm 0.6^\circ$ from axial parallelism, the area and solid angle of view of each layer is substantially independent of x . The integrated emission is then

$$I(t) = \int_0^{v_{rs}t} I_0' (\exp\{\alpha[t - (x/v_{rs})]\} - 1 - \Delta) dx = I_0 [\exp(\alpha t) - \alpha(1+\Delta)t - 1]. \quad (A4)$$

³⁵ W. O. Davies, J. Chem. Phys. **43**, 2809 (1965).