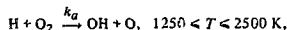


Further Studies of Exponential Branching Rates in Reflected-Shock Heated, Nonstoichiometric $\text{H}_2\text{—CO—O}_2$ Systems*

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More thorough measurements are made of exponentially growing chemiluminescence, viewed end-on, during branched-chain ignition of $\text{H}_2\text{—CO—O}_2\text{—Ar}$ mixtures in reflected shock waves, to try to resolve residual questions from earlier studies by this and related techniques. Systematic variations of spectral bandpass, gas composition, and gas pressure have been made for particular $\text{H}_2:\text{O}_2$ ratios and temperature spans. At $\text{H}_2:\text{O}_2 = 1/3$, with CO present, exponential time constants, ϕ^* , for the CO—O chemiluminescence are independent of spectral bandpass over the 300–600 nm range; with CO absent, there is appreciable $\text{H}_2\text{—O}_2$ system ultraviolet chemiluminescence at $\lambda > 340$ nm, whose presence voids some earlier interpretations predicated on dominance of the $\text{OH } A^2\Sigma^+ \rightarrow X^2\Pi$ spectrum. At $\text{H}_2:\text{O}_2 = 0.1$, ϕ^* of CO—O chemiluminescence exhibits a small and unaccountable variation with extent of dilution of $\text{H}_2\text{—CO—O}_2$ mixtures in noble gas. This effect, diminished but perceptible also at $\text{H}_2:\text{O}_2 = 1/3$, clouds kinetic interpretation of ϕ^* in lean mixtures, but of itself does not reconcile disagreements with infrared and with incident shock CO—O exponential rates. The dilution effect is not found at $\text{H}_2:\text{O}_2 = 10$, where new measurements up to $T = 2400$ K are made and pooled with previous rich ϕ^* results to determine, for



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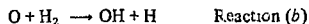
$$k_a = 1.22 \times 10^{17} T^{-0.907} \exp(-8369/T) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

Introduction

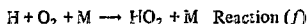
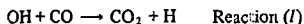
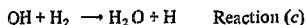
Exponentially accelerating formation of reaction products during the induction period of the gaseous $\text{H}_2\text{—O}_2$ thermal ignition process in shock waves has already been studied over a considerable range of conditions of temperature and composition, and by several independent spectroscopic means [1–11], in combination with two major variants of shock-tube technique, namely incident and reflected shock waves. Mixtures diluted with argon have uniformly been employed,

and CO has been included as an essential constituent in some of these studies.

The time constants for exponential growth of the optical indication of branched chain reaction progress constitute the basic quantitative data from these experiments. Chemical kinetics interpretations are then pursued by accounting for these time constants as a function of the reagent concentrations, the mechanism of the optical indicator process, and the specific rates of some or all of the elementary steps of the following mechanism:



*Work performed under the auspices of the U.S. Atomic Energy Commission.



The most concordant results have been obtained in the H_2 -rich, $1400 \lesssim T \lesssim 1800$ K domain, and these results yield the rate coefficient k_a at these temperatures most conclusively. However, the actual investigations to date have individually been concerned as much with developing and extending techniques as with optimum acquisition of kinetics data (and this fact is often not adequately emphasized in the reporting of these studies or recognized by kinetics-oriented readers), and there remain certain problem areas.

Foremost among these is disagreement of a factor of two among exponential time constants for H_2 -lean mixtures measured by different techniques, and the present study explores and partially resolves this disagreement. New measurements are also made which extend the range of data at $\text{H}_2:\text{O}_2 = 10$ to higher temperatures and over a range of a argon dilution, and the representation of k_a between 1250 and 2500 K is reformulated to correlate the present rich mixture results with those from [1] and [4]. Also, the spectral composition of the exponentially growing radiation in the absence of CO, investigated in [3], is reexamined and certain conclusions rescinded. This work was begun in 1968, before some of the results now available from other laboratories were known or appreciated.

Methods

Shock Wave and Optical Configurations

The present work was done with the combination of reflected shock waves and time-resolved, spatially integrated viewing of the intensity of visible and near ultraviolet chemiluminescent emission that was developed in [1], [2], [3], and [4]. The equipment was common to that employed in [4] and [5]. Spectral bandpasses were selected by combinations of solid inorganic and organic filters (see Fig. 1), and relative intensities of emission were measured continuously during the ignition process by oscillograms of photomultiplier tube currents.

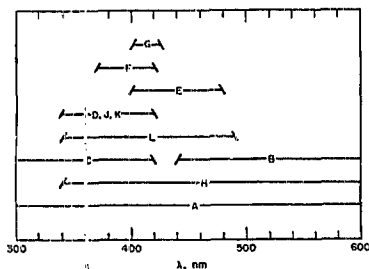


Fig. 1. Spectral bandpasses accepted by Pyrex or silica windows, RCA #6903 and 2020 photomultipliers, and filter combinations as follows, used in exponential acceleration rate measurements: A, no filter; B, Corning #3387; C, Corning #9863; D, Corning #s 9863 and 7380; E, Corning #s 5113 and 3389; F, Corning #s 9863 and 3360; G, interference filter, $\lambda_{\text{max}} = 414$ nm; H, Polymethylmethacrylate sheet; J, Corning #s 7380 and 5970; K, Polymethylmethacrylate sheet and Corning #5970; L, Polymethylmethacrylate sheet and Corning #5850.

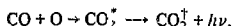
By this end-on method, all spatial elements of the process are viewed in real time. The gas temperature is reckoned from the measured incident shock speed, smoothed and extrapolated for evaluation at the end plate position, together with the equations of state for the original gas composition and the steady mechanical equations for the incident and reflected shock waves. A potential deficiency is that the gas under observation may be subject to progressive conductive cooling in a thin layer next to the end plate, which should be expected to develop in proportion to the square root of the time after shock reflection and to scale with inverse proportionality to the square root of the gas pressure [12]. Also, progressive heating of the interior gas occurs as the result of nonsteady propagation of the reflected shock wave encountering the sidewall boundary layer of the incident shock [13].

In comparison, the other studies cited in the Introduction ([6], [7], [8], [9], [10], and [11]) all employed axially differential viewing of the moving column of gas behind an incident shock wave. The nonidealities in the time and temperature scales of some of these experiments have been

taken into account [6-8]; however, the optical requirements for spatial definition in emission intensity experiments in this configuration restrict the sensitivity available and thereby limit the reaction speeds and uppermost temperatures reached by such studies.

Chemiluminescence Sources

As in much of the previous incident [6-8] and reflected [1, 2, 4] shock wave work, controlled amounts of CO were included in most of the present gas mixtures, so that the CO flame spectrum greatly dominated any luminescence from the purely hydrogen- and oxygen-containing constituents. This spectrum is believed to be effectively continuous under the pressure conditions encountered here, with a spectral distribution dependent upon gas temperature. It is described as CO—O recombination chemiluminescence and represented by the mechanism



in which CO₂^{*} denotes electronically excited CO₂ populated by a still-debated mechanism [14] at a temperature-dependent rate indicative of an activation energy of a few kcal/mole above the potential of ground-state dissociated CO and O atom fragments. CO₂^{*}, the coproduct with the 2.5 to 4 eV photons, is highly vibrationally excited CO₂, which is promptly thermalized and does not reabsorb the spectrum noticeably. Numerous conditions have been characterized [15] under which the intensity of this spectrum, or of a particular portion of it, is proportional to the product of concentrations [CO][O]. Imaginable limitations on the domain of validity of this proportionality have not been conclusively defined [16], and each new application carries the possibility of an interfering effect.

By way of comparison, two of the exponential acceleration studies [10, 11] employed absorption spectrometry specifically sensitive to the population of a single reactive constituent, OH radicals in the ground state. Still another study [5] was based on the intensity of infrared, apparently thermal vibrational emission from the main reaction product, H₂O.

The near ultraviolet emission spectrum from igniting H₂—O₂ mixtures in the absence of CO or other adulterants is also examined in the present work, as it has been in previous exponential acceleration studies [3, 9, 10].

Rate Equations

The chemical rate equations for the early formation of H, O, OH, H₂O, CO₂, and HO₂ by the forward progress of Reactions (a), (b), (c), (f), and (j) above, before the initial H₂, O₂, and CO concentrations are affected, are coupled by and linear in the dependent variables [H], [O], and [OH]. After initial transients, the solution [7] exhibits exponential acceleration illustrated by

$$[\text{O}] = [\text{O}]_0 e^{+\phi(t-t_0)}, \quad (1)$$

where ϕ is the only positive root of the polynomial

$$\begin{aligned} \phi^3 + \{k_a[\text{O}_2] + (k_b + k_c)[\text{H}_2] + k_l[\text{CO}] \\ + k_f[\text{M}][\text{O}_2]\} \phi^2 + \{(k_c[\text{H}_2] + k_l[\text{CO}]) \\ + (k_b[\text{H}_2] + k_f[\text{M}][\text{O}_2]) \\ + k_b k_f[\text{M}][\text{H}_2][\text{O}_2]\} \phi - k_b[\text{H}_2](k_c[\text{H}_2] \\ + k_l[\text{CO}]) + (2k_a - k_f[\text{M}])[\text{O}_2] = 0. \end{aligned} \quad (2)$$

Reactions (f) and (l) are formally included, and best available values of their rate coefficients are ultimately incorporated in treating the data; however, the present experiments were devised to afford much smaller sensitivity than has been obtained to k_f [2] and k_l [7]. Thus, subsequent reactions of HO₂ are neglected and constancy of [CO] during the exponential acceleration of reaction, while formally necessary for Eq. (1), is practically necessary only in rendering the product [CO][O] proportional to the exponentially growing [O].

The intensity of CO flame spectrum chemiluminescence is found to increase exponentially with time, as indicated by satisfactorily straight semilogarithmic plots over two or more decades under many circumstances, and the slopes of these plots are described by the exponential coefficient

ϕ^* . Interpretation based on equality of ϕ^* and ϕ , the root of Eq. (2), depends on proportionality of chemiluminescence intensity to $[\text{CO}][\text{O}]$, with $[\text{CO}]$ constant. The exponential growth coefficient, ϕ^\dagger , for thermal infrared emission of the H_2O product also provides a direct measure of ϕ , as does the exponential growth of absorption by OH.

In previous end-on investigations of ϕ^* and ϕ^\dagger , emphasis on the limiting behavior of Eq. (2) at large $\text{H}_2:\text{O}_2$ ratio,

$$\lim_{\text{H}_2:\text{O}_2 \rightarrow \infty} \phi/2[\text{O}_2] = k_a,$$

has led to graphical and analytical correlations of results by the function $\phi/2[\text{O}_2]$. For the lean mixture portion of the present study, with neglect of the effect of Reaction (1), the corresponding behavior is

$$\lim_{\text{H}_2:\text{O}_2 \rightarrow 0} \phi/[\text{H}_2] = \sqrt{2k_b k_c},$$

and correlation by the function $\phi/[\text{H}_2]$ is introduced.

The related exponential growth coefficient of chemiluminescence from H_2-O_2 ignition without CO is denoted ϕ^{**} . Past results under limited conditions [3, 10] gave the result

$$\phi^{**} \cong 2\phi^* \cong 2\phi,$$

thus indicating a chemiluminescent mechanism

governed kinetically by the association of two of the exponentially accumulating reactive species.

Problem Areas Investigated

ϕ^* in Lean Mixtures

Completion of ϕ^\dagger measurements in the infrared [5] resulted in a clear-cut disparity with the prior CO flame spectrum results obtained in the same shock-tube apparatus [4]. Whereas the data for $\text{H}_2:\text{O}_2 \geq 3$ agreed, disagreement appeared at lower $\text{H}_2:\text{O}_2$ ratios, the infrared values of ϕ^\dagger being systematically smaller. The disparity expanded progressively with decreasing $\text{H}_2:\text{O}_2$ ratio and with increasing temperature, reaching a factor of two at $\text{H}_2:\text{O}_2 = 0.1$, $T \approx 2000$ K, and it was not removed by inclusion of CO in the infrared experimental mixtures.

The subsequently published data by the other techniques have aggravated this difficulty, rather than resolving it. Table 1 illustrates the disparities at 1600 K by the observed values of $\phi/[\text{H}_2]$ obtained in low-density experiments in those studies where $\text{H}_2:\text{O}_2 = 0.1$ mixtures were used, and by the geometric mean of the values derived for k_b and k_c from these studies and from those where other lean compositions were used.

A secondary cause for concern over the behavior of ϕ^* in lean mixtures has been the unexpectedly steep temperature dependence found for ϕ^* by [4] and inferred therefrom for the product $k_b k_c$. A sum of activation energies of 20 kcal/mole or more [4] for these reactions is noticeably larger than has been found from the temperature-

TABLE 1
Illustrative Functions of Exponential Branching Rate Results
in Fuel-Lean $\text{H}_2-(\text{CO})-\text{O}_2$ Mixtures at 1600°K

| Source | $\phi/[\text{H}_2]$ ($\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$) | $\text{H}_2:\text{O}_2$ | $(k_b k_c)^{1/2}$ ($\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$) |
|---------|---|-------------------------|---|
| [4] | 3.2×10^{12a} | 0.10 | 3.9×10^{12} |
| [5] | 1.9×10^{12} | 0.10 | 2.4×10^{12} |
| [10] | $\sim 3 \times 10^{12b}$ | 0.10 | |
| [7] | | | 2.4×10^{12} |
| [11] | 2.5×10^{12} | 0.125 | 3.1×10^{12} |
| Table 3 | — | — | 4.7×10^{12} |

^aWith $\text{CO}:\text{H}_2 = 5$

^bValue estimated from Fig. 4 of [10].

dependent rates of these elementary reactions below 1000 K [17], or up to 2000 K in other lean exponential branching rate work [5, 7, 11].

On the hypothesis that the end-on CO flame spectrum method might have a systematic flaw under lean-mixture conditions, and that such a flaw might be revealed by a greater variation of experimental conditions than had been tested previously (at H₂:O₂ = 0.1, [4] had used but one gas mixture, one initial pressure, and one spectral band), H₂:O₂ = 0.33 and H₂:O₂ = 0.10 mixtures were used in several series of tests.

ϕ^* in Rich Mixtures and k_d

The infrared investigation [5] confirmed the merit of exponential acceleration data at H₂:O₂ = 10 in defining k_d , and extended the range of such measurements up to 2200 K, while demonstrating agreement with the CO flame spectrum data then available [1]. The latter, however, had been restricted to $T \leq 1650$ K by a subsequently remedied [4] limitation of equipment, and although somewhat higher temperatures have subsequently been examined at H₂:O₂ = 10 with incident shock wave methods [6, 10], none of the other techniques offers the sensitivity and precision provided by the spatially integrated CO flame spectrum combination. This gap in the existing data is filled in the present study, and the small influence of newly available high-temperature data on k_b and k_c in the deduction of k_d from ϕ^* data in rich mixtures is also given further attention.

As the present work progressed, a systematic effect of the degree of dilution of the reactants in argon appeared at lean compositions, as is amplified below. It thus became of importance to examine H₂:O₂ = 10 mixtures for the possible presence of a comparable effect in the CO—O ϕ^* data.

Finally, a more satisfactory representation of k_d as a function of temperature is sought, to replace the anomalously low mean-activation-energy result of [4].

Electronic Chemiluminescence in Absence of CO

The near-ultraviolet chemiluminescence growing with an exponential time constant twice that of

the CO flame spectrum in an H₂:O₂ = 0.33 mixture was attributed wholly to the OH $A^2\Sigma \rightarrow X^2\Pi$ fine-line spectrum near 310 nm, in experiments [3] that did not exclude the possibility of a substantial contribution from an indistinctly structured spectrum within the 290 $\leq \lambda \leq 420$ nm band, but merely failed to confirm such a contribution alongside the recognized OH spectrum. This matter is reexamined here, in conjunction with attempts to use electronic chemiluminescence in the absence of CO to resolve the disparities in Table 1.

Results

Effect of Spectral Bandpass

Figure 2 shows time constants, ϕ^* , for a small range of reflected shock wave conditions near 1800 K in experiments having initial H₂ partial pressures of 0.50 Torr and H₂:O₂ = 0.33. The nine points located by capital letters were determined in the new experiments performed in this range with one of the same gas mixture batches used in the H₂O infrared emission study of ϕ^* (mixture G of [5]). The letters denote the spectral bandpass accepted in each experiment in correspondence with Fig. 1. These results lie much closer to the previous CO—O ϕ^* data at H₂:O₂ =

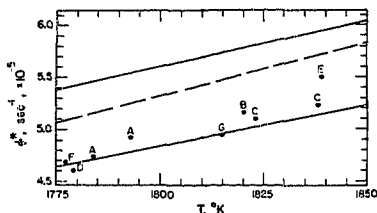


Fig. 2. Exponential branching coefficients for reflected shock waves in the system 0.96% H₂, 2.9% O₂, 2.0% CO, 94.1% Ar, initially at 50 Torr and 290 to 297°K. Lettered points: ϕ^* measured for particular spectral bandpasses (See Fig. 1). Solid curves: Upper and lower extremes of ϕ^* for similar conditions in previous studies by [1] and [2], scaled as $\phi^* / [H_2]$ to the above H₂ concentrations. Dashed curve: ϕ calculated with Eq. (2) and data in Table 3

0.33 [4] than to the infrared ϕ^* data, and thus reconfirm the existing disparity.

The constructive result in Fig. 2 is that the spectral bandpass used does not detectably influence the measured ϕ^* , from which it is concluded that there are not interfering spectra arising with more than one kinetic order with respect to products formed in the branched chain reactions. Possible effects of spectral bandpass were also examined, though less deliberately than exhibited above, in the course of several of the experiments in $H_2:O_2 = 0.10$ mixtures whose main results are presented below. Again, no effect of bandpass was identified.

Effects of Reagent Concentrations in Lean Mixtures

The next attempts within the present study to examine the basis of disagreement among various sources of ϕ^* data in fuel-lean mixtures were undertaken between about 1600 and 1850 K in a fresh $H_2:O_2 = 0.10$ mixture (Mixture I of Table 2 herein), containing 1.5% of H_2 (roughly matching Mixture H of [5]) and 1% CO. The experiments are summarized in Table 2. On the average, the $\phi^*/[H_2]$ values were found to exceed the corresponding values from H_2O infrared experiments

by a factor of about 1.5, but, more strikingly, they fell consistently below those of [4] by more than ten percent. Moreover, addition of sufficient CO to increase its concentration from 1% to 5.7% (Mixture IA of Table 2), thereby closely duplicating the $CO:H_2$ ratio used in [4], failed to raise the $\phi^*/[H_2]$ results perceptibly.

The next step was twofold dilution of this mixture with more argon (Mixture IB), thereby closely matching the complete $H_2:O_2 = 0.10$ gas composition of [4]. The resulting effect upon ϕ^* was unmistakable; in each of three experiments between 1650 and 1800 K, the smoothed curve of the earlier $\phi^*/[H_2]$ results [4] as a function of temperature was reconfirmed within 3%.

Upon the recognition of this unexpected and reproducible dependence of ϕ^* for $H_2:O_2 = 0.1$ mixtures upon the extent of dilution in argon, the seriousness of this effect as a flaw in the reflected shock, CO flame spectrum method of studying chain branching kinetics was explored more extensively. Two further series of $H_2:O_2 = 0.10$ mixtures were examined, which are denoted II through IIC and III through IIIA and represented in Table 2. $\phi^*/[H_2]$ from the end-on CO—O experiments at $H_2:O_2 = 0.1$ are displayed as a

TABLE 2
Particulars of ϕ^* Experiments in Gas Mixtures with $H_2:O_2 = 0.10$

| Mixture | Symbol ^a | % H_2 | CO: H_2 | Diluent and Mole Fraction | P_0 (Torr) | No. of ^b Experiments | Spectral ^c Band pass | $(\phi^*/\%calo)_{avg}$ |
|-----------------------|---------------------|---------|-----------|---------------------------|--------------|---------------------------------|---------------------------------|-------------------------|
| I | ■ | 1.49 | 0.667 | Ar, 0.83 | 25 | 6 | J, A | 0.76 ± 0.05 |
| | ■ | 1.49 | 0.667 | Ar, 0.83 | 50 | 3 | J | 0.84 ± 0.04 |
| IA | ■ | 1.42 | 4.02 | Ar, 0.79 | 25 | 7 | J, A | 0.74 ± 0.04 |
| IB | ● | 0.71 | 4.02 | Ar, 0.89 | 50 | 3 | J | 0.87 ± 0.00 |
| S-P(III) ^d | ● | 0.73 | 5.3 | Ar, 0.89 | 50 | 9 | A | 0.88 ± 0.02 |
| II | ● | 0.63 | 4.71 | Ar, 0.90 | 50 | 15 | H, K, L | 0.84 ± 0.05 |
| IIA | ▲ | 0.25 | 4.71 | Ar, 0.96 | 125 | 14 | H | 0.94 ± 0.04 |
| IIB | × | 0.091 | 4.71 | Ar, 0.99 | 350 | 8 | H | 0.99 ± 0.05 |
| IIC | + | 0.090 | 22.3 | Ar, 0.98 | 350 | 4 | H | 1.04 ± 0.05 |
| III | ▲ | 1.82 | 1.65 | Ar, 0.77 | 19 | 3 | H | 0.73 ± 0.02 |
| | ▲ | 1.82 | 1.65 | Ar, 0.77 | 25 | 5 | H | 0.69 ± 0.05 |
| | ▲ | 1.82 | 1.65 | Ar, 0.77 | 50 | 2 | H | 0.76 ± 0.06 |
| IIIA | ▼ | 1.36 | 1.65 | Ar, 0.68/ He, 0.25 | 25 | 4 | H | 0.77 ± 0.02 |

^aRefer to Figs. 3, 5, and 6.

^bSome of these experiments lie outside the abscissa range of Fig. 3.

^cRefer to Fig. 1.

^dData from [4].

function of temperature in Fig. 3. The ranges of compositions and working densities of these mixtures were broad enough that rate-limiting effects of both Reactions (f) and (l) were quite recognizable, and Fig. 3 serves primarily to illustrate the precision within the measurements grouped according to gas composition and the approximate magnitude of the dilution and other composition effects.

The most elementary conclusion from the range of results shown in Fig. 3 is that the dilution and gas composition effects found here are not of themselves large enough to account for the range of results assembled in Table 1. The following specifics relating to the present experiments must also be noted before we proceed to a more detailed treatment of the assembly of ϕ^* data at H₂:O₂ = 0.10. First, the range of partial pressures of H₂ and O₂ employed in the experiments, and hence, the range of values of ϕ^* , spans at most about a factor of three. The much larger variation in mole fractions of H₂ and O₂ has been coupled

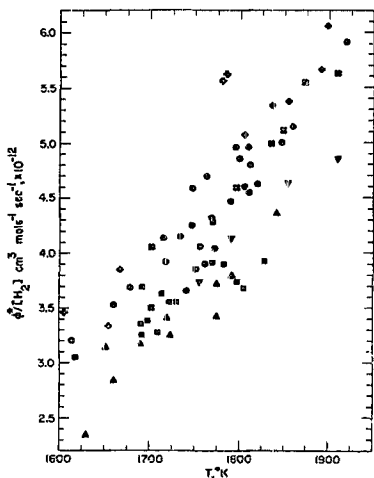


Fig. 3. Exponential branching rates measured by CO flame spectrum chemiluminescence in reflected shock waves, for gas mixtures having H₂:O₂ = 0.10, individually specified and coordinated with symbols in Table 2.

systematically with a corresponding range of total gas pressures, so that, in the main, the systematic effect of progressive dilution of the reagents upon ϕ^* is an effect of changing the amount of diluent in experiments done on the same densities of reactant gases, and on substantially the same time and chemiluminescent signal amplitude scales, and thereby subject to presumably the same potential defects arising from outgassing of impurities, electronics deficiencies, or whatever.

Second, it is important to recognize that the main observed effect of adding diluent is to increase ϕ^* , which is opposite to the expected influence of enhancing the rate of Reaction (f). This latter effect is only noticed qualitatively in the results from the highest pressure set of experiments, with Mixture IIB.

Third, the effect of dilution is not systematically associated with Reaction (l), as the CO:H₂ ratio is constant through the sequence of Mixtures II, IIA, IIB, and covers a fivefold range between Mixtures I and IA.

Finally, the effect of varying the working density of a given mixture is explored to a degree with Mixtures I and III, over ranges of a factor of 2 in the former case and 2.6 in the latter. While the unexpected effects of these variations on the ϕ^* data are not demonstrably nil, neither are they uniform, or so readily recognizable as the effect of gas composition.

Further workup of the data shown in Fig. 3 has been done by solving Eq. (2) for its positive root, which we denote ϕ_{calc} , under the temperature and composition conditions of each experiment, or the basis of independent rate coefficient data for each of Reactions (a), (b), (c), (f), and (l). The values and sources of these data are set out in Table 3, where one sees that the values of k_a used are those developed later in the present paper on the basis of the ϕ^* data from H₂-rich mixtures only, and all the other values are derived from other types of experiments [18–20]. The ratios $\phi^*/\phi_{\text{calc}}$ for the several experiments in each group specified in Table 2 were averaged to give the means and standard deviations in the final column.

This procedure accomplishes two purposes in preparation for the subsequent consideration of these results under Discussion. First, it sorts out accountable effects of Reactions (a), (f), and (l)

TABLE 3
Elementary Reactions and Rate Coefficients Used in Interpreting ϕ^* Data

| Reaction | $k_i(T)^a$ | Temperature basis (K) | Source |
|--------------------------------------|---|-----------------------------|-----------|
| a $H + O_2 \rightarrow OH + O$ | $1.22 \times 10^{17} T^{-9.97} \exp(-16.63/RT)$ | 1250–2500 | this work |
| b $O + H_2 \rightarrow OH + H$ | $2.07 \times 10^{16} \exp(-13.75/RT)$ | 1460–1900 | [18] |
| c $OH + H_2 \rightarrow H_2O + H$ | $5.3 \times 10^{17} \exp(-6.5/RT)$ | 1200–1800 | [19] |
| d $OH + CO \rightarrow CO_2 + H$ | $4.0 \times 10^{12} \exp(-8.0/RT)$ | 1500–2000 | [19] |
| f $H + O_2 + M \rightarrow HO_2 + M$ | 2.2×10^{15} | 1250–1900 | [20] |

^a RT in kcal/mole, k_f in $\text{cm}^6 \text{mole}^{-2} \text{sec}^{-1}$, other k 's in $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$.

from the composition-dependent ϕ^* data at $H_2:O_2 = 0.10$, to permit a more direct assessment of the dilution effect. And second, it provides a basis for comparing the range of dilution-dependent ϕ^* results in lean mixtures with the results to be expected on the basis of Eq. (2) and the independent data on Reactions (b) and (c).

The same sense of effect of dilution can also be seen in Fig. 2, for $H_2:O_2 = 0.33$, where the new data lie low in the band of earlier results, taken at greater but finite dilution, while the calculated line lies above the middle of this band.

Supplementary Experimental Tests in Lean Mixtures

In the course of this study, one operational difference between the CO—O chemiluminescence measurements of ϕ^* and the infrared emission measurements of [5] became apparent. It was determined that, owing to the differences in radiation intensities, backgrounds, and compatible instrumental sensitivities, the infrared measurements of exponential growth rate, for comparable reactant densities and temperatures, were uniformly made over spans of time after shock wave arrival which were later than those that yield the ϕ^* data reported here and in [4]. This difference was particularly acute for the H_2 -lean compositions, where the two spans did not even overlap. As the infrared measurements could not be made at earlier times, some tests of CO—O chemiluminescence growth were conducted in Mixture II at much lower sensitivity and correspondingly later times. Qualitatively, the transition from steep, exponential growth to less steep acceleration was smooth and gradual until $d \ln$

(intensity)/ dt had fallen to a few tenths of its earliest steady value, and only afterward was precipitous decrease in this quantity noticeable over a single decade of growth of intensity.

After the ϕ^* results from Mixture I, IA, and IB had been obtained, another test of the infrared measurements was made using Mixture IB to determine whether a similar effect of dilution might be revealed between these experiments and those of [5] at twice the H_2 and O_2 percentages. Owing to the insensitivity and data scatter experienced in this test, its results were incapable of conclusively confirming or denying the $\sim 20\%$ effect found in the CO—O measurements.

H_2 -rich ϕ^* Measurements

ϕ^* values were determined in 32 new experiments in gas mixtures having $H_2:O_2 = 10.0$, for the conditions summarized in Table 4. Besides extending the data for this $H_2:O_2$ ratio upward to 2350 K, these experiments serve specifically to test for systematic effects of gas density and dilution upon ϕ^* .

The data from all these experiments, plus nine $H_2:O_2 = 10.0$ points from Table I of [1], are represented in Fig. 4. The ordinate in this plot is k_a , and the apparent value from each experiment is derived from the measured ϕ^* by solving Eq. (2) with k_b, k_c, k_f , and k_l taken from independent sources and given in Table 3. The small relative adjustments of the data resulting from this procedure can be gauged by the ratios of the derived k_a to the corresponding values of $\phi^*/2[O_2]$. This ratio varies gradually with temperature from 1.08 at 2350 K to 1.10 near 2000 K, and 1.12 near

TABLE 4
 Particulars of ϕ Experiments at H₂:O₂ = 10

| Mixture | Symbol ^a | % H ₂ | % CO | P ₀ (Torr) | No. of experiments | T Range (K) | (<i>k</i> _{expt} / <i>k</i> _{fit}) _{avg} |
|---------|---------------------|------------------|------|--------------------------|-----------------------|----------------|---|
| IV | ■ | 10.0 | 4.0 | 100 | 11 | 1268–2064 | 0.984 ± 0.061 |
| | ▲ | 10.0 | 4.0 | 35 | 8 | 1544–2347 | 0.982 ± 0.050 |
| IVA | ● | 3.5 | 1.4 | 100 | 13 | 1475–2035 | 1.016 ± 0.080 |
| GS | ◆ | 5.0 | 3.3 | 150 | 9 | 1278–1648 | 1.018 ± 0.071 |

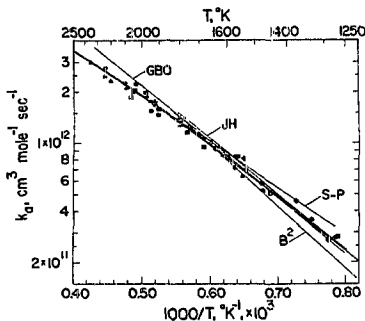
^aRefers to Figs. 4 and 7.

Fig. 4. Arrhenius plot of k_d derived from individual ϕ measurements at H₂:O₂ = 10, for sets of conditions specified and coordinated with symbols in Table 4. Straight line segments: Arrhenius expressions from previous sources GBO [5]; S-P [4]; B² [6]; JH [11]. Heavy curve: this work, Eq. (3), based on 41 points shown, plus 44 experiments at H₂:O₂ = 3.0, from [1, 4].

1500 K, and then rises more abruptly as Reaction (f) becomes influential, reaching 1.29 near 1250 K. Thus, above 1500 K, Fig. 4 faithfully represents the scatter among the data and the agreement, based on the expectation from the chemical mechanism, among the data from mixtures covering threefold ranges of dilution and working density.

Chemiluminescence from H₂—O₂—Ar System

At an early stage in the present study, experiments were undertaken in which time constants ϕ^{**} for near ultraviolet chemiluminescence were measured near 1700 K in a mixture of 1.5% H₂, 15% O₂, 83.5% Ar. An RCA 6903 photomultiplier and a fused silica viewing window were used, so as

to provide as much sensitivity to the OH A²Σ → X²Π emission as to any other near-uv chemiluminescent spectrum.

These experiments showed that $\phi^{**}/[\text{H}_2]$ was consistently larger than $\phi^*/[\text{H}_2]$ in mixtures of similar dilution, by a factor between 1 and 2, but they were imprecise and not convincing in distinguishing whether the ϕ^* data or the infrared data at H₂:O₂ = 0.10 were anomalous.

In the course of these experiments, however, the influence of spectral bandpass was explored more fully than in [3], with the following results:

(i) In the apparatus and at the temperatures used, the exponential rise in emission is preceded by a significant, apparently linearly rising component. This interfering component, whose presence delays the time at which exponential growth may be measured, is greatly reduced by a Corning #9863 filter, which confines the accepted spectral band to $\lambda \leq 420$ nm.

(ii) Most of the intensity (surely not less than 50%, and not demonstrably less than all) of the chemiluminescent component growing exponentially with time constant ϕ^{**} is transmitted by Pyrex and also by a Corning #7380 glass filter ($\lambda \gtrsim 340$ nm), and is therefore not A²Σ → X²Π (0,0) radiation.

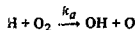
(iii) Attempts to localize the spectral bandpass of ϕ^{**} determinations near 308 nm, either with an f/8.5 grating monochromator (JACO Model 82-000) or an interference filter ($\lambda_{\text{max}} = 306$ nm, $Tr_{\text{max}} = 13.5\%$, $\Delta\lambda_{1/2} = 9$ nm), together with the RCA 6903 (S-13 response) photomultiplier, all in the end-on shock tube configuration of [1-5], did not afford adequately noise-free signals until times so late in the ignition process that the induction

period as measured by OH absorption [10] had passed, and the semilogarithmic plots of intensity were noticeably convex upward.

(iv) Conclusion (ii) above was verified also for 2% H₂, 6% O₂, 92% Ar in experiments near 1050 K, the same conditions employed in [3].

Discussion

High-Temperature Rate Coefficient of



The new data points in Fig. 4 are important in showing the absence of a perceptible effect of gas pressure or dilution upon the value of k_a derived from CO—O ϕ^* measurements in H₂-rich mixtures. This freedom from experimental inconsistencies, found also at H₂:O₂ = 10 by [5] using the infrared diagnostic, rejustifies the extraction of k_a data from these experiments and correlation of the results at different temperatures and from different investigations.

Such correlation over the 1250–2500 K range is illustrated in Arrhenius coordinates in Fig. 4. Existing end-on, CO—O ϕ^* data at H₂:O₂ = 3 [1, 4] were also included in the correlation, k_a values being determined by the same procedure and rate coefficient set (Table 3) used in treating the 10:1 data. It was observed graphically that the k_a data from the 3:1 and 10:1 experiments agreed, and freedom of the 3:1 data from the dilution effect, while never tested directly, is inferred from the trend defined by the experience at H₂:O₂ = 10, 0.33, and 0.10.

To describe the convex upward curvature displayed by both the 3:1 and 10:1 bands of points, and to arrive at a single expression which unifies this whole body of data, the combined k_a values from the 3:1 and 10:1 experiments were least-squares fit to the familiar modified Arrhenius form

$$\log_{10} k = \log_{10} A + \frac{E}{RT} - \ln(10).$$

E was fixed arbitrarily at the value of ΔE_0° , 16.63 kcal/mole, and the residual temperature dependence was incorporated in the value of \underline{A} . The resulting curve is given by

$$k_a = 1.22 \times 10^{17} T^{-0.907} \exp(-16.63 \text{ kcal}/RT) \\ \text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}, \quad (3)$$

by which the local activation energy for 1250 < T < 2500 K is

$$-R d \ln k_a / d(1/T) = 16.63 \text{ kcal/mole} \\ - 0.907 RT. \quad (4)$$

The satisfactory fitting of the 10:1 data by Eq. (3) is exhibited in Fig. 4, and the simultaneous agreement with the 3:1 data can be gauged by the fact that Eq. (3) is based on like numbers of 3:1 and 10:1 data points similarly distributed over the temperature range [1, 4]. Actually, the 3:1 data are somewhat less scattered, particularly above 2000 K [4], and treated by themselves define a slightly steeper curve over 1. Fits of the 3:1 data and 10:1 data individually yielded $\underline{A} = -0.79$ and $\underline{A} = -1.04$, respectively. These individual curves cross near $1000/T = 0.6$ and differ by 9% at the extremes of $1000/T$, 0.4 and 0.8. These disparities and the spread of the data points in Fig. 4 indicate the precision of the present experimental knowledge of k_a provided by end-on CO—O ϕ^* results in the H₂-rich mixtures.

Previous recent determinations of k_a from ϕ^* data at H₂:O₂ ≥ 3 above ~ 1100 K have provided the four straight-line Arrhenius representations plotted in Fig. 4. The first point to note is that between about 1600 and 1900 K, all five determinations of k_a agree within a 10% total spread. This agreement among rich ϕ^* measurements by four techniques in three laboratories is believed to define k_a well enough that the corresponding investigation of the D₂—O₂ system would now be profitable.

Above ~ 1900 K, the present CO—O ϕ^* results at H₂:O₂ = 10 and those at H₂:O₂ = 3 from [4] give k_a values that are clearly lower than those derived from the infrared measurements by [5]. The basis of this disagreement is partly that [5] obtained a cluster of larger $\phi^*/2[\text{O}_2]$ values near 2200 K, and partly that their interpretation included distinctly lower k_b and k_c values than we now favor [18, 19].

Straight extrapolations of the data measured up to ~ 1900 K by [11] and [6], as well as other previous estimates and Arrhenius correlations assembled by Baugh et al. [17], lie above Eq. (3) at $T > 2000$ K. The precision and direct sensitivity to k_a of the CO—O ϕ^* method in rich

mixtures, together with the good experience this method affords below 1900 K, lead us to contend that, at ~2000–2400 K, Eqs. (3) and (4) are to be preferred over previous assessments of the rate coefficient and local activation energy of Reaction (a).

Below ~1500 K, the extension of the S-P line does not satisfactorily follow the rich mixture data, which bend downward, and this extension must now be rejected in favor of Eq. (3). At these temperatures, there remains disagreement between the present results for k_a , corroborated by infrared and OH absorption data, and those from the side-viewed incident shock CO—O measurements of ϕ^* after adjustment of the temperature and time scales for the boundary layer effect [6, 8]. With such an adjustment, the OH absorption data of [11] would also be displaced downward and to the left in Fig. 4, away from the present results in the same sense that the B² results disagree. Present knowledge of the reliability of reflected shock wave technique for somewhat slow reactions on the one hand, and of the correctness of incident shock boundary layer treatments on the other, does not enable a clear choice to be made between the higher k_a values found here over the 1250–1500 K range and the lower ones of [6]. An independent basis of choice is offered by correlation between the 1600–1900 K range and the much-studied 800–1000 K range [17, 21, 22]. Detailed examination of this correlation is left to the concerned reader or compiler.

Theoretical accounting of the steadily diminishing local activation energy of Reaction (a), which is embodied in Eq. (3), is not developed here. Suffice it to recall that Kurzius and Boudart [21] sought to account for the magnitude of k_a and its deuterium isotope effect near 800–1000 K, and concluded that a conventional transition complex description does not succeed. They observed that the model with which they did account for their data also leads to a convex upward Arrhenius plot of k_a , when extended upward to 2000 K. Quantitatively, the summary expression on page 487 of [21] gives values that are higher than Eq. (3) by a factor of 1.14 at 1250 K and 1.41 at 2000 K, so that the calculated curvature by the treatment of Kurzius and Boudart is uniformly smaller than that found here.

Lean Mixture Findings

The data of Figs. 2 and 3 and Table 2 relate to several questions, in two general categories. First, what are the source and extent of the anomalous dilution effect upon ϕ^* found in lean mixtures? And second, how may measurements of ϕ^* in lean mixtures under different circumstances be related to each other and to the ignition kinetics embodied in Eq. (2), particularly the temperature-dependent rates of Reactions (b), (c), and (f)?

Figures 5 and 6 represent the mean ϕ^*/ϕ_{calc} results from Table 2 as functions of gas pressure and gas composition, respectively. The main result is that by either plot a smooth dependence upon dilution is obtained, which suggests short extrapolation to infinite dilution. The facts that these extrapolated intercepts are near unity and that all of the data lie between ~0.7 and 1.1 are an inducement to regard these ϕ^* measurements as providing confirmation of the independently measured set of rate coefficients in Table 3, particularly k_b and k_c , to which ϕ_{calc} is most sensitive for the present gas compositions. However, the range and precision of the data displayed here do not clarify whether the dilution effect upon ϕ^* is to be correlated with working pressure or with mole frac-

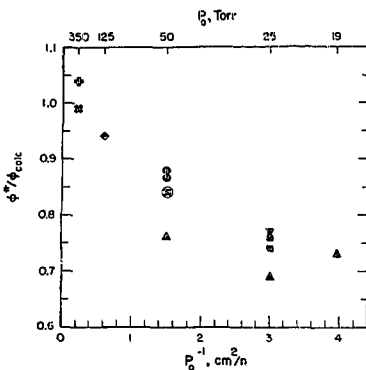


Fig. 5. Dependence of ϕ^* results at H₂:O₂ = 0.10 averaged for each line in Table 2, upon preshock gas pressure, on same ordinate scale as Figs. 6 and 7 and same abscissa scale as Fig. 7.

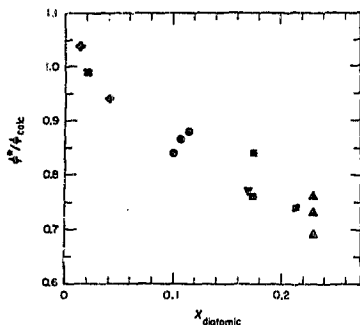


Fig. 6. Dependence of ϕ^* results at $\text{H}_2:\text{O}_2 = 0.10$, summarized as means for each line in Table 2, upon gas mixture composition, on same ordinate scale as Figs. 5 and 7.

tion of diluent. Nor is there a compelling significance to the extrapolated intercept. Figure 7 illustrates the comparative absence of the dilution effect in the 10:1 ϕ^* data, on a scale equivalent to those in Figs. 5 and 6.

As the extent of the dilution effect found in the 1:10 and 1:3 experiments is clearly not large

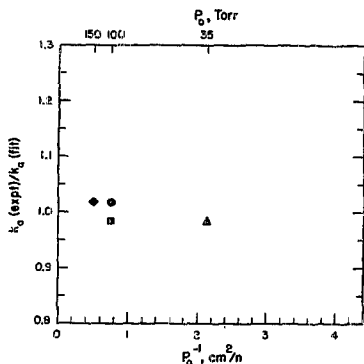


Fig. 7. Dependence of k_0 results from $\text{H}_2:\text{O}_2 = 10$ experiments, averaged for each line in Table 4, upon pre-shock gas pressure, on same ordinate scale as Figs. 5 and 6 and same abscissa scale as Fig. 5.

enough to account for the two-fold differences exhibited in Table 1, other accounting of the discrepancies must be sought. The lower values obtained by end-on infrared measurement are demonstrably attributable to the later time spans of those experiments, which at $\text{H}_2:\text{O}_2 = 0.1$ were also later than the end of the corresponding OH absorption induction periods of [10]. Applicability of this argument to the side-viewed CO—O measurements [7] cannot be verified from the details published.

With the newly available evidence [18, 19] that between 1000 and 2000 K the temperature dependences of both k_b and k_c (Table 3) are steeper than had been expected from data below 1000 K, the steep temperature dependence of ϕ^* in lean mixtures found by [4] need no longer be regarded as anomalous. The general conclusion which can be offered from the present and prior evidence is that end-on CO—O ϕ^* measurements made early in the ignition process in lean mixtures come close to corresponding with the ϕ that satisfies Eq. (2) with separately measured rate coefficients, but that determination of k_b , k_c , and k_l by this means is clouded by the dilution effect. The anomalies found in fitting ϕ^* data from several $\text{H}_2:\text{O}_2$ ratios [4, 5] and in the scaling of the reference emission intensity, I_0^* , with density [4] both depend upon precise knowledge of ϕ , and should be held in abeyance pending satisfactory explanation of the dilution effect.

The cause of the dilution effect may be sought in such areas as the shock tube technique, the CO—O chemiluminescence diagnostic, and the real chemical kinetics of ignition of lean H_2 —(CO)— O_2 mixtures.

A shock tube effect, such as cooling of the gas at the end plate, would be expected to occur just as strongly in rich mixtures, as the experimental gas pressures, time scales, and thermophysical parameters such as C_p/C_v and thermal conductivity do not differ markedly between the sets of conditions in Tables 2 and 4, and this is not borne out. Evidence of the presence or absence of the effect in incident shock measurements of ϕ^* is not available. An indirect indication of a dilution effect of the same qualitative sense as in Figs. 5 and 6 was found in the early [23] induc-

tion time measurements in incident shock waves, particularly at H₂:O₂ = 0.25, and at that time contributed to the failure of the effect of H₂:O₂ ratio to be correctly recognized. Finally, the infrared reflected shock study at H₂:O₂ = 0.1, done at time spans late in the ignition, failed to show an aggravated dilution effect or confirm the small one. Thus, we cannot conclusively associate the effect with shock tube technique.

Association of the dilution effect with the CO—O chemiluminescence is similarly indefinite, as existing ϕ^* measurements using OH absorption have not covered ranges of dilution at fixed H₂:O₂ ratio, and again the attempted infrared test was inconclusive. The present findings merely exclude a spectrally distinguishable interfering component in the chemiluminescence, and they do not exclude the possibility of failure of proportionality between the emission intensity and the product [O] [CO] on a short time scale [16].

One appealing hypothesis is that the dilution effect being seen is associated with a nonthermal vibrational condition of either the H₂ or the O₂, which would be more severe at lower collision frequency. Support for this proposition is diminished by the failure of inclusion of 25% of He in Mixture IIIA to displace ϕ^*/ϕ_{calc} from the bands of points in Figs. 5 and 6. More thorough investigation would be needed to dismiss this hypothesis conclusively.

Aside from the unique association with lean fuel:oxygen ratios, the characteristics of the present experiments which do seem associable with the dilution effect are precision and sensitivity, and the difficulty for further study is that the effect as found to date is awkwardly small. Perhaps mixtures still leaner than H₂:O₂ = 0.1 will enlarge the effect and permit more profitable investigation.

Pure H₂—O₂ System Chemiluminescence

The present finding of strong and/or dominant emission at $\lambda > 340$ nm under the experimental conditions of [3] voids the basis of the deductions made in that work about the kinetics of OH²Σ⁺ formation from O and H atoms. The finding by [3] of the presence of an emission process with $\phi^* = 2\phi$ is not affected, and their discussion of

alternative emitters and emission kinetics remains relevant.

Evidence with respect to the OH A²Σ⁺ → X²Π emission is now confined to that provided by [10] and [9].

J. L. Young and J. J. Damitz assisted in the execution of the experiments, and L. S. Blair provided the supplementary infrared measurements and worked up a portion of the CO—O φ data. Discussions with many colleagues, particularly Dr. R. W. Getzinger and Professor W. C. Gardiner, Jr. have helped guide the series of studies incorporated in this paper.*

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