

Transition from Branching Chain Kinetics to Partial Equilibrium in the
Shock-Induced Combustion of Lean Hydrogen-Oxygen Mixtures

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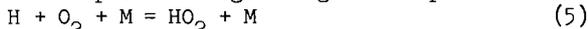
The chemical kinetics of the high-temperature reaction between hydrogen and oxygen has been the subject of numerous experimental studies. For the case of combustion in shock waves through hydrogen-oxygen mixtures highly diluted with argon, the kinetics may be divided into three regimes: in the initiation regime, small concentrations of atoms and/or radicals are generated by slow, unknown reactions; in the induction regime, bimolecular branching chain reactions lead to exponential increase in the concentrations of H, O and OH; in the recombination regime, termolecular reactions cause evaluation of heat and establishment of chemical equilibrium. The induction regime kinetics are thought to be explicable in terms of the mechanism



When the OH radical concentration is high, the fast reaction



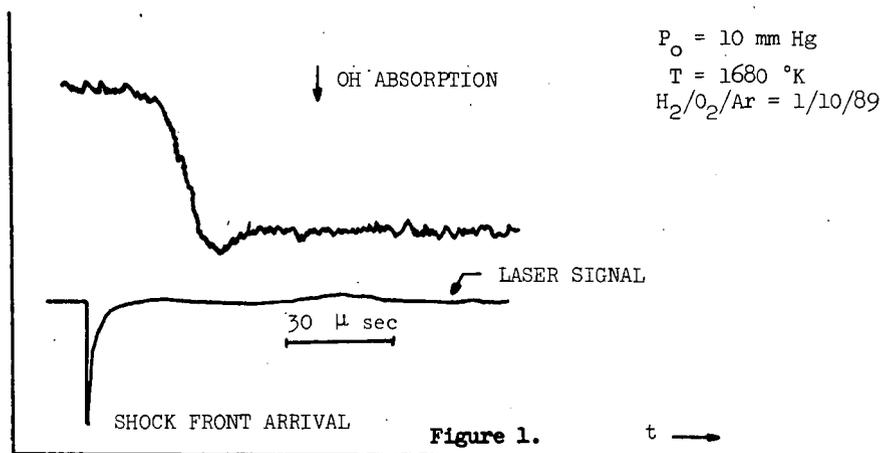
also contributes to interconversion of species. Neglecting the step



which is important for $p > 1$ atm, $T < 1200^\circ\text{K}$, defines the limits of validity of this mechanism. Rate constant expressions for all of these steps, based on a variety of experiments, have been proposed¹. The agreement among the various investigators is good.

The separation between induction and recombination regimes lies essentially in the fact that the termolecular reactions of the latter are far slower than the bimolecular reactions of the former. Steps (1-4) have, as a consequence, almost equal forward and reverse rates during the recombination regime, leading to a condition of partial equilibrium². It was shown recently by Hamilton and Schott³ that in mixtures with $[\text{H}_2]/[\text{O}_2] \equiv R$ either $\gg 1$ or $\ll 1$ the transition between induction regime kinetics, governed by the rates of (1-3) and the partial equilibrium condition, governed by the equilibrium constants of (1-3) could involve transient effects capable of yielding worthwhile information on the rate constants of (1-4). They investigated the situation with $R \gg 1$. They predicted large O-atom spikes, and from the experimental absence of OH spikes, they were able to deduce an upper limit for k_1/k_2 . We have investigated the situation for $R \ll 1$. The OH spikes absent in $R \gg 1$ mixtures are found to be quite pronounced for $R < 1$. Quantitative investigation of incident shocks in $\text{H}_2/\text{O}_2/\text{Ar} = 1/10/89$ mixtures, $p_0 = 10$ torr, $1400 < T < 2500^\circ\text{K}$ is reported here. The experimental technique combined OH concentration measurement by the Bi(3067) method⁴ with conventional shock tube methods.

The OH absorption signal for a run at 1680°K is shown in Fig. 1.



In order to convert the data to graphical form, some approximations are needed. First, the extinction coefficient for the Bi(3067) method fluctuates considerably from run to run. For these experiments each run was used as its own calibration point, and Beer's Law was taken to calculate the ratio $[\text{OH}](\text{spike})/[\text{OH}](\text{partial equilibrium})$, with the level portion of the trace assigned to the partial equilibrium condition, for which $[\text{OH}]$ can be readily computed from the shock speed. To assign error limits to this ratio, the appropriate extreme points were read from the records and likewise substituted into Beer's Law to get the upper and lower limits for the $[\text{OH}](\text{spike})/[\text{OH}](\text{partial equilibrium})$ ratio. Since the full width of the spikes is difficult to determine both on the experimental records and on the computed profiles, we use the apparent full width at half height for the quantitative shape parameter. By apparent half width is meant the width which would be obtained on the accurate computer plotout of the profile by extrapolating the slightly sloped post-spike $[\text{OH}]$ (a small amount of recombination does occur on the time scale of these experiments via Reaction (5)) back to the center of the spike, and then measuring the full width of the spike half way between the back extrapolation and the top. On the records themselves, this means reapplication of Beer's Law to get the correct half height. The results are presented in Figs. 2 and 3.

The first approach to interpret these data is to search for a set of rate constants for the mechanism (1-4) which will predict the correct spike heights and spike durations. This is greatly assisted by the availability of much good data, and a suggestion by Schott that lean mixture maxima would be favored by large values of the ratio k_2/k_3 . We started with the rate constant expression for k_1 given by Baldwin and Melvin^{1b}, the k_2 expression given by Clyne and Thrush^{1c}, and the k_3 and k_4 expressions given by Kaufman and DelGreco^{1a}. A recent experiment by Gutman and Schott^{1f} provides a new value for k_1 which can also be used as input. For the critical k_2 , there are three studies which supercede the consensus of Clyne and Thrush, all giving higher values of k_2 ; these were done by Wong and Potter^{1g}, Westenberg and de Haas^{1e}, and Gutman and Schott^{1f} again. A higher value of k_4 has been reported by Dixon-Lewis, Wilson and Westenberg^{1h}. The hint regarding the k_2/k_3 ratio may be understood in the following way. In order to produce a spike in the OH profile, the induction period reactions must behave in such a way that OH production temporarily exceeds OH destruction as the H_2 concentration suddenly drops from its induction period value to its partial equilibrium value. Reaction (4) unambiguously destroys OH rapidly at this time; Reaction (1) provides reactants for both (2) and (3) at equal rates; this leaves (2) and (3) as the primary generators of the OH profile. Both of them have the same dependence on H_2 , so both will have rates which drop suddenly as the last H_2 is consumed. Overproduction of OH by (2) can then lead to more OH than can be consumed by (3) when H_2 comes into

short supply, and an overshoot occurs. This analysis is rather oversimplified, as our subsequent analysis will show; however, the direction of seeking high values of k_2 is clear. Whether or not it will be fruitful to seek low values of k_3 will depend on the value of k_4 .

First consider the peak heights and half widths which are predicted by numerical integration using the k_1 and k_2 values of Gutman and Schott. (Figs. 2 and 3.) The half widths are approximately correct, but the heights are far lower than the data indicate. Immediately we can conclude that it is unnecessary to investigate further with the k_2 value of Clyne and Thrush, for it is lower than Gutman and Schott's at 1500°K by factor 2. Next, increase the value of k_2 and see what happens. Just as expected, the heights increase; the half widths decrease. By trial and error, a k_2 value 5 times that of Clyne and Thrush, or 2-1/2 times that of Gutman and Schott, is found to give the right height and half width at 1500°K. In subsequent calculation it is found that the right temperature dependence is found also, although the high temperature values are perhaps somewhat high. The influence of k_1 in place of the Gutman and Schott value. It is seen that the difference is minor. Varying k_2 has little effect. When the rates of the reactions are checked, it is found that the lack of effect of k_2 is simply due to the fact that OH is mostly consumed by (4) rather than (3) at the spike time. Therefore, in order to try to reproduce the spike by lowering the OH consumption rate at the time of the spike, k_4 must be reduced. It is indeed possible to increase the heights somewhat by this procedure; however, the predicted half widths are seen to become far too large, and we conclude that it is useless to try to predict the spikes by lowering the OH destruction rate from that predicted by the consensus rate constants.

To summarize this approach to predicting the spikes by numerical integration of the conventional mechanism, we find that reasonably satisfactory agreement is obtained if k_2 is taken as about 2-3 times the value predicted by the expressions of Gutman and Schott, Wong and Potter, or Westenberg and de Haas. Furthermore, this is the only way to predict spikes with this mechanism. The shortcomings of this approach are the disagreement with other values for k_2 and the impossibility of reconciling high values for k_2 with the observed dependence of ignition delays upon R_4 .

There are several other ways in which OH-spikes might be produced. The possibility that the observed oscilloscope traces are due to an inadequacy in the Bi(3067) method arising from its sensitivity to OH($v=0$) may be rejected as a quantitative explanation by noting that at 1500°K only 7% of the OH molecules are in excited vibrational states. The maximum thermal effects of vibrational relaxation are only 3-4% for these mixtures. Trace amounts of impurities could only affect the results by bimolecular catalysis of the recombination reactions or by intervention in the already fast branching mechanism. We see no way to accomplish either of these, although they cannot be rejected on our evidence. Finally, it must be allowed that some combination of causes could be the source of the observed spikes.

We conclude that the observed OH profiles in shock-induced combustion of lean H_2-O_2 -Ar mixtures can be explained on the basis of the conventional mechanism if the rate for $O + H_2 = OH + H$ is assumed to be about twice the current best value from other experiments. Since such an assumption leads to substantial discrepancies in the interpretation of other experiments, we consider this explanation to be suggestive only, and subject to refinement as further experimentation is done on the high-temperature chemistry of the H_2-O_2 reaction.

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Note for Figs. 2 and 3. The solid error bars denote runs made using the Bi(3067) method; the dashed error bars denote runs made using the water lamp method.

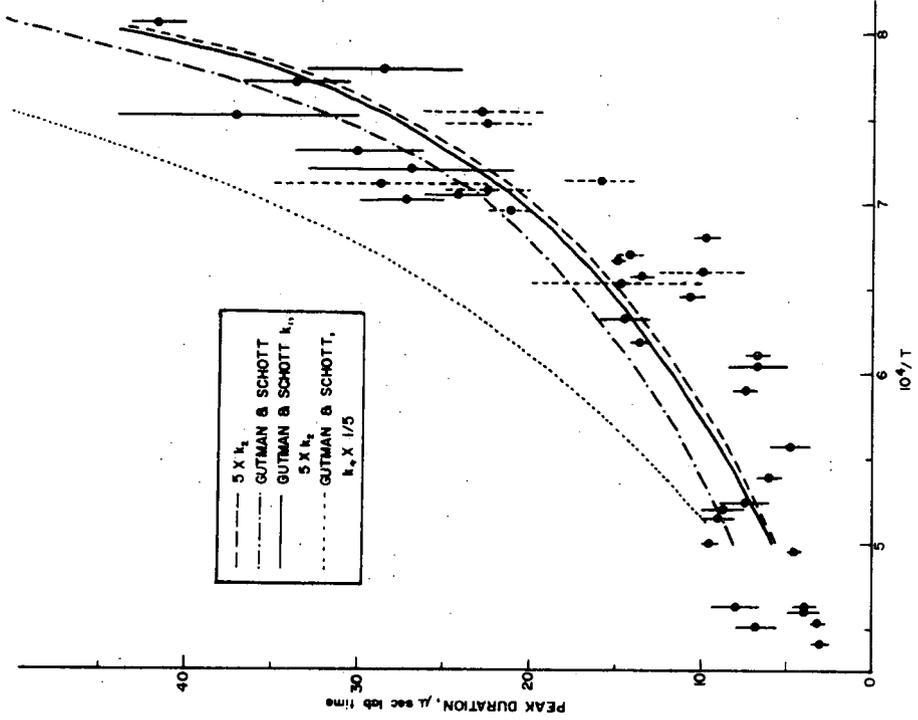


Figure 3.

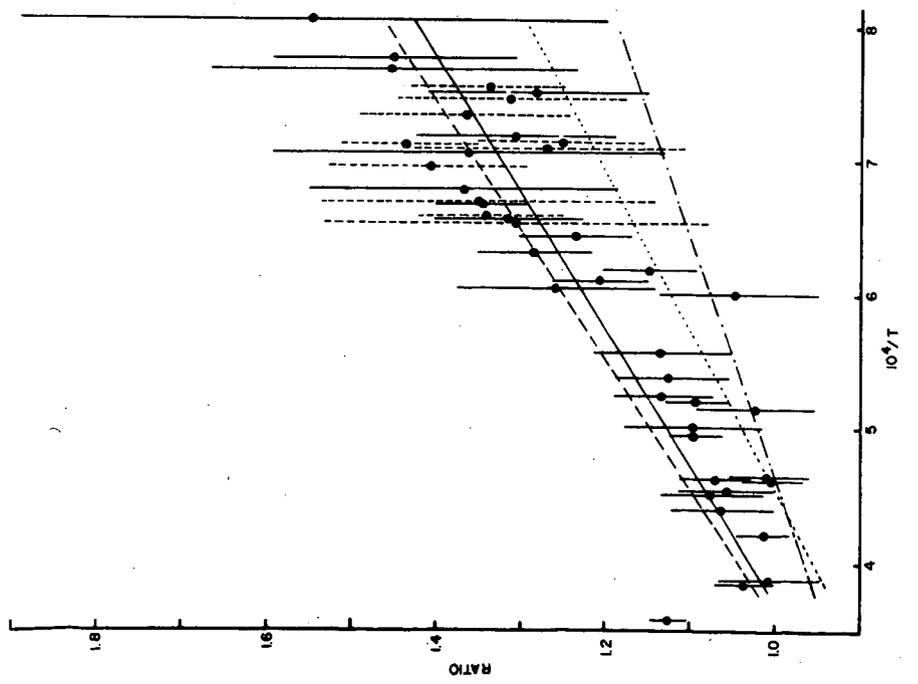


Figure 2.