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POST-INDUCTION KINETICS IN SHOCK INITIATED $H_2 - O_2$ REACTIONS*

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Summary

The course of the shock initiated hydrogen - oxygen reaction after the induction period, during the transition to partial equilibrium, has been investigated by computer integration of the rate equations, and approximate analytic descriptions of particular aspects are developed. $H_2 : O_2$ ratios far from stoichiometric are considered. An earlier suggestion by one of the authors that partial equilibrium conditions with no recombination represent a practical upper limit to the transient atom and radical concentrations is contradicted, and attention is focused on the pronounced "spike" in oxygen atom concentration that modern rate coefficient data predict to occur in fuel-rich mixtures at the time of maximum reaction rates and most rapid O_2 depletion. Failure of measured OH concentrations to exhibit such "spikes" in rich mixtures is used to establish an upper limit to the ratio of rate coefficients k_a/k_c .

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over the range $1156^\circ \leq T \leq 1884^\circ K$.

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Introduction

In an earlier paper,¹ one of us reported observations of the maximum OH concentration developed at the end of the induction period in the shock wave combustion of stoichiometric and nearly stoichiometric hydrogen - oxygen mixtures dilute in argon. At temperatures between about 1000° and 2600°K, these concentrations exceed their ultimate equilibrium values by large factors, and this "overshoot" was accounted for approximately by the notion that the conditions in the reaction mixture at the time of the OH concentration maximum corresponded to a state of partial equilibrium among the three independent reactions of the branching chain mechanism,

which was achieved promptly at the end of the induction period, before the recombination reactions had progressed appreciably. It was suggested, moreover, that the partial equilibrium values represented practical upper limits to the maximum concentrations reached by OH and the other reaction intermediates.

We report here a more thorough investigation of the course of the hydrogen - oxygen reaction at the end of the induction period, which consists

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of the results of numerical integration of the reaction rate equations on a digital computer, complemented by approximate analytic expressions which describe the reaction course in an instructive way. In particular, we have been drawn by recent experimental work^{2,3} to give attention to mixtures far from stoichiometric, both extremely rich and extremely lean. In such mixtures we have found conditions under which the concentration of one or more of the chain carrier species may rise to a peak value considerably in excess of its partial equilibrium value and then drop quickly as partial equilibrium conditions are approached. Such a pronounced maximum, which we term a "spike", is predicted to be exhibited most strikingly by oxygen atoms in rich mixtures.

Computer Methods and Results

The digital computer code which we have developed and used for generating reaction profiles of steady, one dimensional shock waves in inviscid, ideal gas mixtures possessing assumed sets of chemical reaction steps and rate coefficients is an outgrowth of two earlier codes for this purpose.^{4,5} With the initial state of the subject gas (initial density, ρ_0) and the shock velocity, U_0 , as fixed parameters, the Rankine - Hugoniot equations are solved iteratively for a reference condition (normally that of thermal equilibrium with no chemical reaction) behind the shock front. The differential equations for the ensuing changes accompanying the r chemical reactions among the s species are formulated as:

$$\frac{dU}{dy} = \frac{1}{\omega} \sum_{j=1}^S \left(\frac{M}{\rho} - \frac{H_j}{T\theta} \right) \frac{\partial C_j}{\partial y}$$

$$\frac{dC_j}{dy} = \frac{\partial C_j}{\partial y} - \frac{C_j}{U} \frac{dU}{dy} \quad j = 1, \dots, S$$

$$\frac{dp}{dy} = - \frac{\rho_o U_o}{A} \frac{dU}{dy}$$

$$\frac{dT}{dy} = \frac{T}{p} \frac{dp}{dy} - \frac{TH}{\rho} \sum_{j=1}^S \frac{dC_j}{dy} .$$

with the auxiliary relationships:

$$\theta = \sum_{j=1}^S C_j C_{p_j}$$

$$\frac{\rho}{M} = \sum_{j=1}^S C_j$$

$$\omega = \frac{1}{U} + \rho_o U_o \left(\frac{1}{BT\theta} - \frac{1}{A p} \right)$$

$$\frac{\partial C_j}{\partial y} = \frac{1}{U} \sum_{i=1}^r r_i B_{ij} .$$

where U is the gas velocity with respect to the shock wave, y is distance behind the shock front, C_j is the molar concentration of the j^{th} species, H_j and C_{p_j} are the corresponding molar enthalpy and its derivative with

respect to temperature, T , and p is static pressure. A and B denote necessary factors for reckoning units. The partial derivatives $\partial C_j / \partial y$ represent the net contributions to the species concentration changes attributable to the elementary chemical reactions having net stoichiometric coefficients β_{ij} and conventional chemical rates r_i . Additional supplementary relationships are used for such variables as density and time which are carried through the course of the integration.

The code uses the integration algorithm formulated recently by Treanor.⁶ We find that this algorithm affords significant economy in computing time, compared to the ordinary fourth order Runge - Kutta procedure, particularly in the late stages of the hydrogen - oxygen reaction.

The elementary steps of the chemical reaction mechanism are expressed in chemical symbolic form as

The net stoichiometric coefficients are

$$\beta_{ij} = v_{-ij} - v_{ij}$$

and the forward and reverse rate coefficients are related through the equilibrium constant, K_i , by

$$k_i / k_{-i} = K_i.$$

The net rate, r_i , is then given as the sum of the forward and reverse rates, which take the form

$$r_i = r_i^0 - r_{-i}^0 = k_i \left(\prod_{j=1}^S c_j^{v_{ij}} - \frac{1}{K_i} \prod_{j=1}^S c_j^{v_{-ij}} \right).$$

The rate coefficients k_i for ordinary chemical reactions are expressed in the generalized Arrhenius form

$$k_i = A_i T^{m_i} \exp(-E_i/RT).$$

Recombination reactions involving third bodies are handled in the present cases, where a common value of k_i is assigned for all third body species, by excluding third body considerations in assigning v_{ij} and v_{-ij} and multiplying the assigned k_i by

$$\sum_{j=1}^S c_j$$

in the computation of r_i .

The list of elementary reactions included in our numerical investigation is given in Table I. This list is subdivided as follows: The five reactions (a) - (e), including the branching chain sequence (a) - (c) and the metathesis initiation reaction (d), were used for the computations designated as "without recombination." The limited mechanism consisting of reactions (a) - (h) was used for the computations including recombination for the fuel-rich mixtures. The above computations included only the seven species H_2 , O_2 , H_2O , OH , H , O , and Ar . For recombination computations in the fuel-lean cases, the peroxides HO_2 , H_2O_2 , and O_3 , and the complete list of reactions, were included.

Thermochemical quantities for the above species were summarized over the required ranges of temperature in a self-consistent polynomial form.⁷

Coefficients for the polynomials were obtained from elementary theory for Ar and H atoms, and by a least squares fitting of tabulated data⁸ for the other species.

Rate coefficient parameters are included in Table I for those ten cases where the values used represent published information based on experiment.⁹⁻¹⁴ For the remaining eighteen reactions, the coefficients used were arbitrary estimates guided primarily by collision theory. Our conclusions are not sensitive to the values of these coefficients, and we cite the reactions only to indicate the complexity expected to be encountered in a complete description of recombination in stoichiometric and lean mixtures.

The sets of reaction conditions and the combinations of values of k_b and k_c used for the several profile computations are given in Table II. The characteristics of the post-induction period kinetics for the several computational cases indicated in Table II are summarized in Figs. (1) and (2) and the indicated columns in Tables III and IV.

Description of Kinetics

From study of the results of these computations, we notice the following characteristics of the reaction course at the termination of the induction period and during the transition to the subsequent partial equilibrium, slow recombination behavior. The period of exponential growth of reaction rates and product concentrations, with fixed stoichiometry, is ended by the combined effects of depletion of reactants and the commencement of reactions, including reverse reactions, which involve the accumulated products. To be sure, the growth of the reverse reaction rates $r'_{-a} - r'_{-c}$

to values equal to the corresponding forward rates is a necessary and sufficient requirement for the attainment of partial equilibrium conditions. However the numerical computations show that before some of these back reaction rates have become at all significant with respect to the forward rates, the net rates reach substantially simultaneous maxima and decline. This process occurs concurrently with significant consumption of the initial reactants, and is accompanied by marked depletion of the lesser reactant (i.e., of O_2 in rich mixtures or of H_2 in lean) leading to a marked shift in the $H_2 : O_2$ ratio. This is accompanied by a corresponding shift in the instantaneous reaction stoichiometry which of course is necessary to transform the reaction course from that of the induction period, determined only by rate coefficients and initial concentrations, to that of the partial equilibrium situation, determined by element conservation and equilibrium considerations.

The failure of particular back reactions to become important simultaneously with the depletion of reactants in the extreme mixtures is associated with the effect of the excess reactant, which continues to remove certain of the atom or radical intermediates rapidly even after their formation has been slowed dramatically by the depletion of the other reactant. This phenomenon delays the accumulation of the products of the rate-limiting reaction, and thus delays the attainment of the partial equilibrium situation.

We observe in passing, since a detailed consideration of the partial equilibrium - slow recombination regime is outside the scope of the present paper, that the ultimate partial equilibrium situation which is reached in extreme mixtures is one in which certain of the equilibria (reaction (a))

in rich mixtures, reactions (b) and (c) in lean) are characterized by small values of both r'_1 and r'_{-1} . These slowly reached equilibria are very susceptible, relative to the more quickly achieved and more effectively maintained ones, to perturbation by finite recombination rates.

The shift of the reaction stoichiometry around the time of the maxima in $r_a - r_c$ has a particularly dramatic manifestation in rich mixtures. Here the relative values of r_a and r_b early in the reaction are such that oxygen atoms are produced in much greater quantity than can be maintained when O_2 becomes depleted, and C_O exhibits a pronounced maximum, or "spike", immediately after the maximum value of r_a is reached. At this time, when C_{O_2} has decreased to about one-half its initial value and dC_H/dt and $-dC_{O_2}/dt$ are their largest, r_a , which previously has slightly exceeded r_b , falls below it, and C_O commences to decrease. This behavior is illustrated in Fig. 1.

At this time the factors determining C_{OH} , including the growth of r'_{-c} , are also changing markedly, and under some of the hypothetical conditions of our calculations, C_{OH} also exhibits a maximum soon after the maximum in r_a . This maximum is more pronounced when k_c is assumed to be smaller, that is, when the proportion of OH in the early course of the reaction is greater. The ratio k_a/k_c indicated by current literature, however, indicates that the occurrence of OH concentrations significantly in excess of the partial equilibrium level in the shock wave initiated combustion of rich H_2-O_2 mixtures is questionable. The range of available estimates of k_a/k_b , however, is such that occurrence of the C_O "spike" seems quite certain.

For comparison, we note briefly the following characteristics of the computed post-induction kinetics in lean mixtures. First, as Fig. 2 illustrates, reaction (a) emerges after the $r_a - r_c$ maxima as a dominant influence promoting the approach to partial equilibrium. Second, within the combination of circumstances embraced by Table II, there are not computed to be any pronounced excursions of atom or radical species concentrations above the partial equilibrium levels. To be sure, there do occur slight maxima in C_{OH} and C_H in lean mixture computations without recombination, as was reported previously.¹ However these occur significantly later than the $r_a - r_c$ maxima, at a time when r_e and all the reverse rates are significant, and they are not to be classed as "spikes" in the sense of the C_O behavior displayed by rich mixtures.

Also, we may note that the no-recombination computation done for the mildly lean mixture C (see Table II), which was done with the reduced value of k_b and hence favored accumulation of oxygen atoms during the early reaction course, exhibited a maximum C_O five percent greater than the partial equilibrium value. This result indicates, by interpolation, that the C_O "spikes" which are so pronounced in rich mixtures are not necessarily absent in near-stoichiometric mixtures. Their failure to occur in earlier computer investigations^{1,4} is apparently a result of the arbitrary and, in the light of present knowledge, artificially high, value of k_b assumed in those computations.

Quantitative Aspects

To substantiate the interpretation of post-induction kinetics given in the previous section, and to prepare for the consideration of relevant experimental observations, it is appropriate to formulate approximate quantitative expressions for certain aspects of the reaction kinetics. In doing this, we neglect the coupling of the kinetics to the shock wave hydrodynamics assumed throughout the numerical investigation, and consider the reactions as occurring under conventional chemical conditions of constant temperature and density. During the induction period, and in fact throughout the post-induction regime prior to appreciable progress of recombination, such conditions are maintained to a satisfactory approximation in dilute hydrogen - oxygen systems.

The induction period behavior has been treated adequately by several authors,¹⁵ and we reproduce here only enough of the treatment to provide a basis for discussing stoichiometry and the onset of depletion and back reaction effects. For our entire consideration of the early course of the reaction, we restrict our attention to reactions (a)-(d), (f), and (j), which are not higher than first order in product species. The rate equations for the several species are then:

$$\frac{dC_H}{dt} = -r_a + r_b + r_c - 2r_f \quad (1)$$

$$\frac{dC_O}{dt} = r_a - r_b - 2r_j \quad (2)$$

$$\frac{dC_{OH}}{dt} = r_a + r_b - r_c + 2r_d \quad (3)$$

$$\frac{dC_{O_2}}{dt} = -r_a - r_d + r_j \quad (4)$$

$$\frac{dC_{H_2}}{dt} = -r_b - r_c - r_d + r_f \quad (5)$$

$$\frac{dC_{H_2O}}{dt} = r_c \quad (6)$$

During the induction period, r_d , $-r_f$, $-r_j$, $C_{H_2} = C_{H_2}^0$, and $C_{O_2} = C_{O_2}^0$ are regarded as constants, and reverse reactions (a) - (c) are neglected, so that r_a , r_b , and r_c are proportional to C_H , C_O , and C_{OH} , respectively, by the constant factors $g_a = k_a C_{O_2}^0$, $g_b = k_b C_{H_2}^0$, and $g_c = k_c C_{H_2}^0$. Moreover, we presume that r_d , $-r_f$, and $-r_j$ are sufficiently small that as time increases, $r_a - r_c$ dominate Eqs. (1) - (5) and the concentrations are described to a good approximation by:

$$\begin{aligned} C_H^0 e^{\alpha t} = C_H &= \frac{(\alpha + g_b)}{g_a} C_O = \frac{(\alpha + g_b) g_c}{\alpha(\alpha + g_a + g_b)} C_{OH} \\ &= \frac{(\alpha + g_b)}{(\alpha + g_a + g_b)} C_{H_2O} \end{aligned} \quad (7)$$

where α is the positive root of:

$$\alpha^3 + (g_a + g_b + g_c) \alpha^2 + g_b g_c \alpha - 2 g_a g_b g_c = 0$$

and C_H^0 is a constant dependent upon the several g 's and k 's.

We may now examine which of reactions (a) - (c) will first exhibit a significant back reaction by examining the relative values of $Q_i = r'_{-i}/r'_i$, the ratio of the reverse and forward rates.

$$\frac{Q_b}{Q_a} = \frac{K_a C_{O_2} C_H^2}{K_b C_{H_2} C_O^2} \quad (8)$$

$$\frac{Q_c}{Q_a} = \frac{K_a C_{O_2} C_{H_2O} C_H^2}{K_c C_{H_2} C_O C_{OH}^2} \quad (9)$$

During the induction period, these ratios have, from Eq. (7), the values:

$$\frac{Q_b}{Q_a} = \frac{K_a C_{O_2}^0 (\alpha + g_b)^2}{K_b C_{H_2}^0 g_a^2} \quad (10)$$

$$\frac{Q_c}{Q_a} = \frac{K_a C_{O_2}^0 g_c^2 (\alpha + g_b)^2}{K_c C_{H_2}^0 \alpha^2 g_a (\alpha + g_a + g_b)} \quad (11)$$

These ratios, evaluated for the induction period conditions of the several computations summarized in Table III, are presented in columns 2 and 4 therein. From the tabulated numbers, we see that reaction (-c) is the first reverse reaction to become important in very rich mixtures, and that reaction (-a) emerges first in lean mixtures. We also see that the induction period expressions provide a creditable indication of the relative importance

of the three back reactions at the time of the rate maxima, even though Eq. (7) is no longer strictly valid.

We now develop an approximate treatment of the regime of maximum rates and accompanying C_O and possible C_{OH} "spikes", specialized to fuel-rich mixtures. As in the induction period treatment, we use Eqs. (1) - (6) and neglect all rates but $r_a - r_c$, but now allow C_{H_2} and C_{O_2} to vary. From Eq. (4), we write

$$-\frac{dC_{O_2}}{dt} = r_a = k_a C_H C_{O_2} (1 - Q_a) \quad (12)$$

and relate these quantities to dC_H/dt through the stoichiometric relationship appropriate for negligible recombination rates:¹⁶

$$\frac{d}{dt} (C_H + C_{OH} + 2 C_O + 2 C_{O_2}) = 0 \quad (13)$$

by neglecting $\frac{d}{dt} (C_{OH} + 2 C_O)$. This is a reasonable approximation during the induction period for very rich mixtures, and it improves as O_2 becomes depleted and in fact becomes exact at an instant between nearly simultaneous maxima in C_O and C_{OH} . This yields:

$$\frac{dC_H}{dt} \approx -2 \frac{dC_{O_2}}{dt} \quad (14)$$

To proceed, we neglect Q_a in Eq. (12) and formulate:

$$r_a \approx k_a C_H C_{O_2} \approx 1/2 \frac{dC_H}{dt} \quad (15)$$

Integration of Eq. (14) from the initial condition of zero C_H yields:

$$C_{O_2} \approx C_{O_2}^0 (1 - C_H / 2C_{O_2}^0) \quad (16)$$

and combination of this with Eq. (15) and integration yields:

$$C_H \approx \frac{2 C_{O_2}^0}{1 + \exp(-2 k_a C_{O_2}^0 (t - t_m))} \quad (17)$$

$$2 r_a \approx \frac{dC_H}{dt} \approx \frac{4 k_a (C_{O_2}^0)^2 \exp(-2 k_a C_{O_2}^0 (t - t_m))}{\left(1 + \exp(-2 k_a C_{O_2}^0 (t - t_m))\right)^2}$$

where t_m has been selected as the time at which $C_H = 2 C_{O_2}^0$, i.e., at the time of maximum r_a .

To formulate C_O and C_{OH} in this regime, we neglect dC_{OH}/dt in the sum of Eqs. (1) and (3) and write:

$$\frac{dC_H}{dt} \approx 2 r_b = 2 k_b C_O C_{H_2} (1 - Q_b) \quad (18)$$

and similarly neglect dC_O/dt in the sum of Eqs. (1) and (2) and write:

$$\frac{dC_H}{dt} \approx r_c = k_c C_{OH} C_{H_2} (1 - Q_c) \quad (19)$$

Equations (17) - (19) indicate the simultaneity of the maxima in r_a , r_b , and r_c , at $t = t_m$. Concurrent maxima in C_O and C_{OH} are seen to depend upon

substantial constancy of C_{H_2} and negligibility of Q_b and Q_c , respectively. To complete the treatment, we need approximate expressions for C_{H_2} and C_{H_2O} . From no-recombination stoichiometry,¹⁶ we write:

$$C_{H_2} = C_{H_2}^0 - C_{O_2}^0 + C_{O_2} - C_H \approx C_{H_2}^0 - \frac{3}{2} C_H, \quad (20)$$

and from Eqs. (6) and (19), we write:

$$C_{H_2O} = \int_{-\infty}^t r_c dt' \approx C_H. \quad (21)$$

Without reproducing the intermediate details, we state our conclusion that in sufficiently rich mixtures (for $C_{H_2}^0/C_{O_2}^0 = E \gtrsim 4$), near t_m , Q_a is indeed negligible, as are Q_b and differential depletion of H_2 , so that the maximum in C_O is described by:

$$C_{O_{\max}} \approx C_{O_{t=t_m}} = C_{O_m} \approx \frac{k_a C_{O_2}^0}{2 k_b (E - 3/2)}. \quad (22)$$

Simultaneously positive dQ_b/dt and negative dC_{H_2}/dt assure that the true maximum in C_O occurs when $dr_b/dt < 0$, i.e., at $t \gtrsim t_m$.

That this $C_{O_{\max}}$ indeed exceeds the partial equilibrium value by a substantial factor in rich mixtures can be seen by numerical comparison (see Table IV) with C_O at partial equilibrium, without recombination, an approximate expression for which is:

$$C_{O_{pe}} = \frac{C_{H_2O} C_H^2}{K_b K_c C_{H_2}^2} \approx \frac{8 C_{O_2}^o}{K_b K_c (E - 3)^2} \quad (23)$$

which is obtained by evaluation of C_H , C_{H_2} , and C_{H_2O} from Eqs. (17), (20), and (21) at $(t - t_m) \gg \left(2 k_a C_{O_2}^o\right)^{-1}$.

Similar examination of C_{OH} indicates that we cannot neglect Q_c near t_m , and that a maximum in C_{OH} may occur at $t > t_m$ if

$$dr_c/r_c dt + dQ_c/(1 - Q_c)dt - dC_{H_2}/C_{H_2} dt$$

passes through zero at finite t . To estimate the likelihood of this occurring early enough for $C_{OH_{max}}$ to exceed $C_{OH_{pe}}$ by a significant amount, we evaluate C_{OH} at $t = t_m$ and compare it with $C_{OH_{pe}}$. The appropriate expressions are:

$$C_{OH_m} \approx \frac{C_{O_2}^o}{(E - 3/2)} \left(\frac{k_a}{K_c} + \frac{1}{K_c} \right) \quad (24)$$

$$C_{OH_{pe}} = \frac{C_H C_{H_2O}}{K_c C_{H_2}} \approx \frac{4 C_{O_2}^o}{K_c (E - 3)} \quad (25)$$

Columns (5), (6), (10), and (11) in Table IV give the values of C_{O_m} from Eq. (22), $C_{O_{pe}}$, C_{OH_m} from Eq. (24), and $C_{OH_{pe}}$, normalized by division by $C_{O_2}^o$, for the twelve numerical computations performed for the rich mixtures A and B. These are compared with the likewise normalized values of $C_{O_{max}}$ (columns (2) and (3)) and $C_{OH_{max}}$ (columns (7) and (8))

extracted from the numerically integrated reaction profiles. We note that the correspondence between the approximate (Eqs. (22) and (24)) values and the numerical profile values is better for the richer mixture A than for the mildly rich mixture B. Also, the Eqs. (22) and (24) values deviate from the maximum values from the no-recombination profiles by amounts comparable to the differences between the latter and the values from the computations with recombination.

The discrepancies between the approximate (Eqs. (22) and (24)) values and the numerical results for no recombination are due to the approximations in the former. We have traced the bulk of these discrepancies to neglect, in Eq. (16), of C_O and C_{OH} in the integral of Eq. (13). We can correct this approximation to first order in the regime $|t - t_m| \lesssim \left(2 k_a C_{O_2}^0\right)^{-1}$ by replacing Eq. (16) with

$$C_{O_2} = C_{O_2}^0 - 1/2 C_H - 1/2 C_{OH_m} - C_{O_m}$$

and proceeding with the development treating $(1/2 C_{OH_m} + C_{O_m})$ as a constant, $\underline{n} C_{O_2}^0$, satisfactorily given by Eqs. (22) and (24). The resulting expressions replacing Eqs. (22) and (24) are:

$$C_{O_m} \approx \frac{k_a C_{O_2}^0 (1 - \underline{n})^2}{2 k_b (E - 3/2)} \quad (26)$$

$$C_{OH_m} \approx \frac{C_{O_2}^0 (1 - \underline{n})^2}{(E - 3/2)} \left(\frac{k_a}{k_c} + \frac{1}{k_c} \right) \quad (27)$$

The values given by these approximations, presented in columns (4) and (9) of Table IV, are seen to be usually closer to the numerical integration results. The one computation, B-7, involving an only slightly ($E = 4$) rich mixture and a low k_b , shows the onset of failure of the analytic approximations for a rich mixture, the immediate cause being the relatively large Q_a at $r_a = r_{a_{\max}}$. In general, the quantitative validity of the above discussion of rich systems improves as k_b , k_c , and E increase. The best single indication of validity is that α approaches $2 g_a$.

Application to Experiments

The prediction of the C_0 "spike", and its interpretation in the form of Eq. (22) or its numerical refinements, indicates the possibility of a direct determination of the ratio k_a/k_b in the temperature range $1100^\circ \lesssim T \lesssim 2000^\circ K$ by a quantitative measurement of the maximum transient C_0 achieved in the course of the shock wave initiated combustion of rich $H_2 - O_2$ mixtures. At this writing, we have not yet succeeded in completing such experiments, but we¹⁷ have obtained qualitative evidence for the occurrence of this oxygen atom "spike" from uncalibrated, time-resolved photometric measurements of visible continuum emission from shock waves in mixtures containing 2% H_2 , 0.5% O_2 , and 21% CO in argon. These experiments produced nearly symmetrical, short-lived bursts of light emission, at the end of the induction period. Tests with omission of CO or O_2 from the mixture lead us to interpret this emission as being from the radiative recombination of O with CO. The half-width of this "spike", from Eqs. (17) and (18), also offers a direct confirmatory measurement of k_a .

In Eq. (24) and its indicated refinement we also see the possibility of determining k_a/k_c , provided this ratio is comparable to or greater than $1/K_c$. Comparison of Eqs. (24) and (25) shows that a simple determination of k_a/k_c from a peak C_{OH} in excess of $C_{OH_{pe}}$ is not possible unless k_a/k_c exceeds $3/K_c$. In the case of OH, we have available an abundance of quantitative experimental measurements of maximum concentrations in rich mixtures done by ultraviolet line absorption photometry. These have generally^{1,2} shown that the maximum value of C_{OH} does not exceed $C_{OH_{pe}}$, and we use these observations to establish an upper limit to k_a/k_c .

The data from twenty-two experiments covering the ranges of computed partial equilibrium, no-recombination conditions $1156^\circ \leq T \leq 1884^\circ K$ and $0.84 \leq p \leq 4.6$ atm have been utilized. Seventeen of these experiments were from a previous investigation,² and had $E = 8.07$. The remaining five are new ones which we have performed with $E = 13$, using substantially the same equipment and methods as previously. The maximum apparent OH concentrations from these experiments have been treated as follows. On the premises that maximum C_{OH} values significantly in excess of $C_{OH_{pe}}$ would be detectable and interpretable by Eq. (27), if corrected for the effects of finite progress of recombination reactions, and that the experimental C_{OH} might be in error and underestimate the true maximum C_{OH} , we have adjusted the measured maximum C_{OH} values upward, normally by addition of $0.45 C_{OH_{pe}}$. In six cases, values between $0.45 C_{OH_{pe}}$ and $0.60 C_{OH_{pe}}$ were added, in order to bring the adjusted value to $1.15 C_{OH_{pe}}$. These adjusted values, our estimated upper limits to $C_{OH_{max}}$, were used with Eq. (27) to deduce the values of

k_a/k_c presented in Fig. 3 as upper limits to this ratio. In this evaluation, K_c was taken, somewhat arbitrarily, at the partial equilibrium, no-recombination temperature.

In three of the four experiments done below 1250°K, the observed maximum C_{OH} exceeded the computed $C_{OH_{pe}}$ by factors between 1.09 and 1.15, and these apparent maximum C_{OH} values have been used at face value with Eq. (27) to determine the three points shown in Fig. 3 as apparent values of k_a/k_c . The possibility that these measurements were affected by gasdynamic instability effects forces us to present these values as tentative. The margin allowed for this and other uncertainties in estimating the upper limit values is indicated by the separation between the upper limit and face value symbols for these three experiments.

Finally, we include in Fig. 3, for comparison, other pertinent published information^{11,18-20} on the ratio k_a/k_c . The conclusions to be drawn from this figure are self-evident.

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Figure Captions

Fig. 1. Post-induction kinetics for very rich mixture, run A-1 (see Table II), without recombination. (a), net reaction rates of principal binary reactions; (b), C_O and C_{OH} profiles, showing "spikes".

Fig. 2. Post-induction kinetics for very lean mixture, showing reaction rates of principal binary reactions; run D-1 (see Table II), without recombination.

Fig. 3 Upper limits and reported values of k_a/k_c .

Table I. Reaction Mechanism for Numerical Profile Computations.

Designation	Reaction	Rate Coefficient*	Source
(a)	$H + O_2 \rightleftharpoons OH + O$	$2.14 \times 10^{14} \exp(-16,600/RT)$	Ref. 9
(b)	$O + H_2 \rightleftharpoons OH + H$	$(0.4 - 3.6) \times 10^{13} \exp(-9,200/RT)$	Ref. 10†
(c)	$OH + H_2 \rightleftharpoons H_2O + H$	$(2.1 - 18.9) \times 10^{13} \exp(-5,900/RT)$	Ref. 11†
(d)	$H_2 + O_2 \rightleftharpoons 2 OH$		
(e)	$2 OH \rightleftharpoons H_2O + O$	$3.8 \times 10^{12} \exp(-1,000/RT)$	Ref. 11
(f)	$2 H + M \rightleftharpoons H_2 + M$	$9 \times 10^{17} T^{-1}$	Ref. 2
(g)	$H + OH + M \rightleftharpoons H_2O + M$	$9 \times 10^{18} T^{-1}$	Ref. 2
(h)	$H + O + M \rightleftharpoons OH + M$		
(i)	$H + O_2 + M \rightleftharpoons HO_2 + M$	$4.72 \times 10^{14} \exp(+1,600/RT)$	Ref. 12
(j)	$2 O + M \rightleftharpoons O_2 + M$	$1.05 \times 10^{15} T^{-1/2}$	Ref. 13
(k)	$O_3 + M \rightleftharpoons O + O_2 + M$	$3.8 \times 10^{14} \exp(-23,150/RT)$	Ref. 14
(l)	$O + OH + M \rightleftharpoons HO_2 + M$		
(m)	$2 OH + M \rightleftharpoons H_2O_2 + M$		
(n)	$O + O_3 \rightleftharpoons 2 O_2$	$2.4 \times 10^{13} \exp(-5,600/RT)$	Ref. 14
(o)	$O + HO_2 \rightleftharpoons OH + O_2$		
(p)	$H + O_3 \rightleftharpoons OH + O_2$		
(q)	$OH + O_3 \rightleftharpoons HO_2 + O_2$		
(r)	$OH + HO_2 \rightleftharpoons H_2O + O_2$		
(s)	$H + HO_2 \rightleftharpoons H_2O + O$		
(t)	$H + HO_2 \rightleftharpoons H_2 + O_2$		
(u)	$H + HO_2 \rightleftharpoons 2 OH$		

Table I. (Cont.)

Designation	Reaction	Rate Coefficient	Source
(v)	$\text{H} + \text{H}_2\text{O}_2 \rightleftharpoons \text{H}_2 + \text{HO}_2$		
(w)	$\text{H} + \text{H}_2\text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{OH}$		
(x)	$\text{O} + \text{H}_2\text{O}_2 \rightleftharpoons \text{OH} + \text{HO}_2$		
(y)	$\text{O} + \text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$		
(z)	$\text{H}_2 + \text{H}_2\text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}$		
(z')	$\text{O}_2 + \text{H}_2\text{O}_2 \rightleftharpoons 2 \text{HO}_2$		
(y')	$\text{OH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$		

*Bimolecular rate coefficients in units of $\text{cc mole}^{-1} \text{sec}^{-1}$; termolecular rate coefficients in units of $\text{cc}^2 \text{mole}^{-2} \text{sec}^{-1}$; C_M taken as total gas concentration.

†Range obtained by multiplication and division of reference value by factor of 3.

Table II. Summary of Computations used in Post-Induction Kinetics Investigation.

Run No.*	Induction Zone Conditions T, °K p, atm		Rate Coefficients		Recombination Reactions Included Excluded	
			k_b (cc/mole sec) $\times 10^{-13} e^{9,200/RT}$	k_c (cc/mole sec) $\times 10^{-13} e^{5,900/RT}$		
A-1	1161	1.233	1.2	6.3	x	x
A-2	1161	1.233	3.6	6.3	x	x
A-3	1161	1.233	1.2	18.9	x	x
A-4	1161	1.233	1.2	2.1	x	x
A-5	1161	1.233	3.6	18.9	x	
A-6	1161	1.233	0.4	2.1	x	
A-7	1127	1.186	0.4	6.3	x	x
A-8	1161	3.899	1.2	6.3	x	
A-9	1161	0.370	1.2	6.3	x	
A-10	1441	1.624	1.2	6.3	x	x
B-2	1198	1.247	3.6	6.3		x
B-7	1198	1.247	0.4	6.3	x	x
C-7	1217	1.296	0.4	6.3	x	x
D-1	1304	1.535	1.2	6.3	x	x
D-2	1304	1.535	3.6	6.3	x	x
D-3	1304	1.535	1.2	18.9	x	x
D-7	1304	1.535	0.4	6.3	x	x
D-9	1304	0.461	1.2	6.3	x	
D-10	1668	2.095	1.2	6.3	x	x

*Alphabetic part of run number indicates initial Ar : H₂ : O₂ ratios as follows:

A, 91.5 : 8 : 0.5 ; B, 97.5 : 2 : 0.5 ; C, 95 : 1 : 4 ; D, 83 : 1 : 16.

Numerical part indicates correspondence of sets of rate coefficients.

Table III. Depletion and Back Reaction Effects at Rate Maximum for
Reactions without Recombination.

Run	Q_b/Q_a		Q_c/Q_a		Q_a	$C_{H_2}/C_{H_2}^0$	$C_{O_2}/C_{O_2}^0$
	Eq. (10)	Numerical	Eq. (11)	Numerical			
A-1	0.471	0.670	8.89	15.5	0.0096	0.903	0.492
A-2	3.83	5.55	23.5	42.4	0.0034	0.901	0.498
A-3	0.471	0.657	79.6	81.6	0.0043	0.903	0.491
A-4	0.471	0.694	1.00	2.30	0.0248	0.903	0.494
A-7	0.065	0.080	3.70	5.64	0.0240	0.905	0.484
A-10	0.503	0.652	12.7	17.6	0.0114	0.905	0.487
B-2	1.12	1.20	1.91	2.12	0.0775	0.668	0.527
B-7	0.032	0.042	0.579	0.792	0.203	0.739	0.551
C-7	0.015	0.030	0.028	0.063	0.54	0.566	0.922
D-1	0.034	0.065	0.010	0.024	0.53	0.534	0.977
D-2	0.121	0.189	0.012	0.024	0.47	0.520	0.978
D-3	0.047	0.073	0.082	0.097	0.36	0.452	0.972
D-7	0.010	0.023	0.0093	0.024	0.57	0.534	0.975
D-10	0.037	0.060	0.025	0.041	0.45	0.507	0.974

Table IV. Maximum and Partial Equilibrium Values of C_O and C_{OH} for Rich Mixture Computations.

Run	Maximum $C_O/C_{O_2}^o$				$C_{O_{pe}}/C_{O_2}^o$	Maximum $C_{OH}/C_{O_2}^o$				$C_{OH_{pe}}/C_{O_2}^o$
	Recombination Excluded	Recombination Included	Eq.(26)	Eq.(22)		Recombination Excluded	Recombination Included	Eq.(27)	Eq.(24)	
A-1	.024	.0216	.0237	.0249	.000328	.0029	.00268	.00261	.00274	.00215
A-2	.0085	.0079	.0081	.0083	.000328	.0030	.00280	.00269	.00274	.00215
A-3	.024	.0215	.0237	.0249	.000328	.0013*	.00174	.00117	.00122	.00215
A-4	.024	.0212	.0236	.0249	.000328	.0069	.00645	.00690	.00728	.00215
A-5		.0150	.0082	.0083	.000328		.00186	.00120	.00122	.00215
A-6		.0469	.0649	.0747	.000328		.00525	.00635	.00728	.00215
A-7	.057	.0478	.0598	.0678	.000267	.0023	.00202	.00210	.00236	.00177
A-8		.0185	.0237	.0249	.000328		.00229	.00261	.00274	.00215
A-9		.0233	.0237	.0249	.000328		.00285	.00261	.00274	.00215
A-10	.041	.0400	.0422	.0464	.000975	.0081	.00780	.00666	.00724	.00752
B-2	.054		.0474	.0532	.0371	.020*		.0167	.0185	.0248
B-7	.183	.136	.259	.478	.0371	.011*	.0131	.0107	.0185	.0248

*No maximum in C_{OH} was computed; value given is C_{OH} at time of maximum C_O .

Hamilton and Schott Fig. 1a

Hamilton and Schott Fig. 1b

Hamilton and Schott Fig. 2

Hamilton and Schott Fig. 3