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by Richard S. Brokaw
Lewis Research Center
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TECHNICAL PAPER proposed for presentation at Eleventh International Symposium on Combustion sponsored by the Combustion Institute Berkeley, California, August 14-20, 1966

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# IGNITION KINETICS OF THE CARBON MONOXIDE - OXYGEN REACTION

Richard S. Brokaw

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

## SUMMARY

An analytic solution for the ignition kinetics of the dry $CO\text{-}O_2$ reaction is obtained by assuming an initiation reaction followed by the chain-branching steps

$$CO + O \rightarrow CO_2^*$$

$$CO_2^* + O_2 \rightarrow CO_2 + 2O$$

together with chain termination by quenching of $CO_2^*$ and three-body recombination of CO and O. It is concluded that shock-tube induction times on reportedly dry $CO\text{-}O_2$ mixtures cannot be explained by this mechanism. The shock-tube data can be explained by the following scheme, if a water vapor content of 20 ppm or less is assumed:

$$CO + O_2 \xrightarrow{k_i} CO_2 + O$$

$$O + H_2O \xrightarrow{k_5} 2OH$$

$$OH + CO \xrightarrow{k_6} CO_2 + H$$

$$H + O_2 \xrightarrow{k_2'} OH + O$$

The rate constant for the initiation reaction was found to be $k_i = 2.5\times10^9 \exp(-48,000/RT)$ liters mole$^{-1}$ sec$^{-1}$. The rate constant for the reaction between O and $H_2O$ at 1600° K was estimated by two different methods to be $8\times10^8$ and $1.5\times10^9$ liters mole$^{-1}$ sec$^{-1}$. Induction periods

for mixtures with deliberate additions of hydrogen can be fit by adding the steps

$$O + H_2 \xrightarrow{k_3'} OH + H$$

$$OH + H_2 \xrightarrow{k_1'} H_2O + H$$

## INTRODUCTION

The explosive reaction of "dry" carbon monoxide and oxygen has been studied by a number of investigators starting with Hadman, Thompson, and Hinshelwood[1] in 1932. At first glance, one might assume that kinetics leading to ignition should be rather simple and easily elucidated. On the contrary, as recently as 1964, Dickens, Dove, and Linnett[2] wrote that "there is still not general agreement about the reaction mechanism."

These prior studies have been concerned with explosion limits in static systems, and in such systems two factors tend to obscure the elementary kinetics. First, surfaces play a role, and the observed limits are affected by prior surface history and treatment; there is a "memory" effect.[3] Second, the reaction is greatly accelerated by water or hydrogen, and it is difficult indeed to be sure that all traces of hydrogenous substances have been excluded.

Recently Sulzmann, Myers, and Bartle[4,5] have studied the induction period preceding rapid carbon dioxide formation in shock-heated carbon monoxide-oxygen-argon mixtures. The shock tube is ideal for such studies since surface effects are avoided - there is insufficient time for diffusion of chain carriers to and from the walls. Furthermore, there is at least the hope that the water-vapor concentration can be held low enough so that there are insufficient collisions involving water vapor to affect the kinetics.

In this paper, an analytic solution is first developed for the ignition kinetics of the dry carbon monoxide - oxygen system. It is found that the experimental data[4,5] cannot be explained by the mechanism postulated. Next a solution is obtained for the kinetics in the presence of traces of water vapor and hydrogen. This scheme can be fit to the experimental results by assuming a water-vapor mole fraction of about 20 ppm. This value is larger than the reported contamination of 1 ppm; possible rationalizations are discussed. Finally, the experimental data[5] with added hydrogen are adequately explained.

These solutions are developed by using mathematical techniques that have been successfully applied to hydrogen-oxygen ignition.[6-8] The principal assumptions are (1) the induction period is isothermal, (2) the reactants are negligibly depleted during the induction period, and (3) reactions among chain carriers and between chain carriers and products are also negligible.

## IGNITION KINETICS OF DRY CARBON MONOXIDE - OXYGEN SYSTEM

In this section, a solution is developed for a kinetic scheme comprised of the gas-phase reactions suggested by Gordon and Knipe[3]

$$CO + O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CO_2^*, \tag{I}$$

$$CO_2^* + O_2 \xrightarrow{k_2} CO_2 + 2O, \tag{II}$$

$$CO_2^* + M \xrightarrow{k_3} CO_2 + M, \tag{III}$$

$$CO + O + M \xrightarrow{k_4} CO_2 + M, \tag{IV}$$

together with an initiation step,

$$CO + O_2 \xrightarrow{k_i} CO_2 + O. \tag{i}$$

This reaction scheme involves two chain carriers - oxygen atoms and an electronically excited carbon dioxide molecule, $CO_2^*$. The differential equations governing the growth of O and $CO_2^*$ concentrations during the induction period are as follows:

$$d[O]/dt = i - (\nu_1 + \nu_4)[O] + (\nu_{-1} + 2\nu_2)[CO_2^*] \qquad (1)$$

$$d[CO_2^*]/dt = \nu_1[O] - (\nu_{-1} + \nu_2 + \nu_3)[CO_2^*]. \qquad (2)$$

Here we have defined $i \equiv k_i[CO][O_2]$ (the initiation rate) and also $\nu_1 \equiv k_1[CO]$, $\nu_{-1} \equiv k_{-1}$, $\nu_2 \equiv k_2[O_2]$, $\nu_3 \equiv k_3[M]$, and $\nu_4 \equiv k_4[CO][M]$. The $\nu$ are reaction frequencies and have the dimensions of reciprocal time. Since we assume the induction period is isothermal and neglect depletion of the reactants, we take both the initiation rate and the reaction frequencies to be constant during the induction period.

The initiation rate can be eliminated from Eq. (1) by introducing new variables

$$C_O \equiv [O] + \frac{(\nu_{-1} + \nu_2 + \nu_3)i}{\nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)} \qquad (3)$$

and

$$C_{CO_2^*} \equiv [CO_2^*] + \frac{\nu_1 i}{\nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)}. \qquad (4)$$

($C_O$ and $C_{CO_2^*}$ differ appreciably from the actual concentrations [O] and $[CO_2^*]$ only at the very start of the reaction.) Thus i is eliminated, $C_{CO_2^*}$ replaces $[CO_2^*]$, and $C_O$ replaces [O]. A particular solution to the transformed equations is

$$C_O = A_O \exp(\varphi t), \quad C_{CO_2^*} = A_{CO_2^*} \exp(\varphi t). \qquad (5)$$

Substituting Eq. (5) into the differential equations yields the relations

$$-(\nu_1 + \nu_4 + \varphi)A_0 + (\nu_{-1} + 2\nu_2)A_{CO_2^*} = 0 \tag{6}$$

and

$$\nu_1 A_0 - (\nu_{-1} + \nu_2 + \nu_3 + \varphi)A_{CO_2^*} = 0. \tag{7}$$

A nontrivial solution requires that the determinant of the coefficients of $A_0$ and $A_{CO_2^*}$ be zero. This leads to the quadratic equation

$$\varphi^2 + (\nu_1 + \nu_{-1} + \nu_2 + \nu_3 + \nu_4)\varphi - \left[\nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)\right] = 0. \tag{8}$$

One root of this equation is always negative; the other may be positive if $\nu_1\nu_2 > \nu_1\nu_3 + \nu_4(\nu_{-1} + \nu_2 + \nu_3)$. Thus, there is an explosion limit defined by

$$k_4[M] = \frac{k_1\left(k_2[O_2] - k_3[M]\right)}{k_{-1} + k_2[O_2] + k_3[M]}. \tag{9}$$

A very similar result has been obtained by Gordon and Knipe[3] by equating the rates of formation and destruction of O and $CO_2^*$.

Let us call the root of Eq. (8) that may be positive $\varphi_1$ and the root that is always negative $\varphi_2$. Next, define $\lambda_1 \equiv \varphi_1$ and $\lambda_2 \equiv -\varphi_2$. The general solution is

$$\left.\begin{aligned} C_0 &= A_{0,1}\exp(\lambda_1 t) + A_{0,2}\exp(-\lambda_2 t) \\ C_{CO_2^*} &= A_{CO_2^*,1}\exp(\lambda_1 t) + A_{CO_2^*,2}\exp(-\lambda_2 t), \end{aligned}\right\} \tag{10}$$

where

$$\lambda_1 = \frac{b}{2}\left[\left(1 + \frac{4c}{b^2}\right)^{1/2} - 1\right], \tag{11}$$

$$\lambda_2 = \frac{b}{2}\left[\left(1 + \frac{4c}{b^2}\right)^{1/2} + 1\right], \tag{12}$$

and

$$b \equiv \nu_1 + \nu_{-1} + \nu_2 + \nu_3 + \nu_4$$

$$= k_1[CO] + k_{-1} + k_2[O_2] + k_3[M] + k_4[CO][M], \qquad (13)$$

$$c \equiv \nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)$$

$$= k_1k_2[CO][O_2] - k_1k_3[CO][M]$$

$$- k_4[CO][M]\left(k_{-1} + k_2[O_2] + k_3[M]\right). \qquad (14)$$

The preexponential coefficients in Eq. (10) are obtained as follows: Initially the concentrations of $CO_2^*$ and O are zero. Thus, from Eqs. (3), (4), and (10),

$$A_{O,1} + A_{O,2} = (\nu_{-1} + \nu_2 + \nu_3)(i/c), \qquad (15)$$

$$A_{CO_2^*,1} + A_{CO_2^*,2} = \nu_1(i/c), \qquad (16)$$

and from Eq. (7),

$$\nu_1 A_{O,1} = (\nu_{-1} + \nu_2 + \nu_3 + \lambda_1)A_{CO_2^*,1}, \qquad (17)$$

$$\nu_1 A_{O,2} = (\nu_{-1} + \nu_2 + \nu_3 - \lambda_2)A_{CO_2^*,2}. \qquad (18)$$

Equations (15) to (18) can now be solved to obtain

$$A_{O,1} = \frac{\lambda_2}{\lambda_1 + \lambda_2} \frac{(\nu_{-1} + \nu_2 + \nu_3 + \lambda_1)i}{c}, \qquad (19)$$

$$A_{O,2} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{(\nu_{-1} + \nu_2 + \nu_3 - \lambda_2)i}{c}, \qquad (20)$$

$$A_{CO_2^*,1} = \frac{\lambda_2}{\lambda_1 + \lambda_2} \frac{\nu_1 i}{c}, \qquad (21)$$

and

$$A_{CO_2^*,2} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{\nu_1 i}{c}. \qquad (22)$$

The growth of carbon dioxide concentration with time is governed by

$$d[CO_2]/dt = (\nu_2 + \nu_3)[CO_2^*] + \nu_4[O] + i. \tag{23}$$

Since we have the preexponential coefficients of Eqs. (10) [Eqs. (19) to (22)], Eq. (23) can be integrated to give

$$[CO_2](c/i) = (2\nu_1\nu_2 - c)\,\frac{(\lambda_2/\lambda_1)}{\lambda_1 + \lambda_2}\left[\left(e^{\lambda_1 t} - 1\right) - (\lambda_1/\lambda_2)^2\left(e^{-\lambda_2 t} - 1\right)\right]$$

$$+ \nu_4\,\frac{\lambda_2}{\lambda_1 + \lambda_2}\left[\left(e^{\lambda_1 t} - 1\right) + (\lambda_1/\lambda_2)\left(e^{-\lambda_2 t} - 1\right)\right] - 2(\nu_1\nu_2 - c)t. \tag{24}$$

At this point, it is worthwhile to consider the relative magnitudes of $\lambda_1$ and $\lambda_2$. From Eqs. (13) and (14) it can be shown that $1 \geq (4c/b^2) \geq -1$. Thus it follows that in the flammable region $(c > 0)$, $\lambda_1/\lambda_2 \leq 0.1715$, and $(\lambda_1/\lambda_2)^2 \leq 0.0294$. Consequently, the terms involving $\exp(-\lambda_2 t)$ die out quickly, and furthermore these terms have smaller preexponential factors. Hence, to a good approximation,

$$[CO_2](c/i) \cong \frac{\lambda_2}{\lambda_1 + \lambda_2}\left(e^{\lambda_1 t} - 1\right)\left(\frac{2\nu_1\nu_2 - c}{\lambda_1} + \nu_4\right) - 2(\nu_1\nu_2 - c)t. \tag{25}$$

In attempting to analyze the experimental results of Sulzmann, Myers, and Bartle,[4,5] we will assume that the temperature is high enough so that reaction (III), the quenching step, can be neglected, and the pressure is low enough so that chain termination by reaction (IV) is also negligible. In this event the growth of $CO_2$ concentration with time is given by

$$[CO_2] \simeq \frac{k_1[CO][O_2]}{\lambda_1}\left(e^{\lambda_1 t} - 1\right), \tag{26}$$

since $0.85 < \lambda_2/(\lambda_1 + \lambda_2) < 1$.

Figure 1 shows experimental data on the growth of carbon dioxide mole fraction with time for a mixture of 20% CO and 10% $O_2$ in argon at 1597° K and 1.145 atm (taken from Fig. 2 of Ref. 4). In Fig. 1(a), a linear plot, the carbon dioxide mole fraction grows in an accelerating fashion for perhaps 400 μsec. Next, there is a brief period of linear concentration growth followed by a point of inflection and a subsequent decrease in reaction rate. Sulzmann, et al.,[4] define the induction period by extrapolating the linear portion of the curve through the inflection point back to zero carbon dioxide concentration. Thus, their induction time corresponds to a carbon dioxide mole fraction of about $5 \times 10^{-4}$.

In Fig. 1(b), the same data are replotted on semilogarithmic coordinates, and it is clear that the growth of carbon dioxide is exponential, or nearly so, for the first 400 μsec. (The subsequent falloff must be a result either of reactions among chain carriers or depletion of the reactants.) From Fig. 1(b) and Eq. (26), it is found that $\lambda_1 = 1.54 \times 10^4\ \mathrm{sec}^{-1}$. Let us now see if this exponential growth constant is consistent with the postulated reaction mechanism.

Inasmuch as $4c/b^2 \leq 1$, the binomial expansion can be applied to Eq. (11) without undue violence (error less than 20%), with the result

$$\lambda_1 \simeq \frac{k_1 k_2 [CO][O_2]}{k_1[CO] + k_{-1} + k_2[O_2]} . \tag{27}$$

If one assumes that the dissociation of $CO_2^*$ can be neglected, the rate constants $k_1$ and $k_2$ can be chosen to give a reasonable (although not perfect) fit to the data of Sulzmann and co-workers.[4,5]

Detailed balancing, however, suggests that $k_{-1}$ is by no means negligible. We wish to estimate the magnitude of $k_{-1}$ in comparison with $k_1$

and $k_2$. Thus, we are interested in the equilibrium constant $K$ for the reaction

$$CO_2^* \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} CO + O \qquad (I)$$

The entropy change associated with such a process at 1 atm and 1000° to 3000° K can be estimated with some confidence by considering analogous dissociations[9] ($NO_2 \rightleftarrows NO + O$, $\Delta S/R = 17.0$; $SO_2 \rightleftarrows SO + O$, $\Delta S/R = 17.3$; and $CO_2 \rightleftarrows CO + O$, $\Delta S/R = 18.1$). Thus, if we assume that $\Delta S/R = 17$, $K = 7\times10^4 \exp(-\Delta E/RT)$ moles liter$^{-1}$, where $\Delta E$ is the dissociation energy of $CO_2^*$. If $\Delta E = 20$ kcal, $K_{1597^\circ} = 130$; if $\Delta E = 40$ kcal, $K_{1597^\circ} = 0.21$. This is the range of stability for excited carbon dioxide molecules suggested by Clyne and Thrush.[10]

Let us now solve Eq. (27) for $k_1$:

$$\frac{1}{k_1} = \frac{[CO]}{\lambda} - \frac{K}{k_2[O_2]} - \frac{[CO]}{k_2[O_2]}. \qquad (28)$$

The last term on the right may be neglected because $K > 0.21 >> [CO] = 1.75\times10^{-3}$ mole liter$^{-1}$. Since $k_1$ is positive, we conclude that

$$\frac{k_2[O_2]}{K} > \frac{\lambda}{[CO]} = 8.8\times10^6.$$

Next, express $k_2$ in collision theory form,

$$k_2 = PZ \exp(-E_2/RT).$$

Because the dissociation energy of $O_2$ is 7 kcal less than that of $CO_2$, we find that $E_2 \geq \Delta E - 7$ kcal. At 1597° K, $Z \sim 3.5\times10^{11}$, so that the steric factor $P$ must be greater than 200! This is clearly ridiculous.

Thus, we are forced to the conclusion that the experimental ignition-delay data <u>cannot</u> be explained by reactions (I) to (IV).

## IGNITION KINETICS OF CARBON MONOXIDE - OXYGEN SYSTEM IN PRESENCE OF WATER OR HYDROGEN

Since Sulzmann, Myers, and Bartle[4] report that their nominally dry carbon monoxide - oxygen mixtures contained about 1 ppm of water vapor, we must next investigate the kinetics in the presence of traces of water. Furthermore, experiments were performed with small additions of hydrogen,[5] so that we can profitably examine the effect of hydrogen as well.

Once again, we assume the initiation step

$$CO + O_2 \xrightarrow{k_i} CO_2 + O. \qquad (i)$$

The product oxygen atoms react with either water or hydrogen,

$$O + H_2O \xrightarrow{k_5} 2OH \qquad (V)$$

$$O + H_2 \xrightarrow{k_3'} OH + H, \qquad (III')$$

to generate hydroxyl radicals that oxidize both carbon monoxide and hydrogen:

$$OH + CO \xrightarrow{k_6} CO_2 + H \qquad (VI)$$

and

$$OH + H_2 \xrightarrow{k_1'} H_2O + H. \qquad (I')$$

Finally, hydroxyl radicals are regenerated through the step

$$H + O_2 \xrightarrow{k_2'} OH + O. \qquad (II')$$

Reactions (I'), (II'), and (III') are familiar links from the hydrogen - oxygen branched-chain scheme.

The differential equations governing the growth of O, OH, and H concentrations are as follows:

$$dC_O/dt = -(\nu_3' + \nu_5)C_O + \nu_2'C_H, \tag{29}$$

$$dC_{OH}/dt = (\nu_3' + 2\nu_5)C_O - (\nu_1' + \nu_6)C_{OH} + \nu_2'C_H, \tag{30}$$

and

$$dC_H/dt = \nu_3'C_O + (\nu_1' + \nu_6)C_{OH} - \nu_2'C_H. \tag{31}$$

Here we have once again introduced a shorthand notation so that $\nu_1' \equiv k_1'[H_2]$, $\nu_2' \equiv k_2'[O_2]$, $\nu_3' \equiv k_3'[H_2]$, $\nu_5 \equiv k_5[H_2O]$, and $\nu_6 \equiv k_6[CO]$. Also, the initiation rate has been eliminated from the differential equations by introducing new concentration variables,

$$C_O \equiv [O], \tag{32}$$

$$C_{OH} \equiv [OH] + i/(\nu_1' + \nu_6), \tag{33}$$

and

$$C_H \equiv [H] + i/\nu_2'. \tag{34}$$

(Again $C_{OH}$ and $C_H$ differ from [OH] and [H] only early in the indication period.) As before, a particular solution is of the form $C_i = A_i \exp(\varphi t)$, which leads to a cubic equation for $\varphi$,

$$\varphi^3 + (\nu_1' + \nu_2' + \nu_3' + \nu_5 + \nu_6)\varphi^2 + \left[\nu_2'\nu_5 + (\nu_3' + \nu_5)(\nu_1' + \nu_6)\right]\varphi - 2\nu_2'(\nu_3' + \nu_5)(\nu_1' + \nu_6) = 0. \tag{35}$$

Equation (35) has two small roots - one positive and one negative - and one large negative root. In searching for the small roots, a little numerical experimentation reveals that the first term in Eq. (35) can be neglected because these roots <u>are</u> small, and the third term can be neglected because the amounts of water and hydrogen are small so that $\nu_3'$ and $\nu_5$ are also small. Consequently,

$$\varphi_1 \cong -\varphi_2 \cong \left[\frac{2\nu_2'(\nu_3' + \nu_5)(\nu_1' + \nu_6)}{\nu_1' + \nu_2' + \nu_3' + \nu_5 + \nu_6}\right]^{1/2}$$

$$= \left[\frac{2k_2'[O_2]\Big(k_3'[H_2] + k_5[H_2O]\Big)\Big(k_1'[H_2] + k_6[CO]\Big)}{(k_1' + k_3')[H_2] + k_5[H_2O] + k_2'[O_2] + k_6[CO]}\right]^{1/2} \equiv \lambda. \qquad (36)$$

[Equation (36) is in error by at most 5% for an added hydrogen concentration of 0.13%.] Since the coefficient of $\varphi^2$ in Eq. (35) is the negative of the sum of the three roots, the large negative root is

$$\varphi_3 \cong -(\nu_1' + \nu_2' + \nu_3' + \nu_5 + \nu_6). \qquad (37)$$

The coefficients $A_{OH,1}$, $A_{OH,2}$, and $A_{OH,3}$ are found after considerable algebra (and neglecting $\nu_3'$ and $\nu_5$ relative to $\varphi_1$, $\varphi_2$, and $\varphi_3$):

$$A_{OH,1} \cong \frac{1}{2}\,\frac{\nu_2' + \lambda}{\nu_2'}\,\frac{i}{\nu_1' + \nu_6}, \qquad (38)$$

$$A_{OH,2} \cong \frac{1}{2}\,\frac{\nu_2' - \lambda}{\nu_2'}\,\frac{i}{\nu_1' + \nu_6}, \qquad (39)$$

and

$$A_{OH,3} \cong 0 \qquad (40)$$

so that

$$[OH] = \frac{i}{\nu_1' + \nu_6}\left[\cosh(\lambda t) - 1 + \frac{\lambda}{\nu_2'}\sinh(\lambda t)\right]. \qquad (41)$$

The growth of $CO_2$ concentration with time is governed by

$$\frac{d[CO_2]}{dt} = i + \nu_6[OH], \qquad (42)$$

which integrates to give

$$\frac{[\mathrm{CO_2}]}{i} = \frac{\nu_6}{\nu_1{}' + \nu_6}\left[\frac{\sinh(\lambda t)}{\lambda} + \frac{\cosh(\lambda t) - 1}{\nu_2{}'}\right] + \frac{\nu_1{}'t}{\nu_1{}' + \nu_6}. \tag{43}$$

In the absence of added hydrogen and at large times, Eq. (43) simplifies to

$$[\mathrm{CO_2}] \cong \frac{k_i[\mathrm{CO}][\mathrm{O_2}]}{2}\left(\frac{1}{\lambda} + \frac{1}{\nu_2{}'}\right)\exp(\lambda t), \tag{44}$$

which explains the exponential growth of concentration with time shown in Fig. 1(b). Once again, $\lambda$ is determined by the slope of the line. Furthermore, the initiation rate can be determined by extrapolating to an intercept, since $\nu_2{}' = k_2{}'[\mathrm{O_2}]$ is known from studies of the hydrogen-oxygen reaction; in any event, $\nu_2{}'^{-1}$ is small compared with $\lambda^{-1}$.

Equation (43) can be used to calculate induction times by assuming that the end of the induction period can be characterized by some critical concentration of carbon dioxide - Fig. 1(a) suggests a mole fraction of $5\times10^{-4}$. Thus, induction times $\tau$ can be obtained by solution of the transcendental equation

$$\left(\frac{\nu_1{}' + \nu_6}{\nu_6}\right)\frac{\lambda x_{\mathrm{CO_2},\,\mathrm{crit}}}{k_i x_{\mathrm{CO}} x_{\mathrm{O_2}}}\left(\frac{RT}{P}\right)$$

$$= \sinh(\lambda\tau) + \frac{\lambda}{\nu_2{}'}\left[\cosh(\lambda\tau) - 1\right] + \frac{\nu_1{}'}{\nu_6}(\lambda\tau). \tag{45}$$

From Eq. (36), we see that $\lambda$ is proportional to the pressure. Hence, the left side of Eq. (45) is pressure dependent as are the coefficients $\lambda/\nu_2{}'$ and $\nu_1{}'/\nu_6$. Consequently, for a given temperature and composition, Eq. (45) can be solved to obtain a value of $(\lambda\tau)$ that is independent of pressure. Hence, the induction times should be inversely proportional to the pressure, as is observed experimentally.[4,5]

At high temperatures, the induction periods are short so that $\sinh(\lambda t) \rightarrow \lambda t$, $\cosh(\lambda t) \rightarrow 1$, and Eq. (43) reduces to

$$[CO_2] \cong k_i[CO][O_2]t. \tag{46}$$

Under these conditions the induction period is determined largely by the rate of the initiation reaction, and the growth of carbon dioxide concentration with time should be more nearly linear. Such behavior was, in fact, observed (K.G.P. Sulzmann, private communication).

In Fig. 2, the experimental induction periods of Myers, Sulzmann, and Bartle[5] are compared with values calculated from Eq. (45) by assuming that $x_{CO_2,crit} = 5\times10^{-4}$. The rate constant for the initiation reaction has been taken as

$$k_i = 2.5\times10^{9} \exp(-48{,}000/RT) \text{ liters mole}^{-1} \text{ sec}^{-1}. \tag{47}$$

This rate constant was chosen to fit the delays at the highest temperatures and also the linear portion of the curve of concentration growth shown in Fig. 1(b). This rate constant is in close agreement with the value

$$k_i = (3.5\pm1.6)\times10^{9} \exp(-51{,}000\pm7000/RT) \text{ liters mole}^{-1} \text{ sec}^{-1},$$

which Sulzmann, et al.,[4] obtained from measurements of initial slopes of $[CO_2]$ - time histories in the temperature range 2400° to 3000° K. Rate constants for reactions (I'), (II'), and (VI) were taken as recommended by Fristrom and Westenberg.[11]

No further assumptions were needed to fit the data with additions of 0.011%, and 0.13% hydrogen. The agreement between theory and experiment shown in Fig. 2 is gratifying indeed and indicates that both the assumed mechanism and values assigned to the rate constants are substantially correct.

The data without added hydrogen can be fitted by assuming a mole fraction of water vapor of $1.5\times10^{-4}$ and $k_5$ as recommended in Ref. 11. This value is 150 times larger than the reported water-vapor content of about 1 ppm.

From Eq. (36), however, we see that the delay depends on the product of $k_5$ and the water concentration. The value of $k_5$ recommended by Fristrom and Westenberg[11] is based on Kaufmann and Del Greco's[12] measurement of the reverse reaction $2OH \rightarrow H_2O + O$ at 310° K and an activation energy assigned by Kaufmann and Del Greco. They found the rate of the reaction $2OH \rightarrow H_2O + O$ was about 1/80 of the collision frequency. If a steric factor of unity is assumed, (so that the factor 1/80 is ascribed entirely to activation energy), and if the collision frequency is assumed to be proportional to $T^{1/2}$, one can estimate that $k_5$ at 1600° K might be roughly twentyfold larger than the value calculated from Fristrom and Westenberg's recommendation. This value implies a water concentration of 7 ppm. Or, to take another tack, we can try to estimate $k_5$ by assuming that the rate constant is simply the collision frequency times $\exp(-E_5/RT)$ and take $E_5$ as the reaction energy (15.9 kcal at 1600° K).[9] In this manner, we estimate a rate constant some fifteen times larger than the Fristrom and Westenberg value.

There is a third, and perhaps even better way of estimating $k_5$. In Fig. 1(b), the carbon monoxide mole fraction computed from Eq. (43) is plotted as a function of time. Up to about 400 μsec, theory and experiment are in almost perfect accord, but beyond that time the prediction is too high. A reasonable explanation is that the water-vapor concentration is depleted - that most of the water has been converted to H and OH. Thus, we can use the slopes of a curve faired through the experimental data in Fig. 1(b) as an indication of the square root of the water concentration [see Eq. (36)]. Such estimates, shown in the inset in Fig. 1(b), must be high, since carbon dioxide is produced at a steady rate via reactions (VI) and (II') even after all the water vapor has been converted to H and OH.

The depletion of water vapor during the induction period can be related to the growth of carbon dioxide concentration as follows: The rate of destruction of water is

$$-\frac{d[H_2O]}{dt} = k_5[H_2O][O] = i\,\frac{k_5}{\lambda}\,[H_2O]\sinh(\lambda t). \tag{48}$$

This expression can be integrated, at least over the region where $\lambda$ is constant, to give

$$\ln\left(\frac{[H_2O]_0}{[H_2O]}\right) = i\,\frac{k_5}{\lambda^2}\,[\cosh(\lambda t) - 1] \cong \frac{k_i k_5[CO][O_2]}{2\lambda^2}\,\exp(\lambda t). \tag{49}$$

Equations (49) and (44) can be combined to eliminate the time and relate the water and carbon dioxide concentrations

$$\ln\left(\frac{[H_2O]_0}{[H_2O]}\right) = \frac{k_5[CO_2]}{\lambda + \lambda^2/\nu_2'} \cong \frac{k_5}{\lambda}\,[CO_2]. \tag{50}$$

Computed values of the square root of water concentration are also shown in the inset of Fig. 1(b), when $k_5$ is assumed to be $8\times10^8$ moles liter$^{-1}$ sec$^{-1}$. The upper curve was obtained from Eq. (50) by using the experimental carbon dioxide concentrations. [This curve is clearly an upper bound since $CO_2$ formation continues via reactions (II') and (VI) even after the water is consumed.] The lower curve is calculated from the $CO_2$ concentration according to Eq. (44) and is a lower bound. This value of $k_5$ implies a water-vapor content of about 30 ppm.

Finally, after all the water has been converted into H and OH, the carbon dioxide concentration should grow in a linear fashion according to

$$\frac{d[CO_2]}{dt} = k_i[CO][O_2] + \frac{2k_{2'}k_6[O_2][CO]}{k_{2'}[O_2] + k_6[CO]} [H_2O]_0, \tag{51}$$

where $[H_2O]_0$ is the initial moisture content. From Fig. 1(a), at large times (dashed line), we can estimate that $d[CO_2]/dt \sim 0.16$ mole liter$^{-1}$ sec$^{-1}$, which is large compared with the initiation rate. Since values for $k_{2'}$ and $k_6$ are available, the initial water concentration can now be calculated from Eq. (48); it turns out to be about 17 ppm, which leads to $k_5 = 1.5\times10^9$ liters mole$^{-1}$ sec$^{-1}$.

The estimate of $k_5 = 8\times10^8$ (from the dropoff in $CO_2$ growth rate) can be combined with Kaufmann and Del Greco's value at 310° K to obtain

$$k_5 = 3.8\times10^{11} \exp(-19{,}500/RT) \text{ liters mole}^{-1} \text{ sec}^{-1}. \tag{52}$$

The induction periods without hydrogen addition in Fig. 2 have been computed by assuming a water vapor concentration of 20 ppm and $k_5$ from Eq. (52). The data can be fit equally well by assuming lower water-vapor concentrations with correspondingly larger values of $k_5$. The agreement between theory and experiment is good, and strongly supports the kinetic scheme assumed provided that one accepts the idea that the water-vapor concentration may have been 7 to 30 times the value reported by Sulzmann, Myers, and Bartle.[4] This is perhaps a reflection of the problems that often plague accurate measurement of small water-vapor concentrations.

## CONCLUDING REMARKS

The arguments of the preceding sections lead to the following conclusions regarding the oxidation of carbon monoxide:

1. The rate of the reaction $CO + O_2 \rightarrow CO_2 + O$ seems well established, with the rate constant given by Eq. (47). The rate of the reverse reaction $k_{-i}$ can also be obtained by invoking detailed balancing and appropriate thermochemical data[9]

$$k_{-i} = 2\times10^9 \exp(-53{,}000/RT) \text{ liters mole}^{-1} \text{ sec}^{-1}.$$

2. The rate of the reaction $O + H_2O \rightarrow 2OH$ has been estimated by two different methods as $8\times10^8$ and $1.5\times10^9$ liters $\text{mole}^{-1}$ $\text{sec}^{-1}$ near 1600° K.

3. The extraordinary sensitivity of the carbon monoxide oxidation to traces of hydrogen and water vapor is revealed once again. Thus, water-vapor concentrations of about 20 ppm seem to dominate the kinetics in experiments lasting a few tenths of a millisecond.

4. If parts per million of water vapor dominate the kinetics in the millisecond time scale, it seems reasonable that parts per billion of hydrogenous material may well determine the kinetics in static experiments at lower temperatures where reaction times are several seconds or minutes.

5. The data of Sulzmann, et al.,[4,5] cannot be explained by the chain-branching-reaction scheme

$$CO + O \xrightarrow{k_1} CO_2^* \qquad (I)$$

$$CO_2^* + O_2 \xrightarrow{k_2} CO_2 + 2O. \qquad (II)$$

This suggests (together with item 4) that there is <u>no</u> experimental evidence that reaction (II) occurs.

6. Finally, what can we postulate as to the explosion of absolutely hydrogen-free mixtures of carbon monoxide and oxygen? A reasonable guess is that these should be thermal explosions, initiated through the nearly thermoneutral reaction

$$CO + O_2 \xrightarrow{k_1} CO_2 + O$$

with subsequent heat release due to

$$O + O + M \longrightarrow O_2 + M.$$

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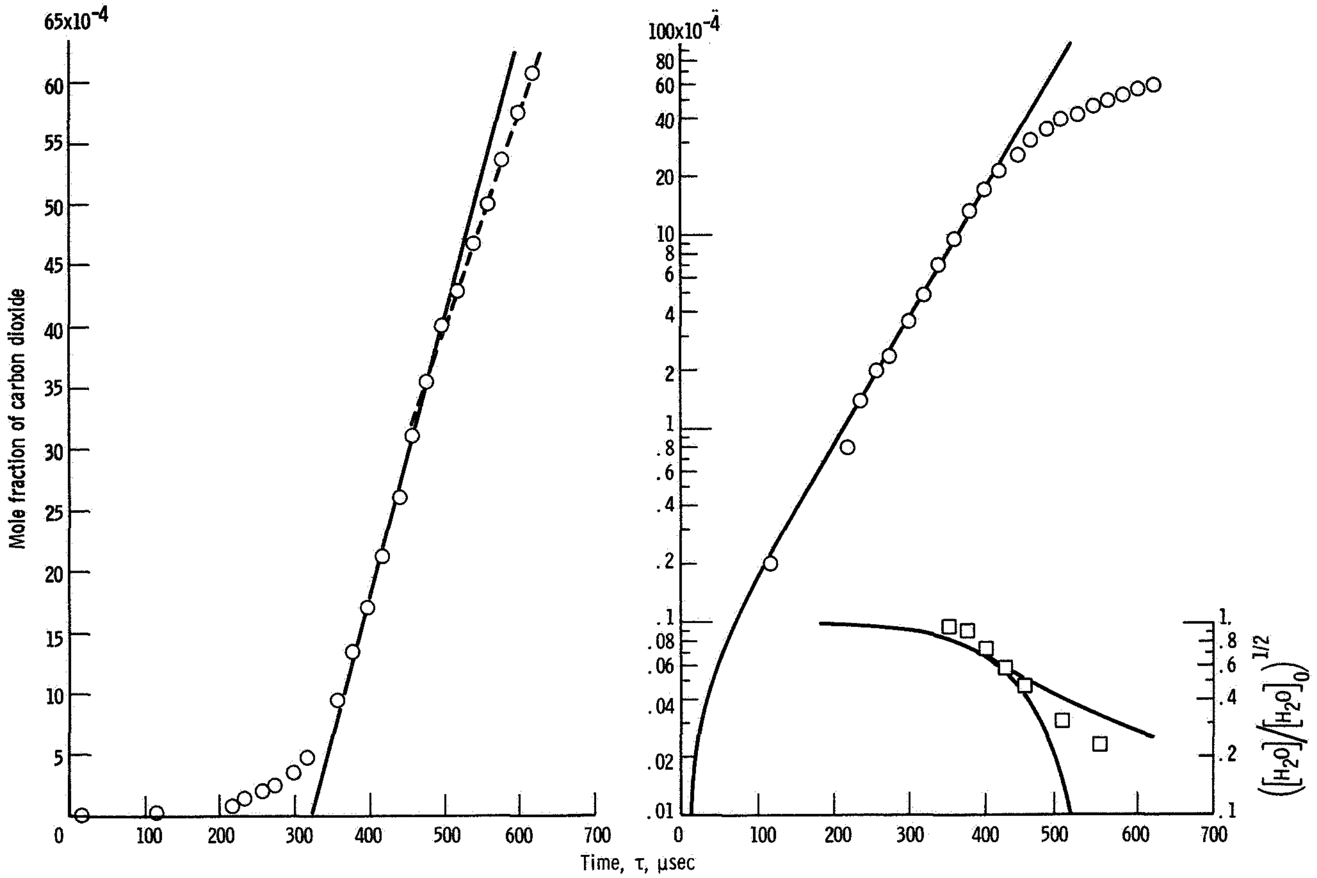
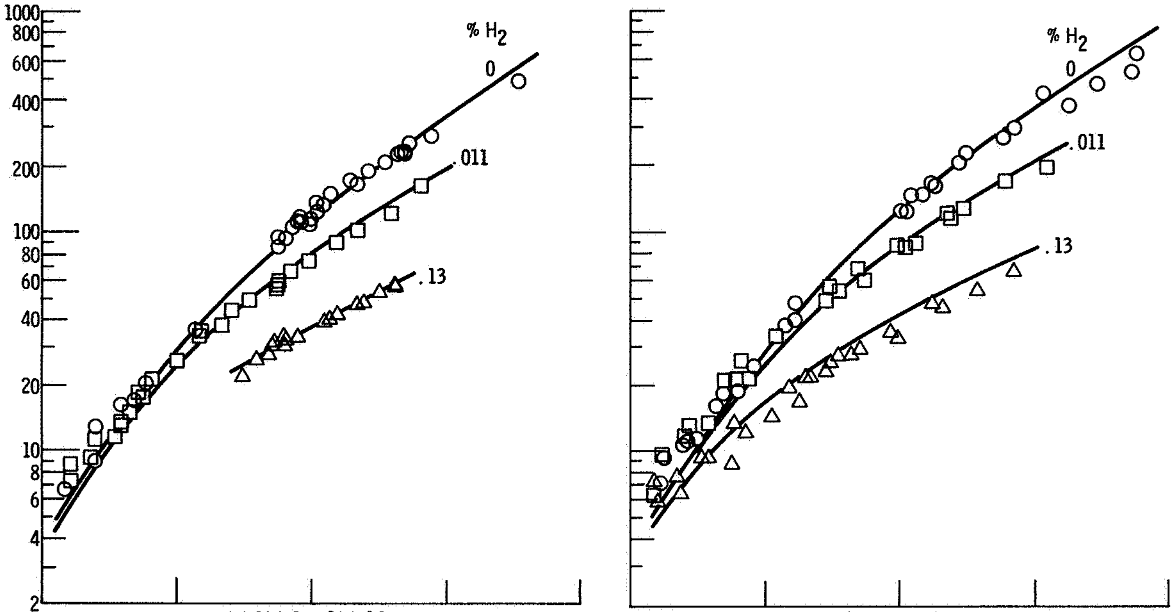


(a)

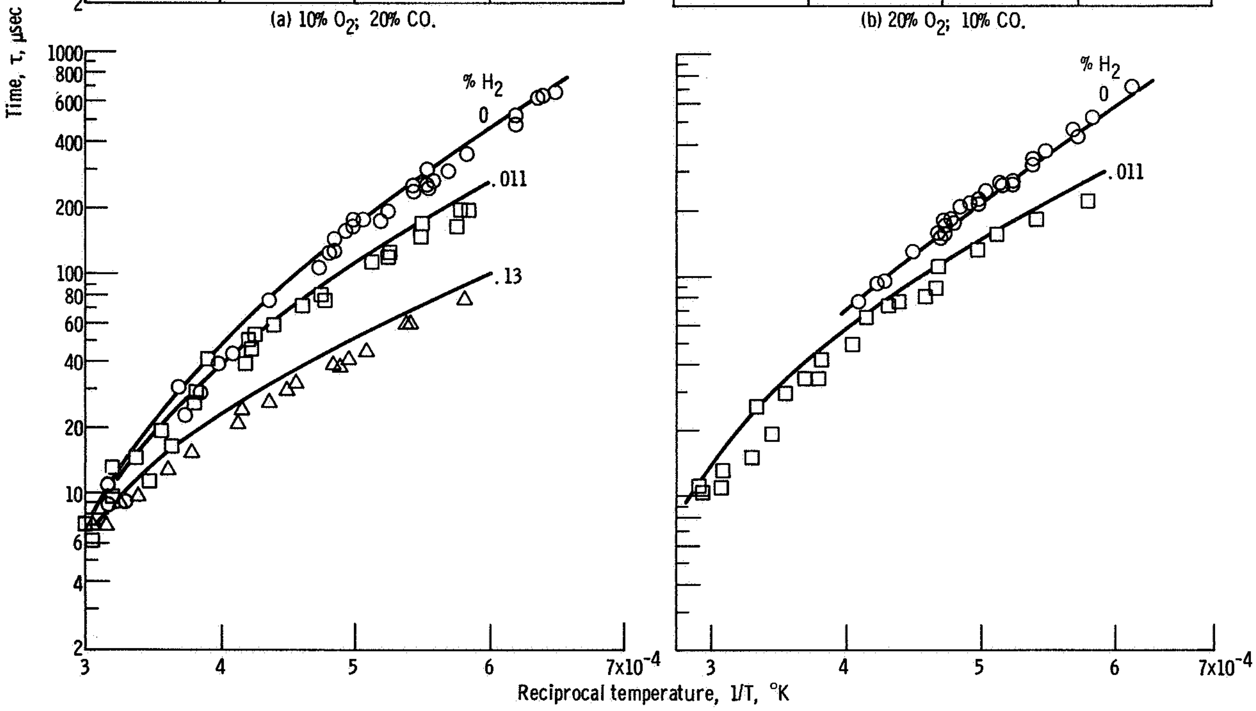
(b)

Fig. 1. - Growth of carbon dioxide concentration with time (Ref. 4). 10% $O_2$; 20% CO; 1.145 atm; 1597° K.



(a) 10% $O_2$; 20% CO.

(b) 20% $O_2$; 10% CO.



(c) 10% $O_2$; 10% CO.

(d) 5% $O_2$; 10% CO.

Fig. 2. - Comparison of computed and experimental induction times as function of reciprocal temperature. (Induction times have been normalized to 1 atm, Ref. 5. Curves labeled 0% $H_2$ have been calculated by assuming 20 ppm water vapor.)