IGNITION KINETICS OF CARBON MONOXIDE - OXYGEN REACTION

by Richard S. Brokaw

Lewis Research Center
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SUMMARY

An analytic solution for the ignition kinetics of the dry carbon monoxide - oxygen reaction is obtained by assuming an initiation reaction followed by the chain-branching steps \( \text{CO} + \text{O} \rightarrow \text{CO}_2^* \) and \( \text{CO}_2^* + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{O} \) together with chain termination by quenching of the electronically excited carbon dioxide molecule, \( \text{CO}_2^* \), and the three-body recombination of carbon monoxide and oxygen atoms. It is concluded that shock-tube induction times on reportedly dry carbon monoxide - oxygen 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 parts per million or less is assumed:

\[
\begin{align*}
\text{CO} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{O}, \\
\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{OH}, \\
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H}, \\
\text{H} + \text{O}_2 & \rightarrow \text{OH} + \text{O}.
\end{align*}
\]

The rate constant for the initiation reaction was found to be \( k_1 = 2.5 \times 10^9 \exp(-48000/RT) \) liters per mole-second. The rate constant for the reaction between oxygen atoms and water at 1600° K was estimated by two different methods to be \( 8 \times 10^8 \) and \( 1.5 \times 10^9 \) liters per mole-second. Induction periods for mixtures with deliberate additions of hydrogen can be fit by adding the steps \( \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \) and \( \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \).

INTRODUCTION

The explosive reaction of "dry" carbon monoxide and oxygen has been studied by a number of investigators starting with Hadman, Thompson, and Hinshelwood (ref. 1) in 1932. At first glance, one might assume that the kinetics leading to ignition should be rather simple and easily elucidated. On the contrary, as recently as 1964, Dickens,

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Dove, and Linnett (ref. 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 (ref. 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 (refs. 4 and 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 because 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 report, an analytic solution is first developed for the ignition kinetics of the dry carbon monoxide-oxygen system. It is found that the experimental data of references 4 and 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 parts per million. This value is larger than the reported contamination of 1 part per million; possible rationalizations are discussed. Finally, the experimental data (ref. 5) with added hydrogen are adequately explained.

These solutions are developed by using mathematical techniques that have been successfully applied to hydrogen-oxygen ignition (refs. 6 to 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.

**SYMBOLS**

A pre-exponential constant, moles liter$^{-1}$

b, c Portmanteau constants defined in equation (13)

C concentration, moles liter$^{-1}$

$\Delta E$ dissociation energy of reaction I, kcal mole$^{-1}$

i rate of initiation reaction, moles liter$^{-1}$ sec$^{-1}$

K equilibrium constant, moles liter$^{-1}$

2
k  specific reaction rate constant
P  steric factor
R  gas constant
ΔS  entropy change of reaction I
T  absolute temperature, °K
t  time, sec
x  mole fraction
Z  collision number
λ  exponential growth constant (eqs. (11) and (36)), sec⁻¹
ν  reaction frequency, sec⁻¹
τ  induction time, sec
φ  roots of equations (8) and (35), sec⁻¹

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 (ref. 3)

\[
\begin{align*}
CO + O & \xrightleftharpoons[\kappa-1]{\kappa_1} CO_2^* \\
CO_2^* + O_2 & \rightarrow CO_2 + 2O \\
CO_2^* + M & \rightarrow CO_2 + M \\
CO + O + M & \rightarrow CO_2 + M
\end{align*}
\]

(III)
This reaction scheme involves two chain carriers - oxygen atoms and an electronically excited carbon dioxide molecule, $\text{CO}_2^*$. The differential equations governing the growth of $\text{O}$ and $\text{CO}_2^*$ concentrations during the induction period are as follows:

\[
\frac{d[\text{O}]}{dt} = i - (\nu_1 + \nu_4)[\text{O}] + (\nu_{-1} + 2\nu_2)[\text{CO}_2^*]
\]

\[
\frac{d[\text{CO}_2^*]}{dt} = \nu_1[\text{O}] - (\nu_{-1} + \nu_2 + \nu_3)[\text{CO}_2^*]
\]

Here $i = k_1[\text{CO}][\text{O}_2]$ (the initiation rate) and also $\nu_1 = k_4[\text{CO}]$, $\nu_{-1} = k_{-1}$, $\nu_2 = k_2[\text{O}_2]$, $\nu_3 = k_3[\text{M}]$, and $\nu_4 = k_4[\text{CO}][\text{M}]$. The $\nu$ are reaction frequencies and have the dimensions of reciprocal time. Since the induction period is assumed isothermal and depletion of the reactants is neglected, both the initiation rate and the reaction frequencies are taken to be constant during the induction period.

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

\[
\text{CO} = [\text{O}] + \frac{(\nu_{-1} + \nu_2 + \nu_3)i}{\nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)}
\]

and

\[
\text{CO}_2^* = [\text{CO}_2^*] + \frac{\nu_1i}{\nu_1\nu_2 - \nu_1\nu_3 - \nu_4(\nu_{-1} + \nu_2 + \nu_3)}
\]

(\text{CO} and \text{CO}_2^* differ appreciably from the actual concentrations [O] and [CO] only at the very start of the reaction.) Thus i is eliminated, $\text{CO}_2^*$ replaces $[\text{CO}_2^*]$, and $\text{CO}$ replaces [O]. A particular solution to the transformed equations is

\[
\begin{align*}
\text{CO} &= A_0 \exp(\varphi t) \\
\text{CO}_2^* &= A_{\text{CO}_2^*} \exp(\varphi t)
\end{align*}
\]
Substituting equation (5) into the differential equations yields the relations

\[-(n_1 + n_4 + \varphi)A_O + (n_{-1} + 2n_2)A_{CO_2} = 0\]  
(6)

and

\[n_1A_O - (n_{-1} + n_2 + n_3 + \varphi)A_{CO_2} = 0\]  
(7)

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

\[\varphi^2 + (n_1 + n_{-1} + n_2 + n_3 + n_4)\varphi - \left[n_1n_2 - n_1n_3 - n_4(n_{-1} + n_2 + n_3)\right] = 0\]  
(8)

One root of this equation is always negative; the other may be positive if $n_1n_2 > n_1n_3 + n_4(n_{-1} + n_2 + n_3)$. Thus, there is an explosion limit defined by

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

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

Call the root of equation (8) that may be positive $\varphi_1$ and the root that is always negative $\varphi_2$. Next, define $\lambda_1 = \varphi_1$ and $\lambda_2 = -\varphi_2$. The general solution is then

\[C_O = A_{O,1} \exp(\lambda_1 t) + A_{O,2} \exp(-\lambda_2 t)\]  
\[C_{CO_2}^* = A_{CO_2^*,1} \exp(\lambda_1 t) + A_{CO_2^*,2} \exp(-\lambda_2 t)\]  
(10)

where

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

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

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

$$= k_1[CO] + k_{-1} + k_2[O_2] + k_3[M] + k_4[CO][M]$$

(13)

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

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

(14)

The pre-exponential coefficients in equation (10) are obtained as follows: Initially the concentrations of CO$_2^*$ and O are zero. Thus, from equations (3), (4), and (10),

$$A_{O,1} + A_{O,2} = (\nu_{-1} + \nu_2 + \nu_3) \frac{1}{c}$$

(15)

$$A_{CO_2^*,1} + A_{CO_2^*,2} = \nu_1 \frac{1}{c}$$

(16)

and from equation (7),

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

(17)

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

(18)

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

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

(19)

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

(20)

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

(21)
and

\[ A_{\text{CO}_2} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{\nu_1}{c} \]  

(22)

The growth of carbon dioxide concentration with time is governed by

\[ \frac{d[\text{CO}_2]}{dt} = (\nu_2 + \nu_3)[\text{CO}_2^*] + \nu_4[\text{O}] + i \]  

(23)

Because the pre-exponential coefficients of equations (10) have been derived (eqs. (19) to (22)), equation (23) can be integrated to give

\[ [\text{CO}_2] = \frac{\lambda_2}{\lambda_1 + \lambda_2} \left( 2\nu_1 \nu_2 - c \right) \left[ \left( e^{\lambda_1 t} - 1 \right) - \left( \frac{\lambda_1}{\lambda_2} \right)^2 \left( e^{-\lambda_2 t} - 1 \right) \right] + \nu_4 \left( \frac{\lambda_2}{\lambda_1 + \lambda_2} \right) \left( e^{\lambda_1 t} - 1 \right) + \left( \frac{\lambda_1}{\lambda_2} \right) \left( e^{-\lambda_2 t} - 1 \right) - 2(\nu_1 \nu_2 - c)t \]  

(24)

At this point, it is worthwhile to consider the relative magnitudes of \( \lambda_1 \) and \( \lambda_2 \). From equations (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 pre-exponential factors. Hence, to a good approximation,

\[ [\text{CO}_2] \approx \frac{\lambda_2}{\lambda_1 + \lambda_2} \left( \frac{\lambda_1}{\lambda_1 + \lambda_2} \right) \left( e^{\lambda_1 t} - 1 \right) \left( \frac{2\nu_1 \nu_2 - c}{\lambda_1} + \nu_4 \right) - 2(\nu_1 \nu_2 - c)t \]  

(25)

In attempting to analyze the experimental results of Sulzmann, Myers, and Bartle (refs. 4 and 5), it will be assumed 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 \( \text{CO}_2 \) concentration with time is given by
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 percent carbon monoxide and 10 percent oxygen in argon at 1597°K and 1.145 atmospheres (taken from fig. 2 of ref. 4). In figure 1(a), a linear plot, the carbon dioxide mole fraction grows in an accelerating fashion for perhaps 400 microseconds. 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. (ref. 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 figure 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 microseconds. (The subsequent falloff must be a result either of reactions among chain carriers or depletion of the reactants.) From figure 1(b) and equation (26), it is found that \( \lambda_1 = 1.54 \times 10^4 \) per second. Is this exponential growth constant consistent with the postulated reaction mechanism?

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

\[
\lambda_1 \approx \frac{k_1 k_2 [CO][O_2]}{k_1 [CO] + k_1^{-1} + k_2 [O_2]} \tag{27}
\]

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 (refs. 4 and 5).

Detailed balancing, however, suggests that \( k_1^{-1} \) is by no means negligible. The magnitude of \( k_1^{-1} \) in comparison with \( k_1 \) and \( k_2 \) can be determined by estimating the equilibrium constant \( K \) for the reaction

\[
CO_2^* \xrightarrow{k_1} CO + O \tag{-I}
\]

The entropy change associated with such a process at 1 atmosphere and 10000°C to 3000°C K can be estimated with some confidence by considering analogous dissociations

\[
(NO_2 = NO + O, \Delta S/R = 17.0; SO_2 = SO + O, \Delta S/R = 17.3; \text{ and } CO_2 = CO + O, \Delta S/R = 18.1, \text{ based on the data of ref. 9}). \]

Thus, if it is assumed that \( \Delta S/R = 17 \), \( K = 7 \times 10^4 \exp(-\Delta E/RT) \) moles per liter, where \( \Delta E \) is the dissociation energy of \( CO_2^* \).

If \( \Delta E = 20 \) kilocalories, \( K_{15970} = 130 \); if \( \Delta E = 40 \) kilocalories, \( K_{15970} = 0.21 \). This is the range of stability for excited carbon dioxide molecules suggested by Clyne and Thrush (ref. 10).

Next solve equation (27) for \( k_1 \):

\[
\frac{1}{k_1} = \frac{\lambda [CO]}{k_2 [O_2]} - \frac{K [CO]}{k_2 [O_2] - k_1^{-1} + k_2 [O_2]} \tag{28}
\]

The last term on the right may be neglected because \( K > 0.21 >> [CO] = 1.75 \times 10^{-3} \) mole per liter. Since \( k_1 \) is positive,
Finally, express $k_2$ in collision theory form,

$$k_2 = PZ \exp \frac{-E_2}{RT}$$

Because the dissociation energy of $O_2$ is 7 kilocalories less than that of $CO_2$, $E_2 > \Delta E - 7$ kilocalories. At $1597^0 K$, $Z \sim 3.5 \times 10^{11}$, so that the steric factor $P$ must be greater than 200! This is clearly ridiculous.

It follows that the experimental ignition-delay data cannot 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 (ref. 4) report that their nominally dry carbon monoxide-oxygen mixtures contained about 1 part per million of water vapor, the kinetics in the presence of traces of water must be investigated next. Furthermore, experiments were performed with small additions of hydrogen (ref. 5), so that the effect of hydrogen can profitably be examined as well.

Once again, assume the initiation step

$$k_1$$

$$CO + O_2 \rightarrow CO_2 + O$$

The product oxygen atoms react with either water or hydrogen

$$k_5$$

$$O + H_2O \rightarrow 2OH$$

(III')

$$k_3, O + H_2 \rightarrow OH + H$$

(V)

to generate hydroxyl radicals that oxidize both carbon monoxide and hydrogen
\[
\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \quad \text{(VI)}
\]

and

\[
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{(I')}\]

Finally, hydroxyl radicals are regenerated through the step

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad \text{(II')}
\]

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:

\[
\frac{dC_O}{dt} = - (\nu_3' + \nu_5)C_O + \nu_2'C_H \quad \text{(29)}
\]

\[
\frac{dC_{OH}}{dt} = (\nu_3' + 2\nu_5)C_O - (\nu_1' + \nu_6)C_{OH} + \nu_2'C_H \quad \text{(30)}
\]

and

\[
\frac{dC_H}{dt} = \nu_3'C_O + (\nu_1' + \nu_6)C_{OH} - \nu_2'C_H \quad \text{(31)}
\]

Here once again a shorthand notation has been introduced so that \(\nu_1' = k_1'[\text{H}_2]\), \(\nu_2' = k_2'[\text{O}_2]\), \(\nu_3' = k_3'[\text{H}_2]\), \(\nu_5' = k_5'[\text{H}_2\text{O}]\), and \(\nu_6' = k_6'[\text{CO}]\). Also, the initiation rate has been eliminated from the differential equations by introducing new concentration variables,

\[
C_O = [O] \quad \text{(32)}
\]

\[
C_{OH} = [OH] + \frac{i}{\nu_1' + \nu_6'} \quad \text{(33)}
\]
and

\[ \text{C}_\text{H} = [\text{H}] + \frac{i}{\nu_2}, \]  
(34)

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

\[ \phi^3 + (\nu_1, + \nu_2, + \nu_3, + \nu_5 + \nu_6)\phi^2 + \left[ \nu_2, \nu_5 + (\nu_3, + \nu_5)(\nu_1, + \nu_6) \right] \phi - 2\nu_2, (\nu_3, + \nu_5)(\nu_1, + \nu_6) = 0 \]

(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 equation (35) can be neglected because these roots are small, and the third term can be neglected because the amounts of water and hydrogen are small so that \( \nu_3, \text{ and } \nu_5 \) are also small. Consequently,

\[ \phi_1 \approx -\phi_2 \approx \frac{2\nu_2, (\nu_3, + \nu_5)(\nu_1, + \nu_6)}{\nu_1, + \nu_2, + \nu_3, + \nu_5 + \nu_6} \]

\[ = \frac{[2k_2, [\text{O}_2](k_3, [\text{H}_2] + k_5, [\text{H}_2\text{O}]) (k_1, [\text{H}_2] + k_6, [\text{CO}])]}{(k_1, + k_3,)[\text{H}_2] + k_5, [\text{H}_2\text{O}] + k_2, [\text{O}_2] + k_6, [\text{CO}]} ^{1/2} \]

(36)

(Eq. (36) is in error by at most 5 percent for an added hydrogen concentration of 0.13 percent.) Since the coefficient of \( \phi^2 \) in equation (35) is the negative of the sum of the three roots, the large negative root is

\[ \phi_3 \approx -(\nu_1, + \nu_2, + \nu_3, + \nu_5 + \nu_6) \]

(37)

The coefficients \( \text{A}_{\text{OH}, 1}, \text{A}_{\text{OH}, 2}, \text{ and } \text{A}_{\text{OH}, 3} \) are found after considerable algebra (and neglecting \( \nu_3, \text{ and } \nu_5 \) relative to \( \phi_1, \phi_2, \text{ and } \phi_3 \))

\[ \text{A}_{\text{OH}, 1} \approx \frac{1}{2} \frac{\nu_2, + \lambda}{\nu_2,} - \frac{i}{\nu_1, + \nu_6} \]

(38)
and

$$A_{OH, 3} \approx 0 \tag{40}$$

so that

$$[OH] = \frac{i}{\nu_1 + \nu_6} \left[ \cosh(\lambda t) - 1 + \frac{\lambda}{\nu_2} \sinh(\lambda t) \right] \tag{41}$$

The growth of CO\textsubscript{2} concentration with time is governed by

$$\frac{d[CO_2]}{dt} = i + \nu_6[OH] \tag{42}$$

which can be integrated to give

$$[CO_2] = \frac{\nu_6}{\nu_1 + \nu_6} \left[ \frac{\sinh(\lambda t)}{\lambda} + \frac{\cosh(\lambda t) - 1}{\nu_2} \right] + \frac{\nu_1 t}{\nu_1 + \nu_6} \tag{43}$$

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

$$[CO_2] \approx \frac{k_1[CO][O_2]}{2} \left( \frac{1}{\lambda} + \frac{1}{\nu_2} \right) \exp(\lambda t) \tag{44}$$

which explains the exponential growth of concentration with time shown in figure 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 $\nu_2 = k_2[O_2]$ 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. Figure 1(a) (p. 8) suggests a mole fraction of $5 \times 10^{-4}$. Thus, induction times $\tau$ can be obtained by solution of the transcendental equation
Figure 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 percent $H_2$ have been calculated by assuming 20 ppm water vapor.)

(a) 10 percent oxygen; 20 percent carbon monoxide.

(b) 20 percent oxygen; 10 percent carbon monoxide.

(c) 10 percent oxygen; 10 percent carbon monoxide.

(d) 5 percent oxygen; 10 percent carbon monoxide.
\[
\frac{(\nu_1 + \nu_6)}{\nu_6} \frac{\lambda x_{CO_2, crit}}{k_1 x_{CO} x_{O_2}} \frac{RT}{P} = \sinh(\lambda T) + \frac{\lambda}{\nu_2'} \left[ \cosh(\lambda T) - 1 \right] + \frac{\nu_1'}{\nu_6'} (\lambda T)
\]  

(45)

From equation (36), it follows that \( \lambda \) is proportional to the pressure. Hence, the left side of equation (45) is pressure independent as are the coefficients \( \lambda/\nu_2 \) and \( \nu_1'/\nu_6' \). Consequently, for a given temperature and composition, equation (45) can be solved to obtain a value of \( \lambda T \) that is independent of pressure. Hence, the induction times should be inversely proportional to the pressure, as is observed experimentally (refs. 4 and 5).

At high temperatures, the induction periods are short so that \( \sinh(\lambda t) \approx \lambda t, \cosh(\lambda t) \approx 1 \), and equation (43) reduces to

\[
[CO_2] \approx k_1 [CO][O_2]^t
\]

(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 figure 2, the experimental induction periods of Myers, Sulzmann, and Bartle (ref. 5) are compared with values calculated from equation (45) by assuming that \( x_{CO_2, crit} = 5 \times 10^{-4} \). The rate constant for the initiation reaction has been taken as

\[ k_1 = 2.5 \times 10^9 \exp\left(-48 \ 000/RT\right) \text{ liters mole}^{-1} \text{ sec}^{-1} \]  

(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 figure 1(b). This rate constant is in close agreement with the value

\[ k_1 = (3.5 \pm 1.6) \times 10^9 \exp\left(-51 \ 000 \pm 7000/RT\right) \text{ liters mole}^{-1} \text{ sec}^{-1} \]

which Sulzmann, et al. (ref. 4), obtained from measurements of initial slopes of \([CO_2] - \text{time histories in the temperature range 2400}^0 \text{ to } 3000^0 \text{ K. Rate constants for reactions (I'), (II'), and (VI) were taken as recommended by Fristrom and Westenberg (ref. 11).}

No further assumptions were needed to fit the data with additions of 0.011 and 0.13 percent hydrogen. The agreement between theory and experiment shown in figure 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 $1.5 \times 10^{-4}$ and $k_5$ as recommended in reference 11. This value is 150 times larger than the reported water-vapor content of about 1 part per million.

From equation (36), however, it follows that the delay depends on the product of $k_5$ and the water concentration. The value of $k_5$ recommended by Fristrom and Westenberg (ref. 11) is based on Kaufmann and Del Greco's measurement (ref. 12) of the reverse reaction $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ at 310° K and an activation energy assigned by Kaufmann and Del Greco. They found the rate of the reaction $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ was about $1/80$ of the collision frequency. If a steric factor of 1 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 about twentyfold larger than the value calculated from Fristrom and Westenberg's recommendation. This value implies a water concentration of 7 parts per million.

Or, to take another tack, $k_5$ can be estimated 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, ref. 9). In this manner, a rate constant is estimated some 15 times larger than the Fristrom and Westenberg value.

There is a third, and perhaps even better way of estimating $k_5$. In figure 1(b), the carbon monoxide mole fraction computed from equation (43) is plotted as a function of time. Up to about 400 microseconds, 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 $\text{H}$ and $\text{OH}$. Thus, the slopes of a curve faired through the experimental data in figure 1(b) can be used as an indication of the square root of the water concentration (see eq. (36)). Such estimates, shown in the inset in figure 1(b), must be high, since carbon dioxide is produced at a steady rate by reactions (VI) and (II') even after all the water vapor has been converted to $\text{H}$ and $\text{OH}$.

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

$$-\frac{d[\text{H}_2\text{O}]}{dt} = k_5[\text{H}_2\text{O}][\text{O}] = \frac{i}{\lambda} \frac{k_5}{[\text{H}_2\text{O}] \sinh(\lambda t)}$$  \hspace{1cm} (48)

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

$$\ln \left( \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} \right) = \frac{i}{\lambda^2} \left[ \cosh(\lambda t) - 1 \right] \approx \frac{k_1k_5[\text{CO}][\text{O}_2]}{2\lambda^2} \exp(\lambda t)$$ \hspace{1cm} (49)
Equations (49) and (44) can be combined to eliminate the time and relate the water and carbon dioxide concentrations

\[
\ln \frac{[H_2O]}{[H_2O]}_0 = \frac{k_5[CO_2]}{\lambda + \frac{\lambda^2}{\nu_2}} \approx \frac{k_5}{\lambda} [CO_2]
\]  

(50)

Computed values of the square root of water concentration are also shown in the inset in figure 1(b), when \(k_5\) is assumed to be \(8 \times 10^8\) moles per liter second. The upper curve was obtained from equation (50) by using the experimental carbon dioxide concentrations. (This curve is clearly an upper bound since \(CO_2\) formation continues by reactions (II') and (VI) even after the water is consumed.) The lower curve is calculated from the \(CO_2\) concentration according to equation (44) and is a lower bound. This value of \(k_5\) implies a water-vapor content of about 30 parts per million.

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

\[
\frac{d[CO_2]}{dt} = k_1[CO][O_2] + \frac{2k_2,k_6[O_2][CO]}{k_2,[O_2] + k_6[CO]} [H_2O]
\]  

(51)

where \([H_2O]\) is the initial moisture content. From figure 1(a), at large times (dashed line), \(d[CO_2]/dt \sim 0.16\) mole per liter-second, 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 equation (48); it turns out to be about 17 parts per million, which leads to \(k_5 = 1.5 \times 10^9\) liters per mole-second.

The estimate of \(k_5 = 8 \times 10^8\) (from the dropoff in \(CO_2\) growth rate) can be combined with Kaufmann and Del Greco’s value at 310°K to obtain

\[
k_5 = 3.8 \times 10^{11} \exp(-19500/RT) \text{ liters mole}^{-1}\text{ sec}^{-1}
\]  

(52)

The induction periods without hydrogen addition in figure 2 have been computed by assuming a water vapor concentration of 20 parts per million and \(k_5\) from equation (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 in refer-
ence 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 \( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \) seems well established, with the rate constant given by equation (47). The rate of the reverse reaction \( k_{-1} \) can also be obtained by invoking detailed balancing and appropriate thermochemical data (ref. 9):

\[ k_{-1} = 2 \times 10^9 \exp(-53,000/RT) \text{ liters mole}^{-1} \text{ sec}^{-1} \]

2. The rate of the reaction \( \text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \) has been estimated by two different methods as \( 8 \times 10^8 \) and \( 1.5 \times 10^9 \) liters per mole-second 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 parts per million 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. (refs. 4 and 5) cannot be explained by the chain-branching-reaction scheme

\[ \text{CO} + \text{O} \xleftrightarrow{\text{k}_1} \text{CO}_2^* \xrightarrow{\text{k}_{-1}} \text{CO}_2 + \text{O} \]  

This suggests (together with item 4) that there is little or no experimental evidence that reaction (II) occurs.

6. Finally, what can be postulated 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

18
\[
\begin{align*}
  k_1 \\
  \text{CO + O}_2 &\rightarrow \text{CO}_2 + \text{O}
\end{align*}
\]

with subsequent heat release due to

\[
\begin{align*}
  \text{O + CO + M} &\rightarrow \text{CO}_2 + \text{M}
\end{align*}
\]

and

\[
\begin{align*}
  \text{O + O + M} &\rightarrow \text{O}_2 + \text{M}
\end{align*}
\]

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—National Aeronautics and Space Act of 1958

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