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IGNITION KINETICS OF CARBON MONOXIDE - OXYGEN REACTION

by Richard S. Brokaw

Lewis Research Center
Cleveland, Ohio

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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 $CO + O \rightarrow CO_2^*$ and $CO_2^* + O_2 \rightarrow CO_2 + 2O$ together with chain termination by quenching of the electronically excited carbon dioxide molecule, 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: $CO + O_2 \xrightarrow{k_i} CO_2 + O$, $O + H_2O \xrightarrow{k_5} 2OH$, $OH + CO \xrightarrow{k_6} CO_2 + H$, $H + O_2 \xrightarrow{k_{2'}} OH + O$. The rate constant for the initiation reaction was found to be $k_i = 2.5\times10^9 \exp(-48\,000/RT)$ liters 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 8×10^8 and 1.5×10^9 liters per mole-second. Induction periods for mixtures with deliberate additions of hydrogen can be fit by adding the steps $O + H_2 \xrightarrow{k_{3'}} OH + H$ and $OH + H_2 \xrightarrow{k_{1'}} H_2O + H$.

INTRODUCTION

The explosive reaction of "dry" carbon monoxide and oxygen has been studied by a number of investigators starting with Hadman, Thompson, and Hinshelwood (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}
ΔE	dissociation energy of reaction I, kcal mole^{-1}
i	rate of initiation reaction, moles liter^{-1} sec^{-1}
K	equilibrium constant, moles liter^{-1}

k	specific reaction rate constant
P	steric factor
R	gas constant
ΔS	entropy change of reaction I
T	absolute temperature, $^{\circ}K$
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)

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

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

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

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

together with an initiation step

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

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:

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

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

Here $i \equiv k_i[CO][O_2]$ (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 ν 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

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

and

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

(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

$$\left.\begin{aligned} C_O &= A_O \exp(\varphi t) \\ C_{CO_2^*} &= A_{CO_2^*} \exp(\varphi t) \end{aligned}\right\} \tag{5}$$

Substituting equation (5) into the differential equations yields the relations

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

and

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

A nontrivial solution requires that the determinant of the coefficients of A_O 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 (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 φ_1 and the root that is always negative φ_2. Next, define $\lambda_1 \equiv \varphi_1$ and $\lambda_2 \equiv -\varphi_2$. The general solution is then

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

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

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

$$= k_1[CO] + k_{-1} + k_2[O_2] + k_3[M] + k_4[CO][M] \tag{13}$$

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

$$= k_1k_2[CO][O_2] - k_1k_3[CO][M] - k_4[CO][M]\left(k_{-1} + k_2[O_2] + k_3[M]\right) \tag{14}$$

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),

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

$$A_{CO_2^*,1} + A_{CO_2^*,2} = \nu_1 \frac{i}{c} \tag{16}$$

and from equation (7),

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

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

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

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

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

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

and

$$A_{CO_2^*,2} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{\nu_1 i}{c} \tag{22}$$

The growth of carbon dioxide concentration with time is governed by

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

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

$$\begin{aligned} [CO_2]\frac{c}{i} = {} & (2\nu_1\nu_2 - c)\frac{\frac{\lambda_2}{\lambda_1}}{\lambda_1 + \lambda_2}\left[\left(e^{\lambda_1 t} - 1\right) - \left(\frac{\lambda_1}{\lambda_2}\right)^2\left(e^{-\lambda_2 t} - 1\right)\right] \\ & + \nu_4\frac{\lambda_2}{\lambda_1 + \lambda_2}\left[\left(e^{\lambda_1 t} - 1\right) + \left(\frac{\lambda_1}{\lambda_2}\right)\left(e^{-\lambda_2 t} - 1\right)\right] - 2(\nu_1\nu_2 - c)t \end{aligned} \tag{24}$$

At this point, it is worthwhile to consider the relative magnitudes of λ_1 and λ_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,

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

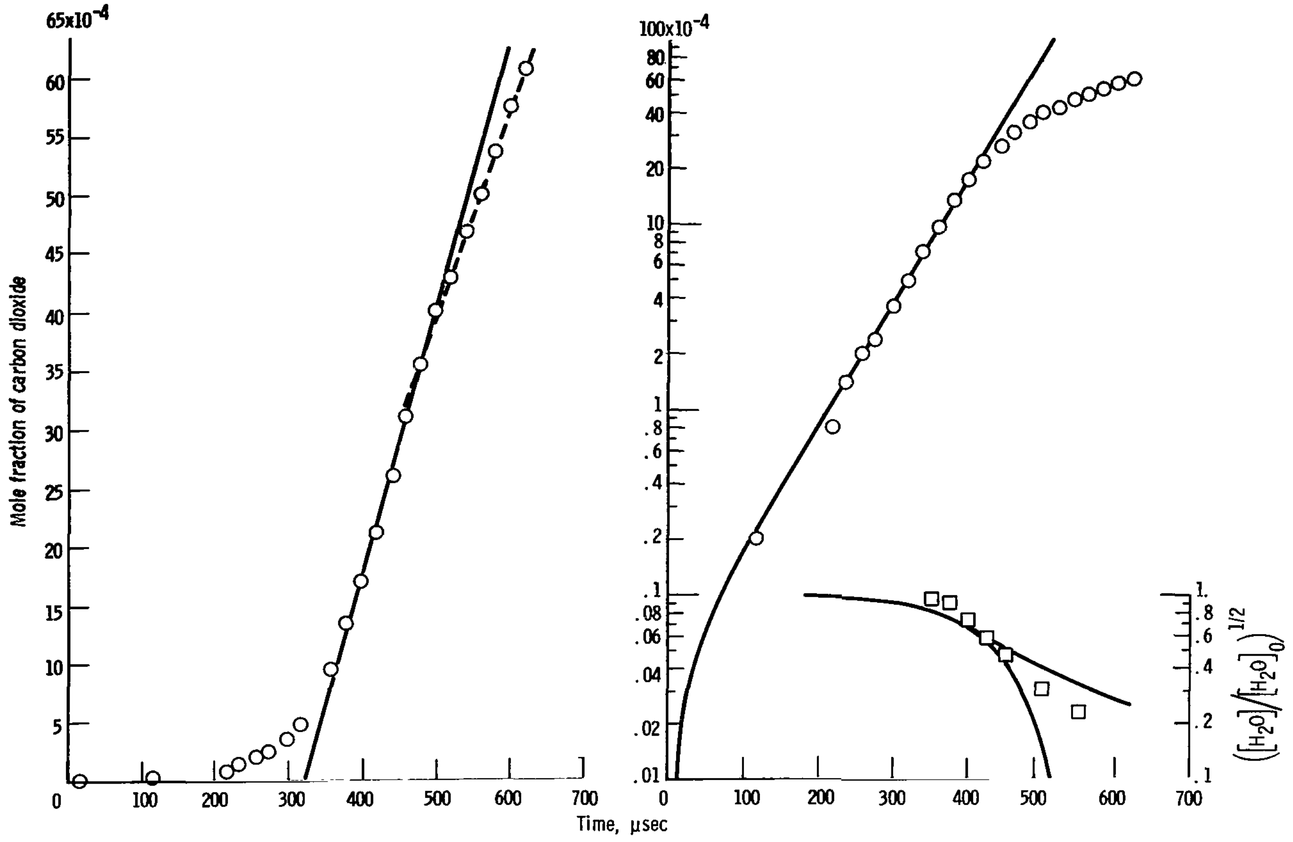
In attempting to analyze the experimental results of Sulzmann, Myers, and Bartle (refs. 4 and 5), it will be assumed that the temperature is high enough so that reaction (III), the quenching step, can be neglected, and the pressure is low enough so that chain termination by reaction (IV) is also negligible.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

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

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 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 5×10^{-4}.

In figure 1(b), the same data are replotted on semilogarithmic coordinates, and it is



(a) Linear plot.

(b) Logarithmic plot.

Figure 1. - Growth of carbon dioxide concentration with time (ref. 4). Oxygen, 10 percent; carbon monoxide, 20 percent; pressure, 1.145 atmospheres; temperature, 1597° K.

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 $\lambda_1 = 1.54\times10^4$ per second. Is this exponential growth constant consistent with the postulated reaction mechanism?

Inasmuch as $4c/b^2 \leq 1$, the binominal expansion can be applied to equation (11) without undue violence (error less than 20 percent), 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 (refs. 4 and 5).

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

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

The entropy change associated with such a process at 1 atmosphere and 1000° to 3000° K can be estimated with some confidence by considering analogous dissociations ($NO_2 \rightleftarrows NO + O$, $\Delta S/R = 17.0$; $SO_2 \rightleftarrows SO + O$, $\Delta S/R = 17.3$; and $CO_2 \rightleftarrows CO + O$, $\Delta S/R = 18.1$, based on the data of ref. 9). Thus, if it is assumed that $\Delta S/R = 17$, $K = 7\times10^4 \exp(-\Delta E/RT)$ moles per liter, where ΔE is the dissociation energy of CO_2^*. If $\Delta E = 20$ kilocalories, $K_{1597^o} = 130$; if $\Delta E = 40$ kilocalories, $K_{1597^o} = 0.21$. 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:

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

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

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

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, $E_2 \geq \Delta E - 7$ kilocalories. At 1597^0 K, $Z \sim 3.5\times10^{11}$, 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

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

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

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

and

$$\mathrm{OH} + \mathrm{H_2} \xrightarrow{k_{1'}} \mathrm{H_2O} + \mathrm{H} \qquad \text{(I')}$$

Finally, hydroxyl radicals are regenerated through the step

$$\mathrm{H} + \mathrm{O_2} \xrightarrow{k_{2'}} \mathrm{OH} + \mathrm{O} \qquad \text{(II')}$$

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:

$$\frac{dC_O}{dt} = -(\nu_{3'} + \nu_5)C_O + \nu_{2'}C_H \qquad (29)$$

$$\frac{dC_{OH}}{dt} = (\nu_{3'} + 2\nu_5)C_O - (\nu_{1'} + \nu_6)C_{OH} + \nu_{2'}C_H \qquad (30)$$

and

$$\frac{dC_H}{dt} = \nu_{3'}C_O + (\nu_{1'} + \nu_6)C_{OH} - \nu_{2'}C_H \qquad (31)$$

Here once again a shorthand notation has been introduced 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,

$$C_O \equiv [O] \qquad (32)$$

$$C_{OH} \equiv [OH] + \frac{i}{\nu_{1'} + \nu_6} \qquad (33)$$

and

$$C_H \equiv [H] + \frac{i}{\nu_{2'}} \tag{34}$$

(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 φ:

$$\varphi^3 + (\nu_{1'} + \nu_{2'} + \nu_{3'} + \nu_5 + \nu_6)\varphi^2 + \left[\nu_{2'}\nu_5 + (\nu_{3'} + \nu_5)(\nu_{1'} + \nu_6)\right]\varphi - 2\nu_{2'}(\nu_{3'} + \nu_5)(\nu_{1'} + \nu_6) = 0 \tag{35}$$

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 equation (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 ν_5 are also small. Consequently,

$$\varphi_1 \cong -\varphi_2 \cong \left[\frac{2\nu_{2'}(\nu_{3'} + \nu_5)(\nu_{1'} + \nu_6)}{\nu_{1'} + \nu_{2'} + \nu_{3'} + \nu_5 + \nu_6}\right]^{1/2}$$

$$= \left[\frac{2k_{2'}[O_2]\Big(k_{3'}[H_2] + k_5[H_2O]\Big)\Big(k_{1'}[H_2] + k_6[CO]\Big)}{(k_{1'} + k_{3'})[H_2] + k_5[H_2O] + k_{2'}[O_2] + k_6[CO]}\right]^{1/2} \equiv \lambda \tag{36}$$

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

$$\varphi_3 \cong -(\nu_{1'} + \nu_{2'} + \nu_{3'} + \nu_5 + \nu_6) \tag{37}$$

The coefficients $A_{OH,1}$, $A_{OH,2}$, and $A_{OH,3}$ are found after considerable algebra (and neglecting $\nu_{3'}$ and ν_5 relative to φ_1, φ_2, and φ_3)

$$A_{OH,1} \cong \frac{1}{2}\,\frac{\nu_{2'} + \lambda}{\nu_{2'}}\,\frac{i}{\nu_{1'} + \nu_6} \tag{38}$$

$$A_{OH,2} \cong \frac{1}{2} \frac{\nu_{2'} - \lambda}{\nu_{2'}} \frac{i}{\nu_{1'} + \nu_6} \tag{39}$$

and

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

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_2 concentration with time is governed by

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

which can be integrated to give

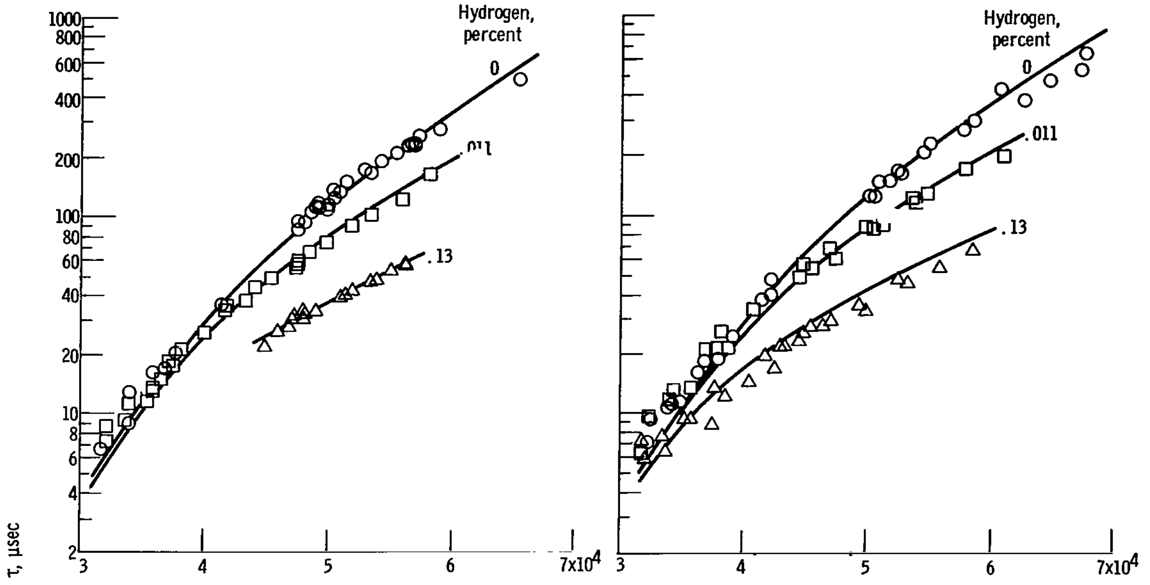
$$\frac{[CO_2]}{i} = \frac{\nu_6}{\nu_{1'} + \nu_6} \left[\frac{\sinh(\lambda t)}{\lambda} + \frac{\cosh(\lambda t) - 1}{\nu_{2'}} \right] + \frac{\nu_{1'} t}{\nu_{1'} + \nu_6} \tag{43}$$

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

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

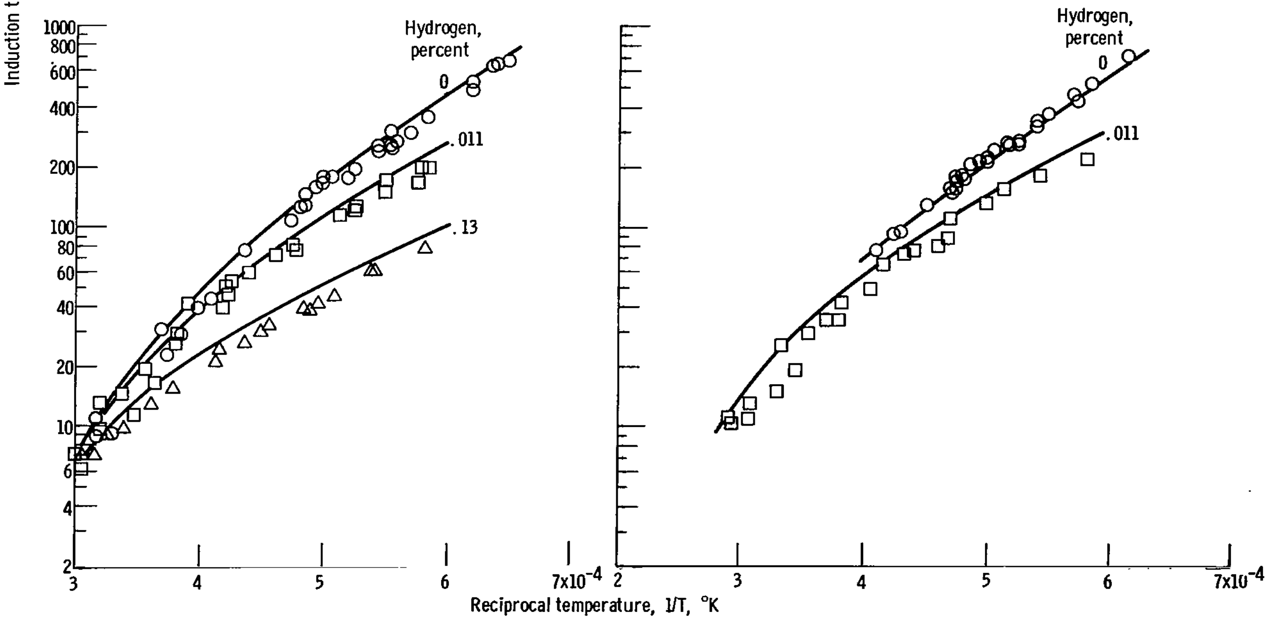
which explains the exponential growth of concentration with time shown in figure 1(b). Once again, λ is determined by the slope of the line. Furthermore, the initiation rate can be determined by extrapolating to an intercept, since $\nu_{2'} = k_{2'}[O_2]$ is known from studies of the hydrogen-oxygen reaction; in any event, $\nu_{2'}^{-1}$ is small compared with λ^{-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 5×10^{-4}. Thus, induction times τ can be obtained by solution of the transcendental equation



(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.

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.)

$$\frac{(\nu_{1'} + \nu_6)}{\nu_6} \frac{\lambda x_{CO_2, crit}}{k_i x_{CO} x_{O_2}} \frac{RT}{P} = \sinh(\lambda\tau) + \frac{\lambda}{\nu_{2'}} \left[\cosh(\lambda\tau) - 1\right] + \frac{\nu_{1'}}{\nu_6} (\lambda\tau) \tag{45}$$

From equation (36), it follows that λ 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 $\lambda\tau$ 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 $\sinh(\lambda t) \rightarrow \lambda t$, $\cosh(\lambda t) \rightarrow 1$, and equation (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 figure 2, the experimental induction periods of Myers, Sulzmann, and Bartle (ref. 5) are compared with values calculated from equation (45) by assuming that $x_{CO_2, crit} = 5\times10^{-4}$. The rate constant for the initiation reaction has been taken as

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

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

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

which Sulzmann, et al. (ref. 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 (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 1.5×10^{-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 $2OH \rightarrow H_2O + O$ 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 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 H and 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 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 λ 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

$$\ln \frac{[H_2O]_O}{[H_2O]} = \frac{k_5[CO_2]}{\lambda + \frac{\lambda^2}{\nu_{2'}}} \cong \frac{k_5}{\lambda}[CO_2] \qquad (50)$$

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 8×10^8 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

$$\frac{d[CO_2]}{dt} = k_i[CO][O_2] + \frac{2k_{2'}k_6[O_2][CO]}{k_{2'}[O_2] + k_6[CO]}[H_2O]_O \qquad (51)$$

where $[H_2O]_O$ 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 $k_5 = 1.5\times10^9$ liters per mole-second.

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

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

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 reference 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 equation (47). The rate of the reverse reaction k_{-i} can also be obtained by invoking detailed balancing and appropriate thermochemical data (ref. 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 8×10^{8} and 1.5×10^{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

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

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

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

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

with subsequent heat release due to

$$O + CO + M \rightarrow CO_2 + M$$

and

$$O + O + M \rightarrow O_2 + M$$

Lewis Research Center,
National Aeronautics and Space Administration,
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