

The Carbon Monoxide-Sensitized Decomposition of Hydrogen Peroxide

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Carbon monoxide accelerates the decomposition of H_2O_2 because the propagation reaction 31 competes with the termination reaction 15:



The accelerating effect of high concentrations of CO requires the introduction of reaction 41, which competes with the termination reaction 10:



A detailed analysis of the results gives $k_{15}/k_{31} = 21 \pm 2$, $k_{41}/k_{10}^{1/2} = (5.8 \pm 1.5) \times 10^{-4} (\text{mm Hg})^{-1/2} \text{ sec}^{-1/2} = 0.012 (\text{liter mole}^{-1} \text{ sec}^{-1})^{1/2}$ at 440°C .



Since $k_{15}/k_1 = 5.0$, $k_{31}/k_1 = 0.24$. When this value is combined with those of other workers, $k_{31}/k_1 = 0.0113 \exp(4768/RT)$. From the known value of k_1 , $k_{31} \approx 2.5 \times 10^8 \exp(-450/RT) \text{ liter mole}^{-1} \text{ sec}^{-1}$, cal units.

Introduction

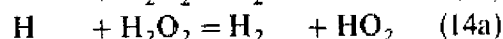
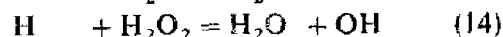
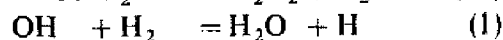
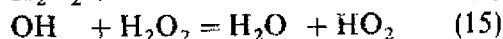
A previous paper [1] showed that, whereas H_2O_2 decomposes homogeneously in an inert atmosphere by a nonchain process involving reactions † 7, 15, and 10, a chain process occurs

in the presence of H_2 through reactions 1 and 14, the chain termination being predominantly through reaction 15 at low concentrations, and through reaction 14a at high H_2 concentrations.

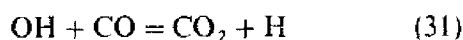
From a study of the accelerating effect of H_2 , the values of k_{15}/k_1 and k_{14a}/k_{14} can be obtained. The values showed no significant variation over the temperature range 440 – 500°C , the mean figures being 5.0 ± 1.0 and 0.143 ± 0.015 , respectively.

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† The nonconsecutive system of numbering adopted is consistent with that used in previous papers in which these reactions are involved.



Reaction 31 of OH radicals with CO is kinetically equivalent to reaction 1, so that a study of the sensitizing effect of CO on H_2O_2 decomposition should permit evaluation of k_{31}/k_1 .



Experimental Procedure

The main experimental procedures have already been described [1]. Use of initial rate measurements was essential because of the variation in the CO : H_2O_2 ratio as the reaction proceeded. The initial rates could not normally be obtained with sufficient accuracy from direct $x-t$ plots because of the pronounced curvature, and therefore they were calculated from appropriate function plots, as described in the previous paper [1]. A temperature of 440°C was used, so that the rate, even with pure CO, was not so high as to make measurement difficult.

The cylinder CO was found to contain traces (0.05–0.1%) of O_2 . Initial attempts to purify the CO by passage over platinized asbestos and copper at 300°C gave a gas free from O_2 but containing detectable amounts of H_2 , presumably formed from traces of H_2O by the water-gas reaction, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Although the amounts of H_2 were not kinetically significant, they were effectively removed by carefully drying the CO by passage through a trap at -80°C , and over P_2O_5 , before admission to the platinized asbestos and copper. A "carbosorb" trap was included to remove any CO_2 produced.

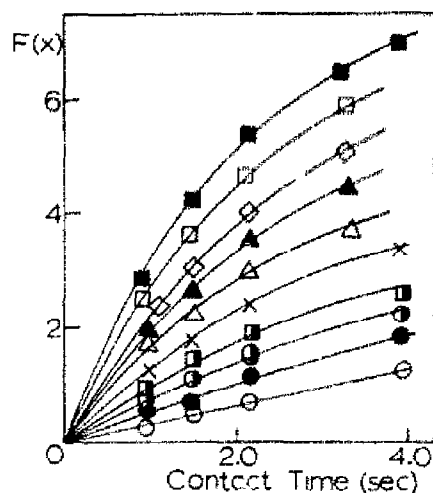


Figure 1. Function plots for decomposition of H_2O_2 at 440°C in presence of CO $n = 0.7$; $[\text{H}_2\text{O}_2] = 0.65$ mm Hg. Mole fraction CO as follows: ○, 0.017; ●, 0.05; ◐, 0.10; ◑, 0.20; ×, 0.30; △, 0.40; ▲, 0.50; ◇, 0.60; ◒, 0.75; ■, 1.0.

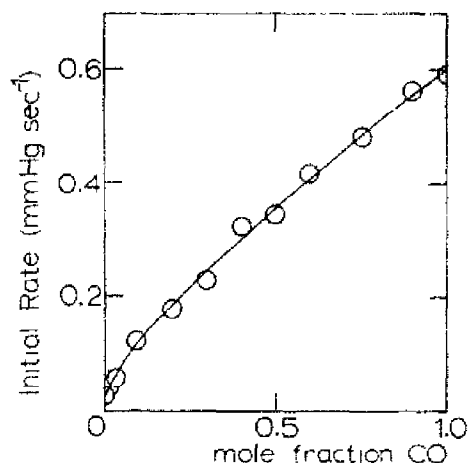


Figure 2. Variation of initial rate of decomposition of H_2O_2 at 440°C with mole fraction of CO. $[\text{H}_2\text{O}_2] = 0.65$ mm Hg. Total pressure = atmospheric.

Results

Figure 1 shows the $F(x)-t$ plots for CO- N_2 mixtures at atmospheric pressure with 0.62–0.66 mm Hg of H_2O_2 , where

$$F(x) = \frac{1/(a-x)^{n-1} - 1/a^{n-1}}{n-1}$$

with $a = 100$ and $x =$ percentage of homogeneous decomposition (corrections for the small

heterogeneous decomposition were made as described earlier [1]. A value of $n = 0.7$ was used for the results in Fig. 1, and this gave linear plots for the mixtures of low CO content, but curved relations for the high-CO mixtures. Initial rates were calculated using the initially linear portions of these functions, both for $n = 0.7$ and for other values of n , by means of the method described in Ref. 1. These values agreed closely, and the average is shown as a function of CO concentration in Fig. 2.

Discussion

A mechanism involving reactions 7, 31, 10, 14, 14a, and 15 gives a rate expression, R_{CO} , in the presence of CO as:

$$R_{CO} = \frac{-d[H_2O_2]}{dt} = 2k_7[H_2O_2][M'_{CO}] \left[\frac{1 + k_{15}[H_2O_2]/k_{31}[CO]}{\beta + k_{15}[H_2O_2]/k_{31}[CO]} \right] \quad (i)$$

where $\beta = k_{14a}/(k_{14} + k_{14a})$.

For very small additions of CO, reaction 15 is the dominant termination process, so that $k_{15}[H_2O_2]/k_{31}[CO] \gg \beta$, and i simplifies to:

$$R_{CO} = 2k_7[H_2O_2][M'_{CO}](1 + k_{31}[CO]/k_{15}[H_2O_2]) \quad (ii)$$

whereas, at high CO, reaction 14a becomes the dominant termination reaction, so that Eq. i simplifies to:

$$R_{CO} = 2k_7[H_2O_2][M'_{CO}](1 + k_{14}/k_{14a}) \quad (iii)$$

Equation ii predicts a linear increase in rate with added CO, whereas expression iii shows that the rate approaches a limiting value independent of CO addition at high CO concentrations. The latter prediction is based on the reasonable assumption that, in view of the similar collision diameters, $[M'_{CO}]$ is not affected by interchange of CO and N₂ (see later discussion). The initial linear increase in Fig. 2 is consistent with the prediction from Eq. ii

and gives a preliminary value for k_{15}/k_{31} of about 20. However, the rate increases continuously with increasing CO addition, contrary to the prediction from expression iii.

This discrepancy is also apparent if Eq. i is rearranged, using the rate R_N with pure N₂, into the form:

$$\frac{R_N}{R_{CO}} \left[1 + \frac{k_{15}[H_2O_2]}{k_{31}[CO]} \right] = \frac{k_{14a}}{k_{14} + k_{14a}} + \frac{k_{15}[H_2O_2]}{k_{31}[CO]} \quad (iv)$$

or

$$\frac{R_N}{R_{CO}} = \frac{k_{14a}}{k_{14} + k_{14a}} + \left(\frac{k_{15}[H_2O_2]}{k_{31}[CO]} \right) \left(1 - \frac{R_N}{R_{CO}} \right) \quad (v)$$

Figure 3 shows that the plot of R_N/R_{CO} against $([H_2O_2]/[CO])(1 - R_N/R_{CO})$ gives a good straight line except at high CO concentrations. The gradient gives the value of $k_{15}/k_{31} = 17.2$, while the intercept of 0.135 is in good agreement with an independent estimate of $k_{14a}/(k_{14} +$

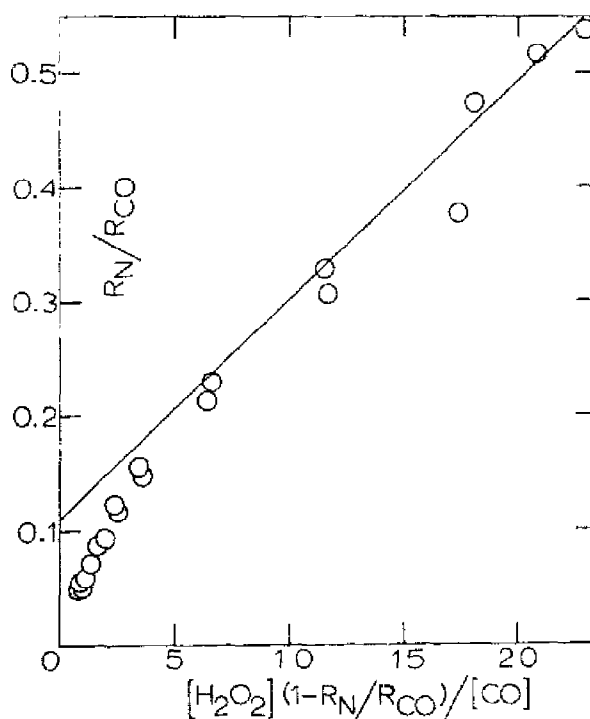


Figure 3. Plot of R_N/R_{CO} against $[H_2O_2](1 - R_N/R_{CO})/[CO]$ at 440°C.

$k_{14a}) = 0.125 \pm 0.015$ at 440–500°C from studies of the H_2 - H_2O_2 system [1].

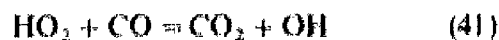
To account for the discrepancy at high CO concentrations, some factor which increases the rate of decomposition at high CO must be found. Since the reaction $HO_2 + H_2 = H_2O_2 + H$ played a small part in the H_2 - H_2O_2 system at high H_2 concentrations [1], and since

$$\frac{-d[H_2O_2]}{dt} = 2k_7[H_2O_2][M'_{CO}] \left[1 + \frac{k_{41}[CO]}{(k_{10}k_7[H_2O_2][M'_{CO}])^{1/2}} \right] \left[\frac{1 + k_{15}[H_2O_2]/k_{31}[CO]}{\beta + k_{15}[H_2O_2]/k_{31}[CO]} \right]$$

To test this expression, a computer program was written giving the rate of reaction for any values of the parameters k_7 , $k_{14a}/(k_{14} + k_{14a})$, k_{15}/k_{31} , and $k_{41}/k_{10}^{1/2}$. The value of k_7 adopted in studies of the H_2 - H_2O_2 system [1] was used, together with the value $k_{14a}/(k_{14} + k_{14a}) = 0.125$ obtained in those studies. For any pair of values of k_{15}/k_{31} , $k_{41}/k_{10}^{1/2}$, the calculated and observed rates were compared for some 15 mixtures and the rms deviation obtained. An optimization program adjusted the values until the rms deviation was a minimum (5.3%) with $k_{15}/k_{31} = 21.2$, $k_{41}/k_{10}^{1/2} = 5.8 \times 10^{-4}$ (mm Hg) $^{-1/2}$ sec $^{-1/2}$; with the absolute deviation a minimum, the corresponding values were 21.5, 5.9×10^{-4} .

The mean value for k_{15}/k_{31} of 21.3 ± 1 may be combined with values of k_{15}/k_1 to obtain k_{31}/k_1 . Studies of the H_2 - H_2O_2 system give a mean value for $k_{15}/k_1 = 5.0 \pm 1.0$ between 440–500°C. When this value is used, k_{31}/k_1 at 440°C is 0.24 ± 0.05 . By following the procedure of Baldwin and Dixon-Lewis [3], this value may be combined (Fig. 4) with lower-temperature estimates by Ung and Back [4], by Dixon-Lewis, Wilson, and Westenberg [5], and by Greiner [6], and with higher-temperature estimates by Fenimore [7] and by Dixon-Lewis, Sutton, and Williams [8], to give $k_{31}/k_1 = 0.0113 \exp[(4700 \pm 400)/RT]$. This is effectively identical to the value of $0.0135 \exp(4600/RT)$ given by Dixon-Lewis, Wilson, and Westenberg [5]. From the best available value [9] of $k_1 = 2.19 \times 10^{10} \exp(-5150/RT)$, $k_{31} = 2.5 \times$

the reaction of HO_2 with CO is some ten times faster [2] at 500°C, reaction 41 is the obvious suggestion:



Addition of this to reactions 7, 10, 31, 14, 14a, and 15 gives the rate expression:

$10^8 \exp(-450/RT)$. This differs from the recently recommended [10] figure* of $5.6 \times 10^8 \exp(-1080/RT)$, but the difference is within the estimated accuracy of either figure.

The value of $k_{41}/k_{10}^{1/2} = 5.8 \times 10^{-4}$ (mm Hg) $^{-1/2}$ sec $^{-1/2}$ at 440°C may be combined with a provisional estimate [2] of $2.1 \pm 0.2 \times 10^{-3}$ (mm Hg) $^{-1/2}$ sec $^{-1/2}$ from studies of the $H_2 + CO + O_2$ system at 500°C to give $(E_{41} - \frac{1}{2}E_{10}) = 23 \pm 5$ kcal mole $^{-1}$, $A_{41}/A_{10}^{1/2} = 6.46 \times 10^3$ (mm Hg sec) $^{-1/2} = 1.36 \times 10^6$ (liter mole $^{-1}$ sec $^{-1}$) $^{1/2}$. If it is assumed [11] that $E_{10} = 0$, $A_{10} = 1.8 \times 10^9$, then $A_{41} = 5.8 \times 10^{10}$ liter mole $^{-1}$ sec $^{-1}$.

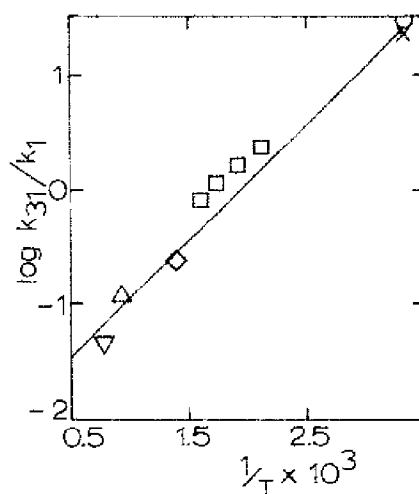


Figure 4. Plot of $\log k_{31}/k_1$ against $1/T$: \circ , Dixon-Lewis, Wilson, and Westenberg [5]; \times , Greiner [6]; \square , Ung and Back [4]; \diamond , present work; \triangle , Dixon-Lewis, Sutton, and Williams [8]; ∇ , Fenimore and Jones [7].

* The value in Ref. 10 has been corrected in Ref. 9.

The values for k_{15}/k_{31} and $k_{41}/k_{10}^{1/2}$ obtained from the optimization program depend on the relative efficiencies assumed for CO and N₂ in reaction 7. Calculations with the efficiency of CO taken as 0.7 and 1.3 times that of N₂ show that the optimum value of k_{15}/k_{31} changes only from 22.5 to 20.5, but that $k_{41}/k_{10}^{1/2}$ changes from 7.7×10^{-4} to 4.4×10^{-4} (mm Hg)^{-1/2} sec^{-1/2}. These changes cause ± 5 kcal mole⁻¹ change in $(E_{41} - \frac{1}{2}E_{10})$. The relative efficiencies of N₂, O₂, He, and Ar appear to be the same [12-14] in reactions 4 and 7, and the H₂ + H₂O₂ system has been satisfactorily interpreted on the assumption that this is true for H₂ also.



The earliest studies [15] of the second limit of the H₂ + CO + O₂ system suggested that CO behaved as an inert gas except at low H₂:CO ratios (<0.1), when CO inhibited the limit through the reaction O + CO → chain termination, which competed with reaction 3. This view seemed confirmed by later studies [16] in KCl-coated vessels, and it would thus appear to be a simple matter to evaluate the relative efficiency of CO from second-limit studies. More recent work [17], however, has suggested three complicating factors:

(a) In KCl-coated vessels, a detailed study [17] over a range of mixture composition suggests that in the presence of CO the surface properties of the vessel change so that there is a significant contribution from quadratic branching, which is otherwise effectively absent. This can cause a rise in the limit at low mole fractions of O₂ when CO replaces N₂.

(b) In CsCl-coated vessels [17, 18], addition of small amounts (up to 5%) of CO causes a sharp drop (up to 10 mm Hg) in the limit, the magnitude of this drop apparently increasing as the O₂ mole fraction is decreased. Although this suggests the occurrence of the reaction H + CO + M = HCO + M, followed by HCO +

O₂ = HO₂ + CO, the decrease in limit at high CO concentrations is almost independent of the O₂ mole fraction and is more consistent with a third-body coefficient of 0.6-0.65 (H₂ = 1) for CO in reaction 4. On present evidence, it is difficult to be certain whether this explanation in terms of homogeneous processes is correct, or whether, as in KCl-coated vessels, there is a change in the surface properties.

(c) The accelerating effect of CO on the slow reaction between H₂ + O₂ in aged boric-acid-coated vessels [2] can be explained only by a contribution from reaction 41, which may therefore play a part, though less important, at the second limit.

A more detailed evaluation of second-limit measurements on the H₂ + CO + O₂ system is thus required before the relative efficiency of CO in reaction 4 can be established with certainty. A lower efficiency than that of N₂ is unlikely, since the limit is never raised by interchange of CO and N₂, except in situation (a) above. An efficiency relative to nitrogen of greater than 1.5 seems unlikely, since this would require no inhibition by the reaction H + CO + M in (b) above. On present evidence, the best assumption is that CO and N₂ have the same relative efficiencies in reaction 7.

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