Lawrence Berkeley National Laboratory
Recent Work

Title
PSEUDO FIRST-ORDER REACTION RATE CONSTANT FOR THE FORMATION OF HYDROMETHYLHYDROPEROXIDE FROM FORMALDEHYDE AND HYDROGEN PEROXIDE

Permalink
https://escholarship.org/uc/item/1c46260t

Authors
Benner, W.H.
Bizjak, M.

Publication Date
1987-12-01

Lawrence Berkeley Laboratory
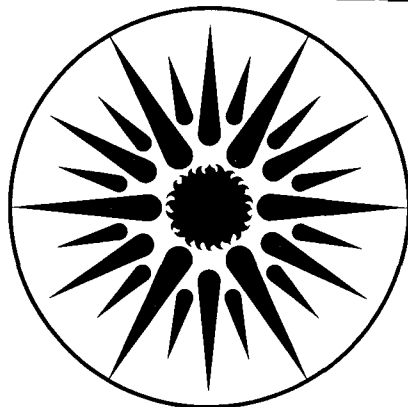## UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

Pseudo First-order Reaction Rate Constant for the Formation of Hydromethylhydroperoxide from Formaldehyde and Hydrogen Peroxide

W.H. Benner and M. Bizjak

December 1987

APPLIED SCIENCE DIVISION

DISCLAIMER

PSEUDO FIRST-ORDER REACTION RATE CONSTANT FOR THE FORMATION OF HYDROMETHYLHYDROPEROXIDE FROM FORMALDEHYDE AND HYDROGEN PEROXIDE*

W.H. Benner† and Mirko Bizjak‡

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

H_2O_2 (0.5-4.0 × 10^{-5} M) and H_2CO (0.0075-0.1 M) were reacted in aqueous solutions buffered at pH between 4.0 and 6.9. The reaction rate constant (k) in

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2][H_2CO]/[H^+]$$

was determined to be 6.47 × 10^{-8} sec^{-1} at 22°C. With this rate expression, estimates of the stability of each reactant in fog and cloud droplets were made.
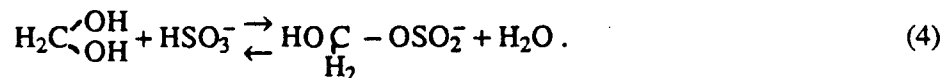
---

†   Author to be contacted.

‡   Current address: Chemical Institute Boris Kidric, Ljubljana, Yugoslavia

Introduction

Formaldehyde and hydrogen peroxide are two of many compounds which competitively influence the oxidation of SO_2 in tropospheric droplets. H_2O_2 and S(IV) react to form sulfate (Martin, 1984) by Equation (1); but if H_2CO is also present, it competes with H_2O_2 to form hydroxymethanesulfonate ion (Munger et al., 1986) as shown in Equations (3) and (4):
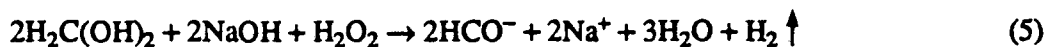
$$- \frac{d[S(IV)]}{dt} = k \cdot [H_2O_2][S(IV)], \text{ where} \tag{1}$$

$$[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^=] \tag{2}$$

$$H_2CO + H_2O \underset{\leftarrow}{\overset{\rightarrow}{}} H_2C \overset{OH}{\underset{OH}{}} \tag{3}$$

$$H_2C \overset{OH}{\underset{OH}{}} + HSO_3^- \underset{\leftarrow}{\overset{\rightarrow}{}} HO \underset{H_2}{C} - OSO_2^- + H_2O . \tag{4}$$

H_2CO in dilute aqueous solutions is highly hydrated (Equation (3)) (Grayson, 1980); Equation (4) was written with the hydrated specie (methylene glycol). The sulfur in hydroxymethanesulfonate ion is not susceptible to attack by H_2O_2 (Richards et al., 1983), and thus the presence of H_2CO in droplets containing S(IV) and H_2O_2 serves to decrease the rate of S(IV) oxidation by decreasing [S(IV)] in Equation (2).

Although the origin of formate ion in droplets is not well documented and is possibly related to the oxidation of H_2CO, in general H_2CO is considered to be very stable and available for reaction with S(IV). Any reaction in droplets involving H_2CO would of course be important because it would indirectly influence S(IV) chemistry as well. A possible reaction that could remove H_2CO from solution is a reaction with H_2O_2. H_2O_2 and H_2CO can react in several ways (Equations (5), (6)), but in dilute acid solution, without catalysts, Equation (6) (Kolthoff and Elving, 1966) greatly predominates with hydroxymethylhydroperoxide (HMP) as a product.

$$2H_2C(OH)_2 + 2NaOH + H_2O_2 \rightarrow 2HCO^- + 2Na^+ + 3H_2O + H_2 \uparrow \tag{5}$$

$$H_2C{\overset{OH}{\underset{OH}{\diagdown}}} + H_2O_2 \overset{k_6}{\underset{k_6}{\underset{\leftarrow}{\rightarrow}}} HO\underset{H_2}{C} - OOH + H_2O \qquad (6)$$
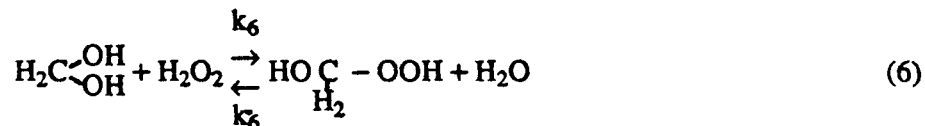
This reaction has been studied by several investigators (Dunicz et al., 1951; Marklund, 1971) and was reported to be pH dependent, but these studies were not validated at the low concentrations of H_2CO and H_2O_2 found in tropospheric droplets. The available data did not allow for a kinetic expression to be developed which included acid or base catalysis so that the importance of this reaction in tropospheric droplets could be evaluated.

Two problems complicate the determination of the rate expression for the reaction of H_2CO and H_2O_2. In aqueous solution H_2CO is not easily distinguished from methylene glycol and HMP also reacts with H_2O_2 to form the dihydroperoxide as in Equation (7).

$$H_2O_2 + HO - \underset{H_2}{C} - OOH \overset{\rightarrow}{\leftarrow} HOO - \underset{H_2}{C} - OOH + H_2O \qquad (7)$$
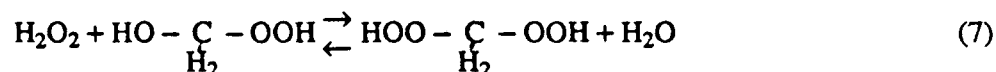
To evaluate the importance of Equation (6) in tropospheric droplets, we chose only to evaluate k_6 under pseudo-first order reaction conditions at room temperature in which $[H_2CO] \gg [H_2O_2]$.

Experimental

H_2O_2 was obtained as a 30% stabilized aqueous solution. Dilutions of this reagent were standardized iodometrically using molybdenate ion to catalyze the reaction between I_3^- and H_2O_2 in acid solution. An approximately 1 M aqueous H_2CO solution was prepared by dissolving paraformaldehyde in water at 35°C. Whatever paraformaldehyde did not dissolve in about 3 days in solution at 35°C was removed by filtration. The filtered solution was kept at 35°C for several weeks and was assumed to be adequately depolymerized because it did not turn cloudy during that time. The H_2CO solution was standardized by titrating residual NaOH when Reaction (5) was conducted with excess NaOH. The concentration of H_2O_2 in a reaction mixture containing buffer, H_2O_2, and H_2CO was determined using a flow injection analysis technique (Madsen and Kromis, 1984). This technique was slightly modified by increasing the buffer

strength of the reagent to 0.128 F so that the reaction mixture buffer (.01 F) did not influence the rate of color development. Reaction mixture pH was controlled with phosphate (pH = 5.5-6.9) or acetate (pH = 4.0-4.9) buffers and actual reaction mixture pH was determined with a properly standardized combination glass electrode. HMP was prepared according to Marklund, 1971. Catalyase was added to an appropriately diluted and pH = 7 buffered solution of HMP to remove residual H_2O_2 and was then quickly analyzed by the H_2O_2 method to demonstrate that HMP is not detected by this H_2O_2 method.

Kinetic data were collected by mixing buffered solutions of H_2CO and H_2O_2 and then at selected times removing aliquots and analyzing for H_2O_2. Both $[H_2CO]_o$ and $[H_2O_2]_o$ were varied, but $[H_2CO]_o$ was always much greater than $[H_2O_2]_o$ so that pseudo first-order kinetics were maintained. When the experimental plot of $[H_2O_2]$ vs. time began to curve, the analysis was stopped and $(\frac{d[H_2O_2]}{dt})_{t=0}$ was calculated by extrapolating the $[H_2O_2]$ vs. time data to $t = 0$.

Results

Eighty-one experiments were conducted in which $[H_2O_2]$ was followed vs. time for a variety of pH's between 4.0 and 6.9, $[H_2CO]_o$ between 7.5×10^{-3} M and 0.1 M, and $[H_2O_2]_o$ between 5×10^{-6} M and 4×10^{-5} M. Typical data are shown in Fig. 1 where 5 different experiments are plotted, each having $[H_2O_2]_o = 2 \times 10^{-5}$ M and $[H_2CO]_o$ between 5×10^{-3} M and 2.5×10^{-2} M for pH = 6.4. If the reaction is first order with respect to H_2CO, then a plot of $(\frac{-d[H_2O_2]}{dt})_{t=0}$ vs. $[H_2CO]_o$ for constant $[H_2O_2]_o$ should be a straight line. This is shown in Fig. 2 and confirms first order kinetics with respect to H_2CO.

Data similar to those presented in Fig. 1 were obtained from additional experiments in which $[H_2O_2]_o$ was varied in solutions also of pH = 6.4. If the reaction is first order with respect to H_2O_2, then a plot of $(\frac{-d[H_2O_2]}{dt})_{t=0}$ vs. $[H_2O_2]_o$ for constant $[H_2CO]$ should also produce a straight line. The straight line in Fig. 3 confirms that the reaction is also first order with respect to H_2O_2.

The effect of pH on the reaction can be seen in Fig. 4 where nearly constant starting concentrations of H_2O_2 and H_2CO were reacted at 6 different pH's. The reaction proceeds faster as the pH is increased, suggesting base catalysis. Since the reactions were conducted in acid solution we chose to describe the effect in terms of $1/[H^+]$ as shown in Equation (8).

$$\left(\frac{-d[H_2O_2]}{dt}\right) = k_8[H_2CO]\,[H_2O_2]\,/[H^+] \qquad (8)$$

When all $\left(\dfrac{-d[H_2O_2]}{dt}\right)_{t=0}$ data were used to prepare a plot of $\left(\dfrac{-d[H_2O_2]}{dt}\right)_{t=0}$ vs. $[H_2CO]\,[H_2O_2]\,/[H^+]$, the data could be approximated by a straight line ($r^2 = 0.98$) as shown in Fig. 5. The slope of the line in Fig. 5 is equal to k_8 and has a value of 6.47×10^{-8} sec^{-1} at room temperature ($22 \pm 2°C$). The reaction is general acid catalyzed because examination of the data showed no effects of shifting from phosphate to acetate buffer.

Discussion

If the reaction rate constant (k_8) determined here is compared to previous work (Marklund, 1971) that did not take into account the effect of acid catalysis in the rate expression, comparison of reaction rates can still be made at a selected published pH value. Marklund reported that k_m in the expression

$$\text{rate} = -k_m[H_2O_2][H_2CO] \text{ at pH} = 5.49$$

was $3.12 \times 10^{-2} M^{-1} \cdot sec^{-1}$, and thus rate $= 3.12 \times 10^{-10} M \cdot sec^{-1}$ when $[H_2O_2] = [H_2CO] = 10^{-4} M$. Using k_8 for identical pH, H_2O_2, and H_2CO concentrations, we calculate that the rate of loss of H_2O_2 using our rate expression (Equation 8) would be $2.00 \times 10^{-10} M \cdot sec^{-1}$. These two rates compare favorably at this pH.

In a study of the oxidation of S(IV) by H_2O_2 in rainwater samples (Lee et al., 1986), the authors reported that rainwater H_2O_2 concentrations ranged from 0.02-100 μM for samples collected on Long Island, New York. Analysis of fogwater samples collected in the San Joaquin Valley in central California were reported to contain total H_2CO (H_2CO + hydroxymethanesulfonate ion) between 32 and 238 μM (Munger et al., 1986). If we take the highest reported concentrations of H_2O_2 and H_2CO from these

studies and assume that they react in a CO_2 buffered droplet at pH = 5.6, then the rate of loss of H_2O_2 can be calculated using Equation (8) and $k_8 = 6.47 \times 10^{-8} sec^{-1}$. The rate of loss of H_2O_2 is $6.13 \times 10^{-10} M \cdot sec^{-1}$. In the same fogwater study (Munger *et al.*, 1986), fogwater also contained 9-350 μM of S(IV). If we use the reaction rate law of Lee *et al.* (1986) for the H_2O_2 + S(IV) reaction, we can calculate that the rate of H_2O_2 loss in our hypothetical droplet by reaction with 230 μM S(IV) is $8.4 \times 10^{-6} M \cdot sec^{-1}$. The result of these comparisons for the competitive reaction of H_2O_2 with H_2CO or S(IV) shows that the reaction of S(IV) with H_2O_2 will dominate because it is 10^4 faster than the reaction between H_2O_2 and H_2CO. This means that the removal of H_2CO by reaction with H_2O_2 is probably negligible in atmospheric droplets.

Conclusions

A colorimetric technique was used to determine H_2O_2 concentrations in the presence of hydroxy-methanehydroperoxide and formaldehyde. The reaction between formaldehyde and hydrogen peroxide was shown to be first order with respect to each and was sensitive to pH. For pH values between 4.0 and 6.9, the following rate expression was obtained,

$$\left(\frac{-d[H_2O_2]}{dt} \right) = k_8[H_2O_2] \, [H_2CO] \, /[H^+],$$

using pseudo-first order reaction conditions in which $[H_2CO] \gg [H_2O_2]$. The reaction rate constant is $6.47 \times 10^{-8} sec^{-1}$. The influence of H^+ was found to be general acid catalyzed. When applied to reactions in atmospheric droplets, the reaction rate at concentrations of formaldehyde and hydrogen peroxide encountered in atmospheric droplets is relatively slow compared to the reaction between dissolved SO_2 and hydrogen peroxide. This indicates that the decomposition of formaldehyde in droplets is slow.

Acknowledgments

References

Dunicz B.L., Perrin D.D. and Style D.W.G. (1951) The reaction between aldehydes and hydrogen peroxide in acid solution; Part 1 - Formaldehyde. *Trans. Faraday Soc.* **47**, 1210-1215.

Grayson M., exec. ed. (1980) *Encyclopaedia of Chemical Technology*, Vol. II, 3d ed. John Wiley, New York.

Kolthoff I.M. and Elving P.J., eds. (1966) *Treatise on Analytical Chemistry*, Part 2, Vol. 13. John Wiley, New York, p. 192.

Lee Y.-N., Shen J., Klotz P.J., Schwartz S.E. and Newman L. (1986) Kinetics of hydrogen peroxide-sulfur (IV) reaction in rainwater collected at a northeastern U.S. site. *J. Geophys. Res.* **91**, 13264-13274.

Madsen B.C. and Kromis M.S. (1984) Flow injection and photometric determination of hydrogen peroxide in rainwater with N-ethyl-N-(sulfopropyl)aniline sodium salt. *Anal. Chem.* **56**, 2849-2850.

Marklund S. (1971) The simultaneous determination of bis(hydroxymethyl)-peroxide (BHMP), hydroxymethylhydroperoxide (HMP), and H_2O_2 with titanium (IV). Equilibria between the peroxides and the stabilities of HMP and BHMP at physiological conditions. *Acta Chem. Scand.* **25**, 3517-3531.

Martin L.R. (1984) Kinetic studies of sulfite oxidation aqueous solution. In SO_2, *NO, and* NO_2 *Oxidation Mechanisms: Atmospheric Considerations* (edited by J.G. Calvert). Butterworth, Boston.

Munger J.W., Tiller C. and Hoffmann M.R. (1986) Identification of hydroxymethanesulfonate in fog water. *Science* **231**, 247-249.

Richards L.W., Anderson J.A., Blumenthal D.L., McDonald J.A., Kok G.L. and Lazrus A.L. (1983) Hydrogen peroxide and sulfur (IV) in Los Angeles cloud water. *Atmospheric Environment* **17**, 911-914; also personal unpublished laboratory data.

Figure Captions

Fig. 1.   Absorbance, which is proportional to $[H_2O_2]$, versus time for various solutions of H_2O_2 and

H_2CO. $[H_2O_2]_o = 2 \times 10^{-5}$ M and each solution was buffered with phosphate at pH = 6.4.

Fig. 2.   Confirmation of reaction being first order with respect to H_2CO. $[H_2O_2]_o = 2 \times 10^{-5}$ M and pH

= 6.4 for all data points. The line has a slope of rate/$[H_2CO]$ and equals 2.58×10^{-6} sec^{-1} at

pH = 6.4 ($r^2 = .99$).

Fig. 3.   Confirmation of reaction being first order with respect to H_2O_2. $[H_2CO]_o = 10^{-2}$ M and pH =

6.4 for all data points. The line has a slope of rate/$[H_2O_2]$ and equals $1.39 \, x \, 10^{-3}$ sec^{-1} at pH =

6.4 ($r^2 = .99$).

Fig. 4.   The influence of solution pH on the rate of disappearance of H_2O_2. $[H_2CO]_o = 1.5 \times 10^{-2}$ M,

and $[H_2O_2]_o \approx 2 \times 10^{-5}$ M.

Fig. 5   Plot of rate of disappearance of H_2O_2 vs. $[H_2O_2][H_2CO]/[H^+]$ for the determination of k_8 (r^2
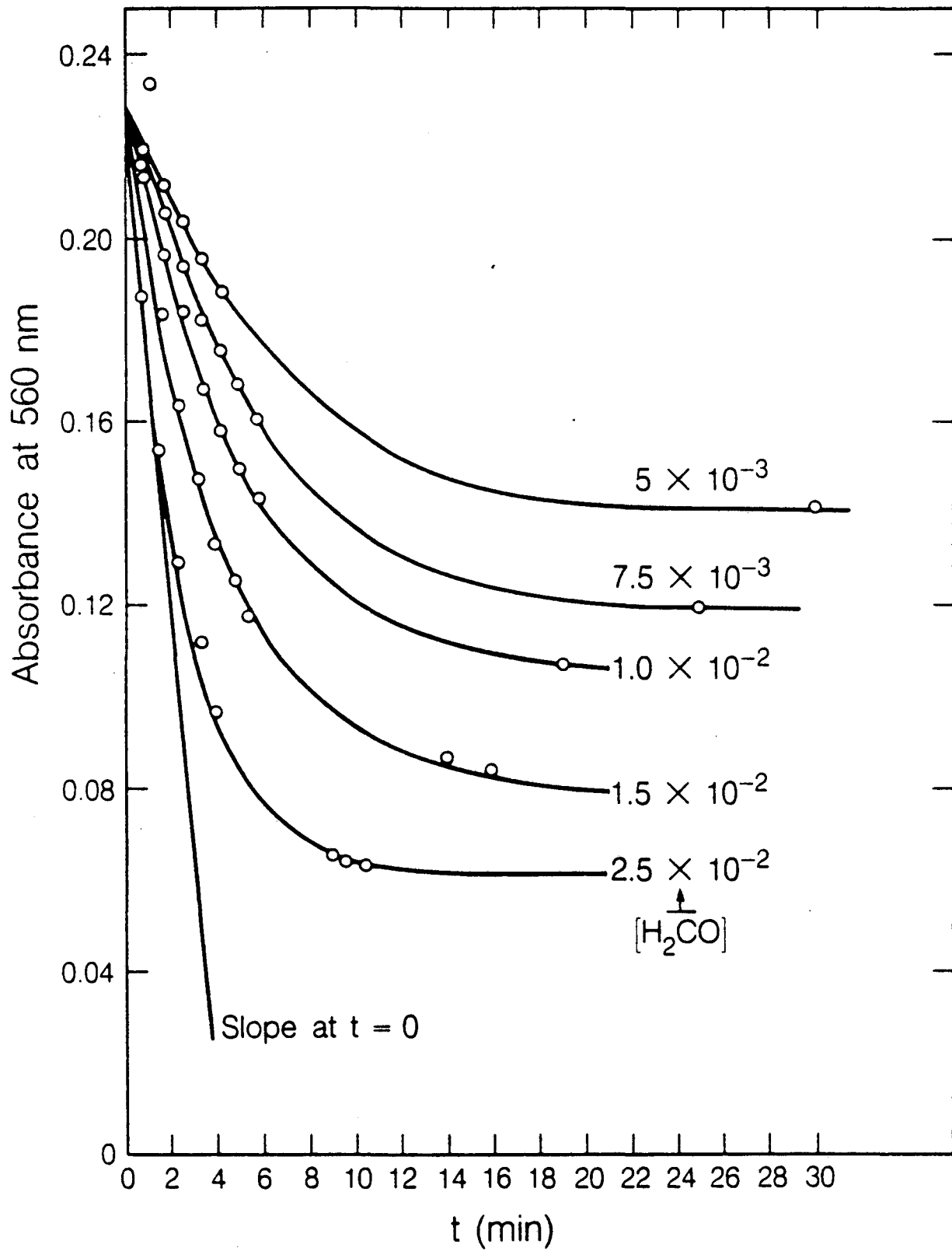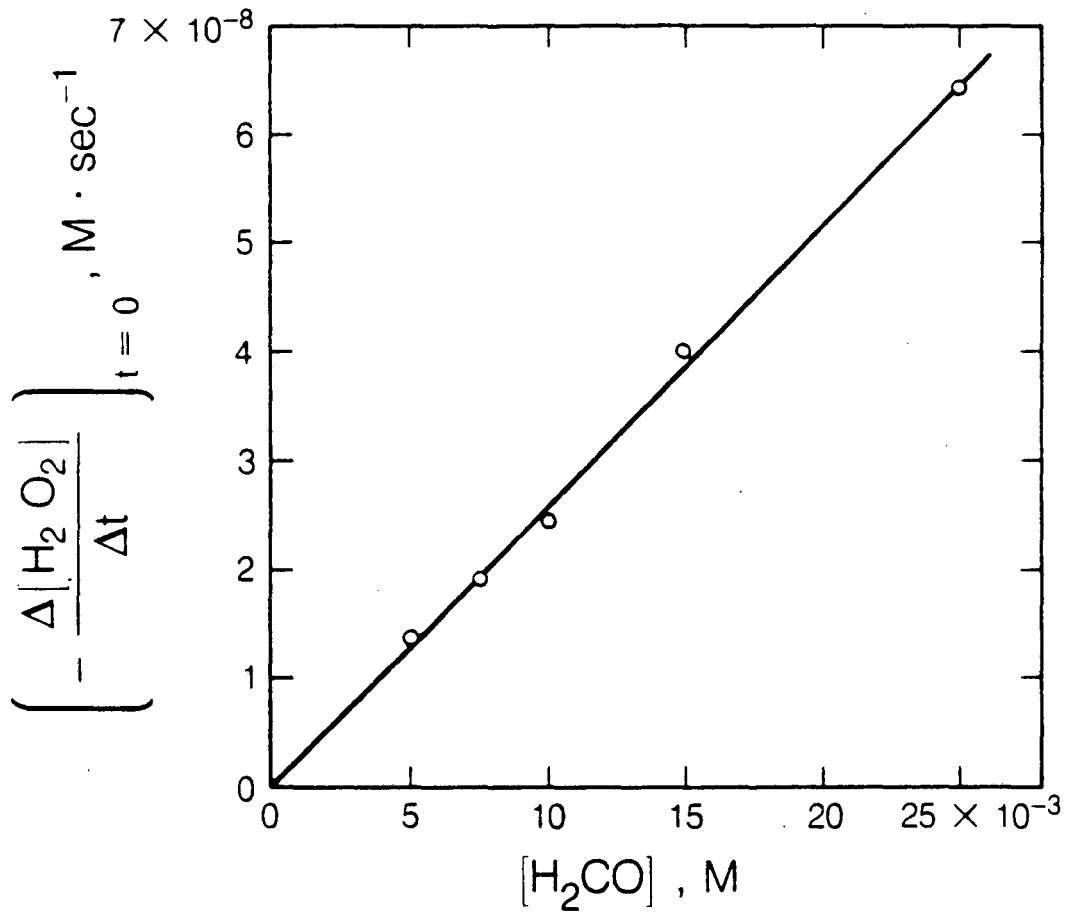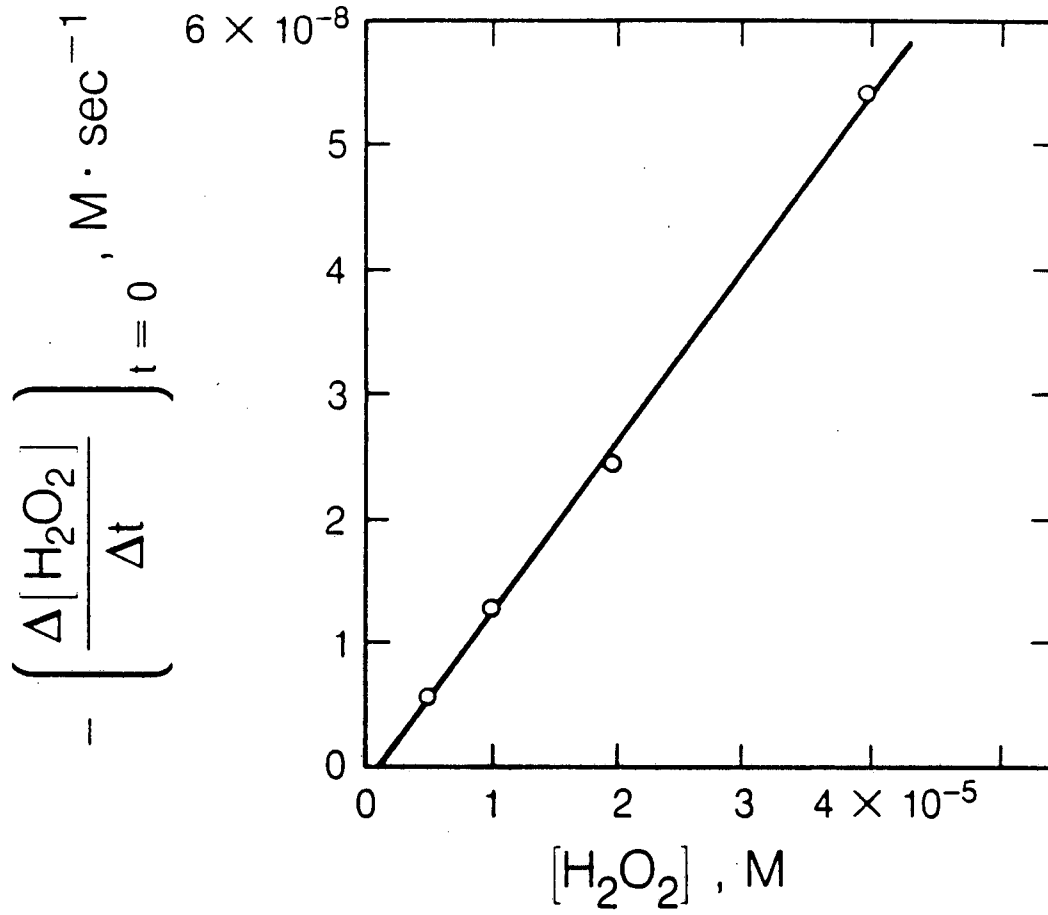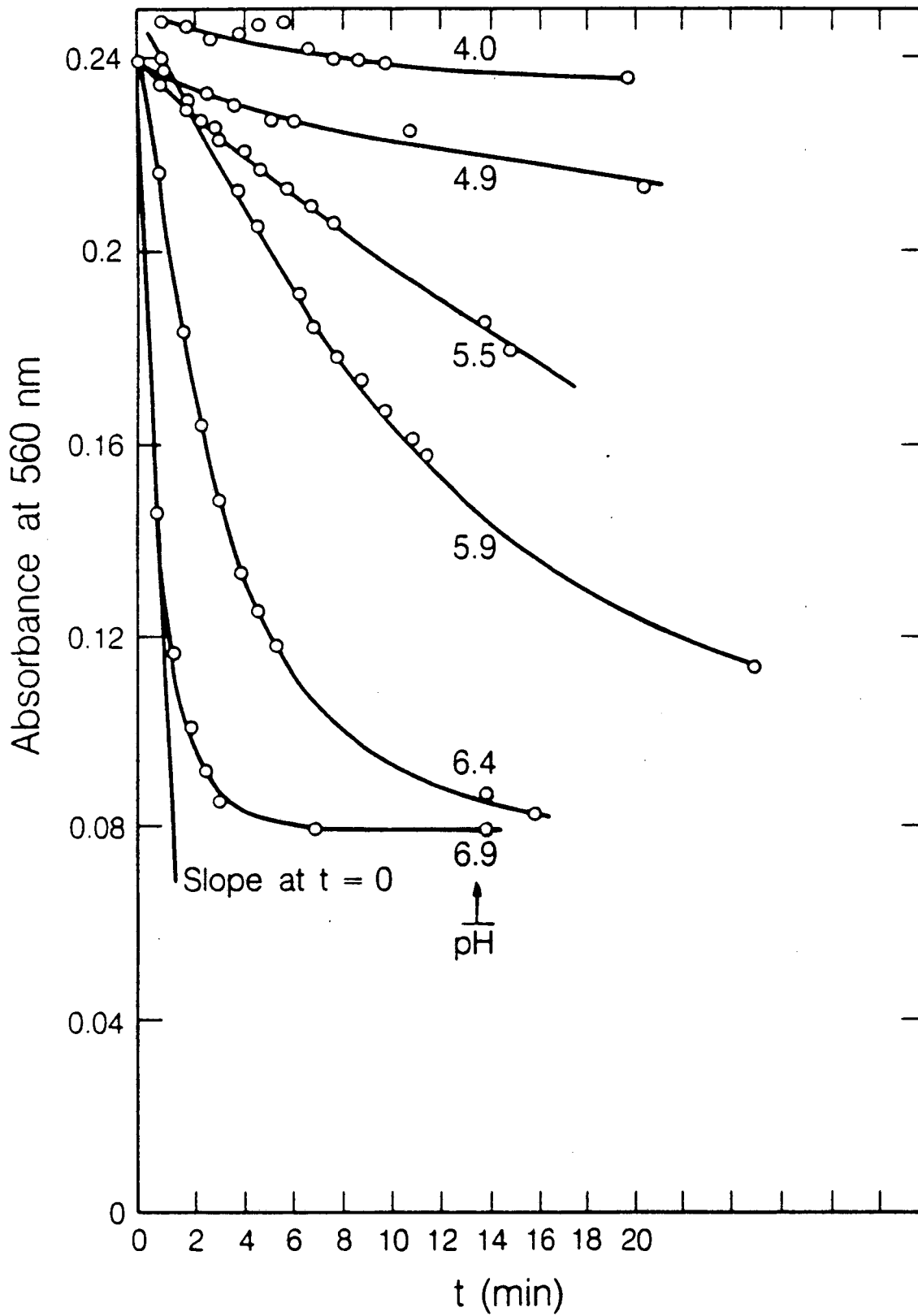
for the indicated line = 0.98).

XBL 8710-8166

Figure 1

The y-axis is labeled $\left(-\dfrac{\Delta[H_2O_2]}{\Delta t}\right)_{t=0}$, $M \cdot sec^{-1}$ with values from 0 to 7×10^{-8}.

The x-axis is labeled $[H_2CO]$, M with values from 0 to 25×10^{-3}.

XBL 8710-8167

Figure 2

6×10^{-8}

$-\left(\dfrac{\Delta\left[H_2O_2\right]}{\Delta t}\right)_{t=0}$, $M \cdot sec^{-1}$

5

4

3

2

1

0

0   1   2   3   4 × 10^{-5}

$\left[H_2O_2\right]$, M

XBL 8710-8169

Figure 3

Figure 4

Figure 5

XBL 8710-8168