# The Effect of Mass Transfer on Apparent Ascorbic Acid Autoxidation Kinetics

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Previous studies of copper-ion catalyzed ascorbic acid autoxidation have indicated zero-order, first-order, or Michaelis-Menten dependence of rate on ascorbic acid or copper concentrations and first- or half-order dependence on oxygen concentration. A simple mathematical model of gas-liquid mass transfer with liquid phase reaction accounts for the various behaviors. Use of an experimental technique that eliminates the mass transfer step shows that the oxidation rate dependence is first order in copper, half order in oxygen, and Michaelis-Menten in ascorbic acid concentrations.

## SCOPE

The reaction between ascorbic acid and oxygen in aqueous solution is catalyzed by copper ion. This reaction has been the subject of many studies because of its importance in food processing and its correspondence to an enzyme catalyzed reaction. There is, however, much disagreement about the dependence of reaction rate on ascorbic acid, copper, and oxygen concentrations (Barron et al., 1936; Dekker and Dickinson, 1940; Silverblatt et al., 1943; Weissberger and LuValle, 1944; Joslyn and Miller, 1949; Khan and Martell, 1967; Ogata et al., 1968; Hanaki, 1969; Shtamm et al., 1974; Skov and Vonderschmitt, 1975; Jameson and Blackburn, 1976). The majority of previous studies have been carried out by contacting gases containing oxygen with solutions of ascorbic acid and copper ion while measuring either the amount of ascorbic acid or the volume of oxygen consumed as the reaction proceeded. It was assumed that oxygen transfer is fast enough to maintain equilibrium between the two phases. Shtamm and Skurlatov (1974) suggest that one reason for discrepancies between sets of experimental results is that dissolved oxygen concentration fails to remain at its saturation level during reaction. The present study uses a mathematical model of the interaction between mass transfer and homogeneous chemical reaction to see if the wide range of reported reaction rates and apparent reaction orders can be explained. Reaction kinetics are studied using an experimental technique in which dissolved oxygen concentration is monitored in a system with no gas-liquid interface, thus eliminating the coupling of mass transfer and reaction.

## CONCLUSIONS AND SIGNIFICANCE

A mathematical model of simultaneous mass transfer and chemical reaction shows that interaction between the two processes can lead to observed kinetics that are much different from true reaction behavior. Not only reaction rate but also apparent reaction order with respect to the concentrations of species present can vary with changes in initial conditions. Reaction orders derived from initial rates can differ from orders obtained from changes of concentration with time.

Application of this model to ascorbic acid autoxidation shows that coupling of oxygen transfer with bulk reaction affects the reaction rate and apparent order with respect to oxygen, ascorbic acid, copper ion, and hydrogen ion concentrations. A wide variety of rate behaviors reported in the literature is used to choose a rate expression that best fits the observations when combined with an independent estimate of the mass transfer coefficient.

A study of the kinetics using an experimental procedure that eliminates the mass transfer step verifies the rate expression chosen by applying the model to literature data. This rate expression contains first-order dependence of rate on copper, Michaelis-Menten dependence on ascorbic acid, and half-order dependence on oxygen concentrations, indicating a chain reaction mechanism.

The work reported in this paper indicates that in gas-liquid reaction systems involving slow chemical reactions, the mass transfer interactive regime may be of considerable experimental importance in kinetic studies. The true kinetic regime, the most desirable region in which to perform experiments, and the mass transfer limited regime, the region in which one obtains no useful information concerning the reaction, have long been recognized. One often can avoid doing experiments in the mass transfer limited regime by increasing the stirrer speed or the gas flow rate. The mass transfer interactive regime, however, may sometimes not be avoided by these methods. This region is large, and a variety of behaviors different from the true reaction kinetics can be observed. The number of reported studies of ascorbic acid autoxidation that were carried out in this regime, even though stirrer speeds or gas flow rates were changed to avoid mass transfer limitations, indicates that disguised kinetics may be common and should be considered when other two-phase reactions are studied. Whenever possible, reaction kinetics should be studied in the absence of mass transfer. The kinetic expression can then be used in a model of simultaneous mass transfer and reaction to qualitatively predict behavior in an open system. Additional work needs to be done to see if mass transfer models that are more realistic than the one used in this study lead to predictions of system behavior that are quantitatively accurate.

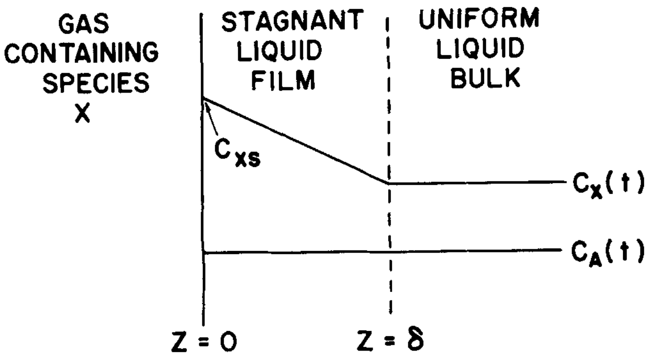

Fig. 1. Film model of mass transfer-reaction system.

The reaction between ascorbic acid and oxygen in water to produce dehydroascorbic acid is efficiently catalyzed by the enzyme, ascorbate oxidase (E.C. 1.10.3.3). This enzyme contains copper ions that are necessary for its activity (Penton and Dawson, 1965). Numerous studies have shown that aqueous copper ion also catalyzes the oxidation of ascorbic acid, although thousands of times less effectively than the enzyme. This reaction thus provides an opportunity to study the activity of various copper complexes in an attempt to elucidate properties of the complex important in catalysis.

In order to compare the activity of different catalysts, it is necessary to have an easily obtainable reference catalyst. It would be convenient to use aqueous copper ion for this purpose. There is, however, much disagreement concerning the magnitude of copper ion activity and the dependence of reaction rate on ascorbic acid, copper, and oxygen concentrations. Typical rate behaviors that have been reported are summarized in Table 1. These studies and many others presented in the literature were performed by contacting stirred solutions of ascorbic acid with oxygen-containing atmospheres while measuring either the amount of ascorbic acid or the volume of oxygen consumed as the reaction proceeded. Such two-phase systems were modeled mathematically to try to account for the variety of observed kinetic behaviors.

## MATHEMATICAL MODEL OF THE SYSTEM

Numerous theoretical models of systems considering mass transfer and chemical reaction have been presented in the literature. These studies have focused primarily on mass transfer (Astarita, 1967; Danckwerts, 1970) or, more recently, on simple chemical reactions (Kulkarni and Doraiswamy, 1975, 1976; Hulbert, 1976). This study considers a simple film model of mass transfer combined with reaction rate expressions that have been proposed for the description of ascorbic acid oxidation. The one-dimensional model used (Figure 1) consists of a gas phase containing species $X$ in contact with a liquid phase containing species $A$. The liquid phase is composed of a stagnant layer of thickness $\delta$ and a well-stirred bulk. The following assumptions are made:

1. The concentrations of $X$ and $A$ in the liquid are small, and the behavior of each species can be approximated by a pseudobinary diffusion equation.
2. The system is isothermal, and physical properties are independent of composition.
3. Quasi steady state conditions exist within the stagnant film.
4. Reaction occurs only in the bulk.

These lead to the following equations and boundary conditions for the film:

$$\mathcal{D}_{AB}\frac{d^2c_{Af}}{dz^2} = 0 \tag{1a}$$

$$\mathcal{D}_{XB}\frac{d^2c_{Xf}}{dz^2} = 0 \tag{1b}$$

$$\left.\begin{array}{lll} \text{At} \quad z = 0, & c_{Xf} = c_{Xs}, & \dfrac{dc_{Af}}{dz} = 0 \\ \text{At} \quad z = \delta, & c_{Xf} = c_X, & c_{Af} = c_A \end{array}\right\} \tag{2}$$

These equations can be solved for the concentration profiles in the film:

$$c_{Af} = c_A \tag{3a}$$

$$c_{Xf} = (c_X - c_{Xs})\frac{z}{\delta} + c_{Xs} \tag{3b}$$

Mass balances on species $A$ and $X$ in the liquid bulk lead to the following equations:

$$\frac{d}{dt}(Vc_A) = R_A V \tag{4a}$$

$$\frac{d}{dt}(Vc_X) = SN_{Xz}|_{z=\delta} + R_X V \tag{4b}$$

From the concentration profile of $X$ in the film, the flux of $X$ into the bulk is

$$N_{Xz}|_{z=\delta} = \mathcal{D}_{XB}\left(\frac{c_{Xs} - c_X}{\delta}\right) \tag{5}$$

If we use rate expressions

$$R_A = -k'c_Ac_X^n \tag{6a}$$

Table 1. Summary of Studies of Ascorbic Acid Oxidation

| Author | Rate dependence on | | |
|---|---|---|---|
| | Ascorbic acid concentration | Copper concentration | Oxygen concentration |
| Barron et al. (1939) | Zero order (from time dependence) | Nonlinear | — |
| Weissberger and LuValle (1944) | First order (from time dependence) | Michaelis-Menten | First order |
| Khan and Martell (1967) | First order (from time dependence) | First order | $a + b[O_2]_s$ |
| Hanaki (1969) | Michaelis-Menten (from initial rates)<br>Zero order (from time dependence) | — | — |
| Ogata et al. (1968) | First order (from time dependence) | First order | $a + b[O_2]_s$ |
| Shtamm et al. (1974) | First order (from initial rates) | First order | Half order |

$$R_X = -mk'c_Ac_X^n \tag{6b}$$

in which $k'$ is a product of specific rate constant, catalyst concentration, and dependence on other concentrations that remain fixed during a single run, the equations describing the bulk and its initial condition become

$$\frac{dc_A}{dt} = -k'c_Ac_X^n \tag{7a}$$

$$\frac{dc_X}{dt} = \frac{S\mathcal{D}_{XB}}{V\delta}(c_{Xs} - c_X) - mk'c_Ac_X^n \tag{7b}$$

$$\text{At} \quad t = 0, \quad c_A = c_{A0}, \quad c_X = c_{Xs} \tag{8}$$

Introduction of dimensionless variables

$$c_A^* = \frac{c_A}{c_{A0}}, \quad c_X^* = \frac{c_X}{c_{Xs}}, \quad t^* = \frac{S\mathcal{D}_{XB}}{V\delta}t \tag{9}$$

gives equations and boundary conditions in which two dimensionless groups appear:

$$\frac{dc_A^*}{dt^*} = -G_1c_A^*(c_X^*)^n \tag{10a}$$

$$\frac{dc_X^*}{dt^*} = 1 - c_X^* - G_1G_2c_A^*(c_X^*)^n \tag{10b}$$

$$\text{At} \quad t^* = 0, \quad c_A^* = 1, \quad c_X^* = 1 \tag{11}$$

$$G_1 = \frac{k'c_{Xs}^nV\delta}{S\mathcal{D}_{XB}} \tag{12a}$$

$$G_2 = \frac{mc_{A0}}{c_{Xs}} \tag{12b}$$

Group $G_1$ is the ratio of the rate constant for chemical reaction in a system always saturated with the gaseous species to the mass transfer coefficient. Group $G_2$ is determined by initial conditions.

### Steady-State Concentration of $X$ in Bulk

The additional assumption that the bulk quickly reaches a steady state concentration of species $X$ allows one to set $dc_X^*/dt^* = 0$. Equations (10*a*) and (10*b*) can then be simplified for $n = 1/2$ and $n = 1$:

$$\frac{-dc_A^*}{dt^*} = \frac{1}{2}G_1^2G_2(c_A^*)^2\left[\sqrt{1 + \frac{4}{G_1^2G_2^2(c_A^*)^2}} - 1\right] \quad \text{for} \quad n = \frac{1}{2} \tag{13}$$

$$\frac{-dc_A^*}{dt^*} = \frac{G_1c_A^*}{1 + G_1G_2c_A^*} \quad \text{for} \quad n = 1 \tag{14}$$

Since many kinetic studies use initial rates and concentrations, it is useful to define a dimensionless initial velocity

$$v_{0i}^* = \frac{V\delta}{S\mathcal{D}_{XB}}\frac{1}{c_{A0}}\left(\frac{-dc_A}{dt}\right)\bigg|_{t=0} = \left(\frac{-dc_A^*}{dt^*}\right)\bigg|_{t^*=0} \tag{15}$$

For $n = 1/2$ and $n = 1$, the expressions for dimensionless initial velocity are

$$v_{02}^* = \frac{1}{2}G_1^2G_2\left[\sqrt{1 + \frac{4}{(G_1G_2)^2}} - 1\right] \quad \text{for} \quad n = \frac{1}{2} \tag{16}$$

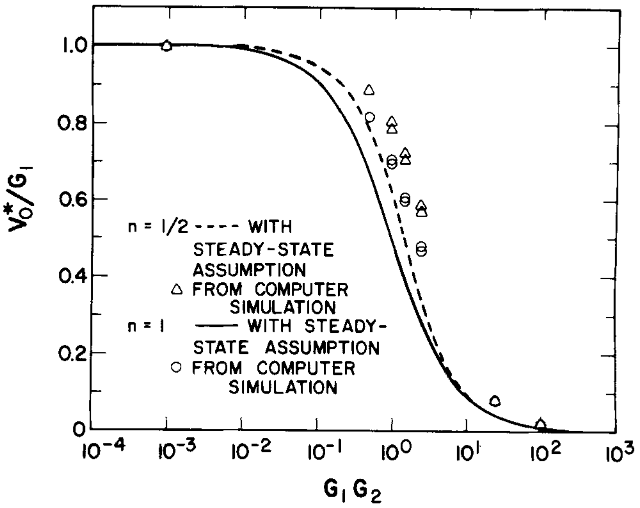

**Fig. 2.** Dependence of dimensionless initial velocity on groups characterizing system conditions.

$$v_{01}^* = \frac{G_1}{1 + G_1G_2} \quad \text{for} \quad n = 1 \tag{17}$$

Kulkarni and Doraiswami (1975) have used effectiveness factors rather than apparent kinetics to summarize the effect of mass transfer on first order reaction. For their case of a film model with reaction confined to the bulk, they obtain an expression for reaction rate that is equivalent to Equation (17).

The information in Equations (16) and (17) is presented in plots of $v_{01}^*/G_1$ and $v_{02}^*/G_1$ vs. $G_1G_2$ in Figure 2. System behavior can be conveniently divided into three regions:

| | |
|---|---|
| Region I | $G_1G_2 < 10^{-2}$ |
| Region II | $10^{-2} < G_1G_2 < 10$ |
| Region III | $10 < G_1G_2$ |

In region I, behavior is virtually identical for $n = 1/2$ and $n = 1$. For small values of $G_1G_2$, Equations (16) and (17) both have the same limiting form:

$$\frac{v_{0i}^*}{G_1} = 1 \tag{18}$$

Converting back to nondimensionless variables, we get

$$v_{0i} = k'c_{A0}c_{Xs}^n \tag{19}$$

Thus, for $n = 1/2$ and $n = 1$, the observed dependence of rate on $k'$ and $c_{A0}$ is first order and on $c_{Xs}$ is $n^{\text{th}}$ order. Experiments performed with $G_1G_2$ in region I will show true kinetic behavior unaffected by mass transfer.

Region III behavior is also virtually identical for $n = 1/2$ and $n = 1$. For large values of $G_1G_2$, Equations (16) and (17) have the limiting form

$$\frac{v_{0i}^*}{G_1} = \frac{1}{G_1G_2} \tag{20}$$

Converting this to dimensional variables gives

$$v_{0i} = \frac{S\mathcal{D}_{XB}}{V\delta}\frac{c_{Xs}}{m} \tag{21}$$

Thus, the dependence of rate on $k'$ and $c_{A0}$ is zero order, and the dependence on $c_{Xs}$ is first order. This is the mass transfer limited regime.

Behavior in region II is more complicated. For $n = 1$, Equation (17) can be transformed into

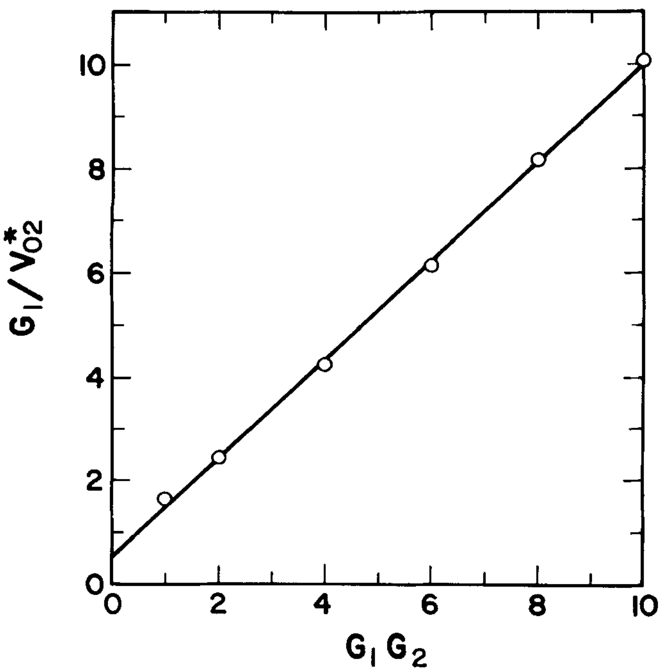

**Fig. 3. Dimensionless Lineweaver-Burk plot using steady state model in Region II with half-order dependence on dissolved gas.**

$$\frac{G_1}{v_{01}^*} = 1 + G_1 G_2 \qquad (22)$$

This is the dimensionless form of the Lineweaver-Burk formulation of Michaelis-Menten kinetics. When converted to dimensional variables, (22) becomes

$$\frac{1}{v_{01}} = \frac{1}{c_{Xs}}\left[\frac{1}{k' c_{A0}} + \frac{mV\delta}{S\mathfrak{D}_{XB}}\right] \qquad (23)$$

Thus, in region II for $n = 1$, initial velocity shows Michaelis-Menten dependence on $k'$ and $c_{A0}$ and first order dependence on $c_{Xs}$.

For $n = \frac{1}{2}$ in region II, if one plots $G_1/v_{02}^*$ vs. $G_1G_2$ for restricted ranges of $G_1G_2$, one obtains graphs that are very nearly linear with nonzero intercepts (Figure 3). These plots indicate that one will observe Michaelis-Menten dependence of initial velocity on $k'$ and $c_{A0}$. The slope and intercept vary with the portion of region II being considered, however.

By calculating $v_{02}^*$ as a function of $c_{Xs}$ for $G_1G_2$ in region II, one sees that the dependence on $c_{Xs}$ varies gradually from half order to first order as $G_1G_2$ increases. In most kinetic studies, the concentration of dissolved gas is varied only a limited amount. As shown in Figure 4, for a restricted range of $c_{Xs}$, the dependence of initial rate on dissolved gas concentration can be interpreted as $v_{02}^* = a + bc_{Xs}$.

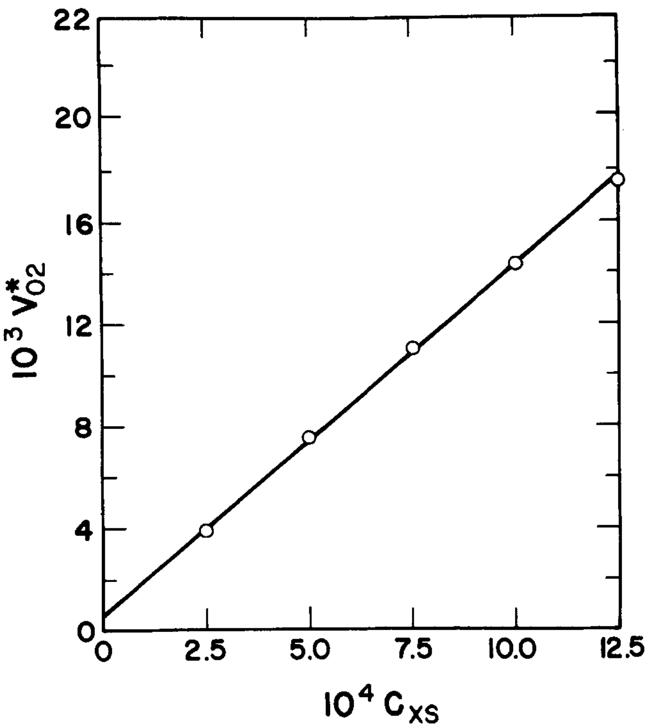

**Fig. 4. Dependence of initial velocity on dissolved gas concentration using steady-state model in region II with half-order dependence on dissolved gas. $G_1 = 0.05$, $G_2 = 50$ at $c_{Xs} = 1.25 \times 10^{-3}$.**

The apparent dependence of initial rate on $k'$, $c_{A0}$, and $c_{Xs}$ for $n = \frac{1}{2}$ and $n = 1$ in all three regions is summarized in Table 2.

### Variable Concentration of *X* in Bulk

In order to check the validity of using the assumption $dc_X^*/dt^* = 0$, Equations (10*a*) and (10*b*) were solved numerically for various values of $G_1$ and $G_2$ using a fourth-order Runge-Kutta technique. The ranges of $G_1$ and $G_2$ were selected to correspond to conditions that have been used in published studies of ascorbic acid oxidation. In order to compare numerically calculated rates and experimentally measured values, it was necessary to establish a correspondence between real and dimensionless times. From papers considering ascorbic acid oxidation, it appears that measurements were taken no more often than once every 30 s. Data given by Shtamm and Skurlatov (1974) enable one to estimate $S\mathfrak{D}_{XB}/V\delta \sim 0.03\ s^{-1}$. With this value, real time of 30 s corresponds to dimensionless time of about 0.9. Simulated data points were therefore generated for $t = 0, 1, 2, \ldots$, although the step size used by the computer program was smaller. For all cases considered, values of $c_X^*(t^*)$ show that after a short period of rapid change, $dc_X^*/dt^*$ is small. It thus appears that over the range of

TABLE 2. PREDICTED DEPENDENCE OF RATE ON $k'$, $c_{A0}$, AND $c_{Xs}$

| | From initial rates | | | From time dependence |
|---|---|---|---|---|
| | $k'$ (Catalyst concentration) | $c_{A0}$ | $c_{Xs}$ | $c_A$ |
| $n = \frac{1}{2}$ | | | | |
| Region I | First order | First order | Half order | First order |
| Region II | Michaelis-Menten | Michaelis-Menten | $a + bc_{Xs}$ | First to zero order |
| Region III | Zero order | Zero order | First order | Zero order |
| $n = 1$ | | | | |
| Region I | First order | First order | First order | First order |
| Region II | Michaelis-Menten | Michaelis-Menten | First order | First to zero order |
| Region III | Zero order | Zero order | First order | Zero order |

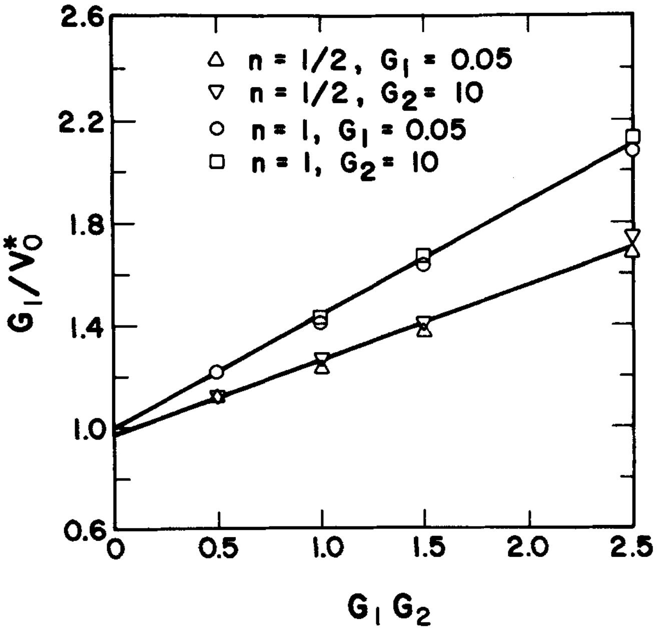

Fig. 5. Dimensionless Lineweaver-Burk plot using simulated data in region II.

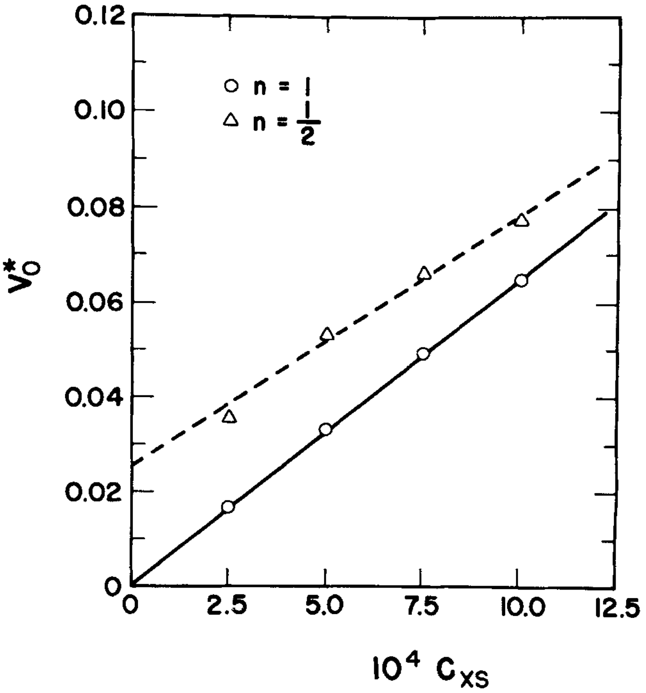

Fig. 6. Dependence of initial velocity on dissolved gas concentration using simulated data in region II. $G_1 = 0.1$, $G_2 = 5$ at $c_{Xs} = 1.25 \times 10^{-3}$.

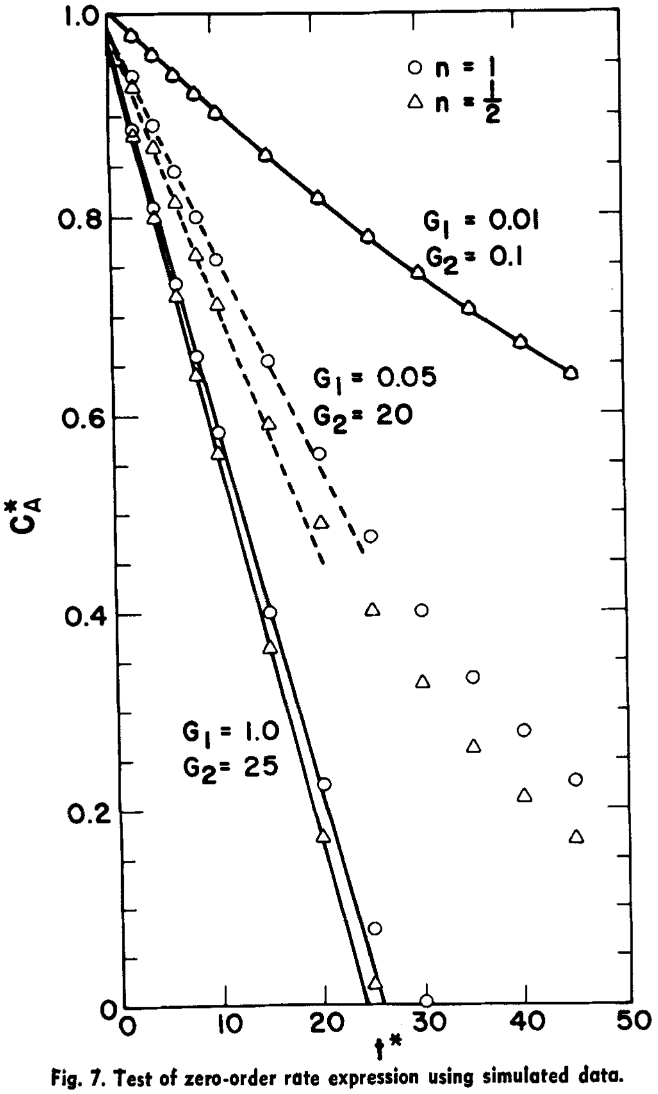

Fig. 7. Test of zero-order rate expression using simulated data.

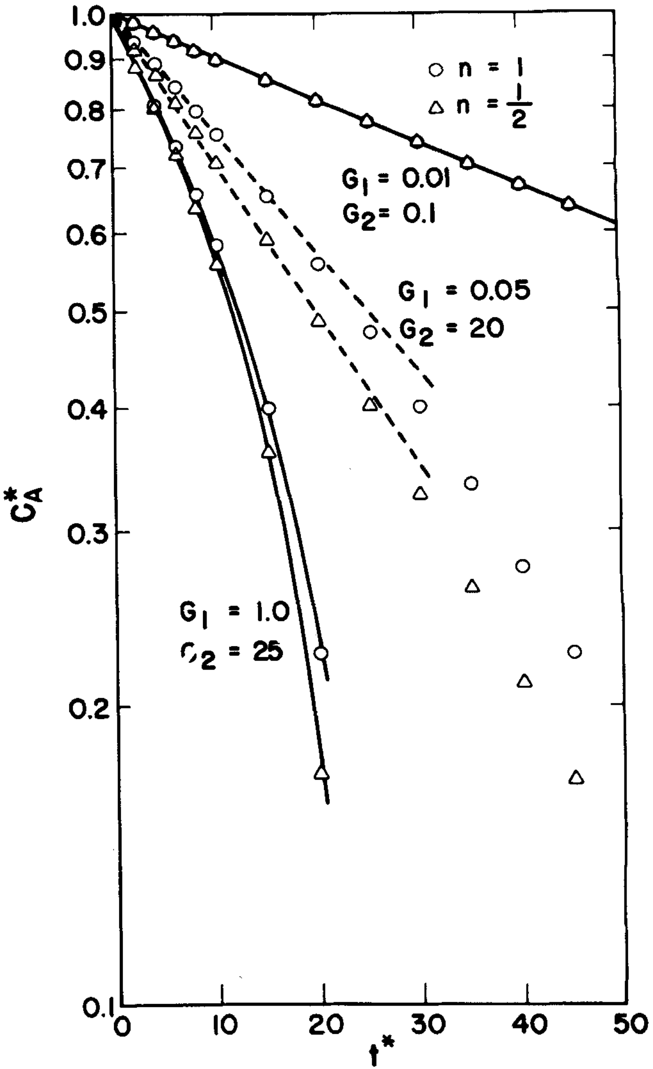

Fig. 8. Test of first-order rate expression using simulated data.

variables studied, conclusions reached using the steady state approximation ought to be qualitatively good.

For each run, computed values of $c_A^*(t^*)$ were used to estimate $v_{0i}^*/G_1$. These points, plotted in Figure 2, lie somewhat above the curves generated from the steady state assumption. In regions I and III, $v_{0i}^*/G_1$ depends *primarily* on $G_1G_2$, whereas in region II, $v_{0i}^*/G_1$ varies considerably with $G_1$ for constant $G_1G_2$.

If one simulates a series of experiments varying $k'$, $c_{A0}$, and $c_{Xs}$ individually in each of the three regions, analysis of estimated initial rates indicates the same dependences predicted using the steady state assumption. Examples of these analyses for region II are presented in Figures 5 and 6. This confirms the conclusion that in the range of variables studied, use of the steady state assumption is justified.

Simulated values of $c_A^*(t^*)$ and integrated rate expressions were also used to investigate the time course of the reaction. The dependence of rate on $c_A$ inferred from these studies is summarized in Table 2. In region I, both initial rates and $c_A^*(t^*)$ show first-order dependence of rate on $c_A$. In region III, both initial rates and $c_A^*(t^*)$ show zero-order dependence on $c_A$. The line fitting $c_A^*(t^*)$ does not, however, go through the initial point (0, 1). In region II, $c_A^*(t^*)$ shows intermediate behavior that can be interpreted as first order in $c_A^*$ for low $G_1G_2$ or zero order in $c_A^*$ for high $G_1G_2$. For intermediate values of $G_1G_2$, the portion of the curve up to 50% conversion can be interpreted as either zero or first order. Examples of simulated runs are shown in Figures 7 and 8.

### Summary of Predictions of Model

The predictions of the model of simultaneous mass transfer and reaction for the dependence of rate on the concentrations of various species are given in Table 2. Region I is the true kinetic regime in which observations give information concerning the reaction. Region II is the mass transfer interactive regime for which observed reaction orders are different than the true orders. Region III is the mass transfer limited regime in which no information concerning the chemical reaction is obtained.

## INTERPRETATION OF PUBLISHED ASCORBIC ACID OXIDATION RATE DATA

Among rate expressions that have been proposed to describe ascorbic acid oxidation are the following forms (Shtamm et al., 1974; Khan and Martell, 1967; Silverblatt et al., 1943; Ogata et al., 1968; Joslyn and Miller, 1949; Dekker and Dickinson, 1940):

$$R_{ASC} = \frac{-k[\mathrm{Cu}][T_A][\mathrm{O_2}]^{1/2}}{K_a + [\mathrm{H^+}]} \tag{24}$$

$$R_{ASC} = \frac{-k[\mathrm{Cu}][T_A][\mathrm{O_2}]}{K_a + [\mathrm{H^+}]} \tag{25}$$

$$R_{ASC} = \frac{-k[\mathrm{Cu}][T_A][\mathrm{O_2}]^{0.4}}{[T_A]^{0.5}[\mathrm{H^+}]^{0.7}} \tag{26}$$

$$R_{ASC} = \frac{-k[\mathrm{Cu}][T_A](a + b[\mathrm{O_2}])}{[\mathrm{H^+}] + (a + b[\mathrm{O_2}])[T_A]} \tag{27}$$

$$R_{ASC} = \frac{-k[\mathrm{Cu}]^{1/2}[T_A]}{[\mathrm{H^+}]^{1/2}} \tag{28}$$

$$R_{ASC} = \frac{-k[\mathrm{Cu}][T_A]}{[\mathrm{H^+}]^2} \tag{29}$$

The most widely supported of these are expressions (24) and (25). These are of the form of expressions (6*a*) and (6*b*) with $n = 1/2$ or 1, $m = 1$, and $k' = k[\mathrm{Cu}]/(K_a + [\mathrm{H^+}])$. These were used in the model of simultaneous mass transfer and homogeneous chemical reaction. Kinetic behaviors predicted by the model were compared to those reported for ascorbic acid oxidation (Table 1) to see which rate expression best fits the observations.

Barron et al. (1936) used high concentrations of ascorbic acid and a wide range of copper concentrations. They report zero time-order dependence on ascorbic acid. Their data indicate first-order dependence on copper at low concentrations and Michaelis-Menten dependence at high concentrations. These observations are in accord with region II models with $n = 1/2$ or 1.

Weissberger and LuValle (1944) used a high concentration of ascorbic acid and report first-order time dependence on ascorbic acid, nonlinear dependence on copper that is linear in the Lineweaver-Burk formulation, and linear dependence on oxygen without specifying the intercept at zero oxygen concentration. These observations are in accord with region II models with $n = 1/2$ or 1.

Khan and Martell (1967) report first-order time dependence on ascorbic acid, first-order dependence on copper, and linear oxygen dependence with a nonzero intercept. These observations are accounted for by a model using $n = 1/2$.

Hanaki (1969) performed experiments at high ascorbic acid concentration and high *p*H and reports zero-order ascorbic acid dependence with respect to time but Michaelis-Menten dependence with respect to initial concentration. These can be explained by region II models with $n = 1/2$ or 1.

Ogata et al. (1968) measured oxidation rates manometrically at various stirring speeds. They found that above a certain speed, observed rate was independent of stirring and concluded mass transfer effects would not affect kinetic observations. They observed first-order dependence on ascorbic acid with respect to time, first-order dependence on copper over a limited range of copper concentration, and a linear dependence on oxygen with a nonzero intercept. These observations are in accord with the region II model with $n = 1/2$. Ogata et al. also investigated the *p*H dependence of the reaction in two ways. They lowered the *p*H by adding increased amounts of ascorbic acid and found that a plot of the logarithm of observed rate constant vs. *p*H was linear with slope 2. They also lowered *p*H by adding nitric acid, keeping the amount of ascorbic acid fixed. Plots of the logarithm of observed rate constant vs. *p*H for these runs showed slopes of 1 at low *p*H but were nonlinear with decreasing slope at higher *p*H. If rate expression (24) or (25) were adequate, then changing the *p*H by adding ascorbic acid should show the same effect on the rate constant as was seen when the *p*H was changed by adding nitric acid. Ogata et al. proposed rate expression (27) to account for different behaviors with the two acids. These observations can also be explained using the mass transfer-reaction model in region II. The model variable that corresponds to their observed rate constant is $v_{02}^*$. As shown, in region II

$$\frac{G_1}{v_{02}^*} = f + gG_1G_2 \tag{30}$$

After rearranging and substituting expressions for $G_1$ and $G_2$ valid for ascorbic acid oxidation, one obtains

$$v_{02}^* = \frac{\alpha}{f([\mathrm{H^+}] + K_a) + \dfrac{g\alpha}{[\mathrm{O_2}]_s}[T_A]_0} \tag{31}$$

where

$$\alpha = k[\mathrm{Cu}][\mathrm{O_2}]_s^{1/2}\frac{V\delta}{S\mathfrak{D}_{\mathrm{O_2}B}}$$

For $[T_A]_0$ constant, as $p$H is decreased, Equation (31) reduces to the limiting form

$$\log v_{02}^* = \log\frac{\alpha}{f} + (p\mathrm{H}) \tag{32}$$

A plot of log ($v_{02}^*$) vs. $p$H will have a slope of 1 at low $p$H, and the slope will decrease as $p$H is raised, as observed by Ogata et al. when nitric acid was used to change $p$H.

In the range of concentrations used by Ogata et al., the dissociation of ascorbic acid will be small, and when no other acid is added, one can approximately relate ascorbic acid concentration and hydrogen ion concentration by the expression

$$[T_A]_0 \simeq \frac{[\mathrm{H^+}]^2}{K_a} \tag{33}$$

Thus, when the $p$H is controlled by the ascorbic acid dissociation equilibrium, Equation (31) is approximated by

$$v_{02}^* \simeq \frac{\alpha}{[\mathrm{H^+}]}\ \frac{1}{f + \left(\dfrac{g\alpha}{[\mathrm{O_2}]_s K_a}\right)[\mathrm{H^+}]} \tag{34}$$

If $g\alpha[\mathrm{H^+}]/([\mathrm{O_2}]_s K_a >> f$, then this reduces to

$$\log v_{02}^* \simeq \log\frac{[\mathrm{O_2}]_s K_a}{g} + 2(p\mathrm{H}) \tag{35}$$

in agreement with observation.

Shtamm and Skurlatov (1974) measured the mass transfer rate of oxygen into a solution with no chemical reaction occurring and were careful to use conditions giving reaction rates far below this value. They also corrected their calculations to account for the fact that dissolved oxygen concentration during reaction is below the saturation level. They performed their experiments in region I and observed true kinetic behavior.

From these analyses, one sees that whereas many observations concerning kinetics of ascorbic acid oxidation can be explained using the mass transfer-reaction model with $n = 1/2$ or with $n = 1$, some of them can be explained only by using $n = 1/2$. Thus, there is evidence that expression (24) is correct.

## EXPERIMENTAL STUDY

In order to avoid the problem of interaction between mass transfer and chemical reaction, a procedure to study the oxidation of ascorbic acid was developed that eliminated mass transfer. A closed vessel that can be completely filled with ascorbic acid solution was fitted with a biological oxygen demand probe and oxygen meter from Yellow Springs Instrument Company to monitor the reaction. A similar approach has been used by Jameson and Blackburn (1976). With a syringe, catalyst solutions of cupric sulfate were injected into the system through a rubber septum. High concentrations of ascorbic acid were used to keep the amount of this species and the $p$H approximately constant during a run. Measurements of oxygen concentration as a function of time were used to estimate initial reaction rates and to investigate several integrated forms of rate expressions. In every case, plots of $[\mathrm{O_2}]$ and log $[\mathrm{O_2}]$ vs. time were not linear, whereas plots of $[\mathrm{O_2}]^{1/2}$ vs. time were linear for over 50% conversion of oxygen. At high conversions, there was some deviation from linearity. The oxygen concentration did not decrease as quickly as expected, perhaps because of competing reactions such as direct oxidation by $\mathrm{H_2O_2}$, a reaction product, or decomposition of $\mathrm{H_2O_2}$ to oxygen and water. These observations imply a rate expression of the form

$$\frac{-d[\mathrm{O_2}]}{dt} = k_{\mathrm{obs}}[\mathrm{O_2}]^{1/2} \tag{36}$$

for which $-k_{\mathrm{obs}}$ equals twice the slope of the linear portion of a plot of $[\mathrm{O_2}]^{1/2}$ vs. time. This finding of half-order dependence on oxygen is in agreement with the work of Jameson and Blackburn (1976) and Shtamm and Skurlatov (1974), as well as the use of expression (24) to interpret data reported for systems involving combined mass transfer and reaction. The half-order dependence on oxygen indicates that the reaction occurs by a chain mechanism. One cannot, however, determine the mechanism from only the overall rate expression. The Appendix describes several proposed mechanisms that would show observed kinetics described by Equation (24).

Having confirmed the half-order dependence on oxygen, the reaction was studied at different concentrations of ascorbic acid, oxygen, and copper ion. A summary of results for a series of runs is presented in Table 3. From potentiometric measurements, the dissociation constant of ascorbic acid is estimated to be $K_a = 4.7 \times 10^{-5}$M, within the range of $4 \times 10^{-5}$ to $9.16 \times 10^{-5}$M reported by others (Ogata et al., 1968; Khan and Martell, 1967). This value was used to check the validity of rate expression (24). A plot of initial velocity vs. $[\mathrm{Cu}][T_A]_0[\mathrm{O_2}]_0^{1/2}/(K_a + [\mathrm{H^+}])$ ought to be linear and extrapolate through the origin. The slope of this plot is the specific rate constant. Using the data presented in Table 3, one obtains a plot that is fairly linear but does not quite go through the origin. When a line through the origin is fitted to these data, the estimate of the rate constant is $k = 0.13\mathrm{M}^{-1/2}\mathrm{s}^{-1}$, the same value obtained by Shtamm and Skurlatov using different experimental methods.

Table 3. Summary of Experimental Observations: Temperature = 25°C

| Run No. | $[T_A]_0(M)$ | $[\mathrm{O_2}]_0(10^{-4}M)$ | $[\mathrm{Cu}](10^{-6}M)$ | $p$H | Initial velocity ($10^{-7}Ms^{-1}$) |
|---|---|---|---|---|---|
| 1 | 0.0400 | 2.28 | 7.5 | 2.86 | 4.35 |
| 2 | 0.0200 | 2.27 | 7.5 | 3.03 | 3.37 |
| 3 | 0.0400 | 5.05 | 7.5 | 2.89 | 6.53 |
| 4 | 0.0200 | 4.91 | 7.5 | 3.01 | 5.98 |
| 5 | 0.0400 | 1.80 | 15.0 | 2.88 | 5.90 |
| 6 | 0.0200 | 2.13 | 15.0 | 3.02 | 6.08 |
| 7 | 0.0400 | 4.04 | 15.0 | 2.85 | 11.2 |
| 8 | 0.0200 | 4.74 | 15.0 | 3.02 | 9.68 |

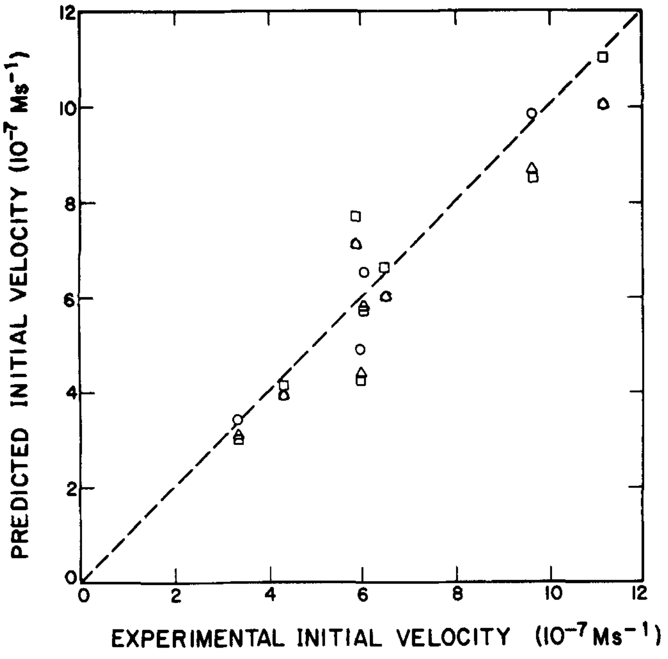

*Fig. 9. Comparison of predicted and experimental initial velocities for conditions specified in Table 3. ○—This work, △—Jameson and Blackburn (1976). □—Shtamm and Skurlatov (1974).*

Jameson and Blackburn (1976) suggest that rate depends on the concentration of unbound copper and propose a rate expression that accounts for formation of copper-ascorbic acid complexes. This is a generalization of Equation (24) and contains additional terms in the denominator. Considering only the copper-ascorbate complex, we get

$$R_{ASC} = R_{O_2} = \frac{-k[\mathrm{Cu}][T_A][O_2]^{1/2}}{K_a + [\mathrm{H}^+] + K_a K^M [T_A]} \quad (37)$$

*If such a model is correct, a plot of* $[O_2]_0^{1/2}$/(initial velocity) vs. $(K_a + [\mathrm{H}^+])/[T_A]_0$ ought to be a family of lines whose slopes and intercepts vary with copper concentration. This is indeed observed for the data in Table 3. From the slopes of the lines, one can estimate the specific rate constant $k$ and from the intercepts, the formation constant for the complex $K^M$. Using initial rate data, $k = 0.32\ \mathrm{M}^{-1/2}\mathrm{s}^{-1}$ and $K^M = 1.2 \times 10^3 \mathrm{M}^{-1}$. Jameson and Blackburn report values corresponding to $K_a = 9.02 \times 10^{-5}$M, $k = 0.19\ \mathrm{M}^{-1/2}\mathrm{s}^{-1}$, and $K^M = 2.1 \times 10^2 \mathrm{M}^{-1}$. They were also able to estimate the formation constant for a second copper-ascorbic acid complex that does not appear to be important in the range of concentrations used in this study. The large differences in the values of the constants estimated in the two studies arises because of the way in which the parameters are determined. The value of $K_a$ is used to calculate $k$, which is then used to calculate $K^M$. Rather than compare values of the parameters, one should look at predicted initial rates for various concentrations. Figure 9 summarizes experimental initial rates and those predicted using parameters estimated by Shtamm and Skurlatov, Jameson and Blackburn, and this study. The agreement among the values is fairly good for both two- and three-parameter models.

It thus appears that Equation (37), or the expanded version given by Jameson and Blackburn, is the best form for describing copper catalyzed ascorbic acid autoxidation kinetics. The use of this equation is not justified, however, for predicting results for combined mass transfer and reaction because of uncertainty in the parameters and the simplicity of the film mass transfer model. For this purpose, the reduced form, Equation (24), is recommended.

## ACKNOWLEDGMENT

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## NOTATION

$a$ = intercept of apparent linear dependence of rate on dissolved gas concentration
A = dehydroascorbic acid
$\dot{\mathrm{A}}\mathrm{H}$ = ascorbate semiquinone
$\mathrm{AH}^-$ = ascorbate anion
$\mathrm{AH}_2$ = ascorbic acid
$b$ = slope of apparent linear dependence of rate on dissolved gas concentration
$c_A$ = concentration of species $A$ in bulk, $M$
$c_{Af}$ = concentration of species $A$ in film, $M$
$c_X$ = concentration of species $X$ in bulk, $M$
$c_{Xf}$ = concentration of species $X$ in film, $M$
$c_{Xs}$ = saturation concentration of $X$ in liquid, $M$
[Cu] = total copper concentration, $M$
$\mathcal{D}_{AB}$ = pseudobinary diffusivity of species $A$ in liquid phase, $\mathrm{m}^2\mathrm{s}^{-1}$
$\mathcal{D}_{XB}$ = pseudobinary diffusivity of species $X$ in liquid phase, $\mathrm{m}^2\mathrm{s}^{-1}$
$f$ = intercept of plot of $G_1/v_{02}^*$ vs. $G_1G_2$
$g$ = slope of plot of $G_1/v_{02}^*$ vs. $G_1G_2$
$G_1$ = dimensionless group relating reaction rate and mass transfer rate
$G_2$ = dimensionless group relating initial reactant concentrations
$[\mathrm{H}^+]$ = hydrogen ion concentration
$k$ = specific rate constant for ascorbic acid oxidation
$k'$ = product of specific rate constant, catalyst concentration, and dependence of rate on species of constant concentration, $\mathrm{M}^{-n}\mathrm{s}^{-1}$
$k_{\mathrm{obs}}$ = observed rate constant from $[O_2]$ as function of time, $\mathrm{M}^{1/2}\mathrm{s}^{-1}$
$k_0$ = rate constant used in proposed mechanisms
$k_i$ = rate constant used in proposed mechanisms
$k_1$ = rate constant used in proposed mechanisms
$k_2$ = rate constant used in proposed mechanisms
$k_3$ = rate constant used in proposed mechanisms
$k_4$ = rate constant used in proposed mechanisms
$K_a$ = dissociation constant for ascorbic acid, M
$K^{DH}$ = formation constant of $[\mathrm{Cu}_2(AH)_2]^{2+}$ dimer
$K^M$ = formation constant for copper-ascorbate complex, $\mathrm{M}^{-1}$
$K^{O_2}$ = formation constant of $[\mathrm{Cu}_2(AH)_2(O_2)]^{2+}$
$m$ = stoichiometric ratio of moles of species $X$ consumed per mole of species $A$
$n$ = order of reaction with respect to oxygen
$N_{Xz}$ = flux of species $X$ in $z$ direction, mole $\mathrm{m}^{-2}\mathrm{s}^{-1}$
$[O_2]$ = dissolved oxygen concentration, M
$R_A$ = rate of production per unit volume of A, $\mathrm{Ms}^{-1}$
$R_{ASC}$ = rate of production per unit volume of ascorbic acid, $\mathrm{Ms}^{-1}$
$R_{O_2}$ = rate of production per unit volume of oxygen, $\mathrm{Ms}^{-1}$
$R_X$ = rate of production per unit volume of $X$, $\mathrm{Ms}^{-1}$
S = surface area, $\mathrm{m}^2$
$t$ = time, s
$[T_A]$ = total ascorbic acid concentration, M
$v_{01}$ = initial velocity of reaction for $n = 1$
$v_{02}$ = initial velocity of reaction for $n = 1/2$
$v_{0i}$ = initial velocity of reaction for $i = 1/n$
$V$ = volume of bulk liquid, $l$

$z$ = distance into liquid phase, m
$\alpha$ = group of constant terms in Equation (31)
$\delta$ = thickness of stagnant layer, m

**Subscripts**

$f$ = value in stagnant film
0 = value at $t = 0$
$s$ = saturation value

**Superscript**

$*$ = dimensionless variable

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## APPENDIX: PROPOSED MECHANISMS

Several chain mechanisms have been proposed to account for the observed dependence of ascorbic acid oxidation rate on concentrations of ascorbic acid, oxygen, copper, and hydrogen ion. All lead to the same overall rate expression but differ in the types of copper compounds involved in the reaction.

Shtamm et al. (1974) propose the following mechanism involving copper (I) and copper (II) compounds:

$$\mathrm{AH_2} \overset{K_a}{\rightleftarrows} \mathrm{AH^-} + \mathrm{H^+} \tag{A1}$$

$$2\mathrm{Cu^{2+}} + \mathrm{AH^-} \xrightarrow{k_i} 2\mathrm{Cu^+} + \mathrm{A} + \mathrm{H^+} \tag{A2}$$

$$\mathrm{Cu^+} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{Cu^{2+}} + \mathrm{O_2}^{\overline{\cdot}} \tag{A3}$$

$$\mathrm{O_2}^{\overline{\cdot}} + \mathrm{H^+} \rightleftarrows \mathrm{HO_2}\cdot \tag{A4}$$

$$\mathrm{HO_2}\cdot + \mathrm{AH^-} \xrightarrow{k_2} \mathrm{HO_2^-} + \dot{\mathrm{A}}\mathrm{H} \tag{A5}$$

$$\dot{\mathrm{A}}\mathrm{H} + \mathrm{Cu^{2+}} \xrightarrow{k_3} \mathrm{Cu^+} + \mathrm{A} + \mathrm{H^+} \tag{A6}$$

$$\mathrm{Cu^+} + \mathrm{HO_2}\cdot \xrightarrow{k_0} \mathrm{Cu^{2+}} + \mathrm{HO_2^-} \tag{A7}$$

Reaction (A2) is a slow process that initiates the chains, reactions (A3) through (A6) propagate them, and (A7) terminates them. If one assumes that the chains are long and that the rate of termination equals the rate of initiation, then the following rate expression is predicted by the mechanism:

$$R_{ASC} = -\left(\frac{k_i k_1 k_2}{k_0}\right)^{1/2} [\mathrm{Cu^{2+}}][\mathrm{AH^-}][\mathrm{O_2}]^{1/2} \tag{A8}$$

Using the ascorbic acid dissociation equilibrium (A1), one can relate ascorbate concentration to total ascorbic acid concentration:

$$[\mathrm{AH^-}] = \frac{K_a[T_A]}{K_a + [\mathrm{H^+}]} \tag{A9}$$

If one considers the copper present in the system to be essentially unbound copper (II), then one can substitute the total copper concentration into the equation. The resulting expression is of the same form as Equation (24):

$$R_{ASC} = -K_a\left(\frac{k_i k_1 k_2}{k_0}\right)^{1/2} \frac{[\mathrm{Cu}][T_A][\mathrm{O_2}]^{1/2}}{K_a + [\mathrm{H^+}]} \tag{A10}$$

Jameson and Blackburn (1976) propose a mechanism involving copper (II) dimers and a copper (III) complex:

$$\mathrm{Cu^{2+}} + \mathrm{AH^-} \overset{K^M}{\rightleftarrows} [\mathrm{Cu(AH)}]^+ \tag{A11}$$

$$2[\mathrm{Cu(AH)}]^+ \overset{K^{DH}}{\rightleftarrows} [\mathrm{Cu_2(AH)_2}]^{2+} \tag{A12}$$

$$[\mathrm{Cu_2(AH)_2}]^{2+} + \mathrm{O_2} \overset{K^{O_2}}{\rightleftarrows} [\mathrm{Cu_2(AH)_2(O_2)}]^{2+} \tag{A13}$$

$$[\mathrm{Cu_2(AH)_2(O_2)}]^{2+} \xrightarrow{k_1} [\mathrm{CuA(O_2H)}]\cdot + \mathrm{Cu^{2+}} + \mathrm{A}^{\overline{\cdot}} + \mathrm{H^+} \tag{A14}$$

$$\mathrm{A}^{\overline{\cdot}} + [\mathrm{Cu_2(AH)_2(O_2)}]^{2+} \xrightarrow{k_2} [\mathrm{CuA(O_2H)}]\cdot + [\mathrm{Cu(AH)}]^+ + \mathrm{A} \tag{A15}$$

$$[\mathrm{CuA(O_2H)}]\cdot \xrightarrow{k_3} \mathrm{A}^{\overline{\cdot}} + \mathrm{HO_2^-} + \mathrm{Cu^{2+}} \tag{A16}$$

$$2[\mathrm{CuA(O_2H)}]\cdot \xrightarrow{k_4} \text{TERMINATION PRODUCTS} \tag{A17}$$

If one assumes that the initiation rate, reaction (A14), is small, then the following rate expression can be derived:

$$R_{ASC} = -k_3 K^M \left(\frac{k_1}{k_4} K^{O_2} K^{DH}\right)^{1/2} [\mathrm{Cu^{2+}}][\mathrm{AH^-}][\mathrm{O_2}]^{1/2} \tag{A18}$$

This is of the form of Equation (A8), and the assumptions made by Shtamm et al. concerning copper and ascorbate concentrations lead to an expression of the form of Equation

(24). If, however, one considers the presence of copper-ascorbate complexes [Equation (A11)], then the expression must be modified. The concentrations of unbound copper and total copper are related by

$$[\mathrm{Cu}]^{2+} = \frac{[\mathrm{Cu}](K_a + [\mathrm{H}^+])}{K_a + [\mathrm{H}^+] + K_a K^M [T_A]} \qquad (A19)$$

Equation (A18) thus can be put into the form of Equation (37):

$$R_{\mathrm{ASC}} = -k_3 K_a K^M \left(\frac{k_1}{k_4} K^{\mathrm{O}_2} K^{DH}\right)^{1/2} \frac{[\mathrm{Cu}][T_A][\mathrm{O}_2]^{1/2}}{K_a + [\mathrm{H}^+] + K_a K^M [T_A]} \qquad (A20)$$

Other mechanisms leading to the same rate expression can also be proposed. One that involves a copper (I)-copper (III) transition rather than copper (II) dimers is as follows:

$$\mathrm{AH}_2 \overset{K_a}{\rightleftarrows} \mathrm{AH}^- + \mathrm{H}^+$$

$$\mathrm{AH}^- + \mathrm{Cu}^{2+} \overset{K^M}{\rightleftarrows} [\mathrm{Cu(II)AH}]^+$$

$$[\mathrm{Cu(II)AH}]^+ + \mathrm{Cu}^{2+} \xrightarrow{k_i} 2\mathrm{Cu}^+ + \mathrm{A} + \mathrm{H}^+$$

$$\mathrm{Cu}^+ + \mathrm{O}_2 \xrightarrow{k_1} [\mathrm{Cu(III)O_2}]^+$$

$$[\mathrm{Cu(III)O_2}]^+ + \mathrm{AH}^- \xrightarrow{k_2} \mathrm{HO_2}^- + [\mathrm{Cu(II)A}]^+$$

$$[\mathrm{Cu(II)A}]^+ \xrightarrow{k_3} \mathrm{Cu}^+ + \mathrm{A}$$

$$\mathrm{Cu}^+ + [\mathrm{Cu(III)O_2}]^+ \xrightarrow{k_t} 2\mathrm{Cu}^{2+} + \mathrm{O_2}^{2-}$$

From this mechanism, expressions (A9) and (A19), and the assumption of equal rates of initiation and termination, a rate expression of the form of Equation (37) results:

$$R_{ASC} = -K_a \left(K^M k_1 k_2 \frac{k_i}{k_t}\right)^{1/2} \frac{[\mathrm{Cu}][T_A][\mathrm{O}_2]^{1/2}}{K_a + [\mathrm{H}^+] + K_a K^M [T_a]} \qquad (A21)$$

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# Absorption of Sulfur Dioxide into Aqueous Sodium Hydroxide and Sodium Sulfite Solutions

The rates of absorption of pure sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions with and without a surface active agent were measured at 25°C using a liquid jet column. For the sulfur dioxide-sodium hydroxide system, the rate of absorption into the solution without surface active agent was higher than that into the solution with surface active agent, indicating the existence of the interfacial turbulence. The absorption rates obtained for the present system under the conditions of no interfacial turbulence were in good agreement with the theoretical predictions based on the penetration theory.

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## SCOPE

The removal of sulfur dioxide from gas mixtures by contacting the gases with an aqueous alkali hydroxide solution is an important industrial absorption process for control of air pollution. However, there have been very few studies of the mechanism of chemical absorption for the $SO_2$-$OH^-$ ions system. Goettler (1967) discussed the chemical absorption mechanism for the sulfur dioxide-sodium hydroxide system in his thesis which reported the results of a theoretical and experimental investigation of simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous sodium hydroxide solutions flowing over a single sphere. A model based on the assumption that the reaction between the dissolved sulfur dioxide and $OH^-$ ions is a two-step instantaneous reaction and two reaction planes are formed within the liquid phase was proposed, and a film theory solution for the reaction factor was presented. However, the direct experimental confirmation of this model was not attempted. Onda et al. (1971) absorbed sulfur dioxide into agar-agar gel containing sodium hydroxide or sodium sulfite at very long exposure times of the liquid in the range 900 to 9 000 s. They studied mainly the behavior of the reaction-plane movement by observing the position of the color change plane in the gel solution containing a indicator. The experimental results for the sulfur dioxide-sodium hydroxide system were found to agree with the penetration theory predictions based on the two reaction plane model proposed by Hikita et al. (1972).

The purposes of the study described in this paper are to obtain reliable data on the absorption rate of sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions at the short exposure times encountered in industrial absorbers, to check for the existence of interfacial turbulence in these absorption systems, to propose reasonable methods of predicting the physical properties of the present systems, and to test the applicability of the two reaction plane model presented by Hikita et al. (1972) to the sulfur dioxide-sodium hydroxide system.

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