STUDIES OF CHEMICAL REDUCTION OF Fe(III)*EDTA IN AN SO_2/NO_x AQUEOUS SCRUBBER SYSTEM

by

W. Li, and T.C. Keener

Department of Civil & Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221

M. Mendelsohn, J.B.L. Harkness, and C.D. Livengood

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STUDIES OF CHEMICAL REDUCTION OF Fe(III)*EDTA IN AN SO$_2$/NO$_x$ AQUEOUS SCRUBBER SYSTEM

W. Li, and T.C. Keener
University of Cincinnati,
Cincinnati, Ohio 45221
U.S.A

M. Mendelsohn, J.B.L. Harkness, and C.D. Livengood
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439
U.S.A

ABSTRACT

Ferrous*EDTA has been found to be an effective scrubbing agent for nitric oxide gas. A major process problem is oxidation of the iron to the ferric species, leading to a significant decrease in NO$_x$-removal capability. Argonne National Laboratory discovered a class of organic compounds that, when used with ferrous*EDTA in a sodium carbonate chemistry, could maintain high levels of NO$_x$ removal. However, those antioxidant/reducing agents (A/R) are not effective in a lime-based chemistry. In recent reports, it has been found that ascorbic acid and related compounds are capable of maintaining stable NO$_x$ removals of about 50% (compared with about 15% without the agent) in a lime-based FGD chemistry with Fe(II)*EDTA. It is believed that the improved performance of Fe(II)*EDTA is due to the catalytic action of ascorbate in the Fe(III)*EDTA reduction system, where Fe(III)*EDTA is reduced by ascorbate and oxidized ascorbate is then reduced back to the ascorbate by sulfite/bisulfite anions, which come from the dissolution of SO$_2$ in the flue gas. In the present work, the kinetics of the reduction of ferric chelate by ascorbate and reduction of oxidized ascorbate by sulfite/bisulfite anions at a typical flue-gas scrubber-system operating temperature (~55°C) have been determined.

STUDIES OF CHEMICAL REDUCTION OF Fe(III).EDTA IN AN SO$_2$/NO$_x$ AQUEOUS SCRUBBER SYSTEM

1 INTRODUCTION

Passage of the 1990 Clean Air Act Amendments has initiated extensive evaluation and planning for strategies to meet these stricter emission requirements. A number of technologies are available to either sulfur dioxide (SO$_2$) or nitrogen oxides (NOx) from flue gas. However, integrated technologies that can simultaneously control both species could offer significant advantages, such as lower capital and operating costs, better system operability and reliability, and possibly lower resource consumption and waste volumes. However, in order to achieve mandated air quality objectives as rapidly as possible, it is clear that emissions control equipment will have to be installed at many existing facilities.

The dominant FGD technology today is wet scrubbing based on limestone, lime, or sodium carbonate. All of these processes are capable of over 90% SO$_2$ removal, but they are largely ineffective for NOx removal due to the low solubility of the principal species, nitric oxide (NO). In view of the large number of wet scrubbers already in place or planned for the near future, a process that promotes NOx removal simply through the addition of chemical additives could have a significant impact on control strategies.

It has been found that some metal chelates, such as ferrous ethylenediaminetetraacetate (EDTA), enhance the absorption of nitrogen oxide by reacting to form a ferrous nitrosyl complex Fe(II)*EDTA*NO.[1,2] The coordinated NO can react with sulfite and bisulfite, which come from dissolution of SO_2 in the flue gas, freeing the ferrous chelate for further reaction with NO.[3] This combined action makes separate regeneration of the Fe(II)*EDTA to release the NO unnecessary. However, a significant process problem is oxidation of the iron in the additive to the inactive ferric state. This oxidation may take place both by direct reaction with dissolved oxygen and by reaction with species produced from decomposition of the Fe(II)*EDTA*NO complex. In some cases, addition of another chemical, specifically an antioxidant and/or reducing agent, has been effective in counteracting the harmful effects of ferrous oxidation. Argonne National Laboratory has found ascorbic acid and related compounds, as an effective antioxidant/reducing agent, capable of maintaining NO_x removals of about 50% with SO_2 removals of over 90% (compared with about 15% without the agent) for more than two hours in a lime-based chemistry with Fe(II)*EDTA, as shown in Figure 1.[4] An investigation was initiated to study the possible catalytic role of ascorbate in the metal-chelate-enhanced process of simultaneous removal of SO_2 and NO_x. This would provide a regenerable source of ascorbate ions and could thus make possible the achieving of stable NO_x removal without continuous addition of the reducing agent.

In this paper, the reduction kinetics of both the reduction of Fe(III)*EDTA by ascorbate and the reduction of oxidized ascorbate by sulfite/bisulfite ions have been established.

4

2 EXPERIMENTAL RESULTS AND DISCUSSION

The experiments that have been performed to investigate the reaction kinetics of reduction of Fe(III)*EDTA by ascorbate ions and the reduction of oxidized ascorbate by sulfite/bisulfite are discussed below.

2.1 REACTION KINETICS OF Fe(III)*EDTA REDUCTION BY ASCORBATE

2.1.1 Experimental Procedure

Jacketed reactors were used in conducting experiments at desired temperatures. The reactor was charged with aqueous $FeCl_3$ solution and aqueous EDTA solution. Nitrogen was bubbled at about 50 cm^3/min (STP) through a ball filter for 20 min to remove dissolved oxygen. The reduction reaction was initiated by injecting 1 L of aqueous L-ascorbic acid sodium salt solution into the reaction flask. Throughout the reaction, N_2 was continuously bubbled through the solution, and the solution was continuously mixed with a magnetic stirring bar. The pH of the reactant solution was adjusted to the desired value with NaOH. Because there was no large change in the progress of the reaction, no buffer solution was needed. At set time intervals, samples of the reaction liquid were taken to determine the concentration of Fe(II) by the 1,10-phenanthroline spectroscopic method.

2.1.2 Results

If the reduction reaction of Fe(III)*EDTA by ascorbic acid is assumed to be first order with respect to the concentration of Fe(III)*EDTA and negative first order with respect to the concentration of Fe(II)*EDTA, the rate equation will be expressed as

$$\frac{-d[Fe(III)]_T}{dt} = k_r \frac{[Fe(III)L]}{[Fe(II)L]} \quad , \tag{1}$$

where $[Fe(III)]_T$ stands for the total concentration of Fe(III) species; L stands for ligand chelate; $[Fe(III)L]$ and $[Fe(II)L]$ refer to the concentrations of ferric and ferrous chelate, respectively; k_r represents the reduction reaction rate constant; and t is time. The integral form of Equation 1 is given by

$$-a_0 \ln (a_0 - x) - x = k_r t - a_0 \ln a_0 \quad , \tag{2}$$

where a_0 refers to the initial concentration of Fe(III)*EDTA and x refers to the concentration of Fe(II)*EDTA at any reaction time. Therefore, $a_0 - x$ denotes the concentration of total Fe(III)*EDTA at any time during the reaction, assuming that this species is the only ferric species present.

Figure 2 shows the conversion of Fe(III) in the reacting solution as a function of time. If these experimental results are expressed as a plot of $-a_0 \ln (a_0 - x) - x$ as a function of time (Figure 3), the straight lines obtained support the assumed rate expression of Equation 1.

Plots of $-a_0 \ln (a_0 - x) - x$ as a function of time while the concentration of ascorbic acid was varied gave essentially straight lines (Figure 4). The calculated reaction rate constants were plotted against the concentration of ascorbic anion in Figure 5. The resulting reaction rate constant is proportional to the concentration of HA^{-1} with a slope of 3.7×10^{-4} s^{-1}. Consequently, the reduction rate can be expressed as first order with respect to the concentration of ascorbic anion.

2.1.3 Discussion

From the kinetic data obtained, an inverse dependence of the specific reaction rate on the hydrogen ion concentration was observed. The rate law describing the reduction may be expressed as

$$ -\frac{d[Fe(III)L]}{dt} = k \frac{[Fe(III)L]}{[Fe(II)L]} T_A \quad , \tag{3} $$

where T_A is the total concentration of unreacted ascorbic acid. Equation 3 may be expressed in the form

7

$$- \frac{d[Fe(III)L]}{dt} = k_1 [H_2A] \frac{[Fe(III)L]}{[Fe(II)L]} + k_2 [HA^{-1}] \frac{[Fe(III)L]}{[Fe(II)L]} \quad , \qquad (4)$$

where k_1 and k_2 are the rate constants for the effect of the metal chelate compound on the neutral and monoionic forms of ascorbic acid, H_2A and HA^{-1}, respectively, assuming that the two species of ascorbic acid react independently with the metal chelate. Equation 4 may be rewritten as

$$- \frac{d[Fe(III)L]}{dt} = k_1 [H_2A] \frac{[Fe(III)L]}{[Fe(II)L]} + k_2 \frac{[H_2A]K_1}{[H^{+1}]} \frac{[Fe(III)L]}{[Fe(II)L]} \quad , \qquad (5)$$

where $[HA^{-1}] = [H_2A]K_1/[H^{+1}]$ and K_1 is the first dissociation constant of ascorbic acid. Then, combining terms in Equation 5 yields the expression

$$- \frac{d[Fe(III)L]}{dt} = [H_2A] \frac{[Fe(III)L]}{[Fe(II)L]} \left(k_1 + k_2 \frac{K_1}{[H^{+1}]} \right) \quad . \qquad (6)$$

Substituting the mass balance expression, $T_A = [H_2A] + [HA^{-1}]$, into Equation 6 gives

$$k = \left(k_1 + k_2 \frac{K_1}{[H^{+1}]} \right) \left(\frac{[H^{+1}]}{[H^{+1}] + K_1} \right) . \qquad (7)$$

8

Figure 6 is a plot of the specific rate constant, k, as a function of the reciprocal of the hydrogen ion concentration. The plot yields a straight line with slope equal to $[H^{+1}]k_2K_1/([H^{+1}] + K_1)$ and a y intercept of $k_1\{[H^{+1}]/([H^{+1}] + K_1)\}$ equal to zero. Therefore, in the ascorbic acid reduction of the metal chelate, k_1 was found to be zero. The results indicate that the nonionized species, H_2A, is totally inactive for the reduction of the metal chelate. The specific reduction rate constant for the ascorbate monoanion, k_2, calculated from Equation 7 at 55°C is 3.5×10^{-4} s^{-1}.

2.2 REACTION KINETICS OF OXIDIZED ASCORBATE REDUCTION BY SULFITE/BISULFITE ANIONS

2.2.1 Experimental Procedure

The same reactor that was used for experiments on reduction of FE(III)*EDTA by ascorbate was charged with dehydroascorbic acid (oxidized ascorbic acid) solution. Nitrogen was bubbled at about 50 cm³/min (STP) through a ball filter for 20 min to remove dissolved oxygen. The reduction reaction was initiated by injecting 10 mL of aqueous sodium sulfite solution into the reaction flask. Throughout the reaction, N_2 was continuously bubbled through the solution, and the solution was continuously mixed with a magnetic stirring bar. The pH of the reactant solution was readjusted with NaOH or HCl to a desired value. In every run, the ionic strength of the solution was adjusted with Na_2SO_4 to a constant value of 1 mol/L. The reaction was monitored by sampling the reaction liquid periodically and determining the concentration of dehydroascorbic acid by the dinitrophenylhydrazine spectroscopic method.

9

2.2.2 Results

The reduction of dehydroascorbic acid was first studied in the presence of an excess of sodium sulfite to ensure pseudo-first-order conditions. Typical examples of the time-dependence of the concentration of Fe(II) in the reaction solution are shown in Figure 7. First-order rate constants were obtained from plots of $\ln[a/(a - x)]$ vs. time by multiplying the slopes by 2.303, where a is the initial concentration of dehydroascorbic acid and x is the concentration of the product (dehydroascorbic acid) at time t. The kinetic traces that resulted in linear first-order plots over at least three half-lives of the reaction are shown in Figure 8.

Concentration dependence studies were performed in the pH range of 2.0 - 7.0 and temperature range of 20 - 55°C. The pseudo-first-order rate constants for the various concentrations of sodium sulfite are given in Table I. The results are presented graphically in Figure 9.

Table I. The Pseudo-First-Order Rate Constants (M^{-1} min^{-1}) for the Sodium Sulfite Dependence of the Reduction of Dehydroascorbic Acid under Different pH Values

Sodium Sulfite Concentration, M	Pseudo-First-Order Rate Constants at $-\log[H^+]$ Values Indicated, 10^{-2} M^{-1} min^{-1}		
	4.0	6.0	7.0
0.005	0.6	0.7	1.3
0.01	1.2	1.4	2.6
0.03	3.6	4.1	7.8
0.05	6.0	6.8	13.1

2.2.3 Discussion

In dehydroascorbic acid reduction, an inverse dependence of specific rate on hydrogen ion concentration was observed. The rate law may be expressed in the form

$$-(\frac{d[DHA]}{dt}) = k'[DHA]T_S \quad , \tag{8}$$

where T_s = total concentration of unreacted sodium sulfite and [DHA] = total concentration of of dehydroascorbic acid. Equation 8 may be expressed in the form

$$-(\frac{d[DHA]}{dt}) = k_1'[SO_3^{2-}][DHA] + k_2'[HSO_3^-][DHA] \quad , \tag{9}$$

where k_1' and k_2' are the rate constants for the effect of the dehydroascorbic acid on the sulfite and bisulfite ions, SO_3^{2-} and HSO_3^-, respectively, assuming that the two species of S^{4+} formed react independently with the dehydroascorbic acid. Equation 9 may be rewritten as

$$-\frac{d[HDA]}{dt} = k_1'[DHA]\frac{K_2[HSO_3^-]}{[H^+]} + k_2'[DHA][HSO_3^-] \quad , \tag{10}$$

where K_2 is the second dissociation constant of sulfurous acid ($=[H^+][SO_3^{2-}]/[HSO_3^-]$). Then combining terms in Equation 10 yields the expression

11

$$-\frac{d[DHA]}{dt} = (\frac{k_1'K_2}{[H^+]} + k_2')[HDA][HSO_3^-] \quad . \tag{11}$$

Substituting the mass balance expression, $T_S = [SO_3^{2-}] + [HSO_3^-]$, into Equation 11 gives

$$k' = k_{Obsd}' = \left(\frac{K_2}{[H^+]}k_1' + k_2'\right)\left(\frac{[H^+]}{K_2 + [H^+]}\right) \quad . \tag{12}$$

Equation 12 can be rewritten as

$$k^* = \frac{k_{Obsd}'(K_2 + [H^+])}{[H^+]} = K_2k_1'\frac{1}{[H^+]} + k_2' \quad . \tag{13}$$

Figure 10 is a plot of the specific constant, k^*, as a function of the reciprocal of the hydrogen ion concentration. The plot gives a straight line with slope equal to K_2k_1' and a y intercept of k_2'. The values of k_1' and k_2' are listed in Table II.

Table II. Specific Rates (M^{-1} min^{-1}) for Dehydroascorbic Acid Reduction by Sulfite Ion

	20°C	55°C
k_1	4.3×10^{-1}	4.7
k_2	6.6×10^{-2}	1.2

3 CONCLUSIONS

This investigation has revealed a very significant catalyzed reaction path for the regeneration of Fe(II)*EDTA by adding ascorbic acid in the SO_2/NO_x scrubber system. This catalytic system can be described as one in which oxidized ferrous is reduced by ascorbate ions and oxidized ascorbate is then reduced by sulfite/bisulfite ions, which come from dissolution of SO_2 in the flue gas. The role of this path can be enhanced by increasing either the temperature or pH. The reaction kinetics have been determined for both reduction reactions at the scrubber operating temperature ($\sim 55°C$). The rate of reduction of Fe(III)*EDTA by ascorbic acid can be expressed as first order with respect to the concentration of both Fe(III)*EDTA and the monoionic species of ascorbic acid, HA^{-1}, and negative first order with respect to Fe(II)*EDTA concentration. The rate of reduction of oxidized ascorbate by sulfite/bisulfite ions can be expressed as first order with respect to the concentration of dehydroascorbic acid and first order with respect to the total sulfite concentration.

4 ACKNOWLEDGMENT

5 REFERENCES

1. Harkness, J.B.L., and R.D. Doctor, 1985, *Development of Combined Nitrogen Oxide/Sulfur Oxide Environmental Control Technology*, Argonne National Laboratory report ANL/ECT-14, Argonne, Ill.

2. Harkness, J.B.L., and R.D. Doctor, 1986, "Simultaneous NO_x/SO_x Removal in Aqueous Scrubber Chemistries," presented at the American Institute of Chemical Engineers National Meeting, New Orleans, La., April.

3. Chang, S.G., and D. Littlejohn, 1990, "Reaction of Ferrous Chelate Nitrosyl Complexes with Sulfite and Bisulfite Ions," *Ind. Eng. Chem. Res.* 29:10-14.

4. Mendelsohn, M.H., C.D. Livengood, and J.B.L. Harkness, 1991, "Combined SO_2/NO_x Control Using Ferrous*EDTA and a Secondary Additive in a Lime-Based Aqueous Scrubber System," 1991 SO_2 Control Symposium, Vol.2, Session 5A -6B, Washington, D.C., Dec. 3-6, 1991.

DISCLAIMER

Figure 1 NO_x Removal with Fe(II)*EDTA and with or without Sodium Ascorbate in Hydrated Lime Chemistry
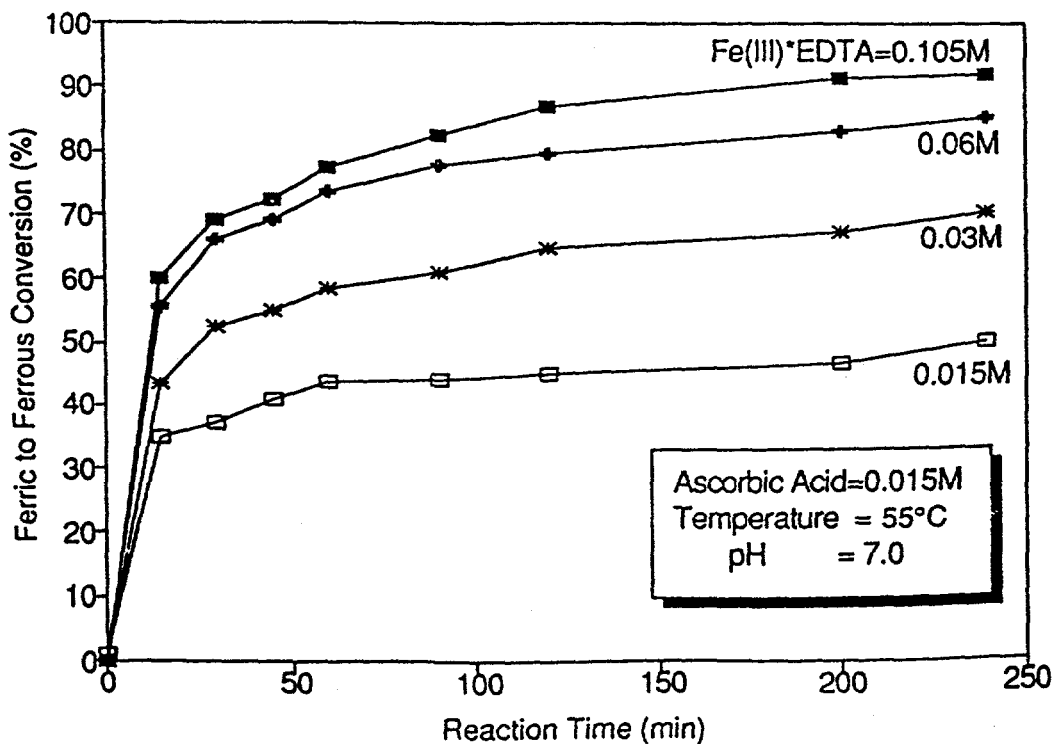
Figure 2   Concentration Of Fe^{+2} Ion in the Reacting Solution at Various Concentrations of Fe(III)*EDTA as a Function of Time
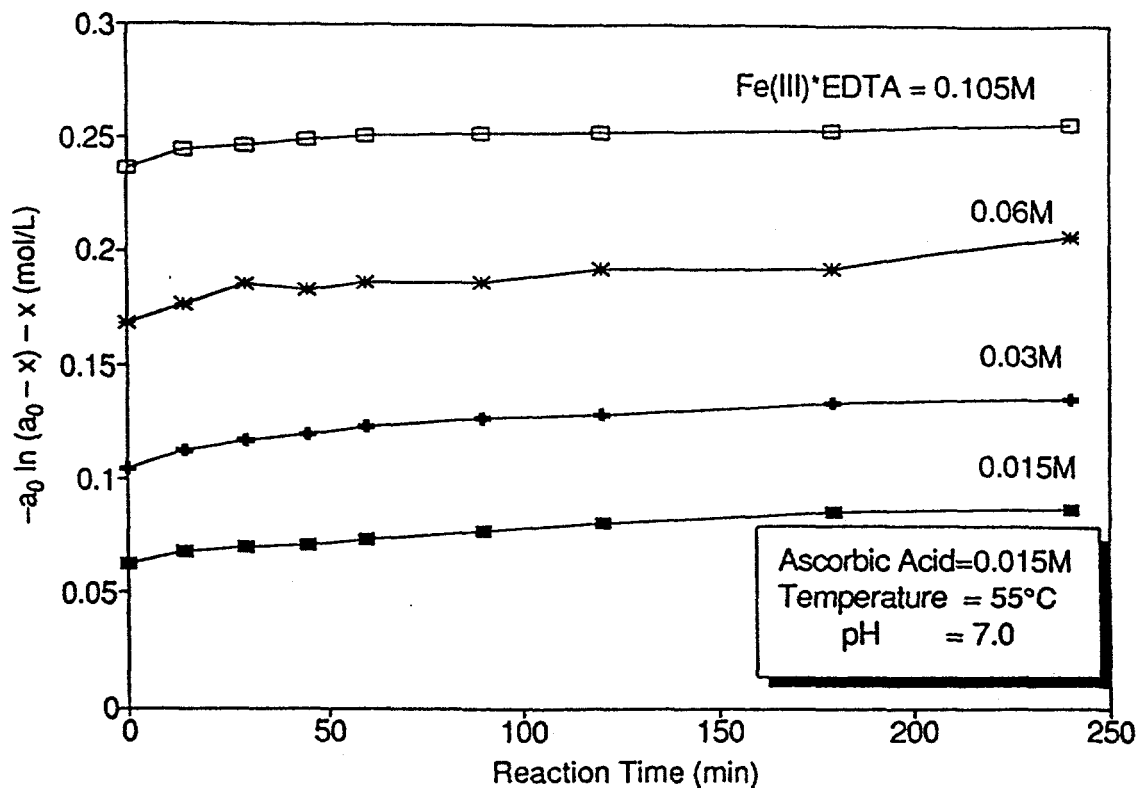
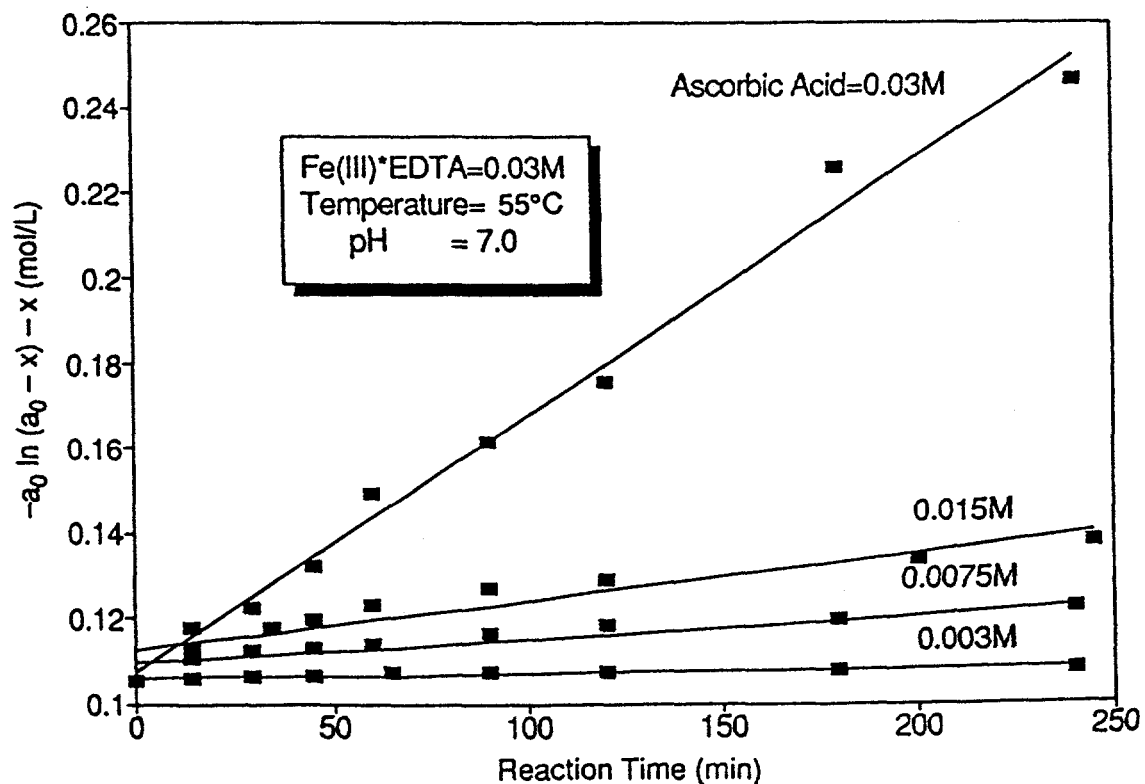**Figure 3 Effect of Fe(III)*EDTA Concentration on the Ascorbic Acid Reduction Reaction at a pH of 7.0**

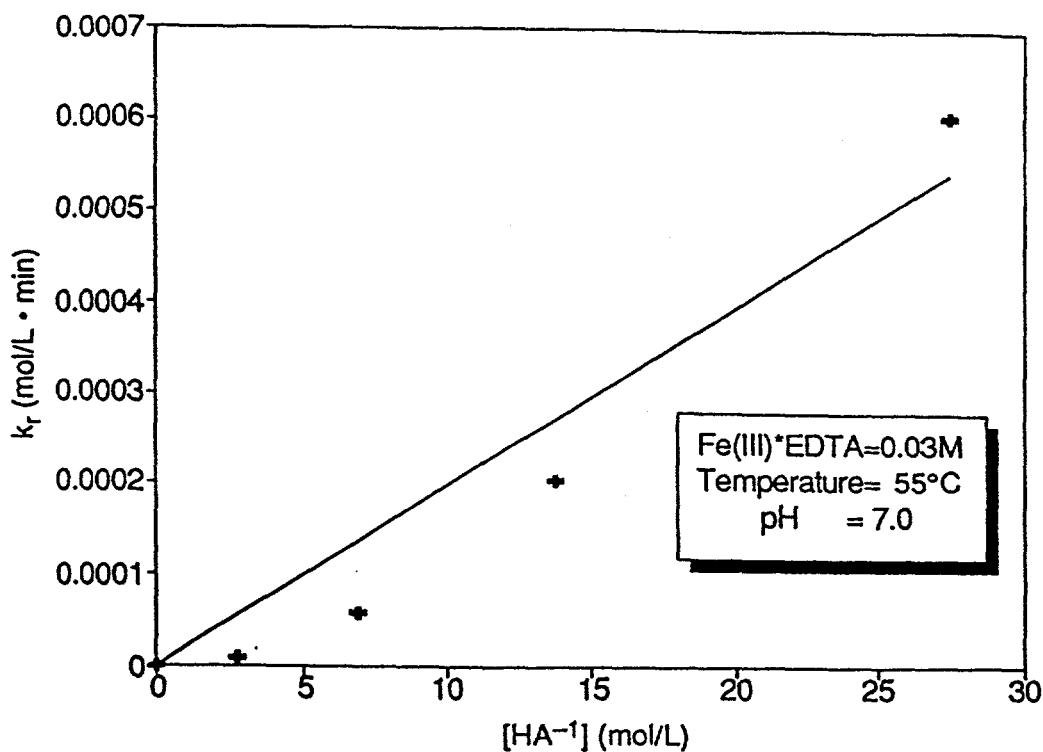**Figure 4   Effect of Ascorbic Acid Concentration on the Reduction Reaction at a pH of 7.0**

Figure 5 Reaction Rate Constant, k_r, for the Reduction of Fe(III)*EDTA Chelate by Ascorbic Acid as a Function of Ascorbic Anion Concentration
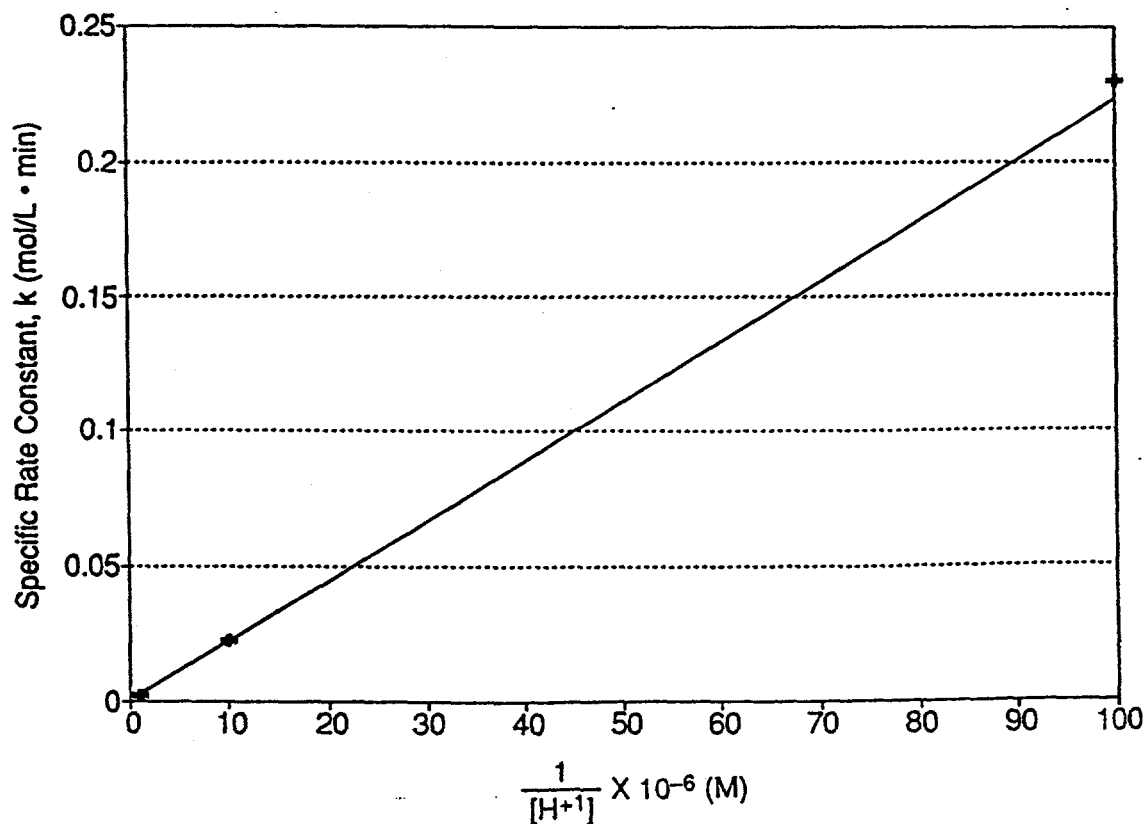

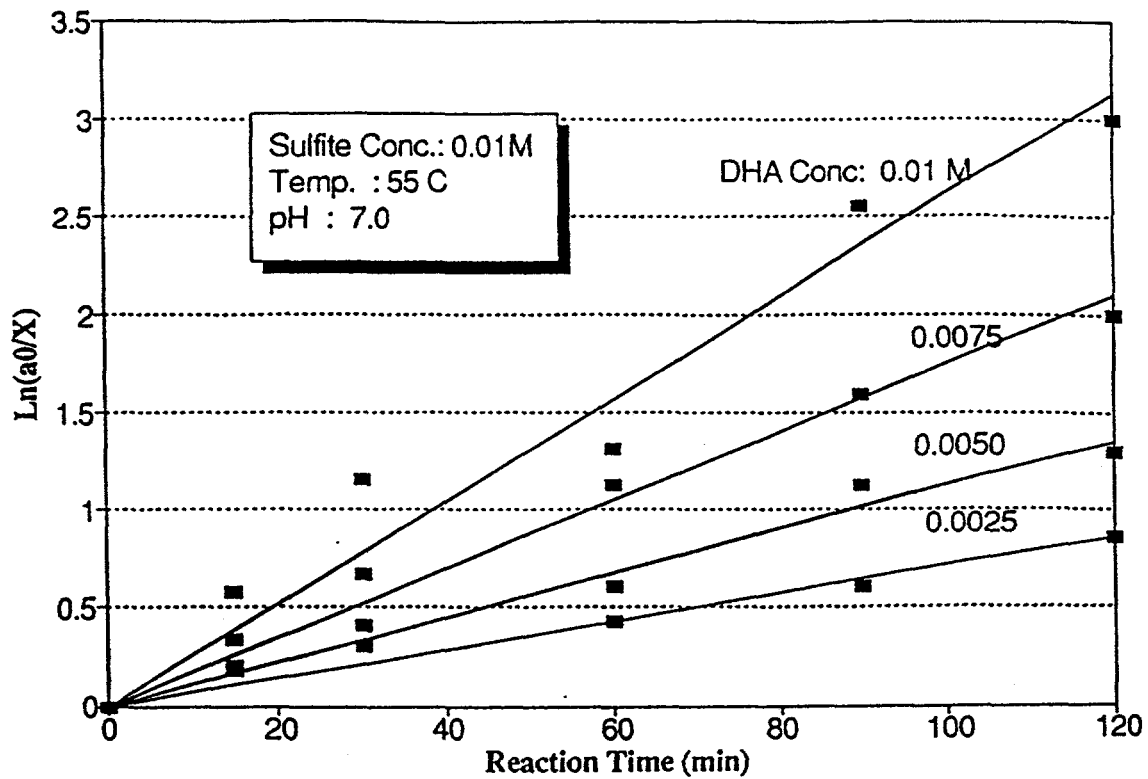**Figure 6** Dependence of the Specific Rate Constant, k, on the Hydrogen Ion Concentration

Figure 7 Concentration of Dehydroascorbic Acid Remaining in the Reacting Solution at Various Initial Concentrations of Dehydroascorbic Acid as a Function of Time
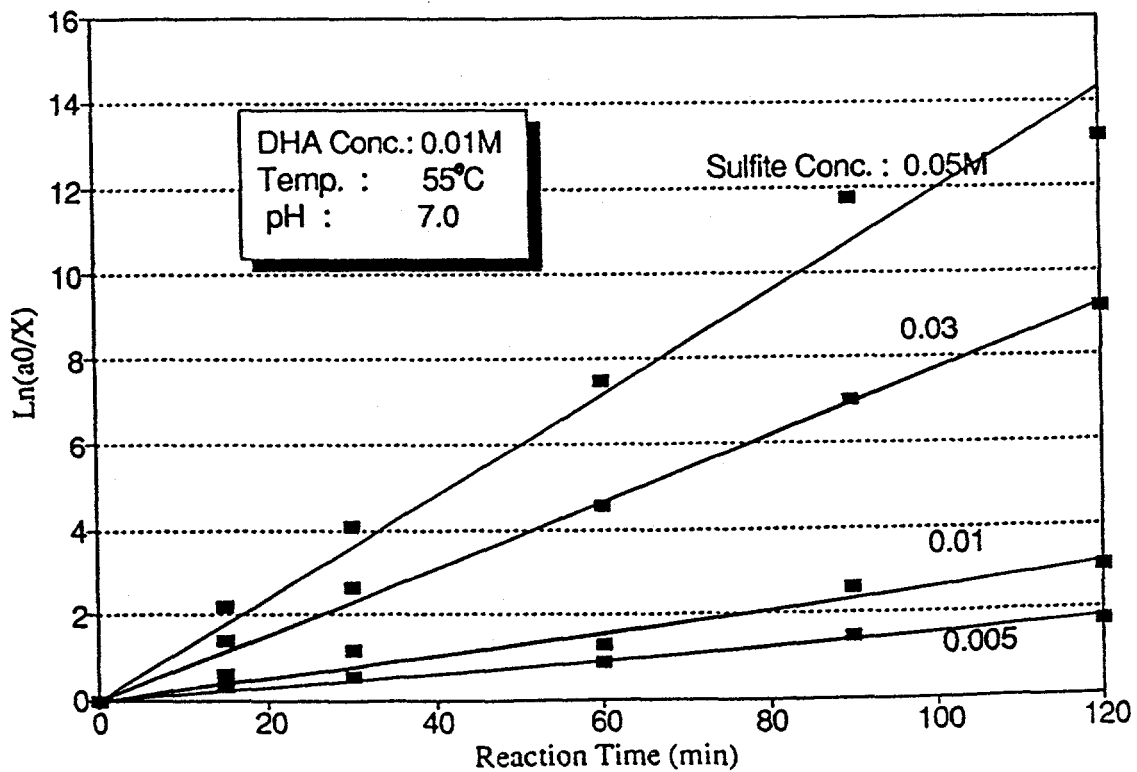

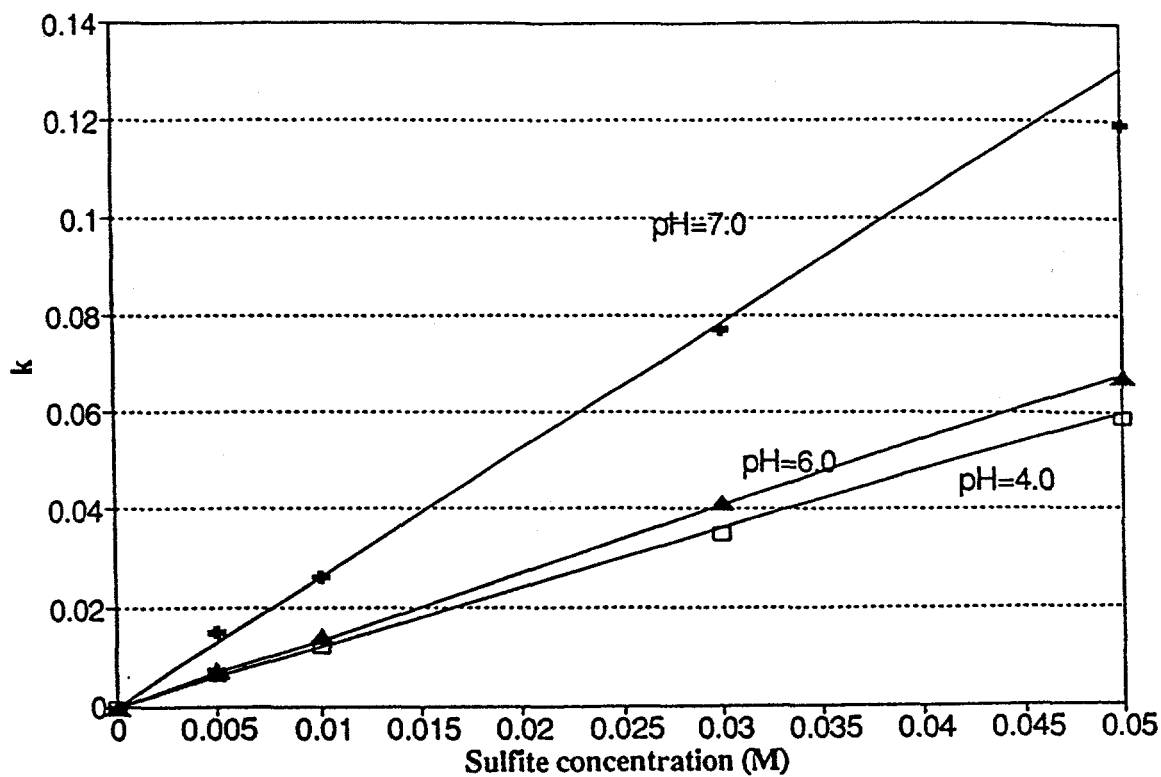**Figure 8** Effect of Dehydroascorbic Acid Concentration on the Reduction Reaction at a pH of 7.0

Figure 9 Reaction Rate Constant, k′, for the Reduction of Dehydroascorbic Acid by Sulfite as a Function of Sodium Sulfite Concentration under different pH Values
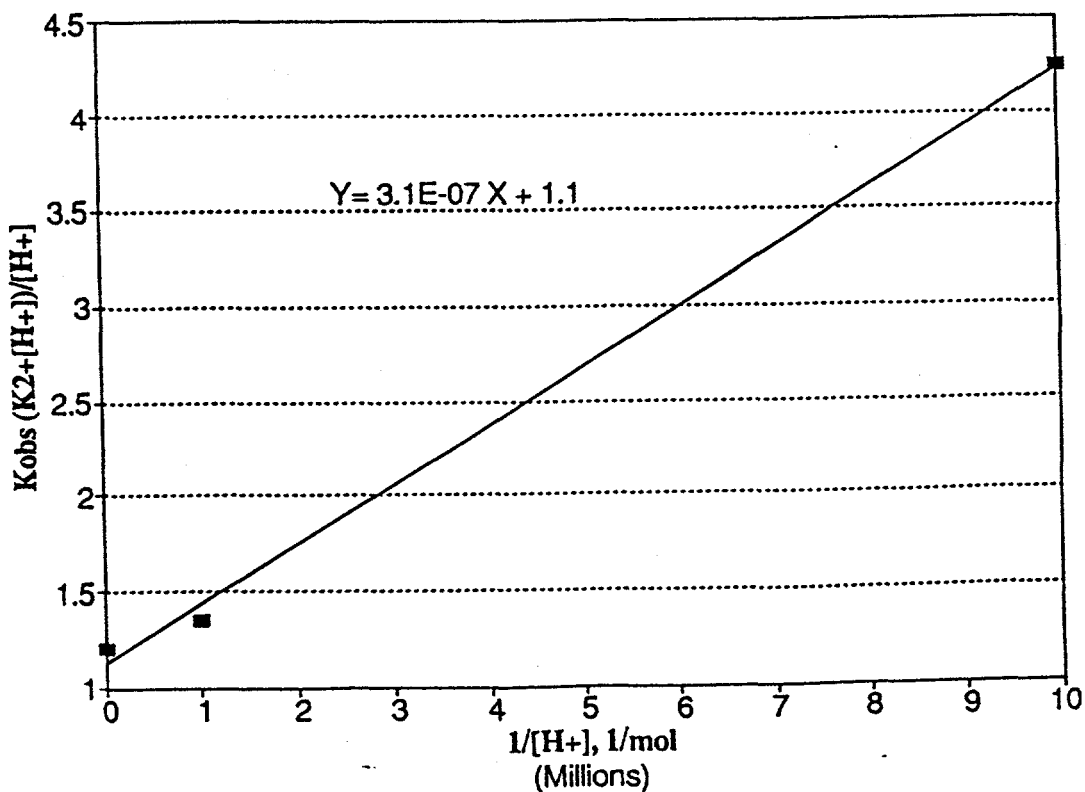

Figure 10 Dependence of the Specific Rate Constant, K*, on the Hydrogen Ion Concentration