Reversible Binding of NO to Fe(II)edta

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The equilibrium constants, enthalpy, and entropy of the reversible binding of nitrogen oxide to Fe(II)edta in an aqueous solution have been measured in the temperature range 38.5 to 70 °C. Experiments were carried out by absorbing NO under O_2 free conditions. The results show that, in the absorption of NO with Fe(II)edta solution, the value of $\Delta H°$ is -15.8 kcal/mol and $\Delta S°$ is -20.7 e.u.

A number of nitrogen monoxide complexes have been known for many years and have attracted the attention of many chemists because the way that NO interacts with transition metal complexes is similar to the way that CO and O_2 interact with those complexes. And recently, the structure of these complexes, the coordination geometry of the NO ligand,[1-4] ways of synthesizing nitrosyl complexes, and the coordinated NO reaction[5] have been under investigation.

In the course of our attempts to develop a method of removing nitrogen monoxide from a flue gas, we found that many of the peptide and amino acid complexes of iron(II) and cobalt(II) bind NO reversibly in aqueous solutions and, therefore, it became necessary to make a detailed investigation of the conditions under which this binding occurs. But only a few data are available with respect to the thermodynamics of this reaction. The experiments reported in this paper were carried out to determine the thermodynamics of the reversible binding of molecular NO to Fe(II)edta.

Although it has been known that the aqueous solution of Fe(II)edta absorbs NO, it has not been known whether Fe(II)edta binds NO reversibly, and the data have not been reported in its thermodynamics in detail. We found that, under O_2 free conditions, a light yellow aqueous solution of Fe(II)edta turns dark green as it absorbs NO, and it turns light yellow again upon heating, in a vacuum or when purged with nitrogen. We have been able to show that these color changes are caused by the following reversible reaction.

$$Fe^{II}edta + NO(g) \rightleftarrows Fe^{II}(NO)edta. \quad (1)$$

In this paper, we discuss the thermodynamics of the coordination of molecular NO to Fe(II)edta in an aqueous solution in the temperature range 38.5 to 70 °C.

Experimental

Materials. Reagent grade iron(II) sulfate and EDTA were used without further purification. The nitrogen monoxide gas that was used was an extra pure mixture of NO and N_2 (NIHON SANSO).

Preparation of Fe(II)edta. The aqueous solution of Fe(II)edta was prepared according to the following method. EDTA was first dissolved in distilled water under O_2 free conditions and the pH of the solution was adjusted to *ca.* 9 by adding a dilute NaOH solution. An equivalent amount of $FeSO_4$ was added to the solution and the pH of the solution was adjusted to the desired values by adding a dilute HCl or NaOH solution.

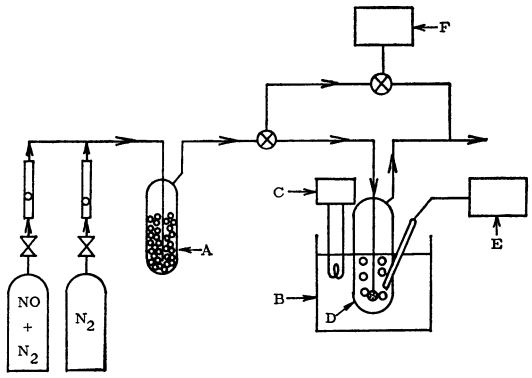

Fig. 1. Schematic diagram of apparatus.
A: gas mixer, B: water bath, C: thermostat
D: absorber, E: pH meter, F: NO_x meter.

The concentration of iron(II) was measured with the usual 1,10-phenanthroline method.[6]

Equilibrium Measurements. Equilibrium constants were determined at 38.5, 55, and 70 °C. A schematic diagram of the apparatus is shown in Fig. 1. The temperature was controlled to within ± 1 °C by a thermostat. All experiments were carried out under O_2 free conditions to avoid irreversible oxidation of the Fe(II)edta. A 100 ml quantity of the Fe(II)-edta solution (0.008—0.036 M) was introduced to an absorber. A mixture of NO and N_2 of known NO concentration was bubbled through the solution and the NO concentration in the outlet gas was measured with Beckman Model 951 NO_x meter. The gas flow rate was 0.73 N.T.P. l/min. NO absorption was carried out until equilibrium was reached, *i.e.* until the NO concentration in the outlet gas became equal to that n the inlet gas.

The amount of NO absorbed was determined by graphical integration of the NO concentration in the outlet gas.

Results and Discussion

To confirm the stoichiometry of NO uptake by Fe(II)edta, we first measured the quantitative NO uptake of an aqueous Fe(II)edta solution. The experiments were performed by absorbing pure NO gas obtained from Matheson Co. with a 0.1 M Fe(II)edta solution at pH 6 at room temperature. It was found from these experiments that 1.0 mol of NO was taken up by each mole of Fe(II)edta initially present, and hence that Fe(II)edta binds NO in a molar ratio of unity. The NO uptake by Fe(II)edta was also found by visible spectroscopy measurements to be reversible.

Figure 2 shows the visible absorption spectrum of the

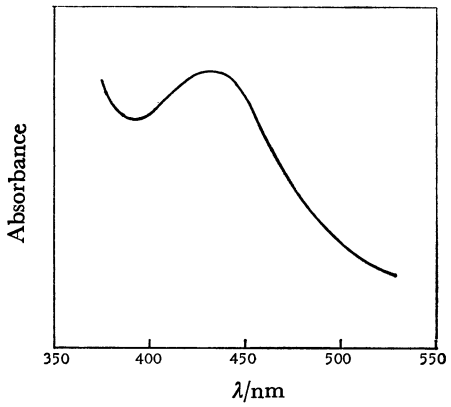

Fig. 2. Spectrum of $Fe^{II}(NO)$ edta at 15 °C.

aqueous Fe(II) (NO)edta solution. The initial light yellow color of the Fe(II)edta solution changes to dark green upon NO absorption and an absorption peak appears at λ=434 nm. When the solution is heated or purged with N_2, it regains its original light yellow color, with the desorption of NO. This indicates that Reaction 1 is completely reversible. Furthermore, the pH of the solution increased from 6.0 to 7.2 after absorbing NO. This increase is probably caused by the displaced carboxylic group since it binds the H^+ in the solution. The expression of the equilibrium constant for Eq. 1 can be written as

$$K_c = \frac{[Fe^{II}(NO)edta]}{[Fe^{II}edta]\cdot[NO]_{aq}} \quad (2)$$

Equation 2 can also be written as

$$K_c = \frac{[Fe^{II}(NO)edta]\cdot H}{\{[Fe^{II}edta]_0 - [Fe^{II}(NO)edta]\}\cdot[NO]_g} \quad (3)$$

where $[Fe^{II}edta]_0$ is the initial molar concentration of Fe(II)edta, $[Fe^{II}(NO)edta]$ is the equilibrium molar concentration of the NO adduct, $[NO]_g$ is the partial pressure of the NO in the gas, and H is the Henry's constant for the solubility of NO in water.

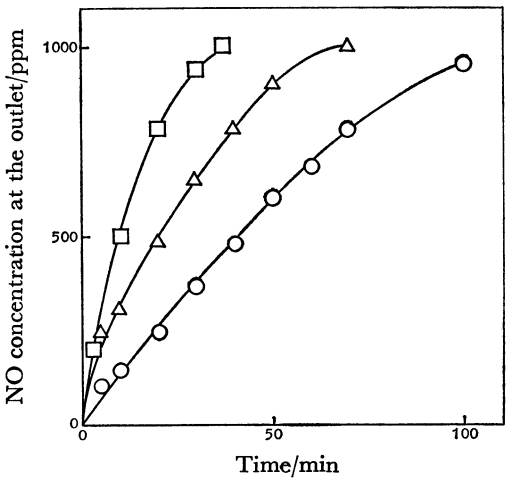

Fig. 3. Graphical illustration of the canges in NO concentration at the absorber outlet.
Inlet gas contents: NO 1000 ppm, N_2 balance, gas flow rate: 730 Nml/min, temperature: 55 °C, pH: 3.0, Fe(II)edta concentration: -□- 0.008 M, -△- 0.016 M, -○- 0.036 M.

Figure 3 shows changes in NO concentration at the absorber outlet for various concentrations of the Fe(II)-edta solution. By graphically integrating the outlet NO concentration curves, the amount of absorbed NO in each solution can be obtained.

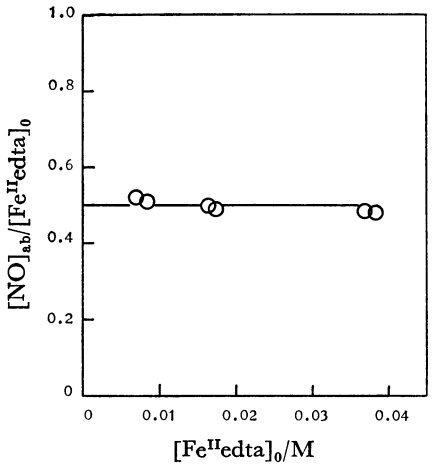

Fig. 4. Effect of $Fe^{II}edta$ concentration on NO absorption.

Figure 4 shows the effect of $[Fe^{II}edta]_0$ on the molar ratio of the absorbed NO to $[Fe^{II}edta]_0$ obtained from Fig. 3. It was found that the ratio was not affected by $[Fe^{II}edta]_0$ of 0.008—0.036 M at pH 3.

The effect of pH on the molar ratio of absorbed NO to total iron(II) ($[Fe^{II}]_0+[Fe^{II}edta]_0$) is shown in Fig. 5. The ratio was not affected by the pH value of the solution in the pH range of 3—6, but this ratio decreased drastically below a pH of 3.

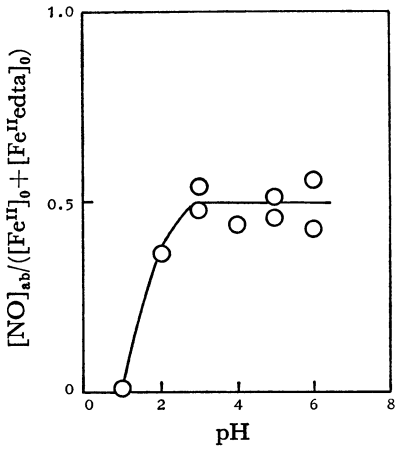

Fig. 5. Effect of pH on NO absorption.
Inlet gas content: NO 1000 ppm, N_2 balance, gas flow rate: 730 Nml/min, temperature: 55 °C, Fe(II): 0.02 M, edta: 0.02 M.

Because Fe(II)edta is very stable and almost 100% of the Fe(II) in the solution exists as Fe(II)edta,[7] in the pH-range 3—6, Eq. 3 can be rewritten as

$$\frac{[Fe^{II}edta]_0}{[NO]_{ab}} = 1 + \frac{H}{[NO]_g\cdot K_c} \quad (4)$$

In this experiment, the NO concentration and tempera-

Table 1. Thermodynamic data for reversible NO coordination to iron complexes

Complex	State	Temperature °C	H/K_c atm	K_c M^{-1}	$\Delta H°$ kcal/mol	$\Delta S°$ e.u.
Fe(II)edta	aqueous solution	38.5	0.18×10^{-3}	3.48×10^{6}		
		55.0	0.850×10^{-3}	0.859×10^{6}	−15.8	−20.7
		70.0	2.38×10^{-3}	0.339×10^{6}		
Fe(II)edta[9]	aqueous solution	60—70	—	—	−14.1	—
Fe(III)Cl(TPP)[10]	solid	25.0	—	3.45 atm^{-1}	−5.26	−15

ture were kept constant and, therefore, $H/[NO]_g$ was constant. This indicates that the equilibrium constant K_c which is defined by Eqs. 2 and 3, is not affected by pH in the range 3—6. But below a pH of 3 the dissociation of Fe(II)edta takes place, which gives rise to a decrease in the NO absorption.

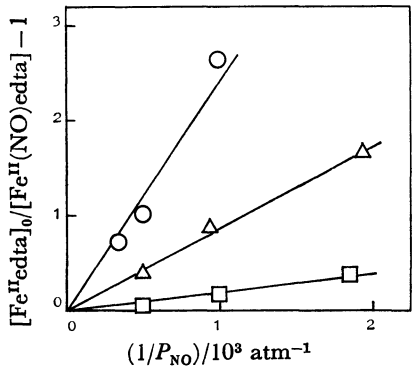

Fig. 6. Plot of $[Fe^{II}\ edta]_0/[Fe^{II}(NO)edta]-1$ *vs.* $1/P_{NO}$
pH: 3.0, temperature: -○- 70 °C, -△- 55 °C, -□- 38.5 °C.

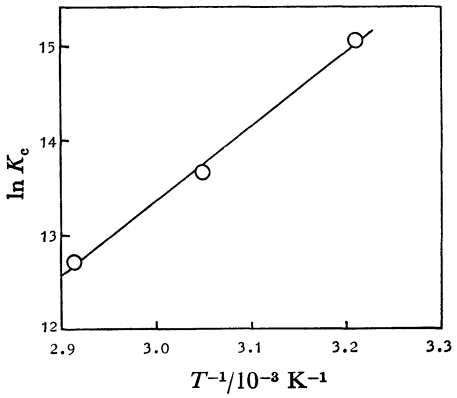

Fig. 7. van't Hoff plot of equilibrium constants for Eq. 1.

Figure 6 shows the relation between $[Fe^{II}edta]_0/[Fe^{II}(NO)edta]-1$ and $1/P_{NO}$ at temperatures of 38.5, 55, and 70 °C. H/K_c can be obtained from the slope of each line for each of these temperatures. Using Henry's constants,[8] the equilibrium constant at each temperature was obtained. These values are summarized in Table 1. Figure 7 shows the van't Hoff plot of these equilibrium constants. The values of thermodynamic quantities obtained from the van't Hoff plot are also given in Table 1. Enthalpy and entropy for Reaction 1 are $\Delta H°=-15.8$ kcal/mol and $\Delta S°=-20.7$ e.u., respectively. Recently Hasui studied the binding of NO to Fe(II)edta in an aqueous solution and measured its equilibrium constants in the temperature range 60—70 °C in the pH range 2.4—8.5.[9] They reported that the enthalpy change for the coordination of NO to Fe(II)edta was $\Delta H°=-14.1$ kcal/mol. This value is approximately same as our data.

The binding of gases with metal complexes is characterized by a small negative change in enthalpy and a relatively large change in entropy to compensate for the enthalpy change. This occurs because a gas loses its translational and rotational degree of freedom by coordination. The stability of such reversible complexes is examined by comparing their $\Delta H°$ values. But to the authors' knowledge, the only available thermodynamic data to date for the reversible binding of NO with iron complexes other than Fe(II)edta are those obtained by Vasca.[10] Their data are shown in Table 1 together with our data. But their data are for NO absorption by Fe(III)Cl (TPP) (TPP=tetraphenyl porphinate)in the solid state. Further extensions of the present work to different solvent systems and ligands will enable us to establish more fully the factors contributing to the stability of reversible NO complexes.

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