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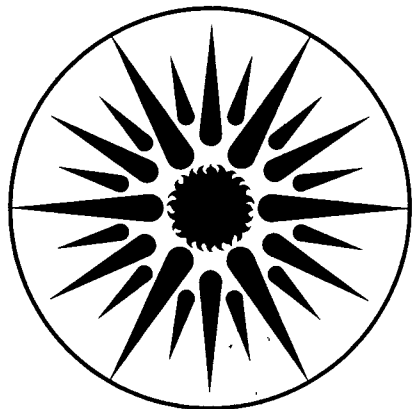
THE STOICHIOMETRY OF FERROUS NITROSYL CHELATES

D. Littlejohn and S.G. Chang

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The Stoichiometry of Ferrous Nitrosyl Chelates**

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The ferrous ion:nitric oxide ratio has been determined for the class of compounds $\text{Fe(II)(L)}_x(\text{NO})_y$, where $L = \text{H}_2\text{O}$, citrate, IDA, NTA and EDTA. All compounds studied were found to have a maximum ferrous ion:nitric oxide ratio of 1:1. In addition, the equilibrium constant for the binding of NO to $\text{Fe(II)(H}_2\text{O)}_6$ was determined to be 470 M^{-1} at pH 3 and 25°C and the equilibrium constant for the binding of NO to Fe(II)(cit) was determined to be $5.7 \times 10^4 \text{ M}^{-1}$ at pH 4 and 25°C .

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A number of ferrous chelates rapidly and reversibly react with nitric oxide in aqueous solutions[1] and have been proposed as agents to aid in the removal of nitric oxide from power plant flue gas streams.[2] There has been some discrepancy in the literature about the stoichiometry of ferrous nitrosyl complexes.[3-6] We have investigated the stoichiometry of the binding of nitric oxide to $\text{Fe(II)(H}_2\text{O)}_6$, Fe(II)(cit) , Fe(II)(IDA) , Fe(II)(NTA) and Fe(II)(EDTA) (cit = citrate, IDA = iminodiacetic acid, NTA = nitrilotriacetic acid, EDTA = ethylenediaminetetracetic acid) by measuring the absorption of NO by solutions of these compounds.

Experimental

Nitric oxide (Matheson, C. P.) was distilled three times and stored at liquid nitrogen temperature prior to use. Reagent grade chelates and ferrous ammonium sulfate were used to prepare the ferrous chelate solutions. All solutions were degassed prior to addition of the ferrous salt. The solutions were treated with concentrated HCl or NaOH to obtain the desired pH. A bulb of known volume was filled to the desired pressure of NO and expanded into an evacuated bulb containing the ferrous chelate solution. Once the pressure had stabilized (approximately 20 seconds), the solution was vigorously stirred. The pressure was monitored until it ceased to decrease, generally about 15 minutes. All pressure determinations were made with a Model 270 Baratron pressure gauge. After correcting for the water vapor pressure, the pressure drop was used to calculate the amount of NO absorbed by the solution. The solubility of NO in aqueous solutions[7] was taken into account to determine the amount bound to the ferrous complexes. All work was done at 25°C.

Results and Discussion

Fe(II)(H₂O)₆ + NO. Even at one atmosphere pressure of NO, Fe(II)(H₂O)₆ did not completely bind with NO, assuming 1:1 stoichiometry, due to the relatively small equilibrium constant for binding.[2,8] The amount of NO absorbed was used to calculate the equilibrium constant as a check of the accuracy of the technique. for $K_{eq} = [Fe(II)(H_2O)_5NO] / [Fe(II)(H_2O)_6][NO_{eq}]$, we obtained a value of $470 \pm 10 M^{-1}$ at pH 3, in excellent agreement with earlier results.[2,8]

Fe(II)(EDTA) + NO. The Fe(II)(EDTA)NO complex has a much larger equilibrium constant than the penta-aquo nitrosyl complex.[6] At nitric oxide pressures of approximately 650 torr, the Fe(II)(EDTA)NO complex was found to have 1:1 stoichiometry over a range of pH 4 to 9. This does not agree with Ogura and Watanabe,[9] who found 1:2 Fe(II):NO stoichiometry using an indirect method.

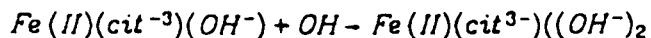
Fe(II)(NTA) + NO. The Fe(II)(NTA)NO complex also has a large equilibrium constant.[10] At pH > 5, the complex had 1:1 stoichiometry over a NO pressure range of 150 to 800 torr. At pH 3, the Fe(II):NO stoichiometry dropped to 1:0.9 because NTA does not bind Fe(II) very effectively at this pH.

Fe(II)(IDA) + NO. IDA does not bind Fe(II) as strongly as the other chelates studied.[9] It was necessary to have IDA concentrations in large excess of those of Fe(II) to ensure that the Fe(II) was completely complexed to IDA. The IDA:Fe(II) ratio was varied from 1:1 to 20:1, and the relative NO absorption increased up to the highest ratios, as shown in Fig. 1. All work was done at pH 4. The complex was found to have 1:1 Fe(II):NO stoichiometry at the highest IDA:Fe(II) ratios. Using the values of the fraction of Fe(II) bound to NO in Fig. 1 and the K_{eq} for Fe(II)(H₂O)₆ + NO, a stability constant for Fe(II) + IDA was determined, assuming that all Fe(II)(IDA) formed would bind with NO. A value of $K_{stab} = [Fe(II)(IDA)] / [Fe(II)][IDA] = 0.9 M^{-1}$ was obtained at pH 4. This does not agree well with the value given by Ogura and Watanabe.[9] It may be that the Fe(II)(IDA)₂ complex alone absorbs NO, and the stability constant we have obtained is for the formation of this complex, whereas the previously reported stability constant is

for Fe(II)(IDA). The assumption that essentially all the Fe(II)(IDA) would bind with NO appears to be valid, as the equilibrium constant reported by Griffiths and Chang for Fe(II)(IDA) + NO is $2.1 \times 10^5 M^{-1}$.

Fe(II)(cit) + NO. The Fe(II)(cit)NO complex was studied over a range of NO pressures and solution pH values with cit:Fe(II) ratios of 2:1 and 10:1. At the highest NO pressures (~700 torr) and pH ~ 4, the Fe(II):NO stoichiometry approached 1:1. At lower NO pressures (~100 torr), the amount of NO bound to Fe(II)(cit) displayed significant pH dependence. Also, at low NO pressures and at pH 7, there was an indication that the apparent equilibrium constant increased with decreasing NO pressure. The apparent equilibrium constant for Fe(II)(cit) + NO \rightarrow Fe(II)(cit)NO vs pH is shown in Fig. 2, along with charge states of citrate as a function of pH (dotted lines). The solid line is for cit:Fe(II) of 2:1 and the dashed line is for cit:Fe(II) of 10:1 where it differs from the 2:1 curve. The maximum value is in good agreement with those obtained by other methods.[11] Hamm, et al.[12] report that only the 2- and 3- charge states of citrate will bind Fe(II). At low pH conditions, a significant amount of Fe(II) is not bound to citrate at cit:Fe(II) = 2:1 because much of the citrate is in the 1- or 0 charge state. Increasing cit:Fe(II) to 10:1 reduces the amount of unbound Fe(II), increasing the apparent equilibrium constant. The decreasing apparent K_{eq} below pH 5 appears to be due to a decreasing fraction of Fe(II) bound to citrate with decreasing pH.

At higher pH conditions, Fe(II)(cit³⁻) forms a complex with OH⁻ that efficiently binds NO.[11] It appears that the decrease in the apparent equilibrium constant observed with increasing pH above pH 5 is due to the formation of a Fe(II)(cit³⁻)(OH⁻)₂ complex, where the second OH⁻ group blocks the NO from binding with the complex. This is supported by a titration curve of a solution of Fe(II) and citric acid, shown in Fig. 3. The curve exhibits a dip in the area between 4 and 5 equivalents of base added, attributable to the process:



The extinction coefficient of Fe(II)(cit) + NO solutions, when corrected for the amount of Fe(II)(cit) bound to NO, is largest around pH 4 and drops with

increasing pH. The rate of absorption of NO, as indicated by the rate of pressure decrease over the solutions at identical initial pressures, increases from pH 3 to 6, and then drops off fairly rapidly. These observations also support the existence of mono- and dihydroxy- Fe(II)(cit) complexes.

In conclusion, it appears that none of the ferrous nitrosyl chelates we have studied exist as dinitrosyls[3-5] under the conditions reported. The equilibrium constants obtained for $\text{Fe(II)(H}_2\text{O)}_6 + \text{NO}$ and $\text{Fe(II)(cit)} + \text{NO}$ are in agreement with the literature values.

Acknowledgements

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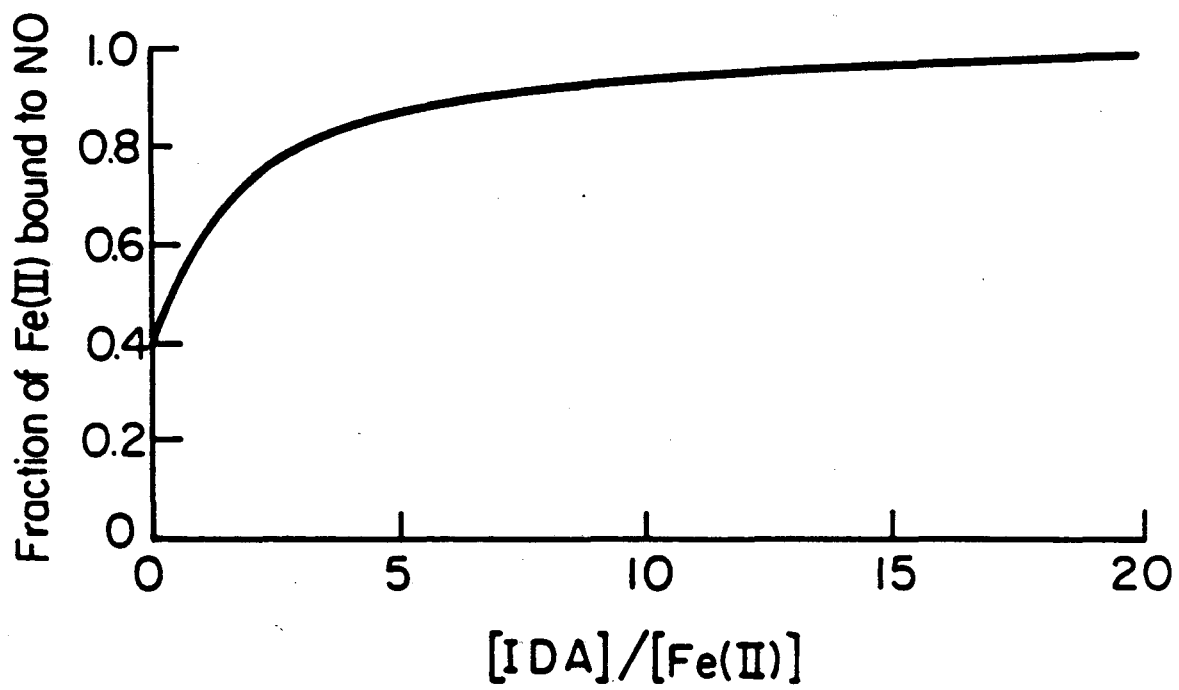
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Figure Captions

Figure 1 Fraction of Fe(II) bound to NO as a function of $[IDA]:[Fe(II)]$.

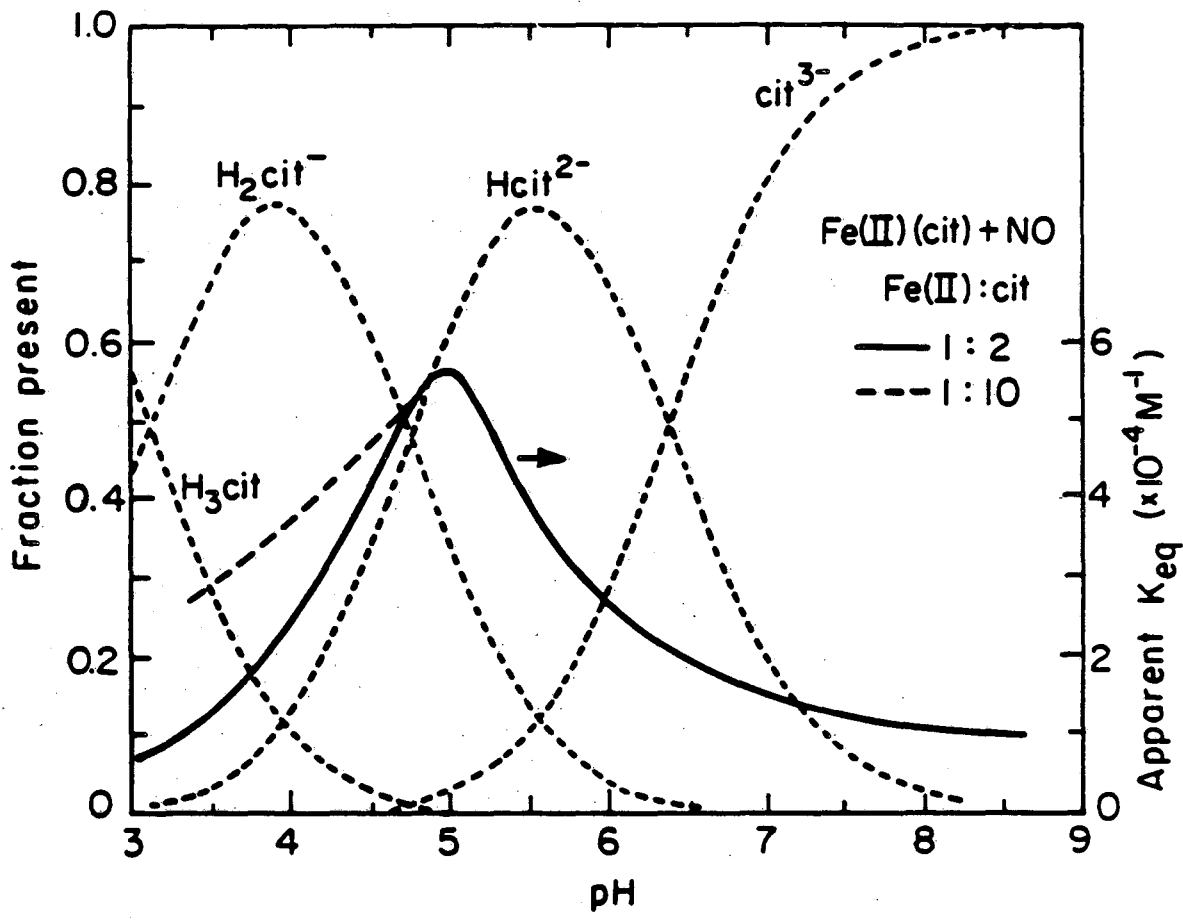
Figure 2 Apparent equilibrium constant of $Fe(II)(cit) + NO = Fe(II)(cit)NO$ and charge states of citrate as a function of pH.

Figure 3 Titration curve of Fe(II) + citric acid.



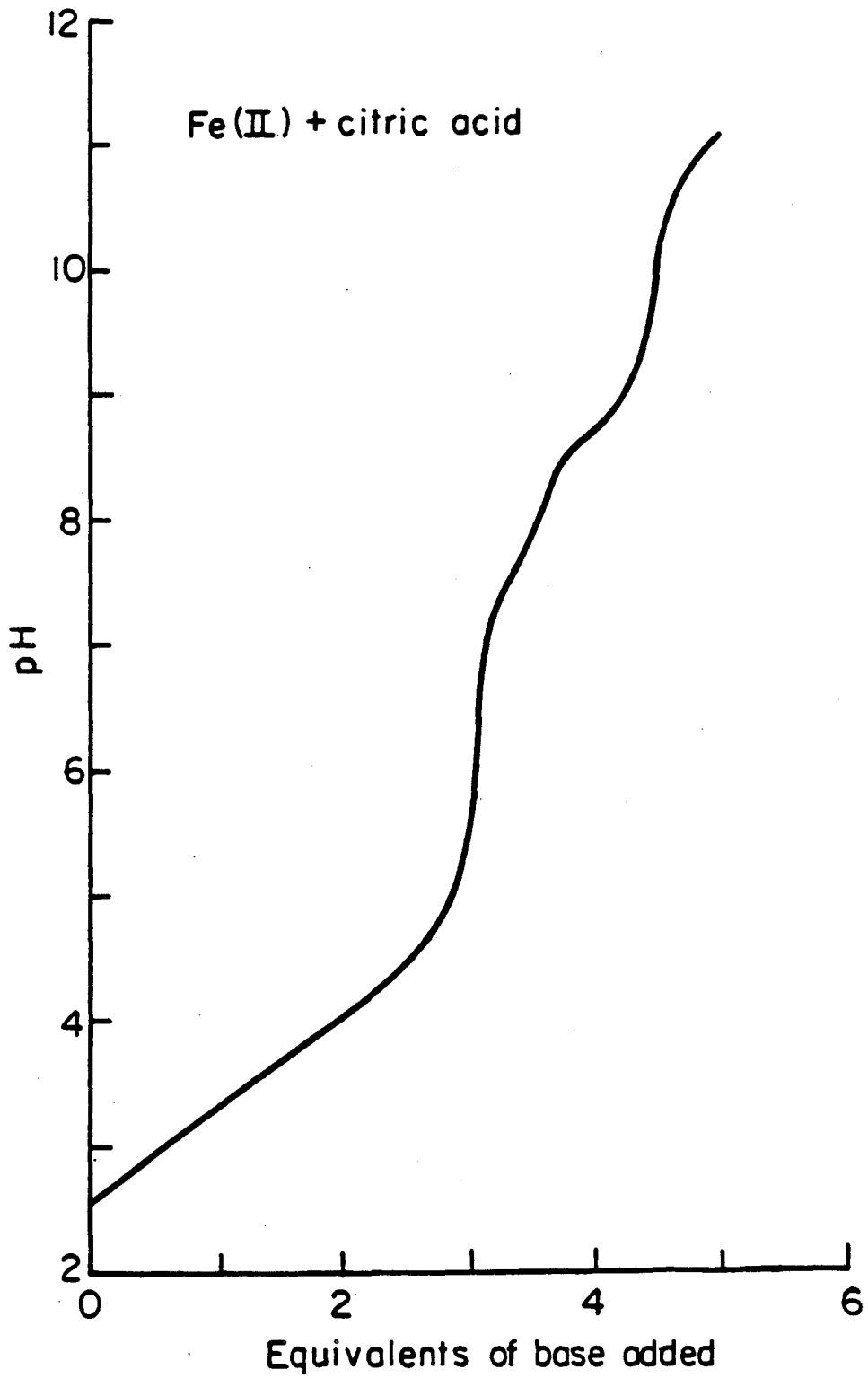
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Fig. 1



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Fig. 2



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Fig. 3

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