formed from the reactants $B^+(^1S_g) + D_2(^1\Sigma_g{}^+)$ arises from what must be a repulsive surface arising at the reaction asymptote from a $(B^+{-}D_2)[^1\Sigma_{(g)}{}^+$ (linear);$^1A'$ (C_s); $^1A_1$ $(C_{2v})]$ surface, the repulsiveness of which could be somewhat mitigated due to the long-range ion-induced dipole attraction $\alpha e^2/(2r^4)$, until it crosses the $(B^+{-}D_2)(^1\Sigma_{(u)}{}^+; {}^1A'; {}^1B_2)$ surface arising from the higher lying reaction asymptotes $B^+(^1P_u) + D_2$ where there could be an adiabatic transition from the surface arising at the asymptote from $B^+(^1S_g) + D_2$ to the equilibrium region intermediate surface arising from $B^+(^1P_u) + D_2$. There is another pair of reactants $B(^2P_u) + D_2{}^+(^2\Sigma_{(g)}{}^+)$ which can also combine to give $(B{-}D_2{}^+)(^{1,3}\Sigma_{(u)}{}^+ + {}^{1,3}\Pi_{(u)}; {}^{1,3}A + {}^{1,3}A' + {}^{1,3}A''; {}^{1,3}B_2 + {}^{1,3}A_1 + {}^{1,3}B_1$. However, it seems reasonable to assume little or no involvement of this latter surface since the products $BD^+(\tilde{X}\,^2\Sigma^+)$ and $BD^+(^2\Pi)$ arise from $B^+ + D$, and it seems to be a general phenomena that for these types of ion–molecule reactions the charge remains with the atom on which it started, provided this atom has the lower ionization potential.[12,13]

In the case of the $BD^+(^2\Pi)$ product the most probable intermediate $(BD{-}D)^+$ from which this product arises is the $(^3\Pi_{(u)}; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1)$ component of $(B{-}D_2)^+(^3\Sigma_{(u)}{}^+ + {}^3\Pi_{(u)}; {}^3A' + {}^3A' + {}^3A''; {}^3B_2 + {}^3A_1 + {}^3B_1) \leftrightarrow (BD{-}D)^+(^3\Pi_{(u)}; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1$ or ${}^3A_2 + {}^3B_2)$ which arises from $B+(^3P_u) + D_2$. While $(B{-}D_2)^+(^1\Sigma_{(u)}{}^+ + {}^1\Pi_{(u)}; {}^1A' + {}^1A' + {}^1A''; {}^1B_2 + {}^1A_1 + {}^1B_1)$ intermediates can arise from the higher reaction asymptote $B^+(^1P_u) + D_2$ these surfaces would be expected to be considerably higher in energy than the $(B^+{-}D_2)$ arising from $B^+(^3P_u) + D_2$. Since the experimentally observed endothermicity as determined from threshold measurements to form $BD^+(^2\Pi)$ from $B^+(^1S_g) + D_2$ is equivalent to the thermochemical endothermicity, this implies that the repulsive $(B^+{-}D_2)(^1\Sigma_{(g)}{}^+; {}^1A'; {}^1A_1)$ surface arising from $B^+(^1S_g)$ cuts the $(B^+{-}D_2)(^3\Pi; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1)$ surface at a point less than or equal to the thermochemical endothermicity. A surface crossing occurs with a change in spin from the singlet to the triplet surface and the $BD^+(^2\Pi) + D(^2S_g)$ arises from the corresponding $(BD{—}D)^+(^3\Pi; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1$ or ${}^3B_2 + {}^3A_2)$ surface.

Thus both the products $BD^+(\tilde{X}\,^2\Sigma^+)$ and $BD^+(^2\Pi)$ can arise from the reactants $B^+(^1S_g) + D_2$ combining at the reaction asymptote along a repulsive surface $(B^+{-}D_2)(^1\Sigma_{(g)}{}^+; {}^1A'; {}^1A_1)$. To form $BD^+(\tilde{X}\,^2\Sigma^+)$ this surface can make an adiabatic transition to the $(B^+{-}D_2)(^1\Sigma_{(u)}{}^+; {}^1A'; {}^1B_2)$ surface [arising from $B^+(^1P_u) + D_2$] leading to the product surface $(BD^+{-}D)(^1\Sigma^+, {}^1A'; {}^1A_1$ or ${}^1B_2)$ giving rise to $BD^+(\tilde{X}\,^2\Sigma^+)$. To form $BD^+(^2\Pi)$ this repulsive $(B^+{-}D_2)$ surface $(^1\Sigma_{(g)}{}^+; {}^1A'; {}^1A_1)$ arising at the reaction asymptote from $B^+(^1S_g) + D_2$ apparently crosses with a change of spin to the surface $(B^+{-}D_2)(^3\Pi; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1)$ [arising at the reaction asymptote from $B^+(^3P_u) + D_2$]. The $BD^+(^2\Pi) + D(^2S_g)$ product arises from the corresponding product surface $(BD^+{-}D)(^3\Pi; {}^3A' + {}^3A''; {}^3A_1 + {}^3B_1$ or ${}^3B_2 + {}^3A_2)$.

Acknowledgment. This work was carried out under the auspices of the U.S. Department of Energy.

Kinetic Study of Ferrous Nitrosyl Complexes

D. Littlejohn and S. G. Chang*

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 *(Received: August 28, 1981)*

The formation and dissociation rate constants and equilibrium constants for the reversible binding of NO to $Fe^{II}(H_2O)_5$, $Fe^{II}(cit)$, $Fe^{II}(acac)_2$, and $Fe^{II}(EDTA)$ in aqueous solution are reported (cit = citrate, acac = acetylacetonate, EDTA = ethylenediaminetetraacetate). The constants were determined (at 25 °C) as follows: $Fe^{II}(H_2O)_5NO$, $k_1 = 7.1 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 1.5 \times 10^3$ s^{-1}, $K = 470$ M^{-1}; $Fe^{II}(cit)NO$, $k_1 = 4.4 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 6.6 \times 10^2$ s^{-1}, $K = 670$ M^{-1}; $Fe^{II}(acac)_2NO$, $k_1 = 4.0 \times 10^2$ M^{-1} s^{-1}, $k_{-1} = 24$ s^{-1}, $K = 17$ M^{-1}; $Fe^{II}(EDTA)NO$, $k_1 \geq 6.0 \times 10^7$ M^{-1} s^{-1}, $k_{-1} \geq 60$ s^{-1}. The visible spectra of the complexes are also reported.

Introduction

Efficient techniques for removing NO_x and SO_2 from power plant flue gases are needed to meet air quality standards. One promising method for removing NO, which is only weakly soluble in aqueous solutions, is the formation of nitrosyl complexes from chelated metal ions.[1] Some metal chelates react rapidly and reversibly with NO. The nitrosyl complexes can react with the absorbed SO_2 to form a variety of products.[1-8]

Although a number of studies have been made of ferrous nitrosyl complexes,[9-11] little work has been done on the kinetics of the formation of these complexes:[12-14]

$$Fe^{II}(L) + NO(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{II}(L)NO(aq) \qquad (1)$$

where L represents the ligand which is complexed to the

---

(1) L. H. Yaverbaum, "Nitrogen Oxides Control and Removal, Recent Developments", Noyes Data Corp., Park Ridge, NJ 1979.

(2) S. B. Oblath, S. S. Markowitz, T. Novakov, and S. G. Chang, *J. Phys. Chem.*, **85**, 1017 (1981).

(3) S. G. Chang, R. Toossi, and T. Novakov, *Atmos. Environ.*, **15**, 1287 (1981).

(4) S. Gomiscek, R. Clem, T. Novakov, and S. G. Chang, *J. Phys. Chem.*, **85**, 2567 (1981).

(5) S. B. Oblath, S. S. Markowitz, T. Novakov, and S. G. Chang, *J. Phys. Chem.*, in press.

(6) S. B. Oblath, S. S. Markowitz, T. Novakov, and S. G. Chang, *Inorg. Chem.*, submitted for publication.

(7) S. G. Chang, paper presented at the Technical Advisory Committee, DOE/Advanced Environmental Control Technology Program, Morgantown, WV, Nov 6–7, 1980; Lawrence Berkeley Laboratory Report LBL-11800, 1980.

(8) S. G. Chang, talk presented at the Symposium on Advances in Flue Gas Desulfurization, American Chemical Society Meeting, Atlanta, GA, March 30, 1981.

(9) N. G. Connelly, *Inorg. Chim. Acta, Rev.*, 47 (1972).

(10) K. G. Caulton, *Coord. Chem. Rev.*, 14, 317 (1975).

(11) J. A. McCleverty, *Chem. Rev.*, **79**, 53 (1979).

(12) K. Kustin, I. A. Taub, and E. Weinstock, *Inorg. Chem.*, **5**, 1079 (1966).

(13) H. Hikita, S. Asai, H. Ishikawa, and S. Hirano, *J. Chem. Eng. Jpn.*, **10**, 120 (1977).

(14) M. Teramoto, S. Hiramine, Y. Shimada, Y. Sugimoto, and H. Teranishi, *J. Chem. Eng. Jpn.*, **11**, 450 (1978).

0022-3654/82/2086-0537$01.25/0

ferrous ion. A study[14] indicates that in one case the forward rate constant is quite rapid, exceeding 10^8 M^{-1} s^{-1} for the $Fe^{II}(EDTA)NO$ complex. This value was obtained indirectly and can be considered only an estimate.

Since no comprehensive study of the kinetics of ferrous nitrosyl complexes has been done, we have started a systematic study of the kinetics and spectra of these complexes with different ligands. We have investigated the kinetics of the following complexes: $Fe^{II}(H_2O)_5NO$, $Fe^{II}(cit)NO$, $Fe^{II}(acac)_2NO$, and $Fe^{II}(EDTA)NO$ (cit = citrate, acac = acetylacetonate, EDTA = ethylenediaminetetraacetate).

Experimental Section

Preparation of Complexes. The exact conditions under which each complex was studied varied somewhat depending on the ligand used; however, the general procedure for preparation was the same. The amount of the desired ligand to be used was measured and added to distilled water, along with H_2SO_4 or KH_2PO_4 for improving solution conductivity, adjusting ionic strength, or buffering. In some experiments the pH of the solution was adjusted with concentrated NaOH. All materials used were reagent grade. The pH of the solution was measured with a Corning Model 135 pH meter, calibrated with Mallinckrodt BuffAR buffer solutions. The ionic strengths of the solutions were as follows: $Fe^{II}(H_2O)_5NO$, $\mu = 0.54$; $Fe^{II}(cit)NO$, $\mu = 0.15$; $Fe^{II}(acac)_2NO$, $\mu = 0.21$; $Fe^{II}(EDTA)NO$, $\mu = 0.15$.

The solution was transferred to a vacuum line and degassed by evacuation of the air over the solution and sonification of the solution under vacuum. An argon atmosphere was placed over the solution and a measured amount of reagent-grade $FeSO_4$ was added. The molar quantity of ligand added was always well in excess of that of the ferrous ion. The solution was again degassed by the procedure mentioned previously.

Nitric oxide (Matheson, C.P.) was distilled 3 times, the first and last portions of each distillate being discarded. The purified nitric oxide was stored in liquid nitrogen until used. The nitric oxide was bubbled through the ferrous complex solution until the nitric oxide pressure over the solution was approximately 1 atm, as determined with a mercury manometer. The solution was then stirred for approximately 15 min to allow the chemical system to equilibrate.

Spectra. The prepared complexes were transferred under oxygen-free conditions to an evacuated 10-cm cell with Pyrex windows. The spectra of the complexes were obtained with a Cary Model 219 double-beam spectrophotometer. The scan conditions under which the spectra were taken were 5 nm s^{-1} with a time constant of 1 s and a slit width of 1.5 nm. The spectra were taken from 800 to 300 nm.

Kinetic Studies. The kinetics of the ferrous nitrosyl complexes were investigated with a temperature-jump apparatus similar to that described by Czerlinski and Eigen.[15] A temperature jump of about 8 °C was created by discharging a 0.25-mF capacitor, charged to 20 kV, through the cell, whose volume is approximately 1.4 cm^3. The discharge time is dependent on the ionic strength of the solution[16] but is generally less than 10 μs.

Light from a G. E. no. 1209 tungsten lamp is passed through a Bausch & Lomb high-intensity monochromator, directed through the cell and onto an RCA 1P28 photomultiplier tube. The signal from the photomultiplier tube is amplified and displayed on an oscilloscope, where it is photographed with a Polaroid camera. The oscilloscope is triggered by the discharge across the spark gap. Data were obtained by transferring the solution containing the ferrous nitrosyl complex from the vacuum line to the temperature-jump cell under oxygen-free conditions, charging the capacitor, and photographing the oscilloscope trace obtained after the discharge of the capacitor. Several shots were taken for each condition, and the results were averaged to get a relaxation time for each condition. The initial cell temperature was not regulated and was at the ambient temperature, 25 ± 2 °C.

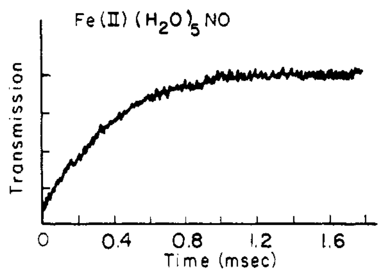

Figure 1. Typical oscilloscope trace for the response of $Fe^{II}(H_2O)_5NO$ solution to a jump in temperature. This initial signal level is at the base line.

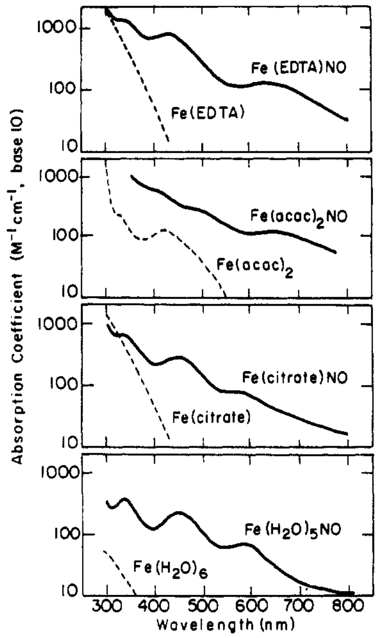

Figure 2. Absorption spectra of ferrous ion complexes from 800 to 300 nm for $Fe^{II}(H_2O)_5NO$, $Fe^{II}(cit)NO$, $Fe^{II}(acac)_2NO$, and $Fe^{II}(EDTA)NO$. The dashed lines represent the absorption spectra of the complexes without NO.

A typical oscilloscope trace is shown in Figure 1. The horizontal scale is 200 μs per division, and the vertical scale is transmission in arbitrary units. The initial signal level is at the bottom of the graph. The complex under investigation when the trace was obtained was $Fe^{II}(H_2O)_5NO$.

Results and Discussion

Spectra. The spectra for the complexes studied are shown in Figure 2. All spectra were taken at 25 °C. The spectra are for $Fe^{II}(H_2O)_5NO$ at pH 0.6, $Fe^{II}(cit)NO$ at pH 5.1, $Fe^{II}(acac)_2NO$ at pH 7.0, and $Fe^{II}(EDTA)NO$ at pH 3.7. The spectra of the complexes without NO are also shown (dashed lines). All complexes were prepared with approximately 1 atm of nitric oxide. Most spectra displayed some dependence on pH. Spectra obtained from complexes in acidic solutions often differed from those

---

(15) G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959).
(16) G. Czerlinski, *Rev. Sci. Instrum.*, **33**, 1184 (1962).

obtained from the same complexes in neutral or basic solutions, probably because of the ligands' presence in depronated forms at higher pH and the smaller tendency of Fe(II) to bind to the ligands at low pH.

With the exception of the $Fe^{II}(acac)_2$ complex, none of the complexes exhibited strong coloration in the absence of nitric oxide. The $Fe^{II}(acac)_2$ complex had a strong yellow coloration with a broad absorption centered at 420 nm. The spectra for the complexes with nitric oxide show three local absorption maxima over the spectral range in which the spectra were taken. The maximum in the near-ultraviolet region occurs between 320 and 360 nm, the maximum in the blue region occurs between 420 and 460 nm, and the maximum in the red region occurs beteen 580 and 660 nm.

The apparent extinction coefficient of the $Fe^{II}(H_2O)_5NO$ complex displayed a linear dependence on the nitric oxide pressure that was over the solution when it was prepared. This effect was not confirmed above a nitric oxide pressure of 1 atm and was not investigated in detail for the other complexes, where it would be expected to occur.

The spectra of the complexes also show a temperature dependence. The apparent extinction coefficients decrease with temperature because of the dissociation of the ferrous nitrosyl complex.

The strength with which the nitric oxide molecule binds to the ferrous complex manifests itself in several ways. A complex in which the nitric oxide is strongly bound will have a larger apparent extinction coefficient, a smaller dependence on nitric oxide pressure, and a smaller temperature dependence than a complex in which the nitric oxide is weakly bound.

The stoichiometries of the ligands bound to the ferrous ion were not checked in this study. The stoichiometries listed in Ringbom[17] have been used.

Kinetics. The response of the ferrous nitrosyl complexes to the temperature jump was monitored at a wavelength that yielded an optical density between 0.1 and 1.0 in the temperature-jump cell. With the exception of $Fe(acac)_2$, the ferrous complexes without nitric oxide did not have any significant absorptions in the visible region. $Fe(acac)_2NO$ was monitored at 480 nm, where there was a large difference in absorption between $Fe(acac)_2$ and $Fe(acac)_2NO$. The difficulty with cavitation in solution immediately following the discharge of the capacitor that was observed by Kustin et al.[12] was generally not a problem with the system in this study.

All of the ferrous nitrosyl complexes investigated in this study displayed a single exponential relaxation in response to the jump in temperature. Consequently, the rate constants can be determined from the equation

$$1/\tau = k_{-1} + k_1([Fe^{II}(L)] + [NO]) \qquad (2)$$

where τ is the relaxation time obtained from photographs of the oscilloscope traces and $[Fe^{II}(L)]$ is the concentration of the ferrous ion complex which is not bound to nitric oxide.

A number of factors must be considered in calculating the concentration of the $Fe^{II}(L)$ concentration. The amount of ferrous ion bound to the ligand in solution must be determined, and corrections must be made for the amount of complex bound to nitric oxide. Minor corrections must be made for hydrolysis and complexation with the buffer in solution.

The nitric oxide concentration in solution was determined from the nitric oxide pressure over the solution and the Henry's constant for nitric oxide. The Henry's law coefficient of 1.9×10^{-3} M atm^{-3} given by Armor[18] was used, with correction made for ionic strength and temperature.

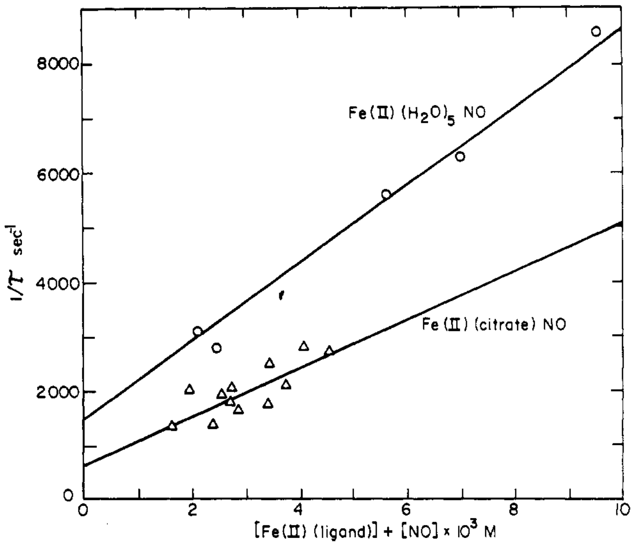

Figure 3. Plot of $[Fe^{II}(ligand)] + [NO]$ vs. reciprocal relaxation time for $Fe^{II}(cit)NO$ and $Fe^{II}(H_2O)_5NO$.

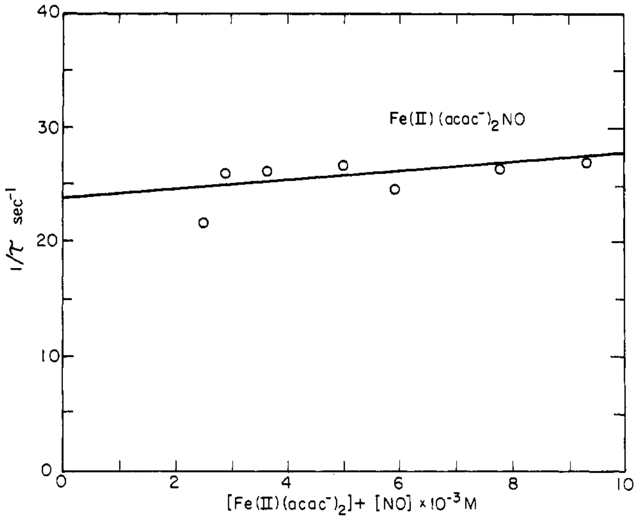

Figure 4. Plot of $[Fe^{II}(acac)_2] + [NO]$ vs. reciprocal relaxation time for $Fe^{II}(acac)_2NO$.

The data were analyzed by assuming a value for K_{eq} where

$$K_{eq} = k_1/k_{-1} \qquad (3)$$

and calculating the concentration of $Fe^{II}(L)$ that should be present. Values for the rate constants k_1 and k_{-1} are obtained from a least-squares fit to the reciprocal relaxation times and the calculated values of $[Fe^{II}(L)] + [NO]$. From these values of k_1 and k_{-1}, a value for K_{eq} is calculated. If the calculated value of K_{eq} differs significantly from the value assumed, the calculations are reiterated until convergence is obtained.

$Fe^{II}(H_2O)_5NO$. Concentrated H_2SO_4 (13.5 mL) was diluted with water to 1.0-L volume for the solution in which the $Fe^{II}(H_2O)_5NO$ complex was prepared. A plot of $1/\tau$ vs. $[Fe^{II}(H_2O)_5] + [NO]$ is shown in Figure 3. The points are the average of the values of $1/\tau$ obtained from each run, and the line is a least-squares fit to all values of $1/\tau$ obtained. The values corresponding to the line are k_1 =

---

(17) A. Ringbom, "Complexation in Analytical Chemistry", Interscience, New York, 1963.

(18) J. N. Armor, *J. Chem. Eng. Data*, 19, 82 (1974).

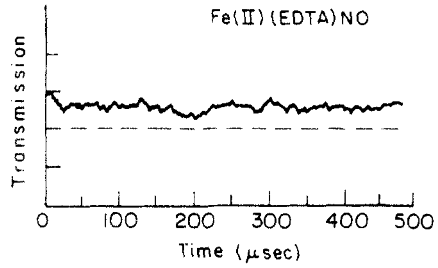

Figure 5. Typical oscilloscope trace for the response of $Fe^{II}(EDTA)NO$ to a jump in temperature. The dashed line indicates the initial signal level.

$(7.1 \pm 1.0) \times 10^5$ M^{-1} s^{-1}, $k_{-1} = (1.5 \pm 0.6) \times 10^3$ s^{-1}, and $K_{eq} = 470 \pm 200$ M^{-1}. These values are in good agreement with those given by Kustin et al.[12] and Hikita et al.[13]

Fe^{II}(cit)NO. Solutions of 0.15 M KH_2PO_4 were adjusted to pH 5.1 with concentrated NaOH. Although phosphate is not a particularly good buffer at this pH, it was used to improve the conductivity of the solution and to adjust the ionic strength. It also does not interact appreciably with ferrous ion. Spot measurements made after the preparation of the complex indicated that the pH did not change appreciably from the initial value. Above pH 4.5, essentially all of the citrate ions are present as the totally deprotonated species.[17] This simplifies the kinetics since only one type of ferrous ion–citrate ion complex will be present. In addition, virtually all of the ferrous ions will be in the form of a ferrous–citrate complex under these conditions. A plot of $1/\tau$ vs. $[Fe^{II}(cit)] + [NO]$ is also shown on Figure 3. It was found that values of $[Fe^{II}(cit)]$ greater than approximately 3.5×10^{-3} M gave erratic and inconsistent relaxations, possibly due to interaction between complex molecules or formation of different types of complexes at high concentrations. The least-squares fit to the values of $1/\tau$ obtained gave the following values for the rate and equilibrium constants: $k_1 = (4.4 \pm 0.8) \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 660 \pm 240$ s^{-1}, and $K_{eq} = 670 \pm 200$ M^{-1}.

$Fe^{II}(acac)_2NO$. The $Fe^{II}(acac)_2NO$ complex was prepared in a 0.15 M KH_2PO_4 solution that had been adjusted to pH 6.6 with concentrated NaOH. This pH was used as a compromise between the tendency of ferrous ions to precipitate at high pH and the inability of acetylacetone to bind ferrous ions at low pH, being in the un-ionized form. Concentrations of acetylacetone were in large excess of the concentrations of ferrous ions used to ensure that almost all of the ferrous ions were bound to acetylacetone in the form of $Fe^{II}(acac)_2$. The relaxation times of $Fe^{II}(acac)_2NO$ were much longer than those of the other complexes studied. A plot of $1/\tau$ vs. $[Fe^{II}(acac)_2] + [NO]$ is shown in Figure 4. A least-squares fit to the data provided the following results: $k_1 = 400 \pm 300$ M^{-1} s^{-1}, $k_{-1} = 24 \pm 2$ s^{-1}, $K_{eq} = 17 \pm 14$ M^{-1}.

Fe^{II}(EDTA)NO. This complex was prepared in 0.15 M KH_2PO_4 solutions adjusted to pH 5.1 with concentrated NaOH. At this pH EDTA binds Fe(II) ions strongly, so that very few free ferrous ions are present in solution. The relaxation times due to the jump in temperature were too fast to be measured with the present system.

A typical trace is shown in Figure 5. The dashed line represents the initial level of the signal. The transmission change in response to the jump in temperature was smaller for Fe^{II}(EDTA)NO than that observed in the other complexes. Consequently, the signal-to-noise ratio was smaller for the Fe^{II}(EDTA)NO complex than that for the other complexes. An upper limit of 10 μs was established for the relaxation time. The limiting factor in the present experimental setup is the length of time that it takes to discharge the capacitor through the solution. Teramoto et al.[14] obtained a value of about 1×10^6 M^{-1} for the equilibrium constant for the formation of Fe^{II}(EDTA)NO, while the values of ΔH and ΔS for the formation of Fe^{II}(EDTA)NO published by Hishinuma et al.[19] yield a value of about 1×10^7 M^{-1} for the equilibrium constant. These results indicate that the equilibrium constant is very high, and essentially all of the Fe^{II}(EDTA) complex will be bound to nitric oxide. Since the concentration of Fe^{II}(EDTA) will be small compared to that of nitric oxide, eq 2 can be approximated as

$$1/\tau \approx k_{-1} + k_1[NO] \qquad (4)$$

The lowest concentration of nitric oxide used in the experiments with EDTA was 1.6×10^{-3} M. Using the upper limit of τ as 10 μs and Teramoto's value of 1×10^6 M^{-1} for K_{eq}, and $K_{eq} = k_1/k_{-1}$, one obtains a value of about 6×10^7 M^{-1} s^{-1} for the lower limit of k_1 and a value of about 60 s^{-1} for the lower limit for k_{-1}. The lower limit for k_1 is in good agreement with the value of $k_1 = 1.7 \times 10^8$ M^{-1} obtained by indirect means by Teramoto et al.

Conclusions

A metal chelate used as a binding agent for NO in a wet flue gas denitrification system must react rapidly and reversibly with NO to be effective.[1] The forward and reverse rate constants and the equilibrium constants for the binding of NO to the metal chelates must be known in order to properly evaluate them. We have investigated four ferrous nitrosyl complexes in this study.

Values for the rate and equilibrium constants for the formation of $Fe^{II}(H_2O)_5NO$ determined in this study are in good agreement with those determined by other groups.[12] The forward and reverse rate constants for the formation of Fe^{II}(cit)NO are somewhat smaller than the values for the $Fe^{II}(H_2O)_5NO$ complex, while the equilibrium constant is larger. The kinetics for the formation and dissociation of the $Fe^{II}(acac)_2NO$ complex are much slower than any other complex studied.

The lower limits for the rate constants for the formation of Fe^{II}(EDTA)NO indicate that the nitric oxide in aqueous solutions reacts very rapidly with the Fe^{II}(EDTA) complex. Since the equilibrium constant strongly favors the nitrosyl form of the complex, this compound provides a very efficient mechanism to bind nitric oxide in solution. It is much more efficient in binding nitric oxide than the $Fe^{II}(H_2O)_5NO$, Fe^{II}(cit)NO, and $Fe^{II}(acac)_2NO$ complexes.

While Fe^{II}(EDTA)NO may be of value in wet flue gas denitrification systems, other compounds may be of equal or greater value. A study[20] indicates that the Fe^{II}(NTA)NO also binds NO rapidly and efficiently. NTA has the advantage of being less expensive than EDTA. Another important consideration is the ability of the nitrosyl complexes to regenerate the metal chelates in a scrubber system by reacting with absorbed SO_2.

Acknowledgment. We thank Professors Leo Brewer, Robert Connick, and Scott Lynn for helpful discussions; and we appreciate the support and encouragement of Mr. Gary Friggen and Mr. Jack Halow. This work was supported by the Morgantown Energy Technology Center, contract no. 81MC14002, through the Assistant Secretary of Fossil Energy of the US Department of Energy under contract no. W-7405-ENG-48.

---

(19) Y. Hishinuma, R. Kaji, H. Akimoto, F. Nakajima, T. Mori, T. Kamo, Y. Arikawa, and S. Nozawa, *Bull. Chem. Soc. Jpn.*, **52**, 2863 (1979).

(20) N. H. Lin, D. Littlejohn, S. G. Chang, *J. Chem. Eng. Data*, submitted for publication.