monodentate binding of the ligand X, so that the alternate path (proposed by Steinhaus for the Ni(trien)$^{2+}$ + Gly reaction) is not favorable. It is likely that other nickel(II) tetraaza ligand complexes that have either planar or *trans*-diaquo geometries and therefore must undergo rearrangement of the tetraaza ligand in order to react with polydentate ligands will react by a mechanism similar to the one proposed in this study.

Registry No. en, 107-15-3; Ni([14]aneN$_4$)$^{2+}$, 46365-93-9; glycine, 56-40-6; oxalic acid, 144-62-7.

Contribution from the Departments of Chemistry, Smith College, Northampton, Massachusetts 01063,
and University of California, San Diego, La Jolla, California 92093

Equilibrium and Kinetic Studies of Substitution Reactions of Fe(TIM)XY^{2+} in Aqueous Solution

ALISON BUTLER[1a] and R. G. LINCK*[1b]

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Equilibrium and rate constants for substitution reactions of some bisligated complexes of Fe(TIM) (TIM is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) in aqueous acetonitrile solutions are reported at 23 °C and an ionic strength of 0.5 M. The equilibrium constant for the replacement of CH_3CN by H_2O (K_1) in Fe(TIM)$(CH_3CN)_2^{2+}$ is 0.023 ± 0.002 whereas the same replacement in Fe(TIM)(CO)CH_3CN^{2+} (K_3) is 1.1 ± 0.1. The mechanism and the rates of establishment of these equilibria are dramatically affected by the π-accepting nature of the trans ligand, namely CH_3CN or CO. Substitution trans to CH_3CN is very rapid, with equilibration occurring on the time scale of milliseconds. On the other hand, the rate of approach to equilibrium in the replacement of CH_3CN for H_2O in Fe(TIM)(CO)CH_3CN^{2+} is complicated by two paths, one in which the ligand trans to the CO is directly replaced and the other in which the CO leaves, equilibration of the coordination sphere of the Fe(II) center occurs, and CO then recoordinates. This rate of approach to equilibrium occurs with a rate constant dependent upon the [CH_3CN], being about 3×10^{-3} s^{-1} at a [CH_3CN] of 1.0 M. In delineation of the complexities of the rate of approach to the equilibrium described by K_3, the rate constant for CO loss from Fe(TIM)(CO)H_2O^{2+} was determined to be 3.6×10^{-3} s^{-1}, and rate constants for all other steps involved were determined.

Introduction

Since the synthesis of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (hereafter abbreviated TIM) by Rose and co-workers in 1969,[2] a number of interesting chemical and physical properties of Fe(TIM)XY^{n+} molecules have been reported.[3-6] These properties led us to consider the possibility that this iron complex could act as a sensitizer for a number of photolytic reactions in aqueous solution. This possibility is given some credence by the report of Rose and co-workers, who have established that the bis(methanol) adduct, Fe(TIM)$(CH_3OH)_2^{2+}$, is oxidized by dioxygen in air and that the resultant Fe(III) complex is then susceptible to photolysis that leads to oxidation of methanol to formaldehyde accompanied by regeneration of the original Fe(II) complex.[4] Moreover, our attention was drawn even more strongly to this molecule by the report of Incorvia and Zink,[5] who found that photolyses of Fe(TIM)(CO)CH_3CN^{2+} are different depending on the solvent in which the photolysis takes place, a result that they interpreted as a highly unusual solvent mediation of a primary photophysical event. We decided, therefore, that further study of this molecule was appropriate to learn more about both its thermal and photolytic properties.

A variety of questions are raised by these considerations, excluding how the processes take place. Among them are the following: What, if any, are the substitutions that take place in Fe(TIM)XY^{2+} in aqueous solutions? What is the time scale in which substitution reactions of the axial ligands take place? What is the affinity of the Fe(TIM)$^{n+}$ center for axial ligands with back-bonding characteristics? What can be said of the inherent oxidation–reduction reactivity of Fe(TIM)XY^{2+}? In this and following reports on this molecule we will address these questions.

Our initial experiments on Fe(TIM)XY^{2+} quickly established that substitution reactions occurred on two separate time scales, one on the order of less than a second and the other on the order of minutes to hours. In this paper we report equilibria occurring when Fe(TIM)$(CH_3CN)_2^{2+}$ and Fe(TIM)(CO)CH_3CN^{2+} are in aqueous acidic acetonitrile solution and the kinetics of the slower processes of substitutions. In future papers, we will discuss the rapid substitution reactions of Fe(TIM)$(CH_3CN)_2^{2+}$, Fe(TIM)$(CH_3CN)H_2O^{2+}$, and Fe(TIM)$(H_2O)_2^{2+}$[7] and results of oxidation–reduction kinetics of Fe(TIM)XY^{2+}.[8]

Experimental Section

Materials. [Fe(TIM)$(CH_3CN)_2$]$(PF_6)_2$ was synthesized according to the procedure of Reichgott and Rose,[4] modified as indicated. Argon was used as an inert gas, and the reaction was stirred for 48 h at 35 °C under a stream of this gas rather than being sealed for 24 h under nitrogen. The crude yield contained a substantial amount of a tan-brown impurity, which was removed by recrystallization; about 0.5 g of the crude material was added to approximately 7 mL of CH_3CN, and the mixture was filtered quickly. Cold ethanol (about 50 mL) was added, and the mixture was filtered as soon as possible. The burgundy-colored solid thus obtained was washed with cold ethanol and cold ether quickly, so as to avoid any oxidation. [Fe(TIM)(CO)CH_3CN]$(PF_6)_2$ was prepared by the published procedure.[3] Solutions of Fe(TIM)XY^{2+} were prepared from the solid material by weight or analyzed for iron content by utilization of the 550-nm peak of Fe(TIM)$(CH_3CN)_2^{2+}$, where the extinction coefficient in

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[1] (a) Part of Ph.D. dissertation research, UCSD. (b) To whom correspondence should be addressed at Smith College.

[2] Baldwin, D. A.; Rose, N. J., paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, MN, April 1969; see Abstracts, No. INOR 020.

[3] Baldwin, D. A.; Pfeiffer, R. M.; Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5152.

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[6] Stynes, D. V.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1973**, 325.

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CH_3CN is 8800 M^{-1} cm^{-1}. Stock solutions of $Fe(TIM)(H_2O)_2^{3+}$ were prepared by allowing a known amount of $Fe(TIM)(CH_3CN)_2^{2+}$ to react with oxygen present in the solution of desired medium.

Vanadous ion solutions were prepared by amalgamated Zn metal reduction of vanadyl perchlorate. Solutions of bromine that were approximately millimolar in concentration were prepared by adding some Br_2 vapor to a solution 0.85 M in HBr. The concentration of Br_2 in the stock solutions was determined by reaction of an aliquot of the solution with ferrous ion, followed by back-titration of the excess Fe(II) with Ce(IV) to a ferroin end point. The first reaction is relatively slow, so care must be taken to let the reaction go to completion. Biacetyl was used from freshly opened bottles or redistilled prior to use. Acetonitrile was dried over CaH_2 and distilled from P_2O_5. The concentration of CH_3CN was determined by the dilution factor. Carbon monoxide was obtained from Matheson as their CP purity grade, 99.5%.

Physical Measurements. All kinetic and equilibrium studies were performed at 23 °C in a medium of 0.5 M ionic strength, composed of 0.1 M $HClO_4$ and 0.4 M $LiClO_4$. The kinetic experiments were followed at fixed wavelengths or by scanning at known time intervals on a Cary Model 14 recording spectrophotometer.

Results and Discussion

Equilibria of $Fe(TIM)XY^{2+}$ Species. Several complexes of $Fe(TIM)XY^{2+}$ are apparent when solid $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ is dissolved in coordinating solvents. When the burgundy-colored solid complex $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ is dissolved in water, under an argon atmosphere, the solution color is deep blue, with $\lambda_{max} = 650$ nm, not the burgundy color of a solution in CH_3CN, where $\lambda_{max} = 550$ nm. This is very similar to the observation made by Rose in methanol solvent,[4] and we take this result to indicate the presence of $Fe(TIM)(H_2O)_2^{2+}$. It is also apparent from this type of experiment that the sensitivity of $Fe(TIM)XY^{2+}$ to oxidation is very much greater when water is the axial ligand than when CH_3CN is. The blue solutions turned yellow when exposed to air or even when stored for extended periods of time. In contrast, solutions of $Fe(TIM)(CH_3CN)_2^{2+}$ in CH_3CN are reasonably stable with respect to oxidation, although over periods of days or weeks some decomposition is evident by the odor of biacetyl over the solutions. We also noted that when $Fe(TIM)(CH_3CN)_2^{2+}$ is dissolved in an aqueous solution of CH_3CN, in which the concentration of the latter is less than about 0.1 M, the color of the solution had a distinctive blue hue to it. Spectral examination of a solution 0.029 M in CH_3CN showed no sign of absorbance at wavelengths where the pure blue solutions of $Fe(TIM)(H_2O)_2^{2+}$ absorb, but it did show absorbance at both 550 nm and at longer wavelengths, about 600 nm—see Figure 1; this indicates that a third material is present in these solutions, a material that is most probably $Fe(TIM)(CH_3CN)H_2O^{2+}$.

In order to study the details of the equilibria involved in the displacement of the first CH_3CN in $Fe(TIM)(CH_3CN)_2^{2+}$ by water, we needed to handle the problem of the ready oxidation of $Fe(TIM)XY^{2+}$ when water is one of the ligands. The experiments were performed by deoxygenating a solution of $Fe(TIM)(H_2O)_2^{3+}$ in the ionic strength medium, establishing temperature equilibration, and then adding the appropriate amount of CH_3CN followed by the subsequent rapid addition of a reducing agent, V^{2+} in this case. The absorbance of this solution at 550 nm was monitored. Experiments to be reported elsewhere[9] showed that this reductant reacted quite rapidly with $Fe(TIM)(H_2O)_2^{3+}$ and, at the levels we added it, had no influence on the absorbance of the solutions measured at either 550 or 650 nm.[10] The range of [Fe(II)] for these experiments was 9×10^{-5} to 1.3×10^{-4} M and the range of $[CH_3CN]$ was 0.012 to 0.146 M; the $[V^{2+}]$, varied from 2.5×10^{-3} to 5×10^{-3} M, had no effect on the values of the equilibrium constants obtained.

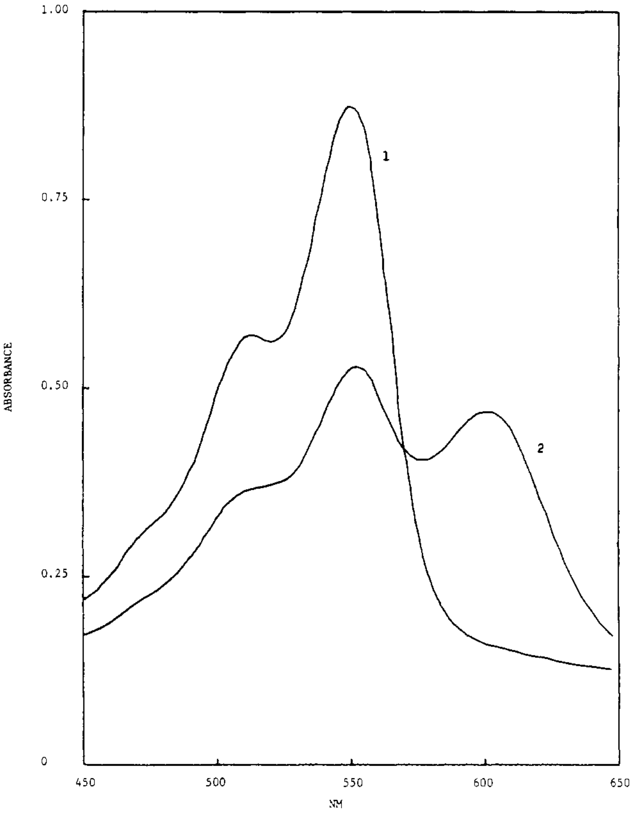

Figure 1. Visible spectra of (1) $Fe(TIM)(CH_3CN)_2^{2+}$ in 1.2 M CH_3CN and of (2) an equilibrium mixture of $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)(CH_3CN)H_2O^{2+}$. Both spectra were recorded immediately after preparation (see text). The total [Fe(II)] in the spectra is 9.2×10^{-5} M.

Given these experimental features, the determination of the equilibrium constant for the reaction indicated in eq 1 is

$$\mathrm{Fe(TIM)(CH_3CN)_2^{2+} + H_2O \overset{K_1}{\rightleftharpoons} Fe(TIM)(H_2O)CH_3CN^{2+} + CH_3CN} \quad (1)$$

straightforward. The expression for the absorbance for this system, assuming that there is no stoichiometrically significant concentration of $Fe(TIM)(H_2O)_2^{2+}$ present (see below) is given in eq 2. In this equation A is the absorbance, l is the cell

$$A/Tl = (\epsilon_1[CH_3CN] + \epsilon_2K_1)/([CH_3CN] + K_1) \quad (2)$$

length, T is the total amount of Fe(II) in the solution, and ϵ_1 and ϵ_2 are the extinction coefficients of $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)(CH_3CN)H_2O^{2+}$, respectively, at the wavelength of observation, 550 nm. Note that water has an activity of unity in our definition of K_1. Since no choice of $[CH_3CN]$ could be found where $Fe(TIM)(CH_3CN)H_2O^{2+}$ was the sole absorbing species at any chosen wavelength, ϵ_2 is not independently obtainable. Neither is ϵ_1, in the sense that the only solutions in which we could be assured that the "only" material is $Fe(TIM)(CH_3CN)_2^{2+}$ are those in which the $[CH_3CN]$ is so high that solvent effects and ion pairing are likely to interfere with the value. Therefore we treated eq 2 as one with three parameters to be fixed, ϵ_1, ϵ_2, and K_1. This equation was analyzed by a nonlinear least-squares technique[11] in terms of the parameters ϵ_1, ϵ_2, and K_1. The resultant values are ϵ_1 =

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(9) Linck, R. G., unpublished results.

(10) Solutions of $Fe(TIM)XY^{2+}$ in the presence of V^{2+} decay slowly. To take this into account, all absorbance values were extrapolated back to the time of mixing in order to determine the absorbance due to the equilibrium mixture of $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)(CH_3CN)H_2O^{2+}$ in the absence of $Fe(TIM)(H_2O)_2^{3+}$.

(11) Moore, R. H.; Ziegler, R. K. *Los Alamos Sci. Lab., [Rep.] LA* **1960**, *LA-2367*.

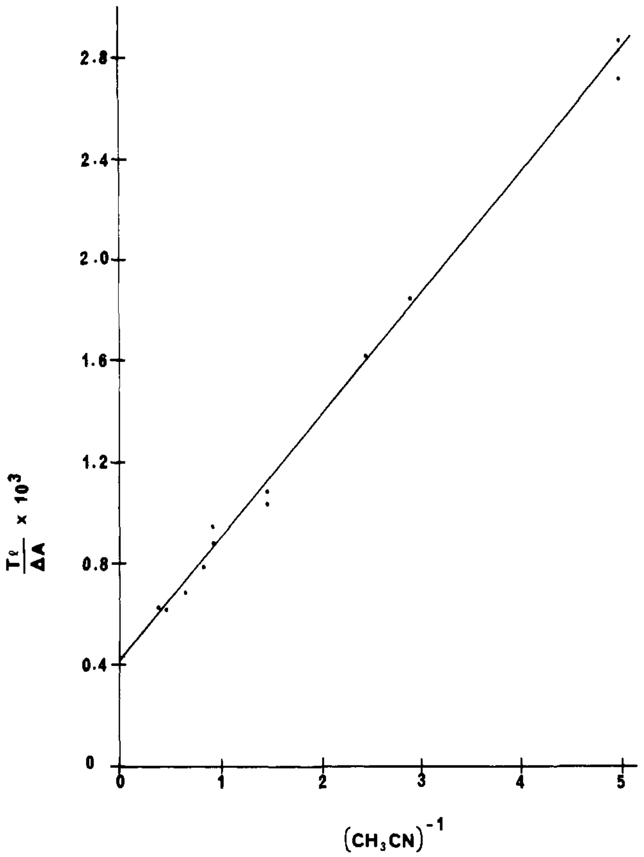

Figure 2. Plot of $-Tl/\Delta A$ vs. $[CH_3CN]^{-1}$ for the determination of K_3.

$(8.44 \pm 0.04) \times 10^3$, $\epsilon_2 = (2.4 \pm 0.2) \times 10^3$, and $K_1 = (2.3 \pm 0.2) \times 10^{-2}$.

Equilibria of Fe(TIM)(CO)X^{2+} Species. Rose and Reichgott report the synthesis of Fe(TIM)(CO)CH_3CN^{2+}. This material was of interest to us with regard to substitution of the ligand trans to CO. Early observations showed that when Fe(TIM)(CO)CH_3CN^{2+} is dissolved in water, under an atmosphere of CO, spectral shifts occur that are partially reversed by the addition of CH_3CN. This process is described in eq 3. We found that Fe(TIM)(CO)CH_3CN^{2+} had a λ_{max} at 435 nm and Fe(TIM)(CO)H_2O^{2+} had its maximum absorbance at 455 nm. The equilibrium constant for this process was measured by noting the change in absorbance obtained by adding CH_3CN to a solution of Fe(TIM)(CO)H_2O^{2+} or by allowing a solution of Fe(TIM)(CO)CH_3CN^{2+} to aquate in aqueous CH_3CN. The appropriate equation for this system is (4), where the symbols common to this equation and eq 2

$$\mathrm{Fe(TIM)(CH_3CN)CO^{2+} + H_2O \overset{K_3}{\rightleftharpoons} Fe(TIM)(H_2O)CO^{2+} + CH_3CN} \quad (3)$$

$$Tl/\Delta A = (\epsilon_3 - \epsilon_4)^{-1} + K_3/((\epsilon_3 - \epsilon_4)[CH_3CN]) \quad (4)$$

have the same meaning and ϵ_3 and ϵ_4 are the extinction coefficients of Fe(TIM)(CO)CH_3CN^{2+} and Fe(TIM)(CO)H_2O^{2+}, respectively. The data are shown in Figure 2; least-squares analysis yields $K_3 = 1.1 \pm 0.1$ M. Similar, but less extensive experiments were carried out in acetone as a solvent. The value for the equilibrium constant corresponding to K_3 in that solvent was found to be about 0.012 M.

It is of interest to compare these results for the substitution equilibrium given in eq 3 with those of Kadish and Chang[12] for the reaction of Ru(TPP)CO (TPP is tetraphenylporphyrin) with various ligands. These authors found that the reaction of Ru(TPP)CO with ligands in CH_2Cl_2 followed the Gutmann donor number[13] order reasonably well, with the exception of acetone. Our data can be analyzed in a similar way if the reaction shown in eq 3 is broken into two steps, the first involving the loss of CH_3CN to form a five-coordinate complex and the second involving recoordination of water to that five-coordinate complex. To make this comparison valid, the standard state of the solvent in eq 3 must be changed from unity to a value appropriate for the molar scale. With this procedure we are able to assess that the reactivity of Fe(TIM)CO^{2+} for water is 0.02 times as effective as it is for CH_3CN and that for acetone is 9×10^{-4} times as effective as that for CH_3CN. Thus, for Fe(TIM)CO^{2+}, neither water nor acetone, both of which have higher donor numbers than does CH_3CN, behaves as expected on the basis of the correlation reported by Kadish and Chang. The situation for acetone may be explained in both systems in that it is sterically hindered by nonbonding interactions between methyl hydrogens and the aromatic ring of these flat tetraaza complexes. We have no explanation for the deviation of water.

From a comparison of K_1 and K_3 it is clear that the equilibrium constant for replacement of CH_3CN by water from various species of the type Fe(TIM)(X)CH_3CN^{2+} is very sensitive to the nature of X: the loss of CH_3CN occurs more readily by a factor of 48 when X is CO than when it is CH_3CN. This feature is made more dramatic if the value for the replacement of CH_3CN by water from Fe(TIM)(CH_3CN)H_2O^{2+} is also considered; this parameter is obtainable by experiments to be reported in a forthcoming paper[7] and has a value of about 2×10^{-3} M. Thus as the ligand trans to the CH_3CN is changed from the electron-withdrawing CO to the less electron-withdrawing CH_3CN and then to electron-donating water, the equilibrium constant decreases by about 3 powers of 10, suggesting that the net electron density at the Fe(II) center is important in influencing the replacement of CH_3CN by the better σ donor water. That this is true is supported by the observation that the low-energy absorptivities of the various complexes show the same trend—see Figure 1. It seems likely that the low-energy absorbance is due to a charge-transfer transition from Fe(II) to the α-diimine linkages. This is supported by the high values of extinction coefficients and the fact that the fine structure of the absorbance, namely the presence of a high-energy shoulder about 1300 cm^{-1} above the main peak, is present in all spectra. The former is indicative of a charge-transfer spectrum; the latter, of the involvement of the diimine linkage rather than that of the axial ligand. The high-energy shoulder 1300 cm^{-1} above the major transition is most likely a vibronic state that is found in several Fe(II)–diimine complexes.[14] That Fe(TIM)(CO)CH_3CN^{2+} absorbs at 435 nm, Fe(TIM)$(CH_3CN)_2{}^{2+}$ at 550 nm, and Fe(TIM)(CH_3CN)H_2O^{2+} at 600 nm indicates that in this series the Fe(II) center is becoming increasingly electron rich. The change of the free energy associated with the substitution of CH_3CN by water follows the change in energy of the absorbance peak linearly. We conclude that CO is quite effective at reducing Fe(II) electron density and that CH_3CN is considerably less effective. This ability is transmitted to the metal, affecting the charge-transfer transitions, and to a trans CH_3CN, affecting the free energy of its replacement by water in a direct manner.

Kinetics of Substitution in Fe(TIM)(CO)X^{2+} Complexes. It was clear from the earliest observations on the CO-containing complexes in the absence of light that substitution of

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[12] Kadish, K. M.; Chang, D. *Inorg. Chem.* **1982**, *21*, 3614.

[13] Gutmann, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978.

[14] Griffiths, L.; Straughan, B. P.; Gardiner, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 305.

Table I. Rate of Approach to Equilibrium (Eq 3)

[CH_3CN], M	10^3k_{obsd}, s^{-1}	$10^2k_{obsd}\delta$,[a] M s^{-2}	$10^2k_{calcd}\delta$,[a] M s^{-2}
0.00	1.95	2.02	1.87
0.09	1.85	2.00	2.11
0.20[b]	2.07	2.44	2.39
0.22	1.82	2.17	2.45
0.34[b]	2.30	2.94	2.79
0.41	2.20	2.91	2.99
0.68[b]	2.53	3.82	3.80
0.80	2.57	4.11	4.21
0.95	2.67	4.55	4.72
1.14	3.06	5.63	5.41
1.53	3.50	7.38	6.94
1.68	3.67	8.13	7.55
1.83	3.55	8.24	8.22
2.29	3.63	9.58	10.3
2.40	3.99	10.8	10.9
2.51	4.25	11.9	11.4

[a] δ is defined in Table III. [b] Experiment done in duplicate; average value quoted.

the ligand trans to CO was quite slow. We have been able to investigate the rate of approach to equilibrium in the substitution process illustrated in eq 3. Experiments were performed by adding $Fe(TIM)(CO)H_2O^{2+}$ to a CH_3CN solution under an atmosphere of CO or by adding $Fe(TIM)(CO)CH_3CN^{2+}$ to the ionic strength diluent. We were not able to carry out the latter experiments by using solid $[Fe(TIM)(CO)CH_3CN](PF_6)_2$ because this compound dissolves slowly in water. If the solid complex was dissolved in a small volume of acetone in the dark and the solution was rapidly diluted with the ionic strength medium, investigation of the rate of approach to equilibrium from the left-hand side of eq 3 was possible. Experiments were conducted with the [CH_3CN] kept below 3 M to minimize the buildup of [$Fe(TIM)(CH_3CN)_2^{2+}$].[7] All kinetic runs gave linear plots of ln $(A_t - A_\infty)$ vs. time. We also investigated the dependence of the rate on [CO]. This experiment is only possible at low concentrations of CH_3CN, since buildup of $Fe(TIM)(CH_3CN)_2^{2+}$ at higher concentrations of CH_3CN would change the nature of the reaction. Under conditions of no excess CH_3CN, the aquations of CH_3CN from $Fe(TIM)(CO)CH_3CN^{2+}$ under an atmosphere of argon and under an atmosphere of CO are the same. The data showing the rate as a function of [CH_3CN] are given in Table I.

As we will show below, analysis of the kinetic data is complicated by a path that is not evident in eq 3. This path is introduced because loss of the ligand trans to CO is so slow that the mechanism involving loss of CO, equilibration of the axial coordination sphere with the solvent, and reattack by CO must be considered. In order to learn whether this supplementary path is feasible, we attempted to determine the rate of loss of CO from $Fe(TIM)(CO)H_2O^{2+}$. Since the equilibrium constant for the loss of CO is very small,[7] the rate must be measured by some process in which the kinetics are dictated by that loss, but with a net stoichiometry that differs from just loss of CO. The observation that the complexes containing CO are relatively inert to oxidation whereas those containing at least one water in the axial coordination position are very sensitive to oxidation suggests such a process. Accordingly, we studied the rate of oxidation of $Fe(TIM)(CO)H_2O^{2+}$ by bromine. In three experiments designed to determine the stoichiometry of the reaction shown in eq 5 we found that the

$$2Fe(TIM)(H_2O)CO^{2+} + Br_2 \rightleftharpoons 2Fe(TIM)(H_2O)_2^{3+} + 2CO + 2Br^- \quad (5)$$

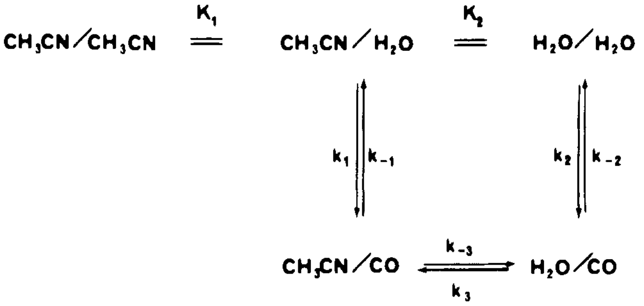
ratio of moles of Fe(II) that disappeared per mole of Br_2 added was 2.08, 2.16, and 1.91, thus confirming the stoichiometry given in that equation.

Table II. Kinetics of Oxidation of $Fe(TIM)(CO)H_2O^{2+}$ by Br_2 (T = 23 °C, I = 0.50 M[a])

$10^4[Br_2]$, M	$10^5[Fe(TIM)(CO)H_2O^{2+}]$, M	10^3k_{obsd}, s^{-1}
6.2	4.77	3.58
6.2	4.77	3.70
6.4	2.39	3.56
6.2	4.65	3.90
7.4	3.10	3.76
3.8	2.39	3.62
3.0	4.30	3.74[b]

[a] [ClO_4^-] = 0.50 M, [H^+] = 0.10 M. [b] Experiment done under an atmosphere of Ar.

Scheme I



To study the kinetics of this reaction, it was necessary to purge the solutions of $Fe(TIM)(CO)H_2O^{2+}$ of excess CO. Accordingly, argon was passed through the solution for at least 12 h. Reactions were run in cells with long path lengths in order to ensure that the [CO] did not build up enough to influence the kinetics as reaction progressed and in the dark in order to avoid any photoinitiated reaction.[7] The rate was measured by following the absorbance at 455 nm; plots of ln $(A_t - A_\infty)$ were linear for up to 90% reaction. The data obtained are given in Table II.

A postulated reaction scheme for the Br_2 oxidation of $Fe(TIM)(CO)H_2O^{2+}$ is given in eq 6–8. If a steady-state as-

$$Fe(TIM)(CO)H_2O^{2+} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} Fe(TIM)(H_2O)_2^{2+} + CO \quad (6)$$

$$Fe(TIM)(H_2O)_2^{2+} + Br_2 \xrightarrow{k_z} Fe(TIM)(H_2O)_2^{3+} + Br^- + Br \quad (7)$$

$$Fe(TIM)(CO)H_2O^{2+} + Br \xrightarrow{\text{fast}} Fe(TIM)(H_2O)_2^{3+} + Br^- + CO \quad (8)$$

sumption is made on [Br][15] and [$Fe(TIM)(H_2O)_2^{2+}$] and if [Br_2] is present in excess, the rate law derived from this set of reactions equates the observed rate constant to the expression given in eq 9. Under conditions where $k_z[Br_2] >> k_2[CO]$, k_{obsd} reduces to $2k_{-2}$.[16] The data shown in Table II confirm the predicted lack of dependence of the observed rate constant on [Br_2]. Therefore, measurement of the oxidation of $Fe(TIM)(CO)H_2O^{2+}$ by Br_2 offers a means of obtaining the rate of loss of CO from $Fe(TIM)(CO)H_2O^{2+}$, k_{-2}.

$$k_{obsd} = (2k_{-2})k_z[Br_2]/(k_z[Br_2] + k_2[CO]) \quad (9)$$

Since the rate of loss of CO from $Fe(TIM)(CO)H_2O^{2+}$ is of the same order of magnitude as the rate of approach to equilibrium between $Fe(TIM)(CO)H_2O^{2+}$ and $Fe(TIM)(CO)CH_3CN^{2+}$, it is clear that the rate of approach to

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(15) Although Br exists as a mixture of Br and Br_2^- under the conditions of this experiment, this has no effect on the analysis, and we ignore it here.

(16) The value of k_z is about 10^6 M^{-1} s^{-1} [8] and k_2[CO] is between 10 and 50 s^{-1} under the conditions of these experiments. Therefore, the [Br_2] could be chosen such that $k_z[Br_2] >> k_2[CO]$.

Table III. Definition of Parameters in Eq 11

parameter	equivalence	value × 10^2
α	$(k_{-1} + k_{-3})k_2K_2$	1.87 ± 0.17 M s^{-2}
β	$(k_{-2} + k_{-3})K_1[CO] + k_3k_2K_2[CO]$	2.51 ± 0.37 s^{-2}
γ	$k_1k_3[CO]$	0.52 ± 0.15 M^{-1} s^{-2}
δ	$(k_1[CH_3CN] + k_2K_2)[CO]$	*a*
$k_1[CO]$		700 ± 80 s^{-1} *b*
$k_2K_2[CO]$		1040 ± 340 s^{-1} *b*
k_{-1}		0.12 ± 0.22
k_{-2}		0.18 ± 0.06
k_3		0.074 ± 0.03
k_{-3}		0.064 ± 0.14

[a] Dependent on the $[CH_3CN]$. [b] From ref 7.

equilibrium must occur, at least partially, by the indirect path shown in Scheme I. If that is the only path for equilibration, then the rate law for the rate constant for the approach to equilibrium is given by eq 10. This equation demands that

$$k_{obsd} = \frac{k_{-1}k_2K_2[CO] + k_1k_{-2}[CO][CH_3CN]}{k_1[CO][CH_3CN] + k_2K_2[CO]} \qquad (10)$$

a plot of $k_{obsd}(k_1[CO][CH_3CN] + k_2K_2[CO])$ vs. $[CH_3CN]$ should be linear. The values of k_1 and k_2K_2 are taken from ref 7 and allow a test of the indirect mechanism. A plot of this kind over a range of $[CH_3CN]$ from 0.091 to 2.51 M is reasonably linear but does show positive deviations when the $[CH_3CN]$ exceeds about 1.2 M. A best straight line through the data gives a value for the slope of 0.038; the value this corresponds to is $k_1k_{-2}[CO]$. From the known values of $k_1[CO]$ as directly measured[7] and k_{-2}, which is the rate of loss of [CO] from $Fe(TIM)(CO)H_2O^{2+}$ available from the bromine oxidation experiments discussed above, the value of the slope can be calculated to be 0.013. Further, the ratio of the intercept to the slope of the plot is equal to the equilibrium constant for the reaction 3; the value determined from the linear least-squares analysis is 0.36, while the value directly determined is 1.1. Clearly, the model where only the indirect path leads to products is not satisfactory. Therefore, only a model in which both direct and indirect paths are present will be able to account for the data.

The rate law for a mechanism involving both direct and indirect paths of substitution, Scheme I, has an observed rate constant for the approach to equilibrium given by eq 11, where

$$k_{obsd} = (\alpha + \beta[CH_3CN] + \gamma[CH_3CN]^2)/\delta \qquad (11)$$

the symbols that stand for combinations of the rate constants used in the scheme are defined in Table III. This rate law demands that a plot of $k_{obsd}\delta$ vs. $[CH_3CN]$ be curved when the term in $[CH_3CN]^2$ becomes large enough, as was observed—see the last paragraph. The best fit to the parameters α, β, and γ can be determined by a nonlinear least-squares approach and yields the values given in Table III. That this fits the observed data reasonably well can be seen from the presentation of the computed values of $k_{obsd}\delta$ given in Table I. The parameters α, β, and γ can be decomposed to determine their constituent rate constants once values of $k_1[CO]$ and $k_2K_2[CO]$ are available.[7] These are also listed in Table III. Note that the value of K_3 determined from the ratio of the kinetic parameters, 0.88, is in reasonable agreement with the value determined from equilibrium absorbance measurements, 1.1.

Comparison of Substitution Rates. The values for the rate constants for loss of ligands from $Fe(TIM)(CO)CH_3CN^{2+}$ and $Fe(TIM)(CO)H_2O^{2+}$ are all within a factor of 2 of 10^{-3} s^{-1}. The values for the loss of CO seem reasonable when compared with rate constants for loss of CO from other low-spin Fe(II) complexes containing this group. Vaska and Yamaji[17] have reported that $Fe(DPGH)_2(py)CO$, where DPGH is the monoanion of diphenylglyoxime and py is pyridine, loses CO with a rate constant of 2.5×10^{-5} s^{-1} in chlorobenzene. Stynes and co-workers[18,19] have observed the rate constant for the loss of CO from $Fe(TIM)(CO)CH_3CN^{2+}$ in CH_3CN to be 4.3×10^{-4} s^{-1} and have also estimated that the Fe(II) complex of 14-ane, a saturated tetraaza ligand similar to TIM but without the methyl groups, has a rate constant for the loss of CO of 7.7 × 10^{-4} s^{-1}. In fact, the rate constants for loss of CO from heme complexes with imidazole or 1-methylimidazole as the trans ligand are in the range (8–28) × 10^{-3} s^{-1}.[20] The tetraaza planar ligand environment seems to hold the rate of loss of CO within a reasonably narrow range, implying that the ligand trans to the CO does not cause a differential bonding effect on the CO between the ground state and the transition state for loss of CO. Since the rate of loss of CO from these complexes is decidedly less rapid than the rate of coordination of CO, the transition state presumably exhibits only weak bonding to the CO and we conclude that the trans ligand does not alter the bonding characteristics of CO very much. On the other hand, the rate of loss of CH_3CN from $Fe(TIM)(CO)CH_3CN^{2+}$ is not consistent with other data for CH_3CN loss from low-spin Fe(II) complexes. For example, Kildahl et al.[21-23] report the rate constant for loss of CH_3CN from $Fe(TIM)(Me\text{-}imd)CH_3CN^{2+}$, where Me-imd is *N*-methylimidazole, to be 195 s^{-1}, whereas the value we find for CH_3CN loss from $Fe(TIM)(CO)CH_3CN^{2+}$ is 1.2×10^{-3} s^{-1}. This 10^5 change is interpretable in terms of a trans effect and will be discussed more fully in a future publication.[7]

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Registry No. $Fe(TIM)(CH_3CN)_2^{2+}$, 49861-52-1; $Fe(TIM)(CO)CH_3CN^{2+}$, 49861-54-3; $Fe(TIM)(CO)H_2O^{2+}$, 90461-83-9; $Fe(TIM)(H_2O)_2^{2+}$, 90461-84-0; Br_2, 7726-95-6.

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