$(CH_3CN)_2]^+$ illustrated in Figure 5 and Table III is consistent with the above-mentioned work.

It is difficult to make an assignment of the spectra of different $[Rh_2(ac)_n(acam)_{4-n}]^+$ cations with respect to the spectra of $[Rh_2(ac)_4]^+$. There are several distinct dissimilarities in the UV–visible spectrum of the $[Rh_2(ac)_4(CH_3CN)_2]^+$ cation and the spectra of the cations of compounds II–V. Firstly, the low-energy ($\delta \rightarrow \delta^*$) band around 800 nm is absent in the cations of compounds II–V. In addition, there is no high-intensity band in the 500-nm region for the $[Rh_2(ac)_4(CH_3CN)_2]^+$ cation.

Plots of λ_{max} for the low-energy band of oxidized compounds II–V were plotted vs. the number of acetamidate ligands. This plot is linear and when extrapolated to zero acetamidate ligands (i.e., the $[Rh_2(ac)_4]^+$ complex) in CH_3CN gives a value of $\lambda_{max} \simeq 550$ nm. This λ_{max} value may be compared to an actual absorbance of 505 nm in this solvent. These differences suggest that different orbital patterns are involved in electronic transitions of the oxidized compound I and the series of oxidized compounds II–V. This observation is consistent with the fact that the oxidized compound I is EPR silent and the oxidized compounds II–V are all EPR active (except for the oxidized compound II in Me_2SO) (Table II).

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Registry No. TBAP, 1923-70-2; $Rh_2(ac)_4$, 15956-28-2; $Rh_2(ac)_4(CH_3CN)_2$, 80419-75-6; $Rh_2(ac)_4(py)_2$, 13987-30-9; $Rh_2(ac)_4(Me_2SO)_2$, 39773-10-9; $Rh_2(ac)_4(PPh_3)_2$, 39773-08-5; $Rh_2(ac)_4(CH_3CN)_2^+$, 92526-07-3; $Rh_2(ac)_4(Me_2SO)_2^+$, 92526-08-4; $Rh_2(ac)_3(acam)(CH_3CN)_2$, 92525-89-8; $Rh_2(ac)_3(acam)(py)_2$, 92543-06-1; $Rh_2(ac)_3(acam)(Me_2SO)_2$, 92525-94-5; $Rh_2(ac)_3(acam)(CH_3CN)_2^+$, 92526-00-6; $Rh_2(ac)_3(acam)(Me_2SO)_2^+$, 92526-09-5; $Rh_2(ac)_2(acam)_2(CH_3CN)_2$, 92525-90-1; $Rh_2(ac)_2(acam)_2(py)_2$, 92525-92-3; $Rh_2(ac)_2(acam)_2(Me_2SO)_2$, 92525-95-6; $Rh_2(ac)_2(acam)_2(PPh_3)_2$, 92525-98-9; $Rh_2(ac)_2(acam)_2(CH_3CN)_2^+$, 92526-01-7; $Rh_2(ac)_2(acam)_2(Me_2SO)_2^+$, 92526-04-0; $Rh_2(ac)(acam)_3(CH_3CN)_2$, 92525-91-2; $Rh_2(ac)(acam)_3(py)_2$, 92525-93-4; $Rh_2(ac)(acam)_3(Me_2SO)_2$, 92525-96-7; $Rh_2(ac)(acam)_3(PPh_3)_2$, 92525-99-0; $Rh_2(ac)(acam)_3(CH_3CN)_2^+$, 92526-02-8; $Rh_2(ac)(acam)_3(Me_2SO)_2^+$, 92526-05-1; $Rh_2(acam)_4(CH_3CN)_2$, 92525-88-7; $Rh_2(acam)_4(py)_2$, 90883-29-7; $Rh_2(acam)_4(Me_2SO)_2$, 92525-97-8; $Rh_2(acam)_4(PPh_3)_2$, 91837-88-6; $Rh_2(acam)_4(CH_3CN)_2^+$, 92526-03-9; $Rh_2(acam)_4(Me_2SO)_2^+$, 92526-06-2; $Rh_2(ac)_3(acam)$, 87985-37-3; $Rh_2(ac)_2(acam)_2$, 87985-38-4; $Rh_2(ac)(acam)_3$, 87985-39-5; $Rh_2(acam)_4$, 87985-40-8.

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Flash Photolysis of $Fe(TIM)CO(X)^{2+}$ Complexes

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The kinetics and mechanism of substitution reactions following flash photolysis of $Fe(TIM)CO(X)^{2+}$ ($X = CH_3CN, H_2O$) in CO-saturated aqueous acetonitrile solutions were studied at 23 °C and at 0.5 M ionic strength. The flash forms a mixture of $Fe(TIM)(CH_3CN)_2^{2+}$, $Fe(TIM)CH_3CN(H_2O)^{2+}$, and $Fe(TIM)CO(H_2O)^{2+}$ with relative amounts depending on the $[CH_3CN]$. When $Fe(TIM)CO(X)^{2+}$ is photolyzed ($\lambda \approx 450$ nm) at $[CH_3CN] > 0.12$ M, the rate of recoordination of CO is between inverse-first and inverse-second order in $[CH_3CN]$ and first-order in both [CO] and the iron complex concentration. Below 0.12 M CH_3CN, the mechanism for CO recoordination is complicated by the rate of establishment of the equilibrium between $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)CH_3CN(H_2O)^{2+}$, which becomes at this $[CH_3CN]$ comparable to the rate of $Fe(TIM)CO(X)^{2+}$ formation. Analysis of the mechanism of substitution shows a dramatic trans effect on the rate of water substitution by CH_3CN. When water is coordinated trans to CO, CH_3CN, and H_2O, the rates of substitution of CH_3CN for water are about 10^{-4}, 10^4, and 10^6 M^{-1} s^{-1}, respectively. Furthermore, the rate for CH_3CN loss (replacement by water) when coordinated trans to CO is 10^{-3} s^{-1}, trans to CH_3CN is 250 s^{-1}, and trans to H_2O is 10^4 s^{-1}, a 10^7 range. These trans-substitution effects are discussed in terms of the π-accepting and σ-donating abilities of the axial ligands. A previously published "solvent-sensitive" process of photolysis is analyzed in terms of these data and is shown to be caused by differential rates of reaction following photolysis.

Introduction

In a previous paper several reactions of carbon monoxide containing complexes of the macrocyclic complex of Fe(II) with 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM) have been reported.[2] These reactions were generally slow, on the time scale of minutes to hours. While we were investigating the properties of $Fe(TIM)CO(CH_3CN)^{2+}$, it was noted, as reported earlier, that the molecule was subject to photolysis in which CO was expelled.[3] The earlier investigators[3] interpreted their observations to imply that the *photolytic* pathway was sensitive to the solvent; in the case of $Fe(TIM)CO(CH_3CN)^{2+}$, photolysis in CH_3CN led to loss of CO and formation of $Fe(TIM)(CH_3CN)_2^{2+}$, whereas photolysis in acetone produced $Fe(TIM)CO(CH_3COCH_3)^{2+}$. Our earliest observations on the photolysis of $Fe(TIM)CO(CH_3CN)^{2+}$ in aqueous CH_3CN solutions indicated that the rate of absorbance changes after photolysis depended critically on the concentration of CH_3CN in the aqueous acetonitrile solutions. This suggests that the conclusions arrived at by Incorvia and Zink[3] may be simply a consequence of different rates of chemical reaction *following* the photolytic step. Because the kinetics of substitution of Fe(II) complexes in low-spin environments has not been well studied, and in order to probe the possibility that there is a more standard explanation for the "solvent-mediated pathway" for photolysis, we have explored the flash photolysis of $Fe(TIM)CO(CH_3CN)^{2+}$ in detail. The results of this investigation offer a rich array of interesting chemistry; they are reported herein.

Experimental Section

Synthesis and Reagents. The syntheses of the iron complexes have been described previously.[2,4] Other reagents were also subject to the procedures used previously.[2]

Flash Photolysis Procedures. All kinetic and equilibrium measurements were made at 23 °C. The ionic strength was maintained

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(1) (a) University of California. (b) Smith College.

(2) Butler, A.; Linck, R. G. *Inorg. Chem.* **1984**, *23*, 2227.

(3) Incorvia, M. J.; Zink, J. I. *J. Chem. Soc., Chem. Commun.* **1977**, 730–731.

(4) Baldwin, D. A.; Pfeiffer, R. M.; Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5152–5158.

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throughout the equilibrium and kinetic experiments at 0.5 M with 0.4 M $LiClO_4$ and 0.1 M $HClO_4$. A stock solution of $Fe(TIM)CO(H_2O)^{2+}$ was made in situ by dissolving $[Fe(TIM)(CH_3CN)_2](PF_6)_2$ in CO-saturated stock ionic strength diluent. The stock solution, which was about 1.5×10^{-3} M in Fe(II), was bubbled with CO for approximately 20 min.

The samples to be photolyzed were made in serum-capped quartz cuvettes. Following saturation of the $LiClO_4$ solutions containing $Fe(TIM)CO(H_2O)^{2+}$ (10^{-5} M) with CO, neat CH_3CN (CO saturated) was added. Evaporation of CH_3CN was prevented by not bubbling the cells with CO after the initial addition of CH_3CN. Typically four successive additions of CO-saturated CH_3CN were made to each cell and flashed between each addition. The temperature of each sample was maintained at 23 °C during CO saturation. In some experiments a small quantity of solid $[Fe(TIM)CO(CH_3CN)](PF_6)_2$ was flushed with CO in a serum-capped 1-cm cell before CO-saturated $LiClO_4$ solution and CH_3CN were added. The flash photolysis reactions were monitored at either 560, 600, or 450 nm. The $[Fe(TIM)CO(X)^{2+}]$ varied between 10^{-5} and 3×10^{-4} M and the $[CH_3CN]$ between 0.031 and 2.55 M.

To vary the partial pressure of CO in these flash photolysis experiments, a serum-capped 1-cm cell containing a small quantity of $[Fe(TIM)CO(CH_3CN)](PF_6)_2$ and a small stir bar was flushed with argon. Portions of ionic strength diluent saturated respectively with carbon monoxide and argon were in turn slowly injected (to avoid the formation of bubbles) through the serum cap followed by argon-degassed acetonitrile (neat) until the cell was filled to the exit needle. The solution was stirred gently, and then the sample was photolyzed. The concentration of CO was varied from 1.1×10^{-4} to 9.84×10^{-4} M (maximum solubility in aqueous solution at 23 °C[5]) at a fixed $[CH_3CN]$. These reactions were monitored at 560 nm.

Flash Photolysis of $Fe(TIM)CO(H_2O)^{2+}$: Second-Order Conditions. A solution of the stock $Fe(TIM)CO(H_2O)^{2+}$ without excess CO was made by passing argon through a CO-saturated solution of $Fe(TIM)CO(H_2O)^{2+}$ for more than 12 h in the dark.[6] Exposure of this sample to light was avoided so that coordinated CO was not photolabilized and subsequently purged with argon. The stock iron complex was diluted into cells and photolyzed. These reactions were monitored at 650 nm.

Flash Photolysis Apparatus. A Durrum stopped-flow spectrophotometer was converted for use as a flash photolysis apparatus. The tube between the mirror compartment and the monochromator compartment was removed and replaced with a black Lucite box. The box was constructed with two quartz windows for monitoring the species and a glass panel to allow excitation. Water was circulated through it to maintain a constant temperature. A camera flash (Vivitar 102) was positioned in line with the cell, and a switch was wired to trigger the flash and the oscilloscope simultaneously. The flash was filtered through a blue Kodak Wrattan filter. Interference filters of the appropriate band-pass were placed between the Lucite box and the photomultiplier tube. The decay of the flash required 2–3 ms. In some experiments a flash photolysis apparatus with a much faster flash decay was used. It has been described previously.[7]

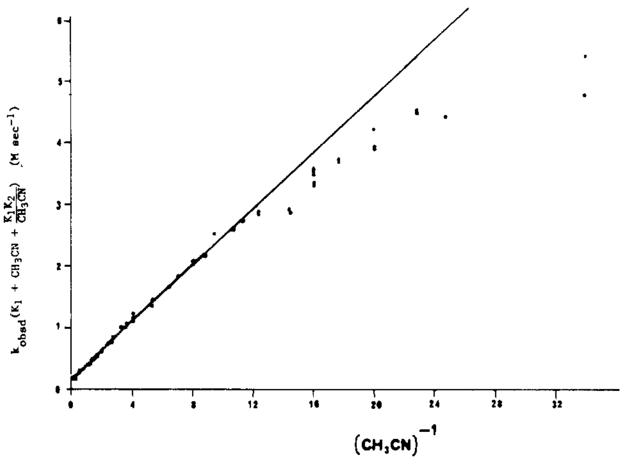

Figure 1. Rate of relaxation to form $Fe(TIM)CO(X)^{2+}$ following photolysis of this molecule as a function of $[CH_3CN]$ in aqueous solution. Conditions: $[CO] = 9.8 \times 10^{-4}$ M; $I = 0.5$ M; $[Fe(II)] \approx 10^{-5}$ M; $T = 23$ °C; wavelength of observation 550 nm.

Results and Discussion

Exposure of the yellow solution of $Fe(TIM)CO(CH_3CN)^{2+}$ to light in aqueous CH_3CN leads to a change in the color to burgundy, a color characteristic of $Fe(TIM)(CH_3CN)_2^{2+}$. Upon removal of the sample from light, the color fades back to yellow (at rates that depend on the $[CH_3CN]$), indicating the reversibility of the reaction (eq 1). Flash photolysis of

$$CH_3CN + Fe(TIM)CO(CH_3CN)^{2+} \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} Fe(TIM)(CH_3CN)_2^{2+} + CO \quad (1)$$

a solution of $Fe(TIM)CO(CH_3CN)^{2+}$ demonstrated that the rate of decay of the absorbance at 551 nm, the maximum of the absorbance for $Fe(TIM)(CH_3CN)_2^{2+}$, was first order in the concentration of $Fe(TIM)XY^{2+}$,[8] where X and Y are either CH_3CN or H_2O, was first order in the concentration of CO, and increases as the $[CH_3CN]$ decreases. The latter dependence indicates that the rate law for the decay of the 551-nm peak is between inverse-first and inverse-second order in $[CH_3CN]$ over a range of $[CH_3CN]$ of 0.031–2.55 M. It has already been established[2] that $Fe(TIM)(CH_3CN)_2^{2+}$ is in equilibrium with $Fe(TIM)(CH_3CN)H_2O^{2+}$, and a value of the equilibrium constant relating these two species has been determined.[2] Other studies[9-12] of $Fe(TIM)XY^{2+}$ and related complexes suggest that both CH_3CN ligands should be replaceable by another ligand.[13] We assume that this feature holds in our case and that two equilibria need to be considered:

$$Fe(TIM)(CH_3CN)_2^{2+} \overset{K_1}{\rightleftharpoons} Fe(TIM)CH_3CN(H_2O)^{2+} + CH_2CN \quad (2)$$

$$Fe(TIM)CH_3CN(H_2O)^{2+} \overset{K_2}{\rightleftharpoons} Fe(TIM)(H_2O)_2^{2+} + CH_3CN \quad (3)$$

If the kinetic pathways for the formation of CO-containing complexes involve the reagents $Fe(TIM)CH_3CN(H_2O)^{2+}$ and $Fe(TIM)(H_2O)_2^{2+}$ (or, in aqueous solution, their kinetically equivalent, $Fe(TIM)CH_3CN^{2+}$ and $Fe(TIM)H_2O^{2+}$, five-coordinate species), as indicated in eq 4 and 5, then a rate law

$$Fe(TIM)CH_3CN(H_2O)^{2+} + CO \xrightarrow{k_1} Fe(TIM)CO(X)^{2+} + H_2O \quad (4)$$

$$Fe(TIM)(H_2O)_2^{2+} + CO \xrightarrow{k_2} Fe(TIM)CO(H_2O)^{2+} + H_2O \quad (5)$$

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(5) "Matheson Unabridged Gas Data Book"; Matheson Gas Products: Secaucus, NJ, 1974.

(6) Carbon monoxide is thermally labile from $Fe(TIM)CO(H_2O)^{2+}$,[2] but until the [CO] falls below the micromolar level, the equilibrium constant favors $Fe(TIM)CO(H_2O)^{2+}$ by more than 100:1. We found for shorter times of standing that the second-order plots after photolysis were invariably curved in such a direction as to indicate that there was excess CO in the solution.

(7) White, D. K.; Cannon, J. C.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 2443–2454.

(8) The symbol $Fe(TIM)XY^{2+}$ represents the complex in which the two axial ligands are water and CH_3CN under equilibrium conditions for the particular concentration of CH_3CN; it is not a single species under most conditions.[2]

(9) Vaska, L.; Yamaji, T. *J. Am. Chem. Soc.* **1971**, *93*, 6673–6674.

(10) Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 590–594.

(11) Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 2192–2199.

(12) Kildahl, N. K.; Balkus, K. J., Jr.; Flynn, M. J. *Inorg. Chem.* **1983**, *22*, 589–592 and references therein.

(13) Cole, T. K.; Linck, R. G., unpublished work. These experiments on the reactions of the $Fe(TIM)XY^{2+}$ with acid at very low concentrations of CH_3CN have verified that a second equilibrium exists and that the extinction coefficient of $Fe(TIM)(H_2O)_2^{2+}$ is about 4400 M^{-1} cm^{-1}.

for the reaction of CO with the species formed after flash photolysis of CO from Fe(TIM)CO(CH_3CN)$^{2+}$ can be derived in terms of these rate and equilibrium constants. Note that we neglect any transition state containing two acetonitriles; this is justified by what follows below. Under conditions where the [CH_3CN] and [CO] are in excess of that of [Fe(II)], the rate constant for the decay of Fe(TIM)XY^{2+} material is as given in eq 6, where $Q = K_1 + [CH_3CN] + K_1K_2/[CH_3CN]$.

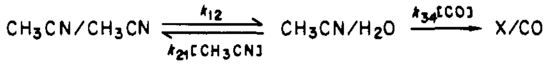
$$k_{obsd} = k_1K_1[CO]/Q + k_2K_1K_2[CO]/[CH_3CN]Q \quad (6)$$

This rate law can be tested by a plot of the function $k_{obsd}Q$ vs. $[CH_3CN]^{-1}$ if values of K_1 and K_2 are available. We have shown[2] that K_1 has a value of 0.023 at 23 °C and 0.5 M ionic strength. However, because of the extreme oxygen sensitivity of Fe(TIM)(H_2O)$_2^{2+}$,[14] the direct determination of K_2 was not judged feasible. Accordingly, we adopt the following "bootstrap" method: For experiments in which the [CH_3CN] was large, the last term in Q should be relatively small compared to the first two terms; under these conditions a plot of $k_{obsd}[K_1 + [CH_3CN]]$ vs. $[CH_3CN]^{-1}$ should be linear. This is true; the expected linear behavior over the range of [CH_3CN] from 0.12 to 2.55 M ($[CH_3CN]^{-1}$ from 0.4 to 8 M^{-1}) is evident (see Figure 1). (Note there is no indication of curvature with a smaller slope at large values of [CH_3CN]; this implies that a pathway with a transition state of composition {Fe(TIM)(CH_3CN)$_2^{2+}$,CO} is not found in the reaction, as assumed above. This we take to be evidence, although not compelling in itself, that the rate of these processes is governed by dissociative pathways, as has been established or assumed in low-spin Fe(II) reactions.[9-12]) From this plot we obtain by least-squares analysis of the points within the range of $[CH_3CN]^{-1}$ from 0 to 8 M^{-1} a value for the intercept of 0.158 ± 0.005 M s^{-1} and for the slope of 0.23 ± 0.06 M^2 s^{-1}. With the value of K_1 equal to 0.023 M and the [CO] in saturated solution taken as 9.84×10^{-4} M,[5] the intercept yields a value of k_1 or $(7.1 \pm 0.8) \times 10^3$ M^{-1} s^{-1} and the slope yields a value of k_2K_2 of 1.06×10^4 s^{-1}.

This value of k_2K_2 allows us to take the second step in obtaining a correct functional relationship for the kinetic data, since direct determination of k_2 would yield a value of K_2. The value of k_2 was determined from the kinetic processes following flash photolysis of a solution of Fe(TIM)CO(H_2O)$^{2+}$ in the absence of CH_3CN under an atmosphere of CO (pseudo-first-order conditions) or under an atmosphere rigorously flushed with Ar to remove all CO (second-order conditions). The second-order rate constant was obtained from a plot of $(A_t - A_\infty)^{-1}$ vs. time, where the A values are the values of the absorbance at 650 nm at time t and at equilibrium, respectively. Such plots were linear for 80% reaction. To obtain a rate constant from the slope of these plots, we need a value of the extinction coefficient for Fe(TIM)(H_2O)$_2^{2+}$. This was obtained from the absorbance of a solution of Fe(TIM)(H_2O)$_2^{3+}$ treated with V^{2+},[13] extrapolated to time of mixing; the appropriate value is about 4400 M^{-1} cm^{-1}. This gives a second-order rate constant of $(1.2 \pm 0.2) \times 10^6$ M^{-1} s^{-1}.[15] Experiments under pseudo-first-order conditions, in which a value for the extinction coefficient is not required, yielded a value of $(1.25 \pm 0.07) \times 10^6$ M^{-1} s^{-1} (two experiments). This value of k_2 yields a value for K_2 of 0.005.

With a value for K_2 a rigorous test of the function given in eq 6 can be achieved. Because the values of $K_1K_2/[CH_3CN]$ are small when [CH_3CN] is greater than moderate, this function does not change data points from the values that they have in Figure 1 at large values of [CH_3CN] and hence does not change the value of the slope and intercept reported above; but, as [CH_3CN] becomes small enough, the last term in Q begins to contribute and causes the curvature of the plot shown in Figure 1 to become *less, but not to disappear*. Some other aspect must be causing the failure of eq 2-5 from completely describing the chemistry of this system.

Scheme I



$$CH_3CN/CH_3CN \underset{k_{21}[CH_3CN]}{\overset{k_{12}}{\rightleftharpoons}} CH_3CN/H_2O \xrightarrow{k_{34}[CO]} X/CO$$

The fact that the rate constant predicted by the model of eq 2-5 is too large at low values of [CH_3CN] means that the feature causing the deviation from the model is an inefficient process for liberating CH_3CN from some species. One possibility consistent with the results of Kildahl[12] is that the assumption of the establishment of rapid equilibria between Fe(TIM)(CH_3CN)$_2^{2+}$, Fe(TIM)CH_3CN(H_2O)$^{2+}$, and Fe(TIM)(H_2O)$_2^{2+}$ does not hold as the [CH_3CN] decreases, a reasonable possibility considering that reactions of low-spin d^6 complexes should not be very rapid.[16] In order to probe this possibility, the simplifying assumption was made that only the equilibration rate between Fe(TIM)(CH_3CN)$_2^{2+}$ and Fe(TIM)CH_3CN(H_2O)$^{2+}$ becomes slow enough to have a kinetic effect (the rationalization for this assumption flows from our analysis as we show below). Under this assumption the kinetics are shown in Scheme I. In this scheme we have abbreviated the Fe(TIM) part of the molecule by a slant, k_{12} and k_{21} are the rate constants that have been introduced by the assumption that the equilibrium is slow, and k_{34}[CO] is a composite rate constant that accounts for both paths to CO-containing products as outlined above, i.e., $k_{34} = k_1 + k_2K_2/[CH_3CN]$. This kinetic scheme has two nonzero relaxation times[17] given by $\lambda_\pm$ (eq 7). The slower of these two

$$\lambda_\pm = 0.5[(k_{21}[CH_3CN] + k_{12} + k_{34}[CO]) \times [(k_{21}[CH_3CN] + k_{12} + k_{34}[CO])^2 - 4k_{12}k_{34}[CO]]^{1/2}] \quad (7)$$

relaxation times, λ_-, is the only observed value under the majority of our experimental conditions. To verify that the breakdown of the equilibrium assumption is true, we employed two methods: (1) a faster flash photolysis apparatus was used to observe λ_+ and (2) the value of λ_- was calculated in the region of low [CH_3CN], where deviation from the rate law given by eq 6 is found, and this calculated value was then compared to the observed rate constant.

To calculate the value of λ_- requires knowledge of k_{12}, k_{21}, and k_{34}. The last is known under the assumption that at a high concentration of CH_3CN the rate of establishment of the equilibrium between Fe(TIM)(CH_3CN)$_2^{2+}$ and Fe(TIM)CH_3CN(H_2O)$^{2+}$ is rapid; that is, λ_- in the region of high [CH_3CN] reduces to k_{obsd} (as can be seen by expansion of the square root term in eq 7). Of the two former rate constants, only one is independent because the value of their ratio is dictated by K_1. Our procedure was then to find the value of k_{12} that reproduced the observed rate constants at low values of [CH_3CN]. Table I gives the fit of the data for a guessed value of k_{12} of 250 s^{-1}. This value is also in agreement with a similar value of k_{12} needed to account for the rapid oxidation of Fe(TIM)XY^{2+} with Br_2 in aqueous solution.[14]

To attempt to resolve the two relaxation times that eq 7 predicts, we used a flash that was nearly 1 order of magnitude faster than that used in the most of our work.[7] Under conditions of this flash system we were able to resolve, albeit poorly, two relaxation times; a typical example is shown in Figure 2. From the two relaxation times of this experiment,

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[14] Flores, M.; Linck, R. G., unpublished work.

[15] Experiments at an ionic strength of 0.01 M gave k of $2.8 \pm 0.3 \times 10^6$ M^{-1} s^{-1}, in reasonable agreement with an expected indifference to ionic strength for a reaction of a neutral species with a charged species.

[16] Taube, H. *Chem. Rev.* **1952**, *50*, 69-126.

[17] Bittrich, H.-J.; Haberland, D.; Just, G. "Methoden chemisch-kinetischen Berechnungen"; Veb Deutschen Verlag fur Grundstoffindustrie: Leipzig, 1979.

Table I. Comparison of Observed and Calculated Relaxation Times

$[CH_3CN]$, M	k_{obsd},[a] s^{-1}	λ_-(calcd),[b] s^{-1}
0.044	65	64
	66	
0.050	50	56
	53	
	53	
	57	
0.063	38	40
	38	
	38	
	41	
	42	

[a] λ_{obsd} = 550 nm. [b] Calculated from eq 7 with a value of k_{12} of 250 s^{-1} and K_1 of 0.023.

Table II. Determination of k_{12} from Fast-Flash Experiment

$[CH_3CN]$, M	λ_+,[a] s^{-1}	λ_-,[a] s^{-1}	$k_{34}[CO]$,[b] s^{-1}	k_{12}, s^{-1}
0.029	1030	75	365	210
0.040	1110	58	270	240
0.049	1170	55	220	290
0.068	1130	35	160	250

[a] λ_{obsd} = 550 nm. [b] Calculated from the parameters obtained in the region of high $[CH_3CN]$.

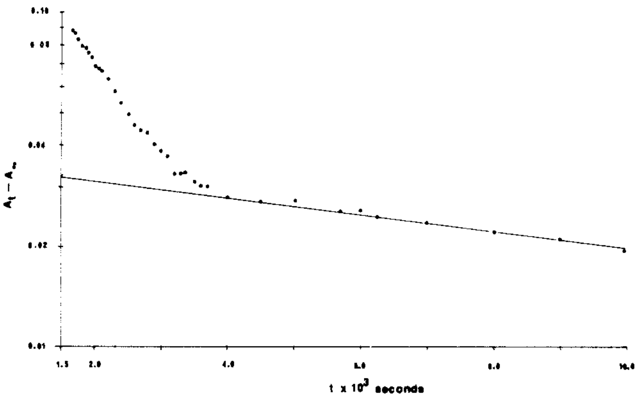

Figure 2. Biphasic kinetic behavior following flash photolysis of $Fe(TIM)CO(X)^{2+}$ at $[CH_3CN]$ of 0.04 M. Conditions: T = 23 °C; [CO] = 9.8×10^{-4} M; [Fe(II)] $\approx 10^{-5}$ M; λ_{obsd} = 550 nm.

both λ_+ and λ_- could be experimentally determined. The product of the two of these is $k_{12}k_{34}[CO]$, and since $k_{34}[CO]$ is known, k_{12} was determined from this product. Table II presents this analysis. It is seen by the value obtained from these data, which averages 250 ± 30 s^{-1}, that the two methods of determination of the breakdown of maintenance of the equilibrium between $Fe(TIM)(CH_3CN)_2^{2+}$ and $Fe(TIM)CH_3CN(H_2O)^{2+}$ at low values of $[Fe(TIM)(CH_3CN)_2^{2+}]$ give the same value of k_{12}.

With the insertion of the rate constants for the processes that were previously taken to be rapidly established equilibria, the reactions describing the substitution processes on $Fe(TIM)XY^{2+}$ are as given in Scheme II, where again the slant is taken to mean the Fe(TIM) fragment of the molecules (and CH_3CN in the solvent is omitted). All rate constants for Scheme II as determined in this paper and ref 2 are listed in Table III. The value of k_1 can be compared to the value of k_{21} determined as outlined above; the values are nearly identical. This is consistent with a dissociative mechanism (leaving group water) if the rate of attack on the five-coordinate species by CH_3CN and CO is similar (see ref 18 for a discussion of the validity of this assumption). We have pursued this technique in estimating the value of k_{32}, which we take to be about the magnitude of k_2. With this assignment of k_{32} and our estimate of K_2, we can fix the value of k_{23}. It is to be noted that these choices of k_{23} and k_{32} are consistent with our evidence that there is no hint of a third relaxation time in the treatment of our data, implying that the equilibrium characterized by K_2 is maintained at equilibrium under all conditions of $[CH_3CN]$ employed in this study: the calculated relaxation time for the K_2 process is about 15 μs at the lowest $[CH_3CN]$ we used, whereas under similar conditions the relaxation time for the K_1 process is about 1 ms.

Scheme II

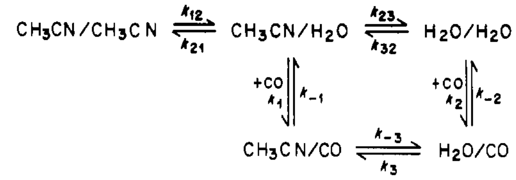

Table III. Summary of Rate Constants for Scheme II

rate const	value	rate const	value
k_{12}	2.5×10^2 s^{-1}	k_{-1}	1.8×10^{-3} s^{-1} [b]
k_{21}	1.1×10^4 M^{-1} s^{-1}	k_2	1.9×10^6 M^{-1} s^{-1}
k_{23}	[1×10^4 s^{-1}][a]	k_{-2}	1.8×10^{-3} s^{-1} [b]
k_{32}	[2×10^6 M^{-1} s^{-1}][a]	k_3	7.5×10^{-4} M^{-1} s^{-1} [b]
k_1	7.1×10^3 M^{-1} s^{-1}	k_{-3}	6.3×10^{-4} s^{-1} [b]

[a] Estimated as outlined in the text. [b] Value obtained for ref 2.

It is apparent from the data in Table III that several striking rate comparisons can be made. For substitution of H_2O by CH_3CN in the complexes $Fe(TIM)X(H_2O)^{2+}$, the relative rate constants for X = CO (k_3), X = CH_3CN (k_{21}), and X = H_2O (k_{32}) are $1:10^8:10^{10}$; and for substitution of CH_3CN by H_2O in the complexes $Fe(TIM)X(CH_3CN)^{2+}$ the relative rate constants for this series of X, k_{-3}, k_{12}, and k_{23}, respectively, are $1:4 \times 10^5:2 \times 10^7$. Clearly, the much stronger π-accepting ligand CO in a trans position causes a much lower rate of substitution than does the weakly π-accepting CH_3CN, which in turn causes a lower rate than does H_2O. This reduction in rate of substitution at a site trans to a strongly π-accepting ligand is consistent with several other studies of low-spin d^6 complexes such as $Fe(DMGH)_2X(py)$, where the rate of loss of pyridine is 10^5 times as fast when X = py as when X = benzyl isocyanide[10], and $Ru(NH_3)_4X(H_2O)^{2+}$,[19] where the rate of loss of water is $>10^4$ faster when X is pyridine than when X is CO. Isied and Taube[19] find that the lability of this last complex correlates rather well with the reduction potential of the Ru(II)/Ru(III) couple, the more positive reduction potential leading to slower substitution rate, consistent with substitution rate and reduction potential being influenced (in opposite directions) dominantly by electron density on the metal center. Such an argument holds equally well for our complexes as we have direct evidence that $Fe(TIM)(CH_3CN)_2^{2+}$ has a higher reduction potential than does $Fe(TIM)CH_3CN(H_2O)^{2+}$ [14] and indirect evidence from the attempted Br_2 oxidation of $Fe(TIM)CO(H_2O)^{2+}$ [2] that this last complex is very hard to oxidize. Stynes has argued[18,20,21] on the basis of a comparison of Ru(II) and Fe(II) complexes with tetraaza macrocyclic ligands of various kinds that a change in spin state occurs in low-spin Fe(II) substitutions in which

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(18) Stynes, D. V.; Hu, Y. S.; Chew, V. *Inorg. Chem.* **1982**, *21*, 1222–1225.

(19) Isied, S. S.; Taube, H. *Inorg. Chem.* **1976**, *15*, 3070–3075.

(20) Pomposa, F.; Carruthers, D.; Stynes, D. V. *Inorg. Chem.* **1982**, *21*, 4245–4248.

(21) Stynes, D. V.; Singh, K.; Ng, B.; Wilshire, S. *Inorg. Chim. Acta* **1982**, *58*, 179–185.

the fifth ligand is one of low ligand field strength,[22] for instance, when CO is the leaving group and water is the trans ligand in the Fe(TIM)XY^{2+} system. The basis for this argument is that there is little rate difference between these two leaving groups in Ru(II) complexes, which are expected to have such large ligand field strengths that the five-coordinate intermediate is expected to stay low-spin independent of the nature of the fifth ligand, but that a substantial rate difference exists for the Fe(II) complexes, as is in fact found for the systems studied here. However, the data on Ru(NH$_3$)$_4$X(H$_2$O)$^{2+}$ [19] violate Stynes's basic argument. We find no compelling evidence in favor of, nor in contradiction to, the spin change argument.

The second useful comparison is between the rate of substitution of the low-spin d^6 center of Fe(TIM)XY^{2+} and other similar d^6 systems. The aforementioned Ru(II) system has rate constants on the order of 10^{-2} M^{-1} s^{-1} for substitution of water when non-π-accepting ligands are in the coordination sphere.[19] The rate of dissociation of pyridine from Fe(DPGH)$_2$(py)$_2$ is 4.2×10^{-3} s^{-1}.[9] These values are to be compared with the rate constants for substitution of ligands on the Fe(TIM) center in the absence of strong π-accepting ligands, that is, with k_{12}, k_{23} (10^2–10^4 s^{-1}), and k_{21} and k_{32} (10^4–10^6 M^{-1} s^{-1}). The more rapid reaction of the Fe(TIM)XY^{2+} complexes seems plausible on the basis of the interpretation that Poon[23] has given for reactions of Co(III) complexes. Evidently the α-diimine linkages are able to allow a delocalization of charge sufficient to lend the transition state some degree of stability.

The strong trans effect on the rate of substitution of Fe(TIM)CO(X)$^{2+}$ has a direct consequence on the photolysis of this molecule. Several years ago Incorvia and Zink[3] reported that the photolysis of Fe(TIM)CO(CH$_3$CN)$^{2+}$ was very sensitive to the nature of the solvent; in fact, they interpreted their results to postulate that the nature of the leaving group changed as the solvent was changed.[24] They observed that photolysis of Fe(TIM)CO(CH$_3$CN)$^{2+}$ in CH$_3$CN led to loss of CO but that photolysis in acetone led to loss of CH$_3$CN to give Fe(TIM)CO(acetone)$^{2+}$. We have duplicated their observations; however, the following analysis will prove that their interpretation of the data is flawed. Our model of their results is as follows: photolysis of Fe(TIM)CO(CH$_3$CN)$^{2+}$ in any solvent leads to loss of CO, but what happens after that is governed by the rate of approach to equilibrium. The uptake of CO is governed in aqueous CH$_3$CN solutions by several pathways, but all require the loss of CH$_3$CN in order to be efficient; thus, in neat CH$_3$CN, the rate of uptake of CO is very slow and observation soon after photolysis (within a few seconds) shows that CO has been photolabilized and that it only returns to the coordination sphere slowly. Photolysis of Fe(TIM)CO(CH$_3$CN)$^{2+}$ in water (and, as we shall show below, acetone behaves similarly) leads also to loss of CO, but if observation of the products is made seconds after removal of the sample from the light source, the system has already relaxed to its equilibrium state in which CO has recoordinated because of the inverse dependence on [CH$_3$CN] in the relaxation process. Since the CO-containing material is formed (in quite dilute CH$_3$CN) by reaction of CO with Fe(TIM)(H$_2$O)$_2$$^{2+}$, the apparent product is Fe(TIM)CO(H$_2$O)$^{2+}$, making it appear that CH$_3$CN has been photolabilized if observation is made some milliseconds after relaxation. Hence, the difference in bonding between CH$_3$CN and water affects the relaxation rate and the "apparent" product observed seconds after photolysis.

A similar phenomenon occurs in acetone. There, the loss of CO by the photolytic pathway is followed by equilibration of acetone into the coordination sites of the Fe(II); but, the uptake of CO is rapid in this molecule, and if observation of products is made seconds after photolysis, the product is Fe(TIM)CO(CH$_3$COCH$_3$)$^{2+}$. Only flash photolysis experiments or low-temperature experiments can establish that the true photolytic pathway is loss of CO under all conditions of solvent that have been studied. The former were performed with water as the solvent; to ensure the correctness of our model, we have made a qualitative study of the photolysis of Fe(TIM)CO(CH$_3$COCH$_3$)$^{2+}$ in acetone at low temperatures. A yellow solution of Fe(TIM)CO(CH$_3$CN)$^{2+}$ in an acetone solution 0.76 M in CH$_3$CN was frozen in liquid nitrogen and photolyzed in sunlight while cold. If the sky is not hazy, the color turns blue, indicating the loss of CO and the uptake of acetone into the coordination sphere of Fe(II). (Note that π-acceptor ligands, CO and isocyanides, cause a transition at considerably higher energies than the weakly π-accepting ligand CH$_3$CN and that oxygen donor ligands, water, methanol, and acetone, absorb at even lower energies.) If the sky is hazy, the color changes only to green, indicating a mixture of Fe(TIM)(CH$_3$COCH$_3$)$_2$$^{2+}$ (blue) and Fe(TIM)CO(CH$_3$COCH$_3$)$^{2+}$ (yellow) and indicating the large rate of relaxation of CO back into the coordination sphere of this Fe(II) complex, so large that it is facile even at reasonably low temperatures and that it can compete with photolytic cleavage of CO in lower light intensities. Thus, both our detailed kinetic study in aqueous solution and the low-temperature photolytic studies in acetone establish photolytic CO bond cleavage occurs for all Fe(TIM)CO(X)$^{2+}$ complexes, followed by a relaxation whose ultimate result is recoordination of CO but whose time course depends on the [CH$_3$CN] in the solution. There is no solvent-dependent pathway for photolysis of Fe(TIM)CO(X)$^{2+}$ complexes.

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Registry No. Fe(TIM)CO(H$_2$O)$^{2+}$, 90461-83-9; Fe(TIM)CO(CH$_3$CN)$^{2+}$, 49861-54-3; CH$_3$CN, 75-05-8; Fe(TIM)(CH$_3$CN)$_2$$^{2+}$, 49861-52-1; Fe(TIM)(CH$_3$CN)(H$_2$O)$^{2+}$, 93184-90-8; Fe(TIM)(CO)(H$_2$O)$^{2+}$, 90461-83-9; CO, 630-08-0; H$_2$O, 7732-18-5.

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[22] We believe all Fe(II) complexes used in our investigation are low spin in their ground state. The basis for this belief is the exceptional similarity of the spectra of the complexes, independent of the ligands. All species, including Fe(TIM)(CH$_3$CN)$_2$$^{2+}$, which is known from direct measurement to be low spin,[4] exhibit a low-energy peak and a higher energy shoulder—see ref 2 for further details.

[23] Poon, C. K. *Coord. Chem. Rev.* **1973**, *10*, 1–35.

[24] Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 2627. These authors have reported a system that shows a solvent dependence on the nature of the leaving group in photolysis. But in their case, Rh(NH$_3$)$_5$Cl^{2+} photosubstitution, the two leaving groups differ in charge; solvents that poorly solvate Cl$^-$ aquation lower the quantum yield for Cl$^-$ loss either by raising the activation barrier for Cl$^-$ loss or by promoting geminate recombination of the resultant solvent cage trapped ion pair. Note, however, even in this case, that neither the quantum yields for the loss of NH$_3$ nor the rate constants for its loss are highly solvent sensitive.