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Photochemical Properties of the Low-Spin Iron(II)–2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene Complexes. An Investigation of the Secondary Thermal Substitution Reactions by Laser and Flash Photolysis

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The photochemical properties of the Fe(II)–TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) complexes have been investigated by laser and flash photolysis. Rapid substitution reactions of the metastable products have been observed in photolyses of $Fe(TIM)(NCS)_2$, $Fe(TIM)(imid)_2^{2+}$, and $Fe(TIM)(CH_3CN)(CO)^{2+}$ in acetonitrile. Also, photolysis induces a transient linkage isomerization of the thiocyanate complex and two photolabilization processes, substitution of CO and CH_3CN, in $Fe(TIM)(CH_3CN)(CO)^{2+}$. A precursor, assigned as pentacoordinated $Fe(TIM)(CO)^{2+}$, was detected in laser flash photolysis. Aspects of the photosubstituion processes in Fe(II)–TIM complexes are discussed.

Introduction

Photosubstitution reactions of the low-spin iron(II) complexes of the macrocyclic TIM ligand[1] have been recently investigated by several authors.[2-5] The nature of the reactive excited state, charge-transfer metal to ligand (CTTL) or ligand field (LF), has been discussed in these studies. In this regard, the photochemical reactivity has been attributed to the population of LF states.[3]

The photolabilization of the ligand is controlled by the solvent.[4] However, the effect that anation of reactive products and intermediates may have upon the product yields has not been investigated. Processes of this kind, anation of metastable species, have been described for photochemical[6-8] and thermal substitutions[9,10] in low-spin cobalt(III) complexes. Moreover, photodissociative and photointerchange mechanisms have been proposed for the photolabilization reactions of the hexacyano and acidopentacyanocobalt(III) complexes.[5-8] In this regard, one may expect some points in common between the photochemical behavior of the low-spin cobalt(III) compounds, complexed with ligands of a large ligand field strength, and isoelectronic iron(II)–macrocyclic species.

Results on the photochemical and thermal secondary reactions of Fe(II)–TIM[1] complexes, investigated by laser and flash photolysis, are reported here.

Experimental Section

Photochemical Procedures. A description of the flash photolysis apparatus was given elsewhere.[11,12] Reactions of the intermediates were investigated by using various concentrations of these species. Different concentrations were produced with flash outputs which corresponded to stored electrical energies between 250 J/flash and 40 J/flash. Cutoff filters, transmissions at wavelengths $\lambda \geq 320$ nm and $\lambda \geq 410$ nm, were used for irradiations of the photolyte in preselected regions.

The laser flash photolysis apparatus was described in detail by Scaiano et al.[13] The directions of the monitoring and excitation beams were adjusted in order to obtain a tight overlap over the 2 mm optical path of the reaction cell. The monitoring pulse had a useful length of a few microseconds. The laser pulse, placed at the beginning of the monitoring interval, had a full width of 20 ns.

Solutions of the complexes were prepared by addition of a given amount of the solid compounds[14] to solvents which were previously deaerated with streams of argon. Also, $Fe(TIM)(CH_3CN)(CO)^{2+}$ was flash irradiated in solutions that were saturated under a given partial pressure of carbon monoxide. The solvent, in these experiments, was first freed of dioxygen with argon streams and was second equilibrated under a mixture of argon and carbon monoxide for 2 h. The ionic strength of the solutions was adjusted to 0.1 M with $NaClO_4$.

The experimental setup, used in continuous wave irradiations, was described in previous reports.[15] Light intensities, 10^{-4}–10^{-5} einstein/(L min), were measured with ferric oxalate[16] or Reinecke salt.[17]

Materials. The complexes $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, $[Fe(TIM)(imid)_2](PF_6)_2$, and $[Fe(TIM)(CH_3CN)(CO)](PF_6)_2$ were obtained by reported procedures.[18] The purity of these complexes was investigated by comparison of their spectra with those reported by other authors.[2,18] These salts were converted into perchlorates by precipitation with solid $NaClO_4$ from acetonitrile or solutions with an excess of the ligands CO or imidazole in acetonitrile.

$[Fe(TIM)(NH_3)_2](PF_6)_2$ was prepared by the method of Incorvia and Zink.[2] A modification of this procedure was used for the synthesis of the $[Fe(TIM)(N(C_2H_5)_3)_2](PF_6)_2$. Indeed, the dry ammonia gas was replaced by addition of triethylamine, in a fivefold excess of the stoichiometric amount, to a solution of the bis(acetonitrile) complex in CH_2Cl_2. This solution was slowly evaporated with streams of argon.

Anal. Calcd for $FeC_{26}N_6H_{54}P_2F_6$: C, 45.87; H, 8.00. Found: C, 45.91; H, 7.99.

$[Fe(TIM)(NCS)_2]$, the bis(acetonitrile) complex (1 g), was dissolved in the minimum amount of deaerated methanol.[19] NaNCS (0.1 g), dissolved in deaerated methanol, was added. The greenish blue precipitate was filtered and dried in vacuo. The air oxidation of the Fe(II) complexes in methanolic solutions was prevented by

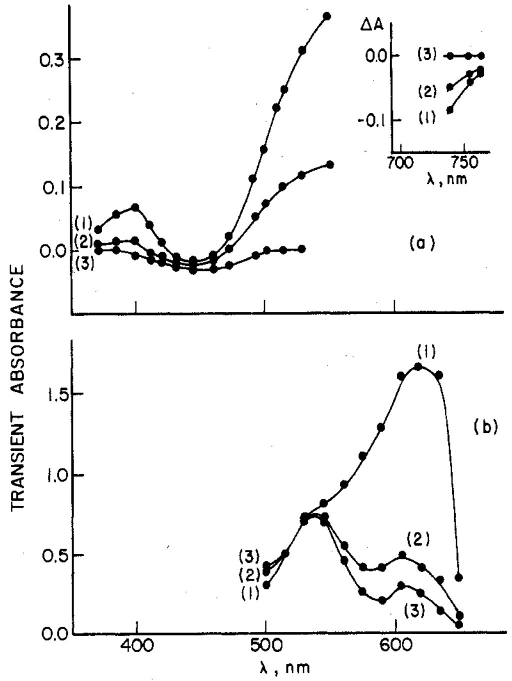

Figure 1. Transient spectra generated in flash photolyses of (a) $Fe(TIM)(NCS)_2$ (reaction times: (1) 50 μs, (2) 540 μs, (3) 4 ms) and (b) $Fe(TIM)(CH_3CN)(CO)^{2+}$ (reaction times: (1) 0 ms, (2) 60 ms, (3) 100 ms).

performing all the manipulations under anaerobic conditions.

Anal. Calcd for $FeC_{16}N_6H_{24}S_2$: C, 45.72; H, 5.76. Found: C, 45.67; H, 5.75.

The absorption spectrum of this complex, obtained in solutions with 10^{-1} M NCS^- (CH_3CN was used as solvent), featured a maximum absorption at $\lambda \sim 675$ nm (ϵ 8.7 × 10^3 M^{-1} cm^{-1}) and a shoulder at $\lambda \sim 625$ nm (ϵ 6.5 × 10^3 M^{-1} cm^{-1}). The same spectrum was obtained with solutions of bis(acetonitrile) complex in acetonitrile which contained 10^{-1} M NCS^-. In addition, this complex was characterized from its infrared spectrum which exhibited characteristic absorptions of the coordinated SCN^- at 2090 and 785 cm^{-1}.[20] These absorptions and the stability of the isothiocyanate complexes of iron(II) suggest that the isolated compound contains nitrogen-bound thiocyanate.[20]

Acetonitrile and methanol were Aldrich spectrometric quality (Gold Label). These solvents were further purified by established procedures.[21,22] The photochemical properties, of the systems studied in this work, did not present differences when each compound was simultaneously investigated in spectrometric or purified solvents. However, some secondary reactions, attributed to impurities, were observed in solutions made with aged acetonitrile. These were avoided by using acetonitrile which was either freshly purified or obtained from new bottles which were opened just before the time of the experiment.

Other chemicals were reagent grade and used without further purifications.

Results and Discussion

Flash photolyses of the Fe(II)–TIM complexes were carried out in deaerated acetonitrile[14] at wavelengths of the CTTL and LF absorptions,[2] $\lambda_{excit} \geq 410$ nm. These irradiations produced transformations in Fe–TIM complexes of SCN^- or imidazole and a stable photolabilization product in the case of $Fe(TIM)(CH_3CN)(CO)^{2+}$. However, each of these systems shows a number of distinctive features which have been discussed below.

(A) $Fe(TIM)(NCS)_2$. Solutions of $Fe(TIM)(NCS)_2$ in deaerated acetonitrile were irradiated at 650 nm ($I_0 \sim 10^{-4}$ einstein/(L min)) for various periods (time ≤120 min). These photolyses failed to produce permanent changes in the solution spectra. However, transient absorbances, Figure 1a, were observed when 10^{-5}–10^{-6} M $Fe(TIM)(NCS)_2$ was flash irradiated in solutions where thiocyanate was in excess (10^{-1}–10^{-4} M SCN^- in acetonitrile). The decay of these absorbances is a complex process. Indeed, the half-life was independent of the amount of the transient generated at zero time and the overall rate constant, k_0, changed linearly with thiocyanate concentration; see Figure 2. These features, summarized in $k_0 = 2.4 \times 10^2 + 9.6 \times 10^4[SCN^-]$ s^{-1}, show that two parallel pathways contribute to the decay of the transient absorbances.[23] The spectrum generated in flash irradiations of $Fe(TIM)(NCS)_2$ in 10^{-1} M NCS^- (Figure 1a), exhibited distinct features at different reaction times. (curves 1–3 in Figure 1a). This time dependence reveals that more than one species is involved in the transformations described above. In this regard, the spectrum at times larger than 10^{-3} s (Figure 1a) can be regarded as the spectrum of the species which disappears by a path independent of the thiocyanate concentration. This species can be assigned as an isomer of $Fe(TIM)(NCS)_2$. It seems feasible that a metastable S-bonded linkage isomer, Fe(TIM)(NCS)(SCN), may be formed in the photochemical reaction. Such a possibility gains some support by taking into consideration that the same linkage isomerism is observed in complexes with other isoelectronic, low-spin, d^6 metal ions.[20] Nevertheless, this metastable S-bonded isomer must be simultaneously formed with another transient product.[24] Some absorptions in the spectrum, obtained for reaction times as short as 50 μs (see (1) in Figure 1a), can be assigned to this species. The same transient absorbances at 500–550 nm were also observed when $Fe(TIM)(CH_3CN)_2^{2+}$ was anated with SCN^- in stop-flow experiments.[25] In this regard, the other transient product of the photolysis can be assigned as $Fe(TIM)(NCS)(CH_3CN)^+$.

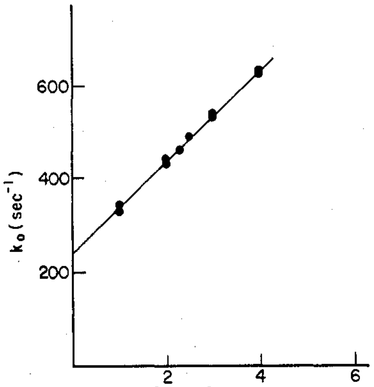

Figure 2. Transient generated in flash photolysis of $Fe(TIM)(NCS)_2$: dependence of the rate constant in thiocyanate concentration; photolysis with 250 J/pulses.

The photochemical formation of the metastable products, Fe(TIM)(NCS)(SCN) and $Fe(TIM)(NCS)(CH_3CN)^+$, occurs in the life of the flash ($t \sim 30$ μs) and it can be described by eq 1 and 2. Moreover, these products must undergo further transformations which restore the spectrum of the parent $Fe(TIM)(NCS)_2$. In this regard, the anation, eq 3 ($k_3 = 9.6 \times 10^4$ M^{-1} s^{-1}), and linkage isomerization, eq 4 ($k_4 = 2.4 \times 10^2$ s^{-1}), account for the decay of the transient absorbances described above.

$$Fe(TIM)(NCS)_2 + h\nu \rightarrow Fe(TIM)(NCS)(SCN) \quad (1)$$

$$Fe(TIM)(NCS)_2 + h\nu \rightarrow Fe(TIM)(CH_3CN)(NCS)^+ + NCS^- \quad (2)$$

$$Fe(TIM)(CH_3CN)(NCS) \xrightarrow{NCS^-} Fe(TIM)(NCS)_2 \quad (3)$$

$$Fe(TIM)(NCS)(SCN) \rightarrow Fe(TIM)(NCS)_2 \quad (4)$$

(B) $Fe(TIM)(imid)_2^{2+}$. Flash photolyses of $Fe(TIM)(imid)_2^{2+}$ in deaerated solutions (solvent CH_3CN; 10^{-3} M ≤

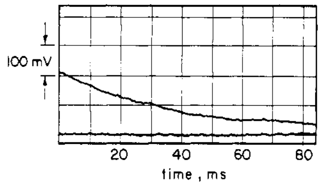

Figure 3. Oscillographic trace obtained in flash photolysis of Fe(TIM)(imid)$_2^{2+}$ (10^{-4}–10^{-5} M) in the presence of 10^{-1} M imidazole (solvent–CH$_3$CN). Observations are at 570 nm.

[imid] $\leq 10^{-1}$ M) produce also transient absorbances with $\lambda_{max} \sim 570$ nm; see Figure 3. These absorbances disappear by a second-order reaction, first order in transient and first order in imidazole concentration, with a rate constant of $k = 2.3 \times 10^2$ M^{-1} s^{-1}.[23] This intermediate can be assigned as a metastable product of the photochemical solvolysis, Fe(TIM)(CH$_3$CN)(imid)$^{2+}$ (eq 5), which recombines with imidazole, eq 6.

$$\text{Fe(TIM)(imid)}_2^{2+} + h\nu \xrightarrow[\text{CH}_3\text{CN}]{\phi} \text{Fe(TIM)(CH}_3\text{CN)(imid)}^{2+} + \text{imid} \quad (5)$$

$$\text{Fe(TIM)(CH}_3\text{CN)(imid)}^{2+} + \text{imid} \rightarrow \text{Fe(TIM)(imid)}_2^{2+} \quad (6)$$

This product can also be described as a pentacoordinate complex, namely, Fe(TIM)(imid)$^{2+}$. However, the results described below for Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ suggest that a pentacoordinate species may be very short-lived for observation in conventional flash photolysis. Moreover, the characterization of Fe(TIM)(CH$_3$CN)(imid)$^{2+}$ or Fe(TIM)(imid)$^{2+}$ as intermediates in substitution reactions between Fe(TIM)(CH$_3$CN)$_2^{2+}$ and imidazole gives some further support to the assignment of these species as metastable products of the photolabilization process.[18b]

(C) Fe(TIM)(CH$_3$CN)(CO)$^{2+}$. Continuous-wave and flash irradiations of the Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ in deaerated CH$_3$CN produce Fe(TIM)(CH$_3$CN)$_2^{2+}$ which is the only stable product of the photochemical reaction. This and the yield of the product, $\phi \sim 0.55 \pm 0.07$ at λ_{excit} 430 nm, agreed well with results that Incorvia and Zink reported for continuous-wave irradiations of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ in acetonitrile.[2] Flash irradiations did not reveal metastable species with lives larger than 30 μs. Indeed, no recombination of the photoproducts CO and Fe(TIM)(CH$_3$CN)$_2^{2+}$, formed in the life of the flash, was detected when carbon monoxide was present in low concentrations, [CO] $< 10^{-5}$ M.

A distinct photochemical reactivity was exhibited by Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ in solutions where carbon monoxide was present in concentrations larger than 10^{-5} M. Insofar as no stable products were detected under these conditions, photochemical transformations were investigated by flash photolysis. Flash irradiations of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$, in solutions saturated under 1 atm of CO, produce transient absorbances, Figure 1a, which are attributed to two distinct species.[23] The long-lived species, $\lambda_{max} \sim 540$ nm, was assigned as Fe(TIM)(CH$_3$CN)$_2^{2+}$. This product reacts with CO reforming the parent complex Fe(TIM)(CH$_3$CN)(CO)$^{2+}$. Indeed, the same reaction rate has been found for the disappearance of this species, Figure 4, and the thermal substitution of CH$_3$CN by CO in Fe(TIM)(CH$_3$CN)$^{2+}$; see Figure 4. A rate constant, $k = (6.6 \pm 0.4)$ M^{-1} s^{-1}, was estimated for the substitution process by using a concentration of carbon monoxide [CO] $\sim 4.0 \times 10^{-3}$ M in these calculations.[26] The short-lived species disappears with a half-life time, $t_{1/2} \sim 37 \times 10^{-3}$ s, which is independent of the transient and carbon monoxide concentrations as it is shown in Table I. The yield of this species was, in addition, proportional to the concentration of carbon monoxide. However, such a dependence was not observed for the yield of Fe(TIM)(CH$_3$CN)$_2^{2+}$; see Table I. This behavior suggests that the bis(acetonitrile) complex and the short-lived species are generated by different precursors. Moreover, the formation of the short-lived species occurs when one of these precursors reacts with carbon monoxide. In this regard, this species can be described as a dicarbonyl complex, {Fe(TIM)(CO)$_2^{2+}$}. The metastable {Fe(TIM)(CO)$_2^{2+}$} and the species Fe(TIM)(CO)$_2^{2+}$ exhibit large differences in their stabilities and absorption spectra.[27] In this regard the intermediate might then be considered an isomer of Fe(TIM)(CO)$_2^{2+}$. Isomerism must be the result of concurrent differences in the coordination sphere of these species and in the spin state of the metal centers.[28] Indeed, the existence of macrocyclic complexes of iron(II) in two spin states and the equilibrium between them has been reported by Busch and co-workers.[29] Evaluation of the promotional energy for these species, see ref 30 and 31, gives a value which is consistent with the metastable nature of {Fe(TIM)(CO)$_2^{2+}$}.[31]

The possible existence of the precursors of the metastable products, generated in photolyses of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ (see above), was further investigated in a nanosecond to microsecond time scale by laser flash photolysis. Transient transformations of the absorption spectrum were observed when Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ was irradiated in deaerated acetonitrile. Figure 5a,b shows a time-resolved bleach of the solution's absorbance, observed at wavelengths $\lambda < 520$ nm, and transient absorbances, observed at $\lambda > 520$ nm. These two transformations obey a first-order rate law with a rate constant,

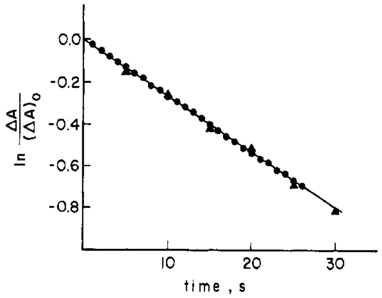

Figure 4. Decay of the long-lived intermediate, ●, generated in flash photolysis of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$, and anation of Fe(TIM)(CH$_3$CN)$_2^{2+}$, ▲. Both reactions were carried out with solutions of CO (4×10^{-3} M) in acetonitrile.

Table I. Decay of Intermediates Generated in Flash Photolyses of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$

$t_{1/2}$,[a] ms	A_0[b]	conditions[c] ([CO], M; J/flash)
	(I) {Fe(TIM)(CO)$_2^{2+}$}	
38	0.211	4.0×10^{-3}; 160
40	0.343	4.0×10^{-3}; 203
39	0.382	4.0×10^{-3}; 250
37	0.267	9.0×10^{-4}; 250
37	0.161	2.5×10^{-4}; 250
d	*d*	$\leqslant 10^{-5}$; 250
	(II) Fe(TIM)(CH$_3$CN)$_2^{2+}$	
26.3×10^3	0.750	4.0×10^{-3}; 250
37.5×10^3	0.712	2.0×10^{-3}; 250
>1 min	0.719	$\leqslant 10^{-5}$; 250

[a] Half-life time determined as an average of two to four determinations. Decay of the absorbance followed at 625 nm (short-lived intermediate) and at 540 nm (long-lived intermediate). [b] Yields of the products; expressed as absorbance produced within the life of the flash at given wavelengths (see *a*). [c] Reactions investigated with solutions of Fe(TIM)(CH$_3$CN)(CO)$^{2+}$ (10^{-4}–10^{-5} M) in acetonitrile. [d] Not observed.

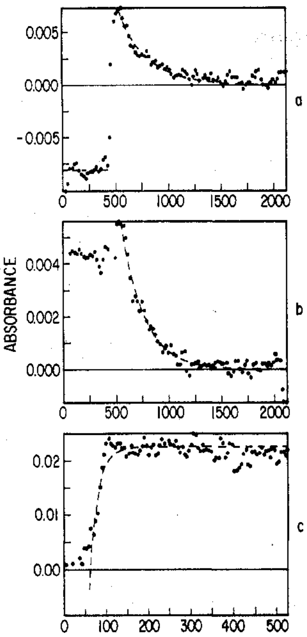

Figure 5. Transient transformations observed in laser flash photolysis of $Fe(TIM)(CH_3CN)(CO)^{2+}$ in acetonitrile. Reactions investigated at (a) λ 560 nm in deaerated solutions, (b) λ 435 nm in deaerated solutions, and (c) λ 580 nm with solutions of the Fe–TIM complex in the presence of 4×10^{-3} M CO.

$k = 4.6 \times 10^7\ s^{-1}$, which is independent of the monitoring wavelength in the region 400–600 nm. In addition, the spectrum, determined after the decay of the transient absorbances (1–2 μs after the laser pulse), was in good agreement with one obtained for the product $Fe(TIM)(CH_3CN)_2^{2+}$; see above. These results and the independence of the $Fe(TIM)(CH_3CN)_2^{2+}$ yield of carbon monoxide concentration (Table I) demonstrate that the decay of this transient does not contribute to the formation of the bis(acetonitrile) complex. Therefore, the observed intermediate must re-form the parent complex.

The interception of the precursor with carbon monoxide (4.0×10^{-3} M CO in deaerated CH_3CN[20]) produces a transient growth of the absorbance at 500–600 nm; see Figure 5c. The new absorbances did not exhibit any decay in a nanosecond–microsecond time scale and their spectrum agreed with one obtained in conventional flash photolysis for the metastable bis(carbonyl) intermediate (see spectrum 1 in Figure 1b). Therefore, this product is formed with a rate constant, $k = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, which has been evaluated from the absorbance growth at 580 nm; see Figure 5c.

A photodissociative mechanism, eq 7–14, explains the results described above.

The photolabilization of CH_3CN and CO, eq 7 and 8, can be induced in the same or in different excited states. Moreover, reaction 10 cannot compete with reaction 9 under the experimental conditions of this work. In this regard, the species observed in laser photolysis must be identified as the monocarbonyl complex in reactions 11 and 12.

The associative solvent attack on a six-coordinate excited state[4] was proposed as an alternative to the photodissociative mechanism. However, the associative mechanism does not provide an appropriate explanation of the reactivity of the shortest lived intermediate. In addition, the existence of pentacoordinate complexes of iron(II) with macrocyclic ligands (see ref 33 and 34) suggests that the formation of a pentacoordinate species must be a more convenient reaction route. Also, the photochemical reactivity of the bis(isothiocyanate) and bis(imidazole) complexes, eq 1–7, can be explained by

$$Fe(TIM)(CH_3CN)(CO)^{2+} \xrightarrow[+h\nu]{\phi_1} Fe(TIM)(CH_3CN)^{2+} + CO \tag{7}$$

$$Fe(TIM)(CH_3CN)(CO)^{2+} \xrightarrow[+h\nu]{\phi_2} Fe(TIM)(CO)^{2+} + CH_3CN \tag{8}$$

$$Fe(TIM)(CH_3CN)^{2+} \xrightarrow{CH_3CN} Fe(TIM)(CH_3CN)_2^{2+} \tag{9}$$

$$Fe(TIM)(CH_3CN)^{2+} \xrightarrow{CO} Fe(TIM)(CH_3CN)(CO)^{2+} \tag{10}$$

$$Fe(TIM)(CO)^{2+} \xrightarrow{CH_3CN} Fe(TIM)(CH_3CN)(CO)^{2+} \tag{11}$$

$$Fe(TIM)(CO)^{2+} \xrightarrow{CO} \{Fe(TIM)(CO)_2^{2+}\} \tag{12}$$

$$Fe(TIM)(CH_3CN)_2^{2+} + CO \rightarrow Fe(TIM)(CH_3CN)(CO)^{2+} \tag{13}$$

$$\{Fe(TIM)(CO)_2^{2+}\} + CH_3CN \rightarrow Fe(TIM)(CH_3CN)(CO)^{2+} \tag{14}$$

assuming that photodissociative processes generate pentacoordinate intermediates. However, the photosubstitution of the coordinate ligands by an interchange mechanism[6] cannot be ruled out.

The photolabilization process was investigated also with $Fe(TIM)(CH_3CN)^{2+}$, $Fe(TIM)(NH_3)_2^{2+}$, and $Fe(TIM)(N(C_2H_5)_3)_2^{2+}$. Transients, with lives larger than 30 μs, were not observed under a wide range of conditions. For example, flash photolyses of $Fe(TIM)(N(C_2H_5)_3)_2^{2+}$ were carried out in 10^{-1}–10^{-3} M $N(C_2H_5)_3$ (solvent; deaerated CH_3CN). The absence of observable intermediates suggests that either or both these complexes are less photoreactive than other compounds (see above) and substitution reactions of the photoproducts re-form the parent complex in less than 30 μs. Such a fast reaction requires a rate constant of $k \geq 5 \times 10^7\ M^{-1}\ s^{-1}$ in the case of the bis(amine) complex.[33]

Concluding Remarks

The results indicated above show that secondary reactions of the primary products may have a significant effect on the value of the quantum yields of the macrocyclic iron complexes. Indeed, the apparent absence of photochemical reactivity in continuous irradiations may be related, in many cases, to the lability of the primary photoproducts. This point is well illustrated by the photochemistries of the complexes $Fe(TIM)(NCS)_2$ and $Fe(TIM)(imid)_2^{2+}$ and the photolabilization of the CH_3CN ligand in $Fe(TIM)(CH_3CN)(CO)^{2+}$. Also this shows that caution must be exerted when product yields, obtained from continuous-wave photolyses, are used as a basis of information about the excited-state properties in these compounds.

The observed photochemistry of the bis(imidazole) complex shows that photoinactivity is not uniquely determined by the presence of a CTTL state with a lower energy than a LF state.[34] Moreover, the experimental conditions, used here for flash photolysis, *show that the major amount of the photochemical reactivity must be associated with the direct population of the CTTL state by absorption of light and/or other state which achieves a very large population at the expense of the CTTL state.*

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Registry No. $Fe(TIM)(NCS)_2$, 69765-88-4; $Fe(TIM)(imid)_2^{2+}$, 49861-53-2; $Fe(TIM)(CH_3CN)(CO)^{2+}$, 49861-54-3; Fe(TIM)-

$(CO)_2{}^{2+}$, 69765-89-5; $Fe(TIM)(CH_3CN)_2{}^{2+}$, 49861-52-1; $[Fe(TIM)(N(C_2H_5)_3)_2](PF_6)_2$, 69765-91-9.

References and Notes

(1) Ligand abbreviations: TIM, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; imid, imidazole.

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(24) Notice that the overall rate constant, k_0, shows *the existence of two parallel and independent pathways* for the decay of the transient absorbances.

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(31) The crossover point occurs for $20Dq > 5(F_2 + 51F_4)$.[30] Therefore, a promotional energy of 10–20 kcal/mol, for a change from low to high spin, is expected for Dq values between 2000 and 2400 cm^{-1}.[32] It is feasible that distortions from an octahedral configuration in $\{Fe(TIM)(CO)_2{}^{2+}\}$ stabilize a high-spin ground state.

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(34) See ref 2 for an assignment of the energies for LF and CTTL transitions.

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Ligand Field Photolysis of *cis*-Tetraamminedichlorochromium(III) and *cis*-α-(Triethylenetetramine)dichlorochromium(III) Cations

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The ligand field photolysis of *cis*-$[Cr(NH_3)_4Cl_5]^+$ in acidic solution results in both amine ($\phi_{H^+} = 0.32$) and chloride ($\phi_{Cl^-} = 0.15$) labilization. The analogous *cis*-α-$[Cr(trien)Cl_2]^+$ ion displays negligible amine loss ($\phi_{H^+} = 0.015$), with chloride aquation dominating ($\phi_{Cl^-} = 0.10$). The photolyses proceed with retention of cis configuration. The total photochemical reactivity ($\phi_{H^+} + \phi_{Cl^-}$) for *cis*-$[CrN_4Cl_2]^+$ is shown to be linearly related to the rate of thermal chloride aquation at 25 °C. The photochemical results are interpreted in terms of the semiempirical photolysis rules and ligand field photolysis models.

Introduction

Among transition metal complexes, the cationic amine complexes of Cr(III) represent one of the most thoroughly studied, if not understood, systems.[1] Elaborate models, both empirical[2] and theoretical,[3,4] have been developed to predict the photolabilized ligand and the relative quantum yields of the photoinduced reaction. The experimental support for these models is surprisingly limited, however, as only complexes of the form $[Cr(N)_5X]^{2+}$ and *trans*-$[Cr(N)_4XY]^+$ (X, Y = halide, pseudohalide, water; N = an amine (NH_3, 1/2(en), etc.)) have been extensively studied.[1] In addition, these models do not account for the stereochemical rearrangements commonly observed upon photolysis of Cr(III) ions.

Theoretical analyses of the stereophotochemistry of d^3 and d^6 systems have recently been presented by Vanquickenborne and Ceulemans,[5,6] in which the chemical processes resulting from ligand field excitation are separated into three distinct steps: (1) ligand labilization, (2) intramolecular distortion of the remaining five-coordinate intermediate, and (3) water attack of the distorted, five-coordinate intermediate. Without discounting the possibility that these processes may be concerted to some extent, a correlation diagram of the second step revealed that for monosubstituted and trans-disubstituted amine complexes of Cr(III), distortion to a trigonal-bipyramidal species was favored for the lowest energy quartet excited state (^4E). In addition, these calculations suggested that cis water attack would be favored over trans attack, accounting for the formation of the cis aquation products generally observed upon ligand field photolysis of these ions.

As part of our investigation of the stereochemistry of ligand field photochemistry of transition-metal complexes, we have investigated the ligand field photochemistry of *cis*-$[Cr(NH_3)_4Cl_2]^+$ and *cis*-α-$[Cr(trien)Cl_2]^+$ (Figure 1). The photochemical behavior of only a few Cr(III) complexes of cis geometry has been reported,[7-9] so an understanding of the photochemistry of these simple ions can provide tests of the photochemical models, as well as allow insight into the stereochemical rearrangements which often accompany Cr(III) photolyses. Photolysis of *cis*-α-$[Cr(trien)Cl_2]^+$ offers a special test of the models which attempt to predict the photolabilized