The conductivity of a neodymium perchlorate solution is presented for comparative purposes and is typical of a 3:1 electrolyte.

The low conductance values obtained for nitrate solutions containing excess ligand indicate that the equilibrium

$$\mathrm{Ln(tren)(NO_3)_3} + \mathrm{tren} \rightleftharpoons \mathrm{Ln(tren)_2(NO_3)_n}^{(3-n)+} + (3-n)\mathrm{NO_3}^- \quad (n = 0, 1)$$

lies predominantly to the left. This behavior is attributed to the coordinating ability of the nitrate group, rather than intrinsic instability of the bis chelate. Thus the thermodynamically favored species in solution is the mono chelate containing three coordinated nitrate groups. Similar results were observed in the diethylenetriamine system, in which $\mathrm{Ln(dien)_2(NO_3)_2}^+$ was established as the favored species in solution, even though $\mathrm{[Ln(dien)_3](NO_3)_3}$ was isolable from solution in pure form. The isolation of pure bis-tren chelates containing at most one coordinated nitrate group is apparently due to a greater insolubility of the bis chelate in acetonitrile, since nitrate displacement is not favored thermodynamically.

Acknowledgments.—The work at St. Louis University was supported in part by a Frederick Gardner Cottrell Grant from Research Corporation. That at Arizona State University was supported by Grant 15941 from the National Science Foundation.

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Photoreduction of Tris(1,10-phenanthroline)iron(III)

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Received April 21, 1971

Tris(1,10-phenanthroline)iron(III) undergoes photoreduction in acidic aqueous media. The effects of acid concentration and added scavengers indicate that water is the electron donor in the photoreaction and that secondary thermal reactions of $\mathrm{Fe(phen)_3}^{3+}$ with OH radicals influence apparent overall quantum yields. Despite the presence of an intense ligand→metal charge-transfer band in the visible spectrum of $\mathrm{Fe(phen)_3}^{3+}$, the complex undergoes photoreduction only in the ultraviolet. The excited state(s) responsible for the observed photochemistry cannot be conclusively identified on the basis of current understanding of the charge-transfer spectrum of $\mathrm{Fe(phen)_3}^{3+}$.

Correlation of redox photochemistry with the locations of charge-transfer excited states (hereafter denoted "CT" states) in coordination compounds is an area of considerable current activity.[1] Although intramolecular CT absorption spectra of metal complexes with 1,10-phenanthroline (subsequently abbreviated "phen") and its relatives have been discussed,[2] photochemistry of phen complexes has received little attention. We have been especially intrigued by a study of photoreduction of $\mathrm{Fe(phen)_3}^{3+}$ published by Baxendale and Bridge[3] in 1955. According to their observations, $\mathrm{Fe(phen)_3}^{3+}$ undergoes efficient photoreduction to $\mathrm{Fe(phen)_3}^{2+}$ only at wavelengths below 300 nm. A spin-allowed $\pi \rightarrow t_2$ CT band[2] appears in the visible region (*ca.* 600 nm), but irradiation in that region effects no photoreduction of $\mathrm{Fe(phen)_3}^{3+}$. Unfortunately, these studies were performed in media containing high concentrations of formic acid, which absorbs in the ultraviolet region and is known to undergo photodecomposition in aqueous solution, yielding OH and CHO radicals as primary products.[4] Because it is highly probable that one or both of the photolysis products of formic acid can react thermally with $\mathrm{Fe(phen)_3}^{3+}$, the significance of the quantum yield data reported by Baxendale and Bridge for wavelengths below 300 nm is dubious. Accordingly, we have performed an investigation of photoreduction of $\mathrm{Fe(phen)_3}^{3+}$ in acidic aqueous media in the absence of extraneous photochemically active solutes.

Experimental Section

Materials.—Tris(1,10-phenanthroline)iron(III) perchlorate was prepared by oxidizing $\mathrm{Fe(phen)_3}^{2+}$ with $\mathrm{Cl_2}$ in aqueous solution; the perchlorate salt of $\mathrm{Fe(phen)_3}^{3+}$ was then precipitated by addition of sodium perchlorate. The solid was washed with 10 *M* aqueous sulfuric acid until supernatants were free of Cl^-; it was dried and stored *in vacuo* in the dark. An nmr spectrum (60 MHz) of this preparation of $\mathrm{Fe(phen)_3}^{3+}$ in concentrated $\mathrm{D_2SO_4}$ agreed well with that published by DeSimone and Drago.[5]

Potassium ferrioxalate[6] and uranyl oxalate[7] for actinometry were prepared and purified by literature procedures. Methyl methacrylate was repeatedly washed with 5% aqueous NaOH to remove inhibitors, washed with distilled water, and then vacuum distilled. The purified material was stored at 4° in the dark in evacuated ampoules until used. Water was distilled twice over alkaline permanganate. Reagent grade $\mathrm{D_2SO_4}$ (Merck Sharp and Dohme of Canada) and $\mathrm{H_2SO_4}$ were used as received.

Methods.—Two photochemical irradiation sources were used. In the first, 2537-Å light from a helical low-pressure mercury lamp was impinged upon cylindrical quartz cuvettes in a merry-

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go-round apparatus; intensities at 2537 Å were of the order of 2×10^{16} quanta sec^{-1}. In the second apparatus, light from a Hanovia 975C98 2500-W xenon lamp was dispersed by a Bausch and Lomb 500-mm monochromator and directed onto the face of rectangular 1-cm spectrophotometer cells. With this apparatus, experiments could be performed at incident wavelengths as low as 225 nm; bandwidths were generally of the order of 6 nm, and intensities (at 270 nm) were *ca.* 9×10^{15} quanta sec^{-1}. The cell housing was thermostated at 30 ± 0.2° by a water bath.

At incident wavelengths greater than 254 nm, ferrioxalate actinometry[6] was employed; for lower wavelengths, uranyl oxalate actinometry[7] with differential spectrophotometric product analysis[8] was used. At 254 nm, both actinometers were employed in comparative runs; less than 6% difference in I_a values determined with the two actionometers was observed. Uranyl oxalate consistently yielded slightly lower I_a values than did ferrioxalate actinometry; none of the yields herein reported have been corrected for this relatively small discrepancy.

Unless otherwise indicated, all solutions contained only $Fe(phen)_3^{3+}$ and sulfuric acid as solutes. Electronic spectra of $Fe(phen)_3^{3+}$ solutions were measured prior to irradiation, in order to ensure absence of dinuclear Fe(III)-phen species[9,10] which absorb strongly in the vicinity of 350 nm; the dinuclear species can be formed as products of thermal decomposition of $Fe(phen)_3^{3+}$.[11] In a given series of experiments, care was exercised to photolyze all solutions to the same fractional decomposition of $Fe(phen)_3^{3+}$ (usually 10% unless otherwise indicated). When necessary, solutions were degassed by techniques previously described.[12] Irradiated solutions were analyzed by visible spectrophotometry at 610 nm (for $Fe(phen)_3^{3+}$) or 500 nm (for $Fe(phen)_3^{2+}$).

Results

Thermal Stability of Complex.—Since relatively high incident intensities were employed, relatively short (≤3 hr) irradiations were performed, even though the quantum yields were small. The thermal stability of $Fe(phen)_3^{3+}$ in aqueous solution increases with increasing acid concentration;[11,13] at sulfuric acid concentrations of 6.0 *M* or greater, thermal stability of $Fe(phen)_3^{3+}$ was sufficient that no detectable dark reaction occurred over the duration of photochemical runs. All quantum yields were obtained under conditions of negligible dark reaction.

Reproducibility of Quantum Yields.—Baxendale and Bridge[3] observed that values of Φ for appearance of $Fe(phen)_3^{2+}$ were erratic unless formic acid (or other oxidant) was present in the solutions. We have observed that Φ for appearance of $Fe(phen)_3^{2+}$ did not vary by more than ±10% upon use of different preparations of the complex. Accordingly, no extraneous solutes were employed, and quantum yields herein reported may be assumed to include a ±10% uncertainty.

Variation of Quantum Yield with Wavelength.—Our results duplicate the observations of Baxendale and Bridge[3] with respect to the unreactivity of $Fe(phen)_3^{3+}$ at all wavelengths between 300 and 660 nm. As noted in Figure 1, Φ for destruction of $Fe(phen)_3^{3+}$ increased rapidly in the ultraviolet spectrum, eventually reaching what appeared to be a limiting value at about 240 nm. Even upon prolonged irradiation at 610 nm, no detectable conversion of $Fe(phen)_3^{3+}$ to $Fe(phen)_3^{2+}$ was observed in 7.5 *M* sulfuric acid; we estimate Φ for destruction of $Fe(phen)_3^{3+}$ to be less than 0.0001 in the region of the visible CT band. Under conditions of constant light intensity, the stoichiometry (*vide infra*) of the photoreduction was independent of incident wavelength.

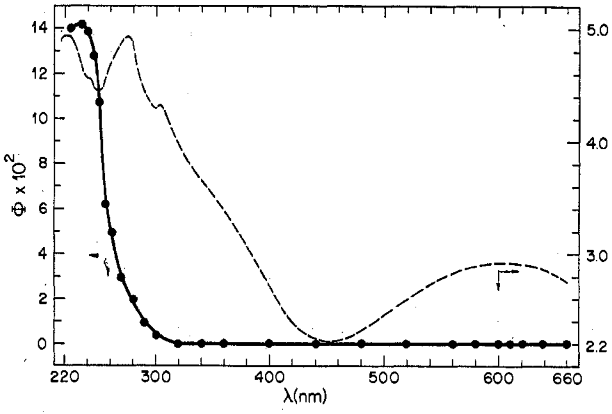

Figure 1.—Variation of quantum yield for disappearance of $Fe(phen)_3^{3+}$ with wavelength (—) and electronic absorption spectrum of $Fe(phen)_3^{3+}$ (----), both in 7.5 *M* H_2SO_4. For the quantum yield plot, the initial concentration of $Fe(phen)_3^{3+}$ was 1.00×10^{-4} *M*.

Variation of Quantum Yield with Solvent Composition.—Quantum yields for destruction of $Fe(phen)_3^{3+}$ were very sensitive to acid concentration (Figure 2).

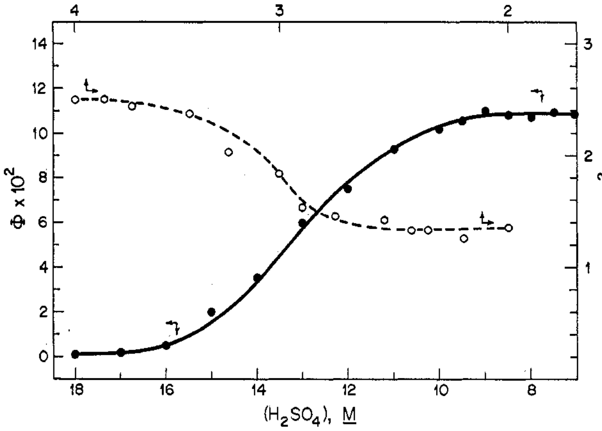

Figure 2.—Variation of quantum yield for disappearance of $Fe(phen)_3^{3+}$ with concentration of H_2SO_4 (—) and with concentration of methyl methacrylate ("MMA," ----). In the MMA plot, the exciting wavelength was 275 nm and the solutions were 7.0 *M* in H_2SO_4. For the H_2SO_4 plot, the exciting wavelength was 250 nm.

For 254-nm irradiation, no detectable photoreaction occurred in 98% (18 *M*) sulfuric acid. As the acid concentration was decreased, the quantum yield increased and eventually reached a limiting value at about 8.5 *M* H_2SO_4.

Chemical Scavenging Experiments.—Degassed solutions 7.2×10^{-4} *M* in $Fe(phen)_3^{3+}$ and 7.0 *M* in sulfuric acid were photolyzed at 275 nm in the presence of various concentrations of methyl methacrylate. After prolonged (2–4 hr) exposures, copious quantities of polymer were recovered. The polymer was recrystallized,[14] dissolved in benzene, and treated with phthalic anhydride.[15] The polymer so treated was then subjected to

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the Rhodamine 6G dye partition test for carboxyl end groups. In all cases, the test was positive, indicating the presence of hydroxyl end groups in the original polymer samples.[15] Polymer obtained in the same manner, but which was not subjected to phthalic anhydride treatment, yielded a negative dye test, as did polymer samples obtained from irradiated "blank" solutions (containing methyl methacrylate but no $Fe(phen)_3{}^{3+}$; because methyl methacrylate absorbs weakly at 270 nm, some polymer was formed by inner-filter photopolymerization). Infrared examination of polymer samples obtained from irradiated $Fe(phen)_3{}^{3+}$ solutions indicated the presence of carboxyl and hydroxyl groups; no other information could be gleaned from the spectra.

The quantum yield for disappearance of $Fe(phen)_3{}^{3+}$ decreased in the presence of methyl methacrylate, as shown in Figure 2.

Stoichiometry of the Reaction.—In contrast to the observations of Baxendale and Bridge,[3] we noted that photochemical conversion of $Fe(phen)_3{}^{3+}$ to $Fe(phen)_3{}^{2+}$ in aqueous sulfuric acid media was not quantitative; the quantity of $Fe(phen)_3{}^{3+}$ consumed was always greater than the quantity of $Fe(phen)_3{}^{2+}$ formed. No detectable quantities of uncomplexed (protonated) phenanthroline or dinuclear Fe(III)-phen species[9,10] were formed, indicating that a quantity of phenanthroline was destroyed. The *ratio* of the quantity of $Fe(phen)_3{}^{2+}$ formed to that of $Fe(phen)_3{}^{3+}$ destroyed was observed to increase as the concentration of sulfuric acid was increased, to increase in the presence of methyl methacrylate, and to decrease as the incident intensity was increased. These data are plotted in Figures 3 and 4.

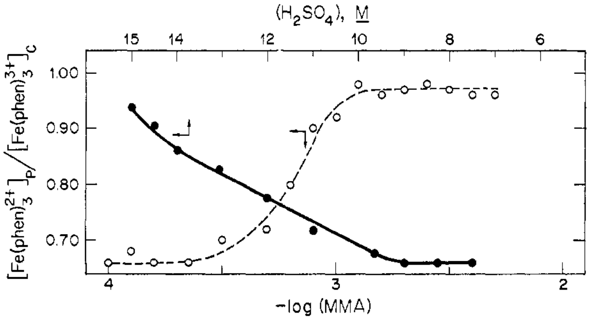

Figure 3.—Variation of ratio of quantity of $Fe(phen)_3{}^{2+}$ produced to that of $Fe(phen)_3{}^{3+}$ consumed with concentration of methyl methacrylate ("MMA," ----) and with concentration of H_2SO_4 (—). In the MMA plot, the solutions were 7.0 *M* in H_2SO_4; the incident wavelength was 270 nm. In the H_2SO_4 plot, the incident wavelength was 250 nm.

In each experiment, the initial concentration of $Fe(phen)_3{}^{3+}$ was 3.3×10^{-4} *M*, and 10% of the $Fe(phen)_3{}^{3+}$ initially present was photochemically consumed. Comparison of Figures 2 and 3 indicates that both Φ and $[Fe(phen)_3{}^{2+}]_p/[Fe(phen)_3{}^{3+}]_c$, when plotted *vs.* methyl methacrylate concentration, plateau at essentially the same concentration. It is also evident that the stoichiometry of the photoreduction approaches unity only in the presence of substantial concentrations of methyl methacrylate.

Dependence of Quantum Yield upon Incident Intensity.—As shown in Figure 4, overall quantum yields for destruction of $Fe(phen)_3{}^{3+}$ increased with increasing light intensity. The quantum yield for appearance of $Fe(phen)_3{}^{2+}$ was, however, virtually independent of incident intensity.

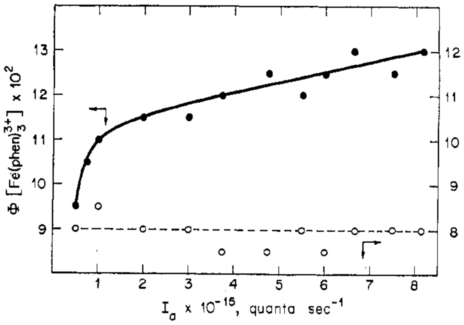

Figure 4.—Dependence of quantum yield for disappearance of $Fe(phen)_3{}^{3+}$ (—) and that for appearance of $Fe(phen)_3{}^{2+}$ (----) with absorbed intensity (I_a). In all cases, the exciting wavelength was 250 nm and the solutions were 7.5 *M* in H_2SO_4 and 3.3×10^{-4} *M* in $Fe(phen)_3{}^{3+}$.

Dependence of Quantum Yield upon Initial Concentration of $Fe(phen)_3{}^{3+}$.—Baxendale and Bridge[3] reported that Φ for photoreduction of $Fe(phen)_3{}^{3+}$ at 365 nm, in the presence of 0.47 *M* formic acid, was approximately linear in the first power of the initial concentration of $Fe(phen)_3{}^{3+}$ over a narrow concentration range. We have observed that Φ is essentially zero at 365 nm. At 270 nm, Φ for consumption of $Fe(phen)_3{}^{3+}$ increases with increasing concentration of $Fe(phen)_3{}^{3+}$ at concentrations greater than *ca.* 7×10^{-6} *M* but is relatively independent of initial concentration below that value. These data are plotted in Figure 5.

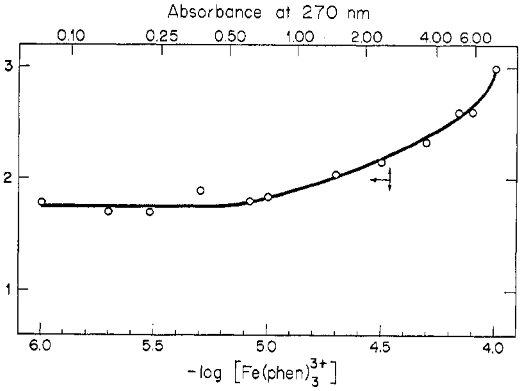

Figure 5.—Variation of quantum yield for disappearance of $Fe(phen)_3{}^{3+}$ with initial concentration of $Fe(phen)_3{}^{3+}$. In all cases, the exciting wavelength was 270 nm and the solutions were 7.5 *M* in H_2SO_4.

Effect of Oxygen upon Quantum Yields.—In 7.5 *M* H_2SO_4, neither the quantum yield nor the stoichiometry of the photoreduction was detectably affected by six freeze-thaw cycles at 10^{-4} Torr. Hence, all quantum yields herein reported were determined in the presence of oxygen.

Discussion

Both photochemical and thermal stabilities of $Fe(phen)_3{}^{3+}$ are maximal in 18 *M* H_2SO_4 and decrease as the acid concentration is decreased.[11,13] Tobe[13] has contended that the critical variable with respect to thermal stability of $Fe(phen)_3{}^{3+}$ in aqueous H_2SO_4 is the concentration of "free" water and has suggested that thermal decomposition of $Fe(phen)_3{}^{3+}$ proceeds by a substitution reaction in which one or more water molecules is weakly bound to iron in the transition state. The pattern of results in the photochemical study also indicates the presence of water to be critical, and indeed it appears justified to conclude that water is the electron donor in the photochemical reduction. Two principal arguments are advanced to support that conclusion. First, it is clear from Figure 2 that the photoreaction proceeds with measurable yield only in the presence of water; thus, the quantum yield is essentially zero in 98% H_2SO_4, increases with decreasing acid concentration, and eventually reaches a limiting value at 8.5 *M* H_2SO_4. Second, chemical scavenging experiments, employing methyl methacrylate as scavenger, and subsequent analysis[14,15] of the polymeric product clearly indicate production of OH radicals in the photoreduction of $Fe(phen)_3{}^{3+}$. These radicals are not formed in inner-filter photopolymerization of methyl methacrylate. Accordingly, we conclude that the photochemical reduction may be represented as

$$Fe(phen)_3{}^{3+} + H_2O \xrightarrow[h\nu]{} Fe(phen)_3{}^{2+} + H^+ + OH$$

The pH change predicted by the equation cannot be measured, due to the very high initial acidity of the solutions.

It is impossible to deduce the nature of interactions between $Fe(phen)_3{}^{3+}$ and water from the photochemical data. It is improbable that nucleophilic attack of water upon electronically excited $Fe(phen)_3{}^{3+}$ could be efficient, owing to the extremely short lifetime of the latter species (as indicated by the fact that $Fe(phen)_3{}^{3+}$ exhibits no photoluminescence in either fluid or glassy media). The electronic absorption spectrum of $Fe(phen)_3{}^{3+}$ in 98% H_2SO_4 is not detectably altered by introduction of water into the solutions; other experimental techniques (nmr or infrared spectroscopy) commonly employed to probe interactions between metal complexes and water are not feasible in solutions of concentrated sulfuric acid. Thus, no evidence for significant interaction between water and ground-state $Fe(phen)_3{}^{3+}$ has been acquired, and the nature of interactions between water and $Fe(phen)_3{}^{3+}$ remains unclear. That water is oxidized concomitant with photoreduction of $Fe(phen)_3{}^{3+}$ is, however, firmly established by the scavenging experiments.

We now consider the origin of the stoichiometric discrepancy (Figures 3 and 4). At least three possible explanations for the observed stoichiometry can be advanced. (a) Phenanthroline, rather than water (*vide supra*), could act as electron donor; some phen would thus be oxidized and ultimately destroyed. (b) The solutions are acidic; hence, a fraction of $Fe(phen)_3{}^{2+}$ formed photochemically could undergo thermal acid hydrolysis. (c) Secondary thermal reactions of $Fe(phen)_3{}^{3+}$ and/or $Fe(phen)_3{}^{2+}$ with transient species formed in photolysis of the former could cause destruction of a portion of one or both complexes.

We conclude that (c) is the major factor influencing the photochemical stoichiometry, and the specific reaction of greatest importance is destruction of $Fe(phen)_3{}^{3+}$ by reaction with OH. The principal evidence supporting that conclusion is the effect of added methyl methacrylate upon the stoichiometry (Figure 3). The principal effect of addition of methyl methacrylate is to decrease Φ for destruction of $Fe(phen)_3{}^{3+}$; Φ for formation of $Fe(phen)_3{}^{2+}$ remains essentially unchanged in the presence of methyl methacrylate. Indeed, at concentrations of methyl methacrylate sufficiently large that the quantum yield for disappearance of $Fe(phen)_3{}^{3+}$ is unaffected by further addition of methyl methacrylate (Figure 2), the stoichiometry of the reaction is 1:1 (Figure 4). It is therefore clear that the methyl methacrylate scavenges a species which reacts thermally with $Fe(phen)_3{}^{3+}$, and it has been shown that the methyl methacrylate scavenges OH radicals produced in the photolysis. The effects of $Fe(phen)_3{}^{3+}$ concentration (Figure 5) and incident intensity (Figure 4) upon Φ and stoichiometry are also consistent with the occurrence of a secondary, thermal reaction which consumes $Fe(phen)_3{}^{3+}$.

Oxidation of the phen ligand by OH (produced in thermal oxidation of OH^- by $Fe(phen)_3{}^{3+}$) has been explicitly considered to be significant,[16] but no direct evidence for such processes has been reported. In order to test the validity of the hypothesis that OH can attack $Fe(phen)_3{}^{3+}$, solutions 0.01 *M* in hydrogen peroxide and 3.3×10^{-4} *M* in $Fe(phen)_3{}^{3+}$ in 4.0 *M* sulfuric acid were photolyzed at 265 nm. Rapid bleaching of the iron complex resulted, and ultraviolet spectral analysis indicated that the phen was destroyed to form nonabsorbing species. Similar events occurred when H_2O_2 was photolyzed in solutions containing $Fe(phen)_3{}^{2+}$ (though the reaction was slower than that with $Fe(phen)_3{}^{3+}$) or with uncomplexed phen. Since ultraviolet photolysis of H_2O_2 in aqueous solution is known to form OH in high yield,[17] it is clear that attack by OH upon $Fe(phen)_3{}^{3+}$ can indeed be responsible for the quantum yields and stoichiometry of photoreduction of the latter. That Φ for formation of $Fe(phen)_3{}^{2+}$ is much less sensitive to such processes than Φ for disappearance of $Fe(phen)_3{}^{3+}$ probably arises from the fact that the photolyses produced only small fractional conversion of $Fe(phen)_3{}^{3+}$ to $Fe(phen)_3{}^{2+}$; hence, the Fe(III) complex was always present in much higher concentration than the Fe(II) species.

That thermal acid hydrolysis of $Fe(phen)_3{}^{2+}$ is partially responsible for the nonquantitative stoichiometry cannot be ruled out, since $Fe(phen)_3{}^{2+}$ is much less stable than $Fe(phen)_3{}^{3+}$ in strongly acidic media. However, thermal acid hydrolysis cannot be the major process, for four reasons. First, the stoichiometric discrepancy becomes smaller as the acid concentration increases (Figure 3). Second, no detectable quantity of "free" phen is formed. Third, ultraviolet spectrophotometry clearly shows that some phen is destroyed in the photolysis. Fourth, the addition of methyl methacrylate (Figure 3) should have no effect on the stoichiometry if acid hydrolysis of $Fe(phen)_3{}^{2+}$ were the principal process responsible for the disparity. Likewise, the possibility that phen is the electron donor in the reaction fails to explain the effect of added methyl methacrylate upon the stoichiometry (Figure 3) or quantum yield (Figure 2) of the photoreduction; at high concentrations of methyl methacrylate, the quantity of phen destroyed is extremely small, yet the photoreduction continues to occur. Accordingly, we conclude that both the quantum yield and stoichiometry of the photoreduction of $Fe(phen)_3{}^{3+}$ are most satisfac-

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torily interpreted in terms of a mechanism involving water as electron donor.

Baxendale and Bridge[3] reported that the quantum yield for disappearance of $\mathrm{Fe(phen)_3}^{3+}$ was linear in the first power of the initial concentration of $\mathrm{Fe(phen)_3}^{3+}$; they therefore proposed that reactions such as

$$[\mathrm{Fe(phen)_3}^{3+}]^* + \mathrm{Fe(phen)_3}^{3+} \longrightarrow \mathrm{Fe(phen)_3}^{2+} + \text{products}$$

were significant. That such a reaction could occur during the short lifetime of excited $\mathrm{Fe(phen)_3}^{3+}$ seems highly improbable, especially since the reaction requires interaction of two tripositive ions. Furthermore, the dependence of Φ upon concentration of $\mathrm{Fe(phen)_3}^{3+}$ becomes important only in strongly absorbing solutions (Figure 5). It is therefore probable that the concentration dependence of Φ arises from the secondary reactions described above, which would more significantly affect apparent Φ values in strongly (and inhomogeneously) absorbing solutions. Again, Φ for appearance of product ($\mathrm{Fe(phen)_3}^{2+}$) is virtually independent of the initial concentration of reactant, which is consistent with previous discussion. Consequently, no justification emerges for postulating interactions between excited and ground-state molecules of $\mathrm{Fe(phen)_3}^{3+}$.

Finally, we consider the unusual wavelength dependence for the photoreduction (Figure 1). It is evident that the low-lying doublet ligand→metal ($\pi \rightarrow t_2$) CT excited state is photochemically inert. The quantum yield data appear to show that spin-allowed intraligand (π, π^*) excited states of $\mathrm{Fe(phen)_3}^{3+}$ are photochemically active. This is an unexpected conclusion, especially since phen does not appear to be the electron donor in photoreduction of $\mathrm{Fe(phen)_3}^{3+}$. Two alternative explanations for the wavelength dependence of the quantum yield can be offered. First, a higher, spin-allowed, CT band (*e.g.*, $\pi \rightarrow e$) may overlap the phen $\pi \rightarrow \pi^*$ bands. Assuming that a higher energy CT band exhibited a molar absorptivity equal to that of the visible CT transition ($\sim 10^3$), it would not be detected in the ultraviolet region due to the much higher intensities of the intraligand bands. Hence, the validity of this hypothesis is not susceptible to experimental verification, and no theoretical studies of the locations of higher CT states in $\mathrm{Fe(phen)_3}^{3+}$ have appeared.

Alternatively, it is possible that, following excitation of a (π, π^*) band in $\mathrm{Fe(phen)_3}^{3+}$, radiationless intersystem crossing to a spin-forbidden, reactive, excited state takes place. Intersystem crossing from singlet to triplet states in free phenanthroline is known to occur[18] and its extent is known to be increased by complexation of phen with metal ions.[19] Again, however, it is difficult to understand why a spin-forbidden ligand-localized excited state would exhibit the observed photochemistry. It might be argued that spin-forbidden CT excited states can ultimately be populated by intersystem crossing. There are no spin-forbidden ($\pi \rightarrow t_{2g}$) CT excited states in $\mathrm{Fe(phen)_3}^{3+}$, but spin-forbidden ($\pi \rightarrow e_g$) excited states are possible. At present, nothing is known about the energetics of spin-forbidden, or spin-allowed ($\pi \rightarrow e$), CT excited states in $\mathrm{Fe(phen)_3}^{3+}$. Hence, the importance of intersystem crossing phenomena in the photochemistry of $\mathrm{Fe(phen)_3}^{3+}$ must remain a matter of conjecture, as the usual experimental techniques employed for evaluating the importance of spin-forbidden excited states in photochemical reactions (energy transfer[20] and esr) are not feasible in this system (because both the spin-allowed and spin-forbidden states are paramagnetic).

It is clear that the interesting and unusual wavelength dependence of photoreduction in $\mathrm{Fe(phen)_3}^{3+}$ cannot now be satisfactorily interpreted. Further theoretical study of CT states (both spin allowed and spin forbidden) in this complex is needed. Furthermore, extensive mixing of metal and ligand orbitals in $\mathrm{Fe(phen)_3}^{3+}$ [5] will render tenuous any attempt to describe the unusual excited-state chemistry of this complex in simple terms.

Acknowledgment.—We thank J. K. Kochi for use of the mercury lamp photolysis apparatus. This work was supported in part by the National Science Foundation (Grant GP-26109) and the Public Health Service (Grant AM 11081).

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Preparation and Studies of Di-μ-nitrogen-decaaquodiruthenium(II) Fluoroborate

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Received May 13, 1971

The preparation of salts containing the ion $\mathrm{(H_2O)_5RuN_2Ru(H_2O)_5}^{4+}$ is described, as are experiments which were directed toward bringing about cleavage of the N≡N bond in the complex by internal disproportionation. In none of the attempts, which included treating the binuclear complex with oxidizing agents, was evidence found for disproportionation.

Introduction

In the work described here we set out to prepare nitrogen complexes derived from $\mathrm{Ru(H_2O)_6}^{2+}$.[1] Besides the intrinsic interest which these species held for us, they appeared to us to be especially promising in searching for evidence of reduction of bound nitrogen. For these purposes they have an obvious advantage over ammine complexes in that the combined

[1] The oxygen-ligand-containing complex $\mathrm{RuN_2(H_2O)_2Cl_2THF}$ has been described by A. K. Shilova, A. E. Shilov, and Z. N. Vostrokhnutova, *Kinet. Katal.*, **9**, 924 (1968); A. K. Shilova and A. E. Shilov, *ibid.*, **10**, 267 (1969).