Inorganica Chimica Acta, 28 (1978) L149–L151

Flash Photolysis of $[Fe(phen)_3]^{3+}$ Ion

GHULAM M. MALIK and GERALD S. LAURENCE*

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001

Received March 21, 1978

The main product of the photolysis of $[Fe(phen)_3]^{3+}$ in sulfuric acid solutions is $[Fe(phen)_3]^{2+}$ [1, 2] but the quantum yield is less than 10^{-4} in the visible absorption band (λ_{max} 602 nm) which corresponds to a spin-allowed $\pi \rightarrow t_2$ ligand-to-metal charge transfer (LMCT) transition. The quantum yield rises rapidly in the region of the $\pi \rightarrow \pi^*$ intraligand band of the phenanthroline. It has been suggested that the initial products of the photochemical reaction are $[Fe(phen)_3]^{2+}$ and OH radicals, and that reactions of the OH radicals with the original complex account for differences between the quantum yields for the loss of $[Fe(phen)_3]^{3+}$, $\phi_{-Fe(III)}$ and for the production of $[Fe(phen)_3]^{2+}$, $\phi_{+Fe(II)}$ [2]. The nature of the primary photochemical reaction remains undetermined. In a study of the oxidation-reduction photochemistry of complexes of phenanthroline and bipyridyl ligands we have investigated the flash photolysis of $[Fe(phen)_3]^{3+}$.

Experimental

Tris-(1,10-phenanthroline)iron(III) perchlorate was prepared by oxidising $[Fe(phen)_3]^{2+}$ (prepared from Analar ferrous sulfate and 1,10-phenanthroline), precipitating with perchloric acid and recrystallising from perchloric acid. All other reagents were reagent grade and all solutions were made up in triple distilled water. No qualitative differences were observed between solutions containing perchloric or sulfuric acids; quantitative differences which were observed could be ascribed to differences in the water activities for the same acid concentrations. The experimental arrangements for flash photolysis were those previously described [3] with the addition of an on-line PDP 11-10 computer for data reduction [4]. Small diameter (6 mm or less) photolysis cells were used to ensure homogeneous absorption of the light from the flash lamp by the intensely absorbing solutions. For this reason the concentrations of $[Fe(phen)_3]^{3+}$ were small (20 μM maximum).

Results

The changes in absorbance following the flash were very dependent on the acid concentration. Between 370 and 565 nm iron(II) complexes of phenanthroline and substituted phenanthrolines absorb more strongly than the iron(III) complexes and there was an immediate ($t_{1/2} < 5$ μsec) increase in absorbance in this region during the light flash (Figure 1). The difference spectrum taken 50 or 100 μsec after the flash showed isosbestic points at 370 ± 2 nm and 565 ± 2 nm, the same as those measured by us for the conversion of $[Fe(phen)_3]^{3+}$ to $[Fe(phen)_3]^{2+}$. These isosbestic points and difference spectrum show that a low-spin iron(II) complex is an initial product of the photochemical reaction.

The fast increase in absorbance during the flash was independent of the acid concentration (0.5 to 10 M $HClO_4$) and was followed by acid independent processes. Between 0.5 and 3.0 M $HClO_4$ there was a further slow *increase* in absorbance (Figure 1) which also showed isosbestic points at 370 and 565 nm 1 sec after the flash. This slow reaction was first order and the rate constant was a linear function of the concentration of $[Fe(phen)_3]^{3+}$ (2 to 20 μM). The second order rate constant was $(8.6 \pm 1) \times 10^6$ M^{-1} sec^{-1} at 22 ± 2 °C and 0.5 M H^+. In 0.5 M acid the yield of iron(II) from the slow reaction was equal to the initial yield of iron(II) during the light flash, but the yield from the slow reaction fell as the

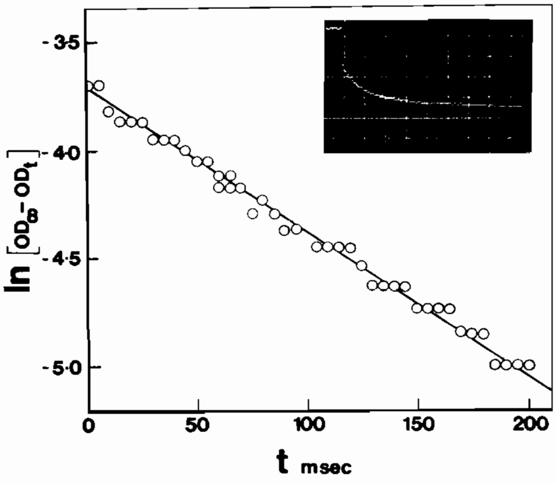


Figure 1. First order plot for the slow formation of $[Fe(phen)_3]^{2+}$ after the flash. The solution was 5 μM in $[Fe(phen)_3]^{3+}$ and 0.5 M in $HClO_4$. The inset shows the original changes in transmittance at 493 nm following the flash. The initial fast process and the slower secondary process are clearly distinguished. The vertical scale is 3% T per division, the horizontal scale 125 msec per division; the lower trace represents the analog-to-digital converter channel number.

---

*Address all correspondence to this author.

acid concentration increased and reached zero at 3.0 *M* $HClO_4$. At this acid concentration no slow secondary reaction was observed and the absorbance remained constant after the initial increase during the light flash.

Above 3.0 *M* acid the initial increase in absorbance was followed by a slow *decay* in which $[Fe(phen)_3]^{3+}$ was regenerated. The extent of this reaction increased with increasing acid concentration and in 10 *M* $HClO_4$ or 15 *M* H_2SO_4 the absorbance at the end of the secondary reaction was almost that before the flash (± 0.1%) at all wavelengths. The overall quantum yield therefore fell to zero at these high acid concentrations where the water activity is almost zero, although the initial quantum yield immediately after the flash remained constant. The rate of decay of the initial increase in absorbance was first order and the rate constant increased as the acid concentration increased. The dependence of the rate constant upon the acid concentration was greater than first order and reflects changes in the water activity in the solutions as well as the hydrogen ion activity. The rate constant reached 550 ± 50 sec^{-1} in 10 *M* $HClO_4$.

As reported previously [1, 2] the photochemical reactions were unaffected by oxygen, and no free ligand was produced. The photolysis of $[Fe(phen)_3]^{3+}$ induces polymerization of methyl methacrylate and it was suggested that the polymerization was induced by OH radicals generated in the primary photochemical step [2]. In scavenger experiments we have been unable to find any evidence for the presence of OH radicals. The quantum yields, and the rates of the secondary processes were unaffected by the addition of methanol, ethanol or t-butanol in concentrations (0.1 *M*) where these react with OH radicals in 0.1 μsec or less. Direct detection of OH radicals was difficult in the strongly absorbing solutions. OH radicals react with Cl^- or Br^- to give radical anions (Cl_2^- and Br_2^-) which absorb strongly at 370 nm where there is an isosbestic point for the photochemical reaction, so that detection of the radical anions was simple at this wavelength. Flash photolysis of solutions of $[Fe(phen)_3]^{3+}$ containing Cl^- or Br^- (10^{-2} *M*) and $HClO_4$ (0.5 *M*), using a filter to eliminate wavelengths < 220 nm from the flash lamp, produced no halogen radical anions. Under these conditions the effective half-life for the production of Cl_2^- or Br_2^- from OH radicals is *ca.* 0.5 μsec. The failure to detect halogen radical anions can only be due to the absence of OH radicals, and not to competitive scavenging of the OH radicals by the $[Fe(phen)_3]^{3+}$, which would require the rate constant for this reaction to be $> 10^{11}$ M^{-1} sec^{-1}. Scavenging of OH radicals by the $[Fe(phen)_3]^{2+}$ produced in the initial step would be even less favourable because of the smaller concentration of $[Fe(phen)_3]^{2+}$. The rate constant for the reaction between OH and $[Fe(phen)_3]^{2+}$ is 10^{10} M^{-1} sec^{-1} [5].

Discussion

As OH radicals are definitely not produced in the initial photochemical reaction, the primary result of light absorption by $[Fe(phen)_3]^{3+}$ at < 300 nm in aqueous solution cannot be electron transfer involving the solvent. The isosbestic points and the difference spectrum immediately after the flash show that one of the primary products is a low-spin iron(II) complex very similar to $[Fe(phen)_3]^{2+}$. At acid concentrations above 3 *M* this species reform the initial $[Fe(phen)_3]^{3+}$ complex by a first order (or a pseudo-first order) process with an acid dependent rate constant. The first order kinetics eliminate the possibility that this thermal back reaction is one between $[Fe(phen)_3]^{2+}$ and a radical in solution. The radical and the $[Fe(phen)_3]^{2+}$ would be formed in equal concentrations as a result of the primary photochemical act and in this case the back reaction would show second order kinetics, even if it were acid dependent.

This thermal back reaction competes with a reaction which produces further $[Fe(phen)_3]^{2+}$ by the reduction of another $[Fe(phen)_3]^{3+}$. This is the dominant one below 3 *M* acid and is the only one observed at 0.5 *M* acid. It cannot be the reduction of $[Fe(phen)_3]^{3+}$ by Fe^{2+}, for which the rate constant is only 3.7 × 10^4 M^{-1} sec^{-1} [6]. The complex acid dependence for the competition between the two secondary reactions suggests that both the water activity and the hydrogen ion activity effect the relative rates of the two reactions. At 3 *M* $HClO_4$ where no slow absorbance change is seen after the flash, the rates of the two reactions are equal.

A reaction scheme in which photochemical ligand-to-metal electron transfer produces an iron(II) complex with a ligand-radical bound to the metal ion (equation 1), followed by the back electron transfer (equation 2) which competes with reaction between the Fe(II)ligand-radical species and $[Fe(phen)_3]^{3+}$ (equation 3) accounts for our observations. Reaction 1 takes place

$$[Fe^{III}(phen)_3]^{3+} \xrightarrow{h\nu} [Fe^{II}(phen)_2(phen\cdot)]^{2+} + H^+ \qquad (1)$$

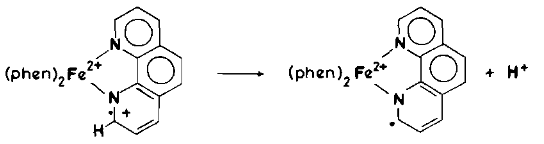
$$[Fe^{II}(phen)_2(phen\cdot)]^{2+} + H^+ \longrightarrow [Fe^{III}(phen)_3]^{3+} \qquad (2)$$

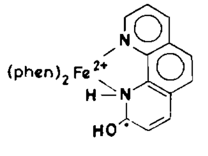
$$[Fe^{III}(phen)_3]^{3+} + [Fe^{II}(phen)_2(phen\cdot)]^{2+} \xrightarrow{H_2O} [Fe^{II}(phen)_3]^{2+} + [Fe^{II}(phen)_2(OH\text{-}phen)]^{2+} \qquad (3)$$

during the flash and reaction 3 is the secondary reaction seen at low acid concentrations which is first order in $[Fe(phen)_3]^{3+}$. A disproportionation reaction similar to reaction 3 occurs in the reaction of OH radicals with $[Fe(phen)_3]^{2+}$ [5]. The reactions account for the 1:1 stoichiometry for the conversion of Fe(III) to Fe(II) at each stage. Ligand-radical complexes have been observed in the reactions of a number of phenanthroline and bipyridyl complexes with OH radicals and in the reduction of $[Ru(bipy)_3]^{3+}$ by OH^- ions [7] and the spectra of the $M(L_2)(L\cdot)$ species are similar to those of the original complexes. However we have not found an absorbance analogous to that observed at 700–800 nm in the oxidation of $[Fe(bipy)_3]^{2+}$ by OH radicals [7].

Scavenging of the Fe(II)ligand-radical intermediate would prevent reaction 3 and reduce the quantum yield for the loss of $[Fe(phen)_3]^{3+}$ to one-half the value in the absence of scavenger, and explains the change in quantum yield observed by Wehry and Ward [2] from 2.5×10^{-2} in the absence of methyl methacrylate to a limiting value of 1.3×10^{-2} in the presence of 10^{-2} *M* monomer. The fall in quantum yield as the acid concentration increases [2] is due to the competition between reactions 2 and 3. We have observed no significant differences between the quantum yields for the loss of $[Fe(phen)_3]^{3+}$ and the production of $[Fe(phen)_3]^{2+}$ (or equivalent) even at 0.5 *M* acid.

The nature of the probable substituted phenanthroline product has not so far been determined because of the small quantum yields (*ca.* 10^{-2}) and the low concentrations (*ca.* 10 *μM*) required for the photochemical experiments, but a hydroxyl-substituted product is most likely, as no free radicals were observed in solution. The loss of a proton after the initial photochemical electron transfer from phenanthroline to the iron will tend to stabilise the Fe(II) ligand-radical complex, equation 1. There is considerable evidence for the existence of covalent hydrate species in aqueous solutions of phenanthroline complexes and the rates of racemization and dissociation of $[Fe(phen)_3]^{3+}$ are strongly dependent on the acid concentration and the water activity [8]. As the water activity falls with increasing acid concentration the proportion of the covalent hydrate falls. The covalent hydrate form of the Fe(II)ligand-radical, or its pseudobase after deprotonation, (I), would be expected to have a larger barrier for the intra-molecular back electron transfer reaction than the unhydrated form, and this would account for the rapid increase in the rate of reaction 2 as the acid concentration increases.





(I)

The covalent hydrate or its base will also provide a pathway for the production in reaction 3 of an $[Fe(phen)_2(OH\text{-}phen)]^{2+}$ complex. Reaction 3 is favoured at low acid concentrations where the covalent hydrate predominates [8]. A similar path has been proposed for the OH^- reduction of $[Fe(phen)_3]^{3+}$ [9]. The reaction scheme appears to be a general one for the photolysis of phenanthroline, substitued phenanthroline, and bipyridyl complexes of +3 transition metal ions as we have found very similar kinetics in a number of such systems [10].

The details of the primary photochemical process are still obscure. The absorption responsible for the photochemical reduction, equation 1, is not the $\pi \rightarrow t_2$ LMCT transition but the intra-ligand $\pi \rightarrow \pi^*$ transition. A photo-reactive LMCT state which may not be populated from the ground state because of spin selection rules may be populated from an excited ligand state by non-radiative processes. While intersystem crossing from a triplet ligand state to a charge transfer doublet or quartet state should be unfavourable, free phenanthroline possesses a triplet state which luminesces at 450 nm and this luminescence is quenched in the iron(III) complex.

Acknowledgements

We wish to acknowledge the award of a Colombo Plan Scholarship to one of us (G.M.M.) and the support of the Australian Research Grants Committee.

References

1 J. H. Baxendale and N. K. Bridge, *J. Phys. Chem., 59,* 783 (1955).
2 R. L. Wehry and R. A. Ward, *Inorg. Chem., 10,* 2660 (1971).
3 B. Falcinella, P. D. Felgate, and G. S. Laurence, *J. Chem. Soc. Dalton,* 1367 (1974).
4 A. T. Thornton and G. S. Laurence, *Int. J. Radiat. Phys. Chem.*, in press.
5 E. S. Floryan and P. Pagsberg, *Int. J. Radiat. Phys. Chem., 8,* 425 (1976).
6 N. Sutin and B. M. Gordon, *J. Am. Chem. Soc., 83,* 70 (1961); M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc., 83,* 1830 (1961).
7 C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A., 72,* 2858 (1975).
8 R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *J. Chem. Soc. Dalton,* 1792 (1977).
9 G. Nord and O. Wernberg, *J. Chem. Soc. Dalton,* 845 (1975).
10 G. M. Malik and G. S. Laurence, to be published.