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ELECTRON TRANSFER REACTIONS OF EXCITED DYES WITH METAL COMPLEXES

Progress Report
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ABSTRACT

A study was initiated of the factors which determine quantum efficiency of transfer of reducing equivalents between excited dye molecules and metal complexes in their ground state and composition and dynamics of formation and decay of related photostationary states. A ruby laser capable of delivering a 3.6 J, 19 nsec flash was acquired and assembly of an apparatus for laser flash photolysis begun. At the same time, conventional flash photolysis was used to pursue investigation of the dependence upon solvent, anions, pH and ionic strength of the kinetics of the spontaneous dark reaction of $Fe(H_2O)_6^{3+}$ with leucothionine and with semithionine, reactions which contribute to the composition and dynamics of formation and decay of the photostationary state of the iron-thionine photoredox reaction. Results are consistent with formation of an intermediate complex between leucothionine and Fe(III), $K_A = 380\ \underline{M}^{-1}$ and $k_{elec.\ transfer} = 0.88\ sec^{-1}$ at ∿22° in water solution at pH2, with sulfate as anion and $\mu = .05 - .1\ \underline{M}$. Under similar conditions in 50 v/v% aqueous CH_3CN, $K_A = 780\ \underline{M}^{-1}$, $k_{elec.\ transfer} = 0.55\ sec^{-1}$. In both solvents, sulfate produces a large positive salt effect. Intermediacy of a complex was not established for the faster reaction of Fe(III) with semithionine under similar conditions: $K_A \cdot k_{elec.\ transfer} \sim 3.5 \times 10^5\ \underline{M}^{-1}sec^{-1}$ in H_2O, $\sim 1.0 \times 10^4$ in 50 v/v% aqueous CH_3CN.

INTRODUCTION

One aspect of work planned for the year beginning May 1, 1976 involved acquisition of those basic components of an apparatus for laser-flash photolytic experiments which could be purchased within the limits of a $15,000 budget and temporary installation of these components so that they could be used in conjunction with the monitoring system of a conventional apparatus for flash photolysis. Another aspect of planned work involved initiation of experiments employing apparatus available at Boston University and laser flash photolytic apparatus in the laboratory of Professor Henry Linschitz at Brandeis University to study electron transfer reactions between selected excited photoredox dyes and metal complexes as well as the ground state back reactions of resulting products.

Since it was the beginning of September before a postdoctoral research associate began work, results described below are more limited than would have been the case if the project had been fully staffed by its inception date at the beginning of May.

APPARATUS FOR LASER FLASH PHOTOLYSIS

Equipment was ordered from Holobeam Laser Inc. on July 12, 1976 and was delivered around December 15, 1976. It consisted of a series 630 ruby laser with a Pockels Cell Q-switch accessory. Claimed performance specifications include 3.6 J output or 190 MW power in a 19 nsec pulse. Planned and unplanned closings of the University during the month of December delayed assembly of working apparatus. By the middle of February "bugs" were still being uncovered and corrective measures were in progress.

EXPERIMENTS EMPLOYING CONVENTIONAL FLASH PHOTOLYTIC APPARATUS

Time resolution provided by our conventional flash photolytic apparatus enables processes with time constants of the order of 10^{-4} sec. or slower to be studied. Such time resolution is not convenient for study of the dynamics of processes involving excited states. It is, however, suitable for investigation of initial products of reaction of excited states with redox quenchers, e.g., the nature and reactions of initially formed dye radicals. It is also suitable in some cases for investigation of ground state back reactions of final products of photodriven reactions. During the report period, conventional flash photolysis technique was used to extend and refine previous exploratory studies (1) of the reaction of Fe(III) with semithionine, $TH_2^{\dot{+}}$, and with leucothionine, TH_3^+ or TH_4^{2+}. (In the balance of this report leucothionine is designated as TH_4^{2+} because measurements were carried out with 10^{-2} $\underline{M}$ concentrations of acid. The pK_a values of the first and second ionization constants of TH_4^{2+} are both probably within the range 5±1. (2)) $TH_2^{\dot{+}}$ is the initial product of reduction of triplet thionine, $^3TH_2^{2+}$, by Fe(II). Leucothionine is formed subsequently by the rapid disproportionation of $TH_2^{\dot{+}}$, eq. 1, and is the major reducing charge carrier when the iron-

$$H^+ + 2\ TH_2^{\dot{+}} \xrightarrow{k_1} TH^+ + TH_4^{2+} \tag{1}$$

thionine photogalvanic cell is illuminated, at least when 50 v/v% aqueous CH_3CN is used as the solvent (3).

Investigation of the reaction between Fe(III) and $TH_2^{\dot{+}}$, reaction 2:

$$2H^+ + TH_2^{\dot{+}} + Fe(III) \xrightarrow{k_2} TH_4^{2+} + Fe(II) \tag{2}$$

employed a competition method which involves knowledge of the specific rate of disproportionation of $TH_2^{\overset{+}{\cdot}}$ in the absence of added Fe(III), reaction 1. Thus values of k_2 were determined under the conditions of investigation of k_1 by measuring dependence of yields of TH^+ on cencentration of Fe(III). Since the reaction of TH_4^{2+} with Fe(III), eq. 3, is much slower than reactions 1 or 2, k_3 can be measured by following the reappearance of TH^+ after

$$TH_4^{2+} + Fe(III) \xrightarrow{k_3} TH_2^{\overset{+}{\cdot}} + 2H^+ + Fe(II) \qquad (3)$$

reactions 1 and 2 are complete. Since the latter reactions also follow reaction 3 and have different stoichiometries, evaluation of k_3 involves estimation of the partitioning of $TH_2^{\overset{+}{\cdot}}$ produced by reaction 3 between reactions 1 and 2.

Previous work (4) had shown that log k_1 varies linearly with Kosower's solvent function, Z, in $10^{-2}\underline{M}$ F_3CSO_3H. During the report period, investigation was initiated of the kinetics of oxidation of $TH_2^{\overset{+}{\cdot}}$ by Fe(III), reaction 2. The immediate objectives of these measurements include determining whether reversible formation of a complex between $TH_2^{\overset{+}{\cdot}}$ and Fe(III) preceeds electron transfer and, if it does, evaluation of the equilibrium and rate constants for the separate steps. In addition, elucidation in depth of the mechanism is to be aided by observing the effects of variation of pH, solvent, nature of anions and ionic strength. During the report period data were obtained in two solvents, water and 50 v/v% aqueous CH_3CN, containing .01$\underline{M}$ H_2SO_4 and $FeSO_4$ and concentrations of $Fe_2(SO_4)_3$ varying from $\sim 3\times10^{-5}$ to $6.10^{-2}\underline{M}$. Resulting equilibrium and rate constants are summarized in Table 1. Whether complexation of Fe(III) and $TH_2^{\overset{+}{\cdot}}$ is involved in the electron transfer process is still subject to question. Since salt effects in these reactions appear to be substantial (see col.5 of Table 1) failure to maintain constant ionic strength introduces errors of unknown magnitude. It appears however that k_2 is more sensitive to solvent (36 fold decrease from H_2O to 50 v/v% aqueous CH_3CN) than is k_1 (4.7 fold decrease). The indicated comparison of k_1 in sulfate and triflate media is inconclusive.

TABLE 1

Values of Association and Rate Constants
for the Reaction of $TH_2^{\dot{+}}$ with Fe(III) in
$10^{-2}\underline{M}$ H_2SO_4 and $FeSO_4$, Varying
Ionic Strength[a] at ∿25°C

Solvent	k_1[b]	$K^{c}_{A,TH_2^{\dot{+}}}$	$k^{d}_{t,TH_2^{\dot{+}}}$	$k_2 = K_{A,TH_2^{\dot{+}}} \times k_{t,TH_2^{\dot{+}}}$
	$10^8\underline{M}^{-1}sec^{-1}$	$\underline{M}^{-1}$	$10^4 sec^{-1}$	$10^4\underline{M}^{-1}sec^{-1}$
H_2O	14.2±1.3(20)[e]	?	?	35±15 (9)[f]
50 v/v% aq. CH_3CN	3.05±.31(2)[e]	0.8	1.2	.96±.25(.65)[f]

a. μ = .05 to .5$\underline{M}$ depending on concentration of $Fe_2(SO_4)_3$.

b. Second order rate constant for disproportionation of $TH_2^{\dot{+}}$, determined with μ = .05$\underline{M}$, H^+ not treated as a reactant.

c. Equilibrium constant for 1:1 association of $TH_2^{\dot{+}}$ with Fe(III).

d. Rate constant for unimolecular electron transfer within the complex.

e. Values of k_1 with $F_3CSO_3^-$ as sole anion, μ = .09, taken from ref. 4.

f. Values of k_2 in sulfate medium with μ = 0.3$\underline{M}$, taken from ref. 1.

The immediate objectives of investigation of the reaction of leucothionine, TH_4^{2+}, with Fe(III) are analogous to the objectives of study of the reaction of TH_2^+ with Fe(III) which are stated above. Considerably more information on the former reaction was collected during the report period. Previous evidence (1) that reaction 3 proceeds via an association complex and subsequent electron transfer was confirmed. Separate association and rate constants, respectively $K_{A,TH_4^{2+}}$ and $k_{t,TH_4^{2+}}$, were evaluated in water and 50 v/v% aqueous CH_3CN. Information was obtained on salt effects with sulfate anion in the aqueous organic solvent. Data are presented in Table 2. As shown in Table 2, failure to take into account disproportionation

TABLE 2

Values of Association and Rate Constants for the Reaction of TH_4^{2+} with Fe(III) in $10^{-2}\underline{M}$ H_2SO_4 and $FeSO_4$ at ∿22°C

Solvent	μ $\underline{M}$	Corrected for Disproportionation of TH_2^+	$K_{A,TH_4^{2+}}$ $\underline{M}^{-1}$	$k_{t,TH_4^{2+}}$ sec^{-1}	$k_3 = K_{A,TH_4^{2+}} \times k_{t,TH_4^{2+}}$ $\underline{M}^{-1}sec^{-1}$
H_2O	.05-.10	yes	380	0.88	334
H_2O	.05-.10	no	380	0.88	334
H_2O	0.3[a]	no	1,745[b]	0.85[b]	1,483
50 v/v% aq.AN	.05-.14	yes	780	0.55	429
50 v/v% aq.AN	.05-.14	no	380	0.69	262
50 v/v% aq.AN	0.2[a]	yes	1,070	1.28	1,370
50 v/v% aq.AN	0.2[a]	no	550	1.39	765

a. Made up with Na_2SO_4.

b. Unpublished work by Dr. Russell Cheney in this laboratory using leucothionine prepared by reduction of TH^+ with H_2/Pd and stopped flow technique.

of $TH_2^{\dot{+}}$ subsequent to its formation by reaction 3 results in substantial errors for data in 50 v/v% aq. CH_3CN. Errors are negligible in H_2O solution, because, as can be estimated from Table 1, $(v_2/v_1)_{H_2O} > (v_2/v_1)_{50\%\ CH_3CN}$ for any set of concentrations. The data of Table 2 indicate relatively small solvent effects on $K_{A,TH_4^{2+}}$, $k_{t,TH_4^{2+}}$ and on k_3, their product. There is a substantial positive salt effect in sulfate solutions. The cause of this effect remains to be determined.

REFERENCES

1. N. N. Lichtin, Report No. NSF/RANN/SE/AER/72-03579/A03/75/4, April 15, 1976, pp. 15-20.
2. H. W. Meyer and W. D. Treadwell, Helv. Chim. Acta, 35, 1444 (1952).
3. P. D. Wildes, N. N. Lichtin and M. Z. Hoffman in Proceedings of the International Symposium on Solar Energy of the Electrochem. Soc., Washington, D.C., May 5-7, 1976, p. 128.
4. P. D. Wildes, N. N. Lichtin and M. Z. Hoffman, J. Amer. Chem. Soc., 97, 2288 (1975).

APPENDIX I

Time and Effort Devoted by Principal and Co-Principal Investigators and Other Personnel

	Summer 1976	Sept. 1, 1976 - April 30, 1977
N. N. Lichtin, Principal Investigator	1 man mo.	1 man mo.
M. Z. Hoffman, Co-Principal Investigator	1 man mo.	0.9 man mo.
T. L. Osif, Research Associate	-	8 man mos.
S. Ray, Graduate Student	1 man mo.	2 man mos.