The rates of formation of the various molecules in benzene solution at 40° was the subject of a computer analysis based on the set of four equations[10]

$$P_4(NCH_3)_6 + C_6H_5N_3 \xrightarrow{k_1} C_6H_5N[P_4(NCH_3)_6] + N_2 \qquad (1)$$

$$C_6H_5N[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_2} (C_6H_5N)_2[P_4(NCH_3)_6] + N_2 \qquad (2)$$

$$(C_6H_5N)_2[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_3} (C_6H_5N)_3[P_4(NCH_3)_6] + N_2 \qquad (3)$$

$$(C_6H_5N)_3[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_4} (C_6H_5N)_4[P_4(NCH_3)_6] + N_2 \qquad (4)$$

Curve fitting of the experimental data, assuming that each reaction is first order in each reagent, leads to the following values for the rate constants: $k_1 \geqslant 50$, $k_2 = 7$, $k_3 = 1.0$, $k_4 = 0.3\ M^{-1}\ \text{hr}^{-1}$. The curves calculated from these rate constants for 1:1, 1:2, 1:3, and 1:4 mole ratios of tetraphosphorus hexamethylhexaimide to phenyl azide are shown in Figure 1.

Quaternization of Other Birdcage Molecules. When various proportions of tetraphosphorus hexaoxide (^{31}P chemical shift of −113.5 ppm) and phenyl azide were mixed together in benzene or methylene chloride, with and without exclusion of light and heating up to 40° for several hours, the only cage-substitution compound which was obtained was the monosubstituted product $P_4O_6(NC_6H_5)$. In addition, there were soluble decomposition products and some of the yellowish white amorphous material which was previously described[11] as being a high polymeric form of P_2O_3 with occasional end groups.

The ^{31}P nmr pattern of $P_4O_6(NC_6H_5)$ in benzene solution consisted of a doublet at −140.6 ppm which exhibited 3 times the peak area of the first-order quartet at +42.7 ppm. J_{PP*} was found to equal 4.4 ± 0.1 Hz. Again, the consistent-area relationship of these peaks in various reaction-product mixtures showed that they belong to a single molecule.

Attempts to prepare phenylimino-substitution products from phosphorus sesquisulfide, P_4S_3, and from white phosphorus, P_4, resulted in failure. In both cases there was no sign of reaction or even of decomposition upon boiling the appropriate carbon disulfide solutions at atmospheric pressure for as long as 6 hr.

Registry No. $[P_4(NCH_3)_6]NC_6H_5$, 39937-16-1; $[P_4(NCH_3)_6](NC_6H_5)_4$, 39937-17-2; $P_4(NCH_3)_6$, 10369-17-2; $P_4(NCH_3)_6(NC_6H_5)_2$, 39937-18-3; $P_4(NCH_3)_6(NC_6H_5)_3$, 40031-97-8; P_4O_6, 12440-00-5; $C_6H_5N_3$, 622-37-7.

Acknowledgment. We wish to thank David L. Baize for writing the computer program for the kinetic study and for assisting with the necessary calculations. We are also indebted to the National Science Foundation (GP-28698X) for partial financial support of this work.

[10] H. Bock and M. Schnoller, *Angew. Chem.*, **80**, 667 (1968); *Chem. Ber.*, **102**, 38 (1969).

[11] J. G. Riess and J. R. Van Wazer, *Inorg. Chem.*, **5**, 178 (1966).

Contribution from the Department of Chemistry,
University of Brasilia, Brasilia-D.F., Brazil

Kinetics of the Dissociation of Binuclear Oxygen-Bridged Complexes of Iron(III) with 1,10-Phenanthroline and 2,2′-Bipyridine

P. G. David* and P. C. de Mello

Received October 20, 1972

The binuclear oxygen-bridged complexes of iron(III) with 1,10-phenanthroline and 2,2′-bipyridine, $Fe_2OL_4Cl_4$ (L = phen or bipy), are high-spin complexes with a linear Fe-O-Fe "bridge."[1-6] While they have the structure $[L_2ClFe\text{-}O\text{-}FeClL_2]^{2+}$ in the solid,[3] dissolution in water effects rapid replacement of coordinated chloride ligands by water molecules.[7] Hence, an aqueous solution of the complex is best represented as $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$.[7] While aqueous solutions of these complexes are indefinitely stable in the dark (they undergo photoreduction on ultraviolet irradiation[7]), they dissociate in acid solutions with complete loss of color. The present work deals with the kinetics of the dissociation of $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$ complexes in dilute nitric acid solutions.

Experimental Section

Materials. The binuclear iron(III) complexes $Fe_2(phen)_4OCl_4$ (hereafter called "DP") and $Fe_2(bipy)_4OCl_4$ (hereafter called "DB") were prepared by literature procedures.[7c,8,9] Water was purified by distillation from potassium permanganate. Reagent grade 1,10-phenanthroline and 2,2′-bipyridine (E. Merck) were purified by recrystallization from aqueous ethanol.[10] All other chemicals were reagent grade and were used without further purification.

Kinetic Runs. The compounds DP and DB have charge-transfer absorption maxima at 28,570 cm^{-1} (ϵ_{max} 9.20 × 10^3 l. mol^{-1} cm^{-1}) and 29,000 cm^{-1} (ϵ_{max} 7.40 × 10^3 l. mol^{-1} cm^{-1}), respectively. These charge-transfer bands were destroyed during the acid dissociation. A spectrophotometric method was used to follow changes in absorbance at the charge-transfer band during dissociation. The products of the dissociation, aquoiron(III) and protonated bipyridine, have very little absorbance in the 28,000–29,000-cm^{-1} region (ϵ ~60 for aquoiron(III) and ~75 for protonated bipyridine), and, hence, the absorption due to aquoiron(III) and protonated bipyridine is negligible at the 10^{-4} M concentrations of the complex used. The protonated phenanthroline has significant absorbance in this region (ϵ for phenH$^+$ at 28,570 cm^{-1} is 800) and hence, was taken into account in calculating the decrease in absorbance during the acid dissociation of DP.

Absorbance changes were recorded on a Unicam SP 700 spectrometer. Suitable volumes of standard aqueous solutions of the complex, sodium nitrate (used to adjust the ionic strength), and nitric acid were mixed rapidly and transferred to a 1-cm quartz cell. The time elapsed between the mixing of the solutions and starting to record the absorbance was 1 min. The spectrometric cell compartments were thermostated at the required temperature

[1] A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

[2] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1014 (1967).

[3] A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. A*, 1561 (1967).

[4] W. M. Reiff, W. A. Baker, and N. E. Erickson, *J. Amer. Chem. Soc.*, 90, 4794 (1968).

[5] M. Wicholas and D. Jayne, *Inorg. Nucl. Chem. Lett.*, 7, 443 (1971).

[6] W. M. Reiff, *J. Chem. Phys.*, 54, 4718 (1971).

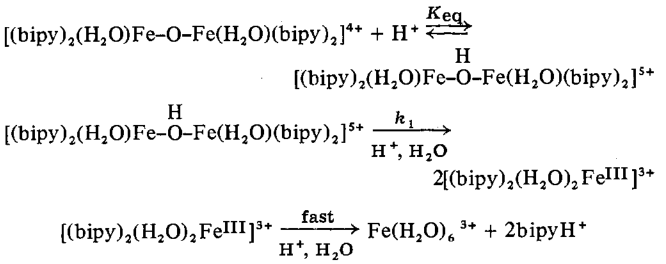
[7] (a) P. G. David, J. G. Richardson, and E. L. Wehry, *Inorg. Nucl. Chem. Lett.*, 7, 251 (1971); (b) *J. Inorg. Nucl. Chem.*, 34, 1333 (1972); (c) P. G. David, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1971.

[8] A. Gaines, Jr., L. P. Hammett, and G. H. Walden, Jr., *J. Amer. Chem. Soc.*, 58, 1668 (1936).

[9] P. G. David, *J. Inorg. Nucl. Chem.*, 35, 1463 (1973).

[10] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, London, 1966, pp 88, 234.

Scheme I

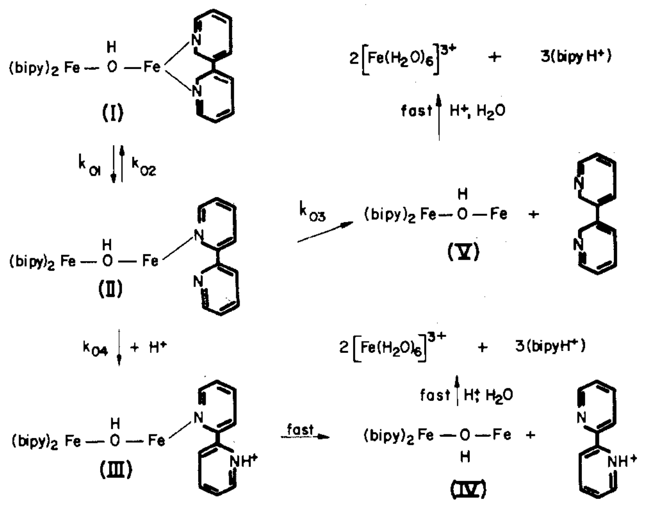


$$[(bipy)_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)(bipy)_2]^{4+} + H^+ \overset{K_{eq}}{\rightleftarrows} [(bipy)_2(H_2O)Fe\text{-}\overset{H}{O}\text{-}Fe(H_2O)(bipy)_2]^{5+}$$

$$[(bipy)_2(H_2O)Fe\text{-}\overset{H}{O}\text{-}Fe(H_2O)(bipy)_2]^{5+} \xrightarrow[H^+,\ H_2O]{k_1} 2[(bipy)_2(H_2O)_2Fe^{III}]^{3+}$$

$$[(bipy)_2(H_2O)_2Fe^{III}]^{3+} \xrightarrow[H^+,\ H_2O]{fast} Fe(H_2O)_6{}^{3+} + 2bipyH^+$$

Scheme II[a]



[a] The coordinated water molecules and one bipy molecule are left out of structures I-V. This scheme is essentially independent of the presence of O-protonated or unprotonated species. In high acid concentrations I will be O protonated, while at low acid concentrations it will be a mixture of protonated and unprotonated species.

by circulating water from a constant-temperature water bath. Solutions used were preequilibrated to the desired temperature before mixing. Activation energies reported in the present work were obtained by following the reaction over a temperature range of 20°.

All kinetic runs were done under pseudo-first-order conditions. The observed rate constants (k_{obsd}) for the acid dissociation were calculated from the slopes of the plots of log ($A_t - A_\infty$) *vs.* time.

Results and Discussion

The observed rate constants (k_{obsd}) for the acid dissociation of DP and DB are given in Table I. The complex DP shows a relatively small acid dependence compared to DB. Both of the complexes show a limiting rate at high acid concentrations and an acid-independent rate at low acid concentrations (Figure 1).

Dissociation of the Bipyridine Complex (DB). Acid dissociation of DB is observed to be first-order in the complex. Dissociation takes place with complete loss of color. No intermediates or isosbestic points were observed. A mechanism based on two parallel reactions (Schemes I and II) is proposed to account for the observed acid-dependent dissociation.

Table I. Rate Data for the Acid Hydrolysis of DB and DP in Aqueous Nitric Acid Solutions[a]

$[HNO_3]$, M	Temp,[b] °C	10^3k_{obsd}, sec^{-1} DP[c]	10^3k_{obsd}, sec^{-1} DB[d]
0.03	20	0.65	2.30
	23	0.92	2.95
	25	0.98	3.50
	30	1.56	5.20
	35	2.52	8.05
	40	3.63	11.22
	45	4.45	
0.05	20		2.50
	23	1.03	
0.10	20		2.77
	23	1.20	
0.20	20		3.38
	23	1.42	
0.40	20		4.20
	23	1.64	
0.60	20		5.12
	23	1.66	
0.80	20		6.05
	23	1.66	7.75
1.00	20		6.05
	23	1.66	7.75

[a] Initial concentrations of DP and DB were 1.0 × 10^{-4} and 1.8 × 10^{-4} M, respectively. Ionic strength was adjusted to 1.20 with sodium nitrate. [b] All ±0.20°. [c] All ±0.05 × 10^{-3} sec^{-1}. [d] All ±0.10 × 10^{-3} sec^{-1}.

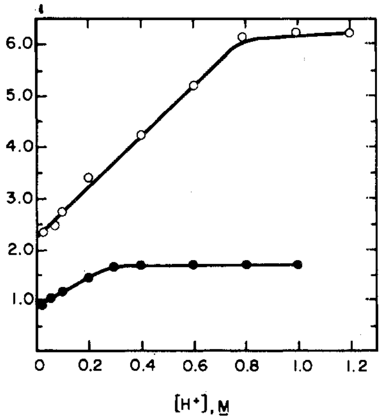


Figure 1. Dependence of the rate of dissociation of DP and DB on nitric acid concentration: ●, DP; ○, DB. In all cases, the ionic strength was adjusted to 1.2 with sodium nitrate.

In Scheme I the rate-determining step is the cleavage of the Fe-O "bridge" of the O-protonated (O for bridge oxygen) species. In Scheme II the rate-determining step is the loss of the first ligand, the loss of the subsequent ligands being very rapid. The mechanism suggested in Scheme II is similar to the one first proposed to explain the acid hydrolysis of $[Fe(bipy)_3]^{2+}$ ion.[11] From Scheme II it is clear that there are two dissociation pathways, one acid dependent and the other acid independent. Assuming steady-state concentration of the intermediate II (in Scheme II), the value of the observed rate constant resulting from the two parallel reactions (Schemes I and II) is given by

$$k_{obsd} = \left[\left(\frac{k_{03} + k_{04}[H^+]}{k_{02} + k_{03} + k_{04}[H^+]}\right)k_{01} + k_1\right]K_{eq}[H^+] \qquad (1)$$

At high acid concentrations (>0.80 M), where a limiting rate is reached, the values of k_{02} and k_{03} are negligible compared to $k_{04}[H^+]$, and thus the rate (for Scheme II) will be determined by k_{01} alone. Hence, $k_\infty = k_{01} + k_1$. Since $[H^+]$ is negligible at very low acidity, the observed rate constant $k_0 = k_{01}k_{03}/(k_{02} + k_{03})$. The values of k_∞ and k_0 for the dissociation of DB at 23° are 7.75 × 10^{-3} and 2.95 × 10^{-3} sec^{-1}, respectively.

If we assume that, under identical conditions of acidity and temperature, k_1 is same for the dissociation of DB and DP (an assumption which may be justified from the identical processes involved and from the identical structures of DB and DP; k_1 for DP is 0.76 × 10^{-3} sec^{-1} at 23°; *vide infra*), we calculate that k_{01} = 6.99 × 10^{-3} sec^{-1} at 23°. The rate constant k_{01} is a measure of the rate at which the first Fe-N bond breaks. At high acid concentrations, each time

---

(11) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 76, 3807 (1954).

an Fe-N bond breaks it results in dissociation. Hence, the ratio $k_0/k_{01} = k_{03}/(k_{02} + k_{03}) = 0.422$ is the probability of the occurrence of the acid-independent dissociation.

The activation energy for the dissociation of DB in 0.03 *M* nitric acid is 14 ± 2 kcal. It is to be noted that this activation energy, since it is obtained at low acid concentration, is a measure of the activation energy indicated with the rate constant $k_{01}k_{03}/(k_{02} + k_{03})$.

Dissociation of the Phenanthroline Complex (DP). As in the case of the bipyridine complex, the binuclear phenanthroline complex $[(phen)_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)(phen)_2]^{4+}$ dissociates in dilute nitric acid with complete loss of color. The dissociation exhibits a first-order dependence on the complex concentration. No intermediate or isosbestic point was observed. But in comparison to DB, DP shows a relatively smaller dependence on the acid concentration (Figure 1).

Because of the rigidity of the phenanthroline rings, half-bonded structures similar to that of III (Scheme II) are not possible. When one Fe-N bond is broken, either reclosure occurs or the second Fe-N bond also breaks off effecting complete dissociation of the phen molecule. Hence, the acid-dependent part of the dissociation depicted in Scheme II (corresponding to k_{04}) is not possible for DP. The dissociation of DP may be described by two parallel reactions: (i) the acid-dependent reaction identical to Scheme I and (ii) the simple dissociation or acid-independent pathway similar to the ones indicated by the rates k_{01}, k_{02}, and k_{03} in Scheme II. Hence, the observed rate constant for the dissociation of DP is

$$k_{\text{obsd}} = \frac{k_{01}k_{03}}{k_{02} + k_{03}} + K_{\text{eq}}k_1[\text{H}^+] \qquad (2)$$

At nitric acid concentrations greater than 0.4 *M*, where a limiting rate is reached, the observed rate constant $k_\infty = k_{01}k_{03}/(k_{02} + k_{03}) + k_1$ and is equal to 1.66×10^{-3} sec^{-1} at 23°. The intercept of the plot of k_{obsd} *vs.* [H$^+$] gives k_0 and is equal to 0.90×10^{-3} sec^{-1} at 23° (Figure 1).[12] Hence, the difference between k_∞ and k_0 is k_1, which is the acid-dependent rate constant (*cf.* Scheme I) for the dissociation of DP, and is equal to 0.76×10^{-3} sec^{-1} at 23°. The slope of the plot of k_{obsd} *vs.* [H$^+$] is equal to $K_{\text{eq}}k_1 = 2.73 \times 10^{-3}$. Since $k_1 = 0.76 \times 10^{-3}$ sec^{-1}, we calculate $K_{\text{eq}} = 3.60$.

The activation energy for the dissociation of DP in 0.03 *M* nitric acid is 16 ± 2 kcal. Within experimental uncertainty, this value is comparable to that for the dissociation of DB. As pointed out in the case of DB, the activation energy for the dissociation of DP is for the rate constant indicated by $k_{01}k_{03}/(k_{02} + k_{03})$.

There is no spectral evidence for the formation of the O-protonated species $[L_2(H_2O)Fe\text{-}OH\text{-}Fe(H_2O)L_2]^{5+}$ in aqueous acid solutions (*cf.* Scheme I). But this is not surprising if we observe that DP and DB behave as acids in aqueous media (a 2.5×10^{-4} *M* solution of the complex has a pH of 4.0). This acidic behavior has been attributed to the presence of the equilibrium[7]

$$\begin{aligned} &[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+} \rightleftarrows \\ &\qquad [L_2(H_2O)Fe\text{-}O\text{-}Fe(OH)L_2]^{3+} + H^+ \\ &\qquad\qquad \upharpoonleft\!\downharpoonright \\ &\qquad [L_2(OH)Fe\text{-}O\text{-}Fe(OH)L_2]^{2+} + H^+ \qquad (3) \end{aligned}$$

But, in addition to the above equilibrium, the presence of an equilibrium of the following type cannot be ruled out

$$[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+} \rightleftarrows [L_2(OH)Fe\text{-}OH\text{-}Fe(H_2O)L_2]^{4+} \qquad (4)$$

It is reasonable to believe that the difference between the absorption maxima of the charge-transfer bands of the O-protonated and unprotonated species will not be more than 5-10 nm and, hence, the electronic absorption spectrum of even an aqueous solution of DB or DP may be an additive superimposition of the spectra due to the O-protonated and unprotonated species. Hence, definitive spectral evidence for the protonated species may not be obtained. Furthermore, it is not unlikely that the O-protonated and unprotonated species have essentially identical electron spectra.

An indirect evidence for the formation of the O-protonated species comes from the reactions of DB and DP with potassium thiocyanate.[9] Addition of potassium thiocyanate to an acidic aqueous solution (pH 1.3) of DP or DB results in the immediate precipitation of $[FeL_2(NCS)_2]^+$, while a mixture of $[FeL_2(NCS)_2]^+$ and $[L_2(NCS)Fe\text{-}O\text{-}Fe(NCS)L_2]^{2+}$ precipitates out in the intermediate pH ranges 1.3-4.0. At high acid concentrations only the O-protonated species exists; protonation at the "bridge" oxygen weakens the Fe-O-Fe bonds, thus accelerating its cleavage. At low acid concentration, where a mixture of $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$ and $[L_2(H_2O)Fe\text{-}OH\text{-}Fe(H_2O)L_2]^{5+}$ exists in solution, reaction with NCS$^-$ results in a mixture of $[FeL_2(NCS)_2]^+$ and $[L_2(NCS)Fe\text{-}O\text{-}Fe(NCS)L_2]^{2+}$.

The reactions of DP and DB with potassium thiocyanate[9] can further be taken as an indirect proof for the occurrence of the dissociation pathway depicted in Scheme I. Formation of $[FeL_2(NCS)]^+$ cannot be explained if Scheme II is the only one responsible for the dissociation reactions of DP and DB. Isolation of $FeL_2(NCS)_2{}^+$ may be taken as a conclusive evidence for the formation of $[FeL_2(H_2O)]^{3+}$ as a transient species (Scheme I) during the acid dissociation reactions.

Registry No. $[(bipy)_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)(bipy)_2]^{4+}$, 24216-38-4; $[(phen)_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)(phen)_2]^{4+}$, 32573-24-3.

---

[12] The difference between the values of the intercept (0.90×10^{-3}) and the k_{obsd} at 0.03 *M* nitric acid (0.92×10^{-3}) is negligible, and, hence, for all practical purposes they may be taken to be the same.

Contribution from the Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

Preparation and Characterization of Chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) Complexes

D. W. Thompson,* W. R. C. Munsey, and Thomas V. Harris

Received November 3, 1972

During the past few years several studies have been reported concerning the synthesis and characterization of hexacoordinate titanium(IV) complexes comprised of two oxygen-chelated 2,4-pentanedionate groups and two monodentate ligands. The most thoroughly studied of these complexes have been the dialkoxy-[1] and dihalobis(2,4-pentanedionato)titanium(IV)[2] complexes. One of the most intriguing

---

[1] J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971), and references cited therein.

[2] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 9, 2048 (1970), and references cited therein.