denyl band occurs near 30,000 cm^{-1}; if present, these bands may be obscured in the currently investigated complexes by the ligand to molybdenum charge-transfer bands. Evidence has been found for a molybdenyl oxygen to molybdenum transition around 52,000 cm^{-1}, which would be expected by analogy to molybdate anion. More work with simple compounds, preferably by reflectance spectroscopy, will be necessary to confirm the existence of a molybdenyl band near 30,000 cm^{-1}.

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Formation and Dissociation Kinetics of Bis(2,4,6-tripyridyl-*s*-triazine)iron(II)

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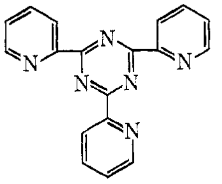
The kinetics of formation of bis(2,4,6-tripyridyl-*s*-triazine)iron(II), $Fe(TPTZ)_2^{2+}$, fit a mechanism where the addition of the first TPTZ is rate determining and the addition of the second TPTZ is much faster. The rate of dissociation of $Fe(TPTZ)_2^{2+}$ is determined using acid, EDTA, or base to cause the reaction. With high concentrations of these scavengers present to react either with Fe(II) or with TPTZ, the rate-determining step shifts to the removal of one TPTZ from $Fe(TPTZ)_2^{2+}$. One of the TPTZ ligands must dissociate completely before EDTA can react; however, EDTA does react with the mono-TPTZ complex. On the other hand, hydrogen ion (above 10^{-3} *M*) and hydroxide ion (above 10^{-10} *M*) react directly with the bis complex to accelerate the dissociation. The $Fe(TPTZ)^{2+}$ complex also shows a strong kinetic preference to react with a neutral TPTZ molecule rather than with the negatively charged EDTA ion.

Introduction

The ligand 2,4,6-tripyridyl-*s*-triazine, TPTZ, first



TPTZ

prepared by Case and Koft,[3] forms a 2:1 iron(II) complex with a molar absorptivity equal to 21,600 at 593 mμ. The complex has been used for iron determinations.[4-6] Only the bis complex has been observed and 1:1 mixtures disproportionate to the bis complex and free iron.[7-9]

Kratochvil and White observed a rapid reaction between EDTA and $Fe(TPTZ)_2^{2+}$ and used the reaction to determine trace levels of EDTA.[10] One of the reasons we examined this reaction was to see if a direct attack of EDTA on the bis-TPTZ complex occurred since such direct attack is not observed in the much slower reaction with tris(1,10-phenanthroline)-iron(II).[11,12] Another reason was to compare the mechanism of dissociation in acid and in base to that of tris(1,10-phenanthroline)iron(II).[11,13-16]

This study shows that EDTA does not react directly with the bis complex although the reaction rates are quite fast requiring stopped-flow techniques. The dissociation kinetics are fascinatingly complex with regard to pH dependence. An additional complication results because of a strong kinetic preference of $Fe(TPTZ)^{2+}$ to react with another TPTZ returning to reactants rather than to react with the electrostatically more attractive EDTA anion to give products.

Experimental Section

The TPTZ (G. F. Smith Chemical Co.) was dissolved with the aid of a few drops of concentrated HCl to give a 3.04×10^{-3} *M* solution. Iron(II) solutions were prepared from fresh ferrous ammonium sulfate. The $Fe(TPTZ)_2^{2+}$ complex was prepared ($\sim 10^{-4}$ *M*) using a slight excess of TPTZ to ensure complete complexation of the metal. Spectrophotometric standardization at 593 mμ was used. EDTA solutions were prepared from the recrystallized sodium salt and standardized against copper.

Constant ionic strength was maintained at 0.10 *M* with KCl. Sodium acetate–acetic acid buffer (0.02 *M*) was used from pH 3.5 to 5.5. At higher and lower pH EDTA served as its own

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[1] Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O85.

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buffer. All pH values were converted to $-\log [H^+]$ by $-\log [H^+] = pH - 0.12$.[17]

Kinetic runs were followed spectrophotometrically by observing the formation or disappearance of $Fe(TPTZ)_2^{2+}$ at 593 mμ, where other absorbing species were almost negligible. Initial concentrations of $Fe(TPTZ)_2$ were $(2-5) \times 10^{-5}$ *M* while EDTA was varied from 5×10^{-4} to 10^{-2} *M*. A stopped-flow apparatus described earlier[18] was used for the faster reactions and a Cary 14 recording spectrophotometer was used for the slower ones. Both instruments were thermostated at 25.0 ± 0.1°.

The reaction between $Fe(TPTZ)_2^{2+}$ and EDTA did not give simple order plots so the initial reaction velocity, $V_i = -d[Fe(TPTZ)_2^{2+}]_i/dt$, was used to determine the mechanism. The presence of dissolved oxygen in the reaction system affects the reaction equilibrium favorably[10] when EDTA is used to force dissociation of $Fe(TPTZ)_2^{2+}$ but does not affect the kinetics. Thus, changing the dissolved oxygen level from 2.6×10^{-4} to 7.7×10^{-4} *M* had no effect on $V_i/[Fe(TPTZ)_2^{2+}]_i$. The iron(II)-EDTA complex is very rapidly oxidized to iron(III)-EDTA and the rate increases with increasing pH.[19] Even at pH 2 the oxidation rate is faster than the observed rate of dissociation of $Fe(TPTZ)_2^{2+}$.

Because of an inconsistency which appeared between our kinetic data and the equilibrium constant for the formation of $Fe(TPTZ)_2^{2+}$, both the protonation constant for TPTZ and the formation constant for $Fe(TPTZ)_2^{2+}$ were redetermined.

The ultraviolet spectrum of TPTZ shows significant shifts at 220, 246, and 290 mμ when the ligand is protonated. Absorbances at these wavelengths were determined for a pH range of 1-6 with a $TPTZ_T$ concentration of $(1.5-1.9) \times 10^{-5}$ *M* at an ionic strength of 0.10 *M* (HCl + KCl) and a temperature of 25.0°. The absorbance-pH curve is approximately S shaped with a midpoint near the reported log K_H value of 3.1.[8] However, the curve cannot be fit with a single protonation constant and requires at least two acid species. Estimated values for $K_H = [HTPTZ^+]/[H^+][TPTZ]$ and $K_{2H} = [H_2TPTZ^{2+}]/[H^+][HTPTZ^+]$ are 3.4×10^3 and 5.4×10^2 M^{-1}, respectively.

The formation constant for $Fe(TPTZ)_2^{2+}$ was determined spectrophotometrically at 593 mμ. A pH range of 4.4-4.5 was used to minimize competition from the protonated TPTZ species. Using 13 different solutions with a range of total Fe(II) of $(1.1-3.1) \times 10^{-5}$ *M* and a range of total TPTZ of $(2.2-6.2) \times 10^{-5}$ *M*, the value of log β_2 is 12.4 ± 0.3 based on the above K_H value. The formation constant also was determined using nine additional solutions in the pH range of 2.9-4.0. A trend exists in the β_2 value if it is calculated on the basis of the single proton constant previously reported. However, this trend is removed by the use of our K_H and K_{2H} values and log $\beta_2 = 12.0 \pm 0.3$. Applying the same proton constant corrections to the previously reported value[8] of log $\beta_2 = 10.24$ gives a new value of 12.7. The larger value for β_2 is consistent with the kinetic data.

Results

The initial velocity (V_i) for the reaction of $Fe(TPTZ)_2^{2+}$ with EDTA (pH 2-8) depends on the EDTA concentration. With an initial concentration of 5.2×10^{-5} *M* $Fe(TPTZ)_2^{2+}$ and EDTA concentrations ranging from 5×10^{-4} to 10^{-2} *M*, a linear relationship is observed when $1/(V_i/[Fe(TPTZ)_2^{2+}]_i)$ is plotted as a function of $1/[EDTA]_i$. This is shown in Figure 1.

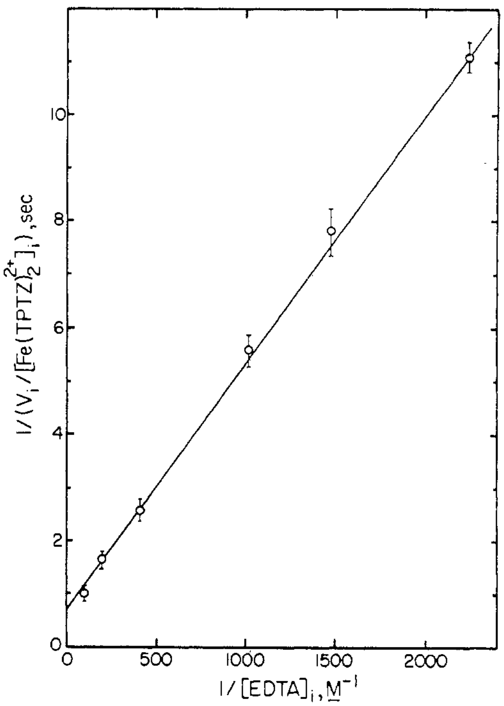

Figure 1.—Double-reciprocal dependence of the initial velocity and EDTA concentration for the reaction of $Fe(TPTZ)_2^{2+}$ with EDTA, $[TPTZ]_i = 4.77 \times 10^{-5}$ *M*, $[Fe(TPTZ)_2^{2+}]_i = 5.2 \times 10^{-5}$ *M*, 25.0°, pH 6.26, and $\mu = 0.10$ *M* KCl.

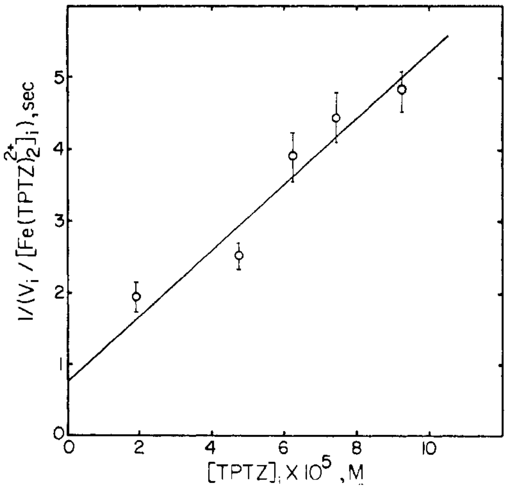

Figure 2.—Reciprocal dependence of the initial velocity on the concentration of excess TPTZ for the reaction of $Fe(TPTZ)_2^{2+}$ with EDTA, $[EDTA]_i = 2.48 \times 10^{-3}$ *M*, $[Fe(TPTZ)_2^{2+}]_i = 5.2 \times 10^{-5}$ *M*, 25.0°, pH 6.26, and $\mu = 0.10$ *M* KCl.

The velocity varies with the free TPTZ concentration, an increase in $[TPTZ]_i$ causing a decrease in $V_i/[Fe(TPTZ)_2^{2+}]_i$. Figure 2 shows the linear relationship between $1/(V_i/[Fe(TPTZ)_2^{2+}]_i)$ and $[TPTZ]_i$. On the other hand, a plot of $1/(V_i/[Fe(TPTZ)_2^{2+}]_i)$ against $[TPTZ]_i^2$ does not give a straight line, thus indicating that only one TPTZ is involved in the rate-determining step.

A mechanism consistent with the kinetic observations is

$$Fe(TPTZ)_2^{2+} \underset{k_{2f}}{\overset{k_{2d}}{\rightleftarrows}} Fe(TPTZ)^{2+} + TPTZ \qquad (1)$$

$$Fe(TPTZ)^{2+} + EDTA \xrightarrow{k_3} Fe^{II}(TPTZ)EDTA \qquad (2)$$

$$Fe^{II}(TPTZ)EDTA \xrightarrow[\text{O}_2\text{ reaction}]{\text{rapid dissociation}} Fe^{III}EDTA^- + TPTZ \qquad (3)$$

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(17) R. G. Bates, "Determination of pH," John Wiley & Sons, Inc., New York, N. Y., 1964, p 74.

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Reaction 3 is fast and does not affect the observed kinetics. The rate of disappearance of reactants equals the rate of formation of products and the steady-state approximation for $Fe(TPTZ)^{2+}$ gives eq 4. Using

$$V = -\frac{d[Fe(TPTZ)_2{}^{2+}]}{dt} = \frac{k_{2d}k_3[Fe(TPTZ)_2{}^{2+}][EDTA]}{k_{2f}[TPTZ] + k_3[EDTA]} \quad (4)$$

the initial velocity we can write eq 5, which agrees

$$\frac{1}{V_i/[Fe(TPTZ)_2{}^{2+}]_i} = \frac{k_{2f}[TPTZ]_i}{k_{2d}k_3[EDTA]_i} + \frac{1}{k_{2d}} \quad (5)$$

with the observed data shown in Figures 1 and 2.

The ratio of k_{2f}/k_3 is calculated from the slope of Figures 1 and 2. This ratio is observed to change with $-\log [H^+]$ and Figure 3 shows this dependence.

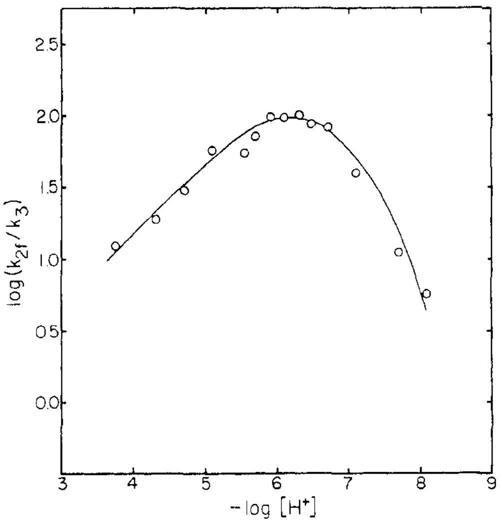

Figure 3.—Effect of hydrogen ion concentration on the ratio of rate constants k_{2f}/k_3 for the reaction of $Fe(TPTZ)_2{}^{2+}$ with EDTA, 25.0° and μ = 0.10 M KCl.

The intercept in each of these plots is $1/k_{2d}$. The rate constant k_{2d} is very pH dependent as shown in Figure 4.

In the pH region 2–8, k_{2d} is determined from the intercepts of plots similar to Figure 1 (three or more EDTA concentrations). In other regions hydrogen ion and hydroxide ion are capable of forcing the dissociation reaction and the points (an average of four kinetic runs) shown in Figure 4 are obtained directly from the first-order dissociation of $Fe(TPTZ)_2{}^{2+}$.

The dissociation rate constant for $Fe(TPTZ)_2{}^{2+}$, k_{2d}, has a complex pH behavior. Figure 4 shows six regions of pH dependence: (1) a limiting rate constant of 0.34 sec^{-1} at high acidity, (2) a proton rate constant of 14.3 M^{-1} sec^{-1} in the vicinity of pH 2, (3) a water dissociation rate constant of 2.6×10^{-2} sec^{-1}—this term is necessary because the minimum is too broad to be accounted for by H^+ and OH^- reactions, (4) a hydroxide ion rate constant of 7.9×10^7 M^{-1} sec^{-1} from pH 4 to 6, (5) a limiting rate constant of 1.7 sec^{-1} in the pH range 7–8, and (6) another hydroxide ion rate constant of 1.3×10^4 M^{-1} sec^{-1} above pH 9.

The kinetics of the formation of $Fe(TPTZ)_2{}^{2+}$ were studied with excess TPTZ and Figure 5 shows a plot of the first-order rate constant, k_{obsd}, as a function of TPTZ concentration. The linear relationship in Figure 5 indicates a first-order dependence rather than a second-order dependence in the TPTZ concentration. From the slope and the acidity constants of TPTZ, the resolved rate constant is 1.3×10^5 M^{-1} sec^{-1}.

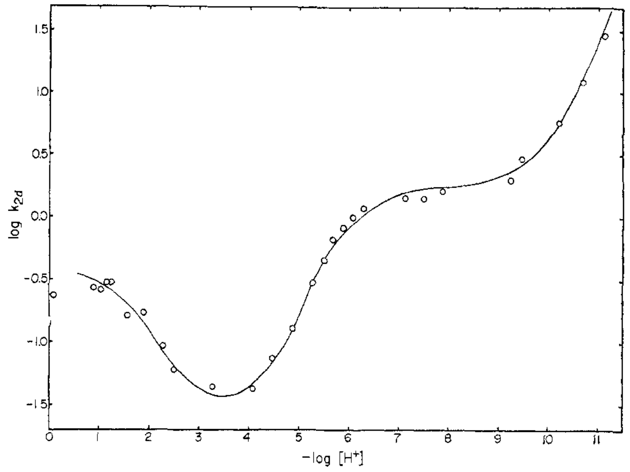

Figure 4.—Effect of acidity on the rate constant for the dissociation of TPTZ from $Fe(TPTZ)_2{}^{2+}$, 25.0°, μ = 0.10 M KCl. The solid line is calculated from eq 15 and rate constants listed in Table I.

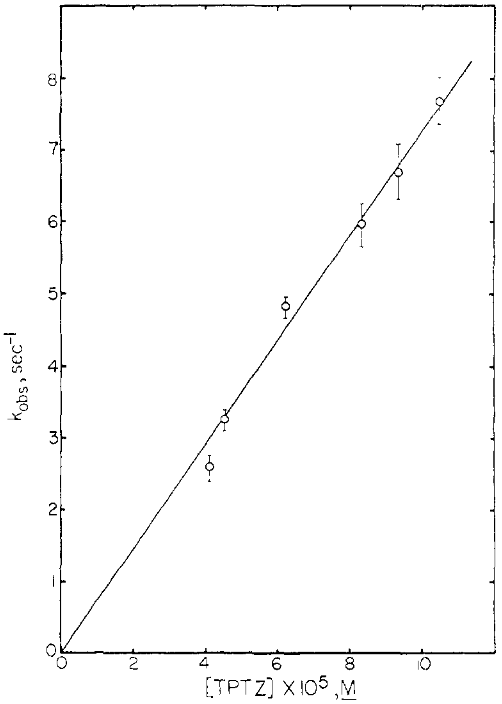

Figure 5.—The effect of TPTZ concentration on the observed pseudo-first order rate constant for the reaction of Fe(II) with TPTZ to form $Fe(TPTZ)_2{}^{2+}$, $[Fe(II)]_i = 8.0 \times 10^{-6}$ M, 25.0°, pH 3.70, and μ = 0.10 M KCl.

Discussion

Kinetics of Formation of $Fe(TPTZ)_2{}^{2+}$.—The formation of $Fe(TPTZ)_2{}^{2+}$ can be treated as a stepwise process as shown in eq 6 and 7. By applying a stationary-

$$Fe(II) + TPTZ \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} Fe(TPTZ)^{2+} \quad (6)$$

$$Fe(TPTZ)^{2+} + TPTZ \xrightarrow{k_{2f}} Fe(TPTZ)_2{}^{2+} \quad (7)$$

state condition to $Fe(TPTZ)^{2+}$, eq 8 follows. Under

$$\text{rate} = k_{\text{obsd}}\,[\text{Fe(II)}] = \frac{k_{1f}k_{2f}[\text{Fe(II)}][\text{TPTZ}]^2}{k_{1d} + k_{2f}[\text{TPTZ}]} \qquad (8)$$

the condition that $k_{2f}[\text{TPTZ}] > k_{1d}$, the rate equals $k_{1f}[\text{Fe(II)}][\text{TPTZ}]$ and with excess TPTZ the rate equals $k_{\text{obsd}}[\text{Fe(II)}]$, where k_{obsd} is $k_{1f}[\text{TPTZ}]$. This is consistent with the observed data presented in Figure 5. Accordingly under the experimental conditions the rate step is the addition of the first ligand. The theory of microscopic reversibility would appear to be violated because the dissociation rate of $Fe(TPTZ)_2^{2+}$ is the loss of the first ligand. However, the dissociation reaction was interrupted by scavengers and a shift in the rate-determining step is possible. In order for the addition of the first TPTZ to be the rate-determining step, there is a definite lower limit for the TPTZ concentration. The [TPTZ] must be greater than 2.0×10^{-6} *M* because the ratio k_{2f}/k_{1d} follows from

$$\beta_2 = \frac{k_{1f}k_{2f}}{k_{2d}k_{1d}} = \frac{k_{2f}}{k_{1d}}\,\frac{1.3 \times 10^5}{2.6 \times 10^{-2}} = 2.5 \times 10^{12} \text{ and } \frac{k_{2f}}{k_{1d}} = 5.0 \times 10^5$$

Under the experimental conditions in Figure 5 the [TPTZ] was greater than 4×10^{-5} *M*, so this condition is satisfied.

An alternate explanation of the first-order dependence in TPTZ would be possible if $Fe(TPTZ)^{2+}$ were formed rapidly and completely in solution. The observed rate constant then would necessitate K_1 and K_2 to be of the same order of magnitude. With the two equilibrium constants so close together, significant concentrations of $Fe(TPTZ)^{2+}$ should be detectable in the stability constant studies. There is no evidence of any $Fe(TPTZ)^{2+}$ being present and it is concluded that this is not an acceptable explanation. Complexes of Fe(II) with terpyridyl also show large differences in the magnitude of successive formation constants,[20] $\log K_1 = 7.1$ and $\log K_2 = 13.9$.

The addition of a second ligand occurring much faster than the first is not unique to TPTZ. Complexes of Fe(II), Ni(II), and Co(II) with terpyridyl also add a second ligand faster than the first.[20]

The magnitude of k_{2f} is illustrated in Figure 3 where the ratio of k_{2f}/k_3 exceeds 100 at pH 6. From electrostatics one would expect the exact opposite. Apparently the tridentate ligands TPTZ and terpyridyl are capable of outer-sphere ligand association with the monoiron(II) complexes which greatly increases the rate of formation of the respective bis complexes.

Dissociation of $Fe(TPTZ)_2^{2+}$.—The reaction of EDTA with $Fe(TPTZ)_2^{2+}$ proceeds through a mechanism that is explained by eq 1 and 2. The requirement that one TPTZ ligand completely dissociate before EDTA can react is similar to the reaction of EDTA with tris(1,10-phenanthroline)iron(II).[12] With the 1,10-phenanthroline complex EDTA can bond to iron(II) when two positions are available whereas with TPTZ there is no reaction until three positions are available probably owing to the bulk of the ligand.

The rate constant for the uncatalyzed dissociation of TPTZ from $Fe(TPTZ)_2^{2+}$, 2.6×10^{-2} sec^{-1}, is larger than those for $Fe(1,10\text{-phen})_3^{2+}$, $Fe(bipy)_3^{2+}$, and $Fe(terpy)_2^{2+}$ and qualitatively parallels the instability constant for the dissociation of the first ligand from the coordinately saturated iron(II). The respective rate constants are in the order: $Fe(TPTZ)_2^{2+}$ (2.6×10^{-2} sec^{-1}) > $Fe(bipy)_3^{2+}$ (1.2×10^{-4} sec^{-1})[15] ~ $Fe(phen)_3^{2+}$ (7.5×10^{-5} sec^{-1})[13] > $Fe(terpy)_2^{2+}$ (1.0×10^{-6} sec^{-1}).[20,21]

Dependence of k_{2d} on pH.—The dissociation rate constant dependence shown in Figure 4 has two plateaus with pH-independent values in acid and in neutral solutions. These values could be due to limiting kinetic steps or to the complete conversion of reactants to an acid form and a hydroxide form, respectively. No spectral evidence and no titrimetric evidence could be found for $Fe(TPTZ)_2OH^+$ from pH 5.4 to 7.5; in the absence of EDTA and O_2 the $Fe(TPTZ)_2^{2+}$ complex does not dissociate in this pH range. Therefore the plateau at pH 7–8 must be due to a limiting dissociation step preceding the reaction with hydroxide ion. This must be only a partial dissociation of TPTZ because under other conditions the dissociation is slower. Figure 6 gives the proposed stepwise dissociation mechanism which is in accord with the distinct regions of pH dependence. Intermediates B and C are necessary in order to account for the water dissociation rate constant and for the two pH plateaus.

The water dissociation path must proceed from A to B to C to products and the steady-state approximation gives

$$k_d = \frac{k_1k_2k_3}{k_2k_3 + k_3k_{-1} + k_{-1}k_{-2}} \qquad (9)$$

A similar mechanism has been proposed[21] for $Fe(terpy)_2^{2+}$ where the last bond rupture of the tridentate ligand is the rate-determining step.

Acid increases the dissociation rate but the limiting value in acid is less than the limiting value at pH 7–8 by a factor of 5. This makes direct H^+ attack on the initial complex very unlikely because there is no evidence of conversion of the reactant to $Fe(TPTZ)_2H^{3+}$, and if the protonated species did form completely its dissociation rate constant would be larger than k_1. The proposed mechanism goes through B to C to D. The expression for the rate constant is

$$k_{2d}(\text{pH 1–3}) = \frac{k_1k_2k_4k_5[\text{H}^+]}{k_{-1}k_{-2}(k_{-4} + k_5) + (k_{-1} + k_2)k_4k_5[\text{H}^+]} \qquad (10)$$

and the limiting value at high acidity is

$$k_{2d}([\text{H}^+] > 1\ M) = \frac{k_1k_2}{k_{-1} + k_2} \qquad (11)$$

Low hydroxide ion accelerates the rate of dissociation indicating a hydroxide intermediate such as E. The

$$k_{2d}(\text{pH 4–7}) = \frac{k_1k_6k_7[\text{OH}^-]}{k_{-1}(k_{-6} + k_7) + k_6k_7[\text{OH}^-]} \qquad (12)$$

plateau at pH 7–8 must be due to a rate step preceding that given in eq 11 because the value is five times larger.

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[20] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

[21] R. Farian, R. Hogg, and R. G. Wilkins, *ibid.*, **7**, 170 (1968).

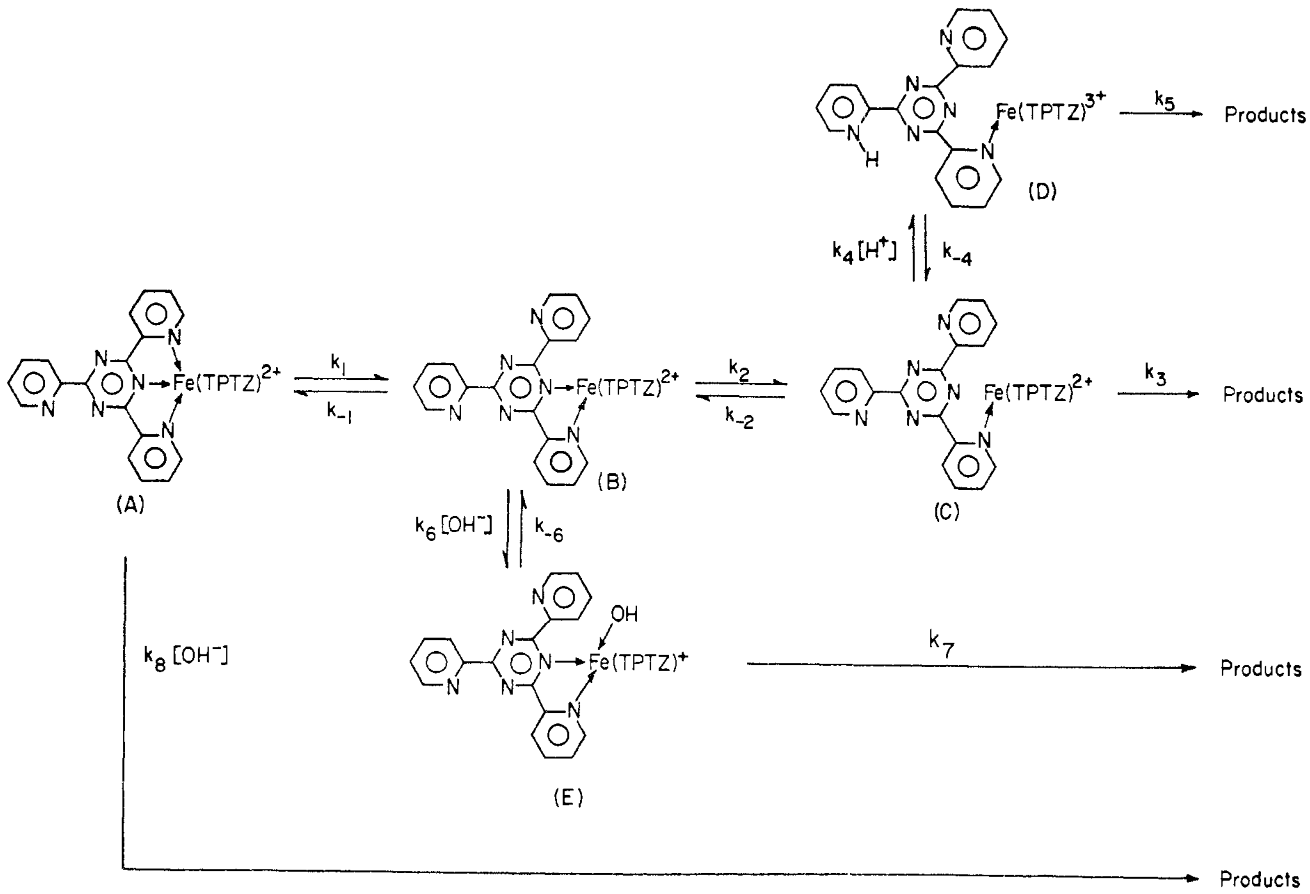

Figure 6.—Stepwise dissociation of TPTZ from Fe(TPTZ)$_2^{2+}$ showing steps proposed in this kinetic study.

TABLE I

RATE CONSTANTS FOR THE DISSOCIATION OF TPTZ FROM Fe(TPTZ)$_2^{2+}$ AT 25.0° AND μ = 0.10 M

Rate constant	Value	Rate constant	Value
$k_1k_2/(k_{-1} + k_2)$	0.34 sec^{-1}	k_1	1.7 sec^{-1}
$k_1k_2k_4k_5/(k_{-1}k_{-2})(k_4 + k_5)$	14.3 M^{-1} sec^{-1}	$k_1k_6k_7/k_{-1}(k_{-6} + k_7)$	7.9 × 10^7 M^{-1} sec^{-1}
k_d	2.6 × 10^{-2} sec^{-1}	k_8	1.3 × 10^4 M^{-1} sec^{-1}

In this pH range the rate of formation of B becomes limiting and

$$k_{2d}(\text{pH } 7\text{–}8) = k_1 \qquad (13)$$

The preceding expressions in eq 9–13 are needed to explain the complex pH dependence. The stepwise dissociation mechanism is reasonable and is similar to terpyridyl and bipyridyl mechanisms. However, above pH 9 a hydroxide dependence reappears. This cannot be attributed to a path with prior rupture of any TPTZ bond because the limiting value of k_1 has already been reached.

Direct reaction of hydroxide ion with tris(1,10-phenanthroline)iron(II)[11] and tris[α-(2-pyridyl)benzylideneaniline]iron(II)[22] have been observed. This type of association mechanism is not general for all metal complexes but does appear quite frequently with iron(II).

$$k_{2d}(\text{pH } 9\text{–}11) = k_8[OH^-] \qquad (14)$$

The solid line shown in Figure 4 is calculated from eq 15. The values for the rate constants are listed in Table I.

$$k_{2d} = \frac{k_1k_2k_4k_5[H^+]}{k_{-1}k_{-2}(k_{-4} + k_5) + (k_{-1} + k_2)k_4k_5[H^+]} + k_d + \frac{k_1k_6k_7[OH^-]}{k_{-1}(k_{-6} + k_7) + k_6k_7[OH^-]} + k_8[OH^-] \qquad (15)$$

Conclusions

(1) The rate of addition of the second TPTZ ligand to iron(II) is much faster (>100 times) than the rate of formation of the mono complex. This behavior also was found for Fe(terpy)$^{2+}$ with terpy.[20] The Fe(TPTZ)$^{2+}$ complex shows a strong kinetic preference to react with a neutral TPTZ molecule rather than with the negatively charged EDTA ion. Thus the effect appears to be the result of outer-sphere association between the complex and the ligand rather than accelerated water loss.

(2) The k_{1f} value of 1.3 × 10^5 M^{-1} sec^{-1} fits the water-exchange rate constants[23] of 3 × 10^6 sec^{-1} and an outer-sphere association constant of 0.04 M for the aquo ion and TPTZ.

(3) EDTA cannot react directly with Fe(TPTZ)$_2^{2+}$ but reacts after the complete dissociation of one TPTZ ligand.

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(22) J. Burgess, *J. Chem. Soc., A*, 497 (1968).

(23) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(4) The k_{2d} value for the TPTZ complex is 4000 times greater than the k_{2d} value for $Fe(terpy)_2^{2+}$, paralleling the relative stability constants of the complexes. In the absence of hydrogen ion or hydroxide ion acceleration of the rate-determining step is the third bond dissociation of TPTZ.

(5) The dissociation of $Fe(TPTZ)_2^{2+}$ is accelerated by hydrogen ion and by hydroxide ion and in both cases prior dissociation steps can become rate limiting. As a result a complete stepwise mechanism can be identified in the loss of the first TPTZ.

(6) Above pH 9 direct reaction is observed between $Fe(TPTZ)_2^{2+}$ and hydroxide ion. This is similar to the reaction of $Fe(phen)_3^{2+}$ with OH^- but with TPTZ the hydroxide ion rate constant is 3000 times greater.[11] Hence hydroxide ion can attack the complex directly as well as taking part in the stepwise dissociation.

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Substitution Reactions of Ruthenium(III)–Ethylenediamine and Related Complexes. I. Acid Hydrolysis of *cis*-Dihalogenobis(ethylenediamine), (—)-1,2-Diaminopropane, Triethylenetetramine, and Ammonia Complexes

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Kinetics and stereochemistry of primary and secondary aquation of *cis*-dihalogenobis(ethylenediamine)ruthenium(III), *cis*-dichlorobis((—)-1,2 diaminopropane)ruthenium(III), *cis*-α-dichlorotriethylenetetramineruthenium(III), and *cis*-dichlorotetraammineruthenium(III) have been studied together with acid hydrolyses of bromo- and iodopentaammineruthenium(III) cations. The aquation reactions take place with complete retention of configuration. Charge has no effect on the rates, while increased chelation results in progressively faster rates. These results can be explained by an SN2 mechanism for aquation. The equilibria pertaining to *cis*-diaquobis(ethylenediamine)ruthenium(III) with chloride or bromide ions and aquopentaammineruthenium(III) with bromide or iodide ions have been studied as a function of temperature. pK_a values of 5.30 ± 0.05 at 23° have been measured for *cis*-$RuXH_2O(en)_2^{2+}$ (X = Cl, Br).

Introduction

The first study of the substitution processes in ruthenium(III) ammines was concerned with the $RuCl(NH_3)_5^{2+}$ cation.[2] Though this complex behaved similarly to Co(III), Cr(III), and Rh(III) with respect to acid hydrolysis, in basic solution loss of the chloro ligand was very fast and therefore similar to the well-known Co(III) system. To obtain information on the stereochemistry of ruthenium(III) reactions we have, therefore, studied the bis-bidentate chelate complexes *cis*-$[RuX_2(en)_2]X$ (X = Cl, Br, I; en = ethylenediamine) and *cis*-$[RuCl_2((-)pn)_2]Cl$ ((—)pn = (—)-1,2-diaminopropane) and the related *cis*-α-$[RuCl_2(trien)]Cl$ (trien = triethylenetetramine) and *cis*-$[RuCl_2(NH_3)_4]Cl$. The initial work on $[RuCl(NH_3)_5]Cl$ has also been extended to include $RuBr(NH_3)_5^{2+}$ and $RuI(NH_3)_5^{2+}$. The syntheses and characterization of these chelate complexes have been described earlier.[3] In this paper the results of kinetic studies in acid solution are given.

Experimental Section

Materials.—*cis*-$[RuCl_2(NH_3)_4]Cl \cdot H_2O$ was obtained by the action of concentrated HCl on $[RuC_2O_4(NH_3)_4]I$[4,5] and was recrystallized as orange needles from dilute HCl (2 *M*). *Anal.* Calcd for $H_{14}N_4Cl_3ORu$: N, 19.1; Cl, 36.2. Found: N, 18.5; Cl, 36.1. The absorption spectrum agreed with previous work[6] and also corresponded closely to that of *cis*-$RuCl_2(en)_2^+$.

***cis*-Bromoaquobis(ethylenediamine)ruthenium(III) *p*-Toluenesulfonate Monohydrate, $[RuBrH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2 \cdot H_2O$.**—This light brown compound was prepared by a method analogous to that described for the corresponding chloro complex. *Anal.* Calcd for $C_{18}H_{34}BrS_2N_4O_8Ru$: C, 31.8; H, 5.0; Br, 11.8; S, 9.4; N, 8.2. Found: C, 31.9; H, 5.0; Br, 12.4; S, 8.6; N, 8.5.

***cis*-Iodoaquobis(ethylenediamine)ruthenium(III) *p*-Toluenesulfonate, $[RuIH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2$.**—This complex could not be obtained pure by the methods[3] which were successful for the chloro and bromoaquo counterparts. In this procedure the addition of ethanol resulted in dissolution of the purple reaction product. For the kinetic studies the complex was best formed *in situ* by treating *cis*-$[RuI_2(en)_2]I \cdot H_2O$ with base followed by acidification with *p*-toluenesulfonic acid.

***cis*-α-Chloroaquotriethylenetetramineruthenium(III) *p*-Toluenesulfonate Monohydrate, $[RuClH_2O(C_6H_{18}N_4)](C_7H_7SO_3)_2 \cdot H_2O$.**—This pale yellow complex was prepared as for the $RuClH_2O(en)_2^{2+}$

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