[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Racemization of Complex Ions. II. Kinetics of the Dissociation and Racemization of Tris-(1,10-phenanthroline)-iron(II) and Tris-(2,2'-dipyridyl)-iron(II) Complexes[1,2]

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The rates of dissociation and racemization of tris-(1,10-phenanthroline)-iron(II) and tris-(2,2'-dipyridyl)-iron(II) ions were determined under similar conditions. Since in each case the rate of racemization is greater than the rate of dissociation, it is concluded that an intramolecular process accounts for much of the observed racemization. It is suggested that this intramolecular rearrangement occurs without opening of the chelate rings. However, a mechanism, involving rupture of a single Fe–N bond, is proposed to account for the acid-dependent dissociation and racemization of $[Fe(dipy)_3]^{+2}$.

The kinetics of racemization of tris-(1,10-phenanthroline)-iron(II) and tris-(2,2'-dipyridyl)-iron(II) ions were recently reported by Davies and Dwyer.[3] They point out that the data obtained for the iron(II) complexes differed from that for the corresponding nickel(II) compounds. The iron(II) complexes have the larger values of the activation energies and the *PZ* term. However, they suggest that in both cases an intramolecular process is involved. In paper I of this series[1] it was shown that these nickel(II) complexes racemized by a dissociation mechanism.

Brown, Ingold and Nyholm[4] infer that a dissociation process is involved because of the near-equivalence of the iron(II) exchange rate[5] and the racemization rate[3] of these iron(II) complexes. However, since the iron(II) exchange was done only qualitatively at room temperature, a better comparison to make would be with the quantitative values for the rates of dissociation.[6,7] Such a comparison reveals that the rate of racemization is in fact faster than the rate of dissociation and thus not consistent with a dissociation mechanism. Unfortunately these independent experiments were not carried out at the same conditions and the differences in rate may be due to secondary effects such as ionic strength or acid concentration. It was, therefore, the purpose of this investigation to determine the rates of these reactions under exactly the same experimental conditions.

Experimental

Preparation of Compounds.—The complex $[Fe(ophen)_3]Cl_2 \cdot 6H_2O$ was prepared and resolved through the antimonyl tartrate by the method of Dwyer and Gyarfas.[8] The preparation and resolution of $[Fe(dipy)_3]Cl_2 \cdot 6H_2O$ through the iodide antimonyl tartrate was likewise carried out as previously described.[9]

Rate of Racemization.—Measurements of optical rotation were made with a Bellingham and Stanley Polarimeter using a sodium vapor lamp. Unfortunately these iron(II) complexes are an intense red color and it was necessary to use very dilute solutions to obtain sufficient light transmission. These solutions, therefore, had small optical rotations and it was difficult to obtain precise kinetic data. All of the data reported are the average of at least three independent determinations. The precision of these data is estimated to be better than 15%.

Solutions of approximately 1×10^{-4} *M* concentration were prepared by the addition of the iron(II) complex to the appropriate solution at 0°. This cold solution was immediately poured into a 1-dm. polarimeter tube equipped with a water jacket and maintained at constant temperature (±0.1°) with circulating water. Measurements were then taken as soon as the equilibrium temperature was reached. The optical rotation at zero time was approximately 0.4° for *d*-$[Fe(ophen)_3]^{+2}$ and approximately 0.7° for *d*-$[Fe(dipy)_3]^{+2}$. With acid solutions of *d*-$[Fe(ophen)_3]^{+2}$ the light intensity does not noticeably change during the period of measurement. In the case of $[Fe(dipy)_3]^{+2}$, however, the rate of dissociation is only a little less than its rate of racemization, and as a result the absorption of light by the solution decreases during the course of these measurements. Therefore, even though the angle of rotation decreases with time, it can still be measured with approximately the same accuracy because of the greater light intensity. The data obtained for the racemization of *d*-$[Fe(dipy)_3]^{+2}$ are more reliable than those for *d*-$[Fe(ophen)_3]^{+2}$ for this reason, and also because the zero time optical rotation was larger for $[Fe(dipy)_3]^{+3}$.

Rate of Dissociation.—The rates of dissociation were determined by the method of Lee, Kolthoff and Leussing.[6] Stock solutions of the iron(II) complexes in water were prepared. A chosen quantity of these solutions was then added to an appropriate amount of an acid solution and the change in optical density over a period of time was observed. A wave length of 510 mμ was used for $[Fe(ophen)_3]^{+2}$ and 520 mμ for $[Fe(dipy)_3]^{+2}$. Measurements were made with a Beckman model DU spectrophotometer using 1-cm. corex cells. The temperature of the reaction mixture was maintained constant (±0.1°) by circulating water through a jacket surrounding the cell compartment. The rate constants were obtained from a plot of the log of the optical density *vs.* time.

Results and Discussion

Rate of Dissociation.—The results of the dissociation experiments are summarized in Table I. The rates of dissociation have been reported[6,7] for somewhat different conditions, and our results are consistent with these previous studies.

Lee, Kolthoff and Leussing[6] have measured the rate of dissociation of $[Fe(ophen)_3]^{+2}$ at 25° in sulfuric acid solutions that were 0.005, 0.05 and 0.5 *M* in the acid, and report $k = 4.5 \times 10^{-3}$ min.$^{-1}$ for all three acidities. Our measurements corrected to 25.0° give a value of $k = 4.2 \times 10^{-3}$ min.$^{-1}$ in 1 *M* HCl. The activation energy in 1 *M* HCl is 32.1 ± 0.5 kcal.

Our data for $[Fe(dipy)_3]^{+2}$ show the same dependence on acidity noted by Baxendale and George,[7] *i.e.*, an increasing rate of dissociation with

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(1) For paper I in this series see THIS JOURNAL, **75**, 5102 (1953).

(2) Taken in part from a thesis submitted by John C. Hayes in partial fulfillment of the requirements for the M.S. degree, 1953.

(3) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **49**, 180 (1953).

(4) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2679 (1953).

(5) S. Ruben, M. D. Kamen, M. B. Allen and P. Nahinsky, THIS JOURNAL, **64**, 2297 (1942).

(6) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *ibid.*, **70**, 3596 (1948).

(7) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(8) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N.S. Wales*, **83**, 263 (1950).

(9) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **85**, 135 (1952).

TABLE I

RATES OF DISSOCIATION OF TRIS-(1,10-PHENANTHROLINE)-IRON(II) ION

Solution	Temp., °C.	$k \times 10^3$ (min.$^{-1}$)
1 M HCl	17.5	1.02
1 M HCl	25.3	4.43
1 M HCl	34.6	22.2

RATES OF DISSOCIATION OF TRIS-(2,2′-DIPYRIDYL)-IRON(II) ION

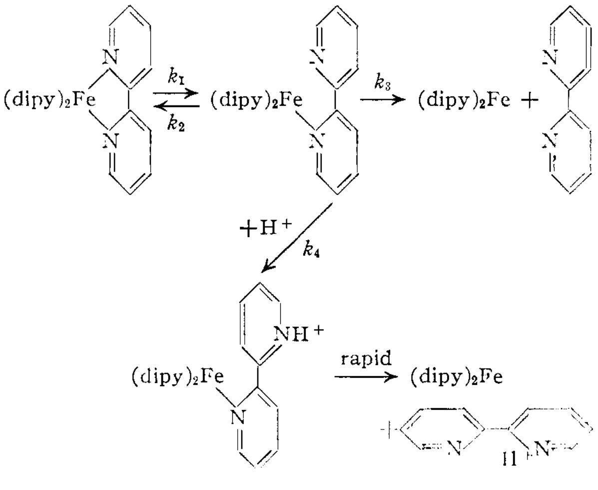
Solution	Temp., °C.	$k \times 10^2$ (min.$^{-1}$)
0.25 M HCl	25.6	2.79
0.5 M HCl	25.6	4.24
1 M HCl	24.4	4.26
1.5 M HCl	17.9	1.52
1.5 M HCl	24.4	4.35
1.5 M HCl	32.4	14.5
2 M HCl	24.4	4.18

increasing acidity until a constant rate is reached for acidities greater than 1 M. Our value for this limiting rate at 25.0° is 4.7×10^{-2}, as compared to 4.4×10^{-2} min.$^{-1}$ reported by Baxendale and George. They report an activation energy of 26.2 kcal. in phthalic acid buffers in the pH range 2.2–2.8, compared to our value of 27.4 ± 0.5 kcal. in 1.5 M HCl.

The observation of an acid-independent dissociation for $[\mathrm{Fe(ophen)_3}]^{+2}$ and an acid-dependent dissociation for $[\mathrm{Fe(dipy)_3}]^{+2}$ is the same as that noted for the corresponding nickel(II) complexes.[1] Baxendale and George[7] have attempted to explain the acid dependence in the case of $(\mathrm{Fe(dipy)_3})^{+2}$ on the basis of the equilibrium

$$[\mathrm{Fe(dipy)_3}]^{+2} + \mathrm{H}^+ \rightleftarrows [\mathrm{Fe(dipy)_3H}]^{+3}$$

They suggested that $[\mathrm{Fe(dipy)_3}]^{+2}$ reacts more slowly than does $[\mathrm{Fe(dipy)_3H}]^{+3}$ and that a limiting rate is reached at high acid concentration where essentially only $[\mathrm{Fe(dipy)_3H}]^{+3}$ is present. If such an equilibrium were involved the absorption spectrum of solutions of $[\mathrm{Fe(dipy)_3}]^{+2}$ in concentrated acid should differ from that in water. Within experimental error no difference was observed whenever the optical densities of 1 M HCl solutions of $[\mathrm{Fe(dipy)_3}]^{+2}$ at 550, 525, 488, 363, 350 and 338 mμ were extrapolated back to zero time. Therefore it would appear that the acid dependence is involved in the kinetics in such a way that at no time is there ever a very large concentration of the protonated species. Unlike 1,10-phenanthroline, the 2,2′-dipyridyl molecule is sufficiently flexible that some activated intermediate may be formed in which it behaves as a monodentate group. The reaction mechanism may thus be shown.



According to this reaction scheme and applying the steady state approximation the observed rate constant, k, will be given by

$$k = k_1\left(\frac{k_3 + k_4[\mathrm{H}^+]}{k_2 + k_3 + k_4[\mathrm{H}^+]}\right)$$

The qualitative behavior of the acid dependence is in agreement with this formula, but a quantitative fit to the data is not possible. Failure to achieve the latter probably results from activity effects which cannot be taken into account. The scheme proposed by Baxendale and George[7] leads to a mathematically equivalent expression and they commented on failure in fitting the data quantitatively.

On the basis of the present scheme the value of k at low acidity is $k_0 = k_1 k_3/(k_2 + k_3)$, and the value of k at high acidity is $k_\infty = k_1$. At 25°, $k_0 = 0.73 \times 10^{-2}$ min.$^{-1}$ and $k_\infty = 4.7 \times 10^{-2}$ min.$^{-1}$. The ratio $k_0/k_\infty = 0.16$, and from the previous expressions we see that k_0/k_∞ also equals $k_3/(k_2 + k_3)$. This means that in solutions of low acidity, for each time a single Fe–N bond breaks the bond will reform approximately 84% of the time and the second bond will break leading to complete dissociation approximately 16% of the time.

TABLE II

RATE OF RACEMIZATION OF TRIS-(1,10-PHENANTHROLINE)-IRON(II) ION

Solution	Temp., °C.	$k \times 10^3$ (min.$^{-1}$) $k_{\mathrm{obs.}}$	$k_{\mathrm{diss.}}$	$k_{\mathrm{intramol.}}$
1 M HCl	15.9	9.9	0.8	9.1
1 M HCl	24.8	40	4.0	36
1 M HCl	30.9	122	11.8	110

RATE OF RACEMIZATION OF TRIS-(2,2′-DIPYRIDYL)-IRON(II) ION

Solution	Temp., °C.	$k \times 10^2$ (min.$^{-1}$) $k_{\mathrm{obs.}}$	$k_{\mathrm{diss.}}$	$k_{\mathrm{intramol.}}$
1.5 M HCl	16.7	1.82	1.26	0.56
1.5 M HCl	25.0	6.43	4.79	1.64
1.5 M HCl	33.9	25.6	18.3	7.3
0.25 M HCl	25.0	5.56	2.56	3.00
0.5 M HCl	25.0	6.05	3.90	2.15
1 M HCl	25.0	6.41	4.69	1.62
2 M HCl	25.0	6.40	4.70	1.70

The assumption of this reaction scheme also implies that the activation energy measured in 1.5 M HCl is the activation energy for the reaction indicated with rate constant k_1. The activation energy measured by Baxendale and George at pH 2.5 would be that for the same reaction modified by the way in which the fraction $k_3/(k_2 + k_3)$ changes with temperature.

Rate of Racemization.—The rates of racemization of these complexes in water had been studied prior to this work.[3] This investigation was carried out in acid solutions so that the results obtained might be compared with the rates of dissociation. These results are given in Table II. The rate constant, k, is obtained from the slope, m, of the log α

TABLE III

RATES FOR INDIVIDUAL PROCESSES LEADING TO RACEMIZATION AT 25.0°

	Intramolecular racemization			Dissociation		
	k (min.$^{-1}$)	E	$\Delta S^\ddagger$	k (min.$^{-1}$)	E	$\Delta S^\ddagger$
$[Fe(ophen)_3]^{+2}$	3.9×10^{-2}	29 ± 2	21 ± 7	0.42×10^{-2}	32.1 ± 0.5	28 ± 2
$[Fe(dipy)_3]^{+2}$	1.6×10^{-2}	26 ± 2	12 ± 7	4.7×10^{-2}	27.4 ± 0.5	17 ± 1
$[Ni(ophen)_3]^{+2}$	$<6.0 \times 10^{-5}$			6.0×10^{-4}	25.0 ± 0.5	2 ± 2
$[Ni(dipy)_3]^{+2}$	$<1.4 \times 10^{-2}$			1.1	21.8 ± 0.5	6 ± 2

vs. t plot by the relationship $k = -2.303m$.[1] The rate of racemization of d-$[Fe(dipy)_3]^{+2}$ increases with increasing concentration of acid and appears to reach a limiting rate at approximately 1 M HCl.

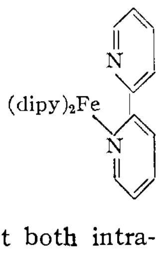
The rate constant for racemization of $[Fe(ophen)_3]^{+2}$ is reported by Davies and Dwyer[3] to be 4.0×10^{-2} min.$^{-1}$ in water and 3.4×10^{-2} min.$^{-1}$ in 0.1 M HCl in water at 25.0°. Our value of 4.0×10^{-2} min.$^{-1}$ in 1 M HCl at 24.8° indicates the fact that the racemization is independent of acidity.

From the results obtained on the racemization of the related Ni complexes[1] it is a reasonable assumption that each dissociation leads to loss of optical activity. Table II lists the rate of dissociation corresponding to the experimental conditions of the racemization, these rates being obtained from our experimental rates of dissociation corrected for temperature differences where necessary. The fact that the racemization is more rapid than the dissociation implies that racemization also takes place by some intramolecular, or non-dissociative, process. The observed rate of racemization will then be the sum of the two rates, and obviously the rate of intramolecular racemization can be obtained by subtracting the rate of dissociation from the total rate. These results are also given in Table II. The activation energies for the intramolecular process can be determined from the data, and they are 29 ± 2 kcal./mole for $[Fe(ophen)_3]^{++}$ and 26 ± 2 kcal./mole for $[Fe(dipy)_3]^{++}$.

The detailed mechanisms of intramolecular rearrangements are not known.[10] However, it has been suggested that either this occurs by means of one[11] or more[12] chelate groups opening up at one end or by the chelate rings shifting around the central atom.[13]

In the case of the intramolecular rearrangement of $[Fe(ophen)_3]^{+2}$ there can be no opening of the chelate rings. This is necessarily true because of the geometry of the 1,10-phenanthroline molecule which is a fixed planar structure with the nitrogen atoms only approximately 2.5 Å. apart. Therefore this molecule cannot behave as a monodentate group and the intramolecular process must involve the movement of these chelate rings about the central atom. We would expect this process to be independent of acidity, and this is the case, since both the total rate of racemization and the rate of dissociation are independent of acidity.

The $[Fe(dipy)_3]^{+2}$ can conceivably undergo intramolecular racemization in two ways. One would be like that of $[Fe(ophen)_3]^{+2}$ which involves shifting, but not breaking, of Fe–N bonds. This process would be acid independent. The second would involve an intramolecular racemization of



Since the life time of this species would decrease with increasing acid concentration, it follows that racemization through such a route decreases with increasing acidity, and approaches zero at high acidities. Examination of the change in the intramolecular rate shows that it decreases with acidity but does not reach zero, indicating that both intramolecular mechanisms are operative.

Obviously racemization does not occur each time a single Fe–N bond is broken as we see that the rate, $k_1 = k_\infty$, of breaking a single bond is 4.7×10^{-2} min.$^{-1}$ at 25.0° while the total rate of racemization is only 3.6×10^{-2} min.$^{-1}$ at the same temperature in water.[3] The results observed are consistent with the picture that following rupture of one bond racemization occurs about 60% of the time before the bond is reformed.

Comparison of Iron(II) and Nickel(II) Complexes.—In Table III the factors involved in these processes have been summarized for both the iron(II) and nickel(II) complexes. A limiting value has been stated for the intramolecular racemization of the nickel(II) complexes, based on failure to observe any racemization by this process. The rate constants stated are for high acidities since for the dipyridyl complexes these are the most meaningful, k for dissociation being k_1, and k for the intramolecular racemization referring only to that process where no bonds are broken.

There is at present no adequate explanation for the greater entropy of activation associated with the dissociation of the iron(II) complexes as compared to that for the nickel(II) compounds. This difference may in some way be related to the role played by the solvent and work is now in progress on the rates of dissociation in non-aqueous solvents.

It has been demonstrated that two mechanisms are operative for both iron(II) complexes, with some evidence that a third also contributes in the case of $[Fe(dipy)_3]^{++}$. It is expected that in other complexes these mechanisms will, in general, compete with each other to account for the total racemization. Small unknown factors may lead to the dominance of one mechanism in any particular case, as has been exemplified by the behavior of the nickel(II) complexes.

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