Reaction Rates of Optically Active Tris(1,10-phenanthroline)* and Tris(2,2'-bipyridyl)* Complexes of Iron(II) in Aqueous Hydroxide and Cyanide Solutions

GWYNETH NORD

Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

At 25°C, total loss of optical activity accompanies the rate-determining second order reaction of $Fe(phen)_3{}^{2+}$ and $Fe(bipy)_3{}^{2+}$ with OH^- and with CN^-. Intramolecular (solvent) racemisation also occurs. Air oxidation of the complexes in alkaline solutions is preceded by the rapidly reversible dissociation of the three chelate ligands.

In our earlier work,[1] we showed that oxygen, although not involved in the rate-determining step, is necessary for the decomposition of $Fe(phen)_3{}^{2+}$ and $Fe(bipy)_3{}^{2+}$ in sodium hydroxide solutions. We further suggested that racemisation rates might provide a useful mechanistic probe for these systems. These rates are presented here for hydroxide, and also for some cyanide solutions, together with the spectrophotometrically determined reaction rates of the complexes in the same media.

EXPERIMENTAL

The complexes were resolved through the antimonyl tartrate and converted to the perchlorate as described in the literature.[2] Reactants and products were identified by their visible absorption spectra.[3,4] Changes in optical rotation of both isomers were measured with a Perkin Elmer, Model 141, polarimeter at 436 nm and at 546 nm, and of optical density with a Cary 14 Recording Spectrophotometer at the maximum of the visible absorption bands of the reactants and (cyanide) products. All measurements were made at 25°C and with three series of solutions with salt concentration adjusted with NaCl or KCl to (0.1 or 1.0) M. These contained (a) NaOH, (b) KCN, and (c) KCN+NaOH ($[OH^-] \geq [CN^-]$) (see tables and legends to the figures). The concentrations of OH^- and CN^- were always much greater than that of the complex, which varied from 10^{-5} M to 10^{-4} M. $Na_2S_2O_4$ (see Ref. 1) was added in most cases to the polarimeter cells. Optical rotation rates were also measured in the pure chloride media (see Table 2).

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* Referred to in this article as *phen* and *bipy*, respectively.

Table 1.

Complex	Medium M	$10^4 k_r$ s^{-1} (25°C)	$10^4 k_d$ s^{-1} (25°C)	$10^4 k_1$ s^{-1} mol^{-1} (25°C)	$10^4 k_2$ s^{-1} mol^{-1} (25°C)
Fe(bipy)$_3^{2+}$	0.1 KCl	6.6	2.0	70	80
	1.0 NaCl	5.9	($\sim$1) [a]	28.8	60
Fe(phen)$_3^{2+}$	1.0 NaCl	5.3	0.3 (0.69) [b]	61	110

[a] Estimated. [b] Ref. 6.

Table 2.

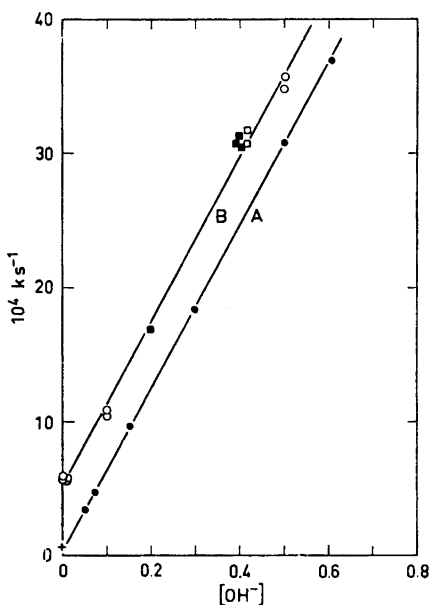| Complex	Medium M	10^4 k_r s^{-1} (25°C)	Reference
Fe(bipy)$_3^{2+}$	0.1 KCl	6.5	This work
	1.0 NaCl	6.0	This work
	Water	6.0	6
Fe(phen)$_3^{2+}$	0.1 KCl	6.5	This work
	1.0 NaCl	5.8	This work
	0.1 HCl	5.7	6
	1.0 HCl	6.7	6 (24.8°C)

Fig. 1. Fe(phen)$_3^{2+}$ in NaOH-NaCl, 1 M. A. Spectrophotometrically determined $k = k_{sp}$. ● perchlorate, present work, + perchlorate in 1 M KCl, Ref. 6. B. Polarimetrically determined $k = k_{pol}$. ○ antimonyltartrate, ■ perchlorate, □ without Na$_2$S$_2$O$_4$ (all others with).
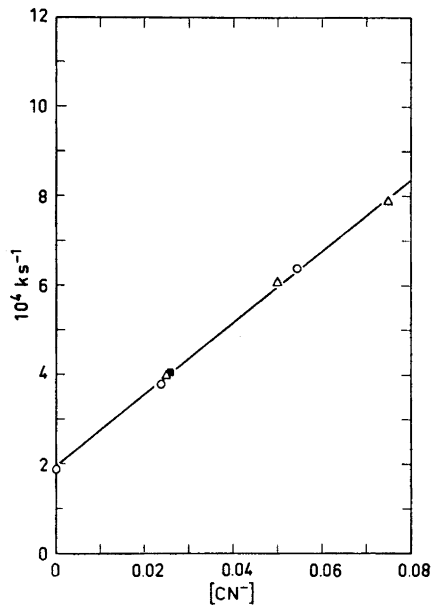
Fig. 2. Fe(bipy)$_2$(ClO$_4$)$_2$.2H$_2$O in KCN-KCl, 0.1 M. ○ $k_{pol} - 4.6 = k_{pol} - (k_r - k_d)$ (see Table 1), △ k_{sp}, Ref. 7, 25.3°C, ■ k_{sp}, this work.
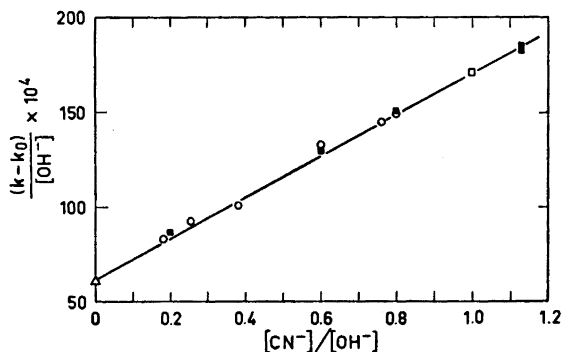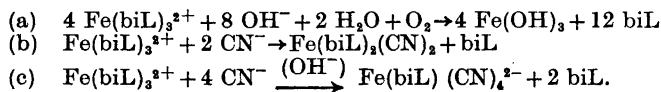
Fig. 3. Fe(phen)$_3$(ClO$_4$)$_2$.2H$_2$O in KCN-NaOH-NaCl, 1 M. ■ $k - k_0 = k_{pol} - k_r = k_{pol} -$ intercept B, Fig. 1, [OH$^-$] = 0.5 M, ○ $k - k_0 = k_{sp} - k_d = k_{sp}$ — intercept A, Fig. 1, [OH$^-$] = (0.1 − 0.4) M, □ $k_1 + k_2$ (see Table 1), △ k_1 (see Table 1).

The rates were all strictly first order in complex and were followed for at least four half lives. All kinetic runs were made in duplicate. The rate constants were calculated from the half lives read from the usual logarithmic plots.

In no case was a product optically active. We did not find the small product activity which has been reported [5] to accompany the reaction of *more concentrated* cyanide solutions (up to 2 M) with ΔFe(phen)$_3^{2+}$ at 0.5°. Because of this report we also investigated series (b) and (c) at 0°C but obtained only racemic products.

The addition of Na$_2$S$_2$O$_4$ did not affect the polarimetrically determined rates although under these conditions no change in optical density was observed in hydroxide solutions of the complex (series (a)). In the presence of O$_2$ for (a), and both in the presence and absence of O$_2$ for (b) and (c), the stoichiometry is given below (*biL* is used for *phen* and *bipy*):

(a) $4 \text{ Fe(biL)}_3^{2+} + 8 \text{ OH}^- + 2 \text{ H}_2\text{O} + \text{O}_2 \rightarrow 4 \text{ Fe(OH)}_3 + 12 \text{ biL}$

(b) $\text{Fe(biL)}_3^{2+} + 2 \text{ CN}^- \rightarrow \text{Fe(biL)}_2(\text{CN})_2 + \text{biL}$

(c) $\text{Fe(biL)}_3^{2+} + 4 \text{ CN}^- \xrightarrow{\text{(OH}^-)} \text{Fe(biL) (CN)}_4^{2-} + 2 \text{ biL}$.
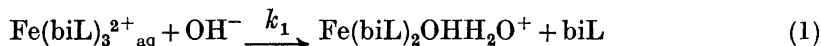
RESULTS AND DISCUSSION

The general rate law in all three sets of solutions (see figures) is:
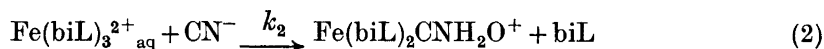
$$- d[\text{Fe(biL)}_3^{2+}]/dt = \{\text{constant} + k_1[\text{OH}^-] + k_2[\text{CN}^-]\}[\text{Fe(biL)}_3^{2+}]$$

The two cyanide products thus do not reflect a change in rate determining step. The spectrophotometric and the polarimetric methods give the same second order constants (k_1 and k_2), which are larger for Fe(phen)$_3^{2+}$ than for Fe(bipy)$_3^{2+}$. The first order constants for racemisation (k_r) are larger than for dissociation (k_d) and are similar to those for the pure salt media and to those published for hydrochloric acid (see Tables 1 and 2).

($k_r - k_d$) is the rate constant for the intramolecular racemisation as defined and discussed in Ref. 6.

We agree with earlier workers that the rate-determining step produces a bis-chelate probably as in eqns. 1 and 2:

$$\text{Fe(biL)}_3^{2+}{}_{aq} + \text{OH}^- \xrightarrow{k_1} \text{Fe(biL)}_2\text{OHH}_2\text{O}^+ + \text{biL} \qquad (1)$$

$$\mathrm{Fe(biL)_3^{2+}}_{aq} + \mathrm{CN}^- \xrightarrow{k_2} \mathrm{Fe(biL)_2CNH_2O^+} + \mathrm{biL} \qquad (2)$$

The decomposition of $\mathrm{Fe(bipy)_2(CN)_2}$ is independent of $[\mathrm{OH}^-]$ and slow $(k = 2.0 \times 10^{-6}\,\mathrm{s}^{-1}$ at $35°\mathrm{C}$; Ref. 7). The corresponding reaction for $\mathrm{Fe(phen)_2(CN)_2}$ would be expected to be even slower. $\mathrm{Fe(biL)_2(CN)_2}$ thus cannot be formed as an intermediate in the presence of comparable concentrations of OH^- and CN^- (series c).

In order to explain the complete conversion to $\mathrm{Fe(biL)(CN)_4}$ it is necessary for OH^- to complete successfully with CN^- for the intermediate species $\mathrm{Fe(biL)_2CNH_2O^+}$. This seems sensible as it only requires a proton shift. The product of this reaction must rapidly form the monochelate. The dissociation of the product of reaction of $\mathrm{Fe(biL)_2OHH_2O^+}$ with OH^- is also required to be rapid. This, unlike $\mathrm{Fe(biL)_2(CN)_2}$ and $\mathrm{Fe(biL)(CN)_4}$ which are spin-paired and robust, would be expected to be spin-free and labile.

The capture and stabilisation of the monochelate iron(II) species by cyanide shows that complete loss of chelate ligand in a series of rapidly reversible steps precedes air oxidation.

Earlier workers [6] have suggested that the mechanism of the intramolecular racemisation may involve an expanded high-spin reactive intermediate. This intermediate does not lead to dissociation of a biL ligand but could well be formed by attack on the complex by a solvent molecule. It therefore could be analogous to the seven-coordinated reactive intermediates which can explain the rate law for the CN^- and OH^- dependent paths. Since loss of optical activity accompanies ligand loss, this common mechanism can adequately accommodate our experimental results.

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