Dependence of Rates of Substitution Reactions of Pentacyanoaquoiron(II) Ion on Ionic Strength

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The second-order rate constants (k) of substitution of water in pentacyanoaquoiron(II) ion by nitrite, thiocyanate, sulphite or nitrobenzene were determined at various ionic strengths (I) in aqueous solution at 25 °C. The following slopes of the plot of log k versus $I^{1/2}$ were obtained: 2.9 (NO_2^-), 2.5 (SCN^-), 4.4 (SO_3^{2-}), and zero (nitrosobenzene).

The mechanistic patterns of octahedral substitutions have continued to be a lively issue in coordination chemistry. The substitution of water in $Fe(CN)_5H_2O^{3-}$ for a variety of entering ligands (Y^n) was found to proceed in aqueous solution according to the second-order rate law:[1,2]

$$— \ d \ ([Fe(CN)_5H_2O^{3-}])/dt = k \ [Fe(CN)_5H_2O^{3-}] \ [Y^n],$$

which can be interpreted in terms of several possible mechanisms including bimolecular and dissociative mode of activation.

In spite of the fact that some indirect evidence was presented in favor of a dissociative mechanism[1-3] it is still tempting to explore the medium effects such as ionic strength on the rates of the substitution reactions of $Fe(CN)_5H_2O^{3-}$.

We report here results showing the influence of ionic strength on the rate of substitution of water in $Fe(CN)_5H_2O^{3-}$ by neutral nitrosobenzene (PhNO), singly charged, NO_2^- and SCN^-, and double charged, SO_3^{2-}, ligands.

EXPERIMENTAL

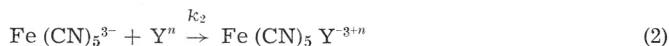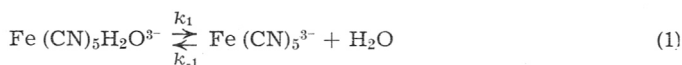The solution of the starting compound $Fe(CN)_5H_2O^{3-}$ was prepared as already described elsewhere[1,2]. The ionic strength of solutions was controlled by the addition of Merck sodium perchlorate. Nitrosobenzene was prepared according to published procedure[4]. All other chemicals were of Merck analytical grade and used without further purification.

A Durrum Stopped-Flow Spectrophotometer D-110 was used for rate measurements at 434 nm following the described procedure[2]. Slower runs were recorded by Cary 16 K Spectrophotometer using 10 cm quartz cells. The reaction solutions were thermostated to ±0.1 K. In all kinetic studies the entering ligand concentration was held in large excess of the pentacyanoaquoiron(II) ion concentration, thus ensuring pseudo-first order conditions.

RESULTS AND DISCUSSION

Substitution of water in $Fe(CN)_5H_2O^{3-}$ has been explained[1,2] in terms of a dissociative mechanism exemplified by eqn. (1)—(2).

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$$Fe\,(CN)_5H_2O^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe\,(CN)_5^{3-} + H_2O \qquad (1)$$

$$Fe\,(CN)_5^{3-} + Y^n \overset{k_2}{\rightarrow} Fe\,(CN)_5\,Y^{-3+n} \qquad (2)$$

The observed pseudo first order rate constant has been represented by eqn. (3).

$$k_{obs.} = \frac{k_1\,k_2\,[Y^n]}{k_{-1}\,[H_2O] + k_2\,[Y^n]} \qquad (3)$$

Assuming that k_{-1} is comparable with k_2 for neutral incoming ligands or even higher than k_2 for negatively charged ligands[1,2], and considering the concentration of water (55.5 mol dm^{-3}) the eqn. (3) can be reduced to $k_{obs.} = k_1 k_2 [Y^n]/$ $/(k_{-1}\,[H_2O])$. The determined second order rate canstant (k) is therefore defined by eqn. (4).

$$k = \frac{k_{obs.}}{[Y^n]} = \frac{k_1\,k_2}{k_{-1}\,[H_2O]} \qquad (4)$$

TABLE I

Dependence of Second Order Rate Constant (k) for Replacement of Water in $Fe(CN)_5H_2O^{3-}$ by Entering Ligand (Y^n) (PhNO, NO_2^-, SCN$^-$ or SO_3^{2-}) on Ionic Strength (I) at 25 ^{0}C. $3 \leqslant [Fe(CN)_5H_2O^{3-}]/10^{-5}$ mol dm$^{-3} \leqslant 6$. PhNO = nitrosobenzene, n = charge of the entering ligand

System No.	$[Y^n]$/mol dm^{-3}	I/mol dm^{-3}	k/dm^3 mol^{-1} s^{-1}
1	PhNO, 0.0005	0.0000	256.00
2	PhNO, 0.0005	0.0010	192.00
3	PhNO, 0.0005	0.0100	220.00
4	PhNO, 0.0005	1.0000	192.00
5	NO_2^-, 0.0001	0.0001	8.06
6	NO_2^-, 0.0001	0.0008	13.20
7	NO_2^-, 0.0100	0.0100	23.10
8	NO_2^-, 0.0100	0.0200	25.66
9	NO_2^-, 0.0100	0.0300	30.13
10	NO_2^-, 0.0100	0.0400	30.13
11	NO_2^-, 0.0100	0.0500	33.00
12	NO_2^-, 0.0100	0.0600	35.53
13	NO_2^-, 0.0100	0.0700	39.60
14	NO_2^-, 0.0100	0.0800	40.76
15	NO_2^-, 0.0100	0.0900	42.00
16	NO_2^-, 0.0100	0.1000	40.76
17	SCN$^-$, 0.0010	0.0010	8.84
18	SCN$^-$, 0.0010	0.0020	13.30
19	SCN$^-$, 0.0010	0.0040	16.10
20	SCN$^-$, 0.0010	0.0050	16.50
21	SCN$^-$, 0.0400	0.1320	48.10
22	SCN$^-$, 0.0400	0.2000	41.50
23	SCN$^-$, 0.0400	0.3000	78.75
24	SO_3^{2-}, 0.0400	0.3000	0.865
25	SO_3^{2-}, 0.0400	0.4000	1.195
26	SO_3^{2-}, 0.0400	0.5000	1.520
27	SO_3^{2-}, 0.0400	0.6000	2.310

According to the Brönsted theory of primary salt effects the postulated mechanism requires the rate to increase with increasing ionic strength in the case of the reactions between $Fe(CN)_5H_2O^{3-}$ and NO_2^-, SCN^- or SO_3^{2-}. The rate of replacement of water by nitrosobenzene should be insensitive to ionic strength. The reported data of systems 1 to 4 of Table I clearly show no dependence of the rate on ionic strength for nitrosobenzene as an entering ligand.

The results of systems 5 to 27 of Table I plotted as $\log k$ versus $I^{1/2}$ gave a straight line with a slope of 2.9 (NO_2^-), 2.5 (SCN^- and 4.4 (SO_3^{2-}).

The variations observed in k as a function of the ionic strength must be caused by proportional changes in k_2, since the fraction $k_1/(k_{-1}[H_2O])$ in eqn. (4) is expected to be identical for all entering ligands.

The figures above are in fair agreement with the predicted values of the slopes for NO_2^- and SCN^- (3.0) and nitrosobenzene (zero) based on the postulated mechanism depicted by eqns. (1)—(2). The only poor agreement is for the reaction with SO_3^{2-} (predicted value 6.1) which could be explained by the higher concentration used, at which SO_3^{2-} might undergo ion association so that Debye-Hückel limiting law does not strictly hold.

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SAŽETAK

Zavisnost konstanti brzine supstitucijskih reakcija pentacijanoakvoferat(II)-iona o ionskoj jakosti

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Mjerene su konstante brzine (k) supstitucije vode u pentacijanoakvoferat(II)--ionu s nitritom, rodanidom, sulfitom i nitrozobenzenom u vodenoj otopini kod različitih ionskih jakosti (I). Ovisnost log k o $I^{1/2}$ daje pravac s nagibom 2.9 (NO_2), 2.5 (SCN^-) i 4.4 (SO_3^{2-}). Brzina reakcije s nitrozobenzenom ne ovisi o ionskoj jakosti otopine. Dobiveni rezultati slažu se s predloženim disocijacijskim mehanizmom za supstitucijske reakcije pentacijanoakvoferat(II)-iona.

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