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Kinetics of Formation and Stability Constants of Aminopentacyanoferrate(II) Complexes*

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The substitution reactions of various ligands on $[Fe(CN)_5H_2O]^{3-}$ are believed to take place either through a D-type mechanism:

$$[Fe(CN)_5H_2O]^{3-} \underset{k_{H_2O}}{\overset{k_{-H_2O}}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + H_2O \quad (1)$$

$$[Fe(CN)_5]^{3-} + L \xrightarrow{k_L} [Fe(CN)_5L]^{3-} \quad (2)$$

or directly through a dissociative interchange (I_d) step (in fact reaction (2) is also reversible, being usually displaced to the right through the use of high [L]) [1a–c].

In either interpretation, the energetics of activation is believed to be controlled by the Fe–OH_2 bond-breaking process, the only differences found when varying L being due to the different rate of diffusion of L towards the iron moiety; this rate in turn is sensitive only to the charge born by L [1b].

Various complexes where L is an aliphatic amine have been previously described, and the first order rate constant for process (3) have been measured [2–4]:

$$[Fe(CN)_5L]^{3-} \xrightarrow{k_{-L}} [Fe(CN)_5]^{3-} + L \quad (3)$$

The results were rather surprising in the sense that k_{-L} was not very sensitive to thenature of L, showing only a minor dependence through an indirect solvation effect. No steric effects could be put into evidence [4].

Now we report the second order rate constants, $k_f = k_L k_{-H_2O}/k_{H_2O}$, for L = NH_3, CH_3NH_2, $C_2H_5NH_2$, n-$C_3H_7NH_2$, n-$C_4H_9NH_2$, $(CH_3)_2NH$ and $(CH_3)_3N$, which were measured in an effort to make evident such effects and also in order to calculate the stability constants of the various complexes.

Experimental

Reagents

As a source for $[Fe(CN)_5H_2O]^{3-}$ solutions, $Na_5[Fe(CN)_5SO_3]\cdot 2H_2O$ was dissolved in deoxigenated distilled water. This material proves to be a more suitable source than $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, used previously by other authors [1a, b, 5, 6] and us [1c], as no slow processes are observed in the kinetic experiments, even in alkaline media and $c_{Fe} = 10^{-3}$ mol dm^{-3}. The aqueous chemistry of $[Fe(CN)_5SO_3]^{5-}$ will be the subject of a separate communication [7]. The solid sulphite complex was prepared according to the literature [8]. All other reagents were similar to those employed in previous work [4].

Kinetic Experiments

These were performed at 25 °C ± 0.2 °C, I = 1 mol dm^{-3} (NaCl) and pH *ca.* 11 (buffer Na_2HPO_4 + NaOH). Iron concentration (10^{-3} mol dm^{-3}) was higher than in previous studies due to experimental difficulties with light sources in the spectrophotometer; this higher concentration, however, did not give rise to difficulties due to the choice of the sulphito-complex as the starting material. A Durrum D-110 stopped-flow spectrophotometer was employed.

In a typical kinetic experiment, a solution of $[Fe(CN)_5SO_3]^{5-}$ was allowed to fully aquate during 15 minutes at 25 °C (for full aquation, it is necessary to keep ionic strength as low as possible [7]) and was then mixed in the mixing chamber with an equal volume of a solution containing the amine under study (at various concentrations ranging from 4×10^{-2} to 4×10^{-1} mol dm^{-3}), pyridine (1×10^{-1} mol dm^{-3}), buffer and adequate amount of NaCl. The change in absorbance attending the formation of $[Fe(CN)_5py]^{3-}$ was monitored at 365 nm. Pyridine was added as a colour indicator, because of the higher molar absorptivity of its complex. Under these conditions, both $[Fe(CN)_5py]^{3-}$ and $[Fe(CN)_5L]^{3-}$ are formed in parallel reactions, the experimental pseudo-first order rate constant being equal to $k_{py}[py] + k_L[L]$. From published values of k_{py}[1a], k_L was computed. Final absorbance data were in good accordance with the expected yield of the pyridine complex.

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TABLE. Rate and Equilibrium Data.

Ligand	10^{-2} k_f (M^{-1} s^{-1})	10^3 k_{-L} (s^{-1})	10^4 K (M^{-1})
n-Butylamine	2.5	5.59	4.5
n-Propylamine	2.0	5.47	3.7
Ethylamine	1.8	5.67	3.2
Ammonia	1.9	16.0	1.2
Methylamine	1.3	2.8	4.7
Dimethylamine	0.80	6.3	1.3
Trimethylamine	0.60	16.7	0.36

Results and Discussion

In the Table we summarize the results, including k_f, previously reported k_{-L} values [4], and the stability constants $K = k_f/k_{-L}$.

In the series $(CH_3)(CH_2)_nNH_2$ (n = 0 to 3), there is a clear similarity in the values of K. Except for CH_3NH_2, also the individual values of k_f and k_{-L} are very close. We cannot offer any obvious explanation for the observed sequence of k_f, which increases as the chain gets longer. As observed in our previous work [4], it is probable that direct correlations of $\Delta G^{\ddagger}$ are difficult to find. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could perhaps give more information but the inherent high scatter of stopped-flow data would probably mask any trend.

On the other hand, steric effects are reflected clearly in the series $(CH_3)_xNH_{3-x}$ (x = 0 to 3). In this case, k_f decreases monotonously as the degree of substitution increases, and this decrease also shows up in the respective stability constant. As pointed out before, it is not possible to attribute the changes in k_{-L} to steric effects [4], the addition of both types of effects giving rise to a marked decrease in the stability of the complex when going from CH_3NH_2 to $(CH_3)_3N$.

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