

A Possible Bimolecular Octahedral Substitution Reaction

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ALTHOUGH it has been suggested that cyanide might prove to be a good nucleophile towards octahedral cobalt(III) reaction centres,¹ the processes studied kinetically up till now have either been of a *redox* character or else have involved reaction of the substrate with the hydroxide that is always formed by the hydrolysis of the cyanide ion in water.² We have recently completed a study of the reactions of the non-electrolyte complex $[\text{Co en}_2\text{SO}_3\text{CN}]$ in aqueous solution and find that the rate of exchange of labelled cyanide increases as the concentration of free cyanide ion in solution is increased. The data, measured at 64.0° in water at constant ionic strength (0.9M with KCl) are presented in the Figure.

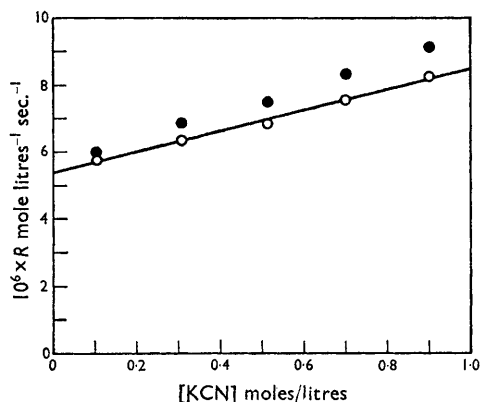


FIGURE. The rate of exchange of labelled KCN with $[\text{Co en}_2\text{SO}_3\text{CN}]$ as a function of potassium cyanide concentration. Concentration of complex = 0.105M, temperature = 64.0°, ionic strength made up to 0.9M with KCl. Uncorrected data ●. Data corrected for the base hydrolysis path ○.

The possibility that the exchange occurs by way of a combination of a reversible aquation and a reversible base hydrolysis could not be discounted and so these reactions were studied independently. Provided the solution is not strongly acidified³ cyanide is the leaving group and this displacement in neutral and basic solutions is indeed reversible at the high concentrations of complex used for the exchange studies (0.1–0.2M). The rate constant for the aquation reaction at 64.0° and 0.9M ionic strength is $2.9 \times 10^{-5} \text{ sec}^{-1}$. The discrepancy between this value and that obtained from

“intercept”/[complex] in the Figure ($= 5.2 \times 10^{-5} \text{ sec}^{-1}$) cannot readily be explained because it is thought that this constant should refer to the cyanide (and hydroxide) independent exchange path which, presumably, is the reversible aquation process. The base hydrolysis reaction follows a second-order rate law and, at 64.0° and $\mu = 0.9\text{M}$ has a rate constant $= 9.5 \times 10^{-4} \text{ l. sec}^{-1} \text{ mole}^{-1}$. The estimation of the concentration of hydroxide present under the conditions of the exchange studies was necessary in order to make corrections for the exchange that took place by way of the reversible base hydrolysis path but the primary data, for the temperature and ionic strength used, were not available. Using the value of $K_w = 1.3 \times 10^{-13} \text{ moles}^2 \text{ l.}^{-2}$ at 64.0° and $\mu = 0.9$ and K_a for HCN = $3.2 \times 10^{-9} \text{ moles/l.}$ at 64.0° and $\mu = 0$ (extrapolated from the data of Izatt *et al.*⁴) it is possible to calculate the hydrolysis constant, $K_{\text{hyd}} \equiv \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = K_w/K_a = 4.1 \times 10^{-5}$

moles/l. Since this constant is the ratio of two other constants that relate to equilibria of the same charge type, the effect of varying the ionic strength is expected, in the first approximation, to cancel out and the value obtained at zero ionic strength should apply equally well to the ionic strength used in the experiments. Since, at the concentrations of potassium cyanide used, $[\text{HCN}] \ll [\text{CN}^-]$, it follows that $[\text{OH}^-] = \sqrt{K_{\text{hyd}}[\text{KCN}]}$ and this square-root relationship further reduces the errors arising from inaccuracies in the equilibrium data. The correction for the small contribution to exchange by way of the reversible base hydrolysis has been made in the Figure where it will be seen that there is still a noticeable linear dependence of the rate of cyanide exchange upon the concentration of potassium cyanide. The second-order rate constant for this direct cyanide exchange, $k_2 = \text{“slope”}/[\text{complex}] = 3.1 \times 10^{-5} \text{ l. sec}^{-1} \text{ mole}^{-1}$ which is only some 30 times smaller than the rate constant for base hydrolysis.

These observations cannot be explained in terms of a unimolecular dissociation of the conjugate base of the complex ($S_N1\text{cb}$) which has been claimed to be the normal mechanism for the base hydrolysis of octahedral cobaltammine complexes⁵ as one would expect to find that the ability of hydroxide and cyanide to generate the amide conjugate base would parallel their basicities,

which differ by a factor of approximately 10^6 . It is not possible, from the kinetics, to distinguish between a classical bimolecular (S_N2) process and an "interchange" mechanism⁶ involving a pre-association between the complex and the cyanide ion. However, the cyanide ion does not possess the mobility of the hydroxide ion (resulting from

a Grotthus proton-jump mechanism), and, since it has been postulated that this mobility is the cause of the almost unique behaviour of hydroxide,⁷ it seems likely the mechanism of the cyanide exchange of $[\text{Coen}_2\text{SO}_3\text{CN}]$ is essentially bimolecular.

(Received, August 22nd, 1966; Com. 619.)

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