The Mechanism and Kinetics of the Substitution of Azide, Thiocyanate, and Cyanide Ions in Aquopentacyanocobaltate(III) and Pentacyanohydroxocobaltate(III)

By **Michael G. Burnett** * and **W. Matthew Gilfillan**, Department of Chemistry, Queen's University, Belfast BT9 5AG

The substitution of pentacyanohydroxocobaltate(III), $[Co(CN)_5(OH)]^{3-}$, by azide ion is shown to take place by the reaction of aquopentacyanocobaltate(III), $[Co(CN)_5(OH_2)]^{2-}$, in equilibrium with it. Deviations from simple second-order rate laws for the substitution of azide, thiocyanate, and cyanide into $[Co(CN)_5(OH_2)]^{2-}$ at unit ionic strength and 40 °C are sufficiently small to be comparable with effects due to ionic activity variation and should not be accepted as evidence of a dissociative (D) mechanism. The reactions are reliably assigned to this class on the basis of activation volumes, solvent effects, and nucleophile competition experiments.

THE substitution of $[Co(CN)_5(OH_2)]^{2-}$ by anionic nucleophiles is considered to be a simple case [1] of a dissociative (D) mechanism.[2] The simplicity of the pentacyanocobaltate systems lies in the reactants being of same sign so that electrostatic repulsions tend to prevent preassociation. The original evidence consisted of an unusually complete series of kinetic investigations [3-6] indicating limiting first-order kinetics at high nucleophile concentrations [3] and the competition [4] between thiocyanate and water for the intermediate $[Co(CN)_5]^{2-}$ formed by the limiting first-order dissociation of $[Co(CN)_5(N_3)]^{3-}$ during hydrolysis. Subsequently solvent effects [7] and activation-volume measurements [8] have confirmed the original conclusions.

Unfortunately the later work of the original authors [5,6,9] showed several experimental discrepancies from the predictions of the dissociative (D) theory. Further kinetic measurements [10] have provided evidence that uncharged nucleophiles do not follow the predictions of the theory, as indeed the original authors themselves suspected.[6] Some of these peculiarities may be explained by the existence of a proton-substitution route in $[Co(CN)_5(OH_2)]^{2-}$ in which the cobalt–oxygen bond of the aquo-ligand remains unbroken and nucleophilic attack occurs at the oxygen atom. Evidence for this pathway has been found [11] in the substitution reaction with $HSeO_3^-$. In short, the system may well not be as simple as it is commonly represented.

The original kinetic evidence for the dissociative substitution of $[Co(CN)_5(OH)]^{3-}$ was less complete and was limited to azide ion substitution.[3] The system has been investigated here as a preliminary to its possible use in testing the validity of the constant ionic strength principle.[12] The results, though generally in agreement with the earlier study,[3] contain crucial discrepancies which largely invalidate the original arguments establishing the direct dissociative substitution of $[Co(CN)_5(OH)]^{3-}$. In the light of these results the study was extended to the substitution of $[Co(CN)_5(OH_2)]^{2-}$ by thiocyanate and azide and here too, despite broad agreement with the original data,[3] important differences exist which imply that the evidence in favour of limiting first-order kinetics may be less clear cut than was originally supposed. The positive results of this study are that the substitution of $[Co(CN)_5(OH)]^{3-}$ takes place *via* $[Co(CN)_5(OH_2)]^{2-}$ and that there is no need to postulate an abnormally high hydroxide ion nucleophile efficiency [3] for the intermediate $[Co(CN)_5]^{2-}$.

EXPERIMENTAL

Reagents.—G.P. grade sodium azide, thiocyanate, and hydroxide were used as received. The remaining sodium salts and perchloric acid were AnalaR grade. $K_2[Co(CN)_5(OH_2)]$ was prepared from G.P. grade $K_3[Co(CN)_6]$ by photolysis using a Pyrex shielded 125-W mercury lamp. A solution of $[Co(CN)_6]^{3-}$ (200 cm^3 of 0.05 mol dm^{-3}) in 0.05 mol dm^{-3} perchloric acid was stirred at room temperature during photolysis for at least 4 h, after which the residual hydrogen cyanide was removed by vacuum distillation, the volume returned to 200 cm^3 and the pH adjusted to between 6 and 7. The photolysed solution contained only reactant and product anions as determined by chromatography using a 1-m column of alumina. $[Co(CN)_5(OH_2)]^{2-}$ was eluted first using 0.1 mol dm^{-3} acetic acid and 1 mol dm^{-3} sodium perchlorate, while $[Co(CN)_6]^{3-}$ was eluted when the sodium perchlorate in the eluant was replaced by sodium chloride.

Apparatus.—The reactions were followed in 1-cm cells thermostatted either in a Unicam SP 500 or a Perkin-Elmer 402 spectrophotometer, unless the half-life was above 20 min when they were thermostatted separately in a light-tight box. Temperature control was better than ±0.05 °C. pK_a measurements were made using an EIL GHS 33 glass electrode and a precision millivoltmeter (Ekco Electrometer N616B), which permitted a discrimination of 0.01 mV. The pH measurements were accurate to ±0.005 pH units when a reference reading was made with 0.01 mol dm^{-3} sodium hydroxide between each experimental observation.

RESULTS

The Substitution of $[Co(CN)_5(OH_2)]^{2-}$.—*Azide.* The reaction of $[Co(CN)_5(OH_2)]^{2-}$ and the azide ion is fully consistent with rate equation (1), in which [Co] and [X] represent the total concentration of the cobalt complexes and the nucleophile respectively.

$$-\frac{d[Co]}{dt} = k_e[Co][X] \qquad (1)$$

The rate constants k_e were measured at 40 °C and unit ionic strength maintained by sodium perchlorate. Most experiments were monitored at

380 and 280 nm but some of the slowest were followed at 280 nm only. The complex concentration commonly used, 1.67×10^{-3} mol dm^{-3}, produces unit absorbance at 280 nm for only 3% reaction, enabling k_e values to be estimated for very slow rates and low conversions. The reaction rates were found to be the same when measured at either frequency in experiments where both sets of absorbance data were available. The faster reactions observed over 3—5 half-lives accurately fitted a first-order rate law as was expected since an excess of nucleophile over complex usually was present. The order with respect to $[Co(CN)_5(OH_2)]^{2-}$ was further confirmed by repeating experiments at 1.67×10^{-4} mol dm^{-3} concentration of complex (Table 1). Reactions at pH 6.4 were performed in the presence of a total concentration of 0.1 mol dm^{-3} of a phosphate buffer containing an equimolar mixture of $[HPO_4]^{2-}$ and $[H_2PO_4]^-$, $k_e = (6.37 \pm 0.32) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} (Table 1), and also in the presence of 0.01 mol dm^{-3} phosphate buffer, $k_e = (6.62 \pm 0.13) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} (Table 1). A final set were performed in 0.01 mol dm^{-3} sodium hydroxide, $k_e = (7.5 \pm 0.3) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} (Table 2). The last group of experiments were analysed assuming that $[Co(CN)_5(OH)]^{3-}$ did not react. The concentration of $[Co(CN)_5(OH_2)]^{2-}$ present was calculated from equilibrium (2),

$$[Co(CN)_5(OH_2)]^{2-} + OH^- \rightleftharpoons [Co(CN)_5(OH)]^{3-} + H_2O \qquad (2)$$

using values of K_2 measured potentiometrically,[13] 2.62×10^3 dm^3 mol^{-1}, and the value of k_e then obtained from equation (3). The back reaction in such alkaline solutions could not be ignored. In these cases the second-order rate

$$-\frac{d[Co]}{dt} = k_e'[Co][X] = \frac{k_e[Co][X]}{(1 + K_2[OH^-])} \qquad (3)$$

constants were estimated from the initial reaction rates during the first half-life and using the experimental absorption coefficients given in Table 3.

TABLE 1

Rate constants k_e for the substitution of 1.67×10^{-3} mol dm^{-3} $[Co(CN)_5(OH_2)]^{2-}$ by the azide ion [a]

Run	$[N_3^-]$/mol dm^{-3}	$10^4 k_e$/dm^3 mol^{-1} s^{-1}		$[N_3^-]$ [b]/mol dm^{-3}	$10^4 k_e$ [c]/dm^3 mol^{-1} s^{-1}	
		obs.	obs.[d]		obs.	calc.
1	0.791	6.61	6.32	0.725	6.03	6.10
2	0.791	6.26		0.725	6.03	6.10
3 [e]	0.791	6.93		0.725	6.03	6.10
4 [e]	0.791	6.19		0.725	6.03	6.10
5	0.600	6.40	6.47	0.600		6.40
6	0.400	6.76	6.53	0.450	6.78	6.81
7	0.100	7.16	6.51	0.142	7.89	7.84
8	0.050	6.02	6.34	0.71	8.80	8.12
9	0.010	6.77	6.06	0.0355	9.30	8.27
10 [e]	0.010	6.19		0.0355	9.30	8.27

[a] At 40 °C and unit ionic strength maintained by $Na[ClO_4]$, pH 6.4. [b] See ref. 3. The complex concentration in these experiments varied from 0.9 to 7.5×10^{-3} mol dm^{-3}. [c] The values of k_e quoted in the last two columns correspond to the azide concentrations in column five which are selected to match as closely as possible the concentrations used in this work and given in column two. The calculated values are obtained from equation (15) of ref. 3. [d] Runs 1—10 were performed in the presence of 0.01 mol dm^{-3} phosphate but the repeat runs in column four were performed with 0.1 mol dm^{-3} phosphate. [e] Runs 3, 4, and 10 are duplicates using 1.67×10^{-4} mol dm^{-3} $[Co(CN)_5(OH_2)]^{2-}$.

TABLE 3

Absorption coefficients [a] used in the measurement of k_e

λ/nm	$[Co(CN)_5(OH_2)]^{2-}$	$[Co(CN)_5(OH)]^{3-}$	$[Co(CN)_5(N_3)]^{3-}$	$[Co(CN)_5(NCS)]^{3-}$	$[Co(CN)_6]^{3-}$
270	100 (225 [b])			14 300(11 700 [b])	
280	100 (140 [b])	250 (219 [c])	8 210 (7 500 [d])		
380	301 (295 [d])	250 (226 [c])	722 (666 [c])		1

[a] In units of dm^3 mol^{-1} cm^{-1} (literature values in parentheses). [b] From ref. 3. [c] From ref. 4. [d] From ref. 6.

The effect of changes in ionic strength between 0.04 and 5 mol dm^{-3} in 0.01 mol dm^{-3} phosphate buffer is shown by the solid line in Figure 1. The results at two extremes of azide concentration, 0.01 and 1 mol dm^{-3} respectively, are indistinguishable up to an ionic strength of 3 mol dm^{-3} but diverge between 3 and 5 mol dm^{-3}. The rate constants measured in a borax buffer (pH 8.9 at $I = 1$ mol dm^{-3}, 0.01 mol dm^{-3} $Na_2B_4O_7$) approach those in phosphate buffers at $I = 1$ mol dm^{-3} but diverge markedly at lower ionic strengths. The divergence probably arises from a specific medium effect since at the lower ionic strengths the greater part of the salt present consists of the buffer.

TABLE 2

Rate constants k_e for the substitution of $[Co(CN)_5(OH_2)]^{2-}$ by the azide ion [a]

Run	$[N_3^-]$/mol dm^{-3}	$10^4 k_e'$ [b]/dm^3 mol^{-1} s^{-1}	$10^4 k_e$ [c]/dm^3 mol^{-1} s^{-1}
1	0.982	0.28	7.6
2	0.982	0.26	7.1
3	0.500	0.27	7.3
4	0.200	0.26	7.1
5	0.100	0.24	6.5
6	0.050	0.32	8.7
7	0.010	0.31	8.4
8 [d]	0.002	0.26	7.1

[a] At 40 °C and unit ionic strength maintained by $Na[ClO_4]$. $[OH^-] = 0.01$ mol dm^{-3}. [b] See ref. 3: quote for 0.01 mol dm^{-3} OH^-, 5.68×10^{-4} mol dm^{-3} $[Co(CN)_5(OH)]^{3-}$, and 0.9 mol dm^{-3} N_3^-, k_e' (obs.) $= 0.21 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, while their equation (15) gives k_e' (calc.) $= 0.21 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. [c] $k_e = k_e'(1 + K_2[OH^-])$; $1 + K_2[OH^-] = [Co]/[Co(CN)_5(OH_2)^{2-}] = 27.2$. [Co] = Total complex concentration = 1.67×10^{-3} mol dm^{-3}. [d] Calculated from rates measured in the first 3% of reaction observed at 280 nm.

A further set of data in 0.01 mol dm^{-3} sodium hydroxide follows the trend set by the borax buffer results although the accuracy in these slow reactions which do not proceed to completion is less than in the other experiments.

Thiocyanate and cyanide. A parallel survey of the substitution by thiocyanate ions was made in 0.01 mol dm^{-3} total phosphate buffer concentration at unit ionic strength (Table 4). In this case, the values of k_e increased from 0.01 mol dm^{-3} to 1 mol dm^{-3} thiocyanate concentration by about 29%. Cyanide substitution had to be studied in 0.01 mol dm^{-3} sodium hydroxide in order to avoid the formation of hydrogen cyanide ($pK_{40\,°C} = 9.19$, $I = 1$ mol dm^{-3}, $Na[ClO_4]$). In this case, a 14% increase was apparent in k_e

between 0.1 and 0.98 mol dm^{-3} cyanide concentration (Table 5). The latter data may be interpreted by equation (3), but the value of K_2 has to be taken throughout as equal to that in sodium perchlorate as the value in sodium cyanide has not been measured. Both sets of results may be summarised by equation (4) in which $10^4\,a = 6.33$ (thiocyanate),

$$k_e = \frac{a}{1 + b[X]} \qquad (4)$$

1.15 (cyanide); and $b = 0.272$ (thiocyanate), 0.233 (cyanide). The effect of ionic strength on k_e for the cyanide ion was similar to that observed for the azide ion (Table 5).

TABLE 4

Rate constants k_e for the substitution of 6.6×10^{-5} mol dm^{-3} $[Co(CN)_5(OH_2)]^{2-}$ by the thiocyanate ion [a]

Run	$[NCS^-]$/mol dm^{-3}	$10^4\,k_e$/dm^3 mol^{-1} s^{-1} obs.	calc. [d]	$[NCS^-]$ [b]/mol dm^{-3}	$10^4\,k_e$ [c]/dm^3 mol^{-1} s^{-1} obs.	calc.
1	0.980	5.18 [e]	5.00	0.900	4.13	4.16
2	0.800	4.80	5.20	0.800	4.40	4.27
3	0.600	6.08	5.44	0.600		4.51
4	0.400	5.83	5.71	0.400	4.75	4.78
5	0.100	6.05	6.16	0.100	5.34	5.25
6	0.050	6.60	6.25	0.050		5.33
7	0.020	5.77	6.30	0.020		5.39
8	0.010	6.72	6.31	0.010		5.41

[a] At 40 °C and unit ionic strength maintained by $Na[ClO_4]$, pH 6.4, 0.01 mol dm^{-3} phosphate. [b] See ref. 3. The complex concentrations in these experiments were $(2.7—4) \times 10^{-4}$ mol dm^{-3}, pH 3.4 controlled by perchloric acid. [c] The values of k_e quoted in the last two columns correspond to thiocyanate concentrations given in column five which are matched as closely as possible to the concentrations used in this work in column two. The calculated values of k_e are obtained from equation (10) of ref. 3. [d] From equation (4) of this work.

$$k_e = 6.33 \times 10^{-4}/(1 + 0.272[NCS^-])$$

[e] The result for 1.01×10^5 N m^{-2} pressure, $k_e = 5.96 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, was reported at $[NCS^-] = 1$ mol dm^{-3} at 40 °C (ref. 8).

DISCUSSION

The results of this study indicate that the substitution of $[Co(CN)_5(OH_2)]^{2-}$ by the azide, thiocyanate, and cyanide ions occurs by a second-order reaction pathway which is subject even at constant ionic strength to a significant secondary salt effect. The conjugate base $[Co(CN)_5(OH)]^{3-}$ is inert to substitution but a slow reaction still occurs *via* the low concentration of $[Co(CN)_5(OH_2)]^{2-}$ in equilibrium with it. Phosphate but not borate buffers slightly catalyse the substitution by azide ions. A survey of the effects of varying ionic strength shows that at higher ionic strength the differing rates induced by the presence of buffers disappears and that the order with respect to the azide ion becomes less than unity.

TABLE 5

Rate constants k_e for the substitution of $[Co(CN)_5(OH_2)]^{2-}$ by the cyanide ion [a]

Run	Ionic strength/mol dm^{-3}	$[CN^-]$/mol dm^{-3}	$10^{-3}K_2$/dm^3 mol^{-1}	$10^4k_e'$/dm^3 mol^{-1} s^{-1} obs.	$1 + K_2[OH^-]$ [b]	10^4k_e/dm^3 mol^{-1} s^{-1} obs. [c]	calc. [d]
1	0.220	0.200	1.48	0.052	15.8	0.82	
2	0.400	0.200	1.78	0.052	18.8	0.98	
3	1.000	0.100	2.62	0.041	27.2	1.12	1.13
4	1.000	0.200	2.62	0.042	27.2	1.14	1.10
5	1.000	0.500	2.62	0.037	27.2	1.01	1.03
6	1.000	0.980	2.62	0.035	27.2	0.95	0.94
7	2.000	0.200	4.79	0.038	48.9	1.86	
8	5.000	0.200	12.6	0.024	127	3.05	

[a] $[OH^-] = 0.01$ mol dm^{-3}, 40 °C. [b] [Co] = Total complex concentration $= 1.67 \times 10^{-3}$ mol dm^{-3}; $1 + K_2[OH^-] = [Co]/[Co(CN)_5(OH_2)^{2-}]$. [c] $k_e = k_e'(1 + K_2[OH^-])$. [d] From equation (4) of this work, $k_e = 1.15 \times 10^{-4}/(1 + 0.233[CN^-])$.

Our conclusions for this system are opposed to those in the previous study[3] although we can substantially reproduce the original experiments. The reason for the difference in interpretation depends mainly on the results of four of these experiments[3] at azide ion concentrations below 0.45 mol dm^{-3}. The rate data in Tables 1, 2, and 4 are accompanied by rate constants calculated from equation (15) of reference 1 and some of the original observations. There are obviously systematic differences which it is tempting to attribute to the variation between the absorption coefficients reported previously and those measured in this work (Table 3). The source of the differences is probably impurities present in the original preparations of $[Co(CN)_5(OH_2)]^{2-}$. We found that these preparations usually gave large absorptions at 270 or 280 nm which were removed on chromatography whilst the band at 380 nm was hardly affected. Thus the previous measurements[3,4,6] are uniformly high in absorption at 270 or 280 nm for $[Co(CN)_5(OH_2)]^{2-}$ and low for the products. However, the first-order analysis used should eliminate these spectroscopic differences. The agreement is actually as good as is usually found in the literature[14] and the important points concern trends induced by changing the conditions. It is our contention that the trends justifying the original mechanism may not exist and that in any case they could easily be distorted by ionic medium effects.

The original experiments indicated that the azide substitution of $[Co(CN)_5(OH_2)]^{3-}$ was less than first-order with respect to the nucleophile at high concentrations. Under alkaline conditions this deviation vanished and the rates eventually became inversely proportional to the hydroxide ion concentration. These results could together only be explained by the mechanism below, from which follows the rate equation (8).

$$[Co(CN)_5(OH_2)]^{2-} + OH^- \rightleftharpoons [Co(CN)_5(OH)]^{3-} + H_2O \quad (2)$$

$$[Co(CN)_5(OH_2)]^{2-} \rightleftharpoons [Co(CN)_5]^{2-} + H_2O \quad (5)$$

$$[Co(CN)_5(OH)]^{3-} \rightleftharpoons [Co(CN)_5]^{2-} + OH^- \quad (6)$$

$$[Co(CN)_5]^{2-} + N_3^- \longrightarrow [Co(CN)_5(N_3)]^{3-} \quad (7)$$

$$k_e = \frac{k_5 + k_6K_2[OH^-]}{\{(k_{-5}[H_2O]/k_7) + (k_{-6}[OH^-]/k_7) + [N_3^-]\}(1 + K_2[OH^-])} \quad (8)$$

The constant K_2 was measured[3] separately using a glass electrode for the hydroxide concentration and spectroscopy to determine the ratio of hydroxo- and aquo-complexes. The constants k_5 and $k_{-5}[H_2O]/k_7$ were fitted under acid conditions and k_6 and k_{-6}/k_7 under alkaline conditions. The statistical correlation of the results and equation (8) is quite exceptional but the necessity for the theory vanishes if the rate is accurately first order in azide ion concentration. Despite a variety of attempts we have found that this is always the case at unit ionic strength.

The simpler approach which has been adopted in this work now becomes just as effective as equation (8). In fact, if the value of K_2 is taken to be that used here (2.62×10^3 dm^3 mol^{-1}) rather than the earlier value[3] (3.54×10^3 dm^3 mol^{-1}), the original measurements taken over a range of pH all fit equation (3) very well (Table 6).

TABLE 6

Values of k_e from experiments at various pH levels

	10^4 k_e'/dm^3 mol^{-1} s^{-1}		10^4 k_e/dm^3 mol^{-1} s^{-1}	
$10^4[OH^-]$/mol dm^{-3}	obs.[a]	calc.[b]	calc.[c]	calc.[d]
1 000	0.020	0.021	6.39	5.26
100	0.204	0.204	7.43	5.60
90	0.228	0.228	6.74	5.60
7.1	2.19	1.86	7.70	6.27
4.2	3.24	2.54	8.08	6.82
0.63	4.94	4.77	6.05	5.76
0.25	5.27	5.29	5.74	5.62
0.003	5.61	5.71	5.61	5.61

[a] The data are taken from Table 4 of ref. 3. The observations were made at 0.9 mol dm^{-3} azide, unit ionic strength, and 40 °C. [b] Calculated using rate equation (8) combined with the original fitted constants, $k_5 = 1.6 \times 10^{-3}$ s^{-1}, $k_6 = 6.5 \times 10^{-4}$ s^{-1}, $K_2 = 3.54 \times 10^3$ dm^3 mol^{-1}, $k_5[H_2O]/k_7 = 1.9$ mol dm^{-3}, $k_{-6}/k_7 = 3 \times 10^3$. [c] Calculated using rate equation (3) and $K_2 = 3.54 \times 10^3$ dm^3 mol^{-1}. [d] Calculated using rate equation (3) and $K_2 = 2.62 \times 10^3$ dm^3 mol^{-1}.

The value of K_2 has been checked using the original method[3] at 40 °C, at unit ionic strength maintained with sodium perchlorate and in a 0.01 mol dm^{-3} carbonate buffer. The result, $K_2 = 2.57 \times 10^3$ dm^3 mol^{-1}, suggests the present potentiometric data are more reliable than the original measurements. The most accurate set of alkaline rate constants (Table 2) suggest that k_e is about 15% larger in the presence of a 30-fold excess of $[Co(CN)_5(OH)]^{3-}$, so an upper limit can be set for reaction (6), $k_6 \leqslant (6 \times 10^{-3})k_5$. The internal consistency of the present data and the general agreement with the original results seems to provide an overwhelming justification for the initial assumption that the $[Co(CN)_5(OH)]^{3-}$ is substitutionally inert. Furthermore, equation (8) is an excellent fit only at the cost of two unlikely numerical results: $k_{-6}/k_7 = 3 \times 10^3$ and $k_6/k_5 = 0.4$. The first ratio seems theoretically anomalous in view of the lack of discrimination which is to be expected of a highly reactive electrophile such as $[Co(CN)_5]^{2-}$ and which is actually to be seen in its reaction with a wide range of other nucleophiles.[15] The second ratio seems equally implausible on more practical grounds. The electrostatic effect of charge separation favours reaction (6) over (5) but this is more than compensated for by the entropy of activation. A group of cyanocobalt systems are available to show the trend in such dissociative reactions (9). A straight line of unit slope roughly fits the data in Table 7 when they are plotted as log k_9 against log K_9, a result which would be expected for dissociative reactions.

$$[Co(CN)_5X]^{(2+n)-} + H_2O \rightleftharpoons [Co(CN)_5(OH_2)]^{2-} + X^{n-} \quad (9)$$

TABLE 7

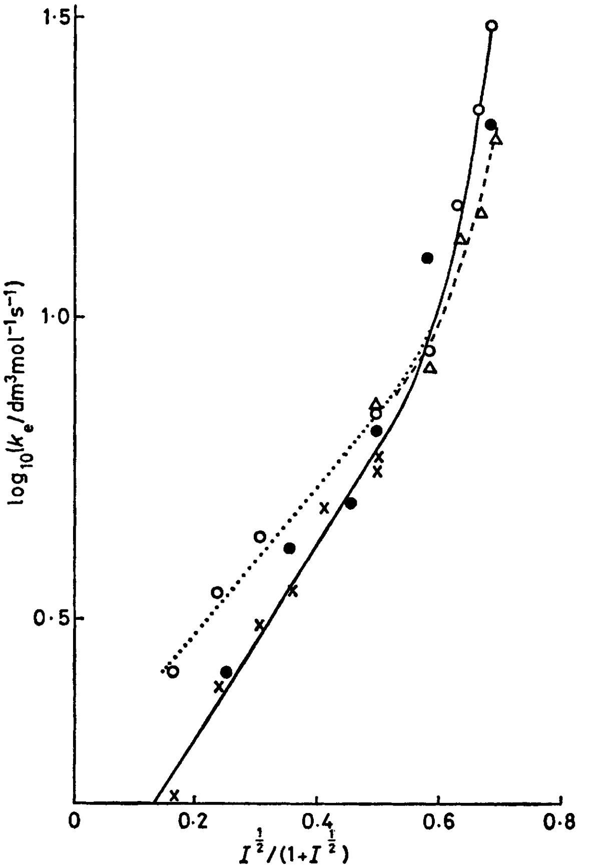
Rate and equilibrium constants for reaction (9) at 40 °C and unit ionic strength

X	N_3^-	NCS^-	I^-	Br^-	Cl^-	N_3H
10^7k_9/s^{-1}	5.5	3.7	74	1 700	5 000	32 000
10^4K_9/mol dm^{-3}	6.5	6.8	238	11 000	46 000	30 000
Ref.	*a*	*a*	*a*	*a*	5	*b*

[a] J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta Rev.*, 1971, **5**, 7. [b] Refs. 3 and 4. The additional data required for p$K(HN_3)$ at unit ionic strength and 40 °C (pK_a = 4.33) were taken from: J. M. Boughton and R. N. Keller, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2851; F. Maggio, V. Romano, and L. Pellerito, *Ann. Chim.* (*Italy*), 1967, **57**, 191; E. A. Burns and F. D. Chang, *J. Phys. Chem.*, 1959, **63**, 1314.

Steps (5) and (6) can be regarded as rate-determining in reactions of the same type as (9). When X = H_2O, the rate-determining step is (5), $K_{9,H_2O} = 1$ mol dm^{-3}, while when X = OH^-, the rate-determining step is (6), $K_{9,OH} = 1/K_2 = 3.8 \times 10^{-4}$ mol dm^{-3}. Since the rate constants of such steps are apparently proportional to the equilibrium constants, $k_6/k_5 = K_{9,OH}/K_{9,H_2O} = 4 \times 10^{-4}$. The fitted value for k_6/k_5 is therefore grossly inconsistent with available dissociative data. A similar decrease in lability between $[Co(CN)_4(SO_3)(OH_2)]^{4-}$ and $[Co(CN)_4(SO_3)(OH)]^{5-}$ has already been reported.[16]

The results with thiocyanate do not duplicate the original data very well but they do confirm a slight decrease in reaction order as the concentration is increased from 0.01 mol dm^{-3} to 1 mol dm^{-3} which is of much the same size as that reported previously.[3] Further confirmation has been independently[10] obtained at 25 °C, although in this case there is only a 10% fall in k_e up to 1 mol dm^{-3}. A similar change has been observed in this work for the cyanide ion although it is inconceivable that the explanation can be mechanistic. The rate of cyanide substitution is only a quarter that of the azide ion so that if reaction (7) is too slow to compete with reactions (−5) or (−6), there is no chance of the cyanide ion being able to do so. Furthermore, the order of reaction with respect to the azide ion falls below 1 at ionic strengths above 3 mol dm^{-3} as was reported previously[3] and is confirmed in the Figure. The magnitudes of these effects and the conditions necessary to obtain them prompt the suspicion that the results are strongly affected by failures of the constant ionic strength principle.[12]



Variation of log k_e with $I^{\frac{1}{2}}/1 + I^{\frac{1}{2}}$ at 40 °C in a sodium perchlorate supported medium: (○) 0.01 mol dm^{-3} phosphate buffer and azide ion, (△) 0.01 mol dm^{-3} phosphate buffer and 1.0 mol dm^{-3} azide ion, (●) 0.01 mol dm^{-3} hydroxide and azide ion, (×) 0.01 mol dm^{-3} borax buffer and azide ion; (——) borax buffer and hydroxide ion, (•••••) phosphate buffer, (– – –) phosphate buffer using 1 mol dm^{-3} azide ion above I = 1 mol dm^{-3}

This hypothesis is currently under investigation but one test is already possible using published data.[13] As a first approximation it would be reasonable to suppose that under acid conditions k_e for the azide ion will be K_5k_7 and that the equilibrium (5) will be unaffected by ionic medium effects. The transition-state expression[12] for reaction (7) is $k_7 = (kT/h)K_7^{\ddagger}$, in which $K_7^{\ddagger}$ is the concentration equilibrium expression for the activation step shown below. The activation equilibrium may be closely modelled in respect of charge and ion size by equilibrium (2). The value[13] of K_2 at unit ionic strength

$$[Co(CN)_5]^{2-} + N_3^- \xrightleftharpoons{K_7^{\ddagger}} \{[Co(CN)_5]^{2-}, N_3^-\}^{\ddagger}$$

and 40 °C changes from 2.11 × 10^3 dm^3 mol^{-1} (NaCl) to 2.63 × 10^3 dm^3 mol^{-1} ($Na[ClO_4]$). On this basis it seems that, even at constant ionic strength, the effect of changing the ionic medium can be large enough to invalidate the mechanistic interpretation of the kinetics during the replacement of one anion by another. The measurements at varying ionic strength shown in the Figure are likewise of no diagnostic value for mechanism in this case since the Brønsted-Bjerrum slope is 2 for both the dissociative and associative models.

In short, the kinetic evidence in favour of the limiting dissociative mechanism of the azide ion seems questionable but the absence of such evidence at unit ionic strength is not surprising since only the most trivial deviations from simple kinetics have ever been reported for such substitutions. However, the remaining undisputed positive evidence of activation-volume measurements,[8] solvent effects,[7] and competition experiments[4] make it highly likely that the reactions are genuinely dissociative (*D*) in character.

We wish to thank Mr. G. Smith and Mr. J. T. Stevenson for their assistance in making the rate measurements required for this study.

[0/1932 *Received*, 15*th December*, 1980]

REFERENCES

[1] C. H. Langford and V. S. Sastri, in ' M.T.P. Int. Review of Science; Inorganic Chemistry, Ser. 1, vol. 9, Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, Butterworths, London, 1972, p. 203.
[2] C. H. Langford and H. B. Gray, ' Ligand Substitution Processes,' W. A. Benjamin Inc., New York, 1965.
[3] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573.
[4] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 583.
[5] R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 237.
[6] R. Barca, J. Ellis, M-S. Tsao, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 243.
[7] M. J. Blandamer, J. Burgess, M. Dupree, and S. J. Hamshere, *J. Chem. Res.* (*S*), 1978, 58; *J. Chem. Res.* (*M*), 1978, 728.
[8] D. A. Palmer, and H. Kelm, *Z. Anorg. Allg. Chem.*, 1979, **450**, 50.
[9] A. Haim, R. Grassi, and W. K. Wilmarth, *Adv. Chem. Ser. 49, Am. Chem. Soc.*, Washington DC, 1965, pp. 31–46.
[10] L. Viaene, J. D'Olieslager, and S. De Jaegere, *Bull. Soc. Chim. Belg.*, 1976, **85**, 89.
[11] W. R. Ashley and Y. Jan, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1099.
[12] B. Perlmutter-Hayman, *Prog. React. Kinet.*, 1971, **6**, 240.
[13] W. M. Gilfillan, Ph.D. Thesis, University of Belfast, 1973.
[14] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.
[15] M. L. Tobe, ' Inorganic Reaction Mechanisms,' Nelson, London, 1972, p. 93.
[16] P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 611.