Kinetics of Acid and Base Hydrolysis of Azido[(*RR*)-1,11-diamino-3,6,9-triazaundecane]cobalt(III)

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The kinetics of hydrolysis of the ion $[Co(Hdtu)N_3]^{2+}$ [Hdtu = (*RR*)-1,11-diamino-3,6,9-triazaundecane] in perchloric acid solutions has been investigated spectrophotometrically and by N_3^- release. Over the range 0·05—0·52M-$HClO_4$ [I = 1·00M ($NaClO_4$)] the reaction follows a rate law of the form $-d\ln[Co(Hdtu)N_3^{2+}]/dt = k_a$, where $k_a = k_1 + k_2[H^+]$. Over the range 0·006—0·03M-$HClO_4$ [I = 1·00M ($NaClO_4$)] the reaction follows a rate expression for opposed first- and second-order reactions. The pseudo-first-order rate constant for the forward reaction has an inverse hydrogen-ion dependence of the form $k_b = k_1' + (k_3/[H^+])$, while the second-order rate constant for the reverse reaction shows a complex dependence on $[H^+]$, of the form $k_c = (k_4/[H^+]) + (k_5/[H^+]^2)$. Activation parameters and a mechanism for the overall reaction are given.

IN previous publications[1,2] we reported the kinetics of isomerization, as well as the acid and base hydrolysis, of [(*RR*)- and (*SS*)-1,11-diamino-3,6,9-triazaundecane]isothiocyanatocobalt(III) ions.* In addition Ni and Garner[3] have reported the kinetics of hydrolysis of the chloro-analogues of these complexes. The *X*-ray crystal structures of the optically active chloro-complexes correspond[4] to diastereoisomeric forms arising from alternative configurations about the secondary nitrogen atom (at the 6-position) common to the two near-coplanar chelate rings. The structures of the other complexes were assigned based on similarity of the i.r. spectra, especially in the NH_2 stretching and bending regions, to those of the chloro-complexes.

In an attempt to provide further insight on the effects of chelation, as well as stereochemistry, on hydrolysis rates of related cobalt(III) complexes, we report here the kinetics of acid and base hydrolysis of azido[(*RR*)-1,11-diamino-3,6,9-triazaundecane]cobalt(III), $[Co(Hdtu)N_3]^{2+}$.

EXPERIMENTAL

All reagents were of analytical grade. The water was doubly distilled and then passed through a mixed-bed cation–anion-exchange resin. 1,11-Diamino-3,6,9-triazaundecane (Hdtu) (practical grade) was used as obtained from Matheson, Coleman, and Bell. Sodium perchlorate was prepared by neutralization of reagent-grade 70% perchloric acid with reagent-grade sodium carbonate and recrystallized three times from hot distilled water. Sodium azide (practical grade), employed in the synthesis of the complex, was used as obtained from Eastman Organic Chemicals. Sodium azide, used for determination of the ionization constants of hydrogen azide, was recrystallized from water as described by Browne.[5]

Preparation of Complexes.—Chloro[(*RR*)-1,11-diamino-3,6,9-triazaundecane]cobalt(III) diperchlorate was prepared and characterized as described in the literature.[6]

Azido[(RR)-1,11-*diamino*-3,6,9-*triazaundecane*]*cobalt*(III) *diperchlorate*. Reddish orange $[Co(Hdtu)N_3](ClO_4)_2$ was prepared from the complex $[Co(Hdtu)Cl](ClO_4)_2$ by the anation reaction with azide. In a typical preparation, the chloro-complex (5 g) was added to 0·4M-$HClO_4$ (50 cm^3) and sodium azide (5 g). The mixture was then heated to 80 °C and maintained at this temperature for 30 min. The solution was then cooled to 25 °C and propan-2-ol–methanol (3 : 1, 250 cm^3) added. The excess of NaN_3 was filtered off and the azido-complex precipitated on cooling in an ice-bath. The perchlorate salt was recrystallized from a minimum volume of 0·2M-$HClO_4$, on addition of propan-2-ol–methanol (3 : 1, 200 cm^3) {Found: C, 20·0; H, 4·90; Co, 11·9; N, 23·3. $[Co(Hdtu)N_3](ClO_4)_2$ requires C, 19·65; H, 4·75; Co, 12·05; N, 22·9%}. Visible, u.v., and i.r. spectra of the perchlorate were identical to those of the tetrachlorozincate(II) salt obtained by House and Garner.[6] The absolute configuration was assigned based on similarity of the i.r. spectra, especially in the NH_2 stretching and bending regions, to the chloro-analogue.

Chromatography of Aquated Solutions.—Solutions of the complex $[Co(Hdtu)N_3]^{2+}$ which had been allowed to aquate in the dark at 80 and 90 °C for 1—2 half-lives under experimental kinetic conditions (as described for low acid concentrations) were adsorbed on a 10 × 1 cm Dowex 50-X8 cation-exchange resin (200—400 mesh) in the hydrogen form and eluted at room temperature with three successive aliquot portions (50 cm^3) of 2·0M-$HClO_4$ followed by three successive portions (50 cm^3) of 3·0M-$HClO_4$.

Kinetic Runs.—Kinetic runs were followed both spectrophotometrically and by azide-ion release. Weighed amounts of the salt $[Co(Hdtu)N_3](ClO_4)_2$ were dissolved in the desired medium made from stock solutions of $NaClO_4$ and $HClO_4$ of known concentrations and made up to the desired volume. Aliquot portions (*ca.* 10 cm^3) were sealed by torch in Pyrex test tubes (20 cm^3). These were then wrapped in aluminium foil to exclude light and placed in oil-baths thermostatted at 80·00 ± 0·02, 90·00 ± 0·03, and 98·00 ± 0·06 °C. Zero-reaction time was taken as 10 min after the ampoules were placed in the temperature bath. The ampoules were then removed at known times and quenched in ice–water. The visible absorption spectrum of each reaction solution was then scanned in 1·00 cm silica cells (against a matching 1·00 cm silica cell filled with an identical solution except for the complex) over the range 600—340 nm with a Cary model 14 recording spectrophotometer at 20 °C. The data were analysed at 520, 510, and 500 nm. In certain runs the reaction was followed by analysis of the released N_3^- ion. Free N_3^- ion and HN_3 in the reaction ampoules were separated from the complexes by adsorbing aliquot portions on a 3 × 2 cm column of H^+ Dowex AG50W-X8 cation-exchange resin (100—200 mesh), prefilled with 0·01M-$HClO_4$. The mixture of N_3^- ion

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* The trivial name tetraethylenepenta-amine has previously been used to describe the *RR* and *SS* ligands.

[1] A. A. El-Awady, *J.C.S. Dalton*, 1972, 1463.

[2] A. A. El-Awady and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3627.

[3] T. Ni and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 1071.

[4] M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Comm.*, 1969, 891.

[5] A. W. Browne, *Inorg. Synth.*, 1939, **1**, 79.

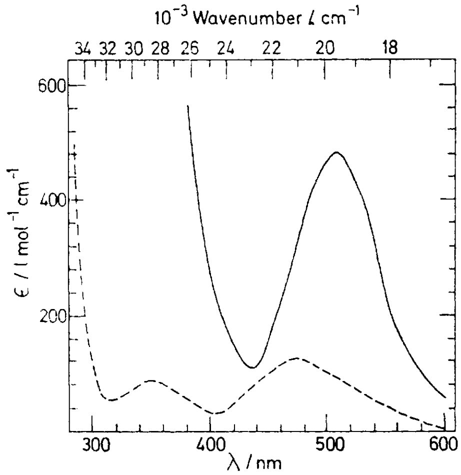
[6] D. A. House and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 272.

and HN_3 was then eluted with 0·01M-$HClO_4$. The total azide concentration was determined by addition of excess of Ce^{IV} and titrating the excess with standard Fe^{II} solution to a Ferroin end point.[7,8]

Ionization Constants.—The ionization constants for hydrogen azide were determined at 70·00, 80·00, and 90·00 °C. Hydrogen azide was made ***in situ*** by mixing a standard solution of perchloric acid with a standard solution of sodium azide.[9] The pH of the resulting solution was measured with a Beckman Expandomatic pH meter, in which the electrodes were left in equilibrium with the solution at the desired temperature for 0·5 h. The pH meter was calibrated against a known buffer at the appropriate temperature. The ionic strength of the solution was maintained at 1·00M.

RESULTS

The Figure presents visible and near-u.v. absorption spectra of aquo- and azido-[1,11-diamino-3,6,9-triazaundecane]cobalt(III). Hydrolysis reactions were studied over the $[H^+]$ range 0·006—0·52M at 80, 90, and 98 °C and an ionic strength of 1·00M ($NaClO_4$). At hydrogen-ion concentrations greater than 0·03M, the reaction obeyed rate law (1), where k_a is a pseudo-first-order rate constant.



Visible and near-u.v. absorption spectra of the salts $[Co(Hdtu)N_3](ClO_4)_2$ (——) and $[Co(Hdtu)H_2O](ClO_4)_3$ (– – – –) at 25 °C in 0·1M-$HClO_4$

The

$$- \text{d}\ln\,[Co(Hdtu)N_3{}^{2+}]/\text{d}t = k_a \qquad (1)$$

reaction was studied by spectrophotometric and azide-ion-release methods. In the former k_a was evaluated for each kinetic run from relation (2), where A_0, A, and A_∞ are optical absorbances at a given wavelength at time zero, t, and 100% hydrolysis of $N_3{}^-$ ligand respectively. The

$$2{\cdot}303 \log_{10} [(A_0 - A_\infty)/(A - A_\infty)] = k_a t \qquad (2)$$

azide-ion-release experiments were fitted to equation (3), where a and x are the initial concentration of the complex

$$2{\cdot}303 \log_{10} [a/(a - x)] = k_a t \qquad (3)$$

and the azide concentration at time t respectively. Plots of equations (2) and (3) were linear up to 70% completion of reaction (the extent to which the reactions were followed). Table 1 presents experimental values of k_a, obtained from least-squares treatment of the data, which were in good agreement with rate constants obtained from gradients of visually drawn rate plots. The values of k_a showed a linear dependence on $[H^+]$ [equation (4)]. Values of k_1 and k_2 obtained by least-squares fit are given in Table 2.

TABLE 1

Pseudo-first-order rate constants for hydrolysis of the ion $[Co(Hdtu)N_3]^{2+}$ at high acid concentrations *

t/°C	[Complex]/ mM	$[HClO_4]$/ M	10^6K_a †/s^{-1}
80·00	1·656	0·1033	2·87 ± 0·02
80·00	1·660	0·2066	4·43 ± 0·03
80·00	1·771	0·3099	6·14 ± 0·05
80·00	1·723	0·4132	8·21 ± 0·04
80·00	1·746	0·5165	9·67 ± 0·06
80·00	8·972	0·4132	8·00 ± 0·05 ‡
90·00	1·954	0·1033	9·88 ± 0·06
90·00	1·833	0·2066	15·48 ± 0·08
90·00	1·938	0·3099	22·64 ± 0·09
90·00	1·883	0·4132	28·0 ± 0·1
90·00	1·890	0·5165	35·5 ± 0·1
90·00	14·08	0·3099	22·77 ± 0·06 ‡
98·00	1·860	0·0516	20·38 ± 0·08
98·00	1·806	0·0620	23·0 ± 0·1
98·00	1·804	0·0723	26·5 ± 0·2
98·00	1·696	0·1033	30·32 ± 0·09
98·00	1·714	0·1550	41·1 ± 0·1
98·00	1·673	0·2066	50·1 ± 0·2
98·00	1·694	0·3099	76·8 ± 0·2
98·00	1·677	0·4132	94·4 ± 0·2
98·00	1·637	0·5165	109·8 ± 0·3
98·00	9·570	0·2066	50·0 ± 0·3 ‡
98·00	5·766	0·0516	21·2 ± 0·1 ‡

* Ionic strength was adjusted to 1·00M with sodium perchlorate. † Weighted averages of values determined at 520, 510, and 500 nm, which agreed within experimental error; errors are standard errors obtained from the least-squares treatment. ‡ From azide-ion-release experiments.

$$k_a = k_1 + k_2[H^+] \qquad (4)$$

TABLE 2

Kinetic parameters for hydrolysis of the ion $[Co(Hdtu)N_3]^{2+}$ at high acid concentrations

t/°C	10^6k_1/s^{-1}	$10^5k_2K_1$/l mol^{-1} s^{-1}
80·00	1·05 ± 0·02	1·68 ± 0·05
90·00	3·7 ± 0·3	5·9 ± 0·1
98·00	11·5 ± 0·5	19·7 ± 0·6

Errors are least-squares standard deviations.

At hydrogen-ion concentrations lower than 0·03M, it was observed that the spectrum of the products was *not* that of the aquo-complexes, but somewhat in between those of the azido- and aquo-complexes. This indicates that the reaction goes to an equilibrium mixture represented by reaction (5). The possibility that the reaction products are

$$[Co(Hdtu)N_3]^{2+} + H_2O \underset{k_c}{\overset{k_b}{\rightleftharpoons}} [Co(Hdtu)H_2O]^{3+} + N_3{}^- \qquad (5)$$

different from those of reaction (5) was excluded on the

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[7] J. W. Arnold, *Ind. and Eng. Chem., Analyt. Edn.*, 1945, **17**, 215.

[8] R. G. Linck, *Inorg. Chem.*, 1972, **11**, 61.

[9] B. W. Clare, D. Cook, E. C. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, 1966, **88**, 1911.

basis of azide-ion-release experiments. In addition, cation-exchange chromatography (see Experimental section) of solutions of the ion $[Co(Hdtu)N_3]^{2+}$ that were allowed to react for 1—2 half-lives gave only two bands, which on elution gave eluates whose spectra corresponded essentially to those of the parent complex and $[Co(Hdtu)H_2O]^{3+}$ (similar results were obtained for the equilibrium mixture). No coloured band remained on the resin column after elution of the aquo-ion.

Experimentally it was found that the reaction followed a rate expression for opposed first- and second-order reactions [equation (6)]. The free azide-ion concentration was calculated from the ionization constant, K_a, of hydrogen azide and the total azide concentration $\Sigma[N_3]$ by use of relation (7), where $K_a \ll [H^+]$. Experimental determination of K_a

$$-d[Co(Hdtu)N_3^{2+}]/dt = k_b[Co(Hdtu)N_3^{2+}] - k_c[Co(Hdtu)H_2O^{3+}][N_3^-] \quad (6)$$

$$[N_3^-] = \frac{K_a\Sigma[N_3]}{K_a + [H^+]} = \frac{K_a\Sigma[N_3]}{[H^+]} \quad (7)$$

gave values of $(5{\cdot}7 \pm 0{\cdot}1) \times 10^{-5}$ and $(6{\cdot}25 \pm 0{\cdot}1) \times 10^{-5}$ mol l^{-1} at 80·00 and 90·00 °C respectively. The starting solutions were chosen so as to satisfy the following conditions: at time $t = 0$, $[Co(Hdtu)N_3^{2+}] = a$ and $[Co(Hdtu)H_2O^{3+}] = [N_3^-] = 0$; at time $t = t$, $[Co(Hdtu)N_3^{2+}] = (a - x)$ and $[Co(Hdtu)H_2O^{3+}] = \Sigma[N_3] = x$; and at equilibrium, $[Co(Hdtu)H_2O^{3+}] = \Sigma[N_3] = x_e$. The simplified expression for opposed first- and second-order reactions is [10] (8), where k_b represents the pseudo-first-order rate constant for the forward reaction.

$$2{\cdot}303 \log_{10} \frac{[ax_e + x(a - x_e)]}{a(x_e - x)} = k_b[(2a - x_e)/x_e]t \quad (8)$$

The reaction was followed both spectrophotometrically and by azide-ion release. In the former, the quantities a, x, and x_e were calculated from the changing absorbance of the reaction mixture and those of pure $[Co(Hdtu)N_3]^{2+}$ and $[Co(Hdtu)H_2O]^{3+}$. Values of k_b were obtained from gradients of plots of $\log\{[ax_e + x(a - x_e)]/a(x_e - x)\}$ against time. These plots were linear over the extent to which the reaction was followed (50—80% completion). Second-order rate constants, k_c, were calculated by use of equation (9). Table 3 lists values of k_b and k_c obtained over the $[H^+]$ range 0·006—0·03M, and at 80·00, 90·00, and

$$k_c = k_b[H^+](a - x_e)/K_a(x_e^2) \quad (9)$$

98·00 °C. At 98 °C, however, it was observed that the reaction mixture developed strong odours due to what we believe to be thermal decomposition of hydrogen azide and/or azide ions. At 80 and 90 °C values of 'x_e' obtained from spectrophotometric and azide-ion-release experiments were in good agreement. At 98°, however, the spectrophotometric x_e value was much larger than that from azide-ion-release experiments. This difference was not observed for values of 'x', however, and only prolonged heating of the solution resulted in decomposition of azide. That no reduction of Co^{III} was taking place was determined by base hydrolysis of the equilibrium mixture, followed by acidification to obtain the aquo-complex, and comparison of the resulting solution spectrum with that calculated from the original concentration of the azido-complex.

Examination of Table 3 shows that the values of k_b decrease with increasing hydrogen-ion concentration. When k_b was corrected for the acid-concentration term (see Discussion section), an inverse $[H^+]$ dependence [equation (10)] was apparent. The second-order rate constant, k_c,

$$k_b = k_1' + (k_3/[H^+]) \quad (10)$$

however showed a complex $[H^+]$ dependence [equation (11)].

$$k_c = (k_4/[H^+]) + (k_5/[H^+]^2) \quad (11)$$

TABLE 3

Rate constants for hydrolysis of the ion $[Co(Hdtu)N_3]^{2+}$ at low acid concentrations *

t/°C	[Complex] mM	$[HClO_4]$ mM	10^6k_b † s^{-1}	k_c † l mol^{-1} s^{-1}
80·00	1·729	6·20	3·7 ± 0·1	98·0 ± 2·0
80·00	1·687	8·26	3·02 ± 0·04	64·5 ± 0·8
80·00	1·695	10·33	2·62 ± 0·04	45·5 ± 0·7
80·00	1·600	12·40	2·38 ± 0·05	34·5 ± 0·7
80·00	1·797	14·46	2·27 ± 0·03	27·7 ± 0·4
80·00	1·677	16·53	2·17 ± 0·05	23·3 ± 0·5
80·00	1·779	18·59	2·10 ± 0·04	18·6 ± 0·4
80·00	1·414	20·66	2·00 ± 0·04	16·6 ± 0·3
80·00	4·976	12·34	2·3 ± 0·1 ‡	33·0 ± 1·0 ‡
90·00	1·679	8·26	11·8 ± 0·1	79·2 ± 0·5
90·00	1·677	10·33	10·22 ± 0·08	56·6 ± 0·4
90·00	1·640	12·40	9·12 ± 0·08	41·6 ± 0·4
90·00	1·615	14·46	8·36 ± 0·04	31·3 ± 0·2
90·00	1·633	16·53	8·02 ± 0·05	25·8 ± 0·2
90·00	1·698	18·59	7·84 ± 0·05	21·9 ± 0·1
90·00	1·652	20·66	7·3 ± 0·1	18·2 ± 0·3
90·00	1·806	25·80	7·15 ± 0·08	13·7 ± 0·2
90·00	1·788	30·99	7·14 ± 0·07	10·1 ± 0·1
90·00	5·850	14·46	8·34 ± 0·07 ‡	31·6 ± 0·3 ‡
90·00	6·230	10·33	9·05 ± 0·08 ‡	56·0 ± 0·5 ‡
98·00	1·750	8·26	30·5 ± 0·1	
98·00	1·694	10·33	27·2 ± 0·2	
98·00	1·725	12·40	24·3 ± 0·2	

* Ionic strength adjusted to 1·00M with sodium perchlorate. † Weighted averages of values determined at 520, 510, and 500 nm. ‡ From azide-ion-release experiments.

Table 4 gives the kinetic parameters of k_b and k_c at low hydrogen-ion concentrations.

TABLE 4

Kinetic parameters for hydrolysis of the ion $[Co(Hdtu)N_3]^{2+}$ at low acid concentrations

t/°C	10^6k_1/ s^{-1}	$10^8k_3K_2$/ mol l^{-1} s^{-1}	k_{-1}/ l mol^{-1} s^{-1}	$k_{-3}K_3$/ s^{-1}
80·00	0·89 ± 0·03	1·63 ± 0·05	37 ± 3	50 ± 4
90·00	3·1 ± 0·3	6·6 ± 0·3	32 ± 2	61 ± 1
98·00	10·8 ± 1·00	15·4 ± 1·0		

Errors are least-squares standard deviations.

DISCUSSION

In order to explain the experimental facts we propose the following series of reactions, which provide a mechanism for the hydrolysis and anation reactions over the $[H^+]$ range covered in this work. Here (12) is a rapid, reversible, equilibrium in which the azide ligand is protonated. Reactions of this type usually occur when the leaving group can be protonated, either because of strong basic character or the ability to form hydrogen bonds. Similar pre-equilibria were suggested for ligands such as F^-, N_3^-, CO_3^{2-}, NO_2^-, *etc.* in the ions $[Co(NH_3)_5X]^{2+}$ and $[Co(en)_2X_2]^+$ (en = ethylenedi-

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[10] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961, p. 187.

amine).[11-15] Reactions (13) and (17) are rapid reversible equilibria associated with proton exchange between the

$$[\mathrm{Co(Hdtu)N_3}]^{2+} + \mathrm{H^+} \xrightleftharpoons{K_1} [\mathrm{Co(Hdtu)(N_3H)}]^{3+} \quad (12)$$

$$[\mathrm{Co(Hdtu)N_3}]^{2+} \xrightleftharpoons{K_2} [\mathrm{Co(dtu)N_3}]^{+} + \mathrm{H^+} \quad (13)$$

$$[\mathrm{Co(Hdtu)N_3}]^{2+} + \mathrm{H_2O} \xrightleftharpoons[k_{-1}]{k_1} [\mathrm{Co(Hdtu)H_2O}]^{3+} + \mathrm{N_3}^- \quad (14)$$

$$[\mathrm{Co(Hdtu)(N_3H)}]^{3+} + \mathrm{H_2O} \xrightleftharpoons[k_{-2}]{k_2} [\mathrm{Co(Hdtu)H_2O}]^{3+} + \mathrm{HN_3} \quad (15)$$

$$[\mathrm{Co(dtu)N_3}]^{+} + \mathrm{H_2O} \xrightleftharpoons[k_{-3}]{k_3} [\mathrm{Co(dtu)H_2O}]^{2+} + \mathrm{N_3}^- \quad (16)$$

$$[\mathrm{Co(Hdtu)H_2O}]^{3+} \xrightleftharpoons{K_3} [\mathrm{Co(dtu)H_2O}]^{2+} + \mathrm{H^+} \quad (17)$$

$$\mathrm{HN_3} \xrightleftharpoons{K_a} \mathrm{H^+} + \mathrm{N_3}^- \quad (18)$$

solvent and the secondary NH (at the 6-position) common to the two coplanar chelate rings.[1,2] This mechanism leads to a rate law of the form (19), in which $[\mathrm{Co(Hdtu)N_3}^{2+}]_\mathrm{T}$ represents the total concentration of the azido-complex in its protonated and unprotonated forms, $[\mathrm{Co(Hdtu)H_2O^{3+}}]_\mathrm{T}$ the total concentration of the aquo-complex in its protonated and unprotonated forms, and $\Sigma[\mathrm{N_3}]$ the total azide concentration. It is to be noted that the reverse reaction of (15) has a transition state with one more hydrogen atom than that of the reverse of (14). Experiments at high acid concentration, however, indicated that the reverse reaction in (15) is negligible. Equation (19) reduces to (20), given that K_a, $K_1[\mathrm{H^+}]^2$, K_2, and K_3 are much less than $[\mathrm{H^+}]$ and $(k_{-2}/K_a)[\mathrm{H^+}] \ll (k_{-1}$ and $k_{-3}K_3/[\mathrm{H^+}])$. The experimental rate constant k_b is given by the first part of (20) while the second-order rate constant k_c will be given by the second part.

$$-\frac{\mathrm{d}[\mathrm{Co(Hdtu)N_3}^{2+}]_\mathrm{T}}{\mathrm{d}t} = \left(\frac{[\mathrm{H^+}]}{[\mathrm{H^+}] + K_1[\mathrm{H^+}]^2 + K_2}\right) \left(k_1 + k_2K_1[\mathrm{H^+}] + \frac{k_3K_2}{[\mathrm{H^+}]}\right)[\mathrm{Co(Hdtu)N_3}^{2+}]_\mathrm{T} - \left\{\frac{[\mathrm{H^+}]K_a}{([\mathrm{H^+}] + K_3)([\mathrm{H^+}] + K_a)}\right\} \left\{k_{-1} + (k_{-2}/K_a)[\mathrm{H^+}] + \frac{k_{-3}K_3}{[\mathrm{H^+}]}\right\}[\mathrm{Co(Hdtu)H_2O^{3+}}]_\mathrm{T}\Sigma[\mathrm{N_3}] \quad [19]$$

$$-\frac{\mathrm{d}[\mathrm{Co(Hdtu)N_3}^{2+}]_\mathrm{T}}{\mathrm{d}t} = \left(k_1 + k_2K_1[\mathrm{H^+}] + \frac{k_3K_2}{[\mathrm{H^+}]}\right)[\mathrm{Co(Hdtu)N_3}^{2+}]_\mathrm{T} - \left(\frac{k_{-1}K_a}{[\mathrm{H^+}]} + \frac{k_{-3}K_3K_a}{[\mathrm{H^+}]^2}\right)[\mathrm{Co(Hdtu)H_2O^{3+}}]_\mathrm{T}\Sigma[\mathrm{N_3}] \quad (20)$$

At high $[\mathrm{H^+}]$ the reverse of reaction (15) and the term $k_3K_2/[\mathrm{H^+}]$ are negligible. The rate constant k_a is given by the relation $k_1 + k_2K_1[\mathrm{H^+}]$, where the term $k_2K_1[\mathrm{H^+}]$ is equal to the experimental rate constant k_2. Activation parameters corresponding to k_1 and k_2K_1 were obtained from linear Arrhenius plots; for k_1 at 363 K $\Delta H^\ddagger = 34{\cdot}0 \pm 0{\cdot}6$ kcal mol^{-1} and $\Delta S^\ddagger = 10 \pm 2$ cal K^{-1} mol^{-1}, while for k_2K_1 $\Delta H^\ddagger = 35 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = 17 \pm 6$ cal K^{-1} mol^{-1}.* These values are of the same order of magnitude as those observed for hydrolysis of the ion $[\mathrm{Co(NH_3)_5N_3}]^{2+}$.[12] Extrapolated values for the rate constants at 25 °C are $k_1 = (1{\cdot}1 \pm 0{\cdot}3) \times 10^{-10}$ s^{-1} and $k_2K_1 = (1{\cdot}5 \pm 0{\cdot}6) \times 10^{-9}$ l mol^{-1} s^{-1}.

At low $[\mathrm{H^+}]$ correction of k_b for the high-acid-concentration term $k_2K_1[\mathrm{H^+}]$ gave a quantity inversely proportional to $[\mathrm{H^+}]$. Plots of the corrected values for k_b against $1/[\mathrm{H^+}]$ gave good straight lines. Table 4 gives the values of k_1 and k_3K_2. Values of k_1 obtained from plots of k_b against $1/[\mathrm{H^+}]$ are in good agreement with those obtained from plots of k_b against $[\mathrm{H^+}]$. Activation parameters for k_3K_2 obtained from linear Arrhenius plots gave $\Delta H^\ddagger = 32 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = -5 \pm 5$ cal K^{-1} mol^{-1} at 363 K. The extrapolated value for k_3K_2 at 25 °C is $(3{\cdot}2 \pm 0{\cdot}9) \times 10^{-12}$ mol l^{-1} s^{-1}. The term k_3K_2 can be viewed as a base-hydrolysis term if it is divided by k_w, the ion product of water. The mechanism would then involve removal of a proton from an amino-group, in a rapid pre-equilibrium, by a hydroxide ion, followed by slow aquation of the conjugate base of the complex. At 25 °C the base-hydrolysis term has the value $(3{\cdot}24 \pm 0{\cdot}9) \times 10^2$ l mol^{-1} s^{-1}, leading to $\Delta S^\ddagger = 41{\cdot}35 \pm 6$ cal K^{-1} mol^{-1}. These values are of the same order of magnitude as those observed for base-hydrolysis reactions of similar systems.[3,12,16]

Kinetic parameters for the anation reaction were obtained from a plot of $k_c[\mathrm{H^+}]/K_a$ against $1/[\mathrm{H^+}]$. Values of k_{-1} and $k_{-3}K_3$ are given in Table 4. Activation parameters for $k_{-3}K_3$ from linear Arrhenius plots were $\Delta H^\ddagger = 4{\cdot}4 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = 39 \pm 4$ cal K^{-1} mol^{-1} at 298 K. The extrapolated values of k_{-1} appear to be temperature independent. A careful study of the anation reaction at high $\mathrm{N_3}^-$ concentrations should be conducted, however, before any final conclusions can be drawn. The most probable transition-state complex for reactions (14) and (16) is a short-lived five-co-ordinate intermediate (see hydrolysis reactions of the isothiocyanato-analogues of this complex, ref. 1). Such dissociative mechanisms have been demonstrated for anation reactions of the ion $[\mathrm{Co(CN)_5H_2O}]^{3-}$ with $\mathrm{N_3}^-$,

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* 1 cal = 4·184 J.

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SCN^-, SO_4^{2-}, *etc.*[17] Ion-pair mechanisms were suggested, however, for anation reactions of the ion $[Co(NH_3)_5H_2O]^{3+}$.[18,19]

The slower hydrolysis rates of $[Co(Hdtu)X]^{2+}$ compared with corresponding ammine or ethylenediamine complexes can be explained as (*i*) a solvent effect,[20] in which the organic groups tend to break up the solvation shell of the complex, whereas the complex makes greater demands on solvation on going to the transition state with separating charges, or (*ii*), as was suggested elsewhere[21] for similar comparisons, the greater ability of 1,11-diamino-3,6,9-triazaundecane to expand the 3*d* shell of the central metal ion. In the series $[Co(Hdtu)X]^{2+}$, the order of reactivity as far as the leaving group is concerned is $Cl^- > N_3^- \approx NCS^-$. The anation reactions, however, suggest that the ion N_3^- is a better nucleophile than NCS^-.

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