Kinetics of the Acid and Base Hydrolysis of αβ*R*- and αβ*S*-Isothiocyanatotetraethylenepentaminecobalt(III) Cations

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The kinetics of the acid hydrolysis of αβ*S*-Co(Htetren)NCS^{2+} in perchloric and acetic acid solutions was investigated, spectrophotometrically and by SCN^- release, while the base hydrolysis of the same complex and its diastereoisomer, αβ*R*, was studied by the spectrophotometric and pH-stat methods. The acid hydrolysis follows a rate expression for opposed first- and second-order reactions. In perchloric acid solutions the pseudo-first-order rate constant for the forward reaction was found to have an inverse hydrogen-ion dependence of the form $k_a = k_1'/[H^+]$ while the second-order rate constant for the reverse reaction showed a similar inverse dependence on $[H^+]$; $k_b = k_{-1}'/[H^+]$. The equilibrium constant for the reaction was independent of $[H^+]$. The reaction was studied over the range 0·002—0·10M-$HClO_4$. At 90·00 °C and 0·0106M-$HClO_4$ ($\mu = 1{\cdot}00$M, $NaClO_4$), $k_a = (4{\cdot}5 \pm 0{\cdot}3) \times 10^{-6}\ s^{-1}$; $k_b = 1{\cdot}82 \times 10^{-2}\ l\ mol^{-1}\ s^{-1}$; and $K_a = 0{\cdot}247 \times 10^{-3}\ mol\ l^{-1}$. In acetic acid solutions and over the acetic acid concentration range 0·10—1·0M the pseudo-first-order rate constant had a hydrogen-ion dependence of the form k_a', $= k_2' + k_3'/[H^+]$, while the second-order rate constant for the reverse reaction as well as the equilibrium constant showed a complex dependence on $[H^+]$, $[AcO^-]$, or both. At 90·00 °C and 1·06M-acetic acid $k_a' = (7{\cdot}2 \pm 0{\cdot}1) \times 10^{-6}\ s^{-1}$, $k_b' = 3{\cdot}8 \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$, and $K_a' = 1{\cdot}871 \times 10^{-3}\ mol\ l^{-1}$. The acid hydrolyses were studied at 90·00 ± 0·03, 95·00 ± 0·03, and 99·90 ± 0·07 °C. The base hydrolyses were studied at 15·00 ± 0·01, 20·00 ± 0·02, and 25 ± 0·02 °C, over the pH range 9·22—10·37. The reactions followed a second-order rate law. At 25·00 °C and $5{\cdot}19 \times 10^{-5}$M-NaOH ($\mu = 1{\cdot}0$M, $NaClO_4$) the pseudo-first-order rate constant for the base hydrolysis of αβ*S*-Co(Htetren)NCS^{2+} has the value $k_c = (5{\cdot}73 \pm 0{\cdot}10) \times 10^{-3}\ s^{-1}$. For the base hydrolysis of αβ*R*-Co(Htetren)NCS^{2+} the pseudo-first-order rate constant has the value $k_d = (5{\cdot}50 \pm 0{\cdot}02) \times 10^{-3}\ s^{-1}$ at 25·00 °C and $6{\cdot}00 \times 10^{-5}$M-NaOH. Values of $\Delta H^‡$ and $\Delta S^‡$ for the various kinetic parameters are reported. Mechanisms for both the acid and base hydrolyses are suggested.

EL-AWADY and GARNER[1] reported the kinetics of isomerizations of αβ*R*-isothiocyanatotetraethylenepentaminecobalt(III) cation, αβ*R*-Co(Htetren)NCS^{2+}, to form its diastereoisomeric form αβS-Co(Htetren)NCS^{2+}. The *X*-ray crystal structures of the optically active chloro-analogues of these compounds correspond[2] to diastereoisomeric forms arising from alternative configurations about the secondary nitrogen atom common to the two near-coplanar chelate rings. The structures of the αβ*R* and αβ*S*-isothiocyanato-salts were assigned, based on the similarity of the i.r. spectra especially in the NH_2 stretching and bending regions, to the chloro-analogues.

Ni and Garner[3] reported the kinetics of the acid hydrolysis of αβ*R*- and αβS-Co(Htetren)Cl^{2+}. In an attempt to provide a further insight on the effects of

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

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

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

chelation as well as stereochemistry on the hydrolysis rates of related cobalt(III) complexes, we report here the results of an investigation on the rates of acid and base hydrolysis of $\alpha\beta R$- and $\alpha\beta S$-Co(Htetren)NCS^{2+}.

EXPERIMENTAL

Materials.—All reagents were of analytical grade. The water was doubly distilled and then passed through a mixed-bed cation–anion-exchange resin. Tetraethylenepentamine(Htetren) (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.

Preparation of Complexes.—$\alpha\beta R$-Hydroxo- and $\alpha\beta R$-aquo-tetraethylenepentaminecobalt(III) perchlorates were prepared and characterized as described.[4]

Reddish orange $\alpha\beta S$-[Co(Htetren)NCS](ClO$_4$)$_2$ was prepared from the corresponding chloride [1] by dissolution in the minimum of 0·01M-HClO$_4$ and precipitation of the perchlorate salt with excess of NaClO$_4$. In a typical preparation the chloride (3 g) was dissolved in 0·01M-perchloric acid (15 ml) and NaClO$_4$ (7 g) was added. The clear mixture was left standing for 3—5 hours and the precipitated salt filtered off. A solution of the perchlorate salt gave no precipitate with AgNO$_3$ indicating the absence of chloride ions {Found: Co, 11·6; ClO$_4$, 39·1. Calc. for [Co(Htetren)NCS](ClO$_4$)$_2$ Co, 11·7; ClO$_4$, 39·4%}.

$\alpha\beta R$-Isothiocyanatotetraethylenepentaminecobalt(III) perchlorate was prepared in solution by dissolving a known weight of the corresponding chloride [1,4] in 0·01M-HClO$_4$ and removing the chloride ions by passing the mixture on a 1 cm diameter × 25 cm column of ClO$_4^-$ Dowex AG1-X8 (100—200 mesh) resin,* and eluting the perchlorate salt with 0·01M-HClO$_4$. The eluant was collected in a volumetric flask and diluted to the mark with distilled water.

Chromatography of Aquated Solutions.—Solutions of $\alpha\beta S$-Co(Htetren)NCS^{2+} which had been allowed to aquate in the dark at 90 °C for 1—2 half-lives under experimental kinetic conditions were adsorbed on a 10 cm × 1 cm diameter cation-exchange resin (200—400 mesh) and eluted at room temperature with four successive 50 ml portions of 1·3M-HClO$_4$, then three successive 50 ml portions of 2·5M-HClO$_4$.

Kinetic Runs.—The kinetic runs for the acid hydrolysis were followed both spectrophotometrically and by thiocyanate release. Weighed amounts of $\alpha\beta S$-[Co(Htetren)-NCS](ClO$_4$)$_2$ were dissolved in the desired medium made from stock solutions of NaClO$_4$, HClO$_4$, and acetic acid of known concentrations and made up to desired volume. Portions (*ca*. 10 ml) were sealed by torch in 20 ml Pyrex test tubes. These were then wrapped in aluminium foil to exclude light and placed in oil-baths thermostatted at 90·00 ± 0·03, 95·00 ± 0·03, and 99·90 ± 0·07 °C. Zero reaction time was taken 10 min after the ampoules were put into the temperature bath. 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 (*vs*. 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 500, 490, 480, and 470 nm.

In certain runs, the reaction was followed by analysis of the released SCN$^-$. Free SCN$^-$ in the reaction ampoules was removed from the complexes by absorbing aliquot portions on a 3 cm × 2 cm diameter column of H$^+$ Dowex AG50W-X8 cation-exchange resin (100—200 mesh), prefilled with 0·001M-HClO$_4$, collecting in 50 ml volumetric flasks, and making up to volume with 0·001M-HClO$_4$. The SCN$^-$ anions in these solutions were determined by the FeSCN$^+$ spectrophotometric method [5] or by Volhard titration with silver nitrate.[6]

The kinetic data for the base hydrolysis were obtained by use of the pH-stat and the spectrophotometric methods simultaneoulsy, with a continuous-flow technique. The pH-stat method [7,8] is suitable for reading as a function of time the volume of base required to keep a sample at a constant pH. Thus, complete reaction-rate curves were obtained by maintaining the pH at a pre-selected value, with continuous correction for the base used during the reaction. A recorded plot, then, of milliequivalents (or volume) of base against time provides a reaction-rate curve. The experimental data were obtained with a Radiometer recording pH-stat and a Cary Model 14 spectrophotometer. The chart paper scale of the syringe recorder was calibrated by titration of the standard sodium hydroxide stock solution, used in all experiments, with a standard solution of potassium hydrogen phthalate. Experimentally the solutions for the kinetic runs for the base hydrolysis were prepared by adding a known weight of the complex (a known volume in case of the $\alpha\beta R$-isomer) to an NaClO$_4$ solution in a volumetric flask, calculated to give a final ionic strength of 1·00. The mixture was then diluted to the mark and mixed thoroughly. This solution (60 ml) was then transferred to the thermostatted reaction vessel and allowed to come to temperature equilibrium with the electrodes for a period of not less than 1 h. Simultaneously the same reaction solution was circulated into a continuous-flow silica cell contained in the thermostatted cell compartment of the Cary spectrophotometer. The solution was transferred with a Varistaltic pump (Manostat Corp.) and the flow rate was maintained at 600 ml/min. The spectrophotometer was calibrated to give zero absorbance reading before the introduction of the reaction solutions into the cell by balancing the absorbance due to the continuous flow cell with use of a neutral density filter and the balance dial on the spectrophotometer. The pH-stat was set to the desired pH and the Cary spectrophotometer was set at a fixed wavelength (490 nm for most experiments and occasionally at 480 nm) and the two instruments started simultaneously. Two independent plots of the reaction were thus obtained. On the pH-stat side the volume of standard sodium hydroxide required to keep the pH at the set value was traced by the recorder; on the spectrophotometer side the change in absorbance as a function of time was recorded. No correction for the volume of added NaOH solution was

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* Conversion of commercial Cl$^-$ Dowex AG1-X8 resin into ClO$_4^-$ form was achieved by washing with 1·5M-NaClO$_4$ until the washings gave a negative test for Cl$^-$ with AgNO$_3$. Excess of ClO$_4^-$ was removed by washing with distilled water.

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

[5] J. M. Veigel and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 1569.

[6] I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, 'Quantitative Chemical Analysis,' Macmillan, London, 1969, pp. 722, 798.

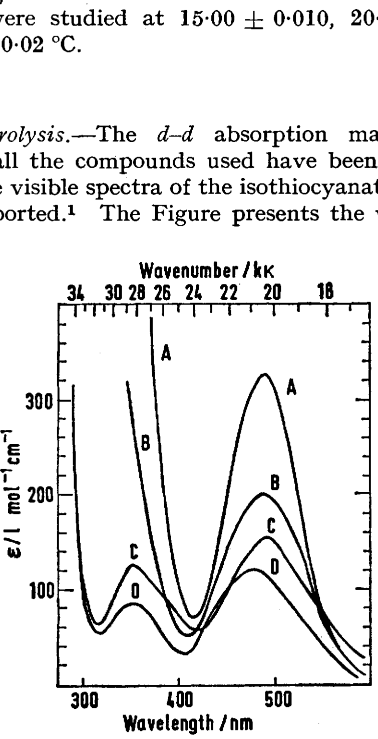
[7] C. F. Jacobsen and J. Leonis, 'Methods of Biochemical Analysis,' vol. IV, Interscience, New York, 1957, pp. 171—210.

[8] H. V. Malmstadt and E. H. Piepmeier, *Analyt. Chem.*, 1965, **37**, 34.

needed since these volumes did not exceed 0·7 ml in any of the experiments performed. The pH of the solutions was checked at the end of the reaction on a Beckman Expandomatic SS-2 pH meter. No difficulty or interference was caused by the precipitation of potassium perchlorate at the liquid junctions in the reference electrode. The base hydrolyses were studied at 15·00 ± 0·010, 20·00 ± 0·02, and 25·00 ± 0·02 °C.

RESULTS

Acid Hydrolysis.—The *d–d* absorption maxima and minima for all the compounds used have been reported.[4] The complete visible spectra of the isothiocyanato-salts has also been reported.[1] The Figure presents the visible and the near-u.v. absorption spectra of the two isothiocyanato-diastereoisomers as well as those of $\alpha\beta R$-aquo- and $\alpha\beta R$-hydroxo-complexes. The positions as well as the molar absorbitivities at the maxima and minima for these complexes are in very good agreement with previously reported values.



Visible and near-u.v. absorption spectra of isothiocyanato-, aquo-, and hydroxo-tetraethylenepentamine complexes of cobalt(III) at 20—25 °C; A, $\alpha\beta S$-Co(Htetren)NCS^{2+}; B, $\alpha\beta R$-Co(Htetren)NCS^{2+}; C, $\alpha\beta R$-Co(Htetren)OH^{2+}; D, $\alpha\beta R$-Co(Htetren)OH$_2^{3+}$

When a known weight of $\alpha\beta S$-[Co(Htetren)NCS](ClO$_4$)$_2$ was dissolved in solution under reaction conditions, the initial absorption spectrum was that of $\alpha\beta S$-Co(Htetren)-NCS^{2+}, but the final spectrum was not that of the known $\alpha\beta R$-Co(Htetren)OH$_2^{3+}$ complex, but somewhat in between the spectra of these two complexes. This indicated that the reaction goes to an equilibrium mixture represented

$$\alpha\beta S\text{-Co(Htetren)NCS}^{2+} + \mathrm{H_2O} \overset{K_a}{\rightleftharpoons} \alpha\beta R\text{- or }\alpha\beta S\text{-Co(Htetren)OH}_2^{3+} + \mathrm{SCN}^- \qquad (1)$$

by the reaction (1) where we assumed that the spectra of the $\alpha\beta R$- and $\alpha\beta S$-aquo-isomers are either identical or nearly so in the spectral region studied (see Discussion section). The possibility that the spectrum of the formed aquo-species is drastically different from that of the $\alpha\beta R$-isomer was excluded on the basis of thiocyanate release experiments. These experiments do show that the reaction is indeed reversible and follows an overall reaction equation of type (1). Preliminary experiments on the thiocyanate anation of $\alpha\beta R$-Co(Htetren)OH$_2^{3+}$ indicated that the back reaction followed second-order kinetics, although this was complicated by isomerizations. Thus addition of SCN$^-$ to the products of aquation of $\alpha\beta S$-Co-(Htetren)NCS^{2+} gave at 90 °C the same spectral changes observed for aquation in reverse.

Experimentally it was observed that the reaction follows a rate expression for opposed first- and second-order reactions of the form (2). Where the forward reaction is

$$\frac{-\partial[\mathrm{A}]}{\partial t} = k_a[\mathrm{A}] - k_b[\mathrm{B}]^2 \qquad (2)$$

done under pseudo-first-order conditions, [A] represents the concentration of $\alpha\beta S$-Co(Htetren)NCS^{2+} and [B] = [Co(Htetren)OH$_2^{3+}$] = [SCN$^-$]. The starting solutions were chosen so as to satisfy the following conditions: at time $t = 0$, [$\alpha\beta S$-Co(Htetren)NCS^{2+}] = a, [Co(Htetren)-OH$_2^{3+}$] = [SCN$^-$] = 0; at time $t = t$, [$\alpha\beta S$-Co(Htetren)-NCS^{2+}] = $(a - X)$, [Co(Htetren)OH$_2^{3+}$] = [SCN$^-$] = X, at time $t = \infty$ (equilibrium), [Co(Htetren)OH$_2^{3+}$] = [SCN$^-$] = X_e. The simplified expression for the opposed first- and second-order reactions is[9] (3), where k_a represents the pseudo-first-order rate constant for the forward reaction.

$$2{\cdot}303 \log \frac{aX_e + X(a - X_e)}{a(X_e - X)} = k_a \frac{(2a - X_e)}{X_e}\, t \qquad (3)$$

The reaction was followed both spectrophotometrically and by thiocyanate release. In the spectrophotometric runs the quantities a, X, and X_e were calculated from the changing absorbance of the reaction mixture and that of pure $\alpha\beta S$-Co(Htetren)NCS^{2+} and $\alpha\beta R$-Co(Htetren)OH$_2^{3+}$. The pseudo-first-order rate constants for the forward reaction were obtained from the slope of the plot of log $\{[aX_e + X(a - X_e)]/a(X_e - X)\}$ against time. These plots were linear up to 60% reaction. The second-order rate constants for the back reaction k_b and the equilibrium constant K_a were calculated by use of equations (4) and (5). The

$$k_b = \frac{k_a(a - X_e)}{(X_e)^2} \qquad (4)$$

$$K_a = \frac{(X_e)^2}{(a - X_e)} \qquad (5)$$

quantity X_e was obtained from a reaction ampoule allowed to react for 10 half-lives. The data for the acid hydrolysis are collected in Tables 1—3.

Base Hydrolysis.—The base hydrolysis (6) was studied

$$\mathrm{Co(Htetren)NCS^{2+} + OH^-} \xrightarrow{k_c} \mathrm{Co(Htetren)OH^{2+} + SCN^-} \qquad (6)$$

under pseudo-first-order conditions, [OH$^-$] being kept constant and the reaction monitored with the pH-stat and the spectrophotometric methods. In the pH-stat method the pseudo-first-order rate constants were obtained from the relation (7) where V_0, V, and V_∞ are the volumes of NaOH added to keep the pH constant, at reaction times zero, time t, and for complete SCN$^-$ release, respectively. In the spectrophotometric method k_c was evaluated for each

$$2{\cdot}303 \log_{10} [(V_\infty - V_0)/(V_\infty - V)] = k_c t \qquad (7)$$

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

TABLE 1

Rate and equilibrium constants for the aquation of αβ*S*-Co(Htetren)NCS^{2+} in perchloric acid solutions *

t/°C	[Complex]/mM	[HClO$_4$]/mM	pH [b]	10^3[H$^+$]/M	10^6k_a †/s^{-1}	10^3k_b †/l mol^{-1} s^{-1}	10^3K_a †/mol l^{-1}
90·00	4·458	2·13	2·78	1·660	22·1 ± 2	89·0	0·249
90·00	4·776	5·03	2·38	4·169	7·9 ± 0·5	32·0	0·246
90·00	5·388	10·65	2·08	8·318	4·5 ± 0·3	18·2	0·247
90·00	9·849	5·03	2·38	4·169	8·0 ± 1·0 [a]	32·0 [a]	0·249 [a]
90·00	10·580	10·65	2·08	8·318	4·3 ± 0·4 [a]	17·2 [a]	0·250 [a]
95·00	4·525	5·03	2·38	4·169	20·0 ± 1·0	73·9	0·270
95·00	4·210	10·65	2·08	8·318	9·9 ± 0·5	37·3	0·265
95·00	4·978	12·90	1·97	10·720	8·2 ± 0·6	29·8	0·275
99·90	5·205	2·13	2·78	1·660	90·1 ± 1·5	307·0	0·293
99·90	4·767	5·03	2·38	4·169	34·6 ± 0·8	112·0	0·310
99·90	4·666	10·65	2·08	8·318	20·7 ± 0·9	67·0	0·308
99·90	5·367	106·50	1·08	83·38	3·2 ± 0·5	10·3	0·311
99·90	27·020	5·03	2·38	4·169	36·0 ± 1·0 [a]	120 [a]	0·300 [a]

* Ionic strength was adjusted to 1·0M with sodium perchlorate. † Weighted averages of values determined at 500, 490, 480, and 470 nm, which agreed within experimental error; errors are standard errors obtained from least-squares treatment.

[a] Thiocyanate release. [b] pH Measured at 20 °C.

TABLE 2

Rate and equilibrium constants for the aquation of αβ*S*-Co(Htetren)NCS^{2+} in acetic acid solutions *

t/°C	[Complex]/mM	[CH$_3$CO$_2$H]/M	pH [b]	10^3[H$^+$]/M	$10^6k_a'$†/s^{-1}	$10^3k_b'$ †/l mol^{-1} s^{-1}	$10^3K_a'$ †/mol l^{-1}
90·00	4·862	0·104	2·83	1·479	22·6 ± 1·0	24·9	0·909
90·00	4·745	0·318	2·57	2·692	12·6 ± 0·3	9·1	1·376
90·00	4·730	1·060	2·27	5·370	7·2 ± 0·1	3·8	1·871
90·00	9·698	0·318	2·57	2·692	15·0 ± 2·5 [a]	11·4 [a]	1·322 [a]
95·00	4·689	0·104	2·83	1·479	46·2 ± 2	49·0	0·951
95·00	4·797	0·318	2·57	2·692	27·3 ± 1	18·9	1·442
95·00	3·682	1·060	2·27	5·370	16·4 ± 0·6	7·6	2·156
95·00	12·970	1·060	2·27	5·370	17·0 ± 0·7 [a]	7·7 [a]	2·200 [a]
99·90	4·693	0·104	2·83	1·479	97·3 ± 2	97·8	0·995
99·90	4·543	0·318	2·57	2·692	61·1 ± 1	36·8	1·663
99·90	3·689	1·060	2·27	5·370	32·5 ± 0·5	13·4	2·429
99·90	34·321	0·318	2·57	2·692	63·0 ± 1·5 [a]	37·0 [a]	1·700 [a]

* Ionic strength was adjusted to 1·0M with sodium perchlorate. † Weighted averages of values determined at 500, 490, 480, and 470 nm which agreed within experimental error; errors are standard errors obtained from least-squares treatment.

[a] Thiocyanate release. [b] pH Measured at 20 °C.

TABLE 3

Rate and equilibrium constants for the aquation of αβ*S*-Co(Htetren)NCS^{2+} in a mixture of acetic and perchloric acid solutions *

t/°C	[Complex]/mM	[CH$_3$CO$_2$H] [a]/M	pH [b]	10^3[H$^+$]/M	$10^6k_a''$ †/s^{-1}	$10^3k_b''$ †/l mol^{-1} s^{-1}	$10^3K_a''$ †/mol l^{-1}
90·00	4·311	0·104	2·65	2·239	15·4 ± 1·2	27·0	0·571
90·00	4·299	0·318	2·45	3·548	10·7 ± 0·7	11·6	0·920
90·00	4·213	1·060	2·17	6·76	6·5 ± 0·2	4·8	1·355
95·00	5·367	0·104	2·65	2·239	30·8 ± 0·9	34·3	0·897
95·00	5·358	0·318	2·45	3·548	19·9 ± 0·4	14·1	1·413
95·00	4·929	1·060	2·17	6·761	13·4 ± 0·2	6·7	2·025
99·90	3·237	0·104	2·65	2·239	70·5 ± 4·0	88·5	0·796
99·90	2·988	0·318	2·45	3·548	41·7 ± 0·7	33·2	1·257
99·90	4·408	1·060	2·17	6·761	27·2 ± 0·3	11·8	2·302

* Ionic strength was adjusted to 1·0M with sodium perchlorate. † Weighted averages of values determined at 500, 490, 480, and 470 nm which agreed within experimental error; errors are standard errors obtained from least-squares treatment.

[a] These solutions contain 1·25 × 10^{-3}M-perchloric acid. [b] pH Measured at 20 °C.

kinetic run by the relation (8) where A_0, A, and A_∞ are the optical absorbances at a given wavelength at reaction time zero, at time t, and at 100% hydrolysis of SCN^-

$$2{\cdot}303 \log_{10} [(A_0 - A_\infty)/(A - A_\infty)] = k_c t \qquad (8)$$

ligand respectively. Plots of equations (7) and (8) were linear up to 85% reaction. Tables 4—6 present rate data for the base hydrolysis of αβ*S*- and αβ*R*-Co(Htetren)NCS^{2+} ions.

The values of the rate constants given in Tables 1—6 are obtained from least-squares treatment of the data and were in good agreement with rate constants obtained from the slopes of the visually drawn rate plots.

The $[OH^-]$ was calculated from the experimental pH values by use of K_w, the ionic product constant for water, at the reaction temperature. These were simply taken as K_w in pure water.[10]

TABLE 4

Pseudo-first-order rate constants for the base hydrolysis of αβ*S*-Co(Htetren)NCS^{2+}

t/°C	pH	$10^5[OH^-]$ / M	[Complex] / mM	10^3k_c(spectro) / s^{-1}	10^3k_c(stat) / s^{-1}
15·00	9·670	2·11	3·38	1·06 ± 0·04	0·93 ± 0·02
15·00	9·900	3·58	5·81	2·09 ± 0·02	2·03 ± 0·04
15·00	10·020	4·74	3·38	3·03 ± 0·05	3·07 ± 0·03
15·00	10·052	5·08	5·81	3·17 ± 0·02	3·00 ± 0·15
15·00	10·158	6·48	5·81	4·04 ± 0·02	3·60 ± 0·15
15·00	10·263	8·25	5·81	5·07 ± 0·02	4·84 ± 0·20
15·00	10·330	9·70	3·38	5·63 ± 0·08	5·41 ± 0·25
20·00	9·247	1·202	6·56	1·12 ± 0·04	1·06 ± 0·07
20·00	9·494	2·123	6·60	1·96 ± 0·02	1·18 ± 0·03
20·00	9·840	4·71	6·60	4·11 ± 0·02	4·15 ± 0·02
20·00	9·670	3·18	6·56	2·67 ± 0·02	2·69 ± 0·10
20·00	9·740	3·74	6·40	3·25 ± 0·02	2·94 ± 0·15
20·00	9·880	5·164	6·40	4·45 ± 0·01	4·30 ± 0·20
20·00	9·952	6·095	6·50	5·58 ± 0·02	5·40 ± 0·02
20·00	10·080	8·19	6·50	6·80 ± 0·10	6·60 ± 0·08
20·00	10·117	8·91	6·40	7·45 ± 0·05	7·22 ± 0·07
25·00	9·326	2·12	6·56	2·35 ± 0·08	1·98 ± 0·20
25·00	9·360	2·29	5·72	2·80 ± 0·06	2·56 ± 0·06
25·00	9·430	2·69	5·72	3·32 ± 0·05	3·33 ± 0·10
25·00	9·500	3·16	5·80	3·25 ± 0·02	3·36 ± 0·03
25·00	9·637	4·34	6·40	4·89 ± 0·10	4·24 ± 0·30
25·00	9·640	4·37	5·80	5·10 ± 0·02	5·22 ± 0·03
25·00	9·715	5·19	6·40	5·72 ± 0·10	5·68 ± 0·15
25·00	9·787	6·12	5·72	6·76 ± 0·02	7·02 ± 0·05
25·00	9·902	7·98	6·40	8·92 ± 0·03	8·96 ± 0·03

Ionic strength adjusted to $\mu = 1{\cdot}00$M with $NaClO_4$. Errors are standard errors obtained from a least-squares treatment.

TABLE 5

Pseudo-first-order rate constants for the base hydrolysis of αβ*R*-Co(Htetren)NCS^{2+}

t/°C	pH	$10^5[OH^-]$/M	[Complex] / mM	10^3k_d(spectro) / s^{-1}	10^3k_d(stat) / s^{-1}
15·00	10·052	5·08	4·87	2·69 ± 0·05	2·66 ± 0·04
15·00	10·158	6·48	4·87	3·40 ± 0·03	3·33 ± 0·05
15·00	10·263	8·25	4·87	4·14 ± 0·08	4·11 ± 0·30
15·00	10·370	10·56	4·81	5·20 ± 0·20	5·40 ± 0·15
20·00	9·743	3·77	3·28	2·23 ± 0·20	2·30 ± 0·30
20·00	9·947	6·03	3·28	3·99 ± 0·10	3·92 ± 0·15
20·00	10·052	7·63	3·28	5·07 ± 0·20	4·91 ± 0·32
20·00	10·152	9·66	3·28	6·56 ± 0·20	6·44 ± 0·34
25·00	9·227	1·69	4·97	1·47 ± 0·06	1·20 ± 0·34
25·00	9·635	4·32	4·97	3·97 ± 0·10	4·14 ± 0·13
25·00	9·740	5·50	3·64	4·49 ± 0·04	4·60 ± 0·2
25·00	9·778	6·00	3·64	5·50 ± 0·02	5·45 ± 0·06
25·00	9·950	8·91	3·64	8·30 ± 0·03	8·20 ± 0·20
25·00	10·052	11·27	3·64	10·23 ± 0·30	10·00 ± 0·40

Ionic strength adjusted to $\mu = 1{\cdot}00$M with $NaClO_4$. Errors are standard errors obtained from a least-squares treatment.

TABLE 6

Second-order rate constants for the base hydrolysis of αβ*S*- and αβ*R*-Co(Htetren)NCS^{2+}

t/°C	$k_{\alpha\beta R}$ / l mol^{-1} s^{-1}	$k_{\alpha\beta S}$ / l mol^{-1} s^{-1}
15·00	51·5 ± 2·2	60·0 ± 2·5
20·00	66·5 ± 1·5	83·0 ± 3·5
25·00	88·5 ± 2·0	108·0 ± 4·0

Errors are least-squares standard deviations.

DISCUSSION

Acid Hydrolysis.—In all our calculations of the spectrophotometric kinetic runs for the acid hydrolysis of

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[10] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 50th edn., The Chemical Rubber Co., Cleveland, Ohio, 1969, p. D-120.

αβ*S*-Co(Htetren)NCS^{2+} we assumed that the hydrolysis product is αβ*R*-Co(Htetren)OH$_2$$^{3+}$, or that the spectra of the αβ*S*-aquo-ion in the region studied is the same or very nearly so. This hypothesis is supported by the good agreement between the spectrophotometric and SCN$^-$ release rate constant values. In addition the aquation products of the αβ*S*- and αβ*R*-chloro-analogues of this compound have always been the αβ*R*-aquo-isomer.[3] However, in the absence of a knowledge of the visible absorption spectra of all the possible geometric and diastereoisomers [2] of the aquo-ion, we cannot exclude the possibility that the product of aquation of αβ*S*-Co(Htetren)NCS^{2+} is an isomer other than the αβ*R*-aquo-form or perhaps a mixture of isomers.

Cation-exchange chromatography (see Experimental section) of solutions of αβ*S*-Co(Htetren)NCS^{2+} that were allowed to react for 1—2 half-lives gave only two bands, which upon elution gave effluents whose visible absorption spectra corresponded essentially to the spectra of the parent complex and αβ*R*-Co(Htetren)OH$_2$$^{3+}$ (similar results were obtained for the equilibrium mixture). No colour was left on the resin column after elution of the apparent αβ*R*-aquo-ion.

In perchloric acid solutions the pseudo-first-order rate constant k_a for the forward reaction and the second-order rate constant k_b for the reverse reaction gave an inverse hydrogen-ion dependence of the form (9) and (10).

$$k_a = k_{1'}/[\mathrm{H^+}] \qquad (9)$$

$$k_b = \frac{k_{-1'}}{[\mathrm{H^+}]} \qquad (10)$$

The equilibrium constant for the reaction showed no hydrogen-ion dependence. A plot of the experimental values of k_a and k_b against [H$^+$], where [H$^+$] is the concentration of perchloric acid in solution, gave good straight lines, the slopes of which are the values of $k_{1'}$ and $k_{-1'}$. These values together with the average value of the equilibrium constant are given in Table 7. These experimental results suggest that the reaction follows a mechanism of the form (11)—(13), where we assumed

$$\alpha\beta S\text{-Co(Htetren)NCS}^{2+} \xrightleftharpoons{K_1} \text{Co(tetren)NCS}^{+} + \mathrm{H}^+ \qquad (11)$$

$$\text{Co(tetren)NCS}^{+} + \mathrm{H_2O} \xrightleftharpoons[k_{-1}]{k_1} \text{Co(tetren)OH}_2{}^{2+} + \text{SCN}^- \qquad (12)$$

$$\text{Co(Htetren)OH}_2{}^{3+} \xrightleftharpoons{K_2} \text{Co(tetren)OH}_2{}^{2+} + \mathrm{H}^+ \qquad (13)$$

that equations (11) and (13) represent rapid reversible equilibria associated with proton exchange between the solvent and the secondary NH common to the two coplanar chelate rings. This mechanism leads to a rate law of the form (14) where C_t is the total isothiocyanato-

$$-\frac{\mathrm{d}C_t}{\mathrm{d}t} = \frac{k_1K_1}{(K_1 + [\mathrm{H^+}])}[C_t] - \frac{k_{-1}K_2}{(K_2 + [\mathrm{H^+}])}[\mathrm{SCN^-}][A_t] \qquad (14)$$

complex in its protonated and unprotonated forms, and A_t is the total aquo-complex in its protonated and unprotonated forms. Given that K_1 and $K_2 \ll [\mathrm{H^+}]$ equation (14) gives the relations (15) and (16) for the rate constants k_a and k_b where the constants $k_{1'}$ and $k_{-1'}$

$$k_a = \frac{k_1K_1}{[\mathrm{H^+}]} \qquad (15)$$

$$k_b = \frac{k_{-1}K_2}{[\mathrm{H^+}]} \qquad (16)$$

in equations (9) and (10) are products of rate and equilibrium constants. On the basis of our data we conclude that reactions such as (17) give very little or no contribution to the overall reaction. Attempts to study the

$$\alpha\beta S\text{-Co(Htetren)NCS}^{2+} + \mathrm{H_2O} \rightleftharpoons \text{Co(Htetren)OH}_2{}^{3+} + \text{SCN}^- \qquad (17)$$

reaction at high hydrogen-ion concentration to verify the possible contribution of reaction (17) were unsuccessful owing to the decomposition of thiocyanate ions;[1] even at 0·1M-HClO$_4$ a foul odour was detected. Activation parameters corresponding to (k_1K_1) and $(k_{-1}K_2)$ were obtained from linear Arrhenius plots. For the forward reaction (k_1K_1), the activation parameters are $\Delta H^{\ddagger}_{298} = 38{\cdot}8 \pm 2{\cdot}0$ kcal mol^{-1} and $\Delta S^{\ddagger}_{298} = 14 \pm 7$ cal mol^{-1} K^{-1}, while for the back reaction $(k_{-1}K_2)$, the parameters are $\Delta H^{\ddagger}_{298} = 31{\cdot}4 \pm 2{\cdot}5$ kcal mol^{-1} and $\Delta S^{\ddagger}_{298} = 11 \pm 8$ cal mol^{-1} K^{-1}. The thermodynamic parameters for the overall reaction at 25 °C are $\Delta H^\circ = 5{\cdot}77 \pm 0{\cdot}03$ kcal mol^{-1}, $\Delta G^\circ = 5{\cdot}96 \pm 0{\cdot}01$ kcal mol^{-1}, and $\Delta S^\circ = -0{\cdot}638$ cal mol^{-1} K^{-1}.

TABLE 7

Rate and equilibrium constants, $k_{1'}$, $k_{-1'}$, and K_a for the acid hydrolysis of αβ*S*-Co(Htetren)NCS^{2+} in perchloric acid

t/°C	$10^{-8}k_{1'}$ * / l mol^{-1} s^{-1}	$10^{-5}k_{-1'}$ */s^{-1}	$10^{-3}K_a$ † / mol l^{-1}
90·00	4·5 ± 0·3	17·7 ± 1·5	0·247
95·00	10·2 ± 0·7	38·0 ± 1·6	0·270
99·90	19·5 ± 1·2	63·2 ± 3·5	0·303

* Errors are least-squares standard deviations. † The K_a values listed are average experimentally obtained values (see Table 1).

In acetic acid solutions, however, the rate constants for the forward and back reactions are apparently functions of both [H$^+$] and [AcO$^-$] concentrations. Table 2 gives the values of these constants in solutions where [H$^+$] = [AcO$^-$]. A comparison of these data with those given in Table 1 for perchloric acid solutions shows that the addition of acetic acid severely retarded the back reaction rates, while the forward reaction rates were slightly decreased. That the apparent retardation is due to the acetate ions and not to acetic acid can be seen by the comparison of the data in Tables 2 and 3. Table 3 gives the values of the constants in solutions where the total (acetate + acetic acid) was kept the same as those of Table 2 while the acetate ion concentration was decreased by addition of perchloric acid.

The effect of added acetate on the aquation and anation rates can be ascribed to an ion pair–ion pair equilibrium (18) in which a less reactive acetate ion pair is formed, where M^{n+} represents the isothiocyanato- or aquo-complex. A similar equilibrium was suggested

$$\mathrm{M}^{n+}(\mathrm{ClO_4}^-)_n + n\mathrm{OAc}^- \overset{K}{\rightleftharpoons} \mathrm{M}^{n+}(\mathrm{OAc}^-)_n + n\mathrm{ClO_4}^- \quad (18)$$

for the explanation of the effect of added NaOAc on the isomerization [11] and acetate exchange [12] of *cis*- and *trans*-$\mathrm{Co(en)_2(OAc)_2ClO_4}$ as well as the solvolysis [13] of *trans*-$\mathrm{Co(en)_2(toluato)_2ClO_4}$. The lower reactivity of the acetate ion pair was attributed by Chester to its structural similarity to a solvated free ion. This effect is the reverse of that generally observed in other solvents.[14-16]

The formation of an ion-pair equilibrium between the acetate ions and the complexes in this investigation can be supported by spectrophotometric evidence. In our study of isomerization of isothiocyanato-complexes [1] in acetic acid solution it was observed that the isosbestic point at 540 nm for the two isomers, although observed in the early stages of the reaction, was subsequently lost and a small spectral shift was observed. This observation was attributed to the small extent of aquation of the αβ*S*-isomer. The present study, however, eliminates this possibility and suggests ion-pairing as an alternative. Addition of acetic acid to αβ*R*-Co(Htetren)-$\mathrm{OH_2}^{3+}$ showed a slight shift in the spectra. The spectral changes, however, are less than 5% and thus did not significantly affect the calculations of spectrophotometric data.

Base Hydrolysis.—The data for the base hydrolysis of the two diastereoisomers shows that the reactions are of the second order overall, first order in the complex, and first order in $[\mathrm{OH}^-]$. This is the general form for the rate law of most base hydrolyses studied. These reactions can be interpreted by any of the mechanisms put forward to discuss base hydrolyses of cobalt(III) complexes. The most obvious of these mechanisms is an associative mechanism [17] S_N2 involving a seven-co-ordinate intermediate. A subdivision of the general S_N2 type mechanism is an ion pair $S_N2$ip [18] and a conjugate base $S_N2$cb.[19]

A more widely accepted mechanism is of the dissociative type S_N1,[20] leading to the formation of an intermediate of reduced co-ordination number. This could involve a rapid formation of a conjugate $S_N1$cb[19] or an ion pair $S_N1$ip.[17] In addition a displacement bimolecular mechanism involving an electron transfer was suggested by Gillard.[21] These and similar mechanisms have been discussed recently.[22-24]

The dissociative mechanisms are more suitable for the base hydrolyses studied here, particularly if one takes into account the effect of acetate ions on the aquation rates (see acid hydrolysis). The severe retardation of the back-reaction rate constants for the acid hydrolysis suggests a five-co-ordinate intermediate for which both the acetate and thiocyanate ions will be in competition. The great similarity between the base hydrolysis rate constants of the two isomers suggests that both reactions take place by the same mechanism. The five-co-ordinate intermediate will not preserve the ring structure of tetraethylenepentamine and this might explain the fact that the final product is αβ*R*-hydroxo-isomer in each case. The apparent activation parameters for base hydrolysis are $\Delta H^{\ddagger}_{\alpha\beta S} = 10{\cdot}07 \pm 2{\cdot}5$ kcal mol^{-1} and $\Delta H^{\ddagger}_{\alpha\beta R} = 9{\cdot}61 \pm 1{\cdot}9$ kcal mol^{-1}. A comparison of these parameters with those obtained from the acid hydrolysis is not possible in the absence of a knowledge of the temperature-dependence of K_w, the ionic product of water, over the entire temperature range of this investigation. In addition a linear Arrhenius plot will not be expected.

The slower hydrolysis rates of $\mathrm{Co(Htetren)X^{2+}}$ than those of the corresponding ammonia or ethylenediamine analogues can be explained as was suggested elsewhere [25,26] for similar comparisons in terms of the greater ability of tetraethylenepentamine to expand the 3*d* shell of the central metal ion. In all of the series studied the labilizing power of non-labile ligands follows the same pattern, $\mathrm{OH^-} > \mathrm{NO_2^-} > \mathrm{Cl^-} \sim \mathrm{CN^-} > \mathrm{NCS^-}$.

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