Kinetics of Base Hydrolysis of the *cis*-Dichloro(1,4,7,10-tetra-azacyclododecane)rhodium(III) and *cis*-Dichloro(1,4,8,11-tetra-azacyclotetradecane)rhodium(III) Cations

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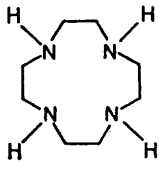
The kinetics of base hydrolysis of the two title cations, *cis*-$[RhCl_2(cyclen)]^+$ (cyclen = 1,4,7,10-tetra-azacyclododecane) and *cis*-$[RhCl_2(cyclam)]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane), have been studied over a range of temperature at I = 0.1 mol dm^{-3} (KCl or $K[NO_3]$). The activation parameters have been obtained and possible mechanisms considered. The base-hydrolysis rate of *cis*-$[RhCl_2(cyclen)]^+$, k_{OH} = 37 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}, is the highest yet reported for halogenorhodium(III) complexes of the $[RhCl_2(N_4)]^+$ type.

RECENTLY there has been considerable interest in the substitution reactions of cobalt(III) complexes of macrocyclic ligands. Poon [1] has reviewed the area with particular emphasis on the hydrolysis of unidentate ligands in cobalt(III) complexes containing macrocyclic N_4 ligands. At the present time few attempts have been made to extend these studies to other metal centres.

Early studies [2] of the base hydrolysis of amine complexes of rhodium(III) suggested that a co-ordinated NH group *trans* to the reaction site was necessary for there to be a significant $[OH^-]$-dependent term in the rate equation. However, it has been shown [3] that *trans*-$[RhCl(en)_2(py)]^{2+}$ and *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl,[4] Br,[4] or I;[5] en = 1,2-diaminoethane, py = pyridine) undergo $[OH^-]$-dependent base hydrolysis. Poë and Vuik [6] have concluded, as a result of a recent study, that base hydrolysis of the complexes *trans*-$[Rh(en)_2X_2]^+$ (X = Cl, Br, or I) does occur if sufficiently high hydroxide-ion concentrations are used. This view has also been confirmed by the recent work of Chung and Bounsall [7] who found that the *trans*-(cyclam)dihalogenorhodium(III) complexes (cyclam = 1,4,8,11-tetra-azacyclotetradecane) were susceptible to base hydrolysis.

As a result of the small ' hole size ' of the macrocycle, the ligand cyclen [1,4,7,10-tetra-azacyclododecane, (1)],



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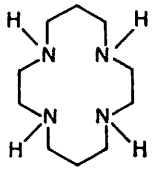


(2)

only forms *cis* complexes with cobalt(III) and rhodium(III).[8] With cyclam (2), both *cis*- and *trans*-dihalogenorhodium(III) complexes can be prepared.[9]

The present paper discussed the kinetics of the base hydrolysis of *cis*-$[RhCl_2(cyclen)]^+$ and *cis*-$[RhCl_2(cyclam)]^+$. The former complex would be expected to be quite susceptible to base hydrolysis and there is no possibility of any stereochemical change occurring during hydrolysis. The determination of the activation parameters allows comparisons to be made regarding the effect of ring size on the reactivity of the chloro-complexes, while the recent work of Chung and Bounsall [7] allows discussion regarding the relative reactivities of the *cis* and *trans* isomers of $[RhCl_2(cyclam)]^+$ towards base hydrolysis.

EXPERIMENTAL

1,4,8,11-Tetra-azacyclotetradecane (cyclam) was prepared as described by Barefield *et al.*[10] and recrystallised from chlorobenzene to give m.p. 183—184 °C (lit.,[10] 185—186 °C). *cis*-Dichloro(1,4,8,11-tetra-azacyclotetradecane)-rhodium(III) chloride was prepared essentially as described by Bounsall and Koprich,[9] and was twice recrystallised from 5 mol dm^{-3} HCl (Found: C, 29.3; H, 6.0; N, 13.6. Calc. for $C_{10}H_{24}Cl_3N_4Rh$: C, 29.3; H, 5.9; N, 13.7%). The *d–d* spectrum had bands at 299 (ε = 304) and 354 nm (ε = 223 dm^3 mol^{-1} cm^{-1}) [lit.,[9] 299 (ε = 308) and 354 nm (ε = 223 dm^3 mol^{-1} cm^{-1})]. The i.r. spectrum was comparable to that reported in the literature, ν(NH) at 3 060 and 3 170 (lit.,[9] 3 060 and 3 175 cm^{-1}). The *trans* complex was prepared as previously described.[9] The ligand 1,4,7,10-tetra-azacyclododecane tetrahydrochloride (cyclen·4HCl) was prepared by the general route briefly outlined by Richman and Atkins,[11] with certain modifications.

NOO'-Tritosyldiethanolamine was prepared as follows.† A four-necked flask (2 dm^3), equipped with a mechanical stirrer, thermometer, and nitrogen inlet tube, was charged with diethanolamine (21 g) and distilled with dry pyridine (192 cm^3). An Erlenmeyer flask containing toluene-*p*-sulphonyl chloride (115 g) was attached by Gooch tubing to the fourth neck of the flask. The reaction mixture was cooled in an ice–salt bath and toluene-*p*-sulphonyl chloride added at such a rate as to keep the temperature below 10 °C. After stirring the reaction mixture under nitrogen for 2 h in an ice-bath, a solution of hydrochloric acid (150 cm^3 of 11.6 mol dm^{-3} diluted to 600 cm^3 with ice and water) was added dropwise. The addition of the first 10 cm^3 of solution was carried out very slowly with rapid stirring, maintaining an internal temperature <5 °C. After the addition was complete the *product* was filtered off, thoroughly washed with ethanol, and dried in a vacuum oven at 50 °C. Yield *ca.* 96 g of a light yellow solid, m.p. 93—95 °C (Found: C, 52.6; H, 5.0; N, 2.7. Calc. for $C_{25}H_{29}NO_6S_3$: C, 52.9; H, 5.1; N, 2.5%).

NN'N''-Tritosyldiethylenetriamine was prepared as fol-

† We are grateful to Dr. T. J. Atkins for details of this procedure.

lows. To a solution of the diethylenetriamine (10.32 g, 0.1 mol) and sodium hydroxide (12.0 g, 0.3 mol) in water (100 cm^3) was added dropwise a solution of toluene-*p*-sulphonyl chloride (57.0 g, 0.3 mol) in diethyl ether (300 cm^3). The reaction mixture was stirred for 1—2 h at room temperature, during which time the *product* slowly crystallised. The colourless tosyl derivative was filtered off, washed with water then ether, and recrystallised from methanol, m.p. 156—158 °C (Found: C, 50.3; H, 5.2; N, 6.9. Calc. for $C_{25}H_{31}N_3O_6S_3 \cdot 1.5H_2O$: C, 50.6; H, 5.8; N, 7.1%).

The tetratosyl derivative of 1,4,7,11-tetra-azacyclododecane was prepared as follows. Tritosyldiethylenetriamine (28 g, 0.05 mol) was dissolved in dry dimethylformamide. Sodium hydride (80% in paraffin oil; 12.5 g, 0.42 mol) was added in small portions and when effervescence ceased the solution was warmed on a water-bath for *ca.* 0.5 h. The solution was cooled to room temperature and the excess of sodium hydride filtered off. The filtrate was transferred to a flask equipped with a thermometer, double-surface condenser, and magnetic stirrer. Tritosyldiethanolamine (28 g, 0.05 mol) dissolved in dimethylformamide (200 cm^3) was added and the mixture heated on an oil-bath for *ca.* 2 h at 110—120 °C with continuous stirring. The solution was cooled to room temperature and water (1 dm^3) added slowly with vigorous stirring. The solid *product* was filtered off, washed thoroughly with water, and dried in a vacuum oven at 60 °C (yield 32 g). The tosyl derivative can be recrystallised from formic acid if required, m.p. 268—271 °C (lit., 273 [12] and 292 °C [13]) (Found: C, 54.7; H, 5.4; N, 7.1. Calc. for $C_{36}H_{44}N_4O_8S_2$: C, 54.8; H, 5.6; N, 7.1%).

The tetratosyl derivative was hydrolysed as follows. Thirty-two grams of the crude product were dissolved in concentrated sulphuric acid (150 cm^3) and the solution heated on an oil-bath with continuous stirring at 110—120 °C for 48 h. The black solution was cooled to room temperature. The reaction mixture was then added slowly with stirring to sodium hydroxide solution (1 dm^3, 8 mol dm^{-3}) cooled in an ice-bath. On completion of the addition the pH was checked to ensure that pH >14 (pK_a values of cyclen are [14] $pK_1 < 1$, pK_2 1.15, pK_3 9.60, and pK_4 10.53). The mixture was allowed to stand at room temperature for *ca.* 2 h to complete the precipitation of sodium sulphate, which was then filtered off. The filtrate was extracted with portions of chloroform (4 × 200 cm^3) and the chloroform removed on a rotary evaporator. The oily *product* was dissolved in methanol (20 cm^3) and concentrated hydrochloric acid (*ca.* 2.5 cm^3) added. The precipitated tetrahydrochloride was filtered off and recrystallised from 50% hydrochloric acid. Yield 4.5 g (35%) (Found: C, 30.2; H, 17.5; N, 7.6. Calc. for $C_8H_{24}Cl_4N_4$: C, 30.2; H, 17.6; N, 7.6%). The ^1H n.m.r. spectrum of the amine tetrahydrochloride (D_2O solution) showed the complete absence of tosyl groups and a single signal at δ 3.34 due to the CH_2 groups; in $S(CD_3)_2O$ the signal occurs at δ 3.41. The detosylation may also be carried out electrochemically as described in the literature.[15,16]

The complex *cis*-[$RhCl_2$(cyclen)]Cl was prepared essentially as described by Collman and Schneider,[8] with the exception that it was recrystallised from 5 mol dm^{-3} hydrochloric acid–ethanol (50 : 50 v/v). The complex had $\lambda_{max.}$ 302 (ε 417; lit.,[8] 430) and 365 nm (ε 518 dm^3 mol^{-1} cm^{-1}; lit.,[8] 535) in aqueous solution (Found: C, 22.9; H, 5.8; N, 13.4. Calc. for $C_8H_{20}Cl_3N_4Rh$: C, 23.0; H, 5.85; N, 13.4%).

Kinetic Measurements.—The kinetics of base hydrolysis of *cis*-[$RhCl_2$(cyclen)]$^+$ were monitored spectrophotometrically. Loss of the first halide ligand was followed at 305 nm (the isosbestic point for loss of the second halide ligand) and hydrolysis of the second halide at 326 nm. Measurements were made with a Gilford 2400S instrument or a Gilford 222 modified SP 500 spectrophotometer. The cell compartment was thermostatted to ±0.1 °C by circulating water. In general the reactions were initiated by the addition of a small quantity of the solid complex on a ' plumper ' to the appropriate buffer solution. The final concentration of the complex was *ca.* 10^{-3} mol dm^{-3}. Loss of the first halide ligand was studied using borax buffers [17] adjusted to $I = 0.1$ mol dm^{-3} with potassium chloride. Potassium nitrate was unsuitable as the supporting electrolyte due to nitrate absorption at *ca.* 290 nm, and potassium perchlorate caused precipitation of the perchlorate complex. Plots of log $(A_t - A_\infty)$ were linear in each case and values of $k_{obs.}$ were obtained from the slopes of such plots.

Loss of the second halide ligand was studied using a variety of buffers [17] in the range pH 6.24—11.88, the ionic strength being adjusted to $I = 0.1$ mol dm^{-3} with potassium chloride. At 326 nm an absorbance increase occurs and values of $k_{obs.}$ were evaluated from linear plots of log $(A_\infty - A_t)$.

The pH of the buffers at the appropriate temperature was determined using a Radiometer 26 pH meter. Values of the hydroxide-ion concentrations were obtained using the appropriate pK_w value,[18] and activity coefficients estimated from the Davies equation.[19]

The kinetics of base hydrolysis of *cis*-[$RhCl_2$(cyclam)]$^+$ were studied using sodium hydroxide solutions in the range 10^{-2}—10^{-1} mol dm^{-3}. Interval scan spectra indicated that for base hydrolysis of the first Cl^- ligand an isosbestic point occurred at 323 nm, while for hydrolysis of the second Cl^- ligand an isosbestic point occurred at 332 nm. Both hydrolyses could be monitored at 254 nm where a marked decrease in absorbance occurred for the two reactions.

The first hydrolysis step was monitored by following the increase in absorbance at 332 nm (the isosbestic point for the second step). Steady infinity values were obtained in all cases although the absorbance changes were relatively small (0.05—0.1A). Loss of the second chloride ligand was monitored in isolation at 254 nm after the elapse of $10t_{\frac{1}{2}}$ for the loss of the first ligand. Plots of log $(A_\infty - A_t)$ or log $(A_t - A_\infty)$ were linear for at least three half-lives in all cases.

Sodium hydroxide solutions were prepared from B.D.H. CVS solutions and were standardised with potassium hydrogenphthalate. The ionic strength was adjusted to 0.1 mol dm^{-3} with potassium nitrate. Sodium perchlorate could not be used as the supporting electrolyte since the perchlorate salt *cis*-[$RhCl_2$(cyclam)][ClO_4] is virtually insoluble in water and immediately precipitated on the addition of *cis*-[$RhCl_2$(cyclam)]$^+$ to perchlorate solutions.

Routine u.v.–visible spectral measurements, including interval scan spectra, were made with a Perkin-Elmer 402 instrument. Hydrogen-1 spectra were recorded on a Perkin-Elmer R32 instrument at 90 MHz using D_2O–DCl solutions and sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal standard. Infrared spectra were obtained of KBr discs or Nujol mulls supported between sodium chloride plates using a Perkin-Elmer 457 spectrophotometer.

RESULTS AND DISCUSSION

The kinetics of base hydrolysis of *cis*-[$RhCl_2$(cyclam)]$^+$ were monitored at 332 nm (the isosbestic point for hydrolysis of the chlorohydroxo-complex). Values of $k_{obs.}$ at constant hydroxide-ion concentration are listed in Table 1. The $k_{obs.}$ values are proportional to the hydroxide-ion concentration giving k_{OH} (= $k_{obs.}/[OH^-]$) equal to 4.56×10^{-2} dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3} (K[NO_3]). The appropriate values of k_{OH} at 30, 36, and 41 °C are 7.22×10^{-2}, 1.67×10^{-1}, and 3.02×10^{-1} dm^3 mol^{-1} s^{-1} respectively giving $\Delta H^{\ddagger}$ = 82.4 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 5.7 J K^{-1} mol^{-1}.

TABLE 1

Kinetics of base hydrolysis of *cis*-[$RhCl_2$(cyclam)]$^+$ at I = 0.1 mol dm^{-3}, monitored at 332 nm

10^2[OH$^-$]/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}	10^2k_{OH}/ dm^3 mol^{-1} s^{-1}
(*a*) At 25 °C		
2.00	0.853	4.3
4.00	1.95	4.9
6.00	2.82	4.7
8.00	3.55	4.4
10.00	4.54	4.5
k_{OH} = (4.6 ± 0.3) × 10^{-2} dm^3 mol^{-1} s^{-1}		
(*b*) At 30 °C		
1.00	0.72	7.2
2.00	1.37	6.9
8.00	6.09	7.6
10.00	7.20	7.2
k_{OH} = (7.2 ± 0.3) × 10^{-2} dm^3 mol^{-1} s^{-1}		
(*c*) At 36 °C		
1.00	1.69	17
2.00	3.38	17
5.00	8.20	16
k_{OH} = (1.7 ± 0.1) × 10^{-1} dm^3 mol^{-1} s^{-1}		
(*d*) At 41 °C		
1.00	2.94	29
2.00	5.96	30
5.00	15.71	31
k_{OH} = (3.0 ± 0.1) × 10^{-1} dm^3 mol^{-1} s^{-1}		

$\Delta H^{\ddagger}$ = 82.4 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}_{298}$ = 5.7 ± 2 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298}$ = 80.7 ± 2 kJ mol^{-1}.

Values of $k_{obs.}$ at constant hydroxide-ion concentration are listed in Table 2 for the hydrolysis of the chlorohydroxo-complex. The $k_{obs.}$ are proportional to the hydroxide-ion concentration giving k_{OH} (= $k_{obs.}/[OH^-]$) equal to 7.1×10^{-3} dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The requisite values at 30 and 35 °C are 1.37×10^{-2} and 2.75×10^{-2} dm^3 mol^{-1} s^{-1} respectively giving $\Delta H^{\ddagger}$ = 106.5 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = 71 J K^{-1} mol^{-1}. The dichloro-complex undergoes base hydrolysis *ca.* 6.5 times faster than the chlorohydroxo-complex at 25 °C. The considerably higher $\Delta H^{\ddagger}$ for the chlorohydroxo-complex is coupled with a much more positive value of $\Delta S^{\ddagger}_{298}$ so that there is not a marked difference in the free energies of activation for the two reactions ($\Delta G^{\ddagger}_{298}$ = 80.7 kJ mol^{-1} for the dichloro-, 85.3 kJ mol^{-1} for the chlorohydroxo-complex). The substantial positive value of $\Delta S^{\ddagger}_{298}$ for the chlorohydroxo-complex is consistent with a dissociative S_N1(CB) mechanism to give a square-pyramidal intermediate.

TABLE 2

Kinetics of base hydrolysis of *cis*-[RhCl(cyclam)(OH)]$^+$ at I = 0.1 mol dm^{-3} (K[NO_3]) monitored at 254 nm

10^2[OH$^-$]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	10^3k_{OH}/ dm^3 mol^{-1} s^{-1}
(*a*) At 25 °C		
6.00	4.25	7.1
	4.30	7.2
	4.10	6.8
8.00	4.80	6.0
	4.75	5.9
	4.90	6.1
10.00	7.70	7.7
	8.65	8.6
	8.65	8.6
k_{OH} = (7.1 ± 1.0) × 10^{-3} dm^3 mol^{-1} s^{-1}		
(*b*) At 30 °C		
1.00	1.32	13
	1.38	14
	1.43	14
	1.33	13
4.00	4.71	12
	5.13	13
5.00	6.55	13
	6.03	12
8.00	12.17	15
	12.67	16
	11.17	14
	12.17	15
k_{OH} = (1.35 ± 0.1) × 10^{-2} dm^3 mol^{-1} s^{-1}		
(*c*) At 35 °C		
2.50	7.8	31
	7.4	30
5.00	12.5	25
	13.2	26
	13.2	26
8.00	18.3	23
	20.4	26
	22.8	28
	25.2	31
k_{OH} = (2.75 ± 0.3) × 10^{-2} dm^3 mol^{-1} s^{-1}		

$\Delta H^{\ddagger}$ = 106.5 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}_{298}$ = 71 ± 4 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298}$ = 85.3 ± 2 kJ mol^{-1}.

cis-[$RhCl_2$(cyclen)]$^+$ *Hydrolysis.*—Interval scan spectra at pH 9.2 established that *cis*-[$RhCl_2$(cyclen)]$^+$ underwent quite rapid hydrolysis. In the early stages of the reaction, tight isosbestic points were observed at 267 and 287 nm with somewhat ' looser ' isosbestic points at 326 and 349 nm. The absorption maxima of the dichloro-complex at 305 and 366 nm both decrease in intensity as the chlorohydroxo-species is formed. Subsequently, slower spectral changes occur with $\lambda_{max.}$ for the lowest-energy band moving to *ca.* 350 nm as the hydroxo-species is produced. Both reactions can be followed in isolation, since loss of the first chloride ligand leads to a marked decrease in absorbance at 305 nm which corresponds to an isosbestic point for hydrolysis of the second chloride ligand. Loss of the second ligand is readily monitored at 326 nm where an absorbance increase occurs. The interval scan measurements are consistent with the sequence of reactions in (i) and (ii).

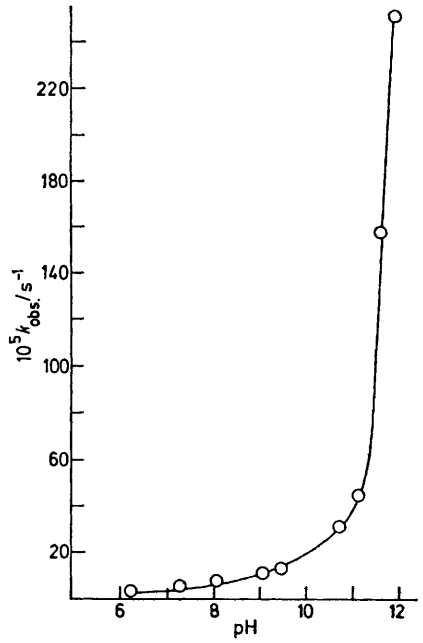
Table 3 lists values of $k_{obs.}$ for the first hydrolysis step. The reaction shows a first-order dependence on the

hydroxide-ion concentration with $k_{OH} = k_{obs.}/[OH^-] = 37.0$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}. The temperature dependence of the first hydrolysis step was

$$cis\text{-}[RhCl_2(cyclen)]^+ + [OH]^- \longrightarrow cis\text{-}[RhCl(cyclen)(OH)]^+ + Cl^- \quad (i)$$

$$cis\text{-}[RhCl(cyclen)(OH)]^+ + [OH]^- \longrightarrow cis\text{-}[Rh(cyclen)(OH)_2]^+ + Cl^- \quad (ii)$$

studied at the additional temperatures of 30, 35, and 45 °C giving $k_{OH} = 74.4$, 137.5, and 332 dm^3 mol^{-1} s^{-1} respectively. The corresponding activation parameters



pH–Rate profile for the hydrolysis of *cis*-[RhCl(cyclen)(OH)]$^+$ at 25 °C and $I = 0.1$ mol dm^{-3}

are $\Delta H^\ddagger = 73.5$ kJ mol^{-1} and $\Delta S^\ddagger = 32$ J K^{-1} mol^{-1}. The complex *cis*-[RhCl$_2$(cyclen)]$^+$ undergoes base hydrolysis some 2×10^4 times faster than *cis*-[RhCl$_2$(en)$_2$]$^+$ and some 800 times faster than *cis*-[RhCl$_2$(cyclam)]$^+$ (Table 4).

The kinetics of the second hydrolysis step were studied over the range pH 6.24—11.88. Values of $k_{obs.}$ are listed in Table 5. A pH–rate profile is shown in the Figure. The reaction shows only a slight pH dependence within the range pH 6.2—10. This dependence can be represented by the equation $k_{obs.} = k_0 + k_{OH}[OH^-]$

TABLE 3

Temperature dependence of the base hydrolysis of *cis*-[RhCl$_2$(cyclen)]$^+$ at $I = 0.1$ mol dm^{-3} (KCl)

pH	10^5[OH$^-$]/ mol dm^{-3}	$10^4 k_{obs.}/s^{-1}$	k_{OH}/ dm^3 mol^{-1} s^{-1}
(*a*) At 25 °C			
8.90	1.04	3.89	37.4
	1.04	3.96	38.1
9.21	2.12	7.96	37.6
	2.12	8.00	37.7
9.42	3.43	12.62	36.8
	3.43	11.17	32.6
9.59	5.07	19.16	37.8
	5.07	19.30	38.1
$k_{OH} = 37.0 \pm 1.5$ dm^3 mol^{-1} s^{-1}			
(*b*) At 30 °C			
8.86	1.23	9.09	73.9
	1.23	9.22	74.9
8.98	1.62	12.34	76.2
	1.62	12.51	77.2
	1.62	12.41	76.6
9.17	2.51	17.70	70.5
	2.51	18.00	71.7
$k_{OH} = 74.4 \pm 2$ dm^3 mol^{-1} s^{-1}			
(*c*) At 35 °C			
8.82	1.80	23.5	130.6
	1.80	27.3	151.7
9.15	3.84	53.8	140.1
	3.84	52.8	137.5
	3.84	53.1	138.3
9.51	8.80	117.5	133.5
	8.80	115.0	130.7
$k_{OH} = 137.5 \pm 4$ dm^3 mol^{-1} s^{-1}			
(*d*) At 45 °C			
87.6	3.02	99.1	328.1
9.43	14.20	478.0	336.6
$k_{OH} = 332 \pm 4$ dm^3 mol^{-1} s^{-1}			

$\Delta H^\ddagger = 73.5 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger_{298} = 32 \pm 2$ J K^{-1} mol^{-1}, and $\Delta G^\ddagger_{298} = 64.0 \pm 2$ kJ mol^{-1}.

where $k_0 = 5.8 \times 10^{-5}$ s^{-1} and $k_{OH} = 2.75 \times 10^{-1}$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}. Values of $k_{obs.}$ were calculated on the basis of this equation (Table 5). The pK_a value for *cis*-[RhCl(cyclen)(OH$_2$)]$^{2+}$ $\rightleftharpoons$ *cis*-[RhCl(cyclen)(OH)]$^+$ would be expected [20] to fall within the range 5—6, so that the hydroxo-species will be present almost exclusively throughout the pH range of the kinetic experiments. The k_0 term could represent aquation of the chlorohydroxo-complex or the kinetically equivalent process of base hydrolysis of the chloroaqua-complex. The pK_a data would suggest that the former process is more mechanistically reasonable. Base hydrolysis of the chlorohydroxo-complex becomes im-

TABLE 4

Rate constants and activation parameters for the base hydrolysis of some *cis*- and *trans*-[RhCl$_2$(N$_4$)]$^+$ complexes at 25 °C

Complex	k_{OH}/ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger_{298}$/ J K^{-1} mol^{-1}	$\Delta G^\ddagger_{298}$/ kJ mol^{-1}	Ref.
cis-[RhCl$_2$(en)$_2$]$^+$	2×10^{-3}				*a*
cis-[RhCl$_2$(trien)]$^+$ [b]	3×10^{-2}				*a*
cis-[RhCl$_2$(cyclam)]$^+$	4.56×10^{-2}	82.4	5.7	80.7	This work
trans-[RhCl$_2$(cyclam)]$^+$	2.74×10^{-3} [c]	147.7	105	116.4	7
cis-[RhCl$_2$(cyclen)]$^+$	37.0	7.35	32	64.0	This work

[a] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 1741. [b] trien = Triethylenetetramine. [c] At $I = 0.3$ mol dm^{-3}.

TABLE 5

Kinetics of hydrolysis of *cis*-[RhCl(cyclen)(OH)]$^+$ at 25 °C and I = 0.1 mol dm^{-3} (KCl)

pH	[OH$^-$]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	$k_{obs.}$(calc.) */ s^{-1}
6.24	2.26×10^{-8}	2.97×10^{-5}	
7.27	2.43×10^{-7}	5.03×10^{-5}	5.81×10^{-5}
8.03	1.40×10^{-6}	7.87×10^{-5}	5.87×10^{-5}
9.09	1.60×10^{-5}	1.04×10^{-4}	0.62×10^{-4}
9.48	3.94×10^{-5}	1.16×10^{-4}	0.69×10^{-4}
10.77	7.68×10^{-4}	3.08×10^{-4}	2.70×10^{-4}
11.13	1.76×10^{-3}	4.42×10^{-4}	5.42×10^{-4}
11.58	4.96×10^{-3}	1.57×10^{-3}	1.42×10^{-3}
11.88	9.89×10^{-3}	2.50×10^{-3}	2.78×10^{-3}

* Calculated from the expression $k_{obs.} = k_0 + k_{OH}[OH^-]$ where $k_0 = 5.8 \times 10^{-5}$ s^{-1} and $k_{OH} = 2.75 \times 10^{-1}$ dm^3 mol^{-1} s^{-1} at 25 °C.

portant at pH >10. For this process, $k_{OH} = 2.75 \times 10^{-1}$ dm^3 mol^{-1} s^{-1} so that hydrolysis of the first halide ligand is some 135 times faster than the second.

Base hydrolysis of *cis*-[RhCl(cyclen)(OH)]$^+$ gives initially *cis*-[Rh(cyclen)(OH)$_2$]$^+$ which will be in equilibrium with its conjugate acid *cis*-[Rh(cyclen)(OH)(OH$_2$)]$^{2+}$. It could be argued that in the presence of an excess of chloride ion (supporting electrolyte) the hydroxoaqua-complex would be rapidly anated back to the starting complex *cis*-[RhCl(cyclen)(OH)]$^+$, so that $k_{obs.}$ would then only give the rate constant for approach to equilibrium. For this reason kinetic runs were carried out at pH 8.10 (tris buffer) * and I = 0.1 mol dm^{-3} using solutions which were 0.09 and 0.01 mol dm^{-3} in chloride (in the latter case $K_2[SO_4]$ was used as the additional supporting electrolyte). For [Cl$^-$] = 0.09 mol dm^{-3} the value of $k_{obs.} = 9.4 \times 10^{-5}$ s^{-1}, while for [Cl$^-$] = 0.01 mol dm^{-3}, $k_{obs.} = 8.3 \times 10^{-5}$ s^{-1}. Since the values of $k_{obs.}$ are essentially independent of a nine-fold variation in [Cl$^-$] there is no evidence for reversibility of this type.

Activation Parameters.—For S_N2 substitutions on cobalt(III), $\Delta S^‡$ has been estimated [21] to be *ca.* −63 J K^{-1} mol^{-1}, while substantial positive entropies of activation (*ca.* 142 J K^{-1} mol^{-1}) are characteristic of the S_N1(CB) mechanism. Values of $\Delta S^‡$ for the base hydrolysis of rhodium(III) and iridium(III) halogeno-complexes tend to be less positive than those of cobalt(III) suggesting more associative character. Thus for the [MCl(NH$_3$)$_5$]$^{2+}$ complexes the values [21] of $\Delta S^‡$ for base hydrolysis are 146 (Co^{III}), 81.6 (Rh^{III}), and 79.5 J K^{-1} mol^{-1} (Ir^{III}). Recent reviews [22] favour an S_N1 mechanism, possibly with some associative character for the base hydrolysis of rhodium(III) and iridium(III) amine complexes. Monacelli and co-workers [20] have also observed markedly less positive values of $\Delta S^‡$ for the base hydrolysis of rhodium(III) complexes compared with the analogous cobalt(III) derivatives. As a result they have suggested that, unless such differences originate in the conjugate-base formation equilibrium, it may indicate for the rhodium complexes that some degree of nucleophilic interaction of a water molecule with the conjugate base occurs, *i.e.* an S_N2(CB) mechanism. For *cis*-[RhCl$_2$(cyclam)]$^+$ the values of $\Delta H^‡$ and $\Delta S^‡$ are 82.4 kJ mol^{-1} and 5.7 J K^{-1} mol^{-1}. The major factor contributing to the much faster hydrolysis rate of *cis*-[RhCl$_2$(cyclen)]$^+$ at 25 °C is the considerably more positive value of $\Delta S^‡$ compared to that of cyclam. Greater strain in the 12- compared to the 14-membered ring complex appears to favour a more dissociative type of reaction.

Since the stereochemical change is not observed with either the *cis* or *trans* complexes on base hydrolysis it is reasonable to assume that any five-co-ordinate intermediate has a square-pyramidal stereochemistry. The crystal-field stabilisation energy for the square-pyramidal stereochemistry is greater in a low-spin d^6 system than for a trigonal-bipyramidal structure. In view of the larger Δ value of Rh^{III} relative to Co^{III}, a square-pyramidal stereochemistry would be expected for five-co-ordinate Rh^{III}.

Values of $\Delta H^‡$ are markedly higher for the *trans*-dichloro-complex than for the two *cis*-dichloro-derivatives. In the *trans* complex the large $\Delta H^‡$ is partially counterbalanced by a substantial positive $\Delta S^‡$. The substantial positive $\Delta S^‡$ for *trans*-[RhCl$_2$(cyclam)]$^+$ is consistent with a dissociative mechanism.

We thank the S.R.C. for support and for the award of a Postdoctoral Fellowship (to P. R. N.).

[8/1489 *Received*, 14*th August*, 1978]

* tris = 2-Amino-2-hydroxymethylpropane-1,3-diol.

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