Structural and Mechanistic Studies of Co-ordination Compounds. Part 21.[1] Base Hydrolysis of Some *trans*-Tetra-aminedichlororuthenium(III) Cations

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The base-hydrolysis kinetics for the release of the first co-ordinated chloride from *trans*-$[RuCl_2L]^+$ [L = $(NH_3)_4$, $(en)_2$ (en = ethylenediamine), 3,7-diazanonane-1,9-diamine, or 1,4,8,11-tetra-azacyclotetradecane] have been studied. All the complexes react by second-order kinetics with complete retention of configuration. The observed increase in reactivity with increased chelation has been explained in terms of the nephelauxetic effect of the amine ligands on the central metal ion. An S_N1(CB) mechanism in which a σ-*trans* effect of the amido-group operates has been proposed to explain the reactions.

In their pioneering work, Broomhead *et al.*[2] suggested that the high rate of base hydrolysis of $[RuCl(NH_3)_5]^{2+}$ could be explained by an S_N2(CB) mechanism since the tendency to π-bond was not great for this second-row d^5 transition-metal complex. Later, Broomhead and Kane-Maguire[3] extended the study to include $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br, or I) and *cis*-$[Ru(en)_2X_2]^+$ (X = Cl or Br, en = ethylenediamine) and found that the release of the first halide from the latter system in dilute Na[OH] was too fast to be followed even at 0 °C. The release of the second halide, essentially from *cis*-$[Ru(en)_2(OH)X]^+$, was also found to be fast and stereoretentive. An S_N1(CB) mechanism was suggested to account for the rates and stereochemistry of the reactions. Recently, Ohyoshi *et al.*[4] reinvestigated the base hydrolysis of $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br, or I) at a higher hydroxide-ion concentration and suggested both S_N2 and S_N2(CB) as possible mechanisms. The aim of the present investigation is to examine the stereochemistry and chelation effect on the base hydrolysis of a series of complexes of the type *trans*-$[RuCl_2L]^+$ (L = $(NH_3)_4$, $(en)_2$, 3,7NH-nd (3,7-diazanonane-1,9-diamine), or cyclam(1,4,8,11-tetra-azacyclotetradecane)] in order to clarify this mechanistic ambiguity.

EXPERIMENTAL

The complexes *trans*-$[RuCl_2(NH_3)_4]^+$,[5-7] *trans*-$[RuCl_2(en)_2]^+$,[8] *trans*-$[Ru\{(R,S)\text{-}3,7NH\text{-}nd\}Cl_2]^+$,[7] and *trans*-$[RuCl_2(cyclam)]^+$ (ref. 8) were prepared by published methods. The base hydrolysis of these complexes in Na[OH] (or buffer) solutions was followed spectrophotometrically *in situ* using a Unicam SP 8000 recording spectrophotometer, equipped with a Weyfringe ADCP digital printer, or an Aminco–Morrow stopped-flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. Experimental details on sampling, data collection, temperature control, and data treatment have been described previously.[1]

RESULTS

Preliminary repetitive spectral scanning during the base hydrolysis of *trans*-$[RuCl_2L]^+$ [L = $(NH_3)_4$ or $(en)_2$] in

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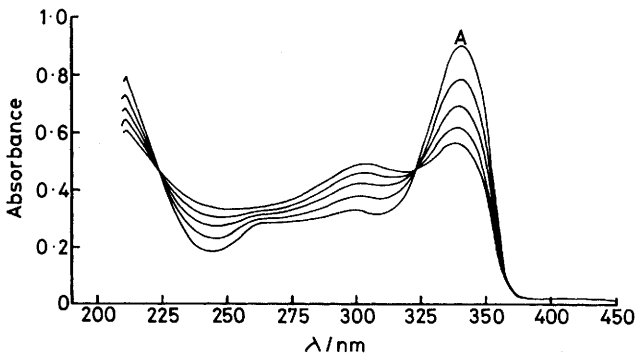
[7] C. K. Poon and D. A. Isabirye, *J.C.S. Dalton*, 1977, 2115.
[8] P. K. Chan, D. A. Isabirye, and C. K. Poon, *Inorg. Chem.*, 1975, **14**, 2579.

Na[OH] indicated well defined isosbestic points [L = $(NH_3)_4$ at 316, $(en)_2$ at 224 and 325 nm (Figure)] for *ca.* 2 half-lives for the release of the first chloride, as confirmed by Volhard's titration. When the reaction was stopped by an excess of toluene-*p*-sulphonic acid and an excess of NaCl was added, the subsequent spectral change was very similar to that occurring on chloride anation of the corresponding *trans*-$[RuCl(L)(OH_2)]^{2+}$, *trans*-$[RuCl_2L]^+$ being the final products.[7] Since it has been demonstrated that the anation of *cis*- and *trans*-aquahalogeno(tetramine)ruthenium(III)



Base hydrolysis of *trans*-$[RuCl_2(en)_2]^+$ in Na[OH] (0.01 mol dm^{-3}) at 20.0 °C. Curve (A) is the initial trace followed successively by traces at 2-min intervals

cations is stereoretentive,[7,9] these observations, following previous argument,[7] strongly suggested that the base-hydrolysis reaction of these complexes is also stereoretentive, as represented by equation (1). After *ca.* 2 half-lives a deviation from the isosbestic points was noted. This was attributed to the beginning of reaction (2) which was also confirmed by Volhard's titration. Since analytically pure samples of the corresponding *trans*-$[RuCl(L)(OH)]^+$ were

$$trans\text{-}[RuCl_2L]^+ + [OH]^- \longrightarrow trans\text{-}[RuCl(L)(OH)]^+ + Cl^- \quad (1)$$

$$trans\text{-}[RuCl(L)(OH)]^+ + [OH]^- \longrightarrow trans\text{-}[RuL(OH)_2]^+ + Cl^- \quad (2)$$

not available, reaction (2) was not followed. The kinetics of reaction (1) were then followed spectrophotometrically at a fixed wavelength [L = $(NH_3)_4$ at 331, $(en)_2$ at 342 nm] for *ca.* 2 half-lives while the isosbestic points were still maintained, and pseudo-first-order rate constants, $k_{obs.}$, were obtained by Guggenheim's method.[10] The second-order rate constants, k_{OH}, were obtained from the gradients of linear plots of $k_{obs.}$ against $[OH^-]$. The base hydrolysis of *trans*-$[RuCl_2(NH_3)_4]^+$ was also followed titrimetrically by Volhard's method by determining the amount of chloride released as a function of time at two different temperatures. The pseudo-first-order rate constant was obtained from a linear plot of $\ln(V_\infty - V_t)$ against time where V_t is the volume of $Ag[NO_3]$ consumed at time t and V_∞ the volume calculated for the complete release of one chloride. These plots are linear to 2 half-lives. The base hydrolysis of *trans*-$[RuCl_2(en)_2]^+$ was also followed in sodium tetraborate–boric acid buffer in order to examine the effect of buffer on the hydrolysis reaction. Here, the spectral change was very similar but the rate constants obtained

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

TABLE 1

Second-order rate constants for the base hydrolysis of *trans*-$[RuCl_2L]^+$ at I = 0.1 mol dm^{-3} adjusted with sodium toluene-*p*-sulphonate

L	θ_c/°C	$[OH^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_{OH}/dm^3 mol^{-1} s^{-1}
$(NH_3)_4$	15.0 [a]	1.0×10^{-1}	1.5×10^{-4}	1.5×10^{-3}
	19.4 [b]	5.0×10^{-2}	$1.3_4 \times 10^{-4}$	
		8.0×10^{-2}	$2.3_3 \times 10^{-4}$	$2.7_9 \times 10^{-3}$
		1.0×10^{-1}	$2.7_6 \times 10^{-4}$	
	20.0 [a]	1.0×10^{-1}	3.1×10^{-4}	3.1×10^{-3}
	21.5 [b]	5.0×10^{-2}	$1.7_6 \times 10^{-4}$	
		8.0×10^{-2}	$2.8_8 \times 10^{-4}$	$3.6_4 \times 10^{-3}$
		1.0×10^{-1}	$3.7_9 \times 10^{-4}$	
	27.6 [b]	5.0×10^{-2}	$4.1_9 \times 10^{-4}$	
		8.0×10^{-2}	$6.9_0 \times 10^{-4}$	$8.6_1 \times 10^{-3}$
		1.0×10^{-1}	$8.7_2 \times 10^{-4}$	
	31.3 [b]	5.0×10^{-2}	$7.1_6 \times 10^{-4}$	
		8.0×10^{-2}	$1.1_5 \times 10^{-3}$	$1.4_4 \times 10^{-2}$
		1.0×10^{-1}	$1.4_6 \times 10^{-3}$	
$(en)_2$	13.7 [b]	6.0×10^{-3}	$5.2_8 \times 10^{-4}$	
		8.0×10^{-3}	$7.2_0 \times 10^{-4}$	$8.8_8 \times 10^{-2}$
		1.0×10^{-2}	$8.8_3 \times 10^{-4}$	
	15.5 [b]	6.0×10^{-3}	$7.2_5 \times 10^{-4}$	
		8.0×10^{-3}	$9.6_0 \times 10^{-4}$	$1.2_1 \times 10^{-1}$
		1.0×10^{-2}	$1.2^1 \times 10^{-3}$	
	19.8 [b]	6.0×10^{-3}	$1.4_4 \times 10^{-3}$	
		8.0×10^{-3}	$2.1_3 \times 10^{-3}$	$2.5_8 \times 10^{-1}$
		1.0×10^{-3}	$2.6_3 \times 10^{-3}$	
	21.8 [b]	4.0×10^{-3}	$1.3_2 \times 10^{-3}$	
		6.0×10^{-3}	$2.2_1 \times 10^{-3}$	$3.5_8 \times 10^{-1}$
		8.0×10^{-3}	$3.3_0 \times 10^{-3}$	
	24.2 [b]	6.0×10^{-3}	$3.2_0 \times 10^{-3}$	$5.3_2 \times 10^{-1}$
		1.0×10^{-2}	$5.3_0 \times 10^{-3}$	
	40.0 [c]	$3.4_3 \times 10^{-5}$	$1.6_7 \times 10^{-4}$	
		$2.2_1 \times 10^{-5}$	$1.1_0 \times 10^{-4}$	5.0
		$1.3_0 \times 10^{-5}$	$6.5_0 \times 10^{-5}$	
3,7NH-nd	15.2 [d]	5.0×10^{-3}	$8.1_0 \times 10^{-2}$	
		1.0×10^{-2}	$1.6_5 \times 10^{-1}$	$1.6_4 \times 10$
		5.0×10^{-2}	$8.2_5 \times 10^{-1}$	
	19.8 [d]	5.0×10^{-3}	$1.6_7 \times 10^{-1}$	
		1.0×10^{-2}	$3.3_3 \times 10^{-1}$	$3.3_3 \times 10$
		5.0×10^{-2}	1.6_7	
	24.6 [d]	5.0×10^{-3}	$3.4_0 \times 10^{-1}$	
		1.0×10^{-2}	$6.8_0 \times 10^{-1}$	$6.7_7 \times 10$
		5.0×10^{-2}	3.3_3	
	29.8 [d]	5.0×10^{-3}	$7.2_8 \times 10^{-1}$	
		1.0×10^{-2}	1.4_3	$1.4_4 \times 10^2$
		5.0×10^{-2}	7.2_1	
cyclam	16.0 [d]	5.0×10^{-3}	$1.2_3 \times 10^{-1}$	
		2.5×10^{-2}	$7.5_0 \times 10^{-1}$	$2.7_8 \times 10$
		5.0×10^{-2}	1.4_4	
	21.1 [d]	5.0×10^{-3}	$3.0_9 \times 10^{-1}$	
		2.5×10^{-2}	1.5_3	$6.0_8 \times 10$
		5.0×10^{-2}	2.9_5	
	23.4 [d]	5.0×10^{-3}	$4.6_6 \times 10^{-1}$	
		2.5×10^{-2}	2.0_0	$8.5_0 \times 10$
		5.0×10^{-2}	4.1_0	
	26.2 [d]	5.0×10^{-3}	$5.4_3 \times 10^{-1}$	
		2.5×10^{-2}	3.2_5	$1.2_9 \times 10^2$
		5.0×10^{-2}	6.4_0	
	27.0 [d]	5.0×10^{-3}	$7.1_0 \times 10^{-1}$	
		2.5×10^{-2}	3.5_5	$1.4_2 \times 10^2$
		5.0×10^{-2}	7.1_0	
	30.1 [d]	5.0×10^{-3}	1.1_5	
		1.0×10^{-2}	2.2_0	$2.2_3 \times 10^2$
		5.0×10^{-2}	$1.1_0 \times 10$	

[a] By titrimetric method; [complex] = 0.01 mol dm^{-3}. [b] By spectrophotometric method using a Unicam SP 8000 recording spectrophotometer; [complex] = 1.0×10^{-4}—3.0×10^{-4} mol dm^{-3}. [c] The reaction was studied in sodium tetraborate–boric acid buffer solution over the range pH 8.62—9.10; [complex] as in footnote *b*. [d] By stopped-flow method; [complex] as in footnote *b*.

were slightly different from those determined in Na[OH]. [At 40.0 °C, $k_{obs.}$ = 5.0 and 6.6 dm^3 mol^{-1} s^{-1} respectively; the latter value was deduced from an Eyring plot of the

primary kinetic data (Table 1).] Details concerning the pH determination and thence $[OH^-]$ calculation, taking into account temperature and ionic-strength effects, have been described previously.[1]

The base hydrolysis of *trans*-$[RuCl_2\{(R,S)$-3,7NH-nd$\}]^+$ and *trans*-$[RuCl_2(cyclam)]^+$ in Na[OH] was too fast to allow repetitive spectral scanning using a Unicam SP 8000 recording spectrophotometer. However, it has been shown that sodium tetraborate buffer had no effect on the position of the isosbestic points for the base hydrolysis of *trans*-$[RuCl_2(en)_2]^+$. Hence, it seems possible to examine the nature of the base hydrolysis of these complexes in sodium tetraborate–boric acid buffer solutions. Here, isosbestic points were maintained for *ca.* 2.5 half-lives (3,7NH-nd at 234 and 336, cyclam at 237 and 342 nm). The stereoretentive nature of the reactions was determined by mixing a known solution of the complex with cooled Na[OH] (*ca.* 1×10^{-3} mol dm^{-3}) at a suitably low temperature. The reaction was allowed to proceed for *ca.* 2 half-lives, after which it was acidified with toluene-*p*-sulphonic acid, followed by addition of an excess of NaCl. The final spectrum, in each of the two cases, was identical to that of the corresponding pure *trans*-dichloro-complex. Kinetically, the base hydrolysis was followed by the stopped-flow method at 348 nm for the 3,7NH-nd and at 352 nm for the cyclam complex. The kinetic data are collected in Table 1.

DISCUSSION

The high sensitivity of ruthenium(III) amine complexes towards hydroxide and stereoretention of configuration, as observed previously [3] for *cis*-$[Ru(en)_2X_2]^+$ (X = Cl or Br), is characteristic of the base hydrolyses studied in this work. Table 2 summarizes the second-order rate constants, k_{OH}, at 25.0 °C and activation parameters for the base hydrolysis of *trans*-$[RuCl_2L]^+$ [L = $(NH_3)_4$, $(en)_2$, 3,7NH-nd, or cyclam]. Three general patterns of behaviour are noted. First, there is a genuine increase in reactivity with increased chelation. Secondly, these reactions are stereoretentive and have relatively substantial positive entropies of activation ($\Delta S^\ddagger$). Thirdly, *cis*-$[RuCl_2(en)_2]^+$ is much more reactive than the corresponding *trans* complex.*

TABLE 2

Effect of increased chelation on the second-order rate constants at 25.0 °C and activation parameters for the base hydrolysis of some complexes of the type *trans*-$[RuCl_2L]^+$

L	k_{OH} / dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}
$(NH_3)_4$	6.1×10^{-3}	97.5 ± 2.0	40 ± 15
$(en)_2$	6.0×10^{-1}	117 ± 2.0	145 ± 15
3,7NH-nd	7.2×10	106 ± 1.5	145 ± 12
cyclam	1.1×10^2	105 ± 1.5	146 ± 12

From the above observations it seems possible to consider the feasibility of various mechanisms for the base hydrolysis of these complexes. A simple bimolecular attack by hydroxide would not be consistent with the present observation. Since the central metal atom becomes less accessible with increased chelation, there should have been a marked decrease in the rate of reaction. Furthermore, an associative mechanism would probably have negative entropies of activation ($\Delta S^\ddagger$).[11] Similarly, it seems unlikely that these complexes react by an ion-pair mechanism.[12] According to this mechanism an increase in the size of the metal complex with increased chelation would probably lead to a smaller ion-pair association constant which in turn would lead to a slower rate. Gillard's redox mechanism,[13] in which a path involving labile cobalt(II) is postulated to account for the rapid base hydrolysis of cobalt(III) amine complexes, is also unlikely to apply to ruthenium(III) amine complexes in view of the non-labile character of Ru^{II} relative to Ru^{III} (*cf.* the considerable lability of Co^{II} relative to Co^{III}).

Nevertheless, if we assume an S_N1(CB) mechanism [14] to be operating, it is possible to explain most of the observations in this work. According to this mechanism, the rapid acid-base equilibrium between hydroxide and the amine complex produces an amido-conjugate base whose dissociation would then largely determine the rate of base hydrolysis of the complex. The lability of the conjugate base, however, depends critically on the efficiency of electron donation from the deprotonated nitrogen to the ruthenium(III) cation either through π or σ bonding, or both. π-Bonding effects are known to result in labilization by a combination of electron repulsion in the ground state and π stabilization of the resulting five-co-ordinate intermediate. This type of labilization is primarily responsible for the stereochemical changes associated with the base hydrolysis of cobalt(III) amine complexes since π stabilization is most effective when the amido-group occupies an equatorial position in a trigonal-bipyramidal five-co-ordinate species. This is most critical when the amido-group is *trans* to the leaving group in a *cis*-dianiono-complex. A *cis*-amido-group, from either a *cis* or a *trans* complex, may still stabilize a square-pyramidal intermediate, which leads to no stereochemical change. In the present study, the absence of any stereochemical change during the base hydrolysis of *cis*- and *trans*-ruthenium(III) amine complexes suggests that trigonal-bipyramidal intermediates having the remaining chlorides in the trigonal plane are not formed. This implies that π stabilization arising from a *trans*-amido-group is not the primary source of the reactivity of the conjugate bases. A π labilization arising from a *cis*-amido-group remains a possibility. If this is the case, one would then expect that both *cis*- and *trans*-$[RuCl_2(en)_2]^+$ should be rather similar in their reactivity since both isomers can generate a *cis*-amido-group. The observed divergence in the reactivity, with the *cis* isomer much more reactive, therefore, also seems to indicate that a π labilization from a *cis*-amido-group is not the source of labilization in these ruthenium(III)

* *cis*-$[RuCl_2(en)_2]^+$ reacts too rapidly [3] to be measured even in 10^{-4} mol dm^{-3} Na[OH] at 0 °C.

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[13] R. D. Gillard, *J. Chem. Soc.* (*A*), 1967, 917.

[14] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 177.

conjugate bases. This deliberation is consistent with the general belief [2,14] that ligand-to-metal π bonding effects are much less important for a larger d^5 ruthenium(III) system than for a d^6 cobalt(III) system, and that the rearrangement of ligands in the five-co-ordinate intermediate to give a trigonal bipyramid is much less favourable in the former system, a second-row transition metal, than in the latter. Recently, the importance of the σ-*trans* effect of non-labile ligands in affecting the kinetic lability of ruthenium(III) amine complexes has been recognized.[7] Sargeson and his co-workers [15] have also argued favourably for the σ-*trans* effect of an amido-group in labilizing cobalt(III) conjugate bases. In the present case, the difference in reactivity between *cis*- and *trans*-$[RuCl_2(en)_2]^+$ can be satisfactorily explained in terms of the σ-*trans* effects of amido-groups in their corresponding conjugate bases. In the conjugate base derived from the *trans* complex, the leaving chloride always lies *cis* to the amido-group, whereas in the *cis* complex it is possible for the leaving chloride to be *trans* to a deprotonated nitrogen. Since corresponding pairs of *cis* and *trans* conjugate bases differ only in the relative positions of the ligands, it seems reasonable to expect, as observed, that the *trans* conjugate base would dissociate much faster, by virtue of the σ-*trans* effect of an amido-group, than the *cis* counterpart.

On the basis of the $S_N1(CB)$ mechanism, the increased reactivity with increased chelation can be explained, in much the same way as for cobalt(III) amine complexes, in terms of the influence of the nephelauxetic effects of amine ligands on the central metal ion.[16,17] It has been shown spectroscopically [16] that the ability of some common saturated amine ligands to delocalize the non-bonding or weakly antibonding $3d$ electrons away from the central cobalt(III) ion increases with increasing chelation, and it seems reasonable to assume that this relative electron-expansion ability may also be true for other metal systems, such as Ru^{III}.[7] Accordingly, the tendency of the central metal ion to attract donor-electron density, and hence the enhancement of the σ-*trans* effect of a deprotonated nitrogen donor in the conjugate base, would also increase with increasing chelation. This effect, therefore, must outweigh the opposing solvation effect,[7] in order to explain the observed increasing base-hydrolysis rate constants with increasing chelation. In adopting this explanation, one would expect that the smaller $3d^6$ cobalt(III) ion with one more d electron than $4d^5$ Ru^{III} might experience a greater influence of the nephelauxetic effect of the amine ligands. However for the corresponding cobalt(III) complexes, the increase in rate constants in going from $(en)_2$ to cyclam is *ca.* 20-fold,[18] whereas the corresponding increase for Ru^{III} is 180. This is probably due in part to the fact that the base hydrolysis of *trans*-$[CoCl_2(en)_2]^+$ is approaching, and that of *trans*-$[CoCl_2(cyclam)]^+$ has reached, a limiting stage,[19,20] so that the relative increase in rates is much smaller than what it would have been. It is also due in part to the fact that the opposing solvation effect is much more important for the smaller cobalt(III) system.

Finally, the observed substantial positive entropies of activation ($\Delta S^{\ddagger}$) are fully consistent with the $S_N1(CB)$ mechanism.[11]

We thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for support, and the Hong Kong Government for the award of a Commonwealth Scholarship (to D. A. I.).

[7/1448 *Received*, 8*th August*, 1977]

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