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Substitution Reactions of Ruthenium(III) Ethylenediamine and Related Complexes. II. Base Hydrolysis of *cis*-Dihalogenobis(ethylenediamine)-, *cis*-Hydroxyhalogenobis(ethylenediamine)-, and Halogenopentaammineruthenium(III) Complexes

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Received February 10, 1969

No stereochemical changes accompany base hydrolysis of the complexes *cis*-$RuX_2(en)_2^+$ and *cis*-$RuXOH(en)_2^+$ (X = Cl, Br, I). In every case hydrolysis is very fast thus resembling the corresponding Co(III) complexes. The kinetics fit the rate law $-d[\text{complex}]/dt = k[OH][\text{complex}]$, and the large rates generally correlate with large values of the log *A* factors (15.0–20.7 sec^{-1}). The kinetics of base hydrolysis of $RuX(NH_3)_5^{2+}$ (X = Br, I) have also been studied. A conjugate base mechanism in which a *trans* effect operates can account for the reactivity and retention of configuration.

Introduction

In previous studies[1] which concerned the base hydrolysis of $RuCl(NH_3)_5^{2+}$ it was shown that the observed rapid loss of the chloro ligand could be understood in terms of a conjugate base mechanism. The rapidity of this base hydrolysis reaction was reminiscent of the behavior of analogous Co(III) complexes. Crystal field stabilization energy arguments together with the smaller electron affinity of Ru(III) when compared to Co(III) let to the prediction that there should be a reduced tendency for π bonding in Ru(III), with consequent reduced likelihood of rearrangement of the conjugate base to a trigonal bipyramid in an SN1CB mechanism. Accordingly we have studied the base hydrolysis of *cis*-$RuX_2(en)_2^+$ (X = halide ion, en = ethylenediamine) complexes in order to see what stereochemical changes might accompany substitution by hydroxide ion.

Preliminary experiments showed that in excess hydroxide replacement of the halide ligands proceeded to completion and that the primary reaction

$$cis\text{-}RuX_2(en)_2^+ + OH^- \longrightarrow cis\text{-}RuXOH(en)_2^+ + X^- \quad (1)$$

was extremely fast, even in 10^{-4} *M* sodium hydroxide at 0°. Attempts to use buffer solutions gave variable results so that this reaction rate has not been measured. However the secondary reaction

$$cis\text{-}RuXOH(en)_2^+ + OH^- \longrightarrow cis\text{-}Ru(OH)_2(en)_2^+ + X^- \quad (2)$$

though still rapid was slow enough to be followed by conventional techniques. Both *cis*-$Ru(OH)_2(en)_2^+$ and $RuOH(NH_3)_5^{2+}$ show further reactions in basic solution but these are slow compared to the replacement of halide.

Experimental Section

Materials.—*cis*-$RuX_2(en)_2^+$ (X = Cl, Br) and $RuX(NH_3)_5^{2+}$ (X = Br, I) were prepared and resolved as previously described.[2,3] Rotations which follow refer to the sodium D line. *cis*-$RuXOH(en)_2^+$ (X = Cl, Br) species were obtained by dissolving *cis*-$[RuXH_2O(en)_2](C_7H_7SO_3)_2 \cdot H_2O$ complexes in dilute sodium hydroxide.

***cis*-Diiodobis(ethylenediamine)ruthenium(III) Iodide Monohydrate, $[RuI_2(C_2H_8N_2)_2]I \cdot H_2O$.**—The complex *cis*-$[RuCl_2(en)_2]Cl \cdot H_2O$ (0.80 g, 0.0023 mol) in water (30 ml) was mixed with silver *p*-toluenesulfonate (1.94 g, 0.0069 mol) and heated near the boiling point for 5 min. The silver chloride was filtered off and the filtrate was poured into a solution of sodium iodide (20 g) in 8 ml of water. A dark purple solid was obtained and this was filtered off and washed with ice water. The yield was 1.14 g. *Anal.* Calcd for $C_4H_{18}I_3N_4ORu$: C, 7.75; H, 2.9; I, 61.4; N, 9.0. Found: C, 7.75; H, 3.0; I, 61.2; N, 8.9. The complex may be recrystallized from 0.5% aqueous sodium iodide solution. Attempts to prepare the diiodo complex by treatment of *cis*-$RuX_2(en)_2^+$ (X = Cl, Br) complexes with sodium iodide gave partially substituted compounds.

For kinetic runs solutions having the desired hydroxide concentrations were made by dilution of freshly prepared and standardized 0.1 *M* sodium hydroxide. Analytical grade sodium *p*-toluenesulfonate was used to maintain constant ionic strength.

Absorption Spectral Studies.—Spectral curves obtained during the base hydrolysis reactions of $RuClOH(en)_2^+$ at successive time intervals are shown in Figure 1. For all of the complexes studied good isosbestic points were obtained over the major part of the reactions. Spectra of the products from treatment of *cis*-$RuX_2(en)_2^+$ (X = Cl, Br, I) with excess sodium hydroxide were identical (λ_{max} 301 mμ, ϵ 2120 ± 50 cm^{-1} M^{-1}) and halide titrations showed that all coordinated halide ligands had been released. Furthermore the spectrum of $RuOH(NH_3)_5^{2+}$ (λ_{max} 297 mμ, ϵ 2145 cm^{-1} M^{-1}) was obtained from $RuBr(NH_3)_5^{2+}$ and $RuI(NH_3)_5^{2+}$ upon base hydrolysis.

Retention and Regeneration Experiments.—Optically active (−)*cis*-$[RuCl_2(en)_2]I$ (0.0565 g) was converted to the soluble chloride salt by shaking with an aqueous suspension of freshly precipitated silver chloride. The silver halides were filtered off and washed with a small amount of water. The filtrate and washings were made up to a volume of 5 ml thus giving a 1.13% solution of (−)*cis*-$[RuCl_2(en)_2]Cl$ which had a rotation of −0.052 ± 0.002° in the sodium D line. Rotations were measured with a Jasco UV-5 automatic polarimeter having a 1-cm path length. Sodium hydroxide (0.12 g) was then added and after 5 min the rotation had increased to −0.069 ± 0.002°. Chloride titration at this stage confirmed that both chloro ligands had been released. Concentrated hydrochloric acid (1 ml) was added giving a final Cl^- concentration of 1.8 *M*. The rotation immediately changed to near zero and then increased over a period of 6 hr to −0.047 ± 0.002°. After correction for dilution this value was identical with the original rotation.

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[1] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

[2] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc., A*, 546 (1967).

[3] K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **227**, 237 (1936).

Solutions obtained from the base hydrolyses of *cis*-$RuBr_2(en)_2^+$ and *cis*-$RuI_2(en)_2^+$ were found to give the calculated spectrum of *cis*-$RuCl_2(en)_2^+$ upon treatment with concentrated hydrochloric acid. (The acid had to be oxygen free, otherwise there was interference from the intensely colored I_3^- species.) Similarly $RuBr(NH_3)_5^{2+}$ could be regenerated almost quantitatively by addition of concentrated HBr to the base-hydrolyzed solution. No regeneration experiments have been carried out with $RuI(NH_3)_5^{2+}$.

Kinetic Studies.—Base hydrolyses of all complexes were found to obey the rate law $-d[\text{complex}]/dt = k_{OH^-}[\text{complex}][OH^-]$. In general the second-order rate constant k_{OH^-} has been evaluated from the plot of k_{obsd} *vs.* $[OH^-]$ where k_{obsd} is a pseudo-first-order rate constant calculated from the slopes of the plots of log $[(A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* time, where A refers to the absorbance of the complex at times t, zero, or infinity.

Results

Verification of both the order of the reactions and the method used in treating the data is contained in Table I. All rate constants were determined at least in duplicate. Most of the rates have been followed spectrophotometrically at the following wavelengths either by the disappearance of the halogeno complex absorption (for $RuBrOH(en)_2^+$, ϵ_{353} is 1260 and for $RuI(NH_3)_5^{2+}$, ϵ_{543} is 1870) or by the appearance of the hydroxy complex spectrum (for $Ru(OH)_2(en)_2^+$, ϵ_{301} is 2120 and for $RuOH(NH_3)_5^{2+}$, ϵ_{297} is 2145). Details of the methods used here have been given previously.[1,4] Some rates have also been measured titrimetrically.[1] For concentrations of hydroxide up to 20-fold in excess of complex there was good adherence to pseudo-first-order kinetics.

TABLE I

KINETIC DATA FOR BASE HYDROLYSIS OF *cis*-$RuXOH(en)_2^+$ AND $RuX(NH_3)_5^{2+}$ COMPLEXES

$10^4[RuClOH(en)_2^+]$,[d] M	$10^3[OH^-]$, M	10^3k_{obsd}, sec^{-1}	k_{OH}, M^{-1} sec^{-1}
1.97	4.75	2.60	0.55[a]
4.35	4.75	2.53	0.53[a]
9.11	4.75	2.62	0.55[a]
4.50	1.97	1.18	0.60, 0.61[a,c]
4.50	3.77	2.31	0.61[a]
4.50	7.0	4.19	0.60[a]
4.50	10.0	5.91	0.59[a]
$10^4[RuBrOH(en_2)^+]$,[d] M			
8.96	10.0	13.4	1.34[a]
4.50	3.77	5.56	1.42[a]
4.50	4.88	6.78	1.39[a]
4.50	7.0	10.3	1.46[a]
4.50	10.0	14.8	1.48[a]
$10^4[RuBr(NH_3)_5^{2+}]$,[e] M			
1.67	3.95	12.9	3.26[a]
2.00	0.988	3.56	3.60[a]
2.00	1.98	6.60, 7.03[f]	3.44[a]
2.00	3.95	12.9, 12.0[f]	3.17[a]
$10^4[RuI(NH_3)_5^{2+}]$, M			
2.10[g]	1.97	10.0	5.07[b]
4.05[g]	1.97	10.1	5.12[b]
2.00[h]	0.988	2.79	2.82[b]
4.00[h]	1.98	5.19	2.62[b]
2.00[h]	2.95	7.17	2.43[b]
4.00[h]	3.95	9.21	2.33[b]
2.00[h]	4.89	10.86	2.22[b]
$10^4[RuCl(NH_3)_5^{2+}]$,[i] M			
2.50	1.98	9.80	4.95[b]
2.50	2.95	13.6	4.60[b]
2.50	3.95	17.7	4.48[b]
2.50	4.94	21.0	4.25[b]

[a] Error ±7%. [b] Error ±5%. [c] By titration. [d] Ionic strength $\mu = 0.01$, temperature 25 ± 0.1°. [e] Temperature 16°, $\mu = 0.001$–0.004. [f] Measured by disappearance of the $RuBr(NH_3)_5^{2+}$ spectrum at 397 mμ. [g] Temperature 24.7 ± 0.1°. [h] Temperature 20 ± 0.1°. [i] Temperature 24.6 ± 0.1°, $\mu = 0.002$–0.005.

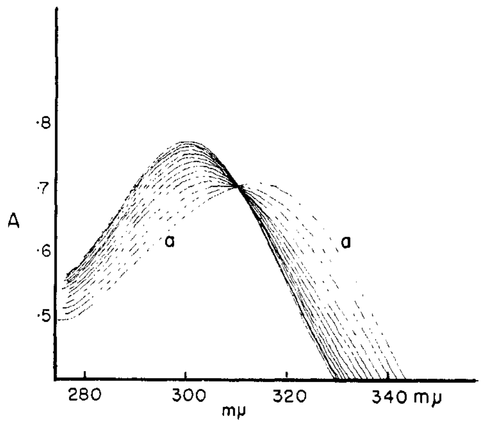

Figure 1.—Spectral changes during base hydrolysis of *cis*-$RuClOH(en)_2^+$ at 25°. [Complex] = 3.6 × 10^{-4} M; $[OH^-]$ = 3.8 × 10^{-3} M. Times of traces (sec): 60 (initial trace a), 120, 180, 260, 350, 420, 510, 590, 710, 830, 990, 1210, 1550, 2000 (final trace).

Discussion

Ruthenium(III) in these systems displays the striking combination of an extremely fast rate of base hydrolysis coupled with a total absence of any stereochemical change. To date this element is the only transition metal which manifests such behavior. It is obvious from the observed over-all second-order rate law that those mechanisms which have been prominent in accounting for the rates of analogous Co(III) complexes again present themselves here.[5-8] Despite the limited amount of data, some discussion of mechanism may be initiated.

Direct bimolecular attack by hydroxide would agree with the rate law and the retention of configuration, provided attack was restricted to the *cis* side of the complex. On the other hand, if symbiotic-effect[9] predictions for an S_N2 mechanism are explored, the fastest rates should be found for the hardest ligand leading to the rate order $Cl^- > Br^- > I^-$ with activation energies increasing along the series, which is contrary to the present findings (Tables I and II).

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(5) D. D. Brown, C. K. Ingold, and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953).

(6) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

(7) S. C. Chan, *J. Chem. Soc.*, *A*, 1124 (1966).

(8) R. D. Gillard, *ibid.*, *A*, 917 (1967).

(9) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).

TABLE II

ARRHENIUS PARAMETERS AND RATE CONSTANTS FOR BASE HYDROLYSIS OF Ru(III) COMPLEXES AT 24.6°

Complex ion	k_{OH^-}, M^{-1} sec^{-1}	E_a, kcal mol^{-1}	Log A (A in sec^{-1})
cis-$RuClOH(en)_2^+$	$0.5^{a,e}$	...	...
cis-$RuBrOH(en)_2^+$	$1.42^{a,d}$	20.3 ± 0.8	15.0 ± 0.6
$RuCl(NH_3)_5^{2+}$	4.95^b	27.3 ± 0.8	20.7 ± 0.6
$RuBr(NH_3)_5^{2+}$	11.3^c	23.1 ± 1.0	18.0 ± 0.8
$RuI(NH_3)_5^{2+}$	5.11^b	24.3 ± 0.2	18.5 ± 0.2

[a] Temperature 25.0 ± 0.1°. [b] $\mu = 0.002$. [c] $\mu = 0.001$. [d] $\mu = 0.004$. [e] $\mu = 0.04$.

The second-order rate law is also consistent with mechanisms involving a preequilibrium between the complex and hydroxide ion to give either a conjugate base[6] or what has been termed an "intimate" ion pair.[7] In the last mentioned mechanism a plot of pseudo-first-order rate constant (k_{obsd}) *vs.* hydroxide should depart from linearity toward high hydroxide concentration (but see ref 10). For the rather narrow range of hydroxide concentrations and within the limits of the experimental accuracy of this work these plots are linear. However this mechanism remains a possibility.

In the conjugate base mechanism the rate expression is

$$-d[\text{complex}]/dt = k_{cB}(K_a/K_w)[OH^-][\text{complex}]$$

where K_a refers to the equilibrium constant for dissociation of a proton from either ammonia or ethylenediamine, K_w is the ionic product for water, and k_{cB} is the rate constant for loss of halide ligand from the conjugate base. This step may be unimolecular or bimolecular with participation of a water molecule. Ruthenium(III) ammines are relatively acidic when compared with Co(III) complexes. For example the base-catalyzed hydrogen-exchange rate constants for $Ru(NH_3)_6^{3+}$ and $Co(NH_3)_6^{3+}$ are 6×10^8 and 1.6×10^6 M^{-1} sec^{-1}, respectively, at 25°. Also the pK_a of $RuClH_2O(en)_2^{2+}$ is 5.3 compared with 6.8 for the corresponding Co(III) complex.[4,11] Therefore values of K_a should be high for Ru(III). While a somewhat faster rate is thus predicted, this factor alone would not lead to the reactivity found. However, the conjugate base mechanism for Ru(III) differs in one respect from the same mechanism applied to Co(III). This arises from the $(t_{2g})^5$ electronic configuration of Ru(III). In the conjugate base mechanism proton loss gives an amido species characterized by the presence of a further lone pair of electrons. Repulsive interaction of this nitrogen lone pair with a $(t_{2g})^6$ metal such as Co(III) may then act as a driving force for rearrangement to a trigonal bipyramid accompanied by ligand loss. Ligand to metal π bonding can then ensue using the cobalt $d_{x^2-y^2}$ orbital.[6] For Ru(III) however this driving force must be reduced. In fact a simple MO picture would indicate a bond order of $^1/_2$ and consequently a stabilization of the stereochemistry of the conjugate base itself, so that no rearrangement need be expected. Similar effects would be predicted for any ligand with an available electron pair of the right symmetry and energy. The fact that loss of the halide ligands is very rapid may suggest that a *trans* effect is operative through effective amido group–ruthenium p_π–d_π interaction. Some information on the relative rates observed in Table I comes from equilibrium studies which show that Ru(III) has less preference for Br^- ligands than for Cl^- or I^-.[4] Since the differences in binding of Br^- and I^- are marginal, other factors such as solvation of the leaving group certainly must be included.

A recent suggestion by Gillard[8] concerning the role of a labile Co(II) pathway in accounting for the rapid base hydrolysis of Co(III) complexes might also be considered here for Ru(III). The availability of such a pathway has been correlated with the ease of reduction to the divalent state, as measured by the third ionization potentials. Literature values are 35.5, 32, 31, and 29.5 eV for Co, Rh, Ru, and Cr, respectively.[6] Thus while the driving force for reduction is less for Ru than for Co or Rh this element shows reactivity in base comparable to Co while Rh displays little or no such reactivity.[12] There would seem to be no general correlation between ease of reduction as measured by this parameter and the rate of base hydrolysis. If an Ru(II) path is important in the reaction with OH^-, then the observed retention of optical activity does mean that any bis(ethylenediamine)ruthenium(II) complex must be relatively inert to racemization.

Acknowledgments.—An award of a CSIRO studentship to Leon Kane-Maguire is gratefully acknowledged.

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