

Kinetics and mechanism of Ruthenium(III) catalyzed oxidation of nucleo substituted acidic medium

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Abstract : The kinetics of aquation and anation reaction have been studied with pentaammineruthenium (III) complexes containing halogenoacetates (fluoro-, dichloro-, bromo-, and iodoacetates). It has been found that the aquation reaction proceeds through two kinds of paths, *i.e.*, the acid-catalysed path and the acid-uncatalysed path, except the cases of dichloro- and trichloroacetate complexes. The aquations of dichloro- and trichloroacetate complexes are not catalysed by a proton because these ligand acids are strong acids. The equilibrium constants between $[\text{RuH}_2\text{O}(\text{NH}_3)_5]^{3+}$ and $[\text{RuO}_2\text{CRX}(\text{NH}_3)_5]^{2+}$ (O_2CRX = halogenoacetate), K_{eq} , were calculated from the anation and aquation rate constants. The k_{aq} and K_{eq} value for the fluoro-, chloro-, di-chloro-, trichloro-, bromo- and iodoacetato complexes are, respectively: K_{aq} , 10×10^{-5} , 7.510^{-5} , 19.110^{-5} , 49.010^{-5} , 6.810^{-5} and $6.710^{-5} \text{ sec}^{-1}$; K_{eq} , 5.210^{-3} , 3.610^{-3} , 9.010^{-3} , 2310^{-3} , 3.510^{-3} and 3.310^{-3} M , at 60 C. The free energy plot, $\log k_{\text{aq}}$ vs. $\log k_{\text{eq}}$, gave a straight line with a gradient of 1.0. It has been concluded that the acid-uncatalysed reaction proceeds via a $\text{S}_{\text{N}}1$ mechanism, while the acid-catalysed reaction seems to take place with a $\text{S}_{\text{N}}2$ mechanism. Some remarks have been made on the molecular interaction between the complex and the acid catalyst.

(Keywords:
)

Introduction

In a previous study reported on the kinetics of acid-hydrolysis for carboxylato pentaammine ruthenium(III) complexes [1]. It was found that one of the reaction paths, *i.e.*, the acid-uncatalysed one, proceeded through a dissociative mechanism; however, the mechanism

for the acid-catalysed path was not clear. We have now extended the study to obtain further information concerning the reaction mechanism. Thus, the aquation and anation rate constants were measured and the reaction mechanisms were discussed on the basis of the free-energy relationship².

Experimental

Materials

All the chemicals used were of reagent grade. Distilled water was used in all kinetic runs. The ionic strength and the acidity of the reaction solution were adjusted with *p*-toluenesulphonic acid and its sodium salt.

Chloropentaammineruthenium (III) Chloride was prepared by the method of Allen *et al.*, [3,4] from ruthenium trichloride and hydrazine hydrate. Found: H, 5.08; N, 23.75%. Calcd for $[\text{RuCl}(\text{NH}_3)_5]\text{Cl}_2$: H, 5.19; N, 23.98%.

Aquopentaammineruthenium(III) *parchlorate* was prepared by the method of Endicott and Taube [5].

Found: H, 3.20; N, 13.74%.

Calcd for $[\text{Ru}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$:
H, 3.42; N, 13.94%.

Halogenoacetatopentaammineruthenium(III) perchlorates were prepared by the method of Stritar and Taube [6] from chloropentaammineruthenium chloride, a halogenoacetate buffer solution and a zinc amalgam.

Found: C, 5.06; H, 3.40; N, 15.00%.
 Calcd for $[\text{RuO}_2\text{CCH}_2\text{F}(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 5.19; H, 3.68; N, 15.15%.

Found: C, 4.77; H, 3.50; N, 14.86%.
 Calcd for $[\text{RuO}_2\text{CCH}_2\text{Cl}(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 5.02; H, 3.59; N, 14.63%.

Found: C, 4.73; H, 3.18; N, 13.73%.
 Calcd for $[\text{RuO}_2\text{CCHCl}_2(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 4.68; H, 3.12; N, 13.65%.

Found: C, 4.58; H, 2.86; N, 12.83%.
 Calcd for $[\text{RuO}_2\text{CCCl}_3(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 4.39; H, 2.74; N, 12.79%.

Found: C, 4.40; H, 3.08; N, 13.14%.
 Calcd for $[\text{RuO}_2\text{CCH}_2\text{Br}(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 4.59; H, 3.25; N, 13.38%.

Found: C, 4.30; H, 2.85; N, 12.17%.
 Calcd for $[\text{RuO}_2\text{CCH}_2\text{I}(\text{NH}_3)_5](\text{ClO}_4)_2$:
 C, 4.21; H, 2.98; N, 12.28%.

Kinetic Runs. The aquation rate was measured spectrophotometrically as previously has been described [1].

The rate of anation is expressed by the ordinary second order rate formula:

$$\frac{dx}{dt} = k_{an}(a-x)(b-x) - k_{aq}x \quad (\text{i})$$

where, x is the concentration of the $[\text{RuO}_2\text{CRX}(\text{NH}_3)_5]^{2+}$ ion at time t and where a and b are the initial concentrations of $[\text{RuH}_2\text{O}(\text{NH}_3)_5]^{3+}$ and the halogenoacetate ion respectively. The last is known from the formal concentration and the acid dissociation constant under the given conditions. When the value of a is negligibly small as compared with b , eq. (i) can be integrated to give;

$$\ln \left[\frac{(x_{\infty} - x)}{x_{\infty}} \right] = -(k_{aq} + bk_{an})t \quad (\text{ii})$$

where, the suffix ∞ denotes the equilibrated state. When the anation is measured by a spectrophotometric method, eq. (ii) is replaced by;

$$\ln \left[\frac{(A_{\infty} - A_t)}{(A_{\infty} - A_0)} \right] = -(k_{aq} + bk_{an})t \quad (\text{iii})$$

where, A_0 , A_t , and A_{∞} are the extinctions of the reaction mixture in the initial state, at time t and in the final state respectively. By plotting $\log (A-A_t)$ vs. t , the apparent rate constant, k_{obs} can be obtained. The equilibrium quotient, k_{eq} , was calculated from the value of k_{aq} and k_{an} .

Results and Discussion

Aquation reactions

The pseudo first-order rate constants, k_{obs} , for the equation of complexes were measured at different hydrogen ion concentrations of the reaction solution. As is illustrated in Fig. 1, the plots of k_{obs} vs. the hydrogen ion concentration gave straight lines for all the complexes. The observed rate constant, k_{obs} , can be expressed by eq. (iv);

$$k_{obs} = k_{H_2O} + k_H[H^+] \quad (\text{iv})$$

where, k_{H_2O} is the acid independent rate constant and k_H is the acid dependent rate constant. In the cases of dichloro- and trichloroaceto complexes, the contribution of the k_H path in eq. (iv) was negligible compared with the k_{H_2O} path; therefore, the rate constant of aquation, k_{obs} , could be approximated as equal to k_{H_2O} . The calculated k_{obs} and values are listed in Table 1, together with the pK_a values of the ligand acids.

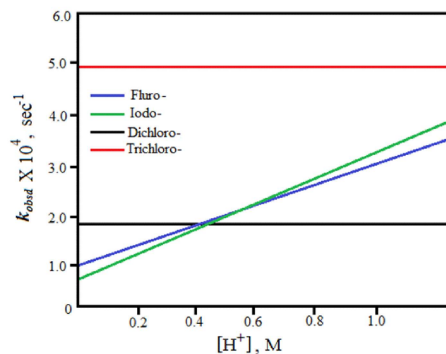


Fig. 1 Relationship between k_{obs} of aquation reaction and the hydrogen ion concentration. (60°C, $\mu=1.0$)

Table 1

Rate constants of acid catalysed and uncatalysed paths in the aquation reaction of halogenoacetatopentaammine ruthenium(III) complexes at $\mu=1.0$.

Complexes	Temperature($^{\circ}$ C)	pK _a [7](35 C)	10 ⁴ (s ⁻¹)	10 ⁴ (M ⁻¹ s ⁻¹)
Fluoroacetato-	40.1	2.624	0.1	0.25
	50.0		0.28	0.82
	60.0		1.0	2.3
	70.0		1.4	7.9
Chloroacetato-	40.0	2.90	0.05	0.44
	50.3		0.17	1.41
	59.8		0.75	2.50
	70.4		1.48	8.4
Bromoacetato-	40.3	2.94	0.10	0.50
	50.0		0.14	1.45
	60.0		0.68	2.6
	69.5		1.7	8.5
Iodoacetato-	40.2	3.21	0.04	0.86
	49.6		0.13	1.50
	60.2		0.67	2.7
	71.8		1.4	8.7
Dichloroacetato-	60.0	1.32	1.91	-
Trichloroacetato-	60.1	0.70	4.90	-

The rates of aquation increase with an increase in the ionic strength. Applying the Bronsted-Bjerrum-Christiansen formulation [8] (eq. v), the dependence of the ionic strength on the k_H value was investigated.

$$\ln k_H = \ln k_{H_2O} + \frac{2AZ_1Z_2\sqrt{\mu}}{1+B\sqrt{\mu}} \quad (\text{iv})$$

where, k_H is the acid dependent rate constant, k_{H_2O} is the same for infinite dilution, Z_1 and Z_2 are the charges on the two reactants, μ is the ionic strength, A is a constant equal to 0.509 for water at 25 $^{\circ}$ C and the B constant is of the order of the magnitude of unity.

The relationship between the values and μ shows according to the simplified equation, eq. (v). Since the present experiment was carried out at $\mu = 1.0$, this relationship is not sufficiently reliable; however, the slopes of the straight lines in Fig. 2 are both nearly +2 and these facts suffice

to show the role of the proton at the transition state in the acid dependent path.

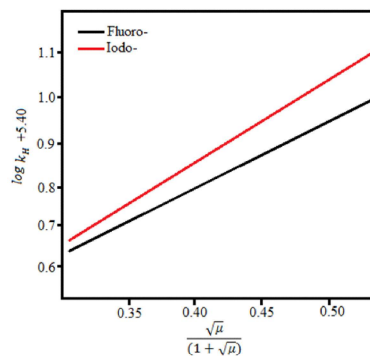
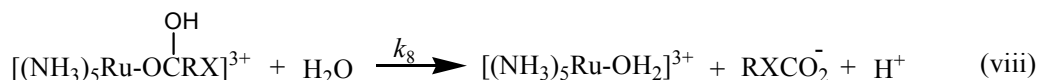


Fig. 2 Relationship between the acid catalysed rate constant k_H and the ionic strength of the solution. (60 $^{\circ}$ C, $[H^+] = 0.025$ M)

These results show that the aquation rate of the complex is dependent on the hydrogen ion concentration and that the two reaction paths

are involved in the reaction. This can be expressed by eq. (vi) for one path and by eq.

(vii) and eq. (viii) for the other path:



The rate constant of the uncatalysed path (eq. vi), k_6 corresponds to k_{aq} . Eq. (vii) and (viii) indicate the acid catalysed path, the rate constant, k_H of which can be expressed by eq. (ix);

$$k_H = k_g K_h \quad (\text{ix})$$

This relationship for the hydrolysis of similar complexes of Co(III), Rh(III) and Ir(III) has previously been reported⁹⁻¹³.

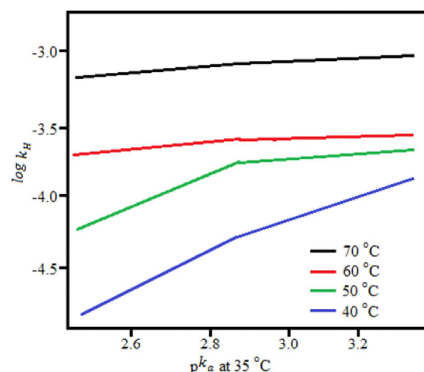
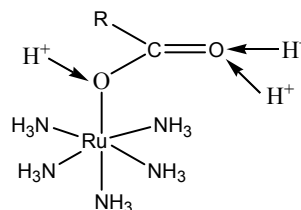


Fig. 3 Relationship between k_H of aquation reactions and pK_a of the ligand acids.

As is shown in Fig. 3, the plot of $\log k_H$ vs. the pK_a value of the ligand acid gives a straight line, with a gradient almost unity at lower reaction temperatures, while the gradient is about zero at higher temperatures, therefore, the weak acid

seems to behave as the strong acid. The smaller values of fluoroacetato complex compared to these of the iodoacetato complex (Table 1) may be due to the smaller tendency of forming a protonated intermediate shown by eq. (vii); that is, the electrostatic effect of the halogen atom is reflected in the constant of eq. (vii), which is important in determining the values.

Some remarks should be made here on the molecular interaction between carboxylatopentaammine ruthenium(III) complexes $[(\text{NH}_3)_5\text{RuOC}(=\text{O})\text{R}^{2+}]$ and the acid catalyst, H^+ . three distinctive modes of interaction can be allowed in view of the orbital symmetry and orbital energies of the two species:



$\text{Ru}-\text{O} = 2.5 \text{ \AA}$; $\text{Ru}-\text{N} = 2.23 \text{ \AA}$; $\text{N}-\text{H} = 1.031 \text{ \AA}$; $\text{Ru}-\text{O} = 2.5 \text{ \AA}$; $\text{C}-\text{O} = 1.28-1.43 \text{ \AA}$, $\angle \text{RuOC} = 105^\circ$; $\text{OCO} = 122.4-130$

The preliminary calculations of the all-valence-shell-electron extended Huckel MO on the above interacting system of $[(\text{NH}_3)_5\text{RuOC}(=\text{O})\text{R}^{2+}] - \text{H}^+$ [14] have demonstrated that the most plausible interaction of the H^+ catalyst occurs

predominantly in the direction of the orbital expansion of the nonbonding lone-pair 2p-orbital on the oxygen atom of the Ru-O bond in terms of the weakening of the Ru-O; in the case of $(\text{NH}_3)_5\text{RuOC}(-\text{O})\text{H}^+$, the bond population of Ru-O (0.085) is lessened to 0.073 by the electrophilic attack of the H^+ catalyst ($\text{H}^+ \text{ Å}$).

Conclusions

It is worthy of emphasis that the single C-O bond is not weakened by the attack of the

catalyst and that, in some measure, the solvent of H_2O participates in the weakening of the Ru-O bond; the details of this will be discussed. The rate constants for various anation reactions are practically the same; that is, there is little assistance by the incoming reaction. In other words, this interchange is the rate determining step for the anation reaction.

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