Substitution Reactions between Penta-ammineaquaruthenium(II) and Thiocyanato, Protonated Acetato, Cyano, and Oxalato Ligands in Aqueous Acidic Solutions

J. Folorunso Ojo, Olusegun Olubuyide,* and Olayinka Oyetunji
Department of Chemistry, University of Ife, Ile-Ife, Nigeria

The substitution reactions between penta-ammineaquaruthenium(II) and thiocyanato (SCN^-), protonated acetato (CH_3COOH), cyano (HCN), and oxalato ($H_2C_2O_4$–$HC_2O_4^-$) ligands (L) have been investigated in aqueous acidic solutions and at an ionic strength 0.20 mol dm^{-3} (LiCl). All the reactions obey the simple second-order rate law (i) and are independent of acid concentration in

$$-d[Ru(NH_3)_5(H_2O)^{2+}]/dt = k_{obs.}[Ru(NH_3)_5(H_2O)^{2+}][L] \quad (i)$$

the range $[H^+] = 1.0 \times 10^{-3}$ to 1.5×10^{-1} mol dm^{-3}. The observed second-order rate constants ($10^2k_{obs.}$/dm^3 mol^{-1} s^{-1}) measured at 25 °C [20.8 ± 1.1 (SCN^-), 11.3 ± 0.7 (HCN), 2.2 ± 0.2 ($H_2C_2O_4$–$HC_2O_4^-$), and 0.36 ± 0.03 (CH_3COOH)] fall within the characteristic range of substitution rate constants for the substitution of many other ligands previously reported and are therefore insensitive to the nature of the ligand. The activation parameters measured for the substitution reactions between penta-ammineaquaruthenium(II) and SCN^- and HCN respectively are as follows: $\Delta H^\ddagger = 88.00 \pm 8.4$ kJ mol^{-1}, $\Delta S^\ddagger = 35.7 \pm 3.1$ J K^{-1} mol^{-1}; $\Delta H^\ddagger = 50.4 \pm 5.4$ kJ mol^{-1}, $\Delta S^\ddagger = -94.0 \pm 9.3$ J K^{-1} mol^{-1}. A dissociative mechanism is proposed for all the reactions.

The substitution of water in penta-ammineaquaruthenium(II)[1,2] and *cis*-tetra-ammineaquaruthenium(II)[3,4] species by various incoming ligands (L) has been characterised by insensitivity to the nature of the ligand. For many neutral ligands,[1,2] the observed second-order rate constants for substitution fall within a narrow range (0.27×10^{-2} to 30.2×10^{-2} dm^3 mol^{-1} s^{-1}). Moreover, the activation parameters[1,2] are uniform for the class of ligands investigated. A dissociative mechanism, involving a rate-determining break-off of the water ligand in penta-ammineaqua- and tetra-ammineaqua-ruthenium(II) species in the transition state has therefore been suggested for these substitution reactions. Hitherto, most of the ligands investigated have been neutral nitrogen-containing heterocyclic ligands.[1,2]

In the present investigation, SCN^- and the protonated ligands HCN, $H_2C_2O_4$–$HC_2O_4^-$, and CH_3COOH are employed. There has not been any report of a *detailed* kinetic study of the substitution of water in penta-ammineaqua-ruthenium(II) by a negatively charged ligand. Although there have been reports[5] of the interaction of HCN with $[Ru(NH_3)_5(H_2O)]^{2+}$, no specific kinetic study of this interaction was made. It is anticipated that if a dissociative mechanism still applies to these reactions, then no significant variation in the second-order rate constants would be observed; moreover, following this, the protonation equilibria that could exist in the oxalate system ($H_2C_2O_4$–$HC_2O_4^-$) should not affect the substitution reactions.

Experimental

Materials.—Stock aqueous acidic solutions of the substituting ligands (SCN^-, HCN, $H_2C_2O_4$, CH_3COOH) were prepared from AnalaR grade samples of their sodium salts. Penta-ammineaquaruthenium(II) ion was generated by zinc amalgam reduction of acidic solutions of $[Ru(NH_3)_5Cl]Cl_2$ in an atmosphere of pure argon gas. Stock solutions of the ruthenium(II) reductant of *ca.* 10^{-2} mol dm^{-3} were prepared from which the appropriate aliquots were taken for the kinetic runs. All runs were performed in an inert gas (argon) medium; HCl and twice-recrystallised LiCl were the reagents used to maintain ionic strength.

Kinetics.—A conventional method using a Pye-Unicam Sp 500 series 2 u.v.–visible spectrophotometer was employed for the kinetic experiments. Absorbance changes were monitored at $\lambda = 324$ nm, the absorption peak[6] for $[Ru(NH_3)_5(H_2O)]^{2+}$ ($\varepsilon = 1.18 \times 10^3$ dm^3 mol^{-1} cm^{-1}), under pseudo-first-order conditions, with the concentration of the substituting ligand in at least ten-fold excess over that of the ruthenium(II) species. The cell compartment was thermostatted to the desired temperature to within ±0.1 °C.

Results

Pseudo-first-order rate plots were linear for at least four half-lives in all cases. The observed second-order rate constants ($k_{obs.}$) fit the rate law (1) and are independent of the acid

$$-\frac{d[Ru(NH_3)_5(H_2O)^{2+}]}{dt} = k_{obs.}[Ru(NH_3)_5(H_2O)^{2+}][L] \quad (1)$$

concentration in the range $[H^+] = 1 \times 10^{-3}$ to 1.5×10^{-1} mol dm^{-3} (Table 1).

At 25 °C and $I = 0.20$ mol dm^{-3} (LiCl), the measured average second-order rate constants ($k_{obs.}$/dm^3 mol^{-1} s^{-1}) for the substitution reactions between $[Ru(NH_3)_5(H_2O)]^{2+}$ and the ligands are $(20.8 \pm 1.1) \times 10^{-2}$ (SCN^-), $(11.3 \pm 0.7) \times 10^{-2}$ (HCN), $(2.2 \pm 0.2) \times 10^{-2}$ ($H_2C_2O_4$–$HC_2O_4^-$), and $(0.36 \pm 0.03) \times 10^{-2}$ (CH_3COOH).

Activation parameters obtained, using least-square analysis from the variation of the observed second-order rate constants with temperature (Table 2), are as follows: $\Delta H^\ddagger = 88.0 \pm 8.4$ kJ mol^{-1}, $\Delta S^\ddagger = 35.7 \pm 3.1$ J K^{-1} mol^{-1} (SCN^-); $\Delta H^\ddagger = 50.4 \pm 5.4$ kJ mol^{-1}, $\Delta S^\ddagger = -94.0 \pm 9.3$ J K^{-1} mol^{-1} (HCN).

Table 1. Average observed second-order rate contants ($k_{obs.}$) for the substitution of water in $[Ru(NH_3)_5(H_2O)]^{2+}$ by SCN^-, CN^-, CH_3COO^- and $H_2C_2O_4$–$HC_2O_4^-$ in aqueous acidic solutions; I = 0.20 mol dm^{-3}, T = 25 °C, $[Ru(NH_3)_5(H_2O)^{2+}]$ = (4.0—8.0) × 10^{-5} mol dm^{-3}

$[H^+]$/ mol dm^{-3}	L	$10^3[L]_T{}^a$/ mol dm^{-3}	$10^2 k_{obs.}{}^b$/dm^3 mol^{-1} s^{-1}
0.150	SCN^-	2.0	22.6
0.100		2.0	19.7
0.050		2.0	20.6
0.010		2.0	19.4
0.010		10	20.6
0.010		20.0	21.8
0.010		40.0	20.1
			c
0.100	HCN	20.0	11.1
0.100		15.0	11.3
0.050		20.0	12.0
0.050		15.0	12.0
0.010		40.0	11.0
0.010		20.0	11.8
0.010		10.0	11.0
0.010		5.0	11.4
0.010		2.0	10.8
0.003		20.0	9.7
0.003		10.0	11.4^f
0.100	CH_3COOH	2.0	0.39
0.100		1.0	0.37
0.050		2.0	0.39
0.050		1.5	0.32
0.010		20.0	0.36
0.010		10.0	0.39
0.010		2.0	0.31
0.010		1.5	0.39
0.001		2.0	0.37
0.001		1.0	0.38
			d
0.100	$H_2C_2O_4$–$HC_2O_4^-$	10.0	2.2
0.100		15.0	2.0
0.010		20.0	2.1
0.010		15.0	2.4
0.010		10.0	2.2
0.001		15.0	2.2
0.001		1.0	2.3
			e

[a] $[L]_T$ = Total ligand concentration. [b] $10^2 k_{obs.}$ Values are the average of at least 3—4 runs at each ligand concentration. [c] Mean 20.8 ± 1.1. [d] Mean 0.36 ± 0.03. [e] Mean 2.2 ± 0.2. [f] Mean 11.3 ± 0.7.

Table 2. Temperature dependence of the rate constants, and activation parameters for the substitution of water in $[Ru(NH_3)_5(H_2O)]^{2+}$ by SCN^- and HCN; I = 0.20 mol dm^{-3} (LiCl)

L	T/°C	$10^2 k_{obs.}$/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
SCN^-	25	20.8		
	32	41.6		
	37	73.9		
	40	103.5	88.0 ± 8.4	35.7 ± 3.1
HCN	25	11.3		
	30	13.8		
	35	19.9		
	40	30.7	50.4 ± 5.4	−94.0 ± 9.3

Discussion

At 25 °C and in the acid concentration range at which this investigation was made, $[H^+]$ = 1.0 × 10^{-3} to 1.5 × 10^{-1} mol dm^{-3}, the cyano, oxalato, and acetato ligands substitute for water in $[Ru(NH_3)_5(H_2O)]^{2+}$ in the protonated forms HCN, $H_2C_2O_4$–$HC_2O_4^-$ and CH_3COOH respectively since the dissociation constants[7] (K_a/mol dm^{-3}) of these protonated forms are 4.93 × 10^{-10} (HCN), 5.90 × 10^{-2} ($H_2C_2O_4$), 6.40 × 10^{-5} ($HC_2O_4^-$), and 1.76 × 10^{-5} (CH_3COOH). The kinetic data in Table 1 show that for the substitution of water in $[Ru(NH_3)_5(H_2O)]^{2+}$ by SCN^-, HCN, $H_2C_2O_4$–$HC_2O_4^-$, and CH_3COOH, the observed second-order rate constants fall within approximately the same narrow range obtained[1–4] previously for a wide variety of ligands, most of which were neutral nitrogen-containing heterocyclic ligands. The enthalpies of activation obtained in this study are likewise of the same order of magnitude as those obtained previously for a wide variety of ligands. These two observations are consistent with the view that the activation process leading to the substitution is a bond-breaking one and so a dissociative mechanism applies. On the basis of this view, the reaction scheme may be written as in equations (2) and (3). The rate law then becomes that in equation (4). Under the conditions of this investigation, equation (5) applies. The rate law (4) then reduces to equation (6) $\{(k_{obs.} = (k_1k_2/k_{-1})[H_2O]\}$.

$$[Ru(NH_3)_5(H_2O)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5]^{2+} + H_2O \qquad (2)$$

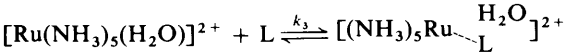
$$[Ru(NH_3)_5]^{2+} + L \xrightarrow{k_2} \text{products} \qquad (3)$$

$$\text{Rate} = \frac{k_1k_2[Ru(NH_3)_5(H_2O)^{2+}][L]}{k_{-1}[H_2O] + k_2[L]} \qquad (4)$$

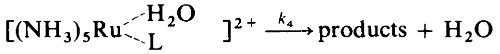
$$k_{-1}[H_2O] \gg k_2[L] \qquad (5)$$

$$\text{Rate} = k_{obs.}[Ru(NH_3)_5(H_2O)^{2+}][L] \qquad (6)$$

The data obtained in this study fit rate law (6). However, an associative pathway represented by equations (7) and (8) would lead to a rate law of the form (9), which is similar and indistinguishable from rate law (6).


(7)

$$[Ru(NH_3)_5(H_2O)]^{2+} + L \overset{k_3}{\rightleftharpoons} \left[(NH_3)_5Ru\begin{smallmatrix}H_2O\\ L\end{smallmatrix}\right]^{2+} \qquad (7)$$


(8)

$$\left[(NH_3)_5Ru\begin{smallmatrix}H_2O\\ L\end{smallmatrix}\right]^{2+} \xrightarrow{k_4} \text{products} + H_2O \qquad (8)$$

$$\text{Rate} = k_3[Ru(NH_3)_5(H_2O)^{2+}][L] \qquad (9)$$

The most powerful argument in favour of the dissociative pathway is the relatively small variations in the observed second-order rate constants as L is varied. The oxalato ligands could exist in the forms $H_2C_2O_4$ and $HC_2O_4^-$ and with very small concentrations of $C_2O_4{}^{2-}$ in the acid concentration range $[H^+]$ = 1.0 × 10^{-3} to 1.0 × 10^{-1} mol dm^{-3} employed in this study (Table 1). Previously,[1] it has been shown that penta-ammineaquaruthenium(II) substitution reactions involving N_2 as the incoming ligand and that involving cationic complexed dinitrogen, $[Ru(NH_3)_5(N_2)]^{2+}$, do not proceed at markedly different rates: for N_2, $k_{obs.}$ = 0.08 dm^3 mol^{-1} s^{-1}, $\Delta H^‡$ = 90 kJ mol^{-1}; for $[Ru(NH_3)_5(N_2)]^{2+}$, $k_{obs.}$ = 0.036 dm^3 mol^{-1} s^{-1}, $\Delta H^‡$ = 81 kJ mol^{-1}. The ratio of roughly two in the measured observed rate constants was attributed solely to a statistical phenomenon arising from the symmetrical N_2 ligand having two potential co-ordination sites for attack while the complexed N_2 in $[Ru(NH_3)_5(N_2)]^{2+}$ has one. Similarly, the $k_{obs.}$ values for the ligands 4-cyanopyridine (0.261 $dm^3 mol^{-1} s^{-1}$) and 4-cyanopyridinium ion (0.238 $dm^3 mol^{-1} s^{-1}$) do not differ by more than 10% even though it might have been expected that the positive charge on the ligand would alter greatly the tendency of the cyanopyridinium ion to form an outer-sphere complex with cationic $[Ru(NH_3)_5(H_2O)]^{2+}$. These four sets of pentaammineaqua substitution reactions have been reported to go through the dissociative mechanism route. The insensitivity of the observed second-order rate constants to acid concentration in the range $[H^+] = 1.0 \times 10^{-3}$ to 1.0×10^{-1} mol dm^{-3} quoted above in this study (for the oxalato ligands, $H_2C_2O_4$–$HC_2O_4^-$) is thus in agreement with the previous report,[1] since $[Ru(NH_3)_5(H_2O)]^{2+}$ does not discriminate between $H_2C_2O_4$ and $HC_2O_4^-$ and thus therefore suggests a dissociative mechanism.

Of the six ligands co-ordinated to Ru^{II} in $[Ru(NH_3)_5(H_2O)]^{2+}$, the aqua ligand is the most labile. π-Acceptor ligands such as pyridine, pyridine derivatives, N_2O, *etc.* have been shown[1,2] to replace water in $[Ru(NH_3)_5(H_2O)]^{2+}$. Moreover, in previous studies[5,8,9] $[Ru(NH_3)_5X]^{(2-n)+}$ (X = NCS, HCN, or C_6H_5NC; n = 0 or 1) have been identified in the interactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with NCS^-, HCN, and C_6H_5NC. In particular for NCS^-, Shepherd and Taube[2] have estimated by a competitive reaction method in the presence of pyrazine, the rate constant for substitution of free NCS^- into $[Ru(NH_3)_5(H_2O)]^{2+}$ to be 4 $dm^3 mol^{-1} s^{-1}$. This may be compared with our rate constant of 0.21 $dm^3 mol^{-1} s^{-1}$ for the substitution of water in $[Ru(NH_3)_5(H_2O)]^{2+}$ by SCN^-. The discrepancy is not surprising because we employed the direct measurement of the rate of disappearance of the $[Ru(NH_3)_5(H_2O)]^{2+}$ at λ = 324 nm, in the substitution of SCN^- into $[Ru(NH_3)_5(H_2O)]^{2+}$, while Shepherd and Taube[2] used the initial rate measurement associated with a system that exhibits *complicated* kinetic behaviour. The final product is the N-bonded isomer $[Ru(NH_3)_5(NCS)]^+$; an absorption peak was observed at λ = 490 nm, in agreement with our conclusion in an earlier report[8] on the reaction of free NCS^- with $[Ru(NH_3)_5(H_2O)]^{2+}$.

The positive value of $\Delta S^\ddagger$ obtained for the substitution reactions involving SCN^- in this study implies that the activated complex states are more disordered than the initial reactant states, and therefore a dissociative process is involved. The negative value of $\Delta S^\ddagger$ obtained for the reaction involving HCN might appear, on the basis of the above argument, to imply an associative[10] mechanism. This is not necessarily so, since similar negative values of $\Delta S^\ddagger$ had been obtained for substitution reactions[1–3] involving a wide variety of other ligands and these reactions were classified as involving a dissociative mechanism. Moreover, Tobe[11] argued that dissociative pathways occurring *via* a trigonal-bipyramidal intermediate give positive $\Delta S^\ddagger$ values, while negative $\Delta S^\ddagger$ values are observed for square-pyramidal intermediates. In addition, since $k_{obs.} = (k_1k_2/k_{-1})[H_2O]$, equation (10) applies so that the

$$\Delta S^\ddagger = (\Delta S_1^\ddagger - \Delta S_{-1}^\ddagger) + \Delta S_2^\ddagger \qquad (10)$$

overall $\Delta S^\ddagger$ term contains contributions from all the three entropy values. The difference in the magnitude and sign of the overall $\Delta S^\ddagger$ terms for SCN^- and HCN substitutions could therefore arise from the relative magnitudes of $\Delta S_2^\ddagger$.

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