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Kinetics and Mechanisms of the Reactions of Iodopentaammineruthenium(III) and Thiocyanate Ions in Aqueous Solution

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Investigations were carried out on the substitution of iodide ion by thiocyanate ion on iodopentaammineruthenium(III) ion in the temperature range 35–50°C. Rate increases linearly with SCN^-. A plot of 'K' *vs.* SCN^- shows positive intercept on rate axis, indicating both SCN^- dependent and SCN^- independent pathways for the substitution reaction. Substitution of SCN^- on aquapentaammine complex has also been investigated to make a comparative study of the two reactions. Both the reactions follow an associative interchange mechanism.

INTRODUCTION

Recently more attention is being given to the reactivity of ruthenium (II)/(III) complexes over to cobalt(III) complexes as it shows a more complex behaviour.[1] Substitution of ligand iodopentaammine complex by the ambidentate ligand thiocyanate is interesting as it may produce linkage isomers. Iodide ion and thiocyanate ion are both soft bases, having nearly equal softness parameters.[2] The present study has been made on the substitution of iodide ion by the thiocyanate in iodopentaammineruthenium (III) complex. To complete the study, anation of aquapentaammine complex ion by the thiocyanate ion has also been incorporated in the present investigation.

EXPERIMENTAL

Preparation of complexes

Iodopentaammineruthenium(III) Iodide

This complex was prepared by titrate method[3]. Aquapentaammineruthenium(III) perchlorate was prepared *in situ* either in aqueous solution or in the solid state after necessary crystallisation from the aqueous phase by the base hydrolysis of chloropentaammineruthenium(III) chloride.[4] An aqueous solution of the chloro complex was treated with one-tenth volume of 0.01 mol

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dm^{-3} sodium hydroxide solution at room temperature for 15–20 min and then neutralised with perchloric acid. The pH of the solution was adjusted to 2.5–3.0, at which the complex ion exists as the aqua species. It was used as such in solution or otherwise recrystallised after evaporation on a rotary evaporator. Purity of the solid compound was checked by analysis.

	% analysis, found (calcd)		
$[Ru(NH_3)_5I]I_2$	18.02	12..10	2.79
	(17.81)	(12.35)	(2.64)
$[Ru(NH_3)_5(H_2O)](ClO_4)_3$	19.72	14.03	2.79
	(20.04)	(13.89)	(2.98)

p-Toluenesulphonic acid (PTS) and its sodium salt (NaPTS) used in this set of experiment were Fluka Puriss grade. Double distilled water and distilled alcohol were used in the preparation of solutions. All other reagents and chemicals used in this study were either of analytical grade or else were purified by suitable methods.

A 'Sicospeck' spectrophotometer was used for recording all the spectra. The pH values of the experimental solutions were recorded with a 'SICO' model pH-Meter.

Kinetic measurements and product identification

The reaction was investigated over a small range of temperature (35–50°C) only as outside this temperature range deviations occur in unimolecular rate plot. The UV-visible spectra of the iodo complex has its absorption maxima at 545 nm and that of the thiocyanato complex at 495 nm along with other bands at 360 and 220 nm. During the reaction course the maxima position shifts from 545 nm to 500 nm and the species formed was found to be different from the thiocyanato complex. The product solution was concentrated on a rotatory evaporator, cooled and ethanol was added, when the least soluble product in aqueous-organic media precipitate out. It was recrystallised from aqueous solution and subjected to elemental analysis and other methods of characterization which are as follows:

% Analysis, found (calcd.): Ru = 25.1 (25..6), C = 7.0 (7.1), N = 23.60 (23.65) and H = 3.3 (3.3) for $Ru_3(NH_3)_{13}(SCN)I_2(SCN)_6$; IR bands ($\nu_{max}$) ($cm^{-1}$) 780, 455; UV-visible spectra (λ_{max}): 220, 360 and 500 nm.

From these observations the compound was characterised as $Ru_3(NH)_{13}(SCN)I_2(SCN)_6$ as observed by Prashad *et al.*[6] This reaction was followed at 500 nm where maximum change in absorbance occurs.

The aquapentaammine complex on similar treatment with thiocyanate ion at the same temperature range shows similar change in spectral pattern, with maxima position shifting from 490 to 495 nm with other bands at 205, 280 and 321 nm. The extinction value at 495 nm changes from near zero to 1000, showing the formation of the thiocyanatopentaammine complex. However, the extinction coefficient of the thicyanato complex has a much higher value.[5] The formation of the thiocyanato complex by the anation reaction is only partial in the present case.

RESULTS AND DISCUSSION

Rate constants as obtained from Guggenheim's plot which shows linearity for 2–3 half lives, for the iodopentaammine and the aquapentaammineruthenium(III) complexes are given in Table-1.

TABLE-1

OBSERVED RATE CONSTANTS (10^4 K, sec^{-1}) by GUGGENHEIM'S METHOD FOR THE REACTION BETWEEN $Ru(NH_3)_5\ X^{2+/3+}$ AND SCN^- ($X = I^-$ or H_2O) (= 40 mts)

X	Temp (°C)	NH_4SCN mol dm^{-3}					
		0.01	0.02	0.03	0.05	0.1	0.2
I^-	35	1.00	1.70	2.00	2.90	5.40	10.40
	40	1.17	2.00	2.60	3.55	6.34	11.95
	45	1.62	2.40	3.20	4.46	7.02	13.24
	50	2.00	2.83	4.02	5.81	8.02	14.88
H_2O	35	0.30	0.62	0.94	1.48	2.90	6.10
	40	0.50	1.00	1.53	2.40	4.82	9.92
	45	0.73	1.45	2.39	3.65	7.00	13.26
	50	1.04	1.98	3.17	5.02	10.06	19.24

Rate increases linearly with thiocyanate concentration for both the complexes. However, for the iodopentaammine complex the plot has a positive intercept on the rate axis while the intercept is zero in the case of the aquapentaammine complex. The rate expression for the iodo complex may be expressed as:

$$\text{Rate} = k_1 \text{ complex} + K_2 \text{ complex } SCN^- \qquad (1)$$

$$K_{obs} = k_1 + k_2\ SCN^- \qquad (2)$$

and for the aqua complex, it is

$$\text{Rate} = k_3 \text{ complex } SCN^- \qquad (3)$$

$$K_{obs} = k_3\ SCN^- \qquad (4)$$

k_1 is the rate constant for the SCN^- free path and k_2 and k_3 are rate constants for SCN^- dependent paths. The derived rate constants k_1, k_2 and k_3 are given in Table-2 along with corresponding activation parameters.

'k_{obs}' versus 'thiocyanate' plot does not show any deviation from linearity up to the highest concentration of the ligand (0.2 mol dm^{-3}) studied. Ion-pair formation does not seem to play any role at any stage of the reaction. Above 55°C, deviation from unimolecular rate plot indicates that a complicated form of the reaction takes place at this stage. Prashad *et al.*[6] observed the formation of a number of products above 55°C. At the experimental temperature range (30–50°C) uniform first order plot was obtained for initial 2 h, but the spectrum does not match with the thiocyanatopentaammine complex[5] as observed in the case of chloro and bromo complexes at 55–70°C range. At this stage the product complex

TABLE-2
RATE CONSTANTS AND ACTIVAATION PARAMETERS *VIA* SCN^- INDEPENDENT (k_1) AND SCN^- DEPENDENT (k_2 OR k_3) PATHS

Complex	Temp. (°C)				H‡	S‡
	35	40	45	50	kJ mol^{-1}	JK^{-1} mol^{-1}
$Ru(NH_3)_5I^{2+}$						
10^4 k_1 sec^{-1}	0.80 ± 0.03	0.87 ± 0.03	1.00 ± 0.05	1.16 ± 0.05	25 ± 5	−196 ± 12
10^4 k_2,$mol^{-1}sec^{-1}$	41.2 ± 1	54.2 ± 2	72 ± 2	98 ± 2	94 ± 4	7 ± 4
$Ru(NH_3)_5{\cdot}H_2O^3$						
10^4 k_3,$mol^{-1}sec^{-1}$	38 ± 1	51.2 ± 1	73.2 ± 2.5	87 ± 1	96 ± 4	15 ± 4

with three ruthenium centres forms. However, at higher temperature (65°C) the trimeric product gives the monomeric product. The rate constant of the thiocyanate independent path obtained from the intercept of 'K_{obs}' versus SCN^- plot, virtually represents aquation of the halo complex in the case of chloro and bromo complexes but it is much greater than the aquation rate constant of the iodopentaammine complex. At 40°C the rate constant for the thiocyanate in dependent path is 8.7×10^{-5} sec^{-1} while that of the iodo complex is only 0.26×10^{-5} sec^{-1}. Activation parameter values also differ from aquation values.[7] By simple reasoning, the intercept does not represent aquation of the pentaammine complex to aquapentaammine species but to some other form of the aquated product. The anating ambidentate ligand thiocyanate with more than one bonding site plays the major role in bringing three ruthenium ions together to give the trimeric product $Ru_3(NH_3)_{13}I_2(SCN)_6$. In this process it acts somewhat like a bridging ligand in bringing two or three complex molecules together. Whether the anation proceeds *via* the aquapentaammine species was investigated by anating the aqua complex with thiocyanate. Nevertheless, the rate constants obtained in the two cases are different. The anating step in the substitution process of the iodopentaammine complex does not involve the aquapentaammine species. The final product formed with the aquapentaammine complex is the nitrogen bonded $Ru(NH_3)_5SCN^{2+}$ species. The derived second order rate constant for the thiocyanate dependent path (k_2 and k_3) of the two complexes does not differ much. The spectral scanning pattern has also much similarity; so there may be some similarity in reaction mechanisms too. As the ion-pair formation has little significance, anation of the aquapentaammine complex most likely proceeds through the associative interchange mechanism which is also the likely process for the substitution of the iodide by thiocyanate ion and observed with water exchange reaction.[8] In conclusion we may say that in the experimental temperature range the thiocyanate ion replaces iodide ion from the pentaammine complex in an associative process simultaneously acting as a bridging ligand between the two or three molecules of the complex ion.

REFERENCES

1. (a) D.E. Richardson and H. Taube, *Coord. Chem. Rev.*, **60**, 107 (1984).
   (b) T.J. Meyer, *Pure Appl. Chem.*, **62**, 1003 (1990).
2. J.A. Davies and F.R. Hartley, *Chem. Rev.*, **81**, 79 (1981).
3. A.D. Allen, F. Bottomley, R.O. Harris, V.P.J. Reinsalu and C.V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).
4. J.A. Broomhead, F. Basolo and R.G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).
5. S.W. Lin and A.F. Schreiner, *Inorg. Chim. Acta*, **5**, 290 (1971).
6. R. Prasad, S.K.S. Yadav and U. Agarwalla, *J. Inorg. Nucl. Chem.*, **43**, 2359 (1981).
7. J.A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **7**, 251, (1968).
8. P. Bernhard, L. Helm, I. Rapaport, A. Ludi and A.E. Merbach, *Inorg. Chem.*, **27**, 873 (1988).

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