SHORT PAPER

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Kinetics of aquation of dichloro tetrapyridine ruthenium(II) complex in binary aqueous solvents

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First-order solvolysis rates of *trans*-dichloro tetrapyridine ruthenium(II) have been measured UV spectrophoto metrically over a wide range of solvent compositions in temperature ranges(40–55°C) in water–2-propanol and water–*t*-butanol mixtures. The rate of solvolysis is faster in the former than in the latter. Plots of log (rate constant) versus the reciprocal of relative permitivity of the co-solvent gave a non-linear relation for both co-solvents, this non-linearity is derived from a large differential effect of solvent structure between the initial and transition states. $\Delta S^{\#}$ of activation correlates well with the extrema in physical properties of the mixtures which are related to changes in solvent structure. Linear plots of $\Delta H^{\#}$ versus $\Delta S^{\#}$ were obtained and the isokinetic temperature indicates that the reaction is entropy controlled.

Keywords: ruthenium, complexes, solvents, solvolysis

We are currently studying the kinetics of reactions of inorganic complexes in mixed aqueous–organic solvents, particularly with a view to assessing the importance of metal-incoming water interaction in transition-state formation for the aquation of a variety of octahedral complexes.[1–7] The previous survey of aquation reactions of the ruthenium complexes takes into consideration, the variety of ligands and the leaving groups attached to the metal[8] ion in order to cover the study of all aquation reactions. The work also includes H NMR study,[9,10] the effects of pH on the rate of aquation. The determination of the activation volume and the thermodynamic parameters of activation were also reported.[11] The present work deals with a kinetic investigation of the aquation of the *trans*-dichloro tetrapyridine ruthenium (II) complex $[Ru(py)_4Cl_2]$. Detailed kinetic studies over a range of solvent composition and temperatures have been carried out for the aquation of this complex with 2-propanol, and *t*-butanol, as co-solvents mixed with water. The co-solvents used were chosen to permit an investigation of the solvolysis in a wide range of relative permittivities when they are mixed with water. The aquation reaction studied is of the form.

$$\textit{trans}\text{-}[Ru(py)_4Cl_2] + H_2O \rightarrow \textit{trans}\text{-}[Ru(py)_4Cl(H_2O)]^+ + Cl^-$$

Experimental

In the present investigation of *trans*-dichloro-tetrapyridine ruthenium (II). $[Ru(Py)_4Cl_2]$ its purity was established by elemental analysis. The rate of aquation of the complex was measured UV-spectrophotometrically, in a wide composition range of water mixed with a co-solvent such as 2-propanol and *t*-butanol.

Materials used

Preparation of the complex: The complex *trans*-$[Ru(Py)_4Cl_2]$ was prepared using the method reported by Poddar and Agarwala.[12] Dichloro bis (triphenyl phosphane) ruthenium (II) complex $[Ru(PPh_3)_2Cl_2]$ (200mg) was taken in pyridine (25ml) and refluxed for 4h under nitrogen. The excess pyridine was removed by evaporating on a water bath, yellow $[Ru(Py)_4Cl_2]$ separated and was filtered, washed with diethyl ether and dried under vacuum.

Kinetics of the aquation reaction

The rate of aquation of the complex was followed UV-spectrophotometrically by measuring the absorption band at $\lambda_{max} = 385$ nm. The measuring flask either containing water or co-solvent was kept in a thermostat which was controlled at the experimental temperature for half an hour till the two solutions reach thermal equilibrium. A weighed sample of the complex (0.8mg) was dissolved with aliquot portions of the thermostatted co-solvent as quickly as possible. The sample was then transferred quantitatively to a 25 ml flask to which the volume of distilled water was added to afford a concentration of 6.56×10^{-5} M. The zero time was recorded and a small amount of the solution was transferred in a 1-cm stoppered silica cell which was previously thermostatted in the cell compartment of the spectrophotometer.

The solution was allowed to stand for 5 minutes to reach thermal equilibrium of the experimental temperature. The build up of the optical density, A_t, at the selected wavelength was followed and recorded at short time intervals. Measurements were carried out till 90% completion of the reaction, the infinity value for each kinetic run was measured.

Full scans of the spectra of the complex were also recorded at different time intervals. The kinetics of aquation were calculated at the desired wavelengths. It was found that results of these measurements were identical with those obtained from the kinetic measurements.

Calculations

Rate constants: For the pseudo-first-order reactions the rate constant (k) for each point was calculated from the first-order rate equation:

$$\mathrm{Ln}\ ([A]\text{–}[AL]_o\ ) = -kt$$

where $[A]$, the concentration at any time (t) and $[A]_o$ is the initial concentration. Thus, k was calculated for each reaction from the slope of plot of log (A_∞–A_t) versus, time, where A_∞ is theoretical absorbance after the reaction is complete, and the absorbance at time *t*. Only points corresponding to 15–75% reaction were taken into consideration.

Results and discussion

Preliminary investigations: Spectra of *trans*-$[Ru(Py)_4Cl_2]$ in organic solvents. The full UV/Vis spectrum of this complex was recorded in 2-propanol and *t*-butanol. The blank was either the organic solvent or water + co-solvent according to the medium of the measured solution. The spectra of *trans*-$[Ru(Py)_4Cl_2]$ in 2-propanol and *t*-butanol showed a broad band with $\lambda_{max} = 385$ nm. The wavelength of the peaks at 385 nm did not shift on the addition of the co-solvent to water.

Rate constants: All kinetic experiments were done under pseudo-first-order conditions. Studying the spectra of the aquation of the complex *trans*-$[Ru(Py)_4Cl_2]$ in 2-propanol–water and *t*-butanol–water mixtures showed that there is a hyperchromic effect. The rate behaviour of some Ru(II) and Fe(II) macrocyclic complexes were studied.[13–15] These complexes showed a simple dissociative (*D*) or interchange (I_d) mechanism and the rate behaviour in our study of *trans*-$[Ru(Py)_4Cl_2]$ was found to follow the same dissociative mechanism.

$$\textit{trans}\text{-}[Ru(Py)_4Cl_2] \underset{k_2}{\overset{k_1}{\leftrightarrow}} [Ru(py)_4Cl]^+ + Cl^-$$

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

$$trans\text{-}[Ru(Py)_4Cl]^+ + H_2O \xrightarrow{k_3} [Ru(py)_4Cl(H_2O)]^+$$

For such mechanism, the observed pseudo-first order rate constant, neglecting the reverse reaction, is given by:

$$k_{obs} = \frac{k_1\, k_3\, [H_2O]}{k_2\, [Cl^-] + k_3[H_2O]}$$

In this study, all aquation reactions were carried out with large excess of water concentration and negligible concentration of chloride ion (Cl^-), under these conditions, the above expression reduces to: $k_{obs} = k_1$

Effect of temperature: The Arrhenius relation was satisfactorily obeyed, as the plots of log k versus the reciprocal of the absolute temperatures were linear. The activation energies ($\Delta E^\#$) of each solvent composition were calculated using a least-square procedure. The activation energy, $\Delta E^\#$, varies non- linearly with the mole fraction of the co-solvent, x_2 This phenomenon may be attributed to the differential effect of the solvent on the initial and transition states.

Thermodynamic activation parameters: (i) In aqueous-2-propanol: These parameters are usually taken as a measure of solvation effects. The free energies $\Delta G^\#$, enthalpies $\Delta H^\#$ and entropies $\Delta S^\#$ of activation were calculated using all the observed rate constants of different solvent compositions and temperatures by applying the least-squares procedure. The values of these parameters and their standard deviations are collected in Table 1. The variation of the thermodynamic parameters of activation with the mole fraction of the co-solvent (x_2), are shown in Fig. 1. The extrema observed for $\Delta H^\#$ and $\Delta S^\#$ (maxima at $x_2 = 0.14$ and 0.36 and minima at $x_2 = 0.19$ and 0.49) were close to those obtained from the physical properties measurement of the same solvent mixtures and from the results of previous studies of the aquation of *trans*-$[Co(4\text{-}MePy)_4 Cl_2]^+$[16] and *trans*-$[Co(4\text{-}EtPy)_4 Cl_2]^+$,[17] in the same solvent mixtures. At low mole fraction of 2-propanol, it was reported[18] that the alkyl chains of this co-solvent induce maximum structure formation within the surrounding flickering "icebergs" of structured water. With further additions of 2-propanol, a situation is reached[19] corresponding roughly to $x_2 \approx$ *ca* 0.1–0.15, in the region of the extremum which appeared in the excess enthalpy of mixing, ΔH^E and the ultrasonic absorption[20] of water-2-propanol mixtures. In this region of mole fraction, the cavities between the structured "icebergs" of water[18] are completely filled by alkyl groups, resulting in the onset of the breakdown of water structure. This structural changes affected differentially the ion solvent interaction in both the initial and transition state, and accordingly the solvolysis rate changes. The isokinetic temperature 300K calculated from the slope of the $\Delta H^\#$ versus $\Delta S^\#$ plot indicated that the solvolysis rate was entropy controlled.[21]

(ii) *In aqueous-t-butanol:* The calculated values of these thermodynamic parameters of activation are compiled in Table 2 and represented graphically in Fig. 2 as a function of the mole fraction of the co-solvent. The activation entropy ($\Delta S^\#$) is negative for the whole range of solvent composition, which indicates that there is non-random distribution of the solvent molecule around the species. Fig. 2 shows that for both $\Delta H^\#$ and $\Delta S^\#$ there is a maximum observed at $x_2 \approx (0.08)$ mole fraction of *t*-butanol, which is similar to that obtained in the aquation reaction of $[Co(Py)_4Cl_2]^+$ in the same solvent mixture[22] and a minimum at $x_2 = 0.16$. The extremum at $x_2 \approx 0.08$ is in the same general region of solvent composition, where ΔH^E ($x_2 \approx 0.08$–0.09) for minimum at 25°C[23] and the ultrasonic absorption ($x_2 = 0.1$)[24] show their extrema. This behaviour is related to sharp changes in solvent structure in the mixture.[24,25] It is suggested[25,26] that the extrema exist at the lower x_2, correspond to the exertion of maximum strain by the branched chain alkyl groups lying in the cavities between the flickering clusters of water[18] on the "clusters" of structured water, and the extrema at higher x_2, correspond to the beginning of the breakdown of the structure of the "clusters" due to the increasing stress within them. The isokinetic temperature, 305 K, calculated from the slope of the $\Delta H^\#$ versus $\Delta S^\#$ plot, indicated[27] that the solvolysis rate was entropy controlled. The non-linear relation of $\Delta S^\#$ with solvent composition (x_2) is an indication of specific solvation effects. The same behaviour and extrema were previously found for aquation of *trans*-$[Co(Py)_4Cl_2]^+$ and *trans*-$[Co(4\text{-}Etpy)_4Cl_2]^+$ in the same solvent mixture.[22,28] This behaviour was interpreted on the assumption that water molecules in the mixed solvent are not randomly distributed, due to strong hydrogen bonding with the co-solvent.

Table 1 Thermodynamic data for the aquation of *trans*-$[Ru(Py)_4Cl_2]$ in water–2-propanol mixtures

Solvent wt.%	$\Delta H^{\#a}$	$\Delta G^{\#a}$	$-\Delta S^{\#b}$
25.25	47.72±2.50	93.03±4.82	151.98±7.79
34.44	84.05±1.64	95.70±3.16	39.07±5.11
44.08	34.82±1.24	93.21±2.40	195.85±3.87
54.17	62.05±2.31	95.71±4.46	112.89±7.20
64.78	89.92±1.57	97.26±3.04	24.62±4.91
75.83	54.43±1.51	94.51±2.92	134.44±4.71
87.59	88.87±1.22	98.14±2.35	31.06±3.79

[a]kJ/mol, [b]J/mol/deg.

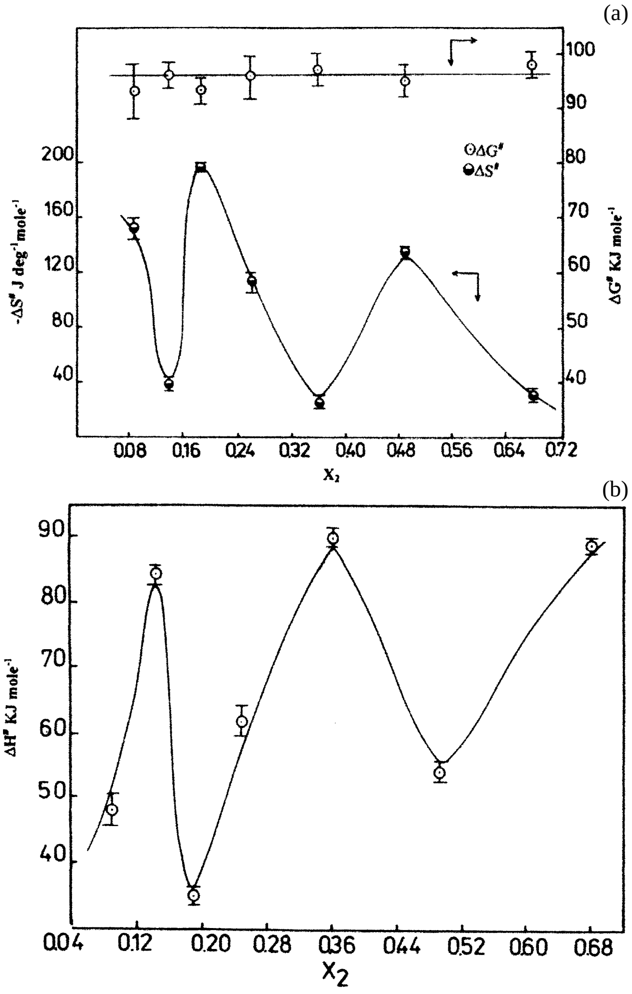

Fig. 1 (a), Dependence of the activation free energies and activation entropies of aquation of *trans*-$[Ru(Py)_4Cl_2]$ on the composition of water–2-propanol mixtures. (b), Dependence of the activation enthalpies of aquation of *trans*-$[Ru(Py)_4Cl_2]$ on the composition of water–2-propanol mixtures.

Table 2 Thermodynamic data for the aquation of *trans*-$[Ru(Py)_4Cl_2]$ in water–*t*-butanol mixtures

Solvent wt/%	$\Delta H^{\#a}$	$\Delta G^{\#a}$	$-\Delta S^{\#b}$
16.35	71.26±2.73	95.82±5.27	82.39±8.52
25.10	124.76±3.55	100.93±6.86	-79.92±11.08
34.27	96.264±9.05	98.83±17.47	8.59±28.23
43.88	52.81±1.48	96.61±2.86	146.90±4.64
35.98	81.74±3.30	98.51±6.37	56.22±10.29
64.60	74.38±4.32	97.08±8.34	76.12±13.47
75.68	96.40±5.71	98.96±11.01	8.57±17.8

[a]kJ/mol, [b]J/mol/deg.

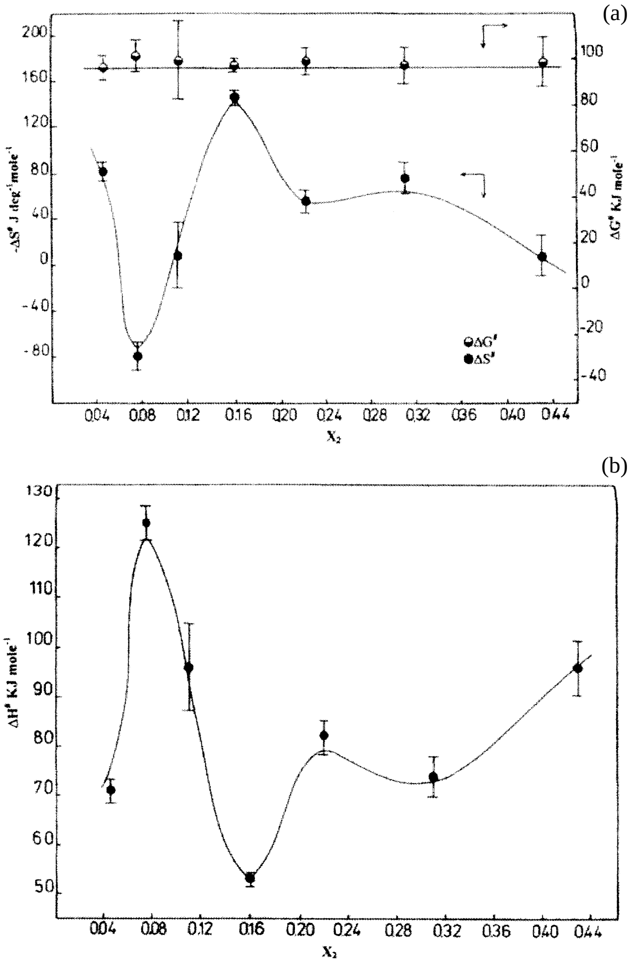

Fig. 2 (a), Dependence of the activation free energies and activation entropies of aquation of *trans*-[Ru(Py)$_4$Cl$_2$] on the composition of water–*t*-bunanil mixtures. (b), Dependence of the activation enthalpies of aquation of *trans*-[Ru(Py)$_4$Cl$_2$] on the composition of water–*t*-butanol mixtures.

Effect of the chloride ion (the leaving group): It was reported that Ru(II)–Py bonds are thermodynamically very stable kinetically, so the leaving group in the aquation of *trans*-[Ru(Py)$_4$Cl$_2$] is only one chloride ion as described in the experimental part. Thus the aquation reaction can be represented by

$$trans\text{-}[Ru(Py)_4Cl_2] + H_2O \rightarrow [Ru(Py)_4(H_2O)Cl]^+ + Cl^-$$

The differential solvation of the species in the ground and the activated state led us to exclude the associative mechanism[29] which involves the formation of a seven coordinate activated complex as

$$trans\text{-}[Ru(Py)_4Cl_2] + H_2O \rightarrow [Ru(Py)_4(H_2O)Cl_2]$$

The presence of such an uncharged intermediate would result in no change in the activation energy, because of similar solvation of the species in the initial and the transition states. Moreover, the simultaneous approach of water molecules towards the substrate and the extension of the Ru–Cl bond is unlikely to arise from the charge inequivalence of the water molecules and the chloride ion in the complex directly. Thus, a slow release of the chloride ion takes place prior to water substitution. These data suggested a dissociative S_N1 mechanism and the slowest step is given by Equation (1) followed by the final fast step as shown in Equation (2).

$$trans\text{-}[Ru(Py)_4Cl_2] \xrightarrow{\text{Slow}} [Ru(Py)_4Cl]^+ + Cl^- \quad (1)$$

$$[Ru(Py)_4Cl]^+ + H_2O \xrightarrow{\text{Fast}} [Ru(Py)_4(H_2O)Cl]^+ \quad (2)$$

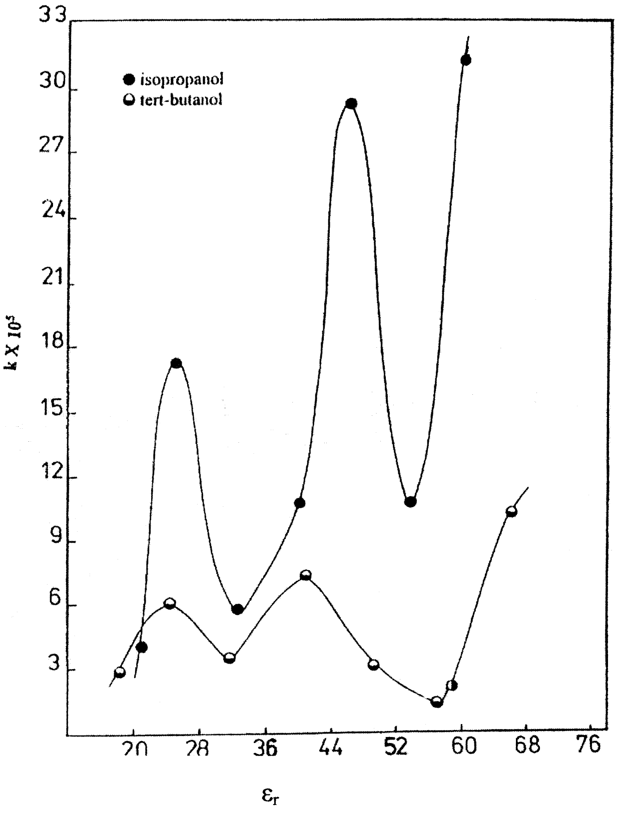

Fig. 3 Variation of isodielectric rate constant of the aquation of *trans*-[Ru(Py)$_4$Cl$_2$] with relative permitivity at 25°C.

Another evidence to exclude the S_N2 associative mechanism is that the pseudo first order rate constant of the solvolysis is independent of the concentration of water. A plot of log (observed rate constants) of the aquation of *trans*-[Ru(Py)$_4$Cl$_2$] against water concentration is non linear. This plot is an indication that the aquation proceeds via a dissociative S_N1 mechanism. These results are consistent with the previously reported data on the axial ligand substitution reactions of Ru(II) and Fe(II) macrocyclic complexes. Kinetic and themodynamic data reported by Kalifa *et al.*[13,15] on the axial ligation reactions of these complexes with some nitrogen, oxygen, phosphorous, and sulfur donors indicate that the reaction mechanism is dissociative (D) and the five coordinate intermediate possesses little or no ability to discriminate between nucleophiles. Comparison between the effects of 2-propanol and *t*-butanol on the kinetics of the aquation of *trans*-[Ru(Py)$_4$Cl$_2$] leads to the following conclusions. In the two investigated solvents, the kinetics of the reaction were controlled by $\Delta S^{\#}$. This conclusion was revealed from the observed non-linear relation between $\Delta H^{\#}$ and the mole fraction of the co-solvent, x_2, log k versus $1/\varepsilon_r$ and the calculated isokinetic temperature. Therefore, the change in solvent structure, due to the addition of the co-solvent to water, must be the dominant influencing factor on the reaction rate.

Figure 3 shows that in the used aqueous organic solvents, the general feature concerning the dielectric rate constant at 25°C, reveals an increasing tendency in the order; 2-propanol–water > *t*-butanol–water through the whole range of relative permittivity used.

The progressive addition of the co-solvent to water causes drastic changes in the structure of both individual solvents.[24,30–32] This change makes each mixture effectively as a new solvent.[33] Specific interaction may occur between one of the components and the species in the medium as permitted by the intrinsic solvent structure. Concerning solvent–solvent interactions, other properties such as solvent basicity and its relative permittivity may affect the rate of aquation of the investigated complex.

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