

Substitution reactions of ruthenium(II) complexes containing heterocyclic ligands: Aquation of bis-bipyridine-di(1, 2, 4-triazole)ruthenium(II) in perchloric acid

Biswanath Chakravarty* & Utpal Kumar Kar

Department of Chemistry, University of Kalyani,
Kalyani 741 235, India

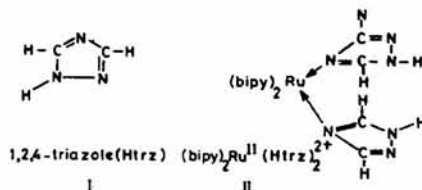
Received 31 January 1994; revised 3 May 1994;
accepted 20 June 1994

Aquation of $[\text{Ru}(\text{bipy})_2(\text{Htrz})_2]^{2+}$, (where Htrz = 1, 2, 4-triazole, a heterocyclic ligand) in the presence of perchloric acid ($0.05\text{--}1.0\text{ mol dm}^{-3}$) has been investigated spectrophotometrically between 21° to 40°C . The reaction proceeds in stages with the formation of monoaqua and diaqua products which subsequently undergoes a redox reaction to give ruthenium(III) and other products. Activation parameters are: $\Delta H^\ddagger$ 64 ± 4 , 64 ± 3 and $73 \pm 4\text{ kJ mol}^{-1}$ and $\Delta S^\ddagger$ -94 ± 8 , -102 ± 8 and $-76 \pm 10\text{ JK}^{-1}\text{ mol}^{-1}$ respectively for the first step and acid-free and acid-catalysed paths of the second step. Compared to chloride complex the triazole complex is more inert due to its higher enthalpy of reaction and bonding properties. Aquation of the complex shows appreciable associative character.

The chemistry of ruthenium(II)-polypyridine complexes is topically interesting because of their wide application in energy conservation processes¹. Lot of work has been done on the mechanistic aspect of these complexes, bulk of which deals with electron-transfer processes²⁻⁴ and a few on thermal substitution reactions⁵⁻⁸. These encompass studies with simple ligands like halides, pseudohalides, nitrogen containing bases and solvated molecules like water, methanol etc. In the present communication we report the aquation reaction of a polypyridine ruthenium(II) complex having the heterocyclic ligand, 1, 2, 4-triazole as two monodentate ligands. The choice of this type of complex bears some significance owing to: (i) the triazole can act both as a monodentate or a bidentate ligand. However, because of its geometry, possibility of chelate formation is remote. Alternatively bidentate coordination would lead to dimerization as observed with the corresponding pyrazolato complex⁹ and (ii) coordination of triazole to $\text{Ru}(\text{bipy})_2^{2+}$ moiety may also

supply information regarding their donor-acceptor properties. This may thus also serve as a useful material for the study of electron-transfer processes.

The structure of the ligand and the complex are represented in I and II.



Experimental

Both the complexes $\text{Ru}(\text{bipy})_2(\text{trz})_2 \cdot \text{H}_2\text{O}$ and $\text{Ru}(\text{bipy})_2(\text{Htrz})_2$, $(\text{PF}_6)_2 \cdot 1/2(\text{CH}_3)_2\text{CO}$ were prepared by following the method of Vos *et al.*¹⁰ Purity of the complexes were checked by their elemental analysis.

All other reagents used in the study were of reagent grade and doubly distilled water was used for making the solutions. As the complex is stable in air, no special precaution was adopted for handling the sample for kinetic measurements or other experimental manipulations.

Kinetic measurements

All the rate measurements were carried out spectrophotometrically at 480 nm ($\log \epsilon = 4.602$) corresponding to the absorption maxima of the ruthenium (II)-triazole complex. In a typical experiment a solution of perchloric acid of appropriate strength and containing requisite amount of sodium perchlorate was thermostated to equilibrate the temperature and then the solid complex was added to give a complex concentration of $5 \times 10^{-4}\text{ mol dm}^{-3}$. The reaction vessel was shaken vigorously and an aliquot of the solution was quickly transferred to the thermostated cell chamber of an ECIL (India) spectrophotometer. The reaction was followed by observing the gradual decrease in absorbance of the solution with time.

The first order rate plot of $\log \{(A_0 - A_\infty)/(A_t - A_\infty)\}$ versus time t (A_0 , A_t and A_∞ denote absorbances at zero time, time t and at the end of the reaction) is non-linear, showing more than one reaction taking place simultaneously. However, semilog plot of $(A_t - A_\infty)$ versus t at later

Table 1—Rate constants for the aquation of $[\text{Ru}(\text{bipy})_2(\text{Htrz})_2]^{2+}$ [Complex] = $5 \times 10^{-4} \text{ mol dm}^{-3}$; $I = 1.0 \text{ mol dm}^{-3}$ (k_1 and k_2 denotes first and second stages of aquation, deviations are within $\pm 3\%$)

Temp. °K	$[\text{HClO}_4]$ mol dm^{-3}	$10^4 k (\text{s}^{-1})$	
		k_1	k_2
294	0.2	3.95	1.32
	0.4	5.43	1.42
	0.6	5.71	1.91
	1.0	6.76	2.08
298	0.25	5.46	1.95
	0.3	5.55	2.22
	0.5	7.10	2.52
	1.0	7.80	3.57
	1.0 (Comp. $1 \times 10^{-3} M$)	7.84	3.71
305	0.1	6.94	2.45
	0.2	8.06	2.96
	0.4	10.60	3.06
	0.6	10.79	3.35
	1.0	12.70	4.99
308	0.05	6.81	3.46
	0.1	8.06	3.75
	0.2	11.00	4.08
	0.3	12.65	4.38
	1.0	14.15	7.04
313	0.1	13.91	4.52
	0.2	16.20	5.22
	0.3	16.67	6.00
	0.4	17.65	6.28
	1.0	19.20	9.77

time shows linearity. The linear portion of the log $(A_t - A_\infty)$ versus time at longer times yields k , the first order rate constant for the slow reaction. A plot of log $\{(A_t - A_\infty) - (A_t - A_\infty)_0\}$ versus time, is also linear [$(A_t - A_\infty)_0$ denotes extrapolated linear portion of the experimental curve to time zero] from the slope of which the rate constant of the fast reaction is obtained. The details of biphasic plot of rate determination is given elsewhere¹¹.

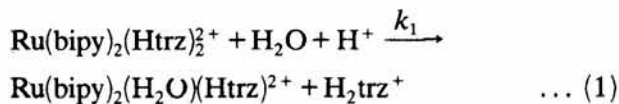
Stoichiometry of the reaction

From the nature of the rate plot it may reasonably be assumed that the reaction takes place in stages. The spectra at an intermediate stage becomes identical with the diaqua complex, which after nearly twelve hours turns to a colourless solution of near zero absorbance. The reaction mixture at the intermediate stage, after quenching

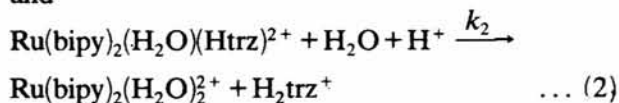
with ice cold water, was passed through an anion exchange column (Amberlite 45, 200-400 mesh) and eluted with water. A yellow coloured solution was obtained and identified as the *cis*-diaqua complex (λ_{max} 350, 495 nm), as the UV-visible spectrum of this matched with that of the authentic compound¹². The diaqua and the hydroxo aqua (may also be present) complexes undergo a slow decomposition in the presence of perchloric acid. The spectrum of the final solution was similar to that described by Cady and Connick¹³, indicating the presence of ruthenium(III) ion. This solution was concentrated on a rotary evaporator and then dried up in a desiccator and the infra red spectra of the residue gave peaks at 681(s), 659(w), 650(s), 648(w), 632(sh) and 622(sh) indicating the presence of bipyridine and 1,2,4-triazole^{14,10}. The 622 cm^{-1} band indicates that the product triazole exists in its protonated form (Htrz).

Results and discussion

The kinetics and stoichiometry of the reaction indicate that the reaction proceeds in stages as shown in Eqs 1 and 2.



and



The values of k_1 and k_2 as obtained from the biphasic plot are recorded in Table 1. The product, diaqua complex of reaction (2) has a *cis* geometry. However, in the presence of normal light it slowly converts to *trans* form, which in turn in the presence of air and acidic aqueous solution converts to *trans* $[\text{Ru}^{\text{III}}(\text{bipy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ complex. Durham *et al.* also observed the same photoisomerization of the *cis*-diaqua complex which further gets oxidised to ruthenium(III) complex in the presence of air¹². The aerial oxidation is accompanied by a slow change in colour from yellow to purple yellow. The λ_{max} of the product complex shifts from 350 to 370 (flat shape). Slow aerial oxidation has also been observed when the reaction was carried out with *p*-toluene sulphonic acid.

Plot of k_1 versus $[\text{H}^+]$ at any particular temperature is non-linear. The reciprocal plot of $[k_1]^{-1}$ versus $[\text{H}^+]^{-1}$ is however, linear, having positive slope and positive intercept. This type of plot fits to the equation of the form (3)

Table 2—Rate constants, protonation constant and activation parameter values for first and second steps of aquation. Deviations are within $\pm 5\%$

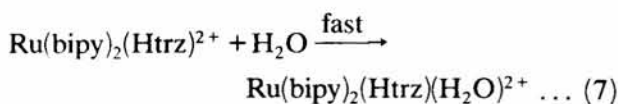
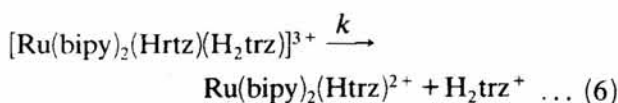
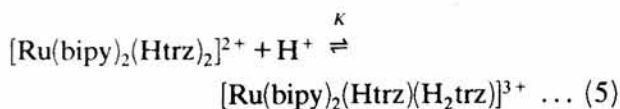
Temp K	$10^3 k_1$ (s^{-1})	$10^4 k_2'$ (s^{-1})	$10^4 k_2''$ ($M^{-1} s^{-1}$)	K (Protonation constant)
294	0.77	1.32	1.00	5.02
298	0.91	1.70	1.60	5.97
305	1.36	2.25	2.52	7.14
308	1.77	3.20	3.75	8.43
313	2.13	4.28	4.72	9.60
$\Delta H^\ddagger$	64 ± 4 ($kJ mol^{-1}$)	63 ± 3	73 ± 4	
$\Delta S^\ddagger$	-94 ± 8 ($JK^{-1} mol^{-1}$)	-102 ± 8	-76 ± 10	

$$-\frac{d}{dt}[\text{complex}] = k_{\text{obs}} = \frac{a[H^+]}{1 + b[H^+]} \quad \dots (3)$$

or

$$1/k_{\text{obs}} = 1/a[H^+] + b/a \quad \dots (4)$$

The detailed steps of the reaction given by Eq. (1) may be shown as:



Hence,

$$\text{Rate} = k[\text{complex}]$$

$$= \frac{kK[\text{complex}][H^+]}{1 + K[H^+]} = k_{\text{obs}} \quad \dots (8)$$

$$\text{or } 1/k_{\text{obs}} = (1/kK)[H^+] + 1/k \quad \dots (9)$$

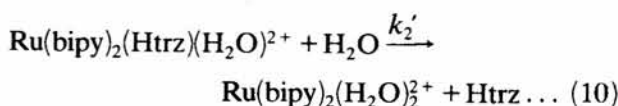
Equation (9) is similar to Eq. (4) in form having $kK = a$ and $k = a/b$. The values of k , the first order rate constant and K , the protonation constant of the complex at various temperature as obtained from the plot of $1/k_1$ versus $1/[H^+]$ are given in Table 2. The corresponding activation parameter values are also given in Table 2.

Plot of k_2 versus $[H^+]$ at a particular tempera-

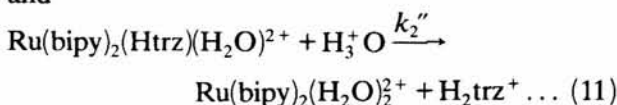
Table 3—Rate and activation parameters for the first stage of aquation of $\text{Ru}(\text{bipy})_2\text{Cl}_2$ and $\text{Ru}(\text{bipy})_2(\text{Htrz})_2^{2+}$

$[H^+]$ mol dm^{-3}	0.05 (35°)	0.1 (32°)	$\Delta H^\ddagger$ ($kJ mol^{-1}$)	$\Delta S^\ddagger$ ($JK^{-1} mol^{-1}$)
$\text{Ru}(\text{bipy})_2\text{Cl}_2$	17.0	22.04	52	-108
$\text{Ru}(\text{bipy})_2(\text{Htrz})_2^{2+}$	6.81	6.94	64	-94

ture is linear having positive slope and positive intercept on rate axis. From the slope and intercept of the plot, the rate constants for acid-free (k_2') and acid-dependent (k_2'') paths were evaluated. The reaction steps of Eq. (2) may be shown as follows:



and



The basic site at one of the triazoles is vulnerable to attack by a protonated solvent molecule. Protonation of one of the nitrogen exerts a pull on the electron cloud of the adjacent nitrogen atom, which in turn exerts a pull on Ru-N bond resulting in its rupture. The vacated position thus created is being filled up with a solvent molecule. The second triazole also dissociates in a similar fashion. In acidic aqueous solution protonation of the basic nitrogen on triazole restricts its coordination ability to act as a bridging ligand. This prevents dimerization of the complex during the course of the reaction. However, in the absence of protonation dimerization may occur¹⁵. The rate constant values for the first stage is several times greater than that of the second stage. Availability of more protonation centres within the di-triazole complex is likely the cause of this rate enhancement. Similar behaviour has also been observed with the nitrite and acetonitrile substituted complexes of $\text{Ru}(\text{bipy})_2^{2+}$ moiety^{7c}. The protonation constant K of the complex is lower than that of the free ligand (K of free ligand is 10.26), showing that the basicity of the ligand decreases on coordination¹⁶.

The activation parameters as obtained from Eyring equation are given in Table 2. The enthalpy values are a little higher compared to other substitution reactions on ruthenium(II) centre. Entropy values are all highly negative. A comparison

of the substitution reaction of this complex with the dichloro complex seems interesting at this stage¹⁷. The rates and the activation parameters (for the first step only) of the two complexes are given in Table 3 for comparison. The inertness of the triazole is due to its ability of acting as a σ and π -donor as well as a π -acceptor utilising its π^* orbitals. This gives a more stable complex. Chloride ion is only a π and σ -donor without having any π -acceptor behaviour. So the chloro complex is of lower stability in accordance with the observed fact. This is also reflected by the lower enthalpy of the dichloro complex. However, the π -bonding properties of triazole are weak, and thus on departure of the first triazole the other one does not show any tendency to chelate formation as the highest occupied metal orbitals have a strong π -character and metal to ligand charge transfer processes are important. The combined effect of higher enthalpy of the reaction as well as the geometry (the bulky size of the ligand) of the complex ion which restricts the approach of the solvent molecule towards itself, gives a lower rate of substitution. It is interesting to mention here that another similarly constituted complex ion, $[\text{Ru}^{\text{II}}(\text{bipy})_2(\text{CN Ptdien})_2]^{4+}$, undergoes aquation by the release of a very bulky ligand-CN Ptdien only very slowly. Half life of this reaction is several hours at room temperature¹⁸. An associative mechanism has been proposed for this reaction. In the present study, smaller rate constant values for the departure of the bulky triazole ligand compared to chloride ion definitely do not indicate a dissociative mode of activation. Solvolysis of a number of ruthenium(II) complexes $[\text{Ru}^{\text{II}}(\text{bipy})_2\text{L}_2]^{n+}$ ($\text{L} = \text{NH}_3$, pyridine, cyanide) in DMF shows associative replacement of the ligand L. [ref. 19]. Considering the nature of reactions of all these ruthenium(II) complexes, it may be proposed that appreciable associative character prevails in the present aquation reaction.

References

- (a) Mavesick A W & Gray H B, *Coordination chemistry XXI IUPAC* (Pergamon) 1981.
(b) Balzani V & Carassiti V, *Photochemistry of coordination compounds* (Academic Press, London) 1970.
- Winkler J R & Sutin N, *Inorg Chem*, 26 (1987) 220.
- Brewer K J, Murphy Jr. W R, Spurlin S R & Petersons, *Inorg Chem*, 25 (1986) 882.
- Book C R, Whitten D C & Meyer T J, *J Am chem Soc*, 96 (1974) 4710.
- Maspero F & Ortaggi G, *Ann Chim (Italy)*, 64 (1974) 115; Davies N R & Mullins T L, *Aust J Chem*, 20 (1967) 657.
- Sagues J A A, Gillard R D, Lancashire R J & Williams P A, *J chem Soc, Dalton* (1979) 193; Herber R H & Nun G, *Inorg Chem*, 27 (1988) 2644.
- (a) Allen R J & Ford P C, *Inorg Chem*, 11 (1972) 679.
(b) Armor J N & Taube H, *J Am chem Soc*, 92 (1970) 6170.
(c) Allen L R, Craft P P, Durham B & Walsh J, *Inorg Chem*, 26 (1987) 53; Constable E C, *Inorg chim Acta*, 82 (1984) 53.
- Kallen T W & Earley J E, *Inorg Chem*, 10 (1971) 1149, 1152; Chakravarty A R & Chakravorty A, *J chem Soc, Dalton* (1982) 1765; Davies N R & Mullins T L, *Aust J Chem*, 21 (1968) 915.
- Sullivan B P, Salmon D J, Meyer T J & Peedi J, *Inorg Chem*, 18 (1978) 3369.
- Vos J G, Haasnoot J G & Vos G, *Inorg chim Acta*, 71 (1983) 155.
- Chakravarty B & Sil A K, *Inorg chim Acta*, 24 (1977) 105.
- Durham B, Wilson S R, Hodgson D J & Meyer T J, *J Am chem Soc*, 102 (1980) 600.
- Cady H H & Connick R E, *J Am chem Soc*, 80 (1958) 2646.
- Linnell R H & Kaozmarezyk A, *J phys Chem*, 65 (1961) 1196.
- (a) Vos G, Haasnoot J G & Groeneveld W L, *Z Naturforsch*, 36b (1981) 802.
(b) Vos G, de Kok A J & Verschoor G C, *Z Naturforsch*, 36b (1981) 809.
- Potts K T, *Chem Revs*, 61 (1961) 87.
- Chakravarty B & Kar U K, *Trans met Chem*, 15 (1990) 183.
- Bignozzi C A & Scandola F, *Inorg Chem*, 23 (1984) 1540.
- Tan S L, De Armond K & Hanck K W, *J electroanal Chem*, 181 (1984) 187.