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Associative Nature of the Photosubstitution of Tris(2,2-bipyridine)ruthenium(II) in Aqueous Acidic Solutions

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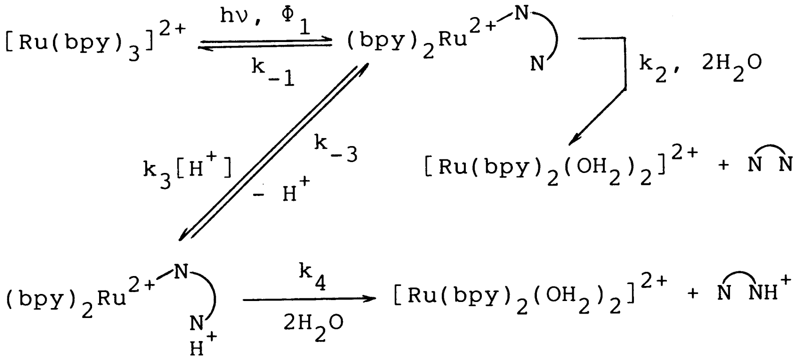
In the photosubstitution of $[Ru(bpy)_3]^{2+}$ in aqueous acidic (HX) solutions, the quantum yield of the initial breaking of a Ru-N(bpy) bond changed 7 fold depending on the kind of X^- in the order, $CF_3SO_3^- < NO_3^- < HSO_4^- < Cl^- < Br^-$. In HCl-NaCl system it increased linearly with increasing $[Cl^-]$. The photosubstitution must have proceeded with a mechanism of associative nature.

The tris(2,2'-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, is among the most important compounds in coordination chemistry which is continuing to play a key role in the development of many fields.[1)] The complex ion undergoes ligand substitution by irradiation of light.[2)] Meyer proposed a dissociative mechanism for the substitution where a five coordinate intermediate with a unidentate bpy ligand formed by dissociative chelate ring opening.[3)] Based on the mechanism he explained the dependence of the substitution quantum yield on the kinds and concentrations of anions in the solution.

In this letter experimental evidence is shown which indicates associative nature of the mechanism of the substitution of $[Ru(bpy)_3]^{2+}$. In the mechanism an anion or a solvent molecule associate with the metal center to form a seven coordinate activated complex which undergoes chelate ring opening with a rupture of a Ru-N(bpy) bond resulting to form the unidentate intermediate.

An aqueous acidic solution of the complex perchlorate ($5X10^{-7}$ mol dm^{-3}) was irradiated by a light (436 nm) under nitrogen atmosphere with stirring at 70.0 °C. In parallel with the decrease in intensity of the emission spectra of the tris complex the absorption spectra of the solution changed with showing isosbestic points. After the irradiation the absorption spectrum in CF_3SO_3H system agreed with that of $[Ru(bpy)_2(OH_2)_2]^{2+}$. A plot of the logalithmic value of an emission intensity of the solution at 590 nm vs. time of irradiation gave a straight line. From the slope of the line, the substitution quauntum yield, Φ_s, was obtained.

The Φ_s increased with the increase in the acid concentration to reach limiting values at $[H^+] > 0.5$ mol dm^{-3} depending on the kind of acid (Fig. 1).[4)] The acid dependence of Φ_s was very similar to that observed for the rate constants of thermal substitution of $[M(bpy)_3]^{2+}$ (M=V(II), Fe(II), Ni(II), etc.).[5)] Since an $[H^+]$ dependence of the rate constants has been related to the formation of a unidentate intermediate, the $[H^+]$ dependence of Φ_s also suggests the formation of the intermediate as:



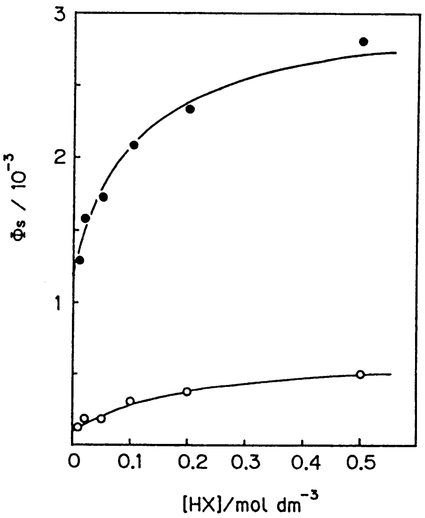


Fig. 1. Plots of Φ_s vs. acid concentration: ○, CF_3SO_3H; ●, HCl(I=1.0 mol dm^{-3}, NaX).

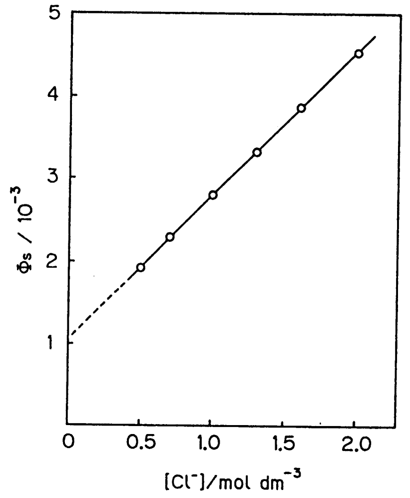


Fig. 2. Plots of Φ_s vs. Cl^- concentration (HCl-NaCl, $[H^+]$=0.5 mol dm^{-3}).

In the intermediate the free end of a unidentate bpy is captured by a proton in acid solution, which prevents the chelate ring closure resulting to assist the substitution. Based on the mechanism the observed quantum yield is expressed as:

$$\Phi_s = \Phi_1\left\{\frac{k_2(k_{-3}+k_4)+k_3k_4[H^+]}{(k_{-1}+k_2)(k_{-3}+k_4)+k_3k_4[H^+]}\right\}$$

Thus a limiting value at high acid concentration corresponds to Φ_1, the quantum yield of the breaking of an initial Ru-N(bpy) bond. A big difference in the limiting values between CF_3SO_3H ($0.66X10^{-3}$) and HCl ($3.0X10^{-3}$) systems (see Fig. 1) suggests the assistance of anions for the breaking of the Ru-N(bpy) bond. The Φ_s measured in 0.5 mol dm^{-3} HCl solution increased linearly with the increase in $[Cl^-]$ (Fig. 2),[4] indicating that the reaction is a first order with respect to $[Cl^-]$, since the Φ_s at $[H^+]$=0.5 mol dm^{-3} roughly equals to Φ_1. These facts suggest again the associative nature of the reaction. The Φ_s's at [HX]= 0.5 mol dm^{-3} (I=1.0 mol dm^{-3}, NaX) increased in the order of X^-, $CF_3SO_3^-$ (0.50) < NO_3^- (1.00) < HSO_4^-(1.85) < Cl^-(2.80) < Br^-(3.37) (values in the parentheses are $\Phi_s/10^{-3}$).[4] The order is consistent with the increasing coordination tendency of the ions to Ru(II) ion. These results strongly indicate that the chelate ring opening, or the breaking of the initial Ru-N(bpy) bond, is assisted by X^-, that is, the reaction proceeds with a mechanism with associative nature, most probably with an interchange mechanism.

References

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3) T. J. Meyer, Pure Appl. Chem., 58, 1193 (1986).
4) Emission intensity stayed almost constant with changing $[H^+]$, $[Cl^-]$, and X^-.
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