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An Acid Dependence of the Photosubstitution of Tris(1,10-phenanthroline)ruthenium(II). Intermediate with a Monodentate Phenanthroline Ligand

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The quantum yield of the photosubstitution of tris(1,10-phenanthroline)ruthenium(II) increased steeply with the increase in acid (HCl or CF_3SO_3H) concentration to reach a plateau at the acid concentration higher than 0.1 mol dm^{-3}, indicating the protonation to a reaction intermediate of the complex, probably to a nitrogen atom in the reaction intermediate with a monodentate phenanthroline ligand.

The aromatic α-diimines, bpy (=2,2'-bipyridine) and phen (=1,10-phenanthroline), have similar properties as ligands in coordination chemistry. The biggest difference between them is their rigidity. Thus, in thermal ligand substitution, $[M(bpy)_3]^{2+}$ (M = V, Fe, and Ni) showed acid dependence[1,2] and $[M(phen)_3]^{2+}$ did not.[2] The acid dependence for the former has been related to the formation of the reaction intermediate with a flexible monodentate bpy ligand, while the acid independence for the latter has been related to the inability of the rigid phen ligand to form such an intermediate in the tris complex:[2] A strong steric repulsion will occur between the rigid monodentate phen and the neighboring phen ligands in the intermediate.[3] Recently Lilie et al. proposed a six coordinate reaction intermediate of $[Cr(phen)_3(H_2O)]^{3+}$ with a monodentate phen ligand for the photosubstitutution of $[Cr(phen)_3]^{3+}$ without any direct evidence for the intermediate.[4] The present paper reports a novel example of the acid dependence of the photosubstitution of tris(1,10-phenanthroline)ruthenium(II), which strongly suggests the existence of the reaction intermediate with a monodentate phen ligand.

The $[Ru(phen)_3]^{2+}$ is very stable in solution in the dark: No changes in the absorption spectrum of the complex were observed even after boiling in 1 mol dm^{-3} HCl solution for hours. However, upon irradiation of N_2-purged acidic solution (HCl or CF_3SO_3H; 0.01-0.5 mol dm^{-3}) of 2.5×10^{-5} mol dm^{-3} $[Ru(phen)_3](ClO_4)_2$ with light (λ = 436 nm) at 70 °C, the intensity of the emission spectra of the tris complex in solution decreased monotonously with time of irradiation, indicating the disappearance of the tris complex. The absorption spectrum of the solution also changed; a profile of the spectral changes in HCl solution was very similar to that observed for $[Ru(bpy)_3]^{2+}$ in HCl solution.[5] The spectral changes in $[Ru(bpy)_3]^{2+}$ system were previously related to the formation of $[Ru(bpy)_2(OH_2)_2]^{2+}$, $[Ru(bpy)_2(OH_2)Cl]^+$, and $[Ru(bpy)_2Cl_2]$.[5] In the photoreaction of $[Ru(phen)_3]^{2+}$ in

HCl solution [Ru(phen)$_2$Cl$_2$] precipitated, whereas in CF$_3$SO$_3$H solution no precipitate was formed. These observation suggest the substitution of a phen ligand in [Ru(phen)$_3$]$^{2+}$ with H_2O and/or Cl$^-$ in the acid solutions.

The substitution rate was expressed by the equation: $(-d[\mathrm{Ru(phen)_3}^{2+}]/dt)_t = \Phi_t I_0(1 - 10^{-A_t \ell})(\varepsilon\ell[\mathrm{Ru(phen)_3}^{2+}]/(A_t\ell))$, where Φ_t is a quantum yield of the photosubstitution at a time t, I_0 is an incident light intensity with a unit of einstein dm^{-3} s^{-1}, A_t is the absorbance per cm at 436 nm of the solution irradiated, ℓ (= 2 cm) is a light-path length of the solution, and ε is a molar absorption coefficient of the tris complex at 436 nm. The concentration of the tris complex in the solution was followed by measuring the emission intensity at 583 nm. The substitution rate was obtained from the gradient at a time t of a curve of [Ru(phen)$_3$$^{2+}$] vs. irradiation time. The quantum yield, Φ_t, thus obtained at a time t for each run showed no dependence on irradiation time in the time range for which the photoreaction was followed (for 0.5-1.3 half-lives). The fact indicated that the contribution of the reverse reaction, i.e., recombination of the liberated phen, to the quantum yield was negligible in the experimental condition.

The quantum yield of the photosubstitution of [Ru(phen)$_3$]$^{2+}$ was drawn as a function of [H$^+$] in Fig. 1. It is evident that in both HCl-NaCl and CF$_3$SO$_3$H-CF$_3$SO$_3$Na systems the Φ increased steeply with the increase in the acid concentration to reach plateaus in solutions of the acid concentration higher than 0.1 mol dm^{-3}. The acid dependence of the Φ indicates the protonation to a reaction intermediate of the Ru complex. (A protonation to a liberated phen ligand cannot explain the acid dependence of the quantum yield, since the Φ's were little influenced by the recombination of the liberated phen.) Since the most plausible position of the protonation in the intermediate must be a nitrogen atom in the ligand, the photosubstitution of [Ru(phen)$_3$]$^{2+}$ proceeds most probably through an intermediate with a monodentate phen ligand. The acid dependence of the photoreaction of the complex is in marked contrast to the thermal ligand substitution (aquation) of other tris 1,10-phenanthroline complexes, [M(phen)$_3$]$^{2+}$ (M= V, Fe, and Ni), of which the first-order rate constant of the reaction didn't show any acid dependence.$^{2)}$

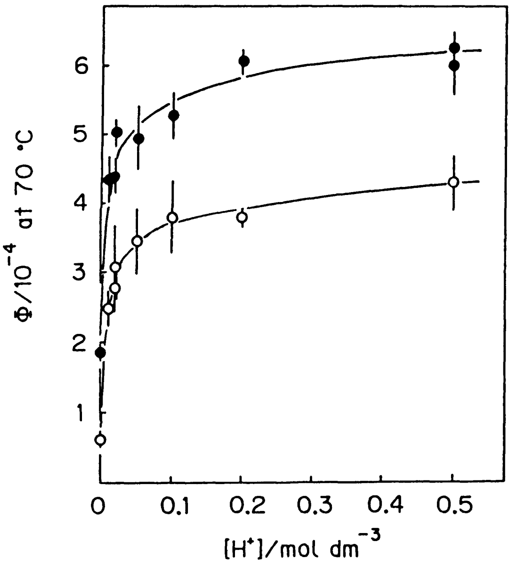
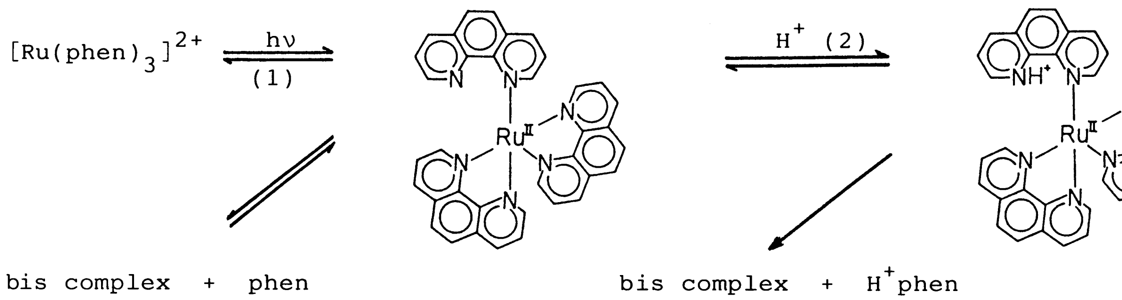


Fig. 1. Plots of the quantum yields, Φ, vs. acid concentration for the photosubstitution of [Ru(phen)$_3$]$^{2+}$: ○, CF$_3$SO$_3$H-CF$_3$SO$_3$Na system; ●, HCl-NaCl system (I=1.00 mol dm^{-3}).

Since the photosubstitution of [Ru(bpy)$_3$]$^{2+}$ has been considered to proceed through an intermediate with a monodentate bpy ligand,$^{5)}$ the reaction of the complex was carried out in HCl solutions to compare with the results obtained here for the phen complex. The results for [Ru(bpy)$_3$]$^{2+}$, shown in Fig. 2, are very similar to those for the photosubstitution of [Ru(phen)$_3$]$^{2+}$ in Fig. 1 and also to those for thermal substitution of $[M(bpy)_3]^{2+}$ (M= V, Fe, and Ni)[1,2] for which the reactions are widely accepted to proceed through a monodentate intermediate. The results suggest again that the ligand substitution of $[Ru(phen)_3]^{2+}$ proceeded through an intermediate with a monodentate phen ligand.

The following scheme was considered for the reaction mechanism:



In the scheme a protonation (path(2)) to the nitrogen atom of the monodentate phen ligand in the intermediate competes with a chelate ring closure of the ligand (path(1)). Thus with the increase in acid concentration, the ring closure is suppressed more efficiently to result in an increment of the quantum yield of the substitution.

In the photosubstitution of $[Ru(bpy)_3](SCN)_2$ in CH_2Cl_2 solution a spectral evidence was obtained of a monodentate intermediate with a lifetime of minutes.[6] On the other hand no direct evidence of the monodentate intermediate has been obtained for phen system. However, the monodentate intermediate is considered to exist at least for a very short period since, in the triplet d-d excited state from which the photoreaction has been considered to occur,[5] the bond distance, Ru-N, between ruthenium(II) and nitrogen atom in the ligand is expected to be appreciably longer than the M-N bond distances of $[M(phen)_3]^{2+}$ (M= V, Fe, and Ni). (The Ru-N bond distance at the excited state is more than 0.2 Å longer[7] than the Fe-N bond distance[8] in the electronic ground state of $[Fe(phen)_3]^{2+}$.) The long Ru-N bond lessens the steric hindrance between the monodentate phen and the neighboring phen ligands. In fact Ru(II) does form a tris complex of a spin-singlet electronic state with a bulky 2,9-dimethyl-1,10-phenanthroline,[9] despite that Fe(II) cannot form a similar complex with the ligand.

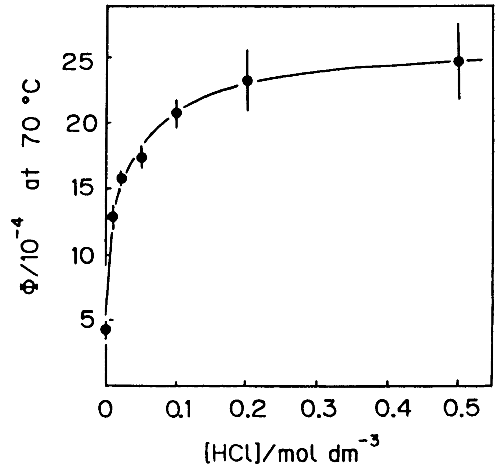


Fig. 2. Plots of the quantum yields, Φ, vs. HCl concentration for the photosubstitution of $[Ru(bpy)_3]^{2+}$ ($I=1.00$ mol dm^{-3}, NaCl).

A protonation may occur to a π-electron system of a ligand in the photoexcited triplet charge-transfer state (^3CT)[10] since in the ^3CT state the excited electron is considered to localize on a phen molecule in solution[11] resulting to form an anionic radical of the phen ligand in the complex. No difference in the emission spectra, however, were observed for $[Ru(phen)_3]^{2+}$ between in 1.0 mol dm^{-3} NaCl solution and in 0.1 mol dm^{-3} HCl solution (I=1.0 mol dm^{-3}, NaCl).

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3) The CPK space-filling model readily shows that the strong steric repulsion exists. Despite of the repulsion DeArmond et al. reported a tris phenanthroline iridium complex with a monodentate phenanthroline ligand. They identified the complex to be six coordinate $[Ir(phen)_2(OH)(phen)]^{2+}$ from elemental analysis and ^1H NMR spectrum (J. L. Kahl, K. W. Hanck, and K. DeArmond, J. Phys. Chem., 83, 2611 (1979)).
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6) B. Durham, J. L. Walsh, C. L. Carter, and T. J. Meyer, Inorg. Chem., 19, 860 (1980).
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