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Mechanisms of the Photosubstitution of Ruthenium(II) Polypyridine Complexes: Formation of an Intermediate with a Monodentate Polypyridine Ligand and Its Reactions

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ABSTRACT

A novel intermediate of the photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy=3,3'-dimethyl-2,2'-bipyridine) with a monodentate dmbpy was identified and its structure in solution was determined. Quantum yields of the formation of the intermediate and of the net photosubstitution of the complex were measured in various solvents. Rate of the thermal rechelation of the monodentate dmbpy in the intermediate was also measured. The data indicated that the formation of the intermediate proceeded by dissociative mechanism. Refered to the dmbpy complex the reactions of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ were concluded to proceed by dissociative interchange mechanism, and $[Ru(bpy)_2(L)_2]^{2+}$ (L=pyridine, imidazole, NH_3, ethylenediamine/2, and picolylamine/2) by dissociative mechanism.

1. INTRODUCTION

Ligand substitution is one of the elementary reactions of photoexcited coordination compounds. Thus, a number of studies have focused on the reaction of tris(polypyridine)ruthenium(II) complexes [1-4]. For the most popular $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) dissociative (D) mechanism has been proposed although the quantum yield of the photosubstitution of the complex changed remarkably depending on solvents, counter anions, and additives [2]. The proposal was based on the fact that the quantum yields of the substitution of py (=pyridine) by X in $[Ru(bpy)_2(py)_2]X_2$ (X = Cl^-, NCS^-, and NO_3^-) were independent of the kind of X. No direct evidence for the mechanism has been obtained so far.

Initial photoproduct of the substitution of a tris(polypyridine)ruthenium(II) complex is considered to be an intermediate with a monodentate polypyridine ligand. Since rechelation of the monodentate polypyridine ligand leads to the reformation of the starting complex, the changes in the net photosubstitution quantum yield, ϕ_S, in different experimental conditions as

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observed for the reaction of $[Ru(bpy)_3]^{2+}$ were related to the changes in the extent of rechelation of the intermediate. Therefore for estimation of the quantum yield of the first breaking of the Ru-ligand bond and for elucidation of its mechanism the quantum yield of the formation of the intermediate should be observed directly. If such an intermediate were observed directly and its thermal and photoreactivities were studied, and the role of the intermediate for the determination of ϕ_s were clarified, we would be able to estimate the quantum yield of the first breaking of the Ru-ligand bond of a tris(polypyridine)ruthenium(II) complex from the net photosubstitution quantum yield. However, neither identification nor reactivity of such an intermediate have been studied so far for the lack of a suitable system.

We have established the formation an intermediate in the photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy=3,3'-dimethyl-2,2'-bipyridine) [5]. Study has been made on the identification of the intermediate with a monodentate dmbpy ligand [6], on the determination of its structure, on the quantum yield of its formation, on thermal rechelation of the dmbpy in the intermediate, on the quantum yield of the net photosubstitution of the complex and on the substitution mechanism in various solvents. Refered to the dmbpy complex the mechanisms of the photosubstitution of other (polypyridine)ruthenium(II) complexes were also clarified.

2. PHOTOSUBSTITUTION OF $[RU(BPY)_2(DMBPY)]^{2+}$

2.1. Identification of the Intermediate [6]

Irradiation of an aqueous solution of $[Ru(bpy)_2(dmbpy)]^{2+}$ caused an instantaneous decrease in absorbance of the solution at 400-460 nm. The absorbance recovered within seconds at 25 °C in the dark. The observation was rationalized by the photochemical formation of an intermediate with a monodentate dmbpy ligand and the thermal back reaction of the intermediate to the original complex [5]. Since the intermediate had a half-life > 10 min in aqueous acidic solution at 0 °C we tried to separate the intermediate to identify it. The complex was flashphotolyzed and the products were analyzed by HPLC using ODS column with an eluent of acetonitrile/water(80/20) containing 0.06 M $LiClO_4$. In its chromatogram a shoulder appeared behind the main peak of the mother complex with three small front peaks of diaqua-, aquaacetonitrile-, and bis(acetonitrile)-bis(bipyridine)ruthenium(II) complexes. Leaving the photolyzed solution for 5 min at 36 °C the shoulder disappeared in the chromatogram and the main peak increased, suggesting that the shoulder was due to the intermediate. In acetonitrile the lifetime of the intermediate was much longer (half-life of 80 min at 25 °C). HPLC analysis of the flashphotolyzed acetonitrile solution gave a chromatogram in which a small front shoulder and a rear shoulder were associated with a main peak. The solution being kept at 80 °C for 10 min, the rear shoulder disappeared and the peak height of the main peak increased. By measuring absorption spectra of the shoulders the rear shoulder was identified to be due to the intermediate, $[\mathrm{Ru(bpy)_2(dmbpy)(MeCN)}]^{2+}$, which showed a similar absorption spectrum to that of $[\mathrm{Ru(bpy)_2(3\text{-}methylpyridine)(MeCN)}]^{2+}$.

^{1}H nmr spectra of the complex were measured in acetonitrile at 10 °C (a) before the photolysis, (b) right after the photolysis, and (c) 5 min at 60 °C after the photolysis. In (a) existed a single methyl signal of dmbpy of the complex. In (b) two weak additional methyl signals of equal intensities were observed with a decrease in the intensity of the original methyl signal. In (c) the two signals disappeared with an increase in the intensity of the original signal. The results demonstrated that the weak signals were those of the intermediate.

2.2. Structure of the Intermediate in Acetonitrile

Chemical shifts of ^{1}H nmr signals of the intermediate was different from those of the corresponding signals of the mother complex. The difference was brought about by the difference in the ring-current shift of the signals caused by aromatic ligands. Thus, the ring-current shifts of the protons of the complex and of the intermediate of various possible structures were calculated [7] and differences in the shifts were obtained between the two systems. Comparing the differences with those of the observed, we could determine the most probable structure of the intermediate. Large upfield shifts (0.9 and 1.5 ppm) of the methyl signals of the intermediate as compared to that of the mother complex indicated that the two py moieties of dmbpy have twisted a right angle to each other in the intermediate. Difference in the chemical shifts of the two methyl signals of the dmbpy of the intermediate by 0.6 ppm indicated that the methyl group of the py ring with Ru-N (py) bond ruptured located above the edge of the py ring of an adjacent bpy in the intermediate. A structural model of the intermediate is drawn in Fig. 1.

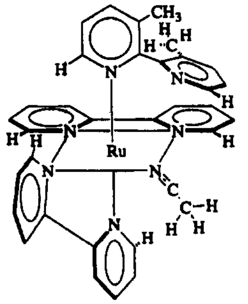

Figure 1. Structural model of the intermediate

2.3. Thermal and Photoreactivities of the Intermediate

An instantaneous decrease in absorbance of a solution of the dmbpy complex by irradiation was confirmed to be caused by a formation of the intermediate with a monodentate dmbpy ligand. Thus, we could obtain the quantum yield of the formation of the intermediate, ϕ_1, from the initial decrease in absorbance right after the irradiation. The rate constant of the rechelation of the monodentate dmbpy in the intermediate, k_{-1}, was obtained from an absorbance recovery process of the irradiated solution in the dark after the photoflash. The net photosubstitution quantum yield of the dmbpy complex, ϕ_s, was obtained from the net decrease in absorbance of a solution of the complex by the photolysis after the completion of the absorbance recovery process. The values of ϕ_1, k_{-1}, and ϕ_s thus obtained in various solvents are listed in Table 1.

The values of k_{-1} were quite small in nitrile solutions. This indicated that a nitrile molecule strongly bound to Ru(II) and could not be readily replace by the free py moiety of the monodentate dmbpy. In alcohols, ketones, and nitriles k_{-1} was larger with a larger size of a solvent molecule in each solvent group. The fact showed that there existed steric repulsion between the coordinated solvent molecule and the monodentate dmbpy ligand, as can be readily expected from the structure of the intermediate (Fig. 1). Thus, the rate of the rechelation differed by a factor as large as 10,000 from acetonitrile to pyridine and methylisobutylketone.

The value of ϕ_s was rather small in all solvent systems (except pyridine) studied. Continuous photolysis of the metal complex in pure water and in aqueous solutions containing NaCl or NaSCN showed that net photosubstitution did not change much in the presence of Cl^-, but the presence of NCS^- considerably enhanced the photosubstitution. In order to elucidate factors

Table 1. Quantum Yield of the Formation of the Intermediate, ϕ_1, Rate Constant of the Rechelation at 25 °C, k_{-1}, and Net Quantum Yield of the Photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$, ϕ_s.

Solvent	ϕ_1	k_{-1}/s^{-1}	ϕ_s
Pyridine	0.033	1.22	0.021
Dimethylformamide	0.023	0.29	0.002
Water	0.028	0.10	0.003
Methanol	0.021	0.35	0.002
Ethanol	---	0.94	—
Acetone	0.021	0.47	0.001
Methylisobutylketone	0.018	1.10	—
Acetonitrile	0.033	0.0001	0.000
Propionitrile	0.019	0.00	0.000
Isobutylonitrile	0.015	0.07	0.001
Benzonitrile	0.004	0.00	0.000
Dichloromethane	0.033*	---	---

* In the presence of saturated Me_4NCl

controling ϕ_s, studies were made on the photosubstitution of $[Ru(bpy)_2(py)X]^{2+}$ ($X=Cl^-$, NCS^-, py, and MeCN) in water. On flash-photolyzing the solution of the complexes, only X was found to dissociate in cases of $X= Cl^-$, py, and MeCN, while for $X=NCS^-$, dissociation of both py and NCS^- was observed. Therefore small value of ϕ_s for $[Ru(bpy)_2(dmbpy)]^{2+}$ in water with and without NaCl and in MeCN was probably brought about by a photosubstitution of X in place of the monodentate dmbpy. The large ϕ_s for X=py must be caused by a facile photosubstitution of dmbpy. A monodentate dmbpy ligand acted as a substituted pyridine. A large ϕ_s in aqueous NaSCN was probably brought about by a facile photosubstitution of the dmbpy in the intermediate to which NCS^- coordinated as in the case of the substitution of py in $[Ru(bpy)_2(py)(NCS)]^+$. Thus, the ϕ_s was not affected by the rate of the rechelation of the monodentate dmbpy but controled by the quantum yield of the photosubstitution of the dmbpy.

2.4. Mechanism of the Photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$

The quantum yields of the formation of the intermediate, ϕ_1,s were almost constant in diverse solvents with different coordinating ability such as pyridine, water, acetonitrile, and Cl^- containing dichloromethane (Table 1). The fact suggested that ϕ_1 was equal to ϕ_0, the quantum yield of the formation of the five coordinate intermediate with a monodentate dmbpy ligand (Fig. 2). Consequently the formation of the intermediate was concluded to proceed by D mechanism.

For the rechelation of the monodentate dmbpy in the intermediate, a free pyridine moiety of the dmbpy needs to twist for coordination against steric repulsion between methyl groups of the dmbpy ligand. Thus in Fig. 2 the rate constant of the rechelation of the unidentate dmbpy ligand, k_{-1}^{o}, must be much smaller than the rate constant of the coordination of a solvent molecule to a five coordinate intermediate, k_s. The relation $k_{-1}^{o} << k_s$ leads to the following relation: $\phi_1 = \phi_0(k_s/(k_s + k_{-1}^{o})) \fallingdotseq \phi_0$. Thus, the largest ϕ_1 of ~ 0.03 in solvents py, water, MeCN, and dichloromethane (Table 1) must be equal to ϕ_0.

The value of ϕ_1 smaller than 0.03 in other solvents must be due to small k_s, which suggest that the coordination of the solvent molecule to the intermediate was hindered sterically by the repulsion between the solvent

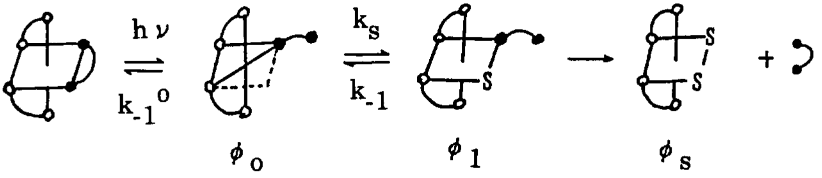

Figure 2. Reaction scheme for the photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$

molecule and the monodentate dmbpy. Such a steric effect is typically observed in a series of nitriles; the larger the size of solvent molecule, the smaller were ϕ_1s (Table 1).

The value of ϕ_0 could also be estimated from an acid dependence of ϕ_s in aqueous acidic solutions. The value of ϕ_s of the complex increased with increasing [HCl] to reach a limiting value at very high acid concentration. The limiting ϕ_s of the dmbpy complex in aqueous solution was equal to ϕ_0 estimated from ϕ_1s in various solvents in Table 1.

3. MECHANISMS OF THE PHOTOSUBSTITUTION OF OTHER (POLYPYRIDINE)RUTHENIUM(II) COMPLEXES

3.1. Mechanism of the photosubstitution of $[Ru(bpy)_3]^{2+}$

Photochemical behavior of $[Ru(bpy)_3]^{2+}$ was compared with that of $[Ru(bpy)_2(dmbpy)]^{2+}$ to elucidate its substitution mechanism. In aqueous acidic solution the quantum yield of the photosubstitution, ϕ_s, increased with the increase in acid concentration to reach a limiting value at high acid concentration. The limiting value depended on the kind of acid and changed by a factor of 7 in the order HBr > HCl > H_2SO_4 > HNO_3 > CF_3SO_3H [8]. The value increased linearly with the increase in [Cl^-] of the solution [8]. These results are in contrast to the phenomena observed for the dmbpy complex where the limiting value of ϕ_s was similar for HCl and CF_3SO_3H and did not depend on [Cl^-].

For $[Ru(bpy)_3]^{2+}$ the limiting value of ϕ_s in aqueous HCl solution was much smaller than ϕ_s in dichloromethane containing Cl^- [2] while for the dmbpy complex ϕ_ss were almost the same in the both solvent systems. An intermediate with a monodentate dmbpy was detected for the dmbpy complex with a half-life of 80 min at 25 ℃ in acetonitrile while for the bpy complex the corresponding intermediate was not detected even in a micro second time scale in the same solvent. The facts suggested that ϕ_0 was small for the bpy complex in aqueous and acetonitrile solutions and therefore the intermediate was not detected for the complex. The complex would not have a quantum yield as large as 0.1 in any solvents other than solvents with low dielectric constant containing anionic nucleophile such as Cl^-, although Meyer has suggested that $[Ru(bpy)_3]^{2+}$ had ϕ_0 of ~ 0.1 as $[Ru(bpy)_2(py)_2]^{2+}$ did [2]. The ligand field strength of bpy is larger than that of $(py)_2$ so that energy difference (ΔE) between emitting ^{3}CT excited state and the reactive ^{3}d-d state is considerably larger for the tris complex than that for $[Ru(bpy)_2(py)_2]^{2+}$ [9]. Therefore apparent activation energy which has contributions of both ΔE and ligand field activation energy for the formation of a five coordinate intermediate from ^{3}d-d state must be considerably larger for $[Ru(bpy)_3]^{2+}$. The discussion is applicable as far as ^{3}d-d state is populated from ^{3}CT state for $[Ru(bpy)_3]^{2+}$. It does not depend whether ^{3}d-d state is populated from ^{3}CT state or directly from ^{1}CT state [10] for $[Ru(bpy)_2(py)_2]^{2+}$.

The results hitherto described suggest strongly that the mechanism of the photosubstitution is different between $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(dmbpy)]^{2+}$. Thus we concluded that the reaction of $[Ru(bpy)_3]^{2+}$ proceeded by dissociative interchange (I_d) mechanism [8].

3.2. Mechanism of the photosubstitution of $[Ru(phen)_3]^{2+}$

The value of ϕ_s increased with the increase in acid concentration to reach a limiting value at high acid concentration in a similar way as observed for $[Ru(bpy)_3]^{2+}$. The acid dependence was explained by the formation of an intermediate with a monodentate phen ligand [11]. The limiting value of ϕ_s at high acid concentration depended on the kind of acid and on $[Cl^-]$. The value of ϕ_s in dichloromethane containing Cl^- or NCS^- was much larger than the limiting ϕ_s in aqueous acidic solutions. The photochemical behavior of the complex was quite similar to that of $[Ru(bpy)_3]^{2+}$. The observation was also parallel to the result obtained for the thermal substitution of $[Fe(phen)_3]^{2+}$ for which ion-pair interchange mechanism was proposed [12]: the substitution rate increased with the increase in the basicity of a nucleophile present in solution, and, in addition, remarkable increase in the rate was observed in the presence of Cl^- or NCS^- in a solvent of low dielectric constant [13]. Thus, the photosubstitution of $[Ru(phen)_3]^{2+}$ was concluded to proceed by I_d mechanism.

3.3. Mechanisms of the photosubstitution of $[Ru(bpy)_2(L)_2]^{2+}$ (L= pyridine, imidazole, NH_3, ethylenediamine/2, and picolylamine/2)

Acid dependence of ϕ_s of these complexes were similar to those observed for $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ except for $[Ru(bpy)_2(NH_3)_2]^{2+}$ of which ϕ_s did not show any acid dependence. At high acid concentration ϕ_s for $[Ru(bpy)_2(L)_2]^{2+}$ did not depend much on the kind of acid nor on $[Cl^-]$ present in the solution. Thus the photosubstitution of the complexes were concluded to proceed by D mechanism.

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