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| journal or publication title | Journal of the Mass Spectrometry Society of Japan |
| volume | 49 |
| number | 5 |
| page range | 183-187 |
| year | 2001 |
| URL | http://hdl.handle.net/10112/5992 |

REGULAR PAPER

Analysis of Photochemical Reactions of Bis(1,10-phenanthroline)-diamineruthenium(II) Complexes by Electrospray Ionization Mass Spectrometry

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(Received March 3, 2001; Accepted May 11, 2001)

The photo ligand substitution reaction of the bisphenanthroline complex $[\text{Ru}(\text{phen})_2\text{B}]^{2+}$ (where phen = 1,10-phenanthroline, B = ethylenediamine (en), trimethylenediamine (tn), or butanediamine (bn)) in acetonitrile solution was studied using electrospray ionization mass spectrometry (ESI-MS). The photochemical reaction of a diamineruthenium(II) complex has been known to proceed by oxidation of a diamine ligand to an α,α' -diimine by oxidative dehydrogenation. The final reaction product was a solvent substituted complex $[\text{Ru}(\text{phen})_2\text{S}_2]^{2+}$, where S is the solvent acetonitrile. We detected two monodentate complexes, an imine complex $[\text{Ru}(\text{phen})_2(\text{B}-2)\text{S}]^{2+}$ and a nitroso complex $[\text{Ru}(\text{phen})_2(\text{en}+14)\text{S}]^{2+}$ in the ESI-MS analysis of the photoreaction products of $[\text{Ru}(\text{phen})_2\text{B}]^{2+}$. These monodentate complexes were not observed with a bipyridine complex $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$ (where bpy = 2,2'-bipyridine, B = en or tn). In addition, photochemical reactivity of the phen complex was found to be higher than that of the bpy complex. The difference in the photochemical reactivity can be explained by the difference in configurational flexibility of the phen and bpy ligands in the ruthenium complexes.

1. Introduction

Oxidative dehydrogenation of aliphatic amine ligands in metal complexes, such as ethylenediamine in a ruthenium(II) complex, has been studied by chemical,¹⁾⁻⁵⁾ electrochemical,^{3), 4)} and photochemical⁶⁾⁻⁸⁾ oxidation reactions. From those studies, the reactions have been considered to proceed first by oxidation of Ru(II) to Ru(III) to form a 17-electron complex, and by stepwise oxidation to form a monoimine and then a diimine complex.^{1), 2), 5), 9)} It was observed that a UV-Vis spectrum of a $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$ (bpy = 2,2'-bipyridine, en = ethylenediamine) complex in acetonitrile showed a high absorption of a metal-to-ligand charge transfer (MLCT) band around 450–500 nm,² and a photochemical reaction of the complex was reported to proceed by the oxidative dehydrogenation as a result of MLCT excitation from the light absorption.^{2), 3), 9), 10)} However, the proposed reaction intermediates, a monoimine complex of Ru(II) or a Ru(III) complex, were too unstable to isolate or identify, and the reaction path of the oxidative dehydrogenation of the diamine ligand remained to be settled.

Electrospray ionization mass spectrometry (ESI-MS) has been used as a powerful technique for detection and identification of reaction products and intermediates, because it has an advantage of a soft ionization process.¹¹⁾⁻¹⁵⁾ We have successfully utilized ESI-MS to analyze the photochemical reaction of $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$ in acetonitrile. By using a deuterium labeled ethylene-

diamine complex, we identified that the photochemical reaction of the complex indeed proceeded through the monoimine intermediate to form the α,α' -diimine complex.⁸⁾ It has been considered that the en complex with MLCT absorption nearby 490 nm would initiate one-electron oxidation of the center Ru(II) metal and transfer an electron to the bpy ligand.¹⁶⁾ The electron transferred to the ligand would be then extracted by dissolved oxygen to produce active oxygen; at the same time, the dehydrogenation reaction would proceed to form the monoimine and then the diimine in the complex.^{7), 8)} We detected a new complex that was formed by addition of one oxygen atom and elimination of two hydrogen atoms from the en ligand.⁷⁾ The new complex was identified as a nitroso-complex by $^{18}\text{O}_2$ experiments.⁸⁾ We also found that the reaction of a complex $[\text{Ru}(\text{bpy})_2(\text{tn})]^{2+}$ (tn = trimethylenediamine) gave the same photochemical reaction products as that of $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$.

Throughout the studies of the photochemical reactions of the bpy complexes with the en or the tn ligand, we have not detected any species that had the breakage of only one side of the bidentate diamine ligand to form a monodentate complex. We report here the ESI-MS analysis of photolysis of $[\text{Ru}(\text{phen})_2\text{B}](\text{PF}_6)_2$ (phen = 1,10-phenanthroline, B = en, tn, or butanediamine (bn)) (Fig. 1). The different reaction products such as the monodentate diamine complexes were observed for the phen complex. The difference in the photochemical reactivity of the bpy and phen complex will be discussed.

2. Experimental

The ESI-MS analysis was performed by a sector-type mass spectrometer (JEOL-D300) with an ESI interface

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constructed in our laboratory. The ESI ion source has been described in detail elsewhere.¹⁴⁾ Briefly, a sample solution was sprayed at the tip of needle biased at 3.5 kV higher than a counter-electrode. The distance between the needle and the counter electrode was 1 cm. This counter electrode was made from a 12 cm long stainless steel capillary tube. Heated N₂ gas (70°C) flowing between the needle and the capillary electrode was used to aid desolvation of sprayed charged droplets. Ions entered a vacuum system through the first and second skimmer cones. The sample solution was infused in a continuous flow at about 2.5 μL min⁻¹ using a syringe pump. The cone voltage was set at 50 volts. A high-pressure Xe lamp (150 W) was used to irradiate sample solutions in a quartz reaction cell (10 × 10 × 50 mm) with light of λ > 420 nm using a UV-cutting off filter. All other light sources were intercepted in the experiments.

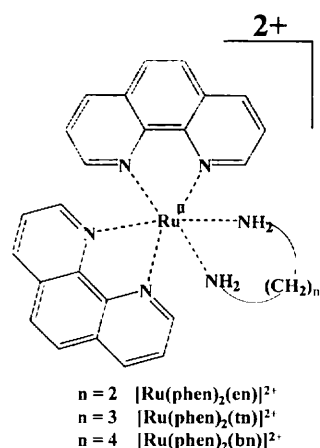


Fig. 1. Structures of the bisphenanthroline complex [Ru(phen)₂B]²⁺ (B=en, tn, or bn).

[Ru(phen)₂B](PF₆)₂ (B=en, tn, or bn) was synthesized in a similar manner as previously published.³⁾ The complex was dissolved in acetonitrile to form 0.2 mM solution. The sample solution was transferred immediately to the quartz cell and irradiated, and the solution collected in a syringe was infused into the mass spectrometer for product analysis. Deuterium labeled acetonitrile-*d*₃ and acetone-*d*₆ were also used as solvents and analyzed in the same manner. All ESI-MS spectra were obtained in the positive ion mode. If necessary, oxygen dissolved in the solvents was removed by replacement with argon gas.

3. Results and Discussion

ESI-MS spectrum of [Ru(phen)₂(en)](PF₆)₂ complex obtained in acetonitrile without light (Fig. 2a) showed two ions at *m/z* 261 [RuL₂(en)]²⁺ and *m/z* 667 [RuL₂(en)]X⁺, where L=phen, X=PF₆. All *m/z* values were calculated with ¹⁰²Ru. A low intensity ion at *m/z* 525 was originated in the impurity from the synthetic starting material. No ion from photochemical reaction was observed. The spectrum after 1 min of light irradiation showed the 2+ and 1+ ions of the oxidized complex at *m/z* 268 [RuL₂(en+14)]²⁺ and *m/z* 681 [RuL₂(en+14)]X⁺, where (en+14) represents the 14 mass units larger species than the en ligand, and has been determined to be the nitroso ligand of H₂N-CH₂-CH₂-NO by ¹⁸O₂ experiments.⁸⁾ The same nitroso complexes were also observed with the bpy complex (B=bpy) (B=en or tn). These nitroso complex ions were not observed when oxygen in the complex solutions was removed by degassing and replaced with argon. The ESI-MS spectrum after 5 min of light irradiation (Fig. 2b) exhibited much higher intensities of the (en+14) complex peaks. In addition, two new peaks, at *m/z* 722 [RuL₂(en+14)S]X⁺ and at *m/z* 289 [RuL₂(en+14)S]²⁺, were detected. These two peaks are formed by

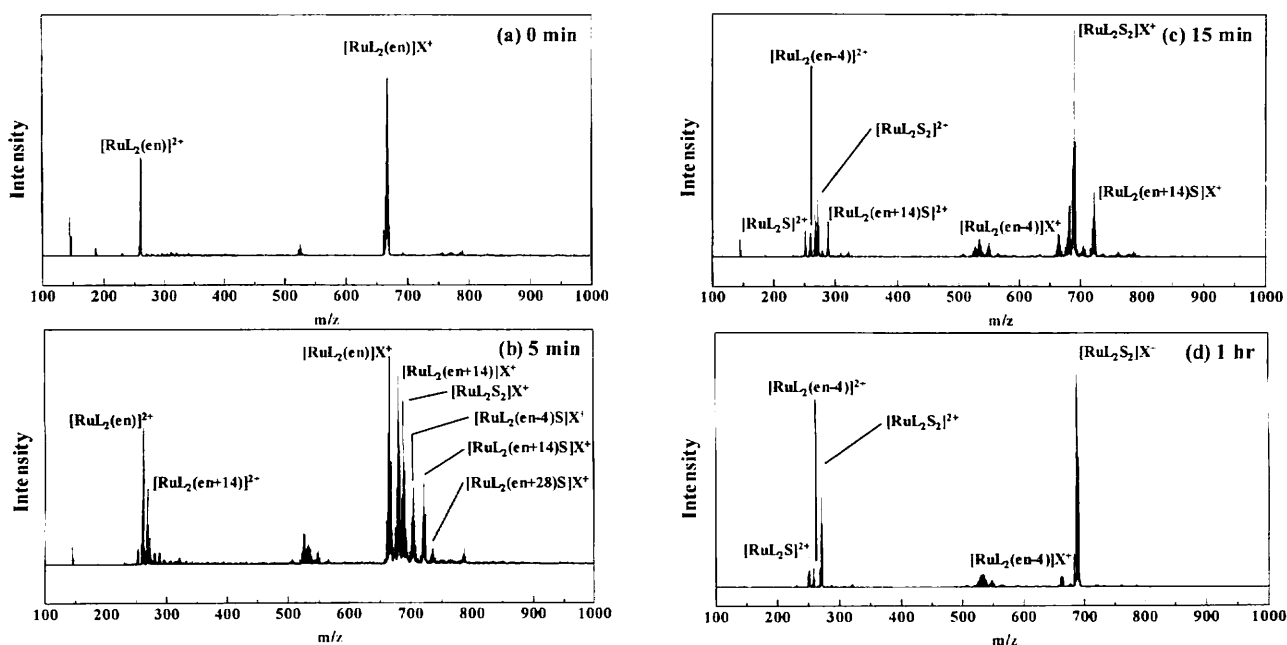
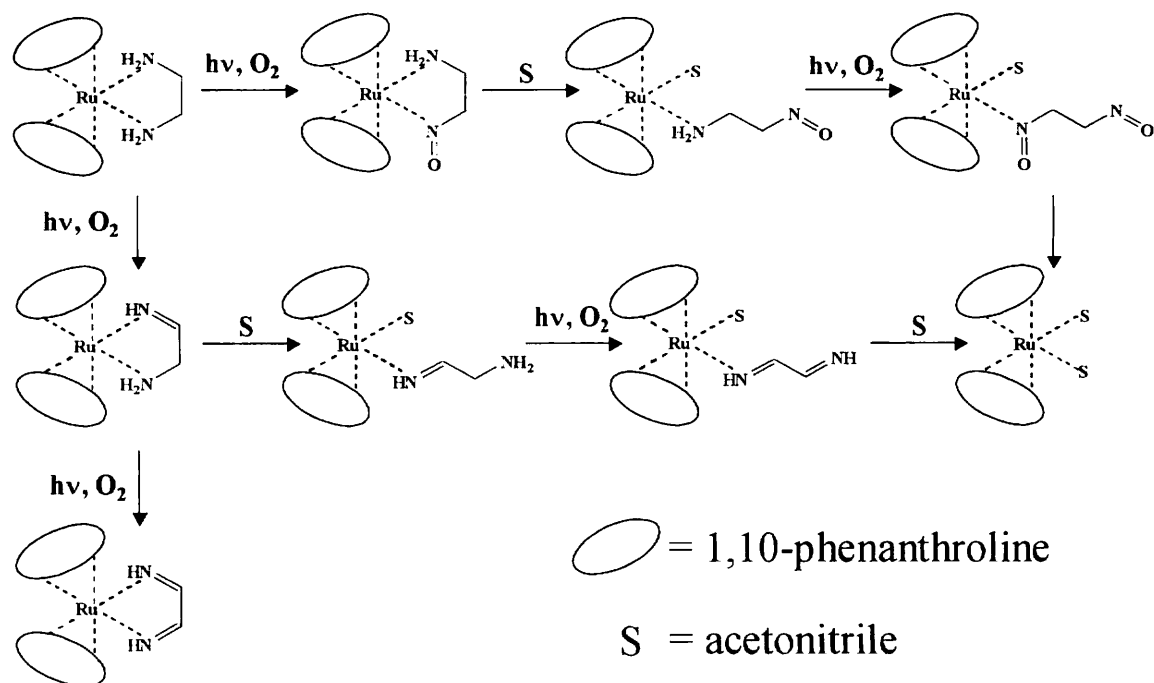


Fig. 2. Positive ESI mass spectra of [Ru(phen)₂(en)](PF₆)₂ with light irradiation; (a) no irradiation (0 min), (b) after 5 min, (c) after 15 min, (d) after 1 hour. The symbols of L, X, and S represent phen, PF₆, and acetonitrile, respectively. (en+14) shows that the mass is 14 mass units larger than that of the en ligand.



Scheme 1. The proposed pathway in the photochemical reaction of $[\text{Ru}(\text{phen})_2(\text{en})](\text{PF}_6)_2$

breakage of the one end of the bidentate nitroso-ligand bonding to Ru(II) and by replacement with a solvent molecule ($\text{S} = \text{acetonitrile}$) to form a monodentate complex ion.

This type of the monodentate complex was not observed in the photochemical reaction of $[\text{Ru}(\text{bpy})_2(\text{en})](\text{PF}_6)_2$. The difference in the photochemical reaction must be due to the difference in the dynamic configurational flexibility of the bpy and phen ligands in the Ru complexes. A bpy ligand possesses the configurational freedom of twist and bow in the molecule. A bpy ligand in the complex can flexibly change its configuration by *cis-trans* isomerization. This fact was reported from the observations of UV and NMR studies.¹⁷⁾⁻²⁰⁾ On the other hand, a phen ligand tends to maintain in a plane structure without twist. The phen ligand in the complex has been reported to form a rigid and stable *trans*-configuration. When the bidentate en ligand of the bpy complex is decoordinated by the irradiation, the decoordinated en ligand can easily undergo recoordination to form a stable complex because the bpy complex has a high degree of flexibility toward configuration changes. But when a phen complex is irradiated the complex tends to isomerize to a rigid and plane *trans* configuration, and the decoordinated en ligand is prevented from recoordination to the Ru metal and results in coordination of a solvent molecule.

The ions observed at m/z 736 and m/z 296 are the monodentate dinitroso-complexes with an acetonitrile ligand $[\text{RuL}_2(\text{en}+28)\text{S}]\text{X}^+$ and $[\text{RuL}_2(\text{en}+28)\text{S}]^{2+}$ ($(\text{en}+28) = \text{ON}-\text{CH}_2-\text{CH}_2-\text{NO}$), respectively. The spectrum obtained after 15 min of the light irradiation (Fig. 2c) showed the solvent-substituted ion at m/z 689 $[\text{RuL}_2\text{S}_2]\text{X}^+$ as the base peak. The ions of m/z 663 and 259 were the diimine complex ions, $[\text{RuL}_2(\text{en}-4)]\text{X}^+$ and $[\text{RuL}_2(\text{en}-4)]^{2+}$, respectively, where $(\text{en}-4)$ is the $\text{HN}=\text{CH}-\text{CH}=\text{NH}$ ligand. The spectrum after one hour

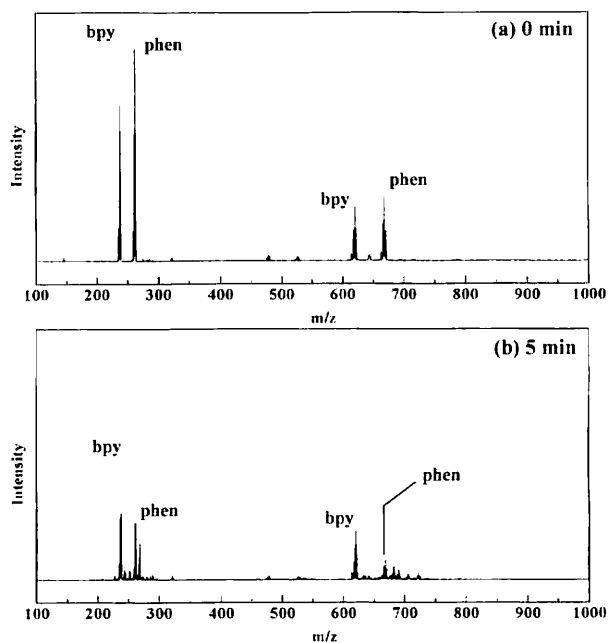


Fig. 3. ESI mass spectra of an equimolar mixture of $[\text{Ru}(\text{bpy})_2(\text{en})](\text{PF}_6)_2$ and $[\text{Ru}(\text{phen})_2(\text{en})](\text{PF}_6)_2$ with light irradiation; (a) no irradiation (0 min), (b) after 5 min. The two spectra are plotted in the same intensity scale.

of light irradiation (Fig. 2d) showed a final photochemical reaction product at m/z 689 $[\text{RuL}_2\text{S}_2]\text{X}^+$ as the base peak. The diimine ion at m/z 663 $[\text{RuL}_2(\text{en}-4)]\text{X}^+$ was also detected in the spectrum as the final reaction product. The same spectral results were obtained from the analysis of the tn and bn complexes.

The photochemical reaction pathway of the $[\text{Ru}(\text{phen})_2(\text{en})]^{2+}$ complex is summarized in Scheme 1. All of the ionic structures shown in the scheme were actu-

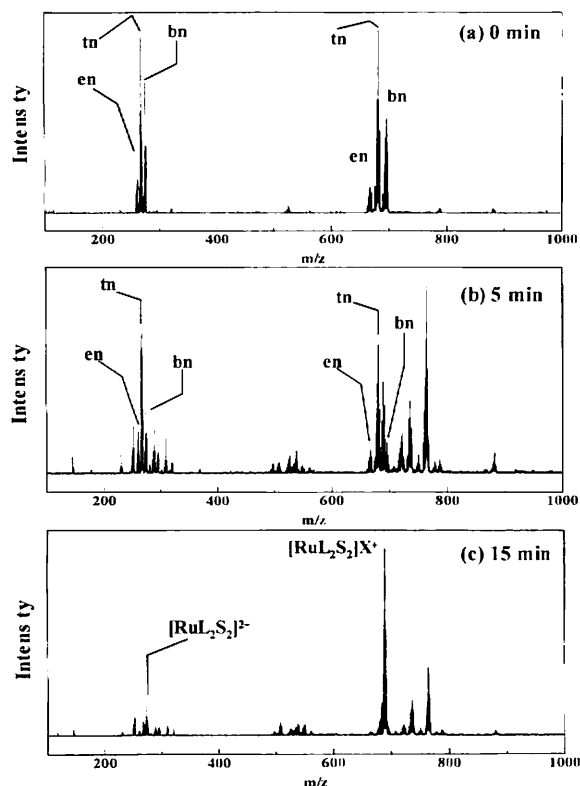


Fig. 4. ESI mass spectra of an equimolar mixture of $[\text{Ru}(\text{phen})_2\text{B}](\text{PF}_6)_2$ ($\text{B}=\text{en}, \text{tn}, \text{or bn}$) with light irradiation; (a) no irradiation (0 min), (b) after 5 min, (c) after 15 min. The spectra are plotted in the same intensity scale.

ally detected in the ESI-MS spectra. Two reaction paths, the nitroso complex and imine complex formation, proceed competitively upon light irradiation. The monodentate intermediates are present in the both pathways. Through these intermediates the solvent substituted complex and the diimine complex will be formed as the final photochemical reaction products.

The experiments were carried out to compare the photochemical reactivity of the $[\text{Ru}(\text{phen})_2(\text{en})](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2(\text{en})](\text{PF}_6)_2$ complexes. The ESI-MS spectrum of an equimolar mixture of the bpy and phen complexes without light (Fig. 3a) showed the 1+ and 2+ ions of the complex in nearly equal intensities. The spectrum obtained after 5 min of light irradiation (Fig. 3b) showed the decrease in both the parent ions of the bpy and phen complexes, but the decrease of the phen complex was more rapid than that of the bpy complex. The spectrum obtained after one hour of light irradiation showed no parent ion of the phen complex, but the parent ion of the bpy complex still remained in the solution. The results indicated that the phen complex is more photochemically reactive than the bpy complex. The reason is that the bpy ligand possesses the higher configuration flexibility, which can re-coordinate the diamine ligand more readily.

In order to study the difference of reactivity among $[\text{Ru}(\text{phen})_2\text{B}](\text{PF}_6)_2$ ($\text{B}=\text{en}, \text{tn}, \text{and bn}$) complexes, the light irradiation experiments were carried out with the 0.1 mM equimolar mixture solution. The spectrum before the irradiation (Fig. 4a) exhibited only the 1+

and 2+ parent ions of each complex. The spectrum after 5 min of the irradiation (Fig. 4b) showed that a decrease in the parent ion was a little greater for the bn complex than those for the en and tn complexes. The spectrum obtained after 15 min of the irradiation (Fig. 4c) showed $[\text{RuL}_2\text{S}_2]\text{X}^+$ as the base peak and the parent ions of the en, tn, and bn complexes were no more detectable. The spectral analysis did not clearly indicate the difference in the photochemical reactivity among the en, tn and bn ligands of the phen complex, but the same experiment on the bpy complexes indicated that the tn ligand was more photo-reactive than the en ligand.

In conclusion, the ESI-MS analysis of the photochemical reactions of the phen complexes $[\text{Ru}(\text{phen})_2\text{B}](\text{PF}_6)_2$ ($\text{B}=\text{en}, \text{tn}, \text{or bn}$) in acetonitrile indicated that the reactions are quite different from that of the analogous bpy complexes. The photochemical reaction of the phen complexes formed the monodentate imine and nitroso complexes, which were not detected with the bpy complexes. The phen complex was more photochemically reactive than the bpy complex. The difference in the reactivity is due to the difference in the dynamic flexibility of the configuration between the phen and bpy ligands in the Ru(II) complexes.

Acknowledgment

This work was partly supported by CREST of JST (Japan Science and Technology).

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Keywords: ESI-MS, Photochemical reactions, Bis(1,10-phenanthroline)diamineruthenium(II) complexes, Intermediate, MLCT