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On-Line Mass Analysis of Reaction Products by Electrospray Ionization. Photosubstitution of Ruthenium(II) Diimine Complexes

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The first observation of photosubstitution products in electrospray mass spectra is reported. The solvent-coordinated Ru(II) complex ions created by photodissociation of Ru(2,2′-bipyrazine)$_3$Cl$_2$, Ru(2,2′-bipyridine)$_3$X$_2$ (X = Cl$^-$ and ClO$_4^-$), and the related complexes in acetonitrile solution were directly detected by on-line electrospray mass spectrometry. The mass spectra were well explained in terms of coordinating ability of counterions and solvent. Collision-induced dissociation in the gas phase was an important process particularly for interpretation of photoproducts such as weakly-bound solvent-coordinated complexes. It was found that the electrospray technique, combined with a flowing photoreaction cell, can potentially be used to identify photoproducts or intermediates.

Introduction

Electrospray mass spectrometry (ES-MS) has recently been shown to be a powerful technique for the measurement of molecular mass of involatile and thermally labile compounds.[1−7] Indeed, these compounds are easily decomposed when they are ionized in the conventional method so that a lot of undesirable fragment ions appear in the mass spectra, which makes it difficult to identify the molecular mass. ES-MS has an attractive advantage of soft ionization. So it provides a quite simple mass pattern and allows us to determine molecular mass accurately with high sensitivity. Therefore, this method has been suited for the measurement of molecular mass of protein and nucleic acid.[3−7] ES-MS was also proved to be an important technique to identify metal complexes.[8−10]

Because of various superiority of ES technique, we felt that ES-MS may be a useful tool for on-line analysis of reaction products or reaction intermediates. In order to make sure this idea, we have examined photosubstitution reactions of metal complexes of bidentate ligands. Photosubstitution reactions of tris(bpz) (bpz = 2,2′-bipyrazine) and tris(bpy) (bpy = 2,2′-bipyridine) Ru(II) complexes and the related compounds in acetonitrile were employed as a model reaction. For these complexes, a large number of papers on photochemical reaction studies have been published.[11−19] The first study for photosubstitution of Ru(II) complexes was reported by Van Houten and Watts.[11] A photochemical release of a bipyridine ligand was observed when Ru(bpy)$_3^{2+}$ in 0.1 M HCl at 95 °C was irradiated with light at 436 nm. It was observed that the absorption band characteristic of Ru(bpy)$_3^{2+}$ was bleached during photolysis to form free bpy in the solution. The next study was a spectrophotometric analysis of the irradiated solution by Gleria et al.[12] By comparing UV and IR spectra of the photolysis products with those of the synthesized complexes, they concluded that the main product of photoreaction was *cis*-Ru(bpy)$_2$Cl$_2$. The more quantitative studies on Ru(bpy)$_3^{2+}$ were reported by Meyer and co-workers.[15] The apparent photochemical stability of Ru(bpy)$_3^{2+}$ in water was due to the dominance of chelatering closure and not of inherently low photochemical reactivity. The comparative chemistry of Ru(bpz)$_3^{2+}$ and Ru(bpy)$_3^{2+}$ was studied using spectroscopic and electrochemical methods by Crutchley and Lever.[16] They showed that the photosubstitution of Ru(bpz)$_3$(PF$_6$)$_2$ in acetonitrile containing chloride ion produced *cis*-Ru(bpz)$_2$(CH$_3$CN)Cl$^+$ with some quantum yield. Very recently, Tachiyashiki et al.[18,19] have identified a solvent-coordinated comprex as the intermediate in the photosubstitution of Ru(bpy)$_2$(dmbpy)$^{2+}$ (dmbpy = 3,3′-dimethyl-2,2′-bipyridine), in which the dmbpy

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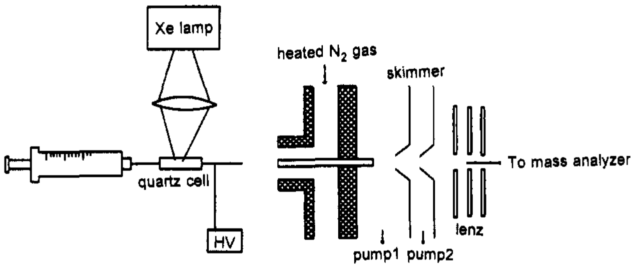

Figure 1. Schematics of electrospray mass spectrometry for on-line analysis of photochemical reaction products. The drawing is not to scale.

ligand coordinated to a Ru(II) ion as a monodentate ligand. The structure of solvent-coordinated complex was determined by means of ^{1}H-NMR. As stated above, mass spectrometry has not been used for identification of the photosubstitution products.

Here, we present the first application of on-line mass analysis to identify products or intermediates in the photolysis of $Ru(bpz)_3^{2+}$, $Ru(bpy)_3^{2+}$, and the related complexes in acetonitrile. The significant advantages for the on-line analysis of ES-MS was expected to be rapid and intact identification and highly sensitive measurement of reaction products. However, not only intact products but also the secondary products formed in the electrospray interface are observed in the ES mass spectra. The problem for implication of the secondary products will be discussed.

Experimental Section

A laboratory-made ES interface was connected to a sector-type mass spectrometer (JEOL-D300). The ES ion source is similar to that designed by Fenn.[2] As illustrated in Figure 1, a sample solution is sprayed at the tip of a needle applied by 3.5 kV higher than a counterelectrode. The distance between the needle and the counterelectrode was 1 cm. This counterelectrode consists of a 12-cm long capillary pipe of stainless steel. A heated N_2 gas (70 °C) flowing between the needle and the capillary electrode was used to aid desolvation of charged droplets sprayed. Ions enter in the vacuum system through the first and the second skimmer. The pressures of these regions were about 10 and 0.1 Torr, respectively. The flow rate of the solution was 2−3 μL/min. An ion beam was focused by a lens system and travels about 20 cm before entering into the main slit. This region is pumped down to the typical pressure of 2×10^{-6} Torr. A rotary pump and a mechanical booster pump for differential pumping stages are floating electrically to depress a discharge. The voltage of the second skimmer determines the translational energy of ions in the mass spectrometer. In the present case, the ion translational energy was 2 keV. The voltages of the capillary electrode and the first skimmer were respectively 100 and 50 V higher than that of the second skimmer.

The sample solution was irradiated with a high-pressure Xe lamp (150 W). A reaction cell is a cylindrical quartz cell of 1 mm in inner diameter, installed at the middle of the needle (Figure 1). The size of a light spot focused by the lens was ca. 5 mm in diameter. A UV-cut filter was used in necessary. It takes about 2 min for a flowing sample to pass across the light area in the cell, and a few tens of seconds to arrive at the tip of needle for spraying. Thus, the present ES mass analysis is able to detect photoproducts with lifetime of more than a few minutes. A light shutter mounted at the exit of the lamp was used to control photoirradiation. $Ru(bpz)_3Cl_2 \cdot 3.5H_2O$ was prepared by the literature methods.[13,16] For measurements of ES mass spectra, all of the samples were dissolved in freshly distilled acetonitrile. Neither acid nor salts to promote the ionization were added unless specified in the text. The sample concentration was <0.1 mM.

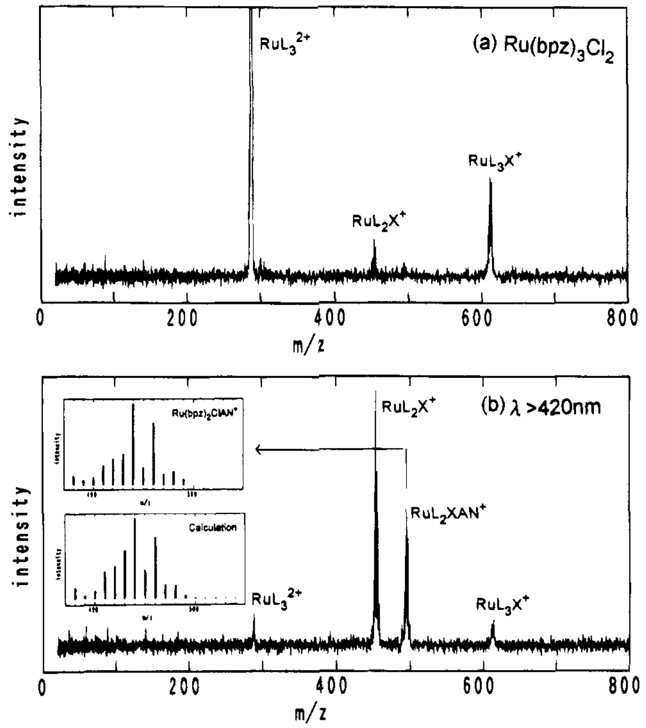

Figure 2. Positive ion ES mass spectra of $Ru(bpz)_3Cl_2$ (bpz = 2,2′-bipyrazine) in acetonitrile solution (0.01 mM) obtained (a) without and (b) with photoirradiation (λ > 420 nm). L is bpz, AN is acetonitrile, and X is Cl^-. The bar graphs in part b represent the experimental and the calculated isotope distribution for the photosubstitution product $Ru(bpz)_2(AN)Cl^+$. The peak $Ru(bpz)_2Cl^+$, which appeared in part a, is probably due to exposure of a room light.

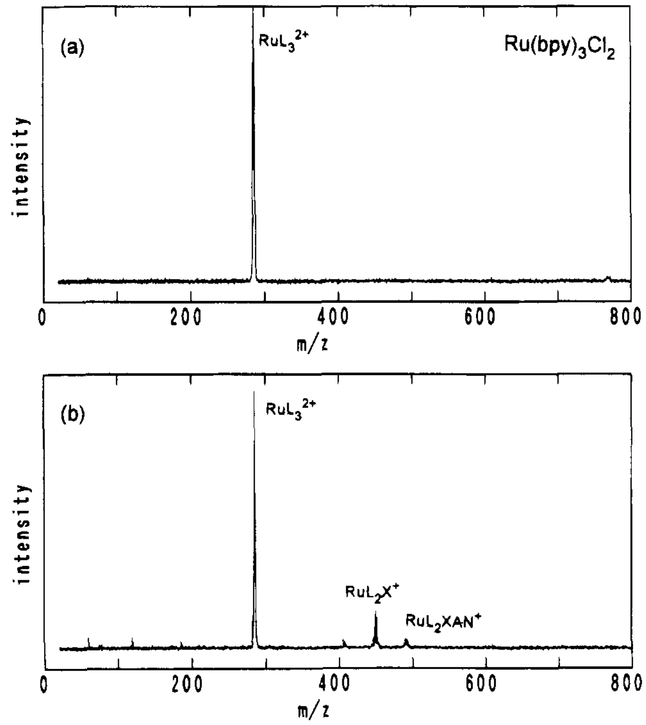

Figure 3. ES mass spectra of $Ru(bpy)_3Cl_2$ (bpy = 2,2′-bipyridine) in acetonitrile (0.1 mM); (a) without and (b) with photoirradiation (λ > 290 nm).

Results and Discussion

Figures 2−4 show the ES mass spectra for $Ru(bpz)_3Cl_2$, $Ru(bpy)_3Cl_2$, and $Ru(bpy)_3(ClO_4)_2$; the upper figure (a) is observed without photoirradiation, while the lower (b) is with photoirradiation. In each complex, spectra a and b were measured under the same experimental conditions. The following abbreviations are used for peak assignment in the spectra: L denotes the bidentate ligand, X is Cl^- or ClO_4^-, and AN is acetonitrile.

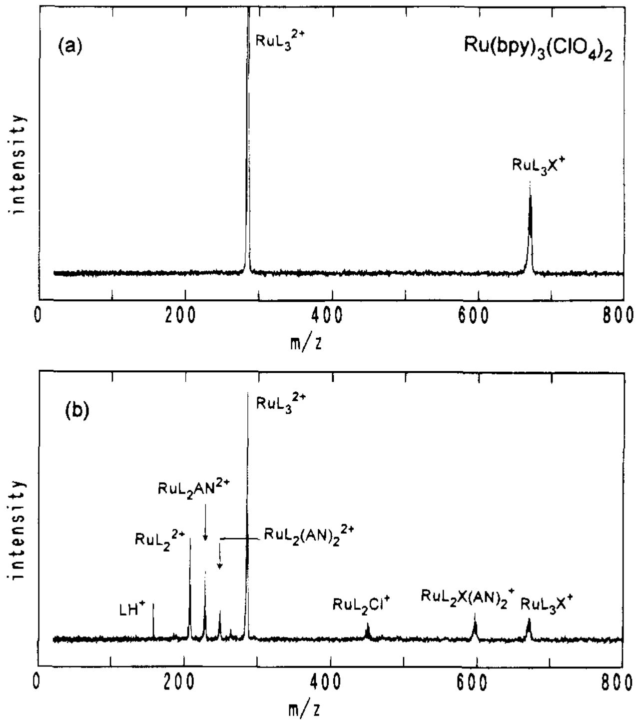

Figure 4. ES mass spectra of $Ru(bpy)_3(ClO_4)_2$ in acetonitrile (0.1 mM); (a) without and (b) with photoirradiation ($\lambda > 420$ nm).

$Ru(bpz)_3Cl_2$ and $Ru(bpy)_3Cl_2$. Figure 2 demonstrates the first on-line observation of photosubstitution reaction in solution by mass spectrometry. Without photoirradiation, a peak of the ion association product $Ru(bpz)_3Cl^+$ is observed in low intensity in addition to the most abundant peak of $Ru(bpz)_3^{2+}$. The ES ionization results from the transfer of ions initially present in solution into the gas phase. Thus, with the first approximation, the ES mass spectra reflect ion-association equilibrium in solution.[10] With irradiation of filtered light ($\lambda > 420$ nm), the intensity of $Ru(bpz)_3^{2+}$ rapidly decreased, while Cl^--coordinated species $Ru(bpz)_2Cl^+$ and $Ru(bpz)_2(AN)Cl^+$ increased. The solvent-coordinated ion $Ru(bpz)_2(AN)Cl^+$ is assigned by comparing isotope distribution with the calculated (Figure 2b). The neutral six-coordinate species $Ru(bpz)_2Cl_2$ is of course produced in the solution, but the neutral species is undetectable.

The 2,2′-bipyridyl complex $Ru(bpy)_3Cl_2$ analogous to $Ru(bpz)_3Cl_2$ was also photoreactive, but its reactivity was much less than that for $Ru(bpz)_3Cl_2$ (Figure 3). A considerable amount of the precursor ion $Ru(bpy)_3^{2+}$ still remained. The formation of Cl^--coordinated species following the photoinduced release of ligand was much less facile for bpy than for bpz. Crutchley and Lever[16] reported, for the first time, that the photosubstitution of $Ru(bpz)_3(PF_6)_2$ was observed in acetonitrile solution containing chloride ion. The quantum yield for the production of Cl^--coordinated species was dependent on the concentration of Cl^-, being greatest at $[Cl^-] = 2$ mM. The quantum yields obtained for the formation of $Ru(bpz)_2(AN)Cl^+$ and $Ru(bpz)_2Cl_2$ were 0.37 and 0.001, respectively. On the other hand, Jones and Cole-Hamilton,[14] under different experimental conditions, obtained a quantum yield of 0.01 for the formation of $Ru(bpy)_2(AN)Cl^+$ in the photosubstitution of $Ru(bpy)_3^{2+}$. Our data shows the same trend as these references: the bpz complex was much more photosensitive than the bpy complex.

It is noted that no complex of monodentate bpz or bpy was clearly detected in the ES mass spectra. The spectroscopic study on the photosubstitution of $Ru(bpz)_3^{2+}$ showed that a complex of monodentate bpz was formed in acetonitrile solution containing 20mM tetraethylammonium chloride, though unidentified.[16] The experimental condition was quite different from ours. It was difficult to obtain clean ES mass spectra for the sample solution containing as much as 1 mM tetraethylammonium chloride. Addition of tetraethylammonium chloride caused the intensity of the signals of Ru(II) complex to be greatly depressed compared with no addition of the electrolyte. Such ion strength effect on ES mass spectra is still unclear.

In Figure 2, the signal intensity of $Ru(bpz)_3Cl^+$ relative to $Ru(bpz)_3^{2+}$ is apparently larger with photoirradiation than without irradiation. This may implicate the production of a different ligand configuration of $Ru(bpz)_3Cl^+$ under photoirradiation. One of the possible configuration is the Cl^--coordinated complex with a monodentate bpz, which is considered to be the intermediate in the stepwise photosubstitution. On the other hand, the configuration of $Ru(bpz)_3Cl^+$ without irradiation must be the ion association between $Ru(bpz)_3^{2+}$ and Cl^-.

$Ru(bpy)_3(ClO_4)_2$. The effect of counterion on the ES mass spectra is shown in Figure 4. A series of doubly charged, solvent-coordinated $Ru(bpy)_2(AN)_n^{2+}$ ($n = 0-2$) were observed for $Ru(bpy)_3(ClO_4)_2$, while not observed for $Ru(bpy)_3Cl_2$. Because the coordinating strength of anion to Ru(II) ion is much stronger for Cl^- than for ClO_4^-, the coordination of Cl^- to the photoproduct $Ru(bpy)_2^{2+}$ easily occurs to form $Ru(bpy)_2(AN)Cl^+$ and $Ru(bpy)_2Cl_2$. Interestingly, the four-coordinated $Ru(bpy)_2^{2+}$ was the most abundant among the series of $RuL_2(AN)_n^{2+}$ ions. It is unlikely that this ion is most stable in the solution. This is due to the secondary reactions such as ligand stripping induced by a collision with a residual gas molecule between two skimmers, called collision-induced dissociation(CID), before the ions enter the mass spectrometer.[8]

$$RuL_2(AN)_2^{2+} \rightarrow RuL_2(AN)^{2+} + AN \qquad (1)$$

$$\rightarrow RuL_2^{2+} + 2AN \qquad (2)$$

The bonding between Ru(II) ion and AN is so weak, compared with bpy, that the CID reactions 1 and 2 are probable paths to give $RuL_2(AN)^{2+}$ and RuL_2^{2+}. The CID release of bpy ligand was never observed in the ES mass spectra of Ru(II) complexes if the collision energy was as low as 50 eV. In the present case, the collision energy was determined from difference between the two skimmer voltages. The bidentate ligand such as bpy is bonded to the Ru(II) ion strongly enough to be against the CID release. The peak intensity of RuL_2X^+ was always larger than that of $RuL_2(AN)X^+$ in the photoirradiation mass spectra of $Ru(bpz)_3Cl_2$, $Ru(bpy)_3Cl_2$, and $Ru(bpy)_2Cl_2$. This must be also related to CID.

Among the singly charged ions, $Ru(bpy)_2(AN)_2(ClO_4)^+$ was only detected as the AN-coordinated species. The four- or five-coordinate ions, as detected in the case of the doubly charged ions, was not observed. The stability of $Ru(bpy)_2(AN)_2(ClO_4)^+$ against the CID release of AN may be due to the formation of ClO_4^- adduct. The AN ligands seem to be surrounded by a ClO_4^- counterion of large radius. It protected the ClO_4^- associated complex from CID reactions like (1) and (2).

Figures 3 and 4 suggest that $Ru(bpy)_3(ClO_4)_2$ is more photoreactive than $Ru(bpy)_3Cl_2$; the ratio of the bis complex to the tris complex is much larger for the former than that for the latter. This is contrary to the results of other studies. The neutral $Ru(bpy)_2Cl_2$ must be a significant photoproduct for irradiation of $Ru(bpy)_3Cl_2$ under the conditions of this study, because Cl^- has higher ability of coodination than ClO_4^-.[20]

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(20) Suggested by the reviewers.

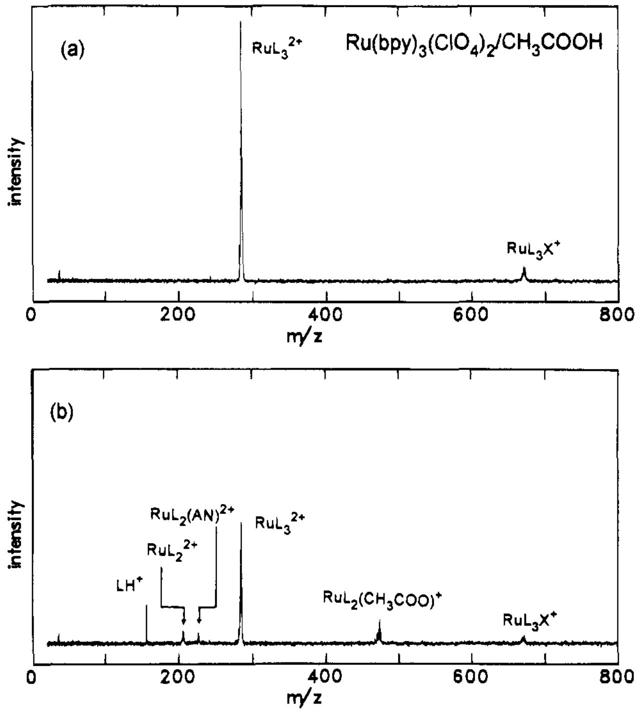

Figure 5. ES mass spectra of $Ru(bpy)_3(ClO_4)_2$ in acetonitrile/acetic acid (2% by volume) solution (0.1 mM) obtained (a) without and (b) with photoirradiation (λ > 420 nm).

The peak of nominal *m/z* 449 in Figure 4b corresponds to $Ru(bpy)_2Cl^+$. This ion was probably formed from the coordination of Cl^- released by a certain photoreaction involving ClO_4^- because Cl^- easily coordinates $Ru(bpy)_2^{2+}$. It should be noticed that the detection of protonated bpy LH^+ was direct evidence for the photoinduced ligand-dissociation of $Ru(bpy)_3^{2+}$ in acetonitrile.

The photosubstitution by acetate ion is shown in Figure 5. $Ru(bpy)_3(ClO_4)_2$ was sprayed with a CH_3CN/CH_3COOH (2% by volume) solution. The formation of an acetate-coordinated complex $Ru(bpy)_2(CH_3COO)^+$ was clearly observed as shown in Figure 5b. However, the addition of acetic acid prevented the formation of the singly charged ion $Ru(bpy)_2(AN)_2(ClO_4)^+$ which was observed in Figure 4. This is because acetate ion has stronger ability of coordination than AN. The photochemical reactivity of $Ru(bpy)_3^{2+}$ was not particularly promoted by the addition of acetic acid.

Other Ru(II) Complexes. The photoirradiation of neutral complex $Ru(bpy)_2Cl_2$ led to the release of not the bpy ligand but the Cl^- ligand and to production of the AN-coordinated complex (Figure 6). It should be noted that the complex ion $Ru(bpy)_2Cl_2^+$ was detected in the ES mass spectra. It is very unlikely that such an oxidized species $Ru^{III}(bpy)_2Cl_2^+$ was present in the solution phase. Thereby the oxidized complex is presumed to be formed by the electrochemical oxidation at the tip of ES needle where the high voltage was applied during spraying. The limit of electrochemical oxidation by this ES process was reported to be $E_{1/2} \sim 1$ V, where $E_{1/2}$ is a half-wave oxidation potential with respect to the saturated calomel electrode(SCE). The $E_{1/2}$ value for $Ru(bpy)_2Cl_2$ is 0.32 V. This problem has recently been discussed by Kebarle and coworkers[21] and Berkel et al.[22]

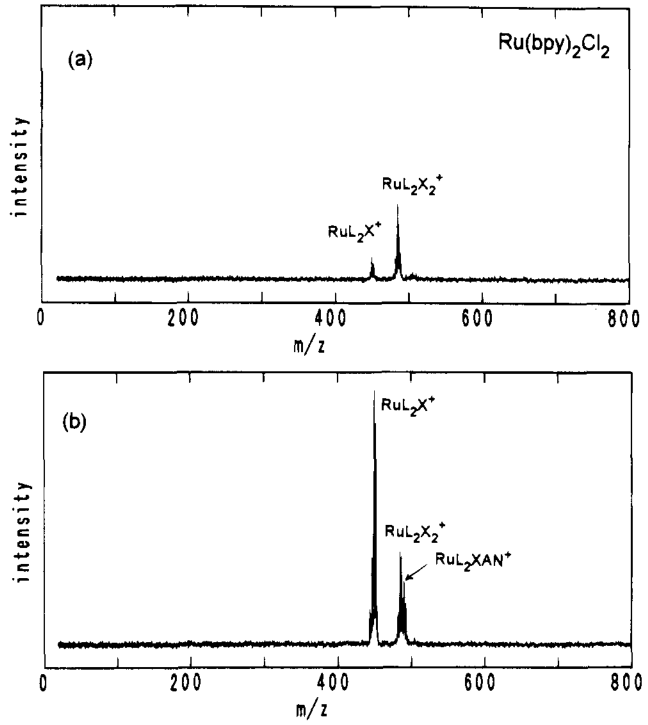

Figure 6. ES mass spectra of $Ru(bpy)_2Cl_2$ in acetonitrile (0.1 mM): (a) without and (b) with photoirradiation (λ > 420 nm).

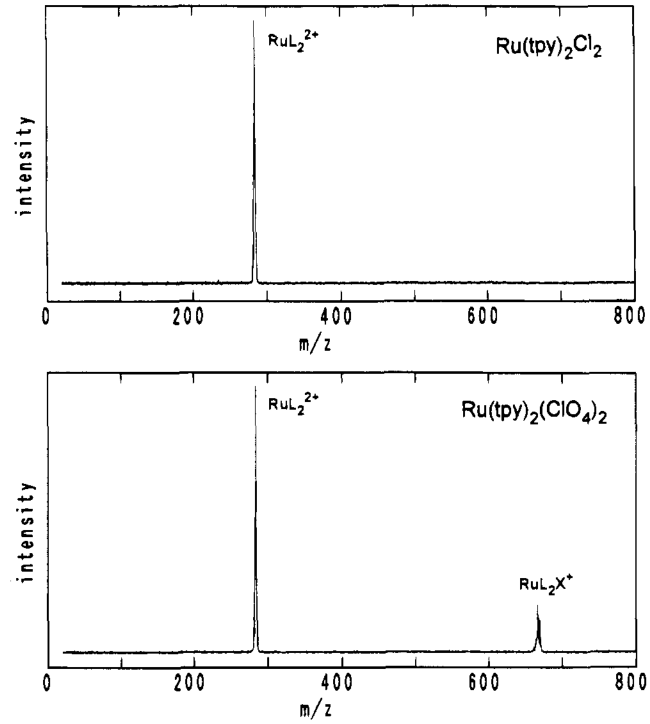

Figure 7. ES mass spectra of (a) $Ru(tpy)_2Cl_2$ (tpy = 2,2′:6′,2″-terpyridine) and (b) $Ru(tpy)_2(ClO_4)_2$ in acetonitrile (0.1 mM) obtained without photoirradiation.

The results of ES measurements for the tridentate tpy complexes $Ru(tpy)_2Cl_2$ and $Ru(tpy)_2(ClO_4)_2$ are shown in Figure 7. There was no change in the mass spectra of these complexes with/without irraiation (λ > 290 nm). The addition of 0.5 mM HCl to promote the photosubstitution caused no effect on the photoproducts. Thus the tridentate tpy complexes are photochemically inert in contrast with bpz, bpy and Cl^-.

As is seen in Figure 7, the counterion adduct $Ru(tpy)_2X^+$ in acetonitrile was much more abundant for X = ClO_4^- than for XCl^-. This trend was the same as $Ru(bpy)_3X_2$ in Figures 3a and 4a. The relative abundance of the counterion-associated complex in the mass spectra is essentially reflective of stability

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in the gas phase rather than in be liquid phase. The results show that the stability of RuL_3X^+ is larger for ClO_4^- than for Cl^-. However, the stability in the gas phase may be reversed because the ion radius of Cl^- is smaller than that of ClO_4^-. The association constant for tetrabutylammonium salts Bu_4NX ($X = Cl^-, Br^-, I^-$, and ClO_4^-) in the solution phase such as alcohol were obtained from the precise conductance measurements by Evans and co-workers.[23] Their data showed that the effective ion radius was larger for Cl^- than for ClO_4^- because Cl^- was more strongly solvated. In other words, the ion association interaction is larger for ClO_4^- than for Cl^- in the solution. If the solvation to anion is the same in acetonitrile, the present ES mass spectra probably look at the solution equilibrium. Finally, it depends upon the mechanism of electrospray ionization what the spectra actually look at. But, the ES mechanism is still under debate.

Conclusions

Here we presented a new application for mass spectroscopic study to photoreaction in solution using the ES interface with reaction cell and analyzed photosubstitution for the Ru(II) chelate complexes. The ES mass spectra for the complexes of bpz, bpy, tpy, and Cl^- ligands were measured for the photoirradiated acetonitrile solution. As a result, the ligand release and the formation of solvent-coordinated ions were observed. However, no photorelease of ligand took place from the tridentate tpy complexes.

The intermediate complexes of monodentate bpz (or bpy) such as $RuL_3(AN)^{2+}$ (L = bpz or bpy) were not able to be explicitly demonstrated in the ES mass spectra; however, $Ru(bpz)_3Cl^+$ formed for irradiation of $Ru(bpz)_3Cl_2$ may be the complex of monodentate bpz even though the evidence for this is indirect. The reason for difficulty in observing the intermediates is that they have too short a lifetime to be detected in the present experimental arrangement. Thus, to detect the short-lived intermediates, we must carry out the photoirradiation at a tip of the ES needle using a more powerful light source than the present one.

One of the difficulties in the ES technique is to introduce the weakly bound complexes, as is, into the mass analyzer. For instance, $Ru(bpy)_2(AN)^{2+}$ and $Ru(bpy)_2^{2+}$ were the secondary products formed by CID of AN-coordinated ion $Ru(bpy)_2(AN)_2^{2+}$ in the gas phase. In this way, the ES mass spectra show in some case not the actual equilibrium in solution, but artifacts formed in the ES interface. Moreover, it may happen that coexisting eiectrolyte prevents the transfer of the actually dissolved ions from droplets into the gas phase so that the sensitivity of the desired ion signal is strongly depressed by the electrolyte.

The present ES-MS method for analysis proved analytically useful for easy identification of photoreaction products in solution. The current method will be able to extend on-line mass analysis for chemical or electrochemical reaction if a reaction cell or an electrolytic cell is installed just on the upper stream of electrospraying.

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