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PHOTOAQUATION OF CIS-DIBROMOTETRAAMMINERUTHENIUM (III) COMPLEX

Akira OHYOSHI, Noriyuki TAKEBAYASHI, and Yutaka HIROSHIMA
Department of Industrial Chemistry, Faculty of Engineering,
Kumamoto University, Kurokami, Kumamoto 860

Studies have been made on the photochemistry of aqueous cis-$Ru(NH_3)_4Br_2^{2+}$. In a solution of pH lower than 2.5, following simple aquation seems to occur; cis-$[Ru(NH_3)_4Br_2]^+ + H_2O \rightarrow$ cis-$[Ru(NH_3)_4BrH_2O]^{2+} + Br^-$. The quantum yield was found to depend on the wavelength of light, but not on the bromide-ion and hydrogen-ion concentrations. The typical value was respectively 5.6×10^{-3}, 2.7×10^{-3}, and 1.4×10^{-3} at the irradiation of 330, 382, and 434 nm light.

Although there have been many studies on the photochemistry of 3d metal complexes, studies of 4d metal analogs, in particular, of the ruthenium complexes are scarce. The recent photochemical study of hexaammine- and chloropentaammineruthenium(III) by Wells and Endicott$^{1)}$ has demonstrated that both the complex ions are very inert when their ultraviolet absorption bands are irradiated, and that the photoinduced aquation of an ammine ligand can be established for each complex with a low quantum yield.

The present paper represents the results of the photochemical studies on the cis-dibromotetraammineruthenium(III) complex to compare with those of the monohalogenopentaammines. The relative reaction rate was determined as a function of hydrogen and bromide ion concentration in a solution, and of the wavelength of the incident radiation.

Photolyses were performed using a JASCO CRM-FA Spectralirradiator with a 2 KW xenon arc lamp. A known volume of sample solution in a rectangular quartz cell with a 1-cm light path length was kept at 25°C, and purified argon gas was passed through the solution during irradiation to avoid an appreciable secondary photolysis or inner filter effects. The solution was irradiated for a preset time period with monitoring the light flux using a JASCO RMI-1 Integrating Radiometer with a thermopile. Absorbed light intensities (I_a) were determined using a ferrioxalate actinometer$^{2)}$ (λ<400 nm) and a Reineckate actinometer$^{3)}$ (λ>400 nm). The concentration of reactant was determined from the absorbance at 441 nm of the first absorption band using a Hitachi 124 spectrophotometer. The pseudo first-order plot gave a straight line for about 120 min at an irradiation rate 2.5×10^3 photons,l^{-1},min^{-1}. Initial slope of this plot was used to calculate an initial rate of complex decomposition. This initial rate was used along with I_a values to calculate a quantum yield.

cis-Dibromotetraammineruthenium(III) complex was prepared by the method of Gleu.$^{4)}$ Found: H, 2.91; N, 13.82%. Calcd for $[RuBr_2(NH_3)_4]Br$: H, 2.94; N, 10.19%.

The progressive changes in the absorption spectrum in an acidic solution is shown in Fig. 1. Two absorption bands in the spectrum can be assigned to the charge transfer absorption from ligand to metal ($\pi \rightarrow t_{2g}$)$^{5)}$, and the band wavelength is in agreement with that calculated by Jϕrgensen's empirical formula$^{6)}$. Figure 1 shows that the absorbance of the first band (442 nm) decreases with the increase of second band (370 nm) which slightly shifts to longer wavelengths with the passage of reaction time. The final spectrum shows a new peak different from that of the two peaks of the initial complex ion. This spectrum suggests that the reaction product is probably cis-monobromoaquotetraammine complex. The similar observation has been described in the aquation study of the dichlorobisethylenediammine-ruthenium(III) complex.[7] Thus we assumed that the photoreaction takes place mainly via the aquation process as follows;

$$\text{cis-}[\mathrm{Ru(NH_3)_4Br_2}]^+ + \mathrm{H_2O} \rightarrow \text{cis-}[\mathrm{Ru(NH_3)_4BrH_2O}]^{2+} + \mathrm{Br^-} \quad (1)$$

We have varied several parameters of the photolysis system to observe their effects on the reaction rate or quantum yield. As is shown in Fig.2, the plotted straight lines indicate that the photoaquation and thermal reaction are both first-order with respect to the complex under given reaction conditions. The thermal reaction is somewhat observed at 25°C, therefore, the net photoreaction rate was determined by subtracting this contribution. Any effects of the bromide ion concentration and of the ionic strength on the reaction rate have not been observed in acidic solutions. This facts indicate that the bromide ion does not concerned in the rate determining step.

The effect of pH on the reaction rate is exhibited in Fig.3. The rate accelaration which observed in pH over the region 2.0 < pH < 3.5 suggests that the additional base hydrolysis participates to the aquation reaction. This fact was confirmed by the spectroscopic observation. All the observations of the changes for the absorption spectrum gave an evidence of partially aquated ruthenium(III) complex species and this formation rate was in agreement with that of the original complex disappearance. Thus, the quantum yield for the photoaquation was determined with the variety

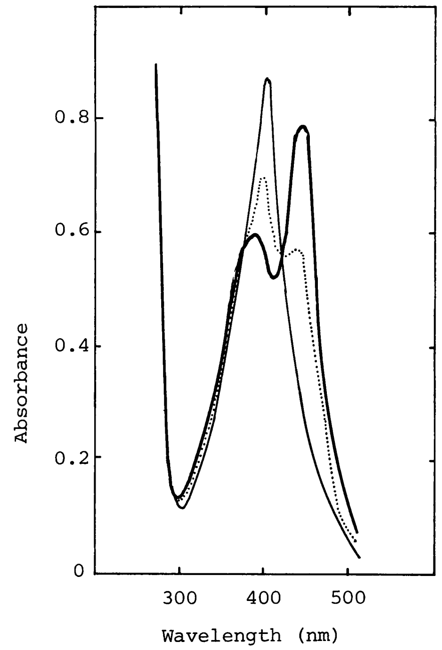
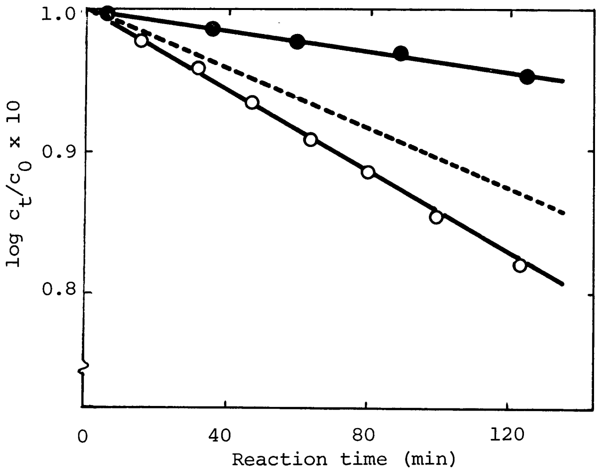


Fig.1. Spectral change of cis-[RuBr$_2$(NH$_3$)$_4$]$^+$ in the photochemical reaction at pH=2.0, 434 nm light irradiation(2.5 x10^{3}photons. l^{-1}.min^{-1}), —— initial spectrum; ············ intermediate spectrum (60 min); ——— final spectrum (300 min).



ig.2. Plots of log c_t/c_0 vs. reaction time at 25°C, pH = 2.2, c_0; initial concentration (5.0×10^{-4}M), c_t; concentration at the reaction time,t.
-o- over all reaction at 434 nm light irradiation, -●- dark reaction, ---- net photoreaction.

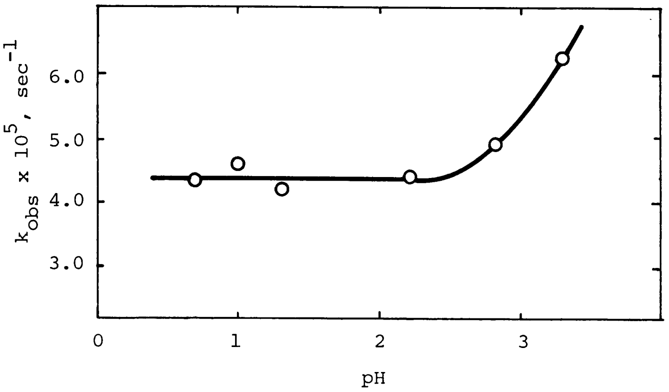


Fig. 3. Effect of pH on the photoreaction rate constant at 434 nm light irradiation, 25°C, [complex]=5.0x10^{-4}M.

Table 1. Spectral data and Quantum yield(Φ) for photoaquation of cis-$[Ru(NH_3)_4Br_2]^+$, in acidic solution.

λ_{max} (nm)	$\varepsilon, 10^3$ ($M^{-1}cm^{-1}$)	light wavelength (nm)	$\Phi, 10^{-3}$
		330	5.6
370	1.30		
		382	2.7
		434	1.4
442	1.66		
		492	≃ 0

of irradiated light wavelength. As is shown in Table 1, the quantum yield is dependent on the light wavelength but it is low comparing with those for the ammine ligand aquation of the chloropentaammineruthenium(III) reported by Wells and Endicott.1) The relatively high yield observed at shorter light wavelength can be regarded as suggestive of population of a charge transfer to metal (CTTM) excited state with a different electronic configuration from that produced by the light irradiation with longer wavelength.

In spite of the same electronic configuration with respect to the central metal, the type of the photochemical reaction of cis-dibromotetraammineruthenium(III) is different from that of the monochloropentaammineruthenium(III), that is, the former is the bromide ligand aquation, while the latter is the ammine ligand aquation. In the other series of photochemical survey, it was found that the cis-dichlorotetraammine complex was remarkably photounreactive, but cis-diiodotetraammine was more photosensitive than cis-dibromotetraammine, for example, the quantum yield for the photoaquation was estimated to be 8.2×10^{-3} at the 408 nm light irradiation. In the case of the halopentaamminecobalt(III) complexes, the type of the photoreaction varied with the kind of halide ligand.8,9) At the same 370 nm light irradiation, the chloride aquation is only observed with 1×10^{-4} yield for the chloropentaammine, while only the photoredox reaction has been observed with 6.6×10^{-3} yield for the iodopentaammine complex. For the bromopentaammine, both the bromide aquation and the redox reaction have been found with the product ratio 1.0 and the quantum yield 2.1×10^{-2}. In the case of the series $[CoX(CN)_5]^{3-}$, X=Cl, Br, and I, Adamson and Sporer8) reported that the quantum yields for aquation decreased in the order I,CN,Br,Cl, which is not the order of the spectrochemical series, but is the order of increasing difficulty of oxidation of the ligand. These facts suggest that the presence or absence of photochemical redox reactions depends on the oxidizability of the ligand. Thus, we concluded that the quantum yield for aquation decreased in the order I,Br,NH_3,Cl.

The fact that the order is preferably that of decreasing oxidizability of the ligand suggests that the primary reaction is one of homolytic bond breaking. A successive reaction is probably the deactivation or the aquation of the species formed by the homolytic bond fission because the quantum yield is independent on the pH in 0.35 ∿ 2.0 range and ionic strength of the reaction solution.

Wells and Endicott1) reported that the quantum yield for the photoaquation of the chloropentaammineruthenium(III) is independent on the light wavelength. It has been interpreted by assuming that the photoreactivity comes from ligand exchange in the lowest energy excited state formed by the CTTM band irradiation. To account for the variation in the quantum yield with wavelength in our results, it may be reasonable to assume that the probability of deactivation process of the primary excited state increases with the decrease in the excitation energy.

The present reaction can be reasonably interpreted according to the "Three-stage Mechanism" proposed by Adamson and Sporer.8) The first stage is homolytic bond breaking.

$$\mathrm{Ru^{III}(NH_3)_4Br_2} + h\nu \rightarrow \mathrm{Ru^{II}(NH_3)_4Br^{\cdot}Br^{\cdot}} \tag{2}$$

The species $\mathrm{Ru^{II}(NH_3)_4Br^{\cdot}Br^{\cdot}}$ is a common precursor which can return to the ground state,

$$\mathrm{Ru^{II}(NH_3)_4Br^{\cdot}Br^{\cdot}} \rightarrow \mathrm{Ru^{III}(NH_3)_4Br_2} \tag{3}$$

In another path, it can react with the water molecule or hydroxy ion,

$$\mathrm{Ru^{II}(NH_3)_4Br^{\cdot}Br^{\cdot}} + \mathrm{H_2O} \rightarrow \mathrm{Ru^{II}(NH_3)_4H_2OBr^{\cdot}Br^{\cdot}} \tag{4}$$

$$\mathrm{Ru^{II}(NH_3)_4Br^{\cdot}Br^{\cdot}} + \mathrm{OH^-} \rightarrow \mathrm{Ru^{II}(NH_3)_4OHBr^{\cdot}Br^{\cdot}} \tag{5}$$

The frequency for the reactions(4) and (5) depends on the acidity of the reaction solution. The product species may be Ru(II) complex with a $\mathrm{Br^{\cdot}}$ radical in the second coordination sphere. This radical species has not yet been detected in our experiment, however it may react in the following way. When the electron transfer from the metal to bromine is favorable energetically, the aquation or base hydrolysis will result.

$$\mathrm{Ru^{II}(NH_3)_4H_2OBr^{\cdot}Br^{\cdot}} \rightarrow \mathrm{Ru^{III}(NH_3)_4H_2OBr} + \mathrm{Br^-} \tag{6}$$

$$\mathrm{Ru^{II}(NH_3)_4OHBr^{\cdot}Br^{\cdot}} \rightarrow \mathrm{Ru^{III}(NH_3)_4OHBr} + \mathrm{Br^-} \tag{7}$$

The sequence of reactions (2)∿(5) seems to be reasonable. The reverse reaction (3) would account for the fact that the quantum yields are less than unity. However, it does not account for the variations in the quantum yield with wavelength. It may be plausible that the probability of the reaction (2) does increase as the excitation energy decreases.

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