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Studies of Ruthenium Complexes. VII.[1] Photochemical Reactions of *cis*-Dihalogenotetraammineruthenium(III) Complexes in Aqueous Solutions

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Studies have been made of the photochemistry of *cis*-dihalogenotetraammineruthenium(III) in aqueous solutions. For the *cis*-dichlorocomplex, no photochemical reaction has been observed by the irradiation of the visible light region. For *cis*-dibromo- and *cis*-diiodo-complexes, a simple aquation of halide ligand seems to occur in a solution with a pH lower than 2.5. The typical values of the quantum yields for the $cis\text{-}[\mathrm{RuX_2(NH_3)_4}]^+ + \mathrm{H_2O} \xrightarrow{h\nu} cis\text{-}[\mathrm{RuX(OH_2)(NH_3)_4}]^{2+} + \mathrm{X}^-$ reaction were 0.27×10^{-2} (382 nm light) and 0.82×10^{-2}(408 nm light) for dibromo- and dichloro-complexes respectively. The quantum yield was dependent on the wavelength of light, but was independent of the concentrations of halide and hydrogen ions. The quantum yield seems to depend on the oxidizability of the ligand or on probability of the deactivation process in the primary excited state. In accounting for the low quantum yield, it seems most probable that the photoexcited complex species is converted to the ground state by non-radiative transitions.

Although there have been many studies of the photochemistry of 3d metal complexes,[2–7] those of 4d metal analogs, in particular of the ruthenium complexes, are scarce. A recent photochemical study of hexaammine- and chloropentaammineruthenium(III)[8] has demonstrated that both of the complex ions are largely unreactive when their ultraviolet absorption bands are irradiated and that the photoinduced aquation of the ammine ligand can be established for each complex with a low quantum yield ($\phi<0.1$). The detectable photoredox process has not been observed by the irradiation of light in the region of charge transfer from ligand to metal(CTTM-band). Qualitatively, it might be expected that absorption in the region of an electron-transfer band would lead to the oxidation-reduction process, while the absorption in the region of a ligand-field band would cause a substitution reaction of the ligand. This photochemical inertness of the t_{2g}^6 ruthenium(III) complexes has been interpreted on the assumption of a small distortion at the excited states with a t_{2g}^5 electronic configuration and on the assumption that the CTTM states are lower in energy than those of the d-d excited states.

In the present study, the photoaquation rates of *cis*-dihalogenotetraammineruthenium(III) complexes were determined as a function of the hydrogen and halide ion concentrations, and the dependence of the quantum yield on the wavelength of the incident radiation was investigated. The results were then discussed in comparison with those of the hexaammine and chloropentaammine complexes of ruthenium(III) and with those of the analogous complexes of cobalt(III) and chromium(III).

Experimental

Materials. All the chemicals used were of a reagent grade. The *cis*-dihalogenotetraammineruthenium(III) halogenides were prepared by the method of Gleu and Breuel.[9] These compounds were analyzed by the usual elemental analysis and were confirmed by means of their spectra.

Photolysis Procedures. The photolyses were performed using a JASCO CRM-FA spectral irradiator equipped with a 2 kW Xenon arc lamp. A known volume of a sample solution in a rectangular quartz cell with a 1-cm light path length was kept at 25 °C; purified argon gas was passed through the solution during irradiation to avoid an appreciable secondary photolysis or inner filter effects. The solution was then irradiated for a preset time period by monitoring the light flux using a JASCO RMI-1 integrating radiometer equipped with a thermopile. The absorbed light intensities (I_a) were determined using a ferrioxalate actinometer[10] ($\lambda<400$ nm) and a reineckate actinometer[11] ($\lambda>400$ nm). The concentration of the reactant was determined from the absorbance of the first absorption band at 352 nm (*cis*-dichlorocomplex), 441 nm (*cis*-dibromocomplex), and 646 nm (*cis*-diiodocomplex) using a Hitachi 124 spectrophotometer. The pseudo first-order plot gave a straight line for about 120 min at an irradiation rate of 2.5×10^3 photons $\mathrm{l^{-1}\,min^{-1}}$. The initial slope of this plot was used to calculate the initial rate of complex decomposition. This rate was used along with the I_a values to calculate the quantum yield.

Results and Discussion

Qualitative Observation of Photoreaction. The progressive changes in the absorption spectrum are shown in Figs. 1 and 2 for two kinds of complexes in acidic and neutral solutions. The two absorption bands in the spectra for the original complexes can be assigned to the charge-transfer absorptions from ligand to metal ($\pi\rightarrow t_{2g}$)[12] from the facts that; (1) their molar absorption coefficients take large values ($10^3\ \mathrm{M^{-1}\,cm^{-1}}$); (2) the plot of the wave number ($\nu_{\max}$) of the CT band from ligand to metal *vs.* the redox potential value of the coordinated halide ligand indicates a linear relationship (Fig. 3); and (3) the $\nu_{\max}$ values obtained from the electronic spectra of the complexes are in agreement with those calculated by Jørgensen's empirical formula.[13]

The changes in the absorption spectra in the neutral solution appear to be different from those in the acidic solutions. The first and second bands of the complexes decrease, and a new peak appears in the UV region. The wavelength of this peak (291 nm) is very close to that of the hydroxo-complex (293 nm) resulting from the base hydrolysis of the corresponding initial complex. Thus, the photochemical reactions presumably proceed as follows:

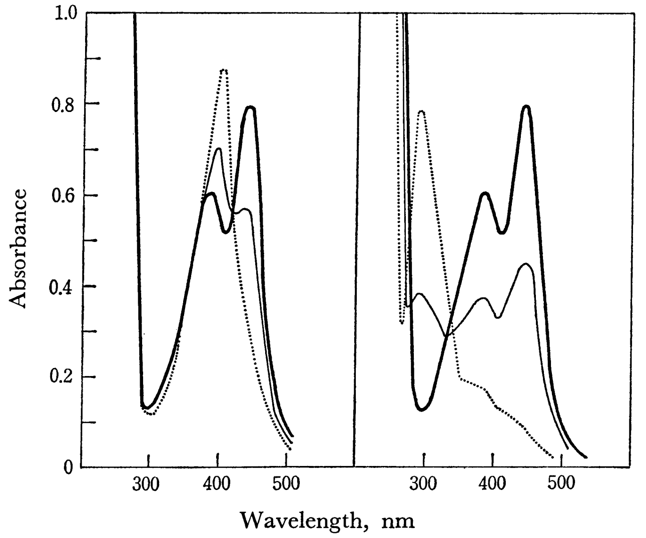

Fig. 1. Spectral change of *cis*-dibromotetraammineruthenium(III) in the photochemical reaction, at pH 2.0 (left), 7.0 (right), 434 nm light irradiation (2.5 $\times 10^3$ photons l^{-1} min^{-1}), 25 °C.
——: initial, ——: intermediate (60 min), ······: final (300 min). [complex]: 5×10^{-4} M, temp: 25 °C.

$$[RuX_2(NH_3)_4]^+ + 2OH^- \xrightarrow{h\nu} [Ru(OH)_2(NH_3)_4]^+ + 2X^- \qquad (1)$$

On the other hand, the changes in the spectra in acidic solutions differ from those in the above case, *i.e.*, the first band decreases with the increase in the second band with the shift toward the longer wavelength as the reaction proceeds. The final spectra (Figs. 1 and 2) show a new peak different from those of the initial complex. In separate experiments where the acid hydrolysis of *cis*-dihalogenotetraammineruthenium(III) were carried out in the dark, similar changes in the absorption spectra were observed throughout the reactions. Similar observations have been reported in the aquation of dichlorobisethylenediammineruthenium(III),[14] and in the study of the preparation of dichlorotetraammine- and chloroaquotetraammineruthenium(II) complexes.[15] All the observations of the changes in the absorption spectrum gave evidence for the formation of a partially-aquated ruthenium(III) complex species, *cis*-$[RuX(OH_2)(NH_3)_4]^{2+}$. Thus, we concluded that the photoreaction took place mainly *via* the aquation process in the acidic solution:

$$cis\text{-}[RuX_2(NH_3)_4]^+ + H_2O \xrightarrow{h\nu} cis\text{-}[RuX(OH_2)(NH_3)_4]^{2+} + X^- \qquad (2)$$

Determination of the Variables Affecting the Photoreaction Rate. Several experiments with various reaction parameters of the photolysis system were carried out in order to investigate their effects on the reaction rate or the quantum yield. The photoreaction rates were determined by measuring the decrease in the absorbance at the first absorption band of the respective complexes under different conditions of light irradiation. The plots of log C_t/C_0 *vs.* the reaction time are exemplified in Fig. 4, where C_t and C_0 denote the con-

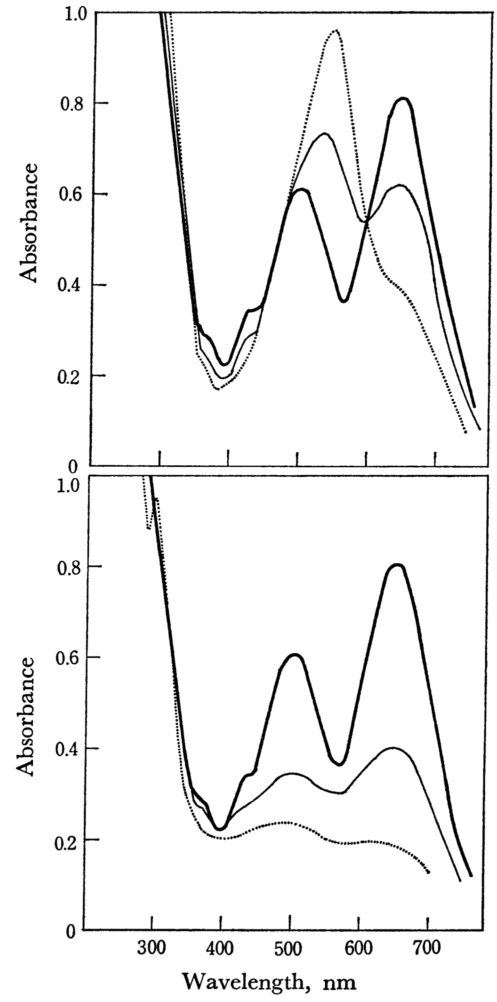

Fig. 2. Spectral change of *cis*-diiodotetraammineruthenium(III) in the photochemical reaction, at pH 2.0 (upper), 7.0 (bottom), 512 nm light irradiation (2.5×10^3 photons l^{-1} min^{-1}), 25°C.
——: initial, ——: intermediate (60 min), ······: final (300 min).

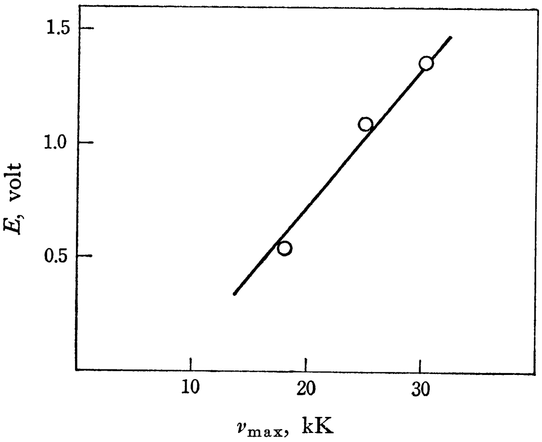

Fig. 3. Relationship between ν_{max} and oxidation potential for halide ligand.

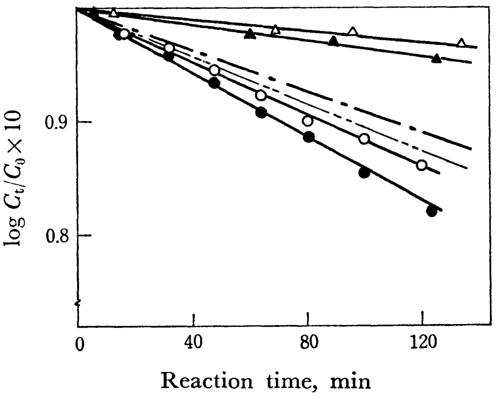

Fig. 4. Plots of log C_t/C_0 *vs.* reaction time at 25 °C, pH 2.2, C_0: initial concentration of complex (5.0×10^{-4} M), C_t: concentration at the reaction time, *t*. [Complex]: 5×10^{-4} M, temp: 25 °C
cis-Dibromotetraammine complex, at 434 nm light irradiation
●: apparent reaction, ▲: thermal reaction
——: net photoreaction
cis-Diiodotetraammine complex, at 512 nm light irradiation
○: apparent reaction, △: thermal reaction
——: net reaction

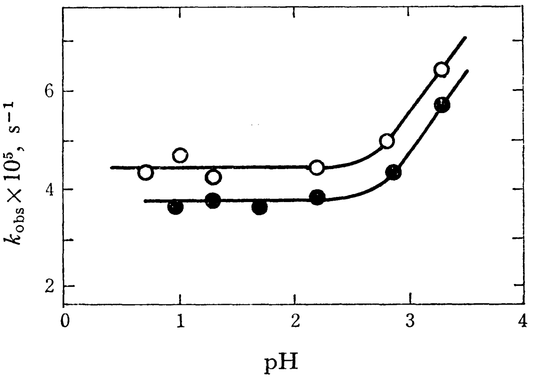

Fig. 5. Effect of pH on the photoreaction rate constant at 434 nm (dibromo-complex) and at 512 nm (diiodo-complex) light irradiation, 25 °C, [complex]: 5.0×10^{-4} M.
-○- dibromo-complex, -●- diiodo-complex

centrations of the reactant complex at the reaction time *t* and at zero, respectively. The straight lines indicate that the photoaquation and thermal reaction are both first-order with respect to the complex concentration under given reaction conditions. The thermal reactions are somewhat observed at 25 °C; therefore, the net photoreaction rates were determined by subtracting these contributions. The photoreaction of the *cis*-dichlorotetraammine complex was found only in the case of ultraviolet light irradiation.

No effects of the halide-ion concentration or of the ionic strength on the reaction rate have been observed in acidic solutions. Three facts indicate that neither the halide ion nor a charged particle is concerned with the rate-determining step.

As is shown in Fig. 5, the effect of pH on the reaction rate has not been observed in a pH range lower than 2.2, while higher than 2.2, the apparent reaction rate increased with an increase in the pH values. Although this fact has not yet been investigated in detail, it may be considered that the base hydrolysis participates to some extent in the aquation reaction. The spectral observations provide evidence for this consideration (Figs. 1 and 2).

Quantum Yield for the Photochemical Aquation Reaction. The quantum yield for the photochemical aquation was determined with different light wavelengths. The results are given in Table 1, along with those of analogous and reference reactions and along with the available data on the thermal aquation reaction rates. The quantum yields for the photoaquation of *cis*-dihalogenotetraammineruthenium(III) complexes are dependent on the light wavelength and are small compared with those for the ammine ligand aquation of the hexaammine- and chloropentaammineruthenium-(III).[8] It was also found that the *cis*-dichlorotetraammine complex was photochemically unreactive and that *cis*-diiodotetraammine was more photosensitive than *cis*-dibromotetraammine in the wavelength region of visible light; for example, the quantum yield was 0.82×10^{-2} (at 408 nm) for the former and 0.27×10^{-2} (at 382 nm) for the latter complex, The relatively high yield observed at shorter wavelengths can be regarded as indicating a CTTM excited state with a different electronic configuration, for it is more populous than that produced by the light irradiation with longer wavelengths. The dependence of the irradiation wavelength on the quantum yield can be interpreted by the mechanism proposed by Adamson and Sporer,[3] which postulated that the first chemical consequence of light absorption is a homolytic bond fission of the metal-ligand bond. When a considerable excessive energy is available, the net quantum yield would be increased by the ease of nascent radicals in escaping their solvent cage. Thus, high quantum yields can be predicted to be favored by the use of the shorter-wavelength light. The homolytic bond fission of the metal ligand may be essentially different from that in the thermally-excited state, because there is no correlation between the photoreactivity and the instability towards thermal aquation as expressed by the rate constants (Table 1). The photoreactivity is rather correlated with the ease of the oxidation of the halide ligand and, hence, with the thermodynamic instability of the complexes towards redox reaction. A similar trend is more evidently observed in the photoreaction of the halogenopentaamminecobalt(III) complexes.[16] The oxidation potential of the halide ligand seems to play the dominant role in determining the photolytic behavior of the halogenoammine complex.

As is shown in Table 1, most studies of the photochemistry of ammine complex ions have dealt with the cobalt(III), chromium(III), and ruthenium(III) systems. These metal complexes differ from each other in photochemical behavior; the photoreactions of cobalt(III) complexes can be either substitution reactions or redox reactions, whereas for chromium(III) and ruthenium(III) complexes only substitution reactions are observed. Although there is no direct comparison of complexes with the same

TABLE 1. PHOTOCHEMICAL REACTIONS OF RUTHENIUM(III) AND OTHER TRANSITION METAL COMPLEXES

Complex	Wavelength Irrad., nm	Product	Quantum yield 10^{-2}	Hydrolysis rate constant, k 10^{-4}, s^{-1}
cis-$RuCl_2(NH_3)_4{}^+$	330—492	no reaction	—[a]	8.68[b]
cis-$RuBr_2(NH_3)_4{}^+$	320	$RuBr(OH_2)(NH_3)_4{}^{2+}$	0.56	7.98
	382		0.27	
	434		0.14	
	492		0.00	
cis-$RuI_2(NH_3)_4{}^+$	408	$RuI(OH_2)(NH_3)_4{}^{2+}$	0.82	3.24
	463		0.33	
	512		0.10	
	642		0.00	
$Ru(NH_3)_6{}^{3+}$	254	$Ru(OH_2)NH_3)_5{}^{3+}$	7[c]	
		$NH_4{}^+$	5	
	321	$Ru(OH_2)(NH_3)^{3+}$	1	
$RuCl(NH_3)_5{}^{2+}$	230	$NH_4{}^+$	1.7	3.28[d]
	254	disappearance	6	
		$NH_4{}^+$	3.2	
		Cl^-	2.9	
	321	disappearance	4[e]	
	321	disappearance	0.8[f]	
		$NH_4{}^+$	2.0	
$Co(NH_3)_6{}^{3+}$	370, 550	disappearance	0.2[g]	
$CoCl(NH_3)_5{}^{2+}$	370	$Co(OH_2)(NH_3)_5{}^{3+}$	1.1	0.017[h]
	550		0.1	
$CoBr(NH_3)_5{}^{2+}$	370	$Co(OH_2)(NH_3)_5{}^{3+}$	21	0.063
		Co(II)	21	
	550	$Co(OH_2)(NH_3)_5{}^{3+}$	0.13	
$CoI(NH_3)_5{}^{2+}$	370	Co(II), I_2	66	0.083
	550	Co(II), I_2	10	
$Cr(NH_3)_6{}^{3+}$	254	$Cr(OH_2)(NH_3)_5{}^{3+}$	49[i]	0.001
$Cr(OH_2)(NH_3)_5{}^{3+}$	320—600	$Cr(OH_2)_2(NH_3)_4{}^{3+}$	25	
$Cr(OH_2)_2(NH_3)_4{}^{3+}$	320—700	$Cr(OH_2)_3(NH_3)_3{}^{3+}$	16	

a) [Complex]$=5.0\times10^{-4}$ M, $I_0=2.5\times10^3$ photons l^{-1} min^{-1}, 25±1 °C, pH 2.0. b) Ref. 14, values for $[RuX_2(en)_2]^+$ at 54.5 °C, $[H^+]=0.1$ M. c) Ref. 8, 25 °C, pH 3. d) Ref. 15, at 80.1 °C. e) 0.5 M C_3H_7OH solution. f) 0.1 M NaCl, 0.5 M C_3H_7OH solution. g) Ref. 17, 25 °C, pH 4. h) Ref. 18. i) Ref. 19, $[H^+]=1-0.05$ M.

ligand, the photoreaction type of the ruthenium(III) complex is the same as that of the chromium(III) complex except that the quantum yield depends on the light wavelength. These differences are presumably due to the greater difficulty of reduction from the trivalent to the divalent state or to the greater instability of the divalent state metal complex.

Photoreaction Mechanism of the cis-*dihalogenotetraammineruthenium(III) Complex.* According to the three-stage mechanism proposed by Adamson and Sporer,[3] the present photochemical reactions can be well interpreted. The first stage is homolytic-bond-breaking:

$$Ru^{III}X_2(NH_3)_4 \xrightarrow{h\nu} Ru^{II}X(NH_3)_4\cdot X^{\cdot} \qquad (3)$$

and

$$Ru^{III}X_2(NH_3)_4 \xrightarrow{h\nu} Ru^{I}(NH_3)_4\cdot X_2{}^{\cdot\cdot} \qquad (4)$$

where X denotes the halide ligand. These intermediate products have not yet been confirmed in our experiment; however, they can react in one of two ways. They can return to the ground state:

$$Ru^{II}X(NH_3)_4\cdot X^{\cdot} \rightarrow Ru^{III}X_2(NH_3)_4 \qquad (5)$$

or

$$Ru^{I}(NH_3)_4\cdot X_2{}^{\cdot\cdot} \rightarrow Ru^{II}X(NH_3)_4\cdot X^{\cdot} \rightarrow Ru^{III}X_2(NH_3)_4 \qquad (6)$$

In another path, they can react with a water molecule in an acidic solution or with the hydroxide ion in neutral and basic solutions:

$$Ru^{II}X(NH_3)_4\cdot X^{\cdot} \begin{cases} \rightarrow + H_2O \rightarrow Ru^{II}X(OH_2)(NH_3)_4\cdot X^{\cdot} & (7) \\ \rightarrow + OH^- \rightarrow Ru^{II}X(OH)(NH_3)_4\cdot X^{\cdot} & (8) \end{cases}$$

$$Ru^{I}(NH_3)_4\cdot X_2{}^{\cdot\cdot} \begin{cases} \rightarrow + 2H_2O \rightarrow Ru^{I}(OH_2)_2(NH_3)_4\cdot X_2{}^{\cdot\cdot} & (9) \\ \rightarrow + 2OH^- \rightarrow Ru^{I}(OH)_2(NH_3)_4\cdot X_2{}^{\cdot\cdot} & (10) \end{cases}$$

The species formed in Reactions (7), (8), and (9), (10) may be ruthenium(II) and ruthenium(I) complexes respectively, with an X˙ radical in the second coordination sphere; however, the formation of the latter complexes may be difficult in view of the coordination ability of ruthenium(I). If the electron transfer from ruthenium(II) to X is energetically favorable, aquation or base hydrolysis proceeds:

$$\mathrm{Ru^{II}X(OH_2)(NH_3)_4 \cdot X^{\cdot} \rightarrow Ru^{III}X(OH_2)(NH_3)_4 + X^-} \qquad (11)$$

$$\mathrm{Ru^{II}X(OH)(NH_3)_4 \cdot X^{\cdot} \rightarrow Ru^{III}X(OH)(NH_3)_4 + X^-} \qquad (12)$$

Wells and Endicott[8] reported that the quantum yield for the photoaquation of the chloropentaammineruthenium(III) is independent of the wavelength. This has been interpreted by assuming that the over-all reaction rate is controlled by the step of ligand-exchange reaction in the lowest-energy excited state formed by the CTTM-band irradiation.

To account for the variation in the quantum yield with the wavelength in our results, it may be reasonable to assume that the probability of the deactivation process (5), (6) of the primary excited state increases with the decrease in the excitation energy, unless the probability of the primary excitation (3), (4) decreases with a decrease in the excitation energy. In particular, the fact that the low quantum yields are different from those for the other metal complexes may be supported by the instability of the radical containing ruthenium(II) or (I) in the deactivation processes (5) and (6).

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