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PHOTO-INDUCED HYDROXIDE ADDITION TO NITROSYL GROUP OF BIS(2,2'-BIPYRIDINE)CHLORONITROSYLRUTHENIUM(2+) IN AQUEOUS SOLUTION

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The irradiation of $[RuCl(bpy)_2NO]^{2+}$ in an aqueous solution at pH$\approx$5 with UV- or solar light brings about the addition of hydroxide to a coordinating NO to give metastable $[RuCl(bpy)_2NO_2H]^+$, which returns to $[RuCl(bpy)_2NO]^{2+}$ in the dark. The reaction produces a reversible change of H^+ concentration. The quantum yields for the formation of $[RuCl(bpy)_2NO_2H]^+$ at 254, 289, 313, and 334 nm are 0.04, 0.04, 0.04, and 0.05, respectively.

Interest in coordinating nitrosyl has been increasing because it shows various reactivities depending on the reaction conditions.1-5) Photoreactions of nitrosyl complexes have been studied mainly on pentacyanonitrosylferrate(2-). Reported photoreactions are elimination of nitrosyl,6-8) oxidation of the complex,7) and reduction of the complex.9-11) On the photochemical behavior of bis(2,2'-bipyridine)chloronitrosylruthenium(2+) in acetonitrile, the substitution of NO by the solvent has been reported.12)

We report here a novel photoreactivity of nitrosyl complex: a photo-induced addition of hydroxide to the coordinating NO in $[RuCl(bpy)_2NO]^{2+}$. The reaction should be interesting, because it is an example which gives information about the electronic interactions between the central metal and ligands in the excited state.

An aqueous solution of $[RuCl(bpy)_2NO](ClO_4)_2$ (2.66×10^{-5} mol dm^{-3}; initial pH$\approx$5.3) deaerated with Ar was irradiated in a 1 cm quartz cell with a stop-cock to isolate it from air. For the irradiation was used either the light from a high pressure mercury lamp or the monochromatic light obtained with a grating monochrometor made by Shimadzu-Bausch and Lomb Co. (dispersion, 7.4 nm mm^{-1}; slit width, 1.5 mm; light source, ultra-high pressure mercury lamp). The photoreaction was followed by means of UV- and visible spectra.

The irradiation of $[RuCl(bpy)_2NO]^{2+}$ with a high pressure mercury lamp in an aqueous solution brought about the UV-spectral change shown in Fig. 1, accompanied by a decrease of pH. Remarkable features of the UV-spectral change are the decrease of the absorption at 323 nm and the increase of the absorption at 287 nm. The existence of isosbestic points during a fairly long irradiation time

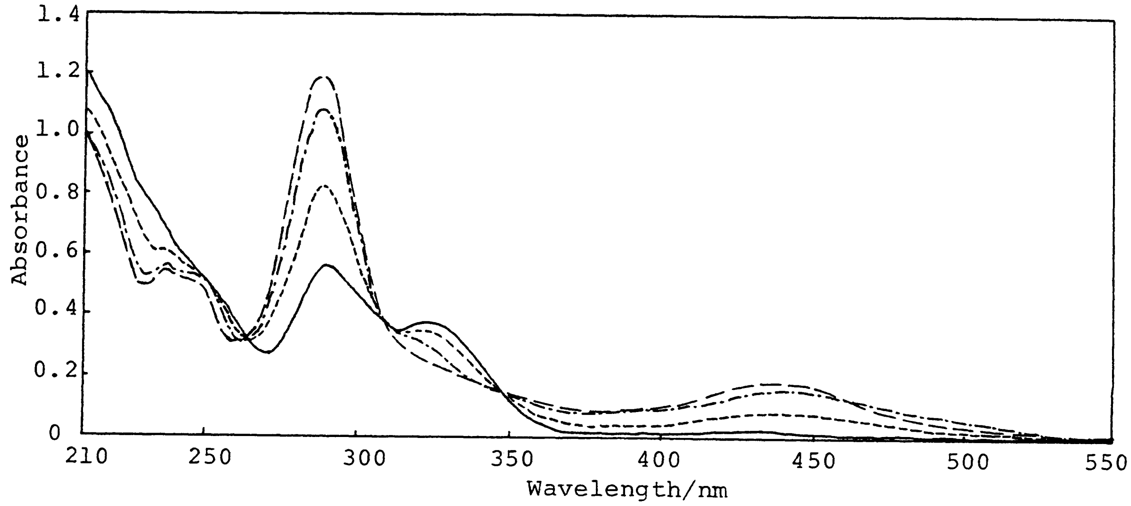

Fig. 1 Spectral change during irradiation of $[RuCl(bpy)_2NO]^{2+}$ with a high pressure mercury lamp

$[Complex] = 2.66 \times 10^{-5}$ mol dm^{-3}; Initial pH, 5.47

———— , Before irradiation; ------ , After irradiation for 6 min;

—·—·— , After irradiation for 12 min

Cf. — — — — , $[RuCl(bpy)_2NO_2H]^+$

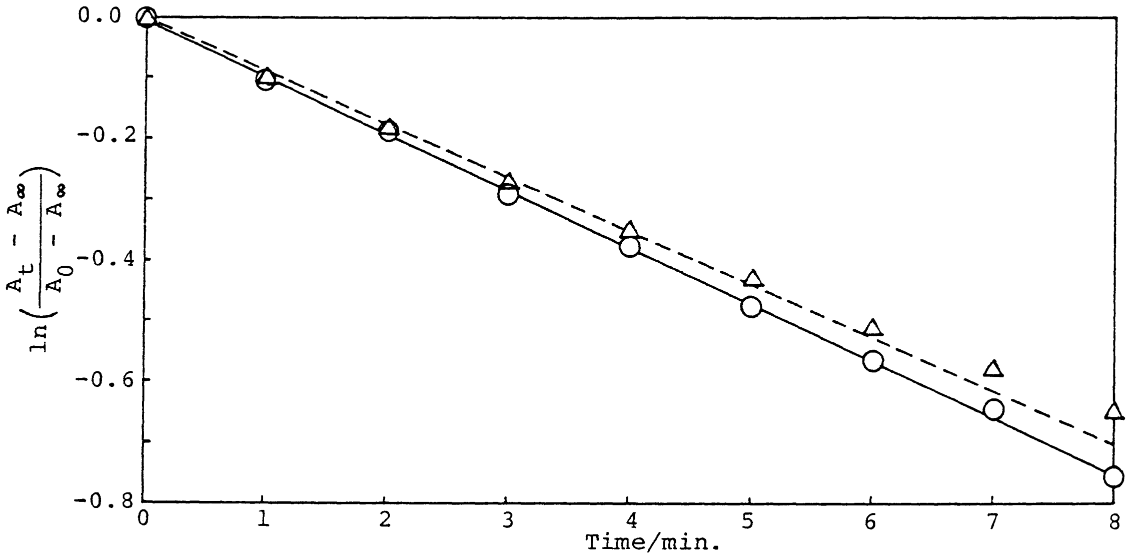

Fig. 2 Pseudo-first order-decay of chemically produced $[RuCl(bpy)_2NO_2H]^+$ (—○—) and photo-generated metastable specis (---△---) at pH 4.57 and at 25 °C. The reactions were followed by absorption at 435 nm.

shows that the photoreaction is without important side reactions.

The UV-spectral change resulting from the irradiation indicates the formation of $[\mathrm{RuCl(bpy)_2NO_2H}]^+$,[13)] which is metastable in the pH range pH < 7. Supports for the formation of $[\mathrm{RuCl(bpy)_2NO_2H}]^+$ are: 1) the rate of reconversion of the photochemically formed species to $[\mathrm{RuCl(bpy)_2NO}]^{2+}$ agrees with that of the chemically produced $[\mathrm{RuCl(bpy)_2NO_2H}]^+$ (Fig. 2) and 2) the pH change induced by the photoreaction agrees with the value calculated on the basis of Equation 1.

$$[\mathrm{RuCl(bpy)_2NO}]^{2+} + \mathrm{H_2O} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} [\mathrm{RuCl(bpy)_2NO_2H}]^{+} + \mathrm{H}^{+} \qquad \text{(Eq. 1)}$$

(Irradiation of the solution of [Complex] = 6.34×10^{-5} mol dm^{-3} and the initial pH = 4.67 with a high pressure mercury lamp for 7 min brought about the formation of 2.0×10^{-5} mol dm^{-3} of $[\mathrm{RuCl(bpy)_2NO_2H}]^+$ and the pH change to 4.36. The increase in $\mathrm{H^+}$ concentration is thus 2.2×10^{-5} mol dm^{-3}.)

The photo-induced addition of hydroxide to the coordinating NO suggests that the NO is electon poor in the excited state, and electron should flow from the NO to the central metal on excitation.

The quantum yields for the formation of $[\mathrm{RuCl(bpy)_2NO_2H}]^+$ at 254, 289, 313, and 334 nm are 0.04, 0.04, 0.04, and 0.05, respectively. Callahan and Meyer assigned the absorption bands at ~290 and 323 nm to π-π^* of coordinating 2,2'-bipyridine and to the electron transfer from $d\pi$(Ru) to π^* of 2,2'-bipyridine, respectively.[12)] The excitation of $d\pi$(Ru)-π^*(bpy) can explain the photochemical addition of $\mathrm{OH^-}$ to the NO: the electronic flow from Ru to bpy induced by the light absorption would cause the increase in the positive charge on the NO. This facilitates the attack of $\mathrm{OH^-}$ to NO. The fact that the quantum yields are almost constant in the irradiation with 254-334 nm light suggests that the reaction proceeds via the lower excited state ($d\pi$(Ru)-π^*(bpy)).

The solar irradiation brought about the same type of spectral change as UV-irradiation. The reaction proceeds backward in the dark. This shows that the solar irradiation as well as UV-irradiation gives a metastable (energetically richer) species and the metastable species returns to the original complex at a slow rate. This is a type of reversible conversion of solar energy to chemical energy.

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13) The pH dependence of the absorbance of UV-spectra of bis(2,2'-bipyridine)-chloronitrosylruthenium(2+) at 325, 360, and 435 nm (Fig. 3) suggests three different forms of the complex in aqueous solutions. These three forms can be ascribed to $[RuCl(bpy)_2NO]^{2+}$ (pH < 6), $[RuCl(bpy)_2NO_2H]^+$ (6 < pH < 11), and $[RuCl(bpy)_2NO_2]$ (pH > 11) as is postulated by Godwin and Meyer (J.B. Godwin and T.J. Meyer, Inorg. Chem., 10, 2150 (1971); W.L. Bowden, W.F. Little, and T.J. Meyer, J. Am. Chem. Soc., 99, 4340 (1977)). The following equiliblia can be concluded:

$$[RuCl(bpy)_2NO]^{2+} \underset{}{\overset{OH^-}{\rightleftharpoons}} \underset{pK_{a_1} = 6.4}{[RuCl(bpy)_2NO_2H]^+} \overset{OH^-(-H_2O)}{\rightleftharpoons} \underset{pK_{a_2} = 11.0}{[RuCl(bpy)_2NO_2]}$$

The formation of NO_2H complex has been suggested for $[Fe(CN)_5NO]^{2-}$ (J.H. Swinehart and P.A. Rock, Inorg. Chem., 5, 573 (1966); J. Mašek and H. Wendt, Inorg. Chim. Acta, 3, 455 (1969)).

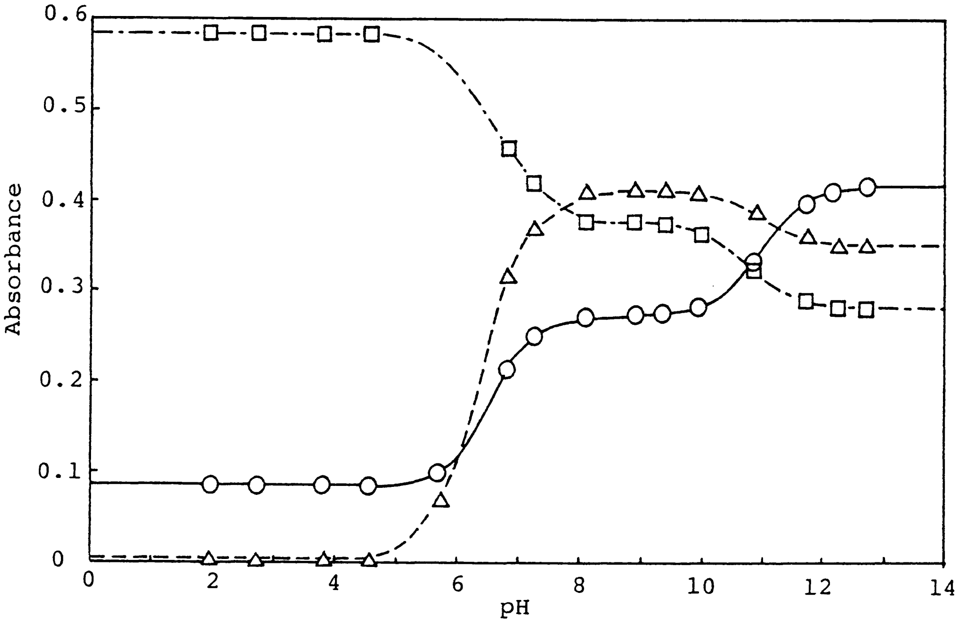

Fig. 3 Dependence of UV-absorption of the complex on pH
[Complex] = 6.2×10^{-5} mol dm^{-3}; —·—□—·—, Absorbance at 325 nm;
—○—, Absorbance at 360 nm; ---△---, Absorbance at 435 nm

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