

Review

Photochemical reactions of rhodium(III) diimine complexes in solid glycerol matrices Ligand-field influences on activation parameters

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Abstract

At temperatures below 150 K in rigid glycerol glasses $[\text{Rh}(\text{CN})_2(\text{s-NN})_2]\text{PF}_6$ complexes display a $^3\pi\pi^* \rightarrow \text{gs}$ phosphorescence characteristic of the s-NN ligand [s-NN = 1,10-phenanthroline (phen), 4-Mephen, 4,7-Me₂phen, and 3,4,7,8-Me₄phen]. Above 150 K but below the melting point of glycerol a temperature-dependent first-order reaction occurs upon irradiation with UV light. The temperature dependences of these photochemical reactions conform to the Arrhenius equation with an activation energy range of 2000–2500 cm⁻¹, which is a range averaging 725 cm⁻¹ lower than that previously reported for $[\text{Rh}(\text{s-NN})_3](\text{PF}_6)_3$ complexes. These results are interpreted in terms of the thermal redistribution of energy from an unreactive $^3\pi\pi^*$ excited term to a close-lying chemically reactive ^3dd level that has been lowered in energy with respect to that of the corresponding $[\text{Rh}(\text{s-NN})_3](\text{PF}_6)_3$ complex. The relationships of the Arrhenius activation energies to the electronic structures of the parent complexes and to the natures of the products are discussed.

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1. Introduction

Photosubstitutional reactions of $[\text{Rh}(\text{diimine})_3]^{3+}$ complexes (tris complexes) in solid glycerol glasses at temperatures above 150 K have been reported [1,2]. These reactions produce single photoproducts that have been tentatively identified as $[\text{Rh}(\text{diimine})_2(\text{diimine:H}^+)(\text{glyceroxide})]^{3+}$ species. The reaction rates were highly temperature-dependent and activation energies were determined. These activation energies were related to the gap between the lowest $^3\pi\pi^*$ level and a higher-lying chemically reactive ^3dd manifold. The initial investigation quantified the effect of tuning the lowest $^3\pi\pi^*$ level, through methyl substitution on the phen backbone, on the photochemical activation energy [2]. In the present contribution the strength of the crystal field around the central rhodium ion has been varied by ligand substitution. Specifically, one of the diimine ligands (tris complexes) has been replaced by two stronger field cyanide ligands (dicyano complexes). Activation energies of the dicyano complexes are then compared with those obtained from the corresponding tris complexes. Finally, the chemical and photophysical natures of the new photoproducts have been investigated.

2. Experimental

2.1. Syntheses

$[\text{Rh}(\text{Cl})_2(\text{s-NN})_2]\text{Cl}$ complexes were anaerobically prepared from RhCl_3 hydrate (2 mmol) and a slight excess of the diimine ligand (4.2 mmol) in a reaction vessel attached to a vacuum line. The reactants were degassed by maintaining them at a pressure below 1 mTorr for ~ 12 h. A 75% aqueous ethanol solvent, rigorously degassed, was condensed on the reactant mixture. The resultant slurry was stirred under gentle warming and after ~ 1 h a yellow-orange solution appeared. The solution was then allowed to evaporate to dryness, and the product was subsequently recrystallized from hot methanol. In all cases, well-formed bright yellow crystals of $[\text{Rh}(\text{Cl})_2(\text{s-NN})_2]\text{Cl}$ were obtained.

The $[\text{Rh}(\text{CN})_2(\text{s-NN})_2]\text{PF}_6$ complexes were prepared anaerobically from $[\text{Rh}(\text{Cl})_2(\text{s-NN})_2]\text{Cl}$ (1 mmol) and a two-fold excess of NaCN (4 mmol) in a reaction vessel attached to a vacuum line. The solid reactants were degassed by maintaining them at a pressure below 1 mTorr for ~ 12 h. Deionized water, carefully degassed by three consecutive freeze–pump–thaw cycles, was then condensed on the reactants. The mixture was stirred under gentle warming. Immediately, while still cold, the slurry turned from yellow to clear producing a white precipitate. Warming was continued until all the precipitate had dissolved and a colorless solution appeared. The solution was removed from the vacuum line and treated with concentrated HCl to remove excess CN^- as HCN gas. The solution was concentrated and cooled in an ice bath whereupon small crystals formed.

To effect purification, the crystals were collected and redissolved in warm water. The crude product was then loaded on a CM-Sephadex-C25 cation exchange column (12 in. \times 1 in. i.d.), which had been equilibrated with deionized water. The column was interfaced with a Pharmacia UV detector and a stripchart recorder to monitor the emerging bands. The eluant was water followed by solutions of NaCl stepped from 0.1 to 0.5N. A very small colorless band came off with the mobile water phase. The largest band, containing the product, came off with the application of 0.1N NaCl. A very small dark impurity band was washed off the column during the 0.5N NaCl step. Hexafluorophosphate salts of the complexes were produced through metathesis of the chlorides with a concentrated, filtered, neutralized solution of NaPF_6 . All complexes were obtained as white powders.

2.2. Sample preparation

Emission and lifetime measurements were performed on 10^{-4} M solutions in glycerol. Photochemical reaction rates were measured on 5×10^{-6} M solutions in rigorously degassed glycerol kept O_2 free with ambient N_2 gas. Photochemical reaction rate measurements were always conducted on fresh samples. For spectroscopic characterization photoproducts were generated through exhaustive photolysis of 10^{-4} M $[\text{Rh}(\text{CN})_2(\text{s-NN})_2]\text{PF}_6$ in glycerol glasses at 200 K. [The glycerol was vigorously degassed prior to use and samples were kept free of O_2 .]

2.3. Spectroscopic measurements

Steady-state emission and lifetime measurements were conducted as described previously [2]. The excitation source was the 325-nm line of a 4-mW HeCd laser. The detection system was a thermoelectrically cooled Hamamatsu R943-02 PMT coupled to an SRS-400 photon counter. For decay-time measurements the excitation beam was modulated mechanically.

2.4. Measurement of activation energies

Photochemical reaction rates were obtained by measuring the rate of disappearance of the characteristic $^3\pi\pi^* \rightarrow \text{gs}$ phosphorescence of the parent $[\text{Rh}(\text{CN})_2(\text{s-NN})_2]\text{PF}_6$ complex. The band was monitored at the emission maximum. The optical setup and the fiber-optic sample rod constructed for measuring the photochemical reaction rates were described previously [2]. Activation energies were determined by fitting the photochemical rates to the Arrhenius equation:

$$\ln k_{\text{obs}} = -(\Delta\varepsilon/k)(1/T) + \ln A$$

where k_{obs} is the observed reaction rate, $\Delta\varepsilon$ the activation energy, and k the Boltzmann constant (in $\text{cm}^{-1} \text{K}^{-1}$).

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