

Oxidation of malononitrile complex of pentaammineruthenium(II)

Sunny Huang, Ingrid Lin, Sabina Wang, Joyce Yeh, Andrew Yeh *

Department of Chemistry, Tunghai Christian University, 181 Taichung-kang Rd. Sec. 3, Taichung 407, Taiwan, ROC

Received 10 May 2004; accepted 4 October 2004

Abstract

The oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ complex by the peroxydisulfate ion in the aqueous solution yields two products, $\text{Ru}(\text{NH}_3)_5\text{NHCOCH}_2\text{CN}^{2+}$ with $\lambda_{\text{max}} = 373$ nm and $\left[(\text{NH}_3)_5\text{RuNCC}(\text{CN})=\text{CCN}(\text{CN})\text{Ru}(\text{NH}_3)_5 \right]^{4+}$ with $\lambda_{\text{max}} = 863$ nm. The distribution of the products and the amount of oxidant required for the maximum yield of the binuclear complex depend on the acidity of the solution. The production of the binuclear complex was favored at lower acid concentrations. The formation of C=C bond in the binuclear complex was characterized by both the spectral and the electrochemical results. A mechanism for the oxidation has been proposed by the kinetic studies in the region of 0.001–0.10 M acid concentrations.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Malononitrile complex; Nitrile hydrolysis; Kinetics and mechanism

1. Introduction

In our recent study [1] of the oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{py}^{2+}$ complex, we found that instead of forming the Ru(III) complex followed by the hydrolysis of the nitrile ligand as was expected for most of the other nitrile complexes of ruthenium(III) amines [2], the oxidation went to ligand and two equivalents of the oxidant were consumed with $[(\text{NH}_3)_5\text{RuNCC}(\text{pyH})=\text{C}(\text{pyH})\text{CNRu}(\text{NH}_3)_5]^{6+}$ as the final product when the reaction was carried out in 0.10 M acid solution. The mechanism of the reaction which leads to this result involves the deprotonation of the α -carbon hydrogen of the ligand. In order to be sure whether this kind of reaction is unique for $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{py}^{2+}$ complex or it can also be applied to other ligands of the type RCH_2CN with labile α -carbon protons, we extend our

study to the oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ complex where the proton on the α -carbon of the ligand is so labile that it cannot be observed in the ^1H NMR spectrum, just like that of the 4-pyridylacetonitrile complex. We did find the formation of the binuclear complex upon oxidation; however, unlike 4-pyridylacetonitrile complex, nitrile hydrolysis was also observed in this system. In this paper, we wish to report the results based on our thermodynamic and kinetic studies.

2. Experimental

2.1. Materials

Malononitrile was purchased from Aldrich and was used as supplied. $[\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}](\text{ClO}_4)_2$ was prepared by following the literature method [3] except that ClO_4^- was used as counter ion to precipitate the complex thus formed. Ion exchange was performed on a glass column with purified Sephadex SP C-25 cation

* Corresponding author. Tel.: +886 4 23590248412; fax: +886 4 23590426.

E-mail address: adyeh@mail.thu.edu.tw (A. Yeh).

resin in the proton form. The doubly distilled water was obtained by passing house line distilled water through an Osmonics P-12 water purification system. All other chemicals were of reagent grade and were used without further purification.

2.2. Synthesis

$[\text{Ru}(\text{NH}_3)_5\text{NHC}(\text{O})\text{CH}_2\text{CN}](\text{ClO}_4)_2$. A 0.22-g (0.49 mmol) amount of $[\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}](\text{ClO}_4)_2$ was dissolved in 20 mL of predeaerated 0.10 M HCl and an equimolar $\text{Na}_2\text{S}_2\text{O}_8$ was added to the solution. After allowing the reaction to proceed for 5 min under argon atmosphere, the solution was then transferred to a Sephadex SP C-25 cationic exchange column. The yellowish amido complex was eluted with 0.2 M HCl (~100 mL) and the eluant was concentrated on a rotary evaporator to ~5 mL. A 1 g amount of NaClO_4 was added and the solution was cooled in an ice bath for 1 h with occasional scratching. The precipitate thus formed was filtered off, washed with ethanol and ether, and dried in vacuum desiccator for 2 h. Yield: 66 mg (29%). *Anal.* Calc. for $\text{RuC}_3\text{N}_7\text{H}_{18}\text{O}_9\text{Cl}_2$: C, 7.70; H, 3.87; N, 20.9. Found: C, 7.37; H, 3.71; N, 19.8%.

$[(\text{Ru}(\text{NH}_3)_5)_2\text{NC}(\text{CN})\text{C}=\text{C}(\text{CN})\text{CN}](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. About 0.30 g (0.66 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}](\text{ClO}_4)_2$ was dissolved in 30 mL of 0.01 M HCl under saturated argon atmosphere and 0.12 g (0.50 mmol) of $\text{Na}_2\text{S}_2\text{O}_8$ was added to the solution. The reaction was allowed to proceed for 20 min under argon. The solution was transferred to a Sephadex SP C-25 cation exchange column. After eluting out the yellow solution stayed in the lower layer with 0.2 M HCl, the blue binuclear complex was eluted with 0.50 M HCl (~50 mL). The eluant was concentrated on a rotary evaporator to ~10 mL, and 2 g NaClO_4 was added and the solution was cooled in an ice bath for ~1 h. The precipitate thus formed was filtered, washed with ethanol and ether, and dried in a vacuum desiccator for 3 h. Yield: 0.40 g (72%). *Anal.* Calc. for $\text{Ru}_2\text{C}_6\text{N}_{14}\text{H}_{32}\text{Cl}_4\text{O}_{17}$: C, 7.86; H, 3.52; N, 21.4. Found: C, 7.97; H, 3.60; N, 20.8%.

2.3. Instruments

UV–Vis spectra were measured on a Hewlett–Packard HP 8453 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 1725X FT-IR spectrophotometer in KBr pellets. The ^1H NMR spectra were obtained in either D_2O or DMSO-d_6 on a Varian Unity 300 spectrophotometer and ^{13}C NMR spectra were performed in DMSO-d_6 on a Bruker Ultrashield™ 400 MHz spectroscopy at Chang Gung University. Electrochemistry was performed on a PAR Model 273A potentiostat/galvanostat system as described previously [4].

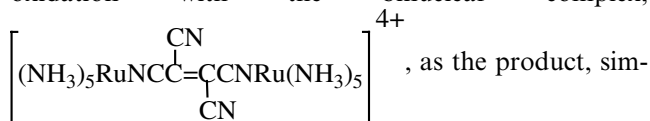
2.4. Kinetic measurements

The rates of oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ complex were carried out on the Hewlett–Packard HP 8453 spectrophotometer. The measurements were performed at an ionic strength of 0.10 (HCl/LiCl) and $T = 25^\circ\text{C}$ with acid concentrations varying from 0.001 to 0.10 M. $[\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}]^{2+}$ complex was oxidized with peroxydisulfate ion and the reactions were monitored by following the formation of $\lambda = 863$ nm, the band maximum of the binuclear complex. The observed rate constants were obtained from the slopes of linear least square fits of $\ln(A_\infty - A_t)$ vs time plots.

3. Results and discussion

3.1. Stoichiometry

The electronic spectra of the complexes under study are shown in Table 1. The $d\pi$ to π_{CN}^* band maximum for the $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ complex was independent of the pH of the solution and was in agreement with the previously reported value [3]. Two cyanide stretching bands (ν_{CN}), both for coordinated and unbounded nitriles, were observed in the IR spectrum, as also shown in Table 1. Similar to that observed in the oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{pyR}^{3+}$ ($\text{R} = \text{H}^+, \text{CH}_3$), the solution turned blue with an absorption at $\lambda = 863$ nm when $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ was oxidized with peroxydisulfate ion. However, unlike that of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{pyR}^{3+}$ complexes where the blue species was the only product, the oxidation of $\text{Ru}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{2+}$ complex yielded two products. In addition to this blue compound, another species which is yellow in color was also formed. The ^1H NMR spectrum of the solution of the blue product showed chemical shifts of ammonia at 4.38 (*trans*) and 3.01 (*cis*) ppm, which fell in the range expected for ruthenium(II) ammine complexes [5]. The $\delta_{\text{NH}_3\text{sym}}$ at 1290 cm^{-1} in the IR spectrum of the isolated product also suggested that the metal center belonged to Ru(II) oxidation states. The exhibition of two ν_{CN} bands at 2230 and 2120 cm^{-1} (Table 1), which agreed well with those of the free (2225 cm^{-1}) and coordinated (2118 cm^{-1}) tetracyanoethylene complex of Ru(II) [7], further indicated that both nitriles of the ligand still remained in the complex. Moreover, the signal for the α -carbon of the ^{13}C NMR spectrum did not appear in the region expected for the $-\text{CH}_2-$ group (11–55 ppm) [6], rather, a δ value at 124 ppm, which falls in the range expected for the $\text{C}=\text{C}$ group, showed up instead. Apparently, the blue species arised from the coupling of the ligand upon oxidation with the binuclear complex,



Download English Version:

<https://daneshyari.com/en/article/10571688>

Download Persian Version:

<https://daneshyari.com/article/10571688>

[Daneshyari.com](https://daneshyari.com)