298 © 1991 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 64, 298—300 (1991) [Vol. 64, No. 1

Synthesis and Reaction of *trans*-Dichlorobis(*o*-phenylenediamine)rhodium(III) Perchlorate with Some Oxidizing Agents

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(Received May 18, 1990)

Synopsis. A new rhodium(III) complex with *o*-phenylenediamine, *trans*-$[RhCl_2\{C_6H_4(NH_2)_2\}_2]ClO_4$ was synthesized and the reaction with oxidizing agents studied. Due to coordination with the rhodium(III) ion the *o*-phenylenediamine (opd) was greatly stabilized against oxidation and the complex was oxidized slowly by periodate via intermediate radical complex to bis(*o*-benzoquinone diimine)dichlororhodium(III) complex which decomposed to the final products.

A number of kinetic studies on the acid or base hydrolysis of various cationic rhodium(III)–amine complexes have been reported.[1–5] Even though *o*-phenylenediamine has the same bidentate function (-N-C-C-N-) as such compounds as ethylenediamine, there has been no report either on the synthesis or on the reactions of rhodium(III) complexes with *o*-phenylenediamine. The reason for this may be that the diamine possibly is oxidized by some oxidizing agents or even by the air and forms 2,4-hexadienedinitrile in the presence of some metal ions which can act as a catalyst for the oxidation reaction.[6–8] In other cases, synthesized metal complexes contain the oxidized state of the amine, *o*-benzoquinonediimine.[9,10] However, many stable complexes of bivalent metal ions such as nickel, cobalt, and so on, with opd have been reported.[11,12]

The authors tried to react rhodium(III) ion with opd in an atmosphere of nitrogen gas, and obtained the new title complex, then the oxidation process of the complex was investigated by means of spectrophotometry. Analysis of the reaction mechanism proved to be extremely difficult in the higher pH region (above 6.5) owing to the rapid and simultaneous oxidation of the coordinated diamine and the base hydrolysis of the complex. For this reason the reaction of the complex with oxidizing agents in the pH region from 5.4 to 6.2 have been focused upon.

In the pH range, reactions appeared to proceed via three steps. These may be looked upon as oxidation of the coordinated opd in the first two steps, then decomposition of the complex in the third step.

Experimental

Synthesis of The Complex. Rhodium(III) chloride trihydrate (1.5 g, 5.7 mmol) and opd (1.8 g, 17 mmol) were dissolved into hot water which had been deaerated by boiling (50 ml). The solution was then refluxed for 5 h under nitrogen gas flow. At the initial step, whitish yellow precipitate formed, but it disappeared with continuing reflux and the solution became clear and yellowish red in color. Then by adding about 5 ml of 70% perchloric acid into the hot solution, yellow crystals were obtained. The collected crystals were recrystallized repeatedly using minimal amounts of hot water.

Analysis. Found: C, 29.14; H, 3.27; N, 11.44; Cl, 21.74%. Calcd for $RhC_{12}H_{16}O_4N_4Cl_3$; C, 29.44; H, 3.29; N, 11.45; Cl, 21.73%.

Reaction Studies. The reactions were studied by measuring absorbance changes in the electronic spectra in the range from 200 to 700 nm using a Shimadzu UV-240 spectrophotometer on solutions containing 10^{-4} mol dm^{-3} of the complex in the presence of 2.12—7.1-fold excess of potassium periodate (KIO_4) as an oxidizing agent. The pH values were adjusted with acetic acid–sodium acetate buffer solutions in the range from pH 5.4 to 6.2, and the ionic strength was set at 0.3 mol dm^{-3} by using sodium perchlorate. The temperature of the solutions was controlled with an electric thermocontroller in the range of ±0.1 °C.

Results and Discussion

The spectra of the complex in aqueous solution showed a peak at 403 nm ($\log \varepsilon = 2.17$) which is typical of the dichlorobis(diamine) type complex ion in a trans form.[1–5]

The spectral change of the complex solution containing potassium periodate at pH 5.85 at 50 °C is shown in Fig. 1. The increase in the absorbance at 420 nm is first order with respect to Rh(III)–opd complex in the first stage, and this may be due to oxidation of the coordinated opd when compared with the spectral change of the solution containing free opd and potassium periodate. The increase in the absorbance could be stopped by addition of hydroxylamine hydrochloride. When free opd was oxidized, formation of the radical was proved by measurements of the ESR spectra for the same solution as was used for the spectral measurements. In this case ESR spectra showed the presence of the radical and the signal disappeared with time. This change in the same as the change of the spectra at 420 nm: At 420 nm, the absorbance increased with time to a maximum, after which it steadily declined.

On the other hand, the increase in the absorbance with time at 420 nm for the complex solution with KIO_4 was much slower than that for the solution containing free opd and KIO_4, indicating the opd must be much resist to oxidation by coordination to the rhodium (k_{obsd} for opd is times greater than that for Rh–opd complex). In this case, ESR spectra did not show the presence of the radical even though the pattern of the spectral change at 420 nm was the same as opd oxidation.

It is assumed that the reaction of Rh(III)–opd with KIO_4 is initiated by a slow loss of an electron from the nitrogen atom of an opd ligand yielding an intermediate short-lived radical complex, $[RhCl_2(opd)(opd^+)]^{2+}$.[13,14] This may be followed by a rapid

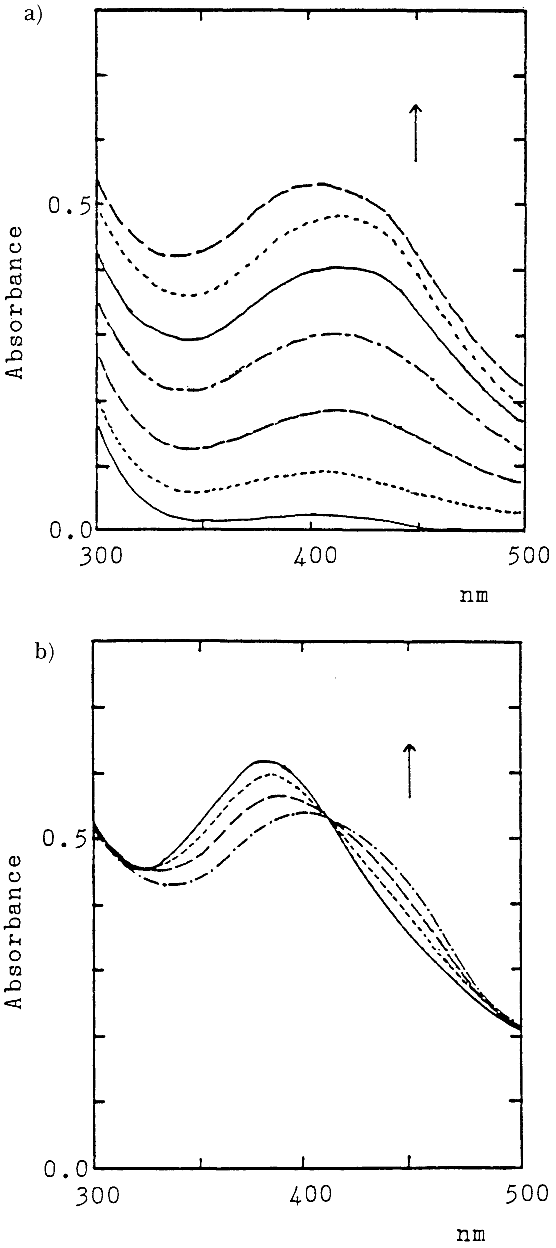

Fig. 1. The spectral change of the complex solution (1.23×10^{-4} M) containing potassium periodate (8.73×10^{-4} M) at pH 5.85 and 50 °C. (M=mol dm^{-3}). (a) From the start (bottom), curves show 20 min. intervals up to 120 min. b) From 130 min. to 180 min. 130 min. 140 min. 150 min. 180 min.

electron loss at another opd ligand in trans position thus forming $[RhCl_2(opd^+)_2]^{3+}$ (420 nm). In this intermediate radical complex, there may be two spin-coupled opd$^+$ radical ions coordinated to Rh(III) in trans-position, forming a diamagnetic complex as in the case of oxidation of the $Ni(opd)_2$ complex ion.[15]

As seen in Fig. 1, after the absorbance at 420 nm approached maximum, the spectra changed showing a new peak at 387 nm with an isosbestic point at 412 nm. In this stage, the color of the solution remained yellow. This step is assumed to be caused by the change of the coordinated opd radical. And this change was zeroth-order with respect to Rh(III)–opd complex. During these oxidation reactions, there may not be significant hydrolysis of the complex itself because the complex solution without the oxidizing agent showed only slight change in this pH region. This second peak at 387 nm, did not appear when free opd was oxidized. That means the second step of oxidation of opd produce a stable state only when opd is coordinated to the rhodium ion. At the last stage, the color of the solution gradually changed from yellow to dark red, implying the formation of *o*-benzoquinonediimine.[9,10,13,15,16] Then the absorbance at 387 nm decreased slowly, and finally an almost black precipitate was formed. The precipitate is thought to be a decomposed and polymerized form of the complex.

The process depends on the pH of the solution. The lower the pH, the slower the reaction rate. However, at pH 6.76, the spectral change is too complicated to analyze, indicating that overlapping of steps must occur at the same time, along with hydrolysis. In such higher pH ranges the absorbance of the peak at 420 nm decreased soon after it reached the maximum without the peak at 387 nm which was seen in the lower pH region.

The processes of the spectral change can be tentatively put as Rh–opd→A (step 1), A→B (step 2), and B→decomposed products (step 3). The examination of the effect of mole ratio of KIO_4 to the complex in the solution revealed that the higher the mole ratio KIO_4/Rh(III)–opd was, the faster the absorbance at 420 nm increased; however, the mole ratio did not much affect the rate of the step-2 change.

The absorption peak at 387 nm also can be observed with an aqueous solution of the complex which contains no other materials (buffer, $NaClO_4$ for adjusting of ionic strength, and KIO_4), although the change is too slow to follow the process quantitatively (it takes one month or more). Being such a slow process, the complex is undoubtedly oxidized even by the air.

Plots of log [A] vs. time in the step 1 change and plots of [B] vs. time in step 2 result in straight lines. From the slopes, pseudo-first-order rate constant, k^{A}_{obsd}, and zeroth-order rate constant, k^{B}_{obsd}, were evaluated. And from the Arrhenous plots, activation energies were also obtained for three different pH values. The results are shown in Table 1, and dependence of the observed rate constants on the concentration of periodate at 60 °C are given in Table 2.

The effects of other oxidizing reagents were investigated. In the case of NaClO, the previously mentioned two peaks at 420 and 387 nm could be observed, but there was no equilibrium between step 1 and step 2. $KMnO_4$ was also examined, but no fruitful results were obtained. At this time, only KIO_4 has given such quantitative results.

The same experiments were done with other Rh(III) complexes with diamines such as ethylenediamine and *cis*-1,2-cyclohexanediamine. However, similar spectral

Table 1. Temperature Dependence of the Rates of Reaction of $[RhCl_2(opd)_2]^+$ with $[KIO_4]$
$[RhCl_2(opd)_2]^+=1.23\times10^{-4}$ M, $[KIO_4]=8.37\times10^{-4}$ M, $I=0.3(NaClO_4)$ M dm^{-3}

Temp/°C	pH=6.17		pH=5.85		pH=5.41	
	$k^{A}_{obsd}\times10^3/s^{-1}$	$k^{B}_{obsd}\times10^8/Ms^{-1}$	$k^{A}_{obsd}\times10^3/s^{-1}$	$k^{B}_{obsd}\times10^8/Ms^{-1}$	$k^{A}_{obsd}\times10^3/s^{-1}$	$k^{B}_{obsd}\times10^8/Ms^{-1}$
50	1.32	7.83	1.23	3.0	0.57	1.30
55	2.30	9.17	1.87	4.0	0.73	1.83
60	3.57	11.2	2.23	5.67	0.86	3.00
E_a/kJ mol^{-1}	89.2	31.7	53.2	56.9	38.3	74.8

Table 2. Dependence of the Observed Rate Constants on the Concentration of Periodate at pH 6.17 and 60 °C, $[RhCl_2(opd)_2^+]=1.23\times10^{-4}$ M, $I=0.3(NaClO_4)$ M dm^{-3}

$KIO_4/[RhCl_2(opd)_2^+]$	$k^{A}_{obsd}\times10^3/s^{-1}$	$k^{B}_{obsd}\times10^8/Ms^{-1}$
2.1	0.90	1.08
3.2	1.12	1.13
5.0	2.67	0.95
7.1	3.57	0.98

changes for the Rh(III)–opd could not be observed.

From our experimental results, it can be concluded that the reaction of the Rh(III)–opd complex with KIO_4 is initiated by the formation of a radical of opd coordinated to Rh(III). After the formation of the opd radical complex, $[Rh^{III}Cl_2\{opd^+\}_2]^{3+}$ is completed, it easily changes to the stable state over time regardless of its concentration (step 2). The opd radical complex is apt to be oxidized by molecular oxygen to benzoquinone diimine complex, $[RhCl_2\{C_6H_4(NH)_2\}_2]^+$,[16] which eventually forms decomposed products.

The authors would like to express their gratitude to Professors Yuzo Nishida and Tatsuji Nisoku of Yamagata University for their arduous work in the ESR measurements.

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