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Studies on Reaction of Dirhodium(II) Aquo Cation with Dioxygen

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Abstract

The reactions of dirhodium(II) aquo cation $\{Rh_{2(aq)}{}^{4+}\}$ with dioxygen were examined. It has been found that the nature of the oxidation product depends upon the concentration of dioxygen in the solution. The dimeric or polymeric $Rh(III)_{(aq)}$ cationic species with a charge of greater than +3 is formed when air oxygen slowly diffuses into a solution containing $Rh_{2(aq)}{}^{4+}$. The paramagnetic cation of proposed formula $[(H_2O)_4Rh(O_2{}^-)(OH)_2Rh(H_2O)_4]^{3+}$ is formed when molecular oxygen is bubbled through a 2–3 M $HClO_4$ solution of $Rh_{2(aq)}{}^{4+}$. This species has been isolated and characterized in solution.

Introduction

Binuclear aquo cations $M_{2(aq)}{}^{4+}$ (M = Mo, Rh) are exceptional in the large group of transition metal aquo complexes [1–3]. Both molybdenum and rhodium aquo dimers are unstable and react easily with dioxygen, however only a few literature data about reactions with the contribution of $Rh_{2(aq)}{}^{4+}$ are available [2–4]. Some information about the Mo aquo complexes at higher oxidation states has been reported [5–7]. The rhodium aquo dimer reacts with dioxygen in different ways depending on the reaction conditions.

The green solution of $Rh_{2(aq)}{}^{4+}$ effected by air oxygen changes slowly to yellow and by molecular oxygen changes its colour faster into violet [3,4]. It has been suggested that the violet reaction product of $Rh_{2(aq)}{}^{4+}$ with O_2 could be the dimer of formula $[(H_2O)_5RhOORh(H_2O)_5]^{4+}$ [3,4].

The compounds containing coordinated O_2 molecule are well known among cobalt complexes [8,9], but are rather rare in the case of rhodium complexes [10–18].

The importance of dioxygen activation by the transition metal complexes in catalytic and in biological processes prompted us to study the reactions occurring in the system: $Rh_{2(aq)}{}^{4+} + O_2$.

Experimental

All chemicals were of the highest purity commonly available.

Water used as a solvent was redistilled from alkaline potassium permanganate in an all glass still.

Argon (99.995% pure) was freed of oxygen by passing the gas through two towers containing amalgamated zinc and a solution of Cr(II) in 0.5 M acid.

Serwa Dowex 50Wx2 cation-exchange resin was used both for ion-exchange columns and for batch equilibration experiments.

Hexaaquorhodium(III) was prepared by the method of Ayres and Forrester [19] in the reaction of $RhCl_3 \cdot 3H_2O$ (Koch-Light Laboratory Ltd) with concentrated (70%) perchloric acid (VEB Laborchemie APOLDA). Solutions were standardized spectrophotometrically by using the known absorption spectrum of $[Rh(H_2O)_6]^{3+}$, with peaks at 311 ($\epsilon = 67.4\ M^{-1}\ cm^{-1}$) and 396 nm ($\epsilon = 62\ M^{-1}\ cm^{-1}$) [20]. Solutions of green aquo Rh(II) dimer were prepared according to the method involving the addition of stoichiometric amounts of $Cr(H_2O)_6{}^{2+}$ to a solution of $Rh(H_2O)_6{}^{3+}$ in 1 M $HClO_4$ [3]. After separation of the different bands on a Dowex 50W-X2 column, the $Rh_{2(aq)}{}^{4+}$ ion was eluted with 3 M $HClO_4$ and gave the literature spectrum with peaks at 402 ($\epsilon = 63\ M^{-1}\ cm^{-1}$ per Rh), 648 ($\epsilon = 46.5\ M^{-1}\ cm^{-1}$) and 250 nm ($\epsilon = 9.85 \times 10^3\ M^{-1}\ cm^{-1}$) [4]. Solutions containing Cr^{2+} were prepared by reduction of $[Cr(H_2O)_6](ClO_4)_3$ (Ventron, GMBH) with amalgamated Zn in 1 M $HClO_4$. Solutions were standardized spectrophotometrically for Cr(II) ($\epsilon = 4.82\ M^{-1}\ cm^{-1}$ at 715 nm, $\epsilon = 0$ at 408 nm) and for Cr(III) ($\epsilon = 15.5\ M^{-1}\ cm^{-1}$ at 408 nm, $\epsilon = 0.3\ M^{-1}\ cm^{-1}$).

The $[H^+]$ of the solutions was determined by titration of the total $[H^+]$ after removal of the metal ions on an Amberlite IR 120(H) ion exchange resin, or potentiometrically.

Experiments involving Cr^{2+} and $Rh_{2(aq)}{}^{4+}$ were carried out under rigorous oxygen-free conditions (Ar). Only teflon needles were used in syringe transfers and residence time on the cation-exchange resin was minimized.

Rhodium was determined gravimetrically as a metal.

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TABLE I. UV–Vis Spectra for Various Aquorhodium Complexes in 3 M $HClO_4$

Complex	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}) per Rh)	Reference
$Rh(H_2O)_6^{3+}$	396(62), 311(67.4)	20
$Rh_{2(aq)}^{4+}$	648(46.5), 402(63), 250(9.85 x 10^3)	4
[$Rh_{2(aq)}^{4+}$ + O_2] yellow product	400(99), 228(2 x 10^4)	this work
$[(H_2O)_4(OH)Rh(O_2^-)Rh(OH)(H_2O)_4]^{3+}$ (violet product)	560(217), 420(140), 235(3.8 x 10^3)	this work

Ultraviolet and visible spectra were recorded on a SPECORD M-40 spectrophotometer. ESR spectra were recorded on a JEOL JS 3X spectrometer. NMR spectra were recorded on a TESLA BS 567 A spectrometer.

Results and Discussion

The reaction of $Rh_{2(aq)}^{4+}$ with dioxygen has been found to be dependent on the diffusion rate of O_2 into the solution. The green solution of $Rh_{2(aq)}^{4+}$ in *ca.* 2 cm layer exposed to the air oxygen changes its colour to yellow. The measurements of UV–Vis spectra in time revealed the decay of the bands at 648, 402 and 250 nm characteristic for $Rh_{2(aq)}^{4+}$ and the formation of new bands at 400 and 228 nm with an isosbestic point at 450 nm (Table I). The cation-exchange behaviour showed the yellow reaction product to have a charge of greater than 3+ per molecule. This yellow compound can be reduced by Cr^{2+} giving $Rh_{2(aq)}^{4+}$. The ESR spectra indicated the yellow species to be diamagnetic. It suggests that oxygen from air produces dimeric or polymeric Rh(III) species.

When the solution of $Rh_{2(aq)}^{4+}$ is exposed to air oxygen in a thin layer (less than 0,5 cm), its colour changes from green to violet. The same effect is observed when dioxygen is bubbled through the solution of $Rh_{2(aq)}^{4+}$. This reaction is accompanied by consumption of H^+ ions that was confirmed by titration of the solution before and after reaction.

The violet complex was prepared by passing dioxygen through the green solution of $Rh_{2(aq)}^{4+}$ in 2–3 M $HClO_4$, placed in a glass reactor equipped with magnetic stirrer. The reaction course was followed spectrophotometrically. After the reaction was completed (no changes in UV–Vis absorption), the reaction mixture was diluted with water and loaded on to a Dowex 50W-X2(H) column. Two distinct bands were observed, an upper yellow band with low intensity and a lower violet, very intensive band. The violet species could be easily eluted by means of 3 M $HClO_4$, while the yellow required a higher concentration of $HClO_4$. Yield of the violet product was about 80% calculated per Rh used.

The remaining rhodium species is the compound whose UV–Vis spectrum corresponds to the yellow oxidation product of $Rh_{2(aq)}^{4+}$ with air oxygen.

The absorption spectrum of the violet complex eluted with 3 M acid has maxima at 560 (ϵ = 217 M^{-1} cm^{-1} per Rh) 420 (ϵ = 140 M^{-1} cm^{-1}), 350sh and 235 nm (ϵ = 3800 M^{-1} cm^{-1}). The ionic charge of the violet complex was determined by the method of Cady and Connick [21]. A charge of +2.9 ± 0.2 per complex species was obtained from four pairs of batch experiments.

The ESR data are summarized in Fig. 1. At room temperature, a single line (a) centred at $g = 2.0414$ was observed. A frozen solution at −140 °C yields spectra (b) showing two g values: $g_{\parallel} = 2.0822$ and $g_{\perp} = 2.0199$ ($g_{av} = 2.0406$) which is very similar to results reported for Rh(II) and Rh(III) complexes with coordinated O_2^- ions (Table II).

The violet complex is stable in concentrated (1–3 M) $HClO_4$. With increasing pH its colour

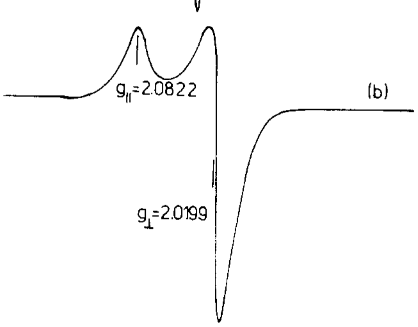

Fig. 1. ESR spectra of $[(H_2O)_4(OH)Rh(O_2^-)Rh(OH)(H_2O)_4]^{3+}$: (a) in 3 M $HClO_4$ solution at room temperature, (b) frozen solution in 3 M $HClO_4$ at −140 °C.

TABLE II. ESR Parameters for Various Superoxide Complexes of Rh(III) and Rh(II)

Complex	ESR signal observed	Reference
Rh(III) complexes		
$[(H_2O)_4(OH)Rh(O_2^-)Rh(OH)(H_2O)_4]^{3+}$	$g_{\parallel} = 2.0822, g_{\perp} = 2.0199, g_{av} = 2.0406, g_{iso} = 2.0414$	this work
trans-$[Rh(en)_2Cl(O_2)]^+$	$g_1 = 2.076, g_2 = 2.022, g_3 = 1.999, g_{av} = 2.033, g_{iso} = 2.033$	11
cis-$[Rh(en)_2Cl(O_2)]^+$	$g_1 = 2.086, g_2 = 2.022, g_3 = 1.992, g_{av} = 2.034, g_{iso} = 2.033$	11
$[\{Rh(en)_2\}_2Cl(NO_2)(\mu\text{-}O_2)]^{3+}$	$g_1 = 2.097, g_2 = 2.030, g_3 = 1.989, g_{av} = 2.039, g_{iso} = 2.037$	11
$[\{Rh(4\text{-}Me\text{-}py)_4Cl\}_2(\mu\text{-}O_2)]^{3+}$	$g_1 = 2.091, g_2 = 2.026, g_3 = 1.989, g_{av} = 2.036,$	11
$[Rh_2L_2Cl_2O_2]^{3+}$ (L = py, pic)	$g_{iso} = 2.019$	10
$[(H_2O)py_4Rh(O_2^-)Rhpy_4(H_2O)](ClO_4)_5$	$g_1 = 2.093, g_2 = 2.029, g_3 = 1.988$	16
$[(H_2O)py_3Rh(O_2^-)Rhpy_3(H_2O)](ClO_4)_4$	$g_1 = 2.094, g_2 = 2.025, g_3 = 2.004$	16
Rh(II) complexes		
$[RhCl_x(DMA)_yO_2^-]$	$g_{\parallel} = 2.10, g_{\perp} = 2.00$ (for the O_2^- ion) $g'_1 = 2.11, g'_2 = 2.04, g'_3 = 1.97$ (for Rh(II))	13
$[RhCl(O_2)(PPr^i_3)_2]$	$g_{\parallel} = 2.04, g_{\perp} = 2.00, g_{iso} = 2.02$ (for the O_2^- ion) $g'_1 = 2.09, g'_2 = 2.07, g'_3 = 1.96, g_{iso} = 2.03$ (for Rh(II))	14
$[Rh(dppe)(H_2O)O_2]BF_4$	$g_{\parallel} = 2.03, g_{\perp} = 2.00$ (for the O_2^- ion) $g'_1, g'_2 = 2.09, g'_3 = 1.97$ (for the Rh(II))	15

changes from violet via dark blue (at pH *ca.* 1) to pink violet (at pH > 7). The bands at 420 and 560 nm shift towards lower energy. At pH *ca.* 7 a yellow–green solid can be precipitated. The violet compound has been found to produce well shaped one electron diffusion cyclic curves in 3 M $HClO_4$ at the Pt electrode [22], while $Rh_{2(aq)}^{4+}$ does not show a similar wave [4]. This complex acts as oxidizing agent towards Cr(II) and J^- in acid solution. $Rh_{2(aq)}^{4+}$ is regenerated in the reaction with Cr(II). The exact titration of violet species with Cr(II) and J^- failed because of instability of the reduction products.

The known stable rhodium complexes with coordinated O_2 molecule are Rh(III) compounds containing the strong donor ligands, e.g. amines [10–12, 16–18]. R. D. Gillard and Pedrosa de Jesus who examined the photochemical generation of Rh(III) complexes with dioxygen have found that if the only reduced state of rhodium in a system is Rh(II), only superoxides are generated [12]. It has been also found that the superoxides of Rh(III) are surprisingly stable in concentrated acid solution [12, 17], while the peroxides undergo a disproportionation reaction [17]. These data and our results allow to assume that the paramagnetic, violet product of the oxidation reaction of $Rh_{2(aq)}^{4+}$ with dioxygen is the cationic complex of formula $[(H_2O)_4(OH)Rh(O_2^-)Rh(OH)(H_2O)_4]^{3+}$.

The magnetic susceptibility of the violet species in 3 M $HClO_4$ solution was measured by the NMR method of Evans [23] modified by Bailay [24]. The solutions of 2.97×10^{-3} and 7.43×10^{-3} M concentration of dimer showed a paramagnetic shift of 1 and 3 Hz respectively. This yielded a corrected [25] susceptibility of 1919×10^{-6} cgsu and 2178×10^{-6} cgsu or μ at 31 °C of 2.18 BM and 2.31 BM per mole of dimer respectively. It seems to confirm the presence of one unpaired electron in the molecule. The violet complex is reactive towards H_2, CO and SO_2. The colour of the solution changes from violet to yellow when effected by these molecules and paramagnetism disappears. However, these reactions are the subject of separate studies.

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