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Photolysis of a Cobalt(III) Complex with a Tetradentate Macrocyclic (N_4) Ligand. Photoredox Reaction

T. G. HOON and C. Y. MOK*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511

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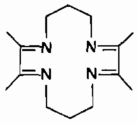
The photolysis of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ *in an aqueous acidic medium has been carried out with incident wavelengths at 254, 265, 313 and 365 nm. Spectrophotometric measurements in the uv, visible, ir and nmr regions show that reduction of the metal centre takes place, but the macrocyclic ligand remains intact. The quantum yield of* $Co^{II}(N_4)$ *formation is small and decreases with decreasing photon energy. Addition of alcohol leads to an appreciable increase in the qunatum yield, and the effect of glycerol is comparable to that shown by 2-propanol or t-butanol. The results are interpreted within the context of the radical-pair model with formation of hydroxyl radicals.*

Introduction

The photo-redox chemistry of cobalt(III) complexes has been the subject of intensive investigations during the past two decades [1]. The bulk of the studies dealt with Werner-type species such as cobalt(III) acidoammine complexes, for which irradiation of the first charge transfer band leads in general to reduction of metal and oxidation of ligand or solvent species with good quantum efficiencies. However, the ligand field bands are generally not very photosensitive [1].

More recently, studies have been extended to cobalt(III) complexes containing quadridentate macrocyclic ligands. These include cobalamins and their model compounds such as cobaloximes and macrocyclic Schiff base complexes [2–10]. Among these systems two kinds of behavior can be noted. For complexes with an alkyl ligand in an axial position, irradiation gives rise to homolytic cleavage of the Co–C bond to form an alkyl radical and a Co(II) species. The quantum efficiencies are comparable to those obtained for cobalt(III) acidoammine systems, and are either constant or do not vary by more than twofold over an extended range of irradiation wavelength [4, 6, 8]. In contrast, for another class of macrocyclic complexes, namely, those with acido ligands in the axial positions, the redox quantum yields are about one to two orders of magnitude lower compared to the alkyl–cobalt complexes. They are also strongly wavelength dependent [5, 7].

Different aspects of the photochemistry of the alkylcobalt systems have been examined, these include the nature of the Co–C bond, the identity of the excited state responsible for reaction, and the fate of the transient species generated in the primary processes [2–4, 8–10]. On the other hand, relatively little attention has been directed toward the photochemistry of macrocyclic complexes with axial acido groups, despite the striking differences in quantum efficiencies. The present work was carried out in the hope to obtain more information on the photochemical behavior of the latter class of compounds, through a study of the photolysis of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ [11] in an aqueous acidic medium.



$Me_4[14]tetraeneN_4$

Experimental

Materials

The complexes *trans*-$[Co(Me_4[14]tetraeneN_4(OH_2)_2](ClO_4)_3$ and *trans*-$[Co(Me_4[14]tetraeneN_4(OH_2)_2](ClO_4)_2$ were prepared according to the methods of Rillema *et al.* [12]. Results of elemental analysis of the former compound are given as follows: % found: C, 24.93; H, 4.83; N, 8.48; Cl, 15.99. % calc.: C, 24.79; H, 4.72; N, 8.44; Cl, 15.69.

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*Author to whom correspondence should be addressed.

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Redistilled water was used as solvent. Other chemicals used were of reagent grade.

Equipment and Apparatus

The light source for photolysis was a Varian high pressure short-arc xenon illuminator, model VIX-150 (a low pressure mercury lamp was used during the early stage of the study). In cases where monochromatic light was required, the light emerging from the illuminator passed through a quartz disc, a grating monochromator (Bausch & Lomb, cat. no. 33-86-75), a collimating lens, and then reached the photolysis cell. The power supply line was regulated with a voltage stabilizer. Most of the irradiation was performed using cylindrical quartz cells of 3.5 cm diameter and 1 cm pathlength. When irradiation was performed for the purpose of product analysis, a larger cylindrical cell of the same diameter but of 5 cm pathlength was used.

Solution spectra were taken on a Unicam SP 8000 Recording Spectrophotometer; absorbance measurements were performed on a SP 500 Series 2 Spectrophotometer.

A Perkin-Elmer model 567 grating Infrared Spectrophotometer and a Perkin-Elmer R12B Nuclear Magnetic Resonance Spectrometer were used for recording ir and nmr spectra.

Measurements of pH were made by means of a Beckman Expandometric SS-2 pH meter.

A vacuum line used for degassing was equipped with an oil diffusion pump and a mechanical pump. System pressure readings were taken with a Pening gauge.

Procedures

Quantum Yield determination

Solutions to be photolyzed were 10^{-4} to 10^{-2} molar in complex and 0.100 molar in perchloric acid. Dissolved oxygen was removed by degassing through four to five freeze–pump–thaw cycles on the vacuum line. Concentration changes were determined spectrophotometrically by measuring the absorbance values at 542 nm, which corresponds to an intense absorption peak of the Co(II) complex. Light intensity was determined by means of the ferrioxalate actinometer.

Characterization of product

The $Co^{II}(N_4)$ produced during photolysis was isolated as solid $Co(N_4)Cl_2(ClO_4)$ through a process described in a previous work [8b] (N_4 denotes a macrocyclic quadridentate ligand which may or may not be identical to the original ligand). One portion of the solid was used for taking infrared spectrum. Another portion, in suspension in a dilute solution of D_2SO_4 in D_2O, was added with a slight excess of $AgNO_3$. The mixture was stirred and heated to about 70 °C. The coagulated AgCl was removed through filtration, and the nmr spectrum of the filtrate was recorded.

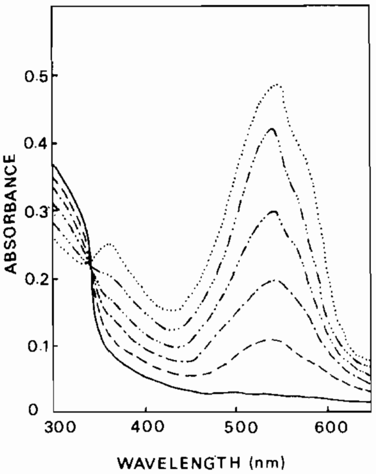

Fig. 1. Spectral changes during photolysis of $Co(Me_4[14]$-tetraene$N_4)(OH_2)_2^{3+}$. Initial concentration of complex = 2.71 × 10^{-4} *M*, $[HClO_4]$ = 1.00 × 10^{-3} *M*. Time of irradiation: ———, 0; – – –, 30; –·–, 90; –··–, 180; –···–, 360; ·······, 720 sec. λ_{irr} = 254 nm.

Detection of radical species

In order to detect formation of radical species, photolysis was carried out with addition of a vinyl monomer. A solution containing the cobalt complex and methyl methacrylate was deaerated by bubbling with Cr^{2+}-scrubbed nitrogen for two hours and irradiated with the xenon lamp, using a combination of Corning filters of serial numbers CS 9-54 and CS 0-53 to cut off radiation below 290 nm so that light absorption was predominantly due to the complex only.

Results and Discussion

The spectra of $[Co(Me_4[14]tetraeneN_4)(OH_2)_2]$-$(ClO_4)_3$ and $[Co(Me_4[14]tetraeneN_4)(OH_2)_2]$-$(ClO_4)_2$ in acidic aqueous solutions agree well with those reported in the literature [13, 14]. For the former complex a major peak appears at 225 nm (ϵ = 2.45 × 10^4 cm^{-1} M^{-1}), corresponding to a charge transfer transition; in the near ultraviolet and visible regions there are low-intensity bands, corresponding to ligand field transitions. In contrast, the spectrum of the Co(II) complex shows two major peaks at 542 and 360 nm (ϵ = 3080 and 1100 cm^{-1} M^{-1} respectively) which have been assigned as charge transfer from metal to ligand transitions [14].

Acidic solutions of $[Co(Me_4[14]tetraeneN_4)$-$(OH_2)_2](ClO_4)_3$ and $[Co(Me_4[14]tetraeneN_4)$-

TABLE I. Infrared and Nmr Analyses of Photo-product.

IR[a]				NMR[d]
$[Co(Me_4[14]tetraeneN_4)Cl_2](ClO_4)^b$				$[Co(Me_4[14]tetraeneN_4)(OH_2)_2]^{3+}$
723(s)	806(m)	829(w)	871(m)	2.47(m)
924(m)	1171(w)	1200(m)	1219(s)	2.98(s)
1263(w)	1290(m)	1334(w)	1598(s)	4.20(m)
$[Co(N_4)Cl_2](ClO_4)^c$				$[Co(N_4)(OH_2)_2]^{3+}$
722(s)	804(m)	830(w)	870(m)	2.45(m)
923(m)	1170(w)	1200(m)	1219(s)	2.97(s)
1263(w)	1291(m)	1335(w)	1596(s)	4.25(m)

[a] Frequencies are in cm^{-1}; m = moderate, w = weak, s = strong. [b] Prepared from $[Co(Me_4[14]tetraeneN_4)(OH_2)_2](ClO_4)_2$. [c] Prepared from photo-product $[Co(N_4)(OH_2)_2](ClO_4)_2$ after irradiation of a solution containing 1.06×10^{-2} *M* $[Co(Me_4[14]tetraeneN_4)(OH_2)_2](ClO_4)_3$ and 1.00×10^{-3} *M* $HClO_4$ to 58% conversion. [d] Chemical shift in δ value (ppm); m = multiplet, s = singlet.

$(OH_2)_2](ClO_4)_2$ exhibited no signs of change when stored in the dark for periods of at least a day. The colour of millimolar solutions of the Co(III) complex was originally pale brown, but during irradiation it gradually changed to the pink colour characteristic of the Co(II) complex. Figure 1 shows the spectral changes during irradiation. The isosbestic point at 340 nm and the emerging peaks at 542 and 360 nm indicate that the product is $Co^{II}(N_4)$.

The infrared spectrum of a $[Co(N_4)Cl_2](ClO_4)$ sample obtained through conversion of the Co(II) species produced photochemically is the same as that of an authentic $[Co(Me_4[14]tetraeneN_4)Cl_2](ClO_4)$ sample. Furthermore, the nmr spectrum of a diaquo Co(III) complex, obtained through conversion of $[Co(N_4)Cl_2](ClO_4)$, was also found to match well with that of the unphotolyzed $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ complex (Table I). The absence of significant variations in both infrared and nmr spectra indicates that the macrocyclic ligand remains intact after photolysis*. If the macrocyclic ligand were directly involved in the primary photoredox process, one would expect irreversible changes of the ligand to take place [15]. The ligand that is oxidized in the primary reaction thus appears to be coordinated water, *i.e.*

$$Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+} \xrightarrow{h\nu} Co(Me_4[14]tetraeneN_4)(OH_2)^{2+} + OH + H^+ \quad (1)$$

The presence of radical species is indicated by the induced polymerization of methyl methacrylate [16]. When a deaerated solution, which was 1.05×10^{-3} *M* in the Co(III) complex, 1.30×10^{-3} *M* in $HClO_4$ and 0.132 *M* in methyl methacrylate, was irradiated for 5 min, the solution became cloudy, further irradiation caused formation of white filmy precipitates. In contrast, irradiation of a deaerated solution of methyl methacrylate for 25 min did not result in observable changes.

During irradiation, the change in pH was caused by at least two factors, namely the change in Co(III) complex concentration and the release of H^+ ions by the photoredox reaction (eqn. (1)). From several determinations of the pH values of solutions containing $HClO_4$ and the Co(III) complex, the pK value of the complex can be estimated to be 3.4 ± 0.2, in good agreement with the literature value of 3.5 [13]. On the other hand, solutions of $[Co(Me_4[14]tetraeneN_4)(OH_2)_2](ClO_4)_2$ were found to be neutral. On this basis the H^+ ion concentration of a photolysed solution can be formulated as follows:

$$[H^+] = [H^+]_s + \Delta[H^+] \quad (2)$$

where $[H^+]_s$ represents the sum of contributions from the hydrolysis of the Co(III) complex and added $HClO_4$, and $\Delta[H^+]$ the contribution from the photoredox reaction. The value of $\Delta[H^+]$ for a given run can be estimated from the pH values of solution before and after photolysis, and a knowledge of the amount of Co(II) produced. The results in Table II show that the Co(II) and H^+ are generated in 1:1 ratio. This is the stoichiometry of reaction (1) and implies that subsequent reactions of the hydroxyl

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*In the cobalt alkyl system of $Co(Me_4[14]tetraeneN_4)(CH_3)(OH_2)^{2+}$, minor structural alterations of the macrocyclic ligand brought about through photolysis could be detected in the i.r. and nmr spectra. See ref. 10.

TABLE II. Increase in Hydrogen Ion Concentration.

Initial conc of Co(III) complex (*M*)	Time of irradiation[a] (min)	Conc of Co^{II} (N_4) (*M*)	$\Delta[H^+]$[b] (*M*)
4.84×10^{-4}	40	3.67×10^{-4}	3.73×10^{-4}
2.14×10^{-3}	45	7.47×10^{-4}	7.58×10^{-4}

[a] The light from the xenon lamp was filtered through the collimating lens only. [b] Increase in H^+ ion concentration due to the photo-redox reaction.

TABLE III. Wavelength Dependence of Quantum Yield.

Initial conc of Co(III) complex[a] (*M*)	Excitation wavelength (nm)	$\Phi_{Co^{II}(N_4)}$[b]
4.91×10^{-4}	254	7.16×10^{-3}
4.58×10^{-4}	265	4.88×10^{-3}
26.0×10^{-4}	313	2.75×10^{-3}
50.0×10^{-4}	365	1.01×10^{-3}

[a] In 0.1 *M* $HClO_4$. [b] Average quantum yield of two determinations, deviations of the individual values are within 10%.

TABLE IV Quantum Yield in Alcohol–Water Mixed Solvents. $\lambda_{irr} = 254$ nm.

Solvent	x_{calc}[a]	$\Phi_{Co^{II}(N_4)}$[b]
Glycerol/water	2.26×10^{-1}	8.95×10^{-2}
t-Butanol/water	2.26×10^{-1}	4.25×10^{-2}
2-Propanol/water	2.26×10^{-1}	7.83×10^{-2}
2-Propanol/water	1.50×10^{-1}	5.84×10^{-2}
2-Propanol/water	7.20×10^{-2}	2.90×10^{-2}
2-Propanol/water	1.92×10^{-2}	1.29×10^{-2}
2-Propanol/water	1.81×10^{-3}	7.36×10^{-3}
2-Propanol/water	1.81×10^{-4}	6.91×10^{-3}

[a] x_{calc} = mol fraction of alcohol; in all cases $[HClO_4]$ = 0.100 *M*, initial concentration of Co(III) complex = $(4.99 \pm 0.05) \times 10^{-4}$ *M*. [b] Average quantum yield of two determinations, deviations of individual values from the average are mostly within 4%.

radicals to not result in any change in the hydrogen ion concentration. Presumably the hydroxyl radicals may combine to form oxygen, as in the case of the photolysis of $Fe(ClO_4)_3$ in acidic solutions [17]; part of the hydroxyl radicals may also react with the Co(II) complex.

The rate of Co(II) formation during irradiation, as calculated from the increase in absorbance at 542 nm, was a constant in the initial stage (within about 7% of conversion). After the initial stage the rate gradually decreased with irradiation time. This decrease in rate reflects the importance of the reverse of reaction (1) as Co(II) is being accumulated. The quantum yield values, calculated from the initial slopes of the increase of Co(II) concentration with time of irradiation, are given in Table III. Though small compared to those observed for Werner-type acidoammine Co(III) complexes, the quantum yield is wavelength-dependent, decreasing toward longer wavelength. This latter feature is common to the acidoammine systems and is in harmony with predictions based on the radical-pair model [1].

The reaction can thus be described as follows:

$$Co^{III}\text{–}OH_2 \xrightarrow{h\nu} CT \tag{3}$$

$$CT \rightarrow [\,Co^{II}, OH, H^+]_{solv\ cage} \tag{4}$$

$$[Co^{II}, OH, H^+]_{solv\ cage} \rightarrow Co^{III}\text{–}OH_2 \tag{5}$$

$$[Co^{II}, OH, H^+]_{solv\ cage} \rightarrow [Co^{II}(S)OH, H^+]_{solv\ cage} \tag{6}$$

$$[Co^{II}(S)OH, H^+]_{solv\ cage} \rightarrow Co^{III}\text{–}OH_2 \tag{7}$$

$$[Co^{II}(S)OH, H^+]_{solv\ cage} \rightarrow Co^{II} + OH + H^+ \tag{8}$$

where only the central metal ion and the ligand directly involved in the photo-reaction are indicated; CT denotes a charge transfer excited state and $[Co^{II}(S)OH, H^+]_{solv\ cage}$ a solvent separated caged species. Relative to step (5), step (6) would be enhanced by an increase in the energy of the incident photons.

In anticipation of a cage effect on the photoredox reaction, we studied the effect of added glycerol. One would expect that a more viscous medium should favour recombination of geminate radical species and thus lead to a lower quantum yield of Co(II) formation in the present case. However, the results showed that with glycerol–water mixed-solvent in which the mole fraction of the alcohol was 0.226, there was a ten-fold increase in quantum yield over that obtained in the absence of alcohol. Substitution of glycerol with 2-propanol or t-butanol

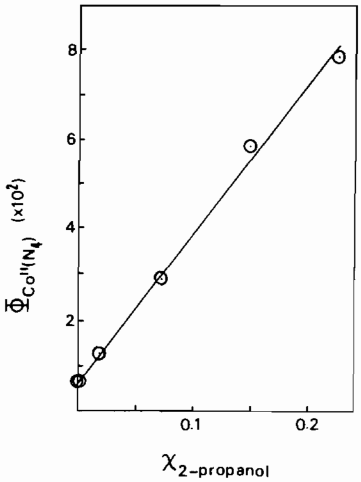
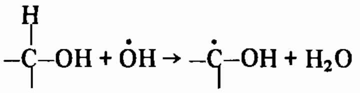


Fig. 2. Variation of quantum yield with 2-propanol concentration.

showed similar effects; the results are given in Table IV. Clearly medium viscosity is not the major factor.

The hydroxyl radical is well known for its ability to abstract an α-hydrogen atom from an alcohol [18]:



$$-\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-OH + \dot{O}H \rightarrow -\underset{|}{\dot{C}}-OH + H_2O \qquad (9)$$

a process which occurs with near diffusion-controlled efficiency [19]. In the case of t-butanol, although no α-hydrogen is present, extraction of a β-hydrogen atom is also efficient [18, 20]. On the other hand another reaction, namely outer-sphere oxidation of alcohol through direct reaction with the charge transfer excited state of the complex, has been shown to take place only with alcohols carrying an α-hydrogen atom [18]. The present observation of comparable effects shown by the three alcohols suggests that abstraction of hydrogen by hydroxyl radicals takes place. Table IV also shows the variation of quantum yield as a function of 2-propanol concentration, and it is evident that only when the mol fraction of alcohol is about 2×10^{-2} (1 molar) or higher, does the quantum yield increase appreciably with alcohol concentration. Requirement of such high alcohol concentration implies scavenging of geminate radicals [21]. Evidently the higher the mol fraction of alcohol, the greater is the probability that an alcohol molecule will be found as a component member of the solvent cage, capable of intercepting geminate species, provided the quenching is near diffusion-controlled. A plot of quantum yield of Co(II) formation against mol fraction of alcohol gives a linear relationship, as shown in Fig. 2. On the basis of the assumption that this linear relationship would extend to higher alcohol concentration range, the slope of the straight line (0.33) can be taken approximately as a lower limit of the quantum yield of the formation of the geminate species. This value is much higher than the yield obtained in the absence of scavenger, and this suggests that geminate recombination occurs with high efficiency*.

Whereas many Werner-type Co(II) complexes are high-spin in their ground states, Co(II) complexes containing quadridentate macrocyclic ligands such as $Me_4[14]tetraeneN_4$ are low-spin [14, 22]. Since the ground state Co(III) complex is singlet, recombination of the radical-pair would be favoured if it has net singlet spin multiplicity [23]. Furthermore, the question of the spin multiplicity of the charge transfer excited state from which homolysis takes place has so far not been adequately resolved. Sensitization techniques have met with only limited success, due to complications such as possible electron transfer reactions [24–26], and ambiguity in donor spin state [27]. For the present system the high efficiency of recombination over separation of the caged radical-pair suggest that the radical-pair, and consequently the charge transfer excited state responsible for reaction, are probably of singlet spin multiplicity.

To conclude, the photoredox reaction of the macrocyclic complex $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ probably takes place from a singlet charge transfer to metal excited state. The small quantum yield of the reaction appears to be the result of very efficient recombination of the geminate radical species.

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*Note that there are two components of geminate recombination, primary and secondary. The quenching process may affect both or just secondary recombination. See ref. 21.

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