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Spectral Evidence for the Formation of Active Intermediates from $RuCl_3$ and $RuCl_2(PPh_3)_3$ with *N*-Methylmorpholine *N*-Oxide (NMO) and Phenyliodosoacetate (PIA) as Mild Oxidants

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Abstract

Electronic, EPR and IR spectral evidence are given for the formation of the following active species: (1) ruthenium(VIII) in ruthenium(III)–PIA system, (2) ruthenium(V) oxo species in ruthenium(III)–*N*-oxide system, and (3) ruthenium(II)–phosphine oxide complex in ruthenium(II)–*N*-oxide system. Cyclic voltammetric studies also suggest the formation of Ru(V) in ruthenium(III)–*N*-oxide system.

Introduction

Sharpless *et al.* [1] have carried out yield oriented studies using ruthenium(III)–*N*-oxide combination for the oxidation of alcohols like geraniol, cholestanol, etc. Muller *et al.* [2] have used iodosobenzene as oxygen transfer agent in combination with ruthenium(III) or ruthenium(II). It has been reported [3, 4] that ruthenium(III) does not undergo a change in the oxidation state when it is used to catalyze the oxidation by PIA.

During the course of systematic investigations on ruthenium(III)-catalyzed oxidation of secondary alcohols using NMO in DMF and PIA in acetic acid, the electronic and EPR spectra of ruthenium(III)–oxidant system were examined in order to characterize the intermediate ruthenium species in solution.

Experimental

Acetic acid was purified by the method due to Orton [5] and DMF was purified according to the method of Faulkner [6]. *N*-methylmorpholine *N*-oxide monohydrate (Fluka) was used as such. Phenyliodosoacetate was prepared by the modified method of Boeseken [7]. $RuCl_3 \cdot 3H_2O$ (Johnson Matthey) was used as such. $RuCl_2(PPh_3)_3$ was prepared according to the method reported by Stephenson and Wilkinson [8]. Solutions of ruthenium(III) were standardized according to the method of Horiuchi [9]. EPR spectra were recorded at 77 K using a Varian spectrometer and electronic spectra using a Shimadzu UV–Vis recording spectrophotometer. IR spectra were recorded with a Perkin-Elmer spectrometer. Voltammograms were taken with Princeton Applied Research Model 173, 175 and 179 electrochemistry system equipped with an X–Y recorder. Voltammograms are obtained with sweep rates of 100–400 mV s^{-1}.

Results and Discussion

(1) $RuCl_3$–PIA System in Acetic Acid as Solvent

Ruthenium(III) chloride in acetic acid has an absorption maximum (Fig. 1a) at 470 nm (ϵ = molar absorption coefficient = 5800 M^{-1} cm^{-1}) and 350 nm ($\epsilon = 3850$ M^{-1} cm^{-1}). For a low spin d^5 system like $RuCl_3$ the expected d–d transitions are $^2T_{2g} \rightarrow {}^2A_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{1g}$ apart from charge transfer bands [10]. Absorption at 470 nm can be attributed to LMCT bands (ligand–metal charge transfer) since the ϵ value is very high. The d–d transitions are obscured by the LMCT bands [11]. Keeping the concentration of $RuCl_3$ constant, if the concentration of PIA is increased, absorption in the region 550–610 nm increases (Figs. 1b and c). However, when a hundred fold excess of PIA is added, the λ_{max} shifts towards 385 nm (Fig. 1d). The spectral shift might be due to the formation of higher oxidation states of ruthenium. Hence Ru(VI), Ru(VII) and Ru(VIII) were prepared as reported in the literature [12] and their electronic spectra are given in Fig. 2. Ru(VI) and Ru(VII) (Figs. 2b and c) are stable only under alkaline conditions [13]. The spectral pattern of an authentic sample of Ru(IV) (Fig. 2d) is entirely different from that of the intermediate formed. From the comparison of Figs. 2a and 1d it is clear that ruthenium(III) is finally oxidized to ruthenium(VIII) by PIA in acetic acid. Ruthenium(VIII) prepared in CCl_4 is stable in acetic acid (Fig. 2f). The species absorbing around 550–610 nm might be ruthenium(V), postulated by earlier workers [14, 15]. The absorp-

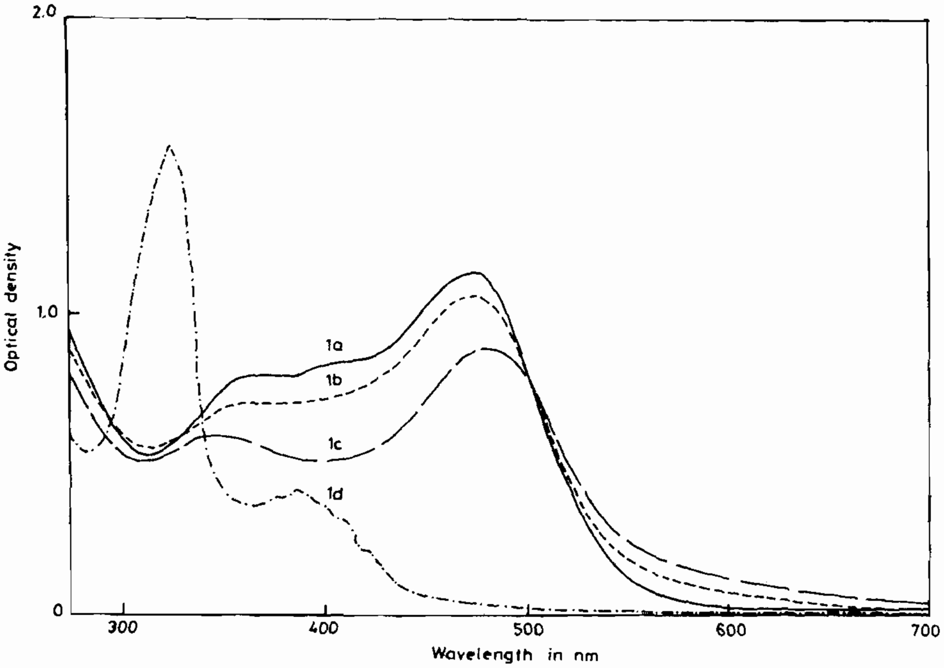

Fig. 1. Absorption spectra of: (1a) $RuCl_3$ (2.0×10^{-4} M) in acetic acid; (1b) $RuCl_3$ (2.0×10^{-4} M) and PIA (1.0×10^{-4} M) in acetic acid; (1c) $RuCl_3$ (2.0×10^{-4} M) and PIA (5.0×10^{-4} M) in acetic acid; (1d) $RuCl_3$ (2.0×10^{-4} M) and PIA (2.0×10^{-2} M) in acetic acid.

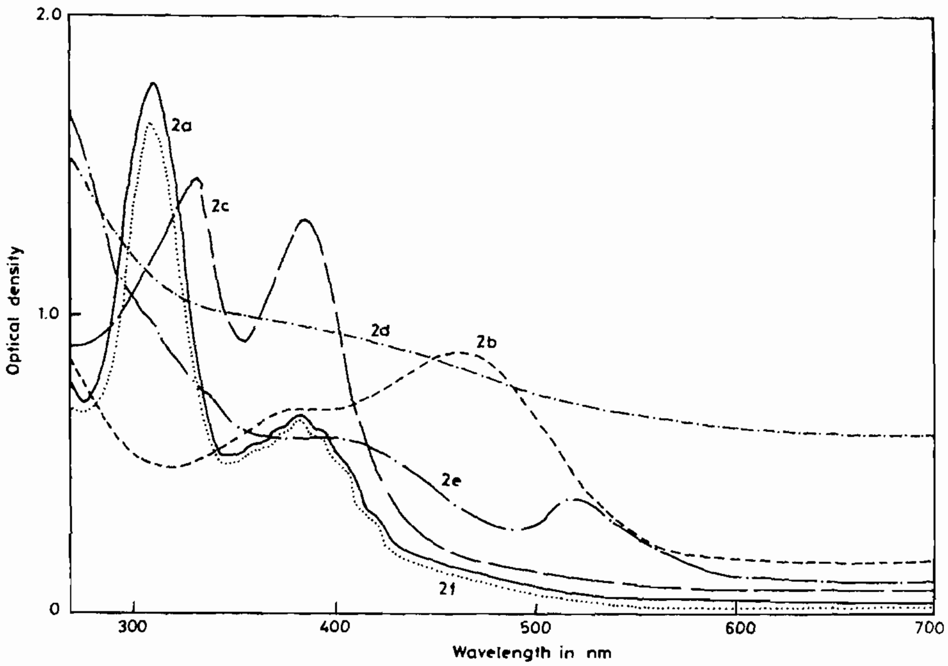

Fig. 2. Absorption spectra of: (2a) Ru(VIII) in CCl_4; (2b) Ru(VI) in NaOH; (2c) Ru(VII) in NaOH; (2d) Ru(IV) in DMF, (2e) Ru(VIII) in CCl_4 + excess of DMF; (2f) Ru(VIII) in CCl_4 + excess of acetic acid.

tion around 550–610 nm ($\epsilon = 2820$ M^{-1} cm^{-1}) can be attributed to the charge transfer band of ruthenium(V). In the presence of excess PIA there is no absorbance due to this intermediate species. EPR spectrum of $RuCl_3$ (low spin, $I = 5/2$) in acetic acid taken at 77 K gives six signals. All the signals disappear over a period of time when excess of PIA is present indicating the formation of ruthenium(VIII), a d^0 system.

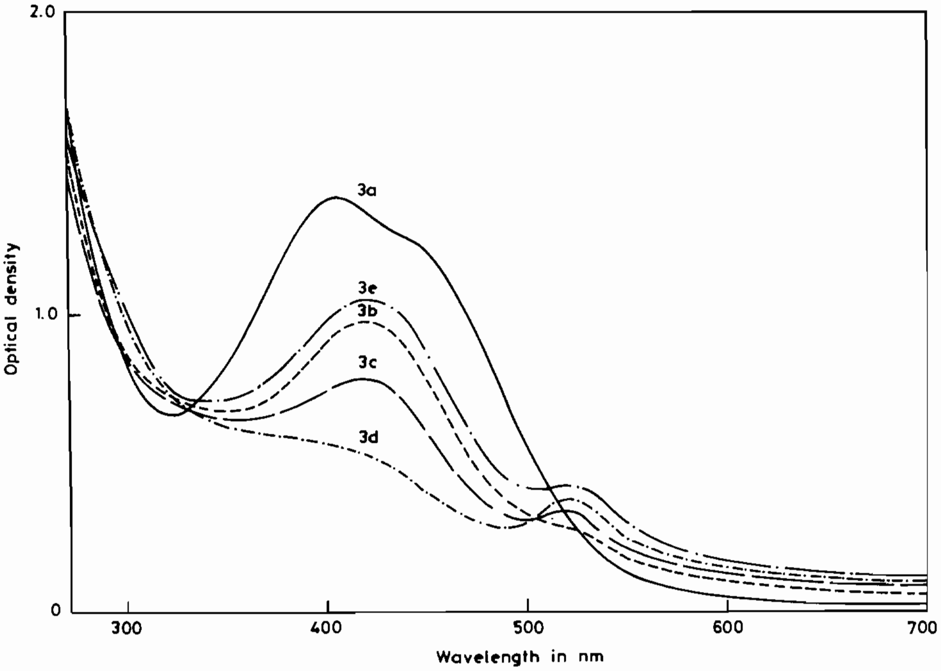

Fig. 3. Absorption spectra of: (3a) $RuCl_3$ (1.96×10^{-4} M) in DMF; (3b) $RuCl_3$ (1.96×10^{-4} M) and NMO (2.0×10^{-4} M) in DMF; (3c) $RuCl_3$ (1.96×10^{-4} M) and NMO (5.0×10^{-4} M) in DMF; (3d) $RuCl_3$ (1.96×10^{-4} M) and NMO (2.0×10^{-2} M) in DMF; (3e) Ru(V) generated electrochemically in DMF.

(2) $RuCl_3$–NMO System in DMF as Solvent

A comparison of the electronic spectra (Figs. 1 and 3) indicates that λ_{max} of $RuCl_3$ is shifted from 470 nm (λ_{max} in acetic acid) to 400 nm ($\epsilon = 7041$ M^{-1} cm^{-1}) in DMF with a shoulder appearing at 450 nm ($\epsilon = 6122$ M^{-1} cm^{-1}). This shift in λ_{max} towards a lower region of λ may be due to the complexation by DMF (Fig. 3a). When the concentration of NMO is increased keeping that of $RuCl_3$ constant (Fig. 3b, c and d) absorption in the region 500–520 nm increases probably due to the formation of an intermediate of higher oxidation state. This intermediate cannot be Ru(IV), Ru(VI) and Ru(VII) (Fig. 2, *vide supra*). The intermediate cannot be Ru(VIII) either, as an authentic sample of RuO_4[Ru(VIII)] is stable only in CCl_4 and acetic acid and it decomposes to give RuO_2 and oxygen in other solvents [16]. The electronic spectrum of RuO_4 in CCl_4 (charge transfer bands at 385 and 330 nm, Fig. 2a) is entirely different when excess of DMF is added (Fig. 2e). From the amount of *N*-oxide estimated titanometrically [17] before and after adding Ru(III), a stoichiometry of 1:1 between $RuCl_3$ and NMO (a two electron oxidant) was established. This suggests the formation of Ru(V). In order to confirm this, EPR studies have been carried out. The EPR spectrum of $RuCl_3$ in DMF (Fig. 4a) consists of six signals. The most intense signal appearing along with DPPH will account for $I = 0$ (due to 70% abundance of even isotopes of ruthenium) and the other signals will account for $I = 5/2$ (due to 30% abundance of odd isotopes of ruthenium). A mixture of $RuCl_3$ and NMO in DMF in the ratio 1:100 left for a long reaction time also gives an EPR spectrum (Fig. 4b) similar to that of $RuCl_3$ in DMF. Though the number of signals expected for Ru(V) is more, all the expected signals are not present. This may be due to the following reasons: (i) zero

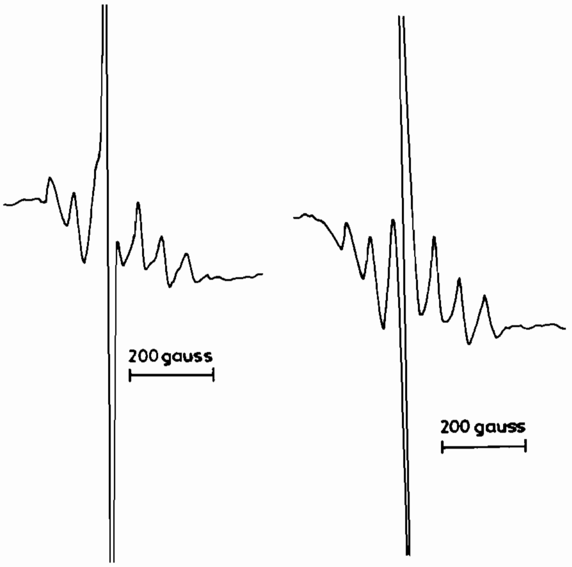

Fig. 4. (4a) EPR spectrum of $RuCl_3$ in DMF frozen at 77 K; (4b) EPR spectrum for the mixture of $RuCl_3$ and *N*-oxide in DMF frozen at 77 K.

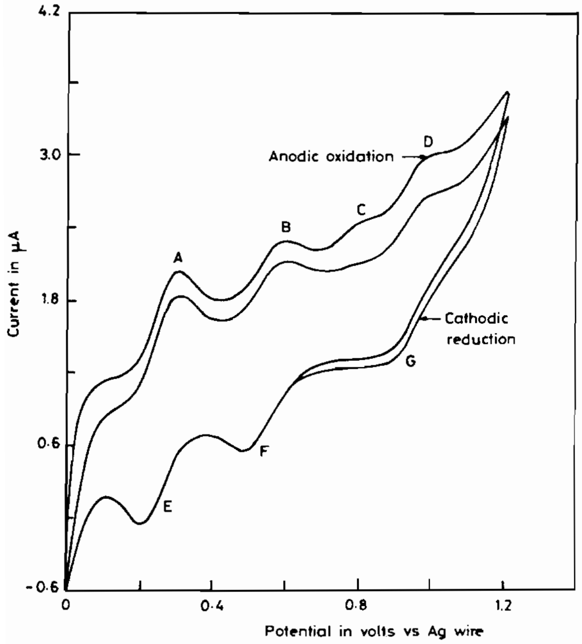

Fig. 5. Voltammogram observed during the anodic oxidation of $RuCl_3$ and cathodic reduction of the higher oxidation states of ruthenium.

field splitting for Ru(V), a d^3 system, may be large and consequently lines corresponding to $-3/2$ to $-1/2$ and $1/2$ to $3/2$ are not seen in the X-band. The $-1/2$ to $1/2$ transition for Ru(V) might be embedded with the lines corresponding to that of Ru(III) unreacted, that is always present in the reaction mixture. (ii) Lines corresponding to Ru(V) might be too broad to be seen unambiguously. Hence EPR studies are inadequate for the detection of Ru(V) species.

Since EPR studies give inconclusive evidence for Ru(V) formation, cyclic voltammetric studies have been carried out using Pt wire, Pt foil and silver wire as working, counter and reference electrodes respectively with tetra-n-butylammonium perchlorate as supporting electrolyte. The voltammogram (Fig. 5) shows four peaks during anodic oxidation of Ru(III) in DMF and three peaks appear during cathodic reduction. Peak A is due to Ru(IV) and B is due to Ru(V). Points C and D correspond to other oxidation states higher than Ru(V). Points E and F are due to Ru(III) and Ru(IV) respectively, formed during cathodic reduction. The difference in potential is 70 mV between A and E and 90 mV between B and F. A difference in potential of 60–70 mV and 90 mV corresponds to one-electron oxidation for reversible and pseudo-reversible processes respectively [18]. The potential corresponding to Ru(V) being 640 mV (Fig. 5) controlled potential electrochemical oxidation of Ru(III) was carried out by applying a voltage of 700 mV so that the electrochemical oxidation does not proceed beyond Ru(V).

The electronic spectrum (Fig. 3e) taken for Ru(V) formed by electrochemical oxidation of Ru(III) is similar to that of the spectrum got for the mixture of Ru(III) and NMO in DMF (Fig. 3b, c and d). The absorption around 520 nm (Fig. 3b, c and d) can account for the charge transfer band of Ru(V) ($\epsilon = 2570\ M^{-1}\ cm^{-1}$). All the three expected d–d transitions for Ru(V) are not seen since the CT bands are very intense and obscure the d–d bands. Thus cyclic voltammetric studies combined with the electronic spectra give a strong evidence for Ru(V) formation.

(3) $RuCl_2(PPh_3)_3$-NMO System

Dichlorotris(triphenylphosphine)ruthenium(II), $[RuCl_2(PPh_3)_3]$, was allowed to react with NMO with a view to find out whether this could behave like ruthenium(III). The electronic spectra indicate that the complex $RuCl_2(PPh_3)_3$ (Fig. 6a) in DMF has absorption bands at 615 ($\epsilon = 388\ M^{-1}\ cm^{-1}$) and 330 nm ($\epsilon = 3107\ M^{-1}\ cm^{-1}$). Ruthenium(II), a d^6 low spin system can have d–d transitions, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ apart from MLCT and LMCT spectra [19]. Charge transfer absorption obscures d–d bands in this species also. Fairly low energy charge transfer absorptions are assigned for MLCT class, for metals like ruthenium(II) [20]. So absorptions at 615 and 330 nm may be due to LMCT and MLCT respectively. When NMO is added to ruthenium(II), a new absorption band appears at 500 nm (Fig. 6b). This may be due to the formation of triphenylphosphine oxide (TPPO) complex [21]. An authentic sample of triphenylphosphine oxide complex of ruthenium(II) is prepared by adding excess of TPPO to $RuCl_3$ in methanol and refluxing the mixture. A comparison of the spectrum taken for the product in solution (Fig. 6c with that of Fig. 6b) indicates that the triphenylphosphine complex of ruthenium in the presence of NMO is converted to triphenylphosphine oxide complex. EPR studies suggest that there is no change in the oxidation state of ruthenium, since no signals appear for both $RuCl_2(PPh_3)_3$ and the mixture of NMO and $RuCl_2(PPh_3)_3$.

In the case of $RuCl_3$–NMO system, IR spectral studies reveal a weak ruthenium–oxygen absorption at 805 cm^{-1} [22] which accounts for the formation of an oxo complex of ruthenium. However this band does not appear for $RuCl_2(PPh_3)_3$–NMO system. Instead ruthenium–triphenylphosphine oxide complex is formed. The detection of complex formation from a shift in the frequency of P–O in triphenylphosphine oxide from 1100 cm^{-1} to a lower region is rendered difficult since most of the peaks of PPh_3 mask the P–O stretching frequency of the triphenylphosphine oxide complex.

All the three active intermediates, *i.e.* ruthenium(VIII), ruthenium(V) oxo species and ruthenium(II)–

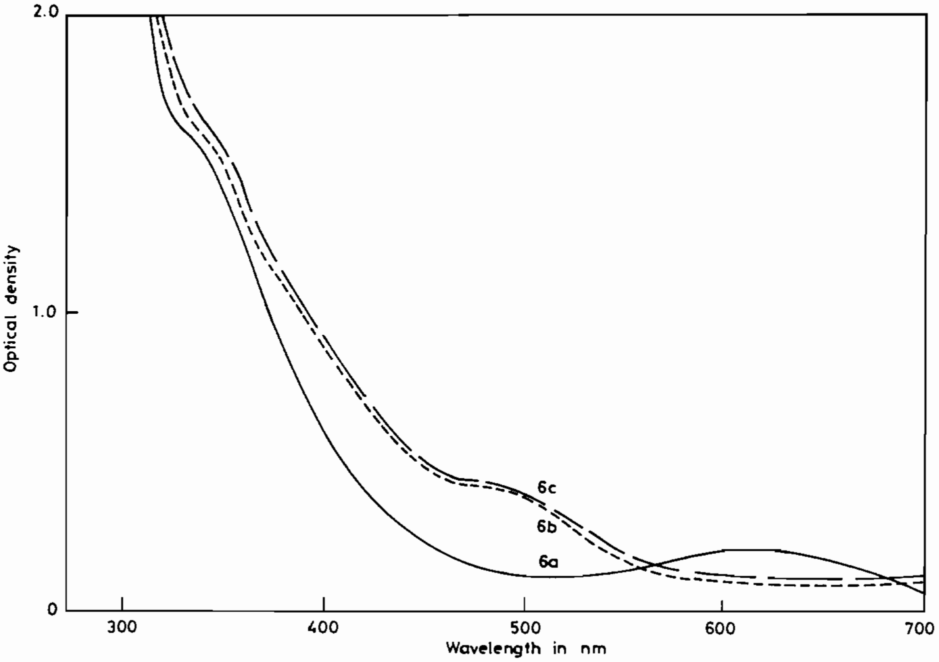

Fig. 6. Absorption spectra of: (6a) $RuCl_2(PPh_3)_3$ (5.15×10^{-4} M) in DMF; (6b) $RuCl_2(PPh_3)_3$ (5.15×10^{-4} M) and NMO (3.0×10^{-2} M) in DMF; (6c) triphenylphosphine oxide complex of Ru(II) in DMF.

triphenylphosphine oxide complex formed in the case of $RuCl_3$–PIA, $RuCl_3$–NMO and $RuCl_2(PPh_3)_3$–NMO respectively, when used in catalytic amounts in the presence of excess of the oxidant are found to oxidize a wide variety of organic substrates like alcohols, carbohydrates, natural products like terpenes, unsaturated compounds, aldehydes and hydrocarbons. $RhCl_3$, $IrCl_3$ are not effective in catalyzing the oxidation of organic substrates as these do not form the oxo species of higher oxidation states with PIA or NMO. This can be explained on the basis of the ability to undergo oxidative addition [23] and the stability of the higher oxidation states [24] of the metals. This tendency decreases across a period as $Ru > Rh > Pd$ and increases down a group as $Fe < Ru < Os$.

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