

RuCl₂(PPh₃)₃ catalyzed oxidation of secondary alcohols with N-methylmorpholine N-oxide

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Abstract. Catalytic amounts of RuCl₂(PPh₃)₃ in the presence of excess of N-methylmorpholine N-oxide (NMO) in DMF, oxidizes secondary alcohols to ketones. Spectral and electrochemical studies reveal the formation of an oxocomplex of Ru(IV), on adding excess of NMO. In the proposed mechanism, the Ru(IV)-oxo complex formed from Ru(II) and NMO, attacks the substrate in the rate determining step.

Keywords. Oxidation; secondary alcohols; N-methylmorpholine N-oxide; catalysis by Ru(II).

1. Introduction

Dichlorotris(triphenylphosphine)ruthenium(II) has wide application as a homogeneous catalyst in hydrogenation, isomerization, hydrosilylation and transfer hydrogenation reactions (Jardine 1984). In many ways it is complementary to Wilkinson's catalyst, RuCl(PPh₃)₃ (Jardine 1981). The oxidation of organic compounds catalyzed by RuCl₂(PPh₃)₃ has not received much attention. At room temperature RuCl₂(PPh₃)₃ catalyzes the oxidation of styrene (Turner and Lyons 1973) and alcohols (Tsuji *et al* 1984) by *t*-butyl hydroperoxide. In the presence of iodosobenzene, RuCl₂(PPh₃)₃ catalyzes the oxidation of alcohols (Muller and Godoy 1981a) and acetylene (Muller and Godoy 1981b). Sharpless *et al* (1976) have carried out reactions using several N-oxides to oxidize cholestanol, geraniol, etc. in the presence of RuCl₂(PPh₃)₃. There are no significant reports on the kinetics of ruthenium(II)-catalyzed oxidation of secondary alcohols. The oxidation of cyclohexanol, 1-phenylethanol and 2-propanol by N-methylmorpholine N-oxide (NMO) in DMF as the solvent is reported in this paper. A suitable mechanism is proposed based on the spectral, electrochemical and kinetic data.

2. Experimental

N-methylmorpholine N-oxide monohydrate (Fluka) was used as such. All the secondary alcohols were purified according to standard procedures. RuCl₂(PPh₃)₃ was prepared as per Stephenson and Wilkinson (1966), while DMF was purified as

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per Faulkner and Bard (1968). Ruthenium(II) solutions were estimated by the thiourea method (Ayres and Young 1950).

Kinetic studies were carried out at $35 \pm 0.1^\circ\text{C}$. The concentration of unreacted NMO at any instant was determined titanometrically as reported earlier (Vijayasri *et al* 1985). For low concentrations of NMO (below 0.05 M) the titanometric method not being very accurate, the ketone formed from the alcohol was estimated spectrophotometrically by the method of Lappin (1951).

Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer while EPR spectra were recorded at 77°K on a Varian E4 spectrometer and IR spectra were recorded on a Perkin-Elmer 983G spectrometer. Voltammograms were recorded on a Princeton Applied Research Model 173, 175 and 179 electrochemistry system equipped with an X-Y recorder. The cell used was of conventional three-electrode design, consisting of Pt-wire as the working electrode, Pt-foil as the counter electrode and silver wire as the reference electrode. Tetra-*n*-butylammonium perchlorate is used as the supporting electrolyte.

3. Results and discussion

Cyclohexanol, 1-phenylethanol and 2-propanol are oxidized by NMO, in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$, to the corresponding ketones. There is no oxidation of the alcohol by NMO in the absence of the catalyst. There is no reaction between $\text{RuCl}_2(\text{PPh}_3)_3$ and the alcohol in the absence of NMO as evidenced by the electronic spectra. Keeping the concentration of the substrate at a large constant value, a plot of $\log[\text{NMO}]$ vs time is linear showing that the order in NMO is unity. The orders with respect to the catalyst and the substrate ($[\text{substrate}] > 0.5 \text{ M}$) are determined to be one and zero respectively from the pseudo first order rate constants (table 1). The order with respect to the substrate is fractional at low concentrations (0.05 to 0.2 M, figure 1). Experimental investigations could not be carried out for concentrations of substrate below 0.05 M owing to inaccuracies in the isolation and estimation of the ketone formed in these cases. The ketone formed by the catalytic oxidation of the alcohol in the concentration range 0.05 to 1.0 M corresponds to that of the NMO consumed which gives a stoichiometry of 1:1 between the substrate and NMO.

The absorption spectrum of $\text{RuCl}_2(\text{PPh}_3)_3$ showed significant changes when the oxidant was present in the system and hence, the electronic and EPR spectra of the $\text{RuCl}_2(\text{PPh}_3)_3$ -NMO system were examined. $\text{RuCl}_2(\text{PPh}_3)_3$ in DMF (figure 2a) has absorption bands at 615 nm ($\epsilon = 388 \text{ M}^{-1} \text{ cm}^{-1}$) and 330 nm ($\epsilon = 3107 \text{ M}^{-1} \text{ cm}^{-1}$). Ruthenium(II) a low spin, d^6 system can have $d-d$ transitions, $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ apart from MLCT and LMCT spectra ($M = \text{metal}$, $L = \text{ligand}$ and $\text{CT} = \text{charge transfer}$). The CT bands generally obscure the $d-d$ bands (Lever 1984b). Absorptions at 330 and 615 nm may be due to LMCT and MLCT respectively. The band at 615 nm is assigned to MLCT as metal ions like ruthenium(II) generate fairly low energy, CT absorption of the MLCT class (Lever 1984a). When NMO is added to ruthenium(II), a new absorption band appears at 385 nm (figure 2b). This new absorption at 385 nm, observed within one to two hours after mixing of $\text{RuCl}_2(\text{PPh}_3)_3$ and NMO, may be due to a higher oxidation

Table 1. Determination of the order of reaction with respect to the reactants at high concentrations of the substrate (temperature = 35 ± 0.1°C; solvent = DMF).

Substrate	$\frac{[NMO]}{(M)}$	$\frac{[S]}{(M)}$	$\frac{[RuCl_2(PPh_3)_3] \times 10^3}{(M)}$	$\frac{k' \times 10^3}{(min^{-1})}$	$\frac{k'}{[Ru(II)]} = \frac{k_1}{M^{-1} min^{-1}}$
Cyclo-hexanol	0.10	1.0	1.0	19.75	19.75
	0.07	1.0	1.0	20.56	20.56
	0.05	1.0	1.0	19.33	19.33
	0.05	0.70	1.0	18.70	18.70
	0.05	0.50	1.0	18.96	18.96
	0.05	1.0	0.75	13.99	19.65
	0.05	1.0	0.50	9.75	19.50
$k_1(\text{mean}) = 19.35 \pm 0.62 \text{ M}^{-1} \text{ min}^{-1}$					
2-Propanol	0.10	1.0	0.75	12.48	16.64
	0.07	1.0	0.75	12.91	17.21
	0.05	1.0	0.75	12.52	16.69
	0.05	0.50	0.75	12.44	16.59
	0.05	0.70	0.75	12.98	17.31
	0.05	1.0	0.50	8.54	17.08
	0.05	1.0	1.00	17.92	17.92
$k_1(\text{mean}) = 17.06 \pm 0.44 \text{ M}^{-1} \text{ min}^{-1}$					
1-Phenyl ethanol	0.10	1.0	0.75	16.61	22.15
	0.07	1.0	0.75	16.39	21.85
	0.05	1.0	0.75	16.44	21.92
	0.05	0.50	0.75	16.46	21.95
	0.05	0.70	0.75	17.02	22.69
	0.05	1.0	1.0	23.33	23.33
	0.05	1.0	0.50	11.08	22.16
$k_1(\text{mean}) = 22.29 \pm 0.50 \text{ M}^{-1} \text{ min}^{-1}$					

k' = pseudo first order rate constant ($[S] \gg [NMO]$);
 k_1 = overall second order rate constant.

state of ruthenium. This can be Ru(IV) since a 1:1 stoichiometry is observed between Ru(II) and NMO. The formation of the Ru(IV) species (d^4 system) could be established by EPR studies since $RuCl_2(PPh_3)_3$ (low spin, d^6 system) is not expected to give EPR signals. However, both $RuCl_2(PPh_3)_3$ as well as a mixture of $RuCl_2(PPh_3)_3$ and NMO are not found to give EPR signals. For d^4 systems like Ru(IV) there are difficulties in detecting EPR signals due to very short spin-lattice relaxation times and large zero field splittings (McGarvey 1966). In the absence of any evidence from EPR studies, cyclic voltammetric studies on solutions of $RuCl_2(PPh_3)_3$ in DMF were undertaken. The voltammogram (figure 3) shows three peaks A_a , B_a and C_a during anodic oxidation and three peaks A_c , B_c and C_c during cathodic reduction. The peak-to-peak potential separations of the oxidative and reductive waves range from 65 to 70 mV, which are characteristic of one-electron reversible process (Bard and Faulkner 1980). Peak A_a and its reduction cycle counterpart A_c can be assigned to Ru(III)/Ru(II) interconversion. Similarly peaks at B_a and B_c can be assigned to Ru(IV)/Ru(III) interconversion. Peaks C_a and C_c can be assigned to Ru(V)/Ru(IV) interconversion. The potential corresponding to Ru^{IV} formation from $RuCl_2(PPh_3)_3$ in DMF is 0.81 V. The species obtained by

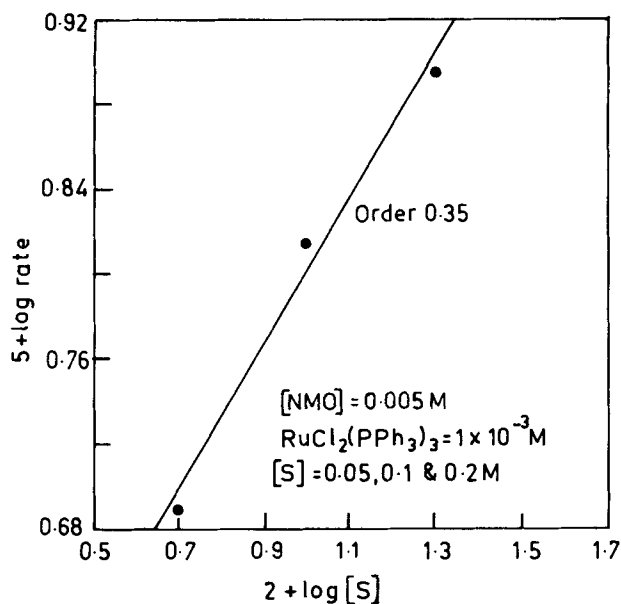


Figure 1. Order with respect to cyclohexanol at low concentrations.

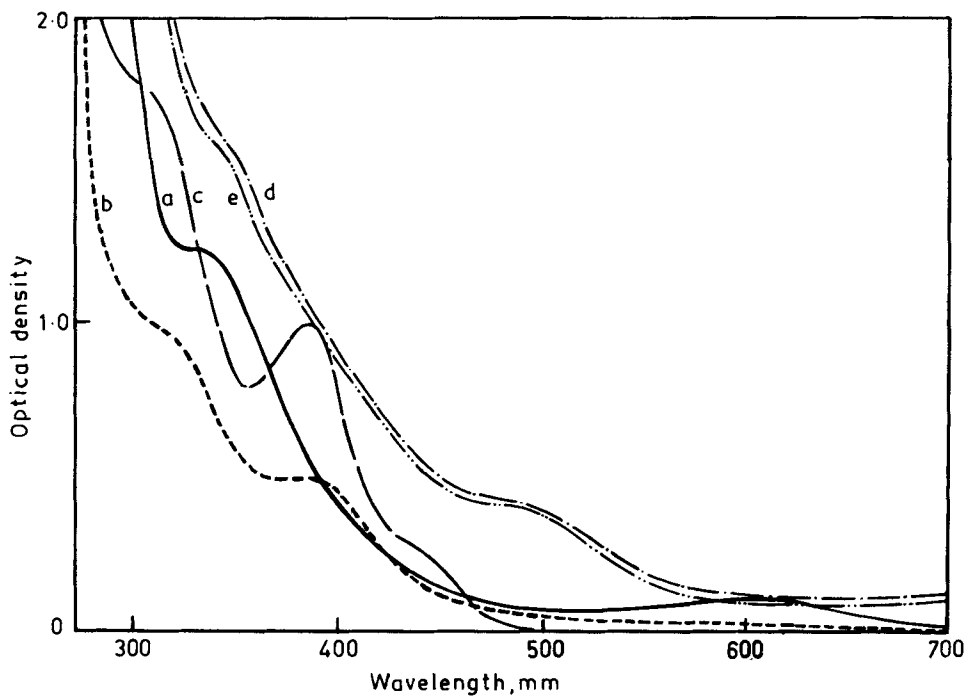


Figure 2. Absorption spectra of (a) $\text{RuCl}_2(\text{PPh}_3)_3 (4 \times 10^{-4} \text{ M})$ in DMF, (b) $\text{RuCl}_2(\text{PPh}_3)_3 (4 \times 10^{-4} \text{ M}) + \text{NMO} (0.2 \text{ M})$ in DMF (spectrum recorded 1 hr after mixing), (c) Ru(IV) generated electrochemically from $\text{RuCl}_2(\text{PPh}_3)_3$ in DMF, (d) triphenylphosphine oxide complex of Ru(II) in DMF, (e) $\text{RuCl}_2(\text{PPh}_3)_3 (5.15 \times 10^{-4} \text{ M}) + \text{NMO} (0.2 \text{ M})$ in DMF (spectrum recorded 24 hr after mixing).

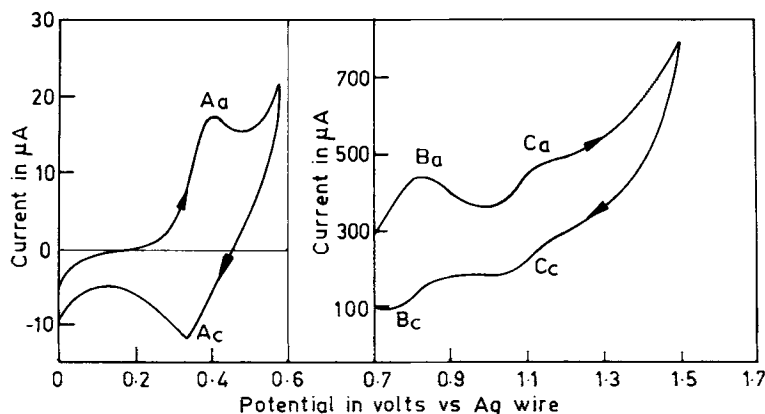


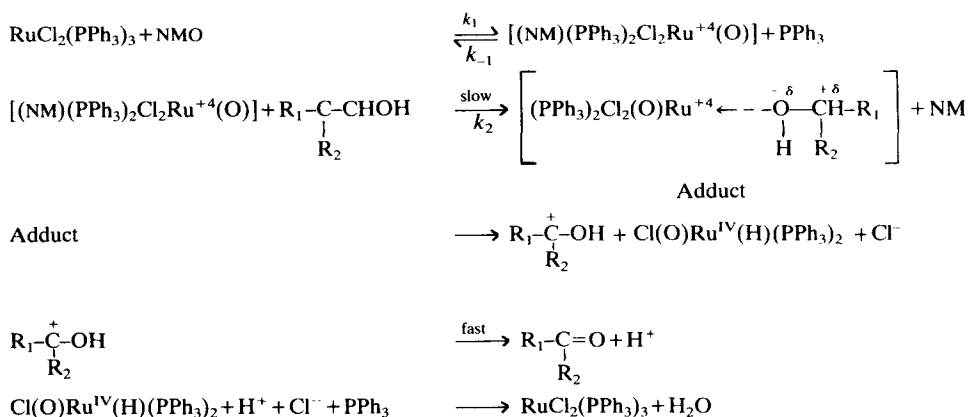
Figure 3. Cyclic voltammograms of RuCl₂(PPh₃)₃ in DMF in the region a. 0 to 0.6 V, b. 0.7 to 1.5 V.

controlled potential oxidation of RuCl₂(PPh₃)₃ in DMF at 1.0 V gives a UV-VIS spectrum (figure 2c) similar to that of the spectrum got immediately after mixing RuCl₂(PPh₃)₃ and NMO (figure 2b). The intermediate can be an oxo or a non-oxo species of Ru(IV). Both the oxo-Ru(IV) complexes, like (trpy)(bpy)Ru^{IV}O⁺² and (bpy)py RuO⁺² (Thompson and Meyer 1982), and non-oxo Ru(IV) amine complexes (Tovrog *et al* 1979) have been used as oxidants for alcohols like 2-propanol. The oxo species of Ru^{IV} is likely to be the active species since N-oxides are known to form metal oxo complexes, the metal undergoing a two-electron change (Powell *et al* 1984). It is difficult to locate the Ru = O frequency in IR as most of the peaks of PPh₃ group of RuCl₂(PPh₃)₃ appear in the region from 700–900 cm⁻¹. Ru(IV) generated electrochemically also oxidizes alcohols in stoichiometric amounts but these Ru(IV) complexes are not found to be stable. Complexes of Ru(IV) like (bpy)py Ru^{IV}O⁺² and (trpy)(bpy)Ru^{IV}O⁺² (Moyer 1981) are known. However, it has not been possible to isolate the Ru^{IV}-oxo complex prepared from RuCl₂(PPh₃)₃. Hence, it has to be formed only *in situ* and used in catalytic amounts with N-oxide. The instability might be due to the PPh₃ ligands which are known to stabilize lower oxidation states.

When the mixture of RuCl₂(PPh₃)₃ and N-oxide is allowed to react for a long time a new absorption band appears at 500 nm (figure 2e). Figure 2e is similar to that of the spectrum of authentic sample of triphenylphosphine oxide complex of Ru(II) (figure 2d). The formation of the triphenylphosphine oxide complex of Ru(II) can be explained only if Ru^{IV} is present as the oxo species. This type of oxygen transfer from Ru^{IV} oxo species to PPh₃ is reported in the case of (bpy)py RuO⁺² (Moyer 1981). The authentic sample of triphenylphosphine oxide complex, prepared *in situ* by passing oxygen through RuCl₂(PPh₃)₃ (Cenini *et al* 1971, 1972), does not oxidize the secondary alcohols. Most of the triphenylphosphine oxide complexes of transition metals are prepared in alcohols like ethanol and 2-propanol as solvents (Cotton *et al* 1960). These solvents are not oxidized by triphenylphosphine oxide complex. Thus the active intermediate is not the triphenylphosphine oxide complex of Ru(II) but an oxo complex of Ru(IV).

Considering the kinetic, spectral and electrochemical results the following mechanism involving the Ru(IV)-oxo species could be given. Within the experimental period of one to two hours the active intermediate is the Ru(IV) oxo species. The formation of a triphenylphosphine oxide complex of Ru(II) after a long reaction time could be explained if the oxygen from the oxo species is transferred to PPh₃. There is inhibition by added triphenylphosphine, provided [PPh₃] is high and so dissociation of PPh₃ from RuCl₂(PPh₃)₃ is given in the first step. In the absence of any inhibition by added N-methylmorpholine (NM) a prior equilibrium step involving this as the product is excluded.

Mechanism:



Ruthenium compounds are known to form adducts with organic compounds (Rajeshwar Rao *et al* 1979). There is no shift in the NMR signal of the -OH proton of the alcohol when RuCl₂(PPh₃)₃ alone is present. But if NMO is present along with RuCl₂(PPh₃)₃ there is a shift in the NMR signal of the -OH proton of the alcohol towards a lower τ value which indicates an adduct formation between Ru(IV) and alcohol. The UV-VIS spectrum of the mixture of RuCl₂(PPh₃)₃ and alcohol is the same as that of RuCl₂(PPh₃)₃ itself, which rules out the possibility of a complex formation between alcohol and RuCl₂(PPh₃)₃. Ruthenium compounds are known to be good hydride ion abstracting agents (Sasson and Rempel 1974). In the present study the kinetic isotopic effect is negligible ($k_{\text{H}}/k_{\text{D}} = 1.1$). This indicates that the cleavage of the C-H bond is not involved in the rate-determining step. The mechanism given above leads to the rate expression (1).

$$\text{Rate} = \frac{k_1 k_2 [\text{RuCl}_2(\text{PPh}_3)_3] [\text{NMO}] [S]}{k_{-1} [\text{PPh}_3] + k_2 [S]}, \quad S = \text{substrate.} \quad (1)$$

Equation (1) can be rearranged to give (2) and (3).

$$\text{Rate} = \frac{k_1 [S] [\text{RuCl}_2(\text{PPh}_3)_3] [\text{NMO}]}{(k_{-1}/k_2) [\text{PPh}_3] + [S]}, \quad (2)$$

$$\frac{1}{\text{rate}} = \frac{k_{-1} [\text{PPh}_3]}{k_1 k_2 [S] [\text{RuCl}_2(\text{PPh}_3)_3] [\text{NMO}]} + \frac{1}{k_1 [\text{RuCl}_2(\text{PPh}_3)_3] [\text{NMO}]} \quad (3)$$

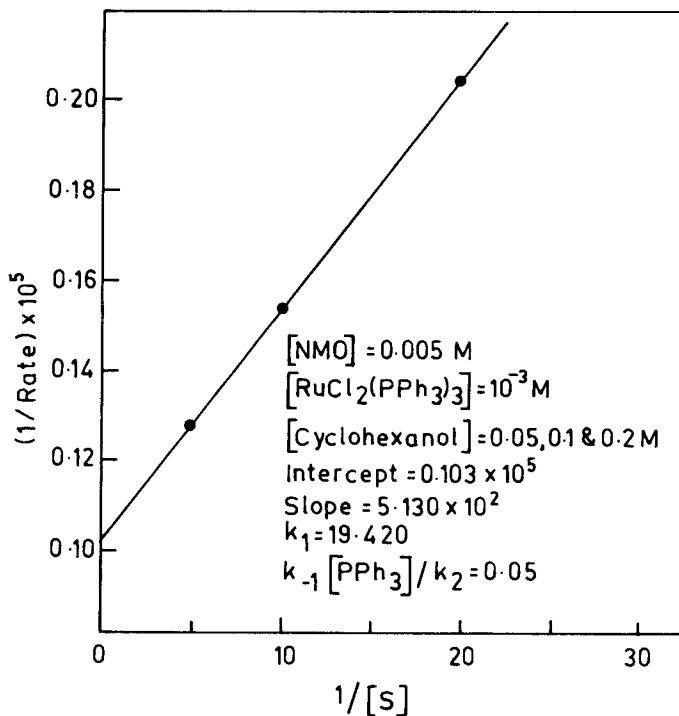


Figure 4. Evaluation of k_1 and $k_{-1}[\text{PPh}_3]/k_2$ from $1/\text{rate}$ vs. $1/[S]$ plot.

From the double reciprocal plot (3) (figure 4) k_1 and $(k_{-1}/k_2)[\text{PPh}_3]$ have been evaluated for a representative substrate like cyclohexanol, $k_1 = 19.42 \text{ M}^{-1} \text{ min}^{-1}$, $(k_{-1}/k_2)[\text{PPh}_3] \approx 0.05$. The concentration of the catalyst being kept constant, $[\text{PPh}_3]$ available from the dissociation step can be considered constant. Under experimental conditions, *i.e.* at low concentrations of the substrate (0.05 to 0.2 M) $(k_{-1}/k_2)[\text{PPh}_3]$ cannot be neglected compared to $[S]$. This explains the observed fractional order in substrate at low concentrations. At high concentrations of the substrate ($[S] > 0.5 \text{ M}$) $(k_{-1}/k_2)[\text{PPh}_3]$ can be neglected when compared to $[S]$. This explains the zero order in substrate in this concentration range. A good agreement between the values of k_1 got from figure 4 and from the pseudo first-order rate constants in the case of cyclohexanol (table 1) supports the mechanism given above.

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