

RUTHENIUM(III)-CATALYSED OXIDATION OF SECONDARY ALCOHOLS BY *N*-METHYLMORPHOLINE *N*-OXIDE (NMO)

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Summary

A catalytic amount of RuCl_3 in the presence of excess of *N*-methylmorpholine *N*-oxide (NMO) in DMF oxidizes secondary alcohols to ketones. Spectral studies reveal the formation of a Ru(V)-oxo species which is formed *in situ* on adding *N*-oxide. The formation of Ru(V) has been established by cyclic voltammetric studies. The mechanism involves the formation of Ru(V)-oxo species in steady state concentrations from Ru(III) and NMO, and this in turn reacts with the substrate in the rate-determining step.

Introduction

Ruthenium(III)-catalysed oxidations of alcohols have been reported using *t*-butyl hydroperoxide [1] and iodosylbenzene [2]. Yield-oriented studies have been carried out using several *N*-oxides to oxidize geraniol, cholestanol, etc. in the presence of ruthenium(III) [3]. In all these cases, *N*-oxides act as two-electron oxidants. In the case of metalloporphyrins, metals such as manganese undergo a change in the oxidation state in addition to complexing with the *N*-oxide [4]. *N*-methylmorpholine *N*-oxide has been used as a secondary oxidant in conjunction with OsO_4 for the oxidation of steroids [5] and for the *cis* hydroxylations of olefins [6, 7]. The oxidation of allylic alcohols [8, 9] by the ruthenium(III)-molecular oxygen system is quite slow, and requires high pressure and temperature. There are no significant reports on the kinetics and mechanism of oxidation of secondary alcohols using a ruthenium(III) *N*-oxide system. The oxidation of cyclohexanol, 1-phenylethanol and 2-propanol by *N*-methylmorpholine *N*-oxide in DMF solvent in the presence of ruthenium(III) is reported in this paper. A mechanism is proposed based on spectral, electrochemical and kinetic investigations.

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Experimental

Materials

N-methylmorpholine *N*-oxide monohydrate (Fluka) was used as received. All the secondary alcohols (Merck) were purified according to standard procedures. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey) was used as received DMF was purified according to the method of Faulkner [10].

Procedure and methods

Measurements of electronic spectra were carried out using a Shimadzu Spectrophotometer. EPR spectra were recorded at liquid nitrogen temperature using a Varian spectrometer. Cyclic voltammetric studies were carried out with a Princeton Applied Research Model 173, 175 and 179 electrochemistry system equipped with an X-Y recorder. Voltammograms were obtained with sweep rates of 100 - 400 mV s^{-1} . Product analysis was carried out with GLC. The RuCl_3 used was the β -form, as confirmed by X-ray diffraction studies. Ru(III) was standardized by the method of Horuchi [11]. Dilute solutions of ruthenium(III) were estimated by the thiourea method [12], the thiourea complex of ruthenium absorbing at 610 nm. All the kinetic studies were carried out at 35 ± 0.1 °C. The concentration of NMO remaining at any instant was determined titanometrically as reported earlier [13]. However, for concentrations of NMO less than 0.05 M the titanometric method was not satisfactory, the ketone formed from the alcohol was therefore converted to the corresponding 2,4-dinitrophenylhydrazone and its concentration determined spectrophotometrically by the method of Lappin [14]. The amount of ketone formed as determined spectrophotometrically corresponded to the amount of NMO consumed. At all concentrations a stoichiometry of 1:1 between the substrate and *N*-oxide in the presence of catalytic amounts of RuCl_3 was established.

Results and discussion

Cyclohexanol, 1-phenylethanol and 2-propanol are oxidized by NMO in the presence of RuCl_3 as catalyst to the corresponding ketones. There is no uncatalysed reaction. When the concentration of the substrate is kept at a constant large value, a plot of $\log[\text{NMO}]$ versus time is linear for all the three alcohols, thereby showing that the order in NMO is unity. Pseudo-first-order plots to show the effect of varying the concentration of NMO for a representative alcohol, *viz* cyclohexanol, are given in Fig. 1. From the pseudo-first-order rate constants (k') the orders with respect to the catalyst and the substrate (high concentrations, $[\text{substrate}] > 0.5$ M) are determined to be one (Fig. 2) and zero respectively (Table 1). The order with respect to the substrate is fractional at low concentrations (0.05 - 0.2 M, Fig. 3).

The observed orders could be accounted for by the Schemes 1 - 3. The three Schemes and the corresponding rate expressions are given below:

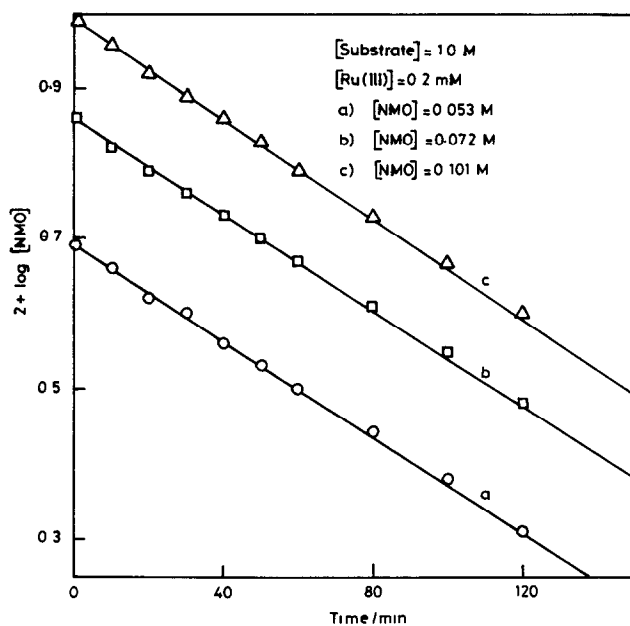


Fig 1 Pseudo-first-order plots to show the effect of varying the concentration of NMO for RuCl_3 -catalysed oxidation of a representative substrate, *viz* cyclohexanol

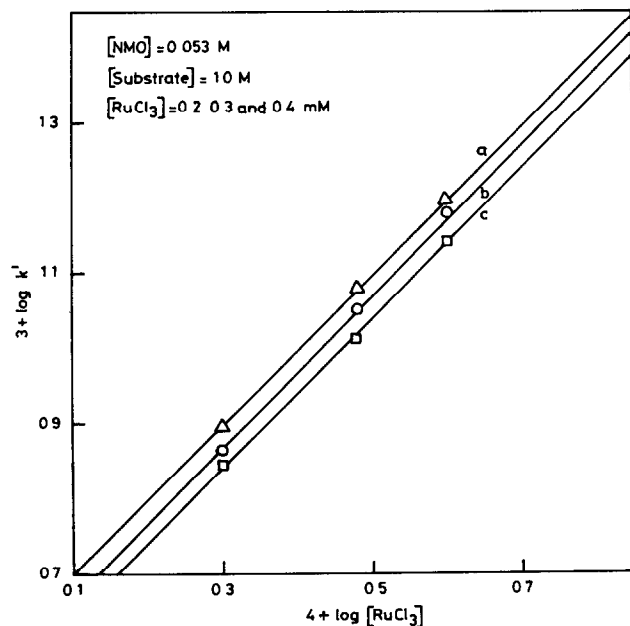


Fig 2 Determination of order with respect to the catalyst, RuCl_3 for (a) 1-phenylethanol, (b) cyclohexanol and (c) 2-propanol

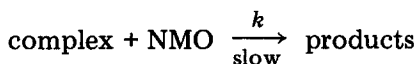
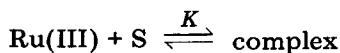
TABLE 1

Determination of the orders with respect to the reactants at high concentrations of the substrate, temperature $35 \pm 0.1^\circ\text{C}$, solvent DMF

Substrate	[NMO] (M)	[S] (M)	10^4 [RuCl ₃] (M)	$10^3 k'$ (min ⁻¹)	$\frac{k'{}^a}{[\text{RuCl}_3]} = k_1{}^b$ (M ⁻¹ min ⁻¹)
cyclohexanol	0.101	1.00	2.0	7.45	37.24
	0.072	1.00	2.0	7.00	35.01
	0.053	1.00	2.0	7.29	36.45
	0.053	0.70	2.0	7.22	36.08
	0.053	0.50	2.0	7.12	35.60
	0.053	1.00	3.0	11.19	37.29
	0.053	1.00	4.0	14.96	37.40
k_1 (mean) = $36.44 \pm 0.86 \text{ M}^{-1} \text{ min}^{-1}$					
2-propanol	0.101	1.00	2.0	6.23	31.13
	0.072	1.00	2.0	7.08	35.39
	0.053	1.00	2.0	6.98	34.92
	0.053	0.70	2.0	6.78	33.92
	0.053	0.50	2.0	6.63	33.16
	0.053	1.00	3.0	10.30	34.35
	0.053	1.00	4.0	13.86	34.66
k_1 (mean) = $33.93 \pm 1.32 \text{ M}^{-1} \text{ min}^{-1}$					
1-phenylethanol	0.101	1.00	2.0	7.76	38.32
	0.072	1.00	2.0	7.89	39.45
	0.053	1.00	2.0	7.87	39.34
	0.053	0.70	2.0	7.68	39.38
	0.053	0.50	2.0	7.70	38.52
	0.053	1.00	3.0	11.92	39.73
	0.053	1.00	4.0	15.64	39.09
k_1 (mean) = $38.97 \pm 0.53 \text{ M}^{-1} \text{ min}^{-1}$					

^a k' = Pseudo-first-order rate constant ($[\text{S}] \gg [\text{NMO}]$) (For k' the correlation factor varies from 0.990 to 0.999)

^b k_1 = Overall second-order rate constant



Scheme 1

Considering the complex to be in equilibrium with the reactants and expressing $[\text{Ru(III)}]_{\text{free}}$ in terms of $[\text{Ru(III)}]_{\text{total}}$, the rate expression (1) is obtained.

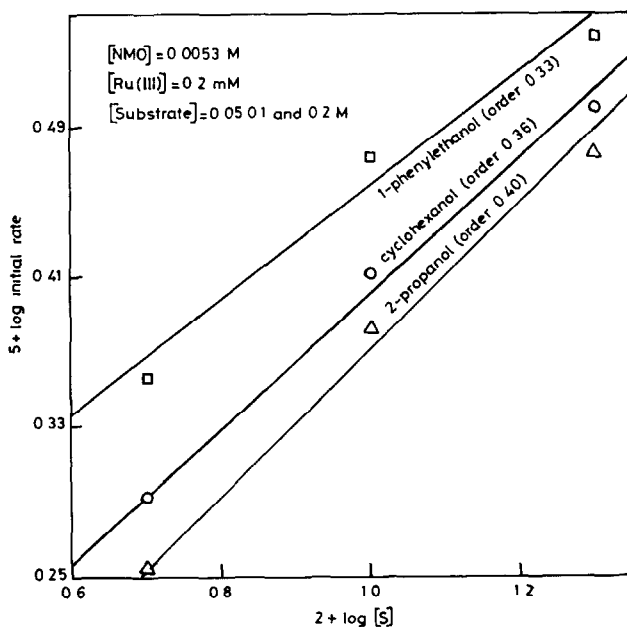
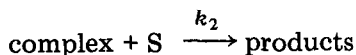
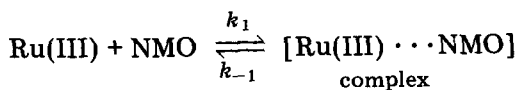


Fig 3 Determination of order with respect to the substrates at low concentrations

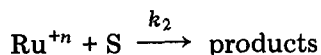
$$\text{rate} = \frac{kK[S][\text{NMO}][\text{Ru(III)}]_{\text{T}}}{1 + K[S]} \quad (1)$$



Scheme 2

Using the steady-state approximation to express the concentration of the complex, the rate expression (2) is obtained

$$\text{rate} = \frac{k_1 k_2 [\text{Ru(III)}][\text{NMO}][\text{S}]}{k_{-1} + k_2 [\text{S}]} \quad (2)$$



Scheme 3

If the steady-state approximation is used to express the concentration of Ru^{+n} ($n > 3$), the rate expression (2) is obtained.

The assumption of a fast prior equilibrium step in mechanisms 2 and 3 leads to the rate expression (3).

$$\text{rate} = \frac{k_2 K [\text{S}] [\text{NMO}] [\text{Ru(III)}]_T}{1 + k [\text{NMO}]} \quad (3)$$

Rate expression (3) does not account for the fractional order in the substrate. Also, one would expect the order with respect to NMO to be a variable, being zero at high concentrations and one at low concentrations. In the range of concentrations studied, the order with respect to NMO is always unity. There is no spectral change when alcohol alone is added to Ru(III). From the titanometric method of estimation of NMO [13] before and after adding RuCl_3 , it is found that RuCl_3 undergoes a change of oxidation state. These results rule out Schemes 1 and 2.

Electronic spectral studies have been carried out in order to discover the nature of the intermediate formed during the course of the reaction between Ru(III) and NMO. RuCl_3 in DMF has an absorption maximum at 405 nm (Fig. 4a, $\epsilon = 7041 \text{ M}^{-1} \text{ cm}^{-1}$), with a shoulder appearing at 450 nm ($\epsilon = 6122 \text{ M}^{-1} \text{ cm}^{-1}$). Absorption at 405 nm can be attributed to LMCT bands (Ligand-Metal Charge Transfer) since the ϵ value is high. The d-d

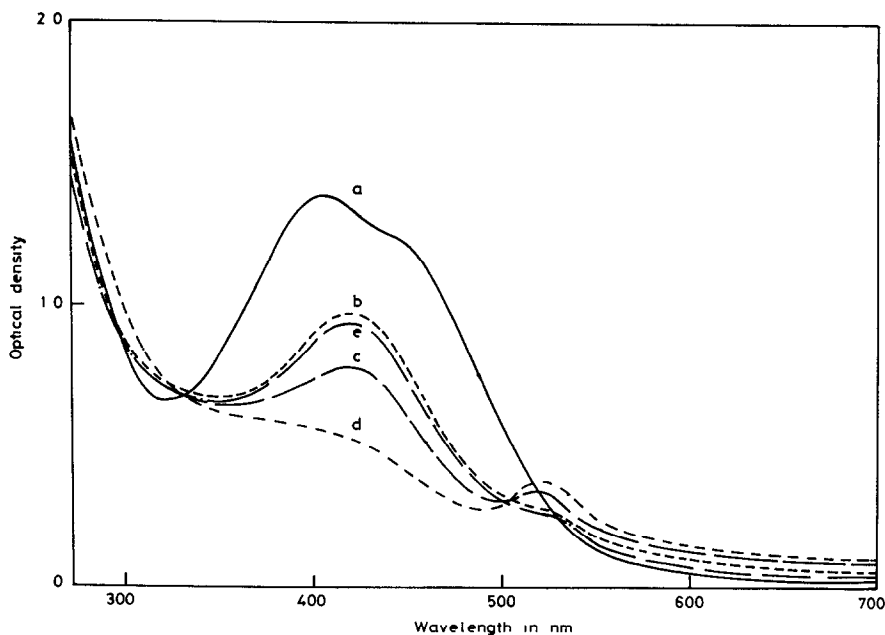


Fig. 4 Absorption spectra of (a) RuCl_3 ($1.96 \times 10^{-4} \text{ M}$) in DMF, (b) RuCl_3 ($1.96 \times 10^{-4} \text{ M}$) and NMO ($2.0 \times 10^{-4} \text{ M}$) in DMF, (c) RuCl_3 ($1.96 \times 10^{-4} \text{ M}$) and NMO ($5.0 \times 10^{-4} \text{ M}$) in DMF, (d) RuCl_3 ($1.96 \times 10^{-4}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

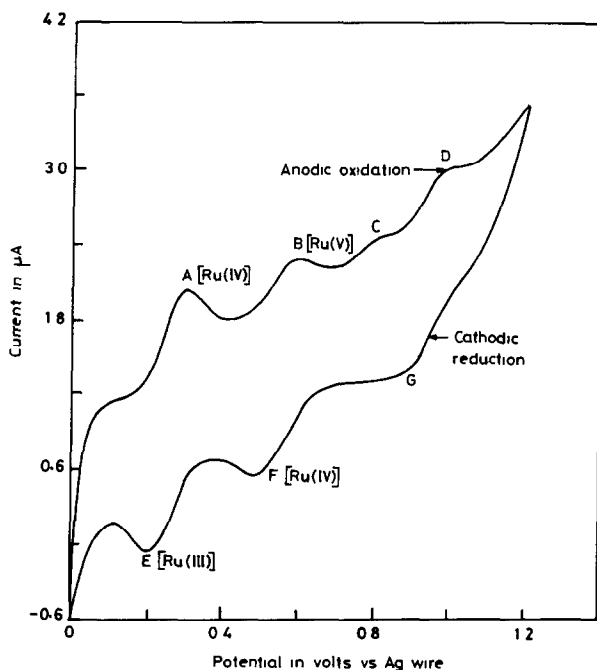


Fig 5 Voltammogram observed during the anodic oxidation of RuCl_3 and cathodic reduction of the higher oxidation states of ruthenium

transitions are obscured by the LMCT bands [15]. On keeping the concentration of RuCl_3 constant, if the concentration of NMO is increased, a new absorption at 520 - 600 nm appears (Fig. 4b, c and d). That this is due to Ru(V) is established from cyclic voltammetric studies.

Cyclic voltammetric studies have been carried out with Pt wire, Pt foil and Ag wire as the working, counter and reference electrodes, respectively, and tetra(n-butyl) ammonium perchlorate as the supporting electrolyte. The voltammogram (Fig. 5) shows four peaks A, B, C and D during anodic oxidation, and three peaks E, F and G during the reduction cycle. The peak-to-peak potential separation between A and E is 90 mV. Peak A and its reduction cycle counterpart E can be assigned to Ru(IV)/Ru(III) interconversion. The peak-to-peak potential separation between B and F is 60 mV. Peak B and its reduction cycle counterpart F can be assigned to Ru(V)/Ru(IV) interconversion. A difference in potential of 60 mV and 90 mV corresponds to that of a one-electron oxidation for a reversible and a pseudo-reversible process, respectively [16]. Peaks C and D are due to other oxidation states higher than Ru(V) . The voltammogram is not scanned beyond 1.2 V, as the supporting electrolyte begins to oxidize above 1.2 volts. The potential corresponding to Ru(V) is 640 mV *versus* silver wire. Controlled-potential electrochemical oxidation of Ru(III) was carried out by applying a potential of 700 mV, so as to stop the electrochemical oxidation of Ru(III) at Ru(V) . The electronic spectrum taken (Fig. 4e) for the Ru(V) formed electro-

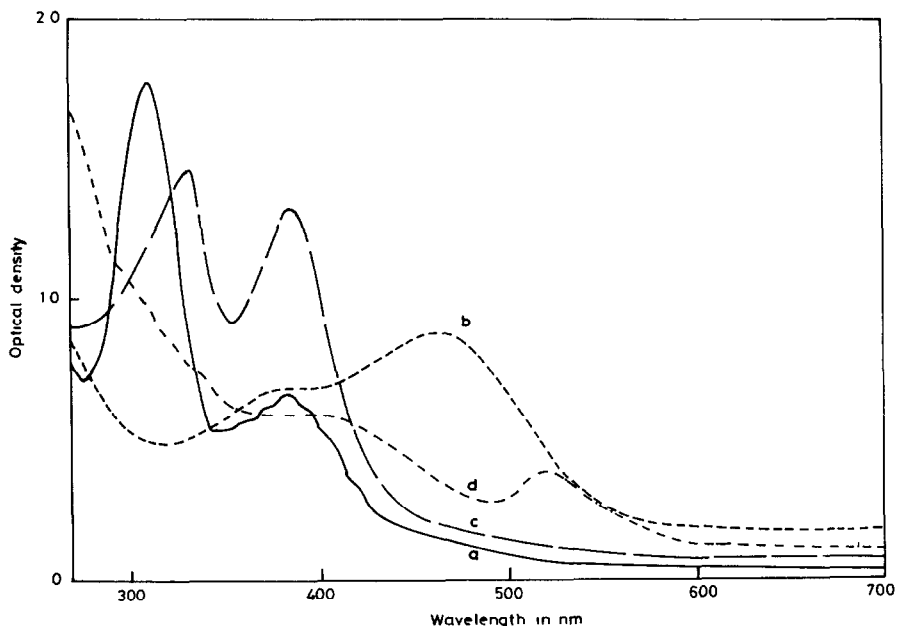


Fig 6 Absorption spectra of (a) Ru(VIII) in CCl_4 , (b) Ru(VI) in NaOH, (c) Ru(VII) in NaOH, (d) Ru(VIII) in CCl_4 + excess of DMF

chemically is similar to the spectrum obtained for the mixture of Ru(III) and NMO (Fig. 4b, c and d). Thus the cyclic voltammetric studies, combined with UV-Visible spectral studies, reveal the formation of Ru(V) as the active intermediate. Similar UV-Visible spectral patterns obtained for the non-oxo Ru(V) species formed electrochemically in DMF and oxo Ru(V) species obtained from RuCl_3 -NMO system in DMF might indicate a weak Ru-O bond. This is also evidenced from the IR spectrum, which shows a weak absorption at 805 cm^{-1} that would account for a loose oxo complex of ruthenium [17]

The stoichiometry of 1.1 observed between RuCl_3 and NMO (a two-electron oxidant) also supports the formation of Ru(V). The formation of other higher oxidation states of ruthenium, namely Ru(IV), Ru(VI), Ru(VII) and Ru(VIII), is not likely due to the reasons mentioned below. Ru(VI), Ru(VII) and Ru(VIII) were prepared as reported in the literature [18] and their electronic spectra are given in Fig 6. Ru(VI) and Ru(VII) (Fig. 6b and c) are stable only under alkaline conditions [19]. The intermediate cannot be $\text{RuO}_2[\text{Ru(IV)}]$, as the spectral pattern reported [20] is entirely different from Fig. 4b, c and d. Moreover, the reaction mixture of Ru(III) and NMO does not leave any final black residue of RuO_2 (RuO_2 is insoluble in DMF). The intermediate cannot be Ru(VIII) (RuO_4) either, as this is stable only in CCl_4 . The electronic spectrum of Ru(VIII) in CCl_4 (Fig 6a) is entirely different when an excess of DMF is added (Fig. 6e).

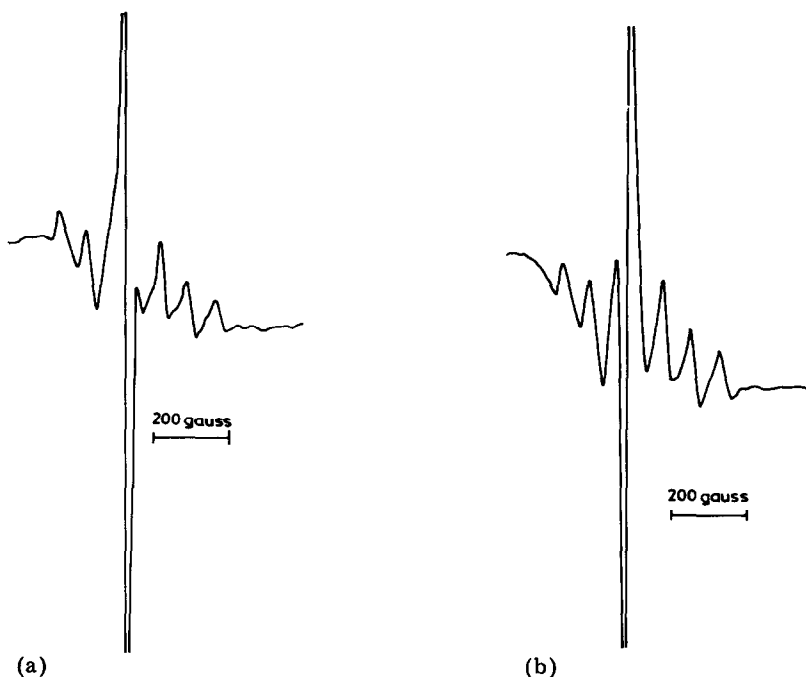


Fig 7 (a) EPR spectrum of RuCl_3 in DMF frozen at 77 K (b) EPR spectrum for the mixture of RuCl_3 and *N*-oxide in DMF frozen at 77 K

EPR studies have also been carried out in order to confirm the formation of Ru(V) . The EPR spectrum of RuCl_3 in DMF (Fig 7a) consists of six signals at 77 K. (At room temperature, ruthenium compounds do not give EPR signals.) The most intense signal appearing with DPPH will account for $I = 0$ (due to a 70% abundance of even isotopes of ruthenium), and the other signals will account for $I = 5/2$ (due to a 30% abundance of odd isotopes of ruthenium). A mixture of RuCl_3 and NMO in DMF after a long reaction time also gives an EPR spectrum (Fig. 7b) similar to that of RuCl_3 in DMF. Though the number of signals expected for Ru(V) is greater, all the expected signals are not seen. The following reasons could be given for obtaining similar EPR spectral patterns for both RuCl_3 and Ru(V) (obtained from RuCl_3 and NMO):

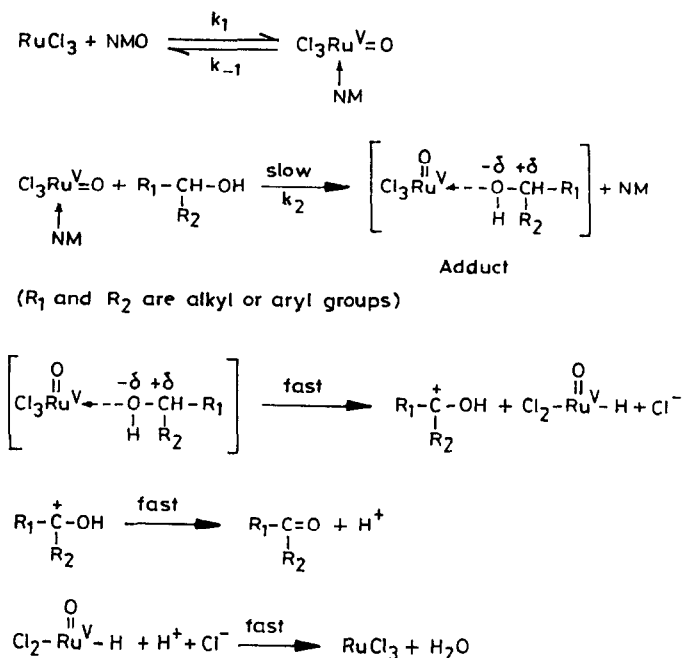
(i) EPR spectra were taken at low temperature, *i.e.* 77 K, where there is a chance for electrons to pair up due to the splitting of t_{2g} levels, in which case a d^3 system, *i.e.* Ru(V) , can have a doublet paramagnetic ground state $(d_{xy})^2(d\pi)^1$ ($d\pi = d_{xz}$ or d_{yz}) which will also account for only one unpaired electron. This type of doublet paramagnetic ground state representation has been given in the case of Ru(V) dioxo complexes [21].

(ii) Zero-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 lines corresponding to those of unreacted Ru(III), which is always present in the reaction mixture and hence the presence of Ru(V) is unidentifiable by EPR

(iii) Lines corresponding to Ru(V) might be too broad to be seen unambiguously. Due to the reasons mentioned above, EPR studies do not give conclusive evidence for Ru(V) formation

The intermediate Ru(V) oxo complex cannot be isolated, and can be prepared only *in situ* by oxidizing catalytic amounts of RuCl₃ using NMO. Recently a novel Ru(V) dioxo species, [Ru(V)(tmc)(O₂)]ClO₄ (tmc = tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been synthesized and characterized [21], which supports the existence of Ru(V) monomer complex and Ru(V) mono oxo species like [Ru(V)(tmc)(O)Cl]⁺₂, generated electrochemically *in situ*, is reported to catalyse oxidation of alcohols [22]. On the basis of the kinetic, spectral and electrochemical investigations, the following mechanism (Scheme 4) could be proposed:



Scheme 4

In the absence of any inhibition by added *N*-methylmorpholine (NM), a prior equilibrium step involving this as the product is excluded. Ruthenium compounds are known to form adducts with organic compounds [23]. There is a shift in the NMR signal ($\Delta\tau = 0.4$ units) of the hydroxylic proton of the alcohol towards a lower τ value in the presence of a mixture of Ru(III) and

NMO, which indicates an adduct formation between Ru(V) and alcohol. The shift in the NMR signal of the hydroxylic proton observed on adding a paramagnetic metal compound to an alcohol indicates a loose complexation between alcohol and metal compound [24]. There is no shift in the NMR signal when Ru(III) and alcohol are present in the absence of NMO, which rules out the possibility of adduct formation between Ru(III) and alcohol. Mere addition of NMO also does not affect the position of the hydroxylic proton. Ruthenium compounds are known to be good hydride ion abstracting agents [25]. In order to find out whether hydride ion abstraction is the rate-determining step, primary kinetic isotopic studies have been carried out using 2-propanol- d_8 and 2-propanol. As the value of k_H/k_D is rather small (1.2), the hydride ion abstraction step is not likely to be rate-determining. The above mechanism leads to the rate expression (2):

$$\text{rate} = \frac{k_1 k_2 [S][\text{NMO}][\text{Ru(III)}]}{k_{-1} + k_2 [S]} \quad (2)$$

Equation (2) can be rearranged to give eqn (4)

$$\frac{1}{\text{rate}} = \frac{k_{-1}}{k_1 k_2 [\text{Ru(III)}][S][\text{NMO}]} + \frac{1}{k_1 [\text{Ru(III)}][\text{NMO}]} \quad (4)$$

Equation (4) can be verified using the data obtained for low concentrations of the substrate (0.05 - 0.2 M). The values of k_1 , the second order rate constant and k_{-1}/k_2 evaluated from the plots of $1/\text{rate}$ versus $1/[S]$ at constant Ru(III) and [NMO] (Fig. 8) for all the three alcohols are given in Table 2. At high concentrations of the substrate (>0.5 M), k_{-1} is negligible compared to $k_2[S]$. This explains the zero order in substrate at high concentrations. There is a good agreement between the values of k_1 in Tables 1 and 2, which supports the given mechanism 4. k_{-1} is not negligible compared to $k_2[S]$ for low concentrations of the substrate (0.05 - 0.2 M) and so the order in substrate is fractional. Thus mechanism 4 explains all the experimental observations. Experimental investigations could not be carried out for concentrations of substrate below 0.05 M, owing to the inaccuracies involved in the isolation and estimation of the ketone formed in these cases. Attempts were not made to calculate k_1/k_{-1} from the spectral studies, since ruthenium(III) has considerable absorption in the region where the Ru(III)-NMO system absorbs (Fig. 4).

The order of reactivity among the secondary alcohols has been compared by carrying out reactions at low substrate concentrations where a fractional order is observed. Among the non-cyclic alcohols, the order of reactivity is given as benzhydrol $>$ 1-phenylethanol $>$ 2-propanol (Table 3), in accordance with polar effect [26]. Among the cyclic alcohols the order of reactivity (Table 3) is cycloheptanol $>$ cyclopentanol $>$ cyclohexanol. Such a reactivity pattern can be explained on the basis of bond hybridization changes [27]. Though the variation in rates among the alcohols is small, the relative rates mentioned in Table 4 cannot be considered as constants, which indicates that the substrate is taking part in the rate-determining step.

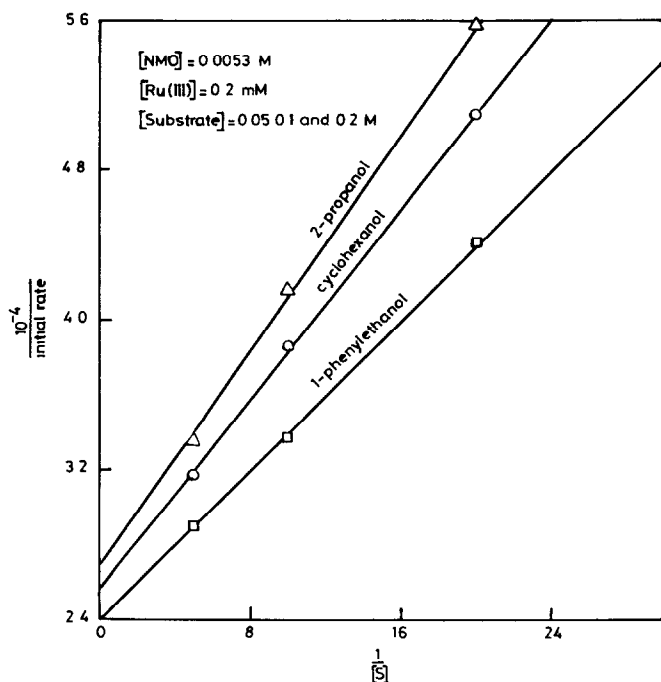


Fig 8 Evaluation of k_1 and k_{-1}/k_2 from the double reciprocal plots for $RuCl_3$ -catalysed oxidation of secondary alcohols by NMO

TABLE 2

Evaluation of k_1 and k_{-1}/k_2 from the double reciprocal plots (Fig 8)

Substrate	k_1 ($M^{-1} \text{ min}^{-1}$)	$\frac{k_{-1}}{k_2}$ (M)
cyclohexanol	35.72	0.044
1-phenylethanol	38.80	0.041
2-propanol	34.50	0.050

Conditions $[NMO] = 0.005 M$, $[RuCl_3] = 2 \times 10^{-4} M$, $[S] = 0.05, 0.1 \text{ and } 0.2 M$, temperature $35 \pm 0.1^\circ C$, solvent DMF

From the structure proposed for the adduct in the Scheme 4, one would expect that the partial positive charge on the secondary carbon atom will be delocalized by electron-donating groups in the *para*-position of the benzene ring in 1-phenylethanol. Hence various substituted 1-phenylethanols were employed in order to determine the nature of the transition state. The slope (ρ) of the Hammett plot (Fig. 9, Table 4) is -0.3 . Though definite information cannot be drawn from the very small value of ρ , it does indicate that the substrate is involved in the rate-determining step.

TABLE 3

Initial rates for various secondary alcohols at low concentrations of the substrate

Substrate	10^5 initial rate ($M \text{ min}^{-1}$)	Relative rates
2-propanol	1.70	1.00
1-phenylethanol	2.13	1.15
benzhydrol	2.64	1.55
cycloheptanol	2.47	1.40
cyclopentanol	2.29	1.29
cyclohexanol	1.87	1.00

Conditions $[\text{NMO}] = 0.005 \text{ M}$, $[\text{Ru}^{+3}] = 2 \times 10^{-4} \text{ M}$, $[\text{S}] = 0.05 \text{ M}$, temperature $35 \pm 0.1 \text{ }^\circ\text{C}$, solvent DMF

TABLE 4

Pseudo-first-order rate constants for the oxidation of a few *p*-substituted 1-phenylethanols and their corresponding substituent constants

Substituted 1-phenylethanol	$3 + \log k'$	σ
1-(4-nitrophenyl)ethanol	0.51	0.78
1-(4-chlorophenyl)ethanol	0.66	0.28
1-phenylethanol	0.74	0
1-(4-methylphenyl)ethanol	0.80	-0.17
1-(4-methoxyphenyl)ethanol	0.82	-0.27

Conditions $[\text{NMO}] = 0.005 \text{ M}$, $[\text{RuCl}_3] = 2 \times 10^{-4} \text{ M}$, $[\text{S}] = 0.1 \text{ M}$, temperature $35 \pm 0.1 \text{ }^\circ\text{C}$, solvent DMF

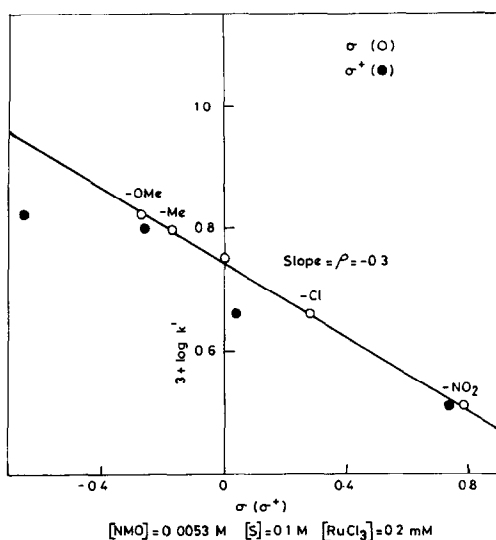


Fig 9 Plot of $\log k'$ for RuCl_3 -catalyzed oxidation of *p*-substituted 1-phenylethanols by NMO in DMF against Hammett σ values of the substituents

The function of the system $\text{RuCl}_3\text{-NMO}$ is similar to oxidations catalysed by cytochrome P-450. In the case of cytochrome P-450-oxidant system, the metal porphyrins form active metal-oxo species in an unusual oxidation state which reacts with the substrate and in so doing the metalloporphyrin is regenerated. In the case of the $\text{RuCl}_3\text{-NMO}$ system, a Ru(V) oxo species is the active intermediate which oxidizes alcohols and finally Ru(III) is regenerated. In the case of the $\text{Fe(TPP)Cl-iodosobenzene}$ system, the formation of a Fe(V) oxo species has been suggested [28], whereas in the case of the $\text{Fe(TPP)Cl-}m\text{-chloroperbenzoic acid}$ [29, 30], $\text{Fe(TPP)Cl } N\text{-oxide}$ [31] and $\text{Ru(III)porphyrin-iodosobenzene}$ systems [32], the oxo metal(IV)porphyrin cation radical has been shown to be the active intermediate. In the case of $\text{Mn(TPP)Cl-catalysed}$ oxidations, the Mn(V) oxo complex [4] and Mn(IV) oxy radicals [33] have been shown as active intermediates with $N\text{-oxide}$ and iodobenzene, respectively. In the case of the $\text{Cr(TPP)Cl-iodosobenzene}$ system, the Cr(V) species has been isolated and characterized [34]. Since the Ru(III)-NMO system is a non-porphyrin system, the formation of a Ru(IV) oxo species is not possible. Ru(IV) oxy radical formation is also not possible since there is no evidence for free radical intermediates in the Ru(III)-NMO system.

The chlorides of other Group VIII metals such as Rh and Ir are not effective in catalysing the oxidation of organic substrates, probably because the higher oxidation states are not formed easily with NMO. Ir(III) , Rh(III) and metal chlorides of the iron triad are very inert towards oxidation with NMO, except in porphyrins of iron and manganese. In the case of the latter, the oxidative addition becomes facile since the porphyrin ring system increases the nucleophilicity of the metal. The ability to undergo oxidative addition [35] and the stability of the higher oxidation states of the metal [36] decrease across the period as $\text{Ru} > \text{Rh} > \text{Pd}$ and increase down the group $\text{Fe} < \text{Ru} < \text{Os}$.

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