

# Oxidation of Organic Substrates by *N*-Methylmorpholine *N*-Oxide catalysed by Ruthenium Complexes

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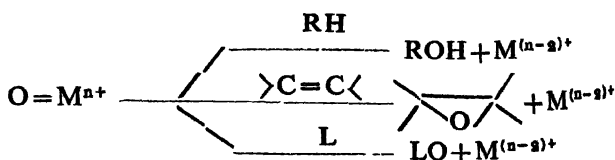
**C**ATALYSIS by metal complexes plays an important role in hydrogenation, hydroformylation, polymerisation and oxidation reactions. Hydrogenation reactions have been thoroughly investigated and mechanisms well established<sup>1</sup>. Mechanisms of oxidation reactions using hydroperoxide in the presence of complexes of Mo, V, W and Ti and peracids are also well documented<sup>2,3</sup>. Cytochrome P-450 is a class of enzymes that catalyse the monooxygenation of a variety of organic substrates by dioxygen and the reduced form of nicotinamide adenine dinucleotide phosphate (NADPH) or single oxygen donors such as iodosoarenes<sup>4</sup>. The use of synthetic metalloporphyrins as models for the enzyme for aliphatic hydroxylation and alkene epoxidation is now firmly established. Primary oxidants like iodosobenzene<sup>5,6</sup>, alkyl hydroperoxides<sup>7,8</sup>, *p*-cyano-*N,N*-dimethylaniline *N*-oxide<sup>9,10</sup> and molecular oxygen<sup>11,12</sup> have been reported. From these model studies it has been reported that higher valent metal-oxo species is responsible for cytochrome P-450 catalysed epoxidation and hydroxylation reactions. Sharpless and coworkers carried out a yield-oriented study of the oxidation of cholestanol, geraniol etc. by *N*-methylmorpholine *N*-oxide (NMO) and *N,N*-dimethylaniline *N*-oxide in the presence of ruthenium complexes as catalysts<sup>13</sup>. The precise role played by NMO and the mode of action of the catalyst are however not known. Kinetic and spectral studies have been carried out in the case of oxidation of organic substrates by *N*-methylmorpholine *N*-oxide catalysed by ruthenium complexes to arrive at a suitable mechanism and also to characterise the active intermediates.

Electronic spectral studies indicated that Ru<sup>III</sup> and Ru<sup>II</sup> species undergo a change in the oxidation state in presence of NMO. Cyclic voltammetric, epr and ir studies conclusively prove the species to be Ru<sup>V</sup>=O in the case of Ru<sup>III</sup>, and Ru<sup>IV</sup>=O in the case of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>14</sup>.

The stoichiometric oxidation of organic substrates by oxometal (M=O) reagents such as permanganate<sup>15</sup>, chromic acid and chromyl compounds<sup>16</sup>, SeO<sub>2</sub><sup>17</sup>, OsO<sub>4</sub><sup>18</sup>, RuO<sub>4</sub><sup>19</sup> and MnO<sub>2</sub><sup>20</sup> is well-known. These reagents have traditionally played an important role in organic synthesis because of their capacity for selective oxygen transfer to a wide variety of substrates under mild conditions. Participation by one or more M=O groups is a key mechanistic feature common to all

these reactions<sup>16–20</sup>. A second group of oxidation reactions involving oxometal reagents is the heterogeneous gas-phase oxidation of hydrocarbons over metal oxide catalysts<sup>21</sup>. These reactions are performed at elevated temperatures (300–600°) and form the basis for a number of important petrochemical processes. The third group of oxidation reactions involving oxometal group is the biochemical oxidation (epoxidation of alkenes and hydroxylation of alkanes) brought about by cytochrome P-450 group of enzymes in living systems<sup>4</sup>.

Oxometal groups are capable of effecting the following types of oxidative transformations,

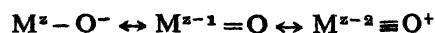


where, L is trialkylphosphines and dialkylsulphides.

Oxidation/reduction of a generalised molecule X/XO by formal gain or loss of an oxygen atom as in reaction (1) is widely used.



Here the oxygen donor is reduced and the oxygen acceptor is oxidised with the result that the atom transferred is maintained as oxide in reactant and product. The oxidation state of the metal is increased by two units for each oxygen atom added. These oxo ligands are stabilised at highly oxidised metal centres and the oxidation state should not be less than four. Oxometal groups are described by canonical forms

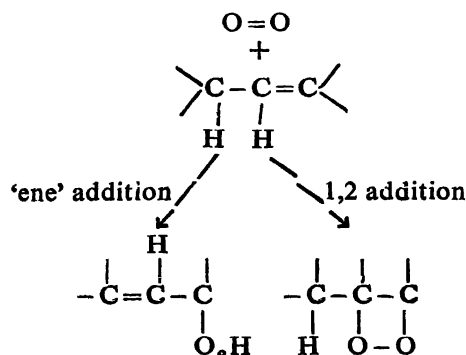


which shows that the metal must be a  $\pi$ -acceptor. Metal atoms with configuration  $d^0$ – $d^4$  have vacant or half filled  $\pi$ -acceptor orbitals necessary for this interaction<sup>22</sup>.

*Interaction of Ru<sup>V</sup>=O with alkenes, sulphides and triphenylphosphine :*

*Interaction of Ru<sup>V</sup>=O with alkenes :* The interaction of olefins with oxometal reagents as with other reagents can involve reaction either at the double bond or at the allylic C–H bond. This competition

is reflected in the reaction of olefins with the simplest oxo species, namely, singlet oxygen<sup>23</sup>.

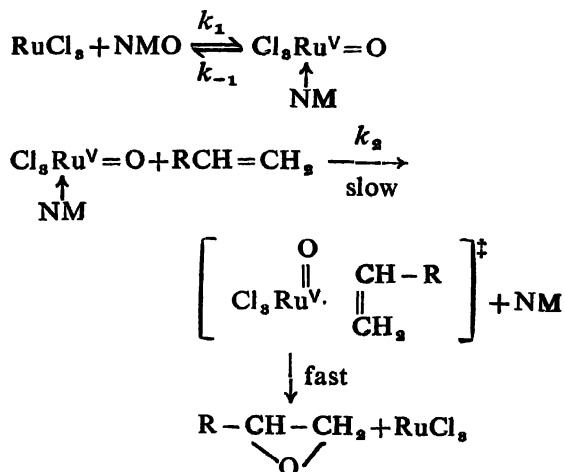


Reaction at the double bond results in an epoxide whereas allylic oxidation gives the unsaturated ketone with other oxidants (oxygen gives hydroperoxides). In both these reactions there is a net oxygen atom transfer. The substitutionally inert polypyridyl and related oxo complexes of Ru<sup>IV</sup>, e.g. [(bpy)<sub>3</sub>(py)Ru<sup>IV</sup>(O)]<sup>3+</sup> (bpy = bipyridine, py = pyridine), bring about the allylic oxidation of cyclohexene in acetonitrile at 25° to give cyclohexenone<sup>24</sup>. Aerobic oxidation of olefins with [Ru(tmp)(O)<sub>2</sub>]<sup>+</sup> (tmp = tetramesityl porphyrin) results in an epoxide at ambient temperature and pressure<sup>25</sup>; no cyclohexenone is detected. Ru<sup>V</sup>=O formed from RuCl<sub>3</sub> and NMO gives rise to cyclohexene oxide and not cyclohexenone<sup>26</sup>. Terminal and cyclic olefins give rise to the corresponding epoxides. Chloroolefins give rise to the corresponding epichlorohydrins.

Among cyclic olefins the order of reactivity is cycloheptene > cyclooctene > cyclohexene, which can be explained in terms of the strain in the molecule. Among terminal alkenes (1-hexene, 1-heptene and 1-octene) the change in rate as the chain length increases is not appreciable to warrant an explanation. The order of reactivity of three representative olefins, styrene (aromatic) > cyclohexene (alicyclic) > 1-octene (aliphatic), is in accordance with the fact that olefins are acting as nucleophiles and the active oxidant is electrophilic. Acetylenic compounds like phenylacetylene and 1-octyne are not oxidised as they are more resistant to electrophilic attack. The chloroolefins are oxidised slowly because of the presence of an electron-withdrawing chlorine atom in the vicinity of the double bond. Thus the epoxidation reaction is governed by both steric and polar factors. A(2+2) cycloaddition is envisaged across the Ru<sup>V</sup>=O bond for the oxygen atom transfer to give an epoxide.

Kinetic studies indicate that the reaction is first order each in NMO and catalyst. The order with respect to the substrate is variable being zero at high and one at low concentrations respectively. In case of styrene, the order remained fractional even at high concentrations of styrene. A stoichiometry of 1 : 1 is observed between the substrate and

NMO in presence of the catalyst. In absence of any information regarding the complex formation between an alkene and the catalyst, a mechanism is proposed in which Ru<sup>V</sup>=O species formed in steady state concentrations from RuCl<sub>3</sub> and NMO reacts with the substrate in the rate-determining step to give the product.



This mechanism leads to the rate-expression (equation 2),

$$\text{Initial rate} = V_1 = \frac{k_1 k_2 [\text{Ru}^{\text{III}}][\text{S}][\text{NMO}]}{(k_{-1} + k_2 [\text{S}])} \quad (2)$$

Equation (2) upon rearrangement gives equation (3),

$$\frac{1}{V_1} = \frac{k_{-1}}{k_1 k_2 [\text{Ru}^{\text{III}}][\text{S}][\text{NMO}]} + \frac{1}{k_1 [\text{Ru}^{\text{III}}][\text{NMO}]} \quad (3)$$

Equation (3) was verified using the kinetic data obtained with the substrate at low concentrations. The plot of 1/rate vs 1/[S] at constant [Ru<sup>III</sup>] and [NMO], at low concentrations of the substrate where a first order dependence was observed, are linear. There is good agreement between the values of  $k_1$  determined from this double-reciprocal plot and that obtained under zero order conditions in the substrate (Table 1). The variable order in the substrate is explained on the basis of the relative magnitude of  $k_{-1}/k_2$  and [S]. In the case of styrene  $k_1$  could not be calculated since even at high [styrene] the order is fractional<sup>27</sup>.

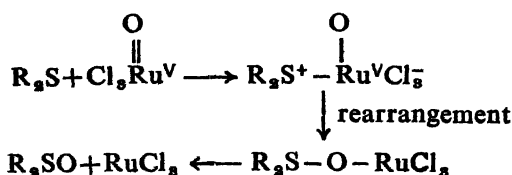
TABLE 1—EVALUATION OF  $k_1$  AND  $k_{-1}/k_2$  FROM DOUBLE-RECIPROCAL PLOT

Substrate	$k_1$ (dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> )		$k_{-1}/k_2$ M
	From pseudo-first order plot	From double-reciprocal plot	
Cyclohexene	11.43 ± 0.13	11.36	0.109
1-Octene	8.43 ± 0.048	8.30	0.058
Styrene	—	—	2.085

RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub> promotes the epoxidation of alkenes at a slower rate than RuCl<sub>3</sub>. This is because only higher valent metaloxo species

( $\text{Ru}^{\text{V}}=\text{O}$  compared to  $\text{Ru}^{\text{IV}}=\text{O}$ ) having a relatively polar  $\text{M}^+-\text{O}^-$  bond can effect (2+2) cycloaddition effectively<sup>28</sup>.

**Interaction of  $\text{Ru}^{\text{V}}=\text{O}$  with sulphides and triphenylphosphine:**  $\text{RuCl}_3/\text{NMO}$  system not only oxidises alkenes but also oxidises more nucleophilic substrates like sulphides and phosphines where there is a net oxygen atom transfer from NMO to the substrate. Amines are not oxidised since they get strongly coordinated to the catalyst. The resulting complex is inactive for catalysis. The order of reactivity is phosphines > sulphides > olefins, which is in accordance with the fact that the substrates are acting as nucleophiles and that the active oxidant is electrophilic. Among the various representative sulphides the order of reactivity is dibutyl sulphide  $\approx$  dibenzyl sulphide (alkyl sulphide) > phenyl methyl sulphide (aralkyl sulphide) > diphenyl sulphide (aryl sulphide). The reactivity pattern can be attributed to steric factors rather than to polar effects. In the oxidation of sulphides and triphenylphosphine, oxygen atom transfer proceeds presumably by prior attack of the nucleophilic substrate at the positive metal centre rather than on the oxygen atom, as the former is mechanistically more reasonable (in analogy with the nucleophilic addition to carbonyl compounds in organic chemistry)<sup>29</sup>. The mechanism of oxygen atom transfer can be represented schematically as



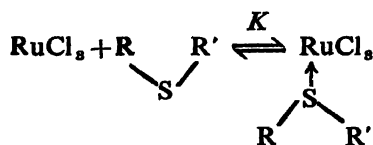
The reaction is found to be first order each in the catalyst and NMO. The order with respect to the substrate is variable being zero and fractional at high and low concentrations respectively. Electronic spectral measurements indicate complex formation between the catalyst and the substrate. A complex formed between an electron-donor and an electron-acceptor still retains the absorptions of the individual components ( $\text{RuCl}_3$ , as the sulphide does not absorb in the region 300–700 nm) modified to a greater or lesser extent, together with one or more absorptions characteristic of the complex as a whole. Using the Scott equation<sup>30</sup>, the equilibrium constant for complex formation is obtained by measuring the decrease in the absorbance at 420 nm. This equation is a modification of the Benesi–Hildebrand equation which requires an extrapolation to concentrated solutions while the Scott equation involves an extrapolation to dilute solutions.

**Scott equation:**

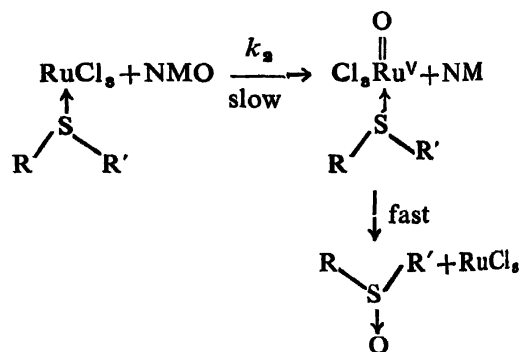
$$\frac{[\text{D}]_0[\text{A}]_0}{\Delta \text{O.D.}} = \frac{[\text{D}]_0}{\epsilon} + \frac{1}{K\epsilon}$$

where  $[\text{D}]_0$  and  $[\text{A}]_0$  are the initial concentration of donor and acceptor respectively,  $\epsilon$  is the extinction

coefficient and  $K$  the equilibrium constant. From the plot of  $[\text{D}]_0[\text{A}]_0/\Delta \text{O.D.}$  vs  $[\text{D}]_0$ , the equilibrium constant for complex formation was calculated by taking the slope/intercept ratio (Table 2). On the basis of kinetic and spectral studies the following mechanism is proposed,



(where, R and R' are alkyl, aryl or aralkyl group)



The above scheme leads to the rate expression (equation 4),

$$\text{Initial rate} = V_1 = \frac{Kk_2[\text{Ru}^{\text{III}}]_0[\text{S}][\text{NMO}]}{(1 + K[\text{S}])} \quad (4)$$

This upon rearrangement gives equation (5),

$$\frac{1}{V_1} = \frac{1}{Kk_2[\text{Ru}^{\text{III}}]_0[\text{S}][\text{NMO}]} + \frac{1}{k_2[\text{Ru}^{\text{III}}]_0[\text{NMO}]} \quad (5)$$

A plot of  $1/\text{initial rate}$  vs  $1/[\text{substrate}]$  is linear. From the intercept ( $1/k_2$ ) and slope ( $1/Kk_2$ ) of the double-reciprocal plot,  $k_2$  (overall second order rate constant) and  $K$  (equilibrium constant) were calculated. The overall second order rate constant calculated from the double-reciprocal plot agrees well with the value obtained under zero order conditions with respect to the substrate (Table 2). The equilibrium constant calculated spectrophotometrically agrees well with the value obtained kinetically (Table 2). The variable order with respect to the substrate can be explained based on the relative magnitude of  $K[\text{S}]$  as compared to 1 in equation (4)<sup>31</sup>.

Besides  $\text{RuCl}_3$ , the complexes of ruthenium in the +2 oxidation state like  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_2(\text{DMSO})_4$ , are also effective for the oxidation of sulphides. The kinetic behaviour of  $\text{RuCl}_2(\text{PPh}_3)_3$ -catalysed oxidation of sulphides and the spectral observations are similar to those observed with  $\text{RuCl}_3$ . Hence a similar mechanism is proposed and verified<sup>32</sup>. In case of *cis*- $\text{RuCl}_2(\text{DMSO})_4$ -catalysed oxidation of organic

TABLE 2—EVALUATION OF  $K$  AND  $k_2$  FROM DOUBLE-RECIPROCAL PLOT

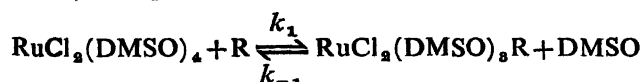
Substrate	$K$ (dm <sup>3</sup> mol <sup>-1</sup> )		$k_2$ (dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> )	
	From double-reciprocal plot	Spectrophotometric measurements	From double-reciprocal plot	Under zero order conditions with respect to [S]
Dibenzyl sulphide	27.7	28.69 ± 0.23	18.6	18.78 ± 0.18
Dibutyl sulphide	30.7	29.36 ± 0.46	19.9	19.01 ± 0.21
Phenylmethyl sulphide	27.7	27.20 ± 0.31	15.4	16.63 ± 0.18
Triphenylphosphine	121.0	121.20 ± 1.13	21.9	21.82 ± 0.18

sulphides by NMO, an induction period is observed. The induction period decreases as [catalyst] increases and at [catalyst] = 5 mM, the induction period vanishes. The induction period however does not depend on the order of addition of the reactants. The induction period might be due to the following.

(i) Dissociation of a ligand :

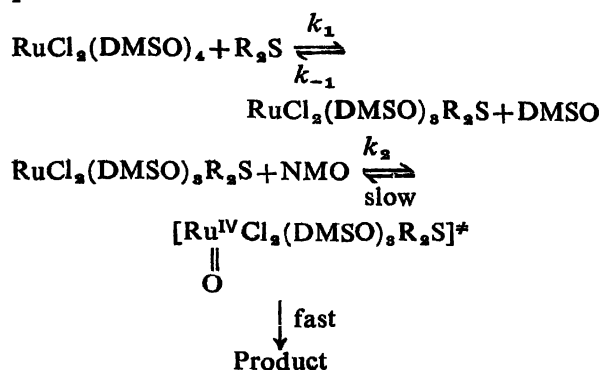


(ii) Displacement of a ligand :



where, R is sulphide ( $\text{R}_2\text{S}$ ) or NMO.

The inability to detect the coordinatively unsaturated species or to infer from the experimental results that the induction period may be attributed to the formation of  $\text{RuCl}_2(\text{DMSO})_3$  rules out the dissociation mechanism. If the induction period is due to the formation of the active species, viz.  $\text{RuCl}_2(\text{DMSO})_3\text{R}$ , one would expect the induction period to decrease by keeping the [catalyst] constant and varying that of the sulphide or NMO individually. It was found that the induction period was minimised only on varying the [sulphide]. Of the four DMSO ligands in the complex, viz.  $\text{RuCl}_2(\text{DMSO})_4$ , the one coordinated to ruthenium via the oxygen is reported to be labile<sup>33,34</sup>. Hence the first step is suggested to be the replacement of this ligand by the sulphide to give the active species  $[\text{RuCl}_2(\text{DMSO})_3\text{R}_2\text{S}]$ . Uv-visible, ir and cyclic voltammetric experiments confirm the formation of  $\text{Ru}^{\text{IV}}=\text{O}$  on adding NMO to  $\text{RuCl}_2(\text{DMSO})_4$ . Based on the kinetic and spectral studies the following mechanism is proposed.



The above scheme leads to the rate expression (equation 6),

$$\text{Initial rate} = V_1 = \frac{k_1 k_2 [\text{RuCl}_2(\text{DMSO})_4][\text{S}][\text{NMO}]}{k_{-1}[\text{DMSO}] + k_2[\text{NMO}]} \quad (6)$$

This upon rearrangement gives equation (7),

$$\frac{1}{V_1} = \frac{k_{-1}[\text{DMSO}]}{k_1 k_2 [\text{RuCl}_2(\text{DMSO})_4][\text{NMO}][\text{S}]} + \frac{1}{k_1 [\text{RuCl}_2(\text{DMSO})_4][\text{S}]} \quad (7)$$

A plot of  $1/V_1$  vs  $1/[\text{NMO}]$  at constant [catalyst] and [substrate] is linear. From the intercept the overall second order rate constant,  $k_1$  was calculated. The overall second order rate constant calculated from the double-reciprocal plot agrees well with the value calculated under zero order conditions with respect to NMO (Table 3). The variable order with respect to NMO can be explained based on the relative magnitudes of  $k_{-1}[\text{DMSO}]/k_2$  and  $[\text{NMO}]$  (Table 3). Among the three catalysts used for the oxidation of sulphides by NMO, the order of catalytic activity is  $\text{RuCl}_2(\text{PPh}_3)_3 > \text{RuCl}_3 > \text{RuCl}_2(\text{DMSO})_4$ .

TABLE 3—EVALUATION OF  $k_1$  AND  $k_{-1}/k_2$  FROM DOUBLE-RECIPROCAL PLOT

Substrate	$k$ (dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> )		$k_{-1}/k_2$ <i>M</i>
	Under zero order conditions with respect to [NMO]	From double-reciprocal plot	
Dibutyl sulphide	0.059 ± 0.003	0.06	0.004 7
Dibenzyl sulphide	0.065 ± 0.002	0.066	0.005 4
Phenyl methyl sulphide	0.048 ± 0.001	0.049	0.004 8

The  $\text{Mn}^{\text{V}}=\text{O}$  and  $\text{Fe}^{\text{V}}=\text{O}$  species resulting from the interaction of metalloporphyrin salts of manganese and iron with single oxygen donors like iodosobenzene<sup>5,6</sup>, percarboxylic acids<sup>7</sup>, hydroperoxides<sup>7,8</sup> and *p*-cyano-*N,N*-dimethylaniline *N*-oxide<sup>9,10</sup> are more powerful oxidants than  $\text{Ru}^{\text{V}}=\text{O}$ . Hence these are able to effect hydroxylation of alkanes whereas  $\text{Ru}^{\text{V}}=\text{O}$  can not.

The oxidation by ruthenium complexes/NMO system is similar to the oxidations catalysed by cytochrome P-450. In case of cytochrome P-450 oxidant system, the metalloporphyrin forms active metal-oxo species in an unusual oxidation state which reacts with the substrate, transferring the

oxygen atom to regenerate the metalloporphyrin<sup>4</sup>. In the case of ruthenium complexes/NMO system the active metal-oxo species transfers its oxygen atom to the substrate and gets regenerated. Unlike the metalloporphyrins of Mn and Fe, the formation of Ru<sup>IV</sup> oxy radical and Ru<sup>IV</sup> cation radical from Ru<sup>V</sup>=O species respectively is ruled out since Ru<sup>III</sup>-NMO system is a non-prophyrin system and does not exhibit any free radical behaviour.

IrCl<sub>3</sub>, RhCl<sub>3</sub>, RhCl(PPh<sub>3</sub>)<sub>3</sub> and metal chlorides of the iron triad are inert in catalysing the oxidation of alkenes, sulphides, phosphines and alcohols under conditions similar to those employed in the case of RuCl<sub>3</sub>. This is explained in terms of the ability to undergo oxidative addition and the stability of higher oxidation states of the metal which decreases across a period Ru>Rh>Pd and increases down a group Fe<Ru<Os<sup>5,6</sup>.

Oxidative addition and stability of higher oxidation increases

Oxidative addition and stability of higher oxidation state increases ↓

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

OsO<sub>4</sub> should be, and in fact, is a good catalyst in conjunction with trimethylamine *N*-oxide or NMO for the hydroxylation of C=C to give glycols<sup>8,9</sup>. One would expect the porphyrins of Mn and Fe to be good catalysts for the epoxidation of alkenes by NMO as it is for *p*-cyano-*N,N*-dimethylaniline *N*-oxide because in the case of porphyrin systems the oxidative addition becomes facile due to the presence of the porphyrin ligand which increases the nucleophilicity of the central metal atom. However, the porphyrin salts of manganese and iron that were prepared failed to epoxidise alkenes. Instead the reduction product of NMO, viz. *N*-methylmorpholine (NM) undergoes demethylation and oxidation giving formaldehyde and morpholine.

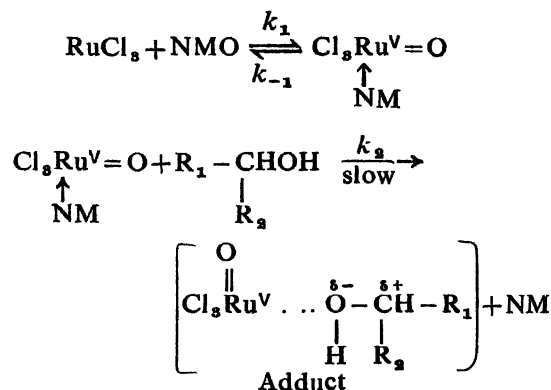
#### Oxidation of alcohols by RuCl<sub>3</sub>/NMO system :

A variety of catalysed reactions for the oxidation of alcohols invariably involve ruthenium as the key atom. Ruthenium compounds are known to be good hydride ion abstracting agents<sup>8,7</sup> and the hydride ion abstraction may or may not be rate determining. Both primary and secondary alcohols are oxidised by ruthenium complexes/NMO to form aldehydes and ketones respectively<sup>8,8,9</sup>. Aldehydes are not oxidised further to the acids independently by this system. The aldehydes act as catalyst poisons. Unsaturated alcohols like cinnamyl and propargyl alcohol, are selectively oxidised at the alcoholic group. This is an important characteristic of ruthenium complexes/NMO system. These reactions do not exhibit any free radical behaviour nor are they inhibited by *N*-methylmorpholine.

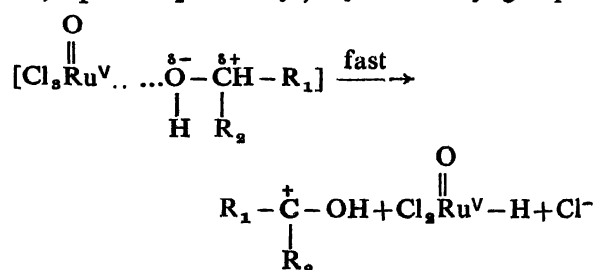
Among the non-cyclic secondary alcohols the order of reactivity is found to be benzhydrol>1-phenylethanol>1-propanol. This is in accord with

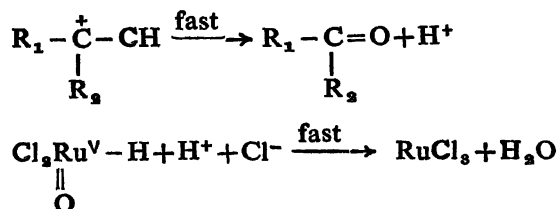
the polar effect. The order of reactivity among cyclic alcohols is cycloheptanol>cyclopentanol>cyclohexanol, which can be explained on the basis of the bond hybridisation changes. Reactions tried with substituted 1-phenylethanol gave a  $\rho$  value of -0.3 which indicates a positively charged transition state. Though the magnitude of  $\rho$  value is small it does indicate the participation of the substrate in the rate-determining step. Primary alcohols react faster than secondary alcohols. This is because the slow step is the adduct formation and the carbocation is formed in the fast step.

The reaction is first order each in catalyst and NMO. The order with respect to the substrate is variable being zero and fractional at high and low concentrations respectively. Ruthenium complexes are known to form adducts with organic compounds<sup>4,0</sup>. The shift in the nmr signal ( $\Delta\tau=0.4$  units) of the hydroxylic proton of the alcohol in the presence of Ru<sup>V</sup> towards a lower value indicates adduct formation between Ru<sup>V</sup> and alcohol. The shift in the nmr signal of the hydroxylic proton of the alcohol observed on adding a paramagnetic metal compound indicates loose complex formation between alcohol and metal compound<sup>4,1</sup>. There is no complex formed between the catalyst and alcohol as shown by uv-visible and nmr spectra. A comparison of the Ru<sup>III</sup>-catalysed oxidation of an alcohol and its corresponding deuterated analogue shows no kinetic isotope effect. Hence the cleavage of the C-H bond of the substrate is not likely to be the rate-determining step. A mechanism is proposed where Ru<sup>V</sup>=O species formed in steady state concentrations from RuCl<sub>3</sub> and NMO reacts with the substrate in the slow step<sup>8,8</sup>.



where, R<sub>1</sub> and R<sub>2</sub> are alkyl, aryl or aralkyl groups.





This mechanism leads to the rate expression (equation 8),

$$\text{Initial rate} = V_1 = \frac{k_1 k_2 [\text{Ru}^{\text{III}}][\text{S}][\text{NMO}]}{(k_{-1} + k_2[\text{S}])} \quad (8)$$

Equation (8) upon rearrangement gives equation (9),

$$\frac{1}{V_1} = \frac{k_{-1}}{k_1 k_2 [\text{Ru}^{\text{III}}][\text{S}][\text{NMO}]} + \frac{1}{k_1 [\text{Ru}^{\text{III}}][\text{NMO}]} \quad (9)$$

A plot of  $1/\text{initial rate}$  vs  $1/[\text{substrate}]$ , in the region where the order with respect to the substrate is fractional, is linear. The values of  $k_1$  and  $k_{-1}/k_2$  obtained from this plot are given in Table 4. The variable orders in the substrate can be explained based on the relative magnitude of  $k_{-1}/k_2$  and  $[\text{S}]$ . There is good agreement between the values of  $k_1$  determined under zero order conditions with respect to the substrate and that obtained from the double-reciprocal plot (Table 4).

TABLE 4—EVALUATION OF  $k_1$  AND  $k_{-1}/k_2$  FROM DOUBLE-RECIPROCAL PLOT

Substrate	$k_1$ ( $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ )		$k_{-1}/k_2$ $M$
	From pseudo-first order plot	From double-reciprocal plot	
Cyclohexanol	36.41	36.57	0.049
1-Phenylethanol	39.05	38.98	0.041
2-Propanol	34.41	34.94	0.053

The orders of reactivity of linear primary alcohols  $\text{C}_2 - \text{C}_{20}$  have been compared in the region where the order with respect to the substrate is fractional. The rate increases in the order,  $\text{C}_2 < \text{C}_3 < \text{C}_4 < \text{C}_5 < \text{C}_6$  which might be attributed to the polar effect of the alkyl group. However from  $\text{C}_7$  onwards a different trend is observed (Table 5, Fig. 1):  $\text{C}_7 \approx \text{C}_8 < \text{C}_9 \approx \text{C}_{10} < \text{C}_{11} > \text{C}_{12} < \text{C}_{13} > \text{C}_{14} < \text{C}_{15} > \text{C}_{16} < \text{C}_{17} > \text{C}_{18} < \text{C}_{19} > \text{C}_{20}$ ; even number alcohols:  $\text{C}_2 < \text{C}_4 < \text{C}_6 < \text{C}_8 < \text{C}_{10} < \text{C}_{12} < \text{C}_{14} < \text{C}_{16} < \text{C}_{18} < \text{C}_{20}$ ; odd number alcohols:  $\text{C}_1 < \text{C}_3 < \text{C}_5 < \text{C}_7 < \text{C}_9 < \text{C}_{11} < \text{C}_{13} < \text{C}_{15} < \text{C}_{17} < \text{C}_{19}$ . This behaviour does not correspond to the variation in some of the known properties of the alcohols like the boiling point refractive index, density and melting point.

$\text{Ru}^{\text{III}}/\text{NMO}$  system is also capable of oxidising carbohydrates like glucose, mannose, galactose, arabinose and xylose to the corresponding lactone. The low percentage yield obtained in the case of carbohydrates might be due to the large size of these substrates<sup>4,5</sup>.

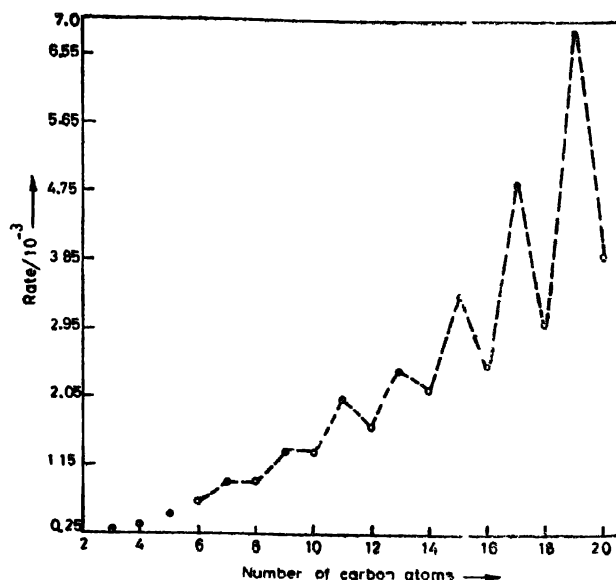


Fig. 1. Rates of oxidation of linear primary alcohols with variation in chain length: (●) Odd number and (○) even number of carbon atoms.

TABLE 5—RELATIVE RATES FOR OXIDATION OF VARIOUS ALCOHOLS

Substrate	Initial rate $\times 10^4$	Relative rate
Ethanol	0.26	1.00
Propanol	2.63	1.14
Butanol	0.84	1.30
Pentanol	0.49	1.88
Hexanol	0.66	2.51
Heptanol	0.95	3.63
Octanol	0.93	3.54
Nonanol	1.32	5.01
Decanol	1.27	4.82
Undecanol	1.99	7.58
Dodecanol	1.69	6.43
Tridecanol	2.81	10.68
Tetradecanol	2.18	8.29
Pentadecanol	3.46	13.15
Hexadecanol	2.45	9.32
Heptadecanol	5.01	19.05
Octadecanol	3.07	11.67
Nonadecanol	6.85	26.04
1-Eicosanol	3.98	15.13

The major problem faced in homogeneous catalysis is the separation of the catalyst from the product at the end of the reaction which can be achieved by filtration in the case of polymer supported catalysts. The recovered catalyst can be used again.  $\text{RuCl}_3(\text{PPh}_3)_3$  was anchored on phosphinated polystyrene divinyl benzene and it is found to catalyse the oxidation of alcohols by NMO in benzene as the solvent<sup>4,5</sup>. Though the oxidation of secondary alcohol by homogeneous catalyst is six times faster than in the case of the same reaction with the anchored catalyst, the anchored catalyst can be recovered and the recovered catalyst is found to be as effective as the original one for the oxidation of alcohols.

## Conclusions :

(i) Ruthenium complexes/NMO system oxidises alcohols, olefins, sulphides and triphenylphosphine. (ii) The reaction proceeds via the formation of a higher valent metal-oxo species as the active intermediate. (iii) The active oxidant is electrophilic and the greater the nucleophilicity of the substrate the greater is the rate of reaction. (iv) In the oxidation of olefins, sulphides and triphenyl phosphine there is a net oxygen atom transfer, the oxygen from NMO being transferred via the catalyst. (v) In the oxidation of alcohols the reaction proceeds by hydride ion abstraction.

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