

characteristic of an aromatic proton adjacent to an oxygen substituent.

On the basis of these observations the product was identified as 7-hydroxy coumarin which was finally confirmed by direct comparison with an authentic sample (m.p., m.m.p., UV, IR, NMR).

In control experiment the compound (I) was added to medium without bacterial inoculum and incubated similarly. After 48 hr of incubation the medium was extracted with chloroform and evaporated as described above when a solid mass was obtained which was found to be the original compound by direct comparison.

Similar experiment with compound (II) furnished compound (III).

The authors express their thanks to Prof. B. B. Biswas for encouragement

21 July 1986

1. Charney, W. and Herzog, H. L., In: *Microbial transformations of steroids*, Academic Press, New York, 1967.
2. Iizuka, H. and Naito, A., In: *Microbial transformation of steroids and alkaloids*, University of Tokyo Press, Tokyo, and University Park Press, State College, PA, 1967.

RUTHENIUM(III)-CATALYZED EPOXIDATION OF OLEFINS BY N-METHYLMORPHOLINE N-OXIDE

G. CAROLING, J. RAJARAM and J. C. KURIACOSE

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India.

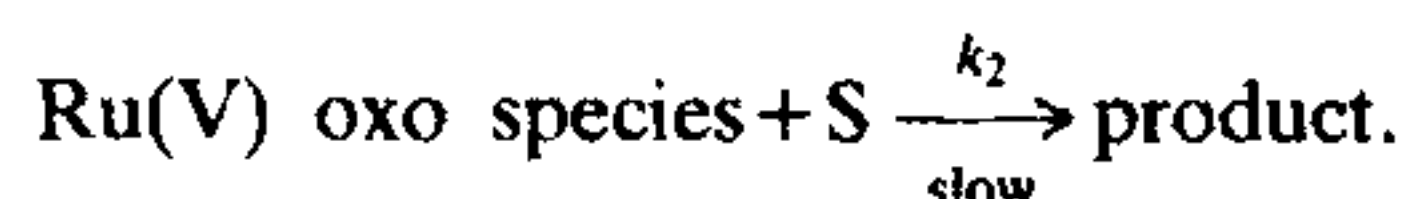
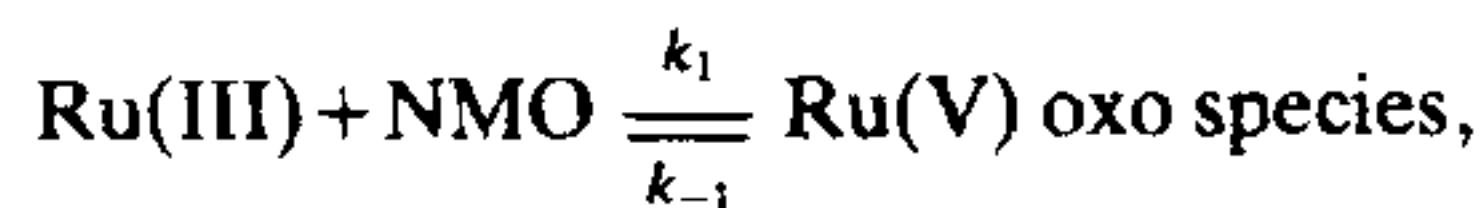
ALKYLHYDROPEROXIDES in combination with complexes of molybdenum, vanadium, tungsten and titanium have been used for the epoxidation of olefins¹. The kinetics, mechanism and factors governing catalytic activity in such epoxidations have been investigated^{2,3}. In the presence of catalytic amounts of (tetraphenyl-porphinato) manganese(III), p-cyano-N,N-dimethylaniline-N-oxide epoxidises cyclohexene⁴. However, olefins are converted into the corresponding glycols by tertiary amine-N-oxides like trimethylamine-N-oxide and N-methylmorpholine-N-oxide (NMO) in the presence of catalytic amounts of OsO₄⁵⁻⁷. Vijayasri *et al*⁸ reported that in the presence of Ru(III) as

catalyst in DMF, NMO oxidizes secondary alcohols to the corresponding ketones. Studies on the use of RuCl₃-NMO combination in DMF as solvent to epoxidize olefinic substrates like cyclohexene, styrene and terminal alkenes are reported in this communication.

The kinetic investigations were carried out at 35 ± 0.1°C. Oxygen-free nitrogen was bubbled into the reaction mixture to provide an inert atmosphere. The concentration of NMO remaining at any instant was determined titanometrically⁹ as reported earlier⁸. In the case of non-aromatic substrates the progress of the reaction, especially at low concentrations of the substrate was followed iodometrically. The reaction mixture was quenched with a known excess of bromine in acetic acid and the unreacted bromine was treated with excess of KI. The iodine liberated was titrated against standard sodium thiosulphate.

The stoichiometry of the reaction is in agreement with the equation $\text{Alkene} + \text{NMO} \xrightarrow{\text{catalyst}} \text{epoxide} + \text{N-methylmorpholine}$. There was no reaction between substrate and NMO in the absence of a catalyst. All the alkenes investigated so far are found to give rise to the corresponding epoxides. This was confirmed by gas chromatographic analysis using an FFAP column and comparison of the retention times with those of authentic samples.

The reactions were carried out under pseudo first order conditions by maintaining [substrate] ≫ [NMO]. The reaction was first order in NMO and catalyst. However, the order with respect to the substrate, as determined from the pseudo first order plots, varied depending on the concentration of substrate. Vijayasri *et al*¹⁰ established the formation of Ru(V) species by spectral and cyclic voltametric studies. Accordingly the following mechanism could be proposed for the epoxidation of olefins.



Assuming the Ru(V) oxo species to be in steady state concentrations one can deduce the following rate expression.

$$\begin{aligned} \text{Rate} &= \frac{-d[\text{NMO}]}{dt} = \frac{k_1 k_2 [\text{Ru(III)}] [\text{NMO}] [\text{S}]}{k_{-1} + k_2 [\text{S}]} \\ &= \frac{k_1 [\text{Ru(III)}] [\text{NMO}] [\text{S}]}{(k_{-1}/k_2) + [\text{S}]} \end{aligned} \quad (1)$$

The variable orders in the substrate could be accounted for on the basis of relative magnitudes of k_{-1}/k_2 and $[S]$. Equation (1) can be rearranged to give (2).

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

Equation (2) has been verified by plotting $1/\text{rate}$ against $1/[S]$ using the data obtained for low concentrations of the substrate, at constant concentration of Ru(III) and NMO. At high substrate concentrations, $k_{-1}/k_2 < [S]$ and so the reaction is zero order in the substrate. A comparison (table 1) of the values of k_1 obtained from the linear plots with those obtained from the pseudo first order rate constants (k_{obs}) supports the proposed mechanism.

Table 1 Evaluation of rate constants from double reciprocal plots at low concentrations of substrate

Substrate	k_1 in $\text{M}^{-1} \text{min}^{-1}$		(k_{-1}/k_2)
	From pseudo first order plots	From double reciprocal plots	
Cyclohexene	11.42 ± 0.13	11.36	0.109
1-Octene	8.43 ± 0.34	8.30	0.053

Since the olefinic substrates can form complexes with transition metal ions, spectral studies are in progress to investigate this possibility. Further work in epoxidizing a variety of olefinic substrates as well as amines, sulphides, etc is in progress.

Financial assistance by CSIR is acknowledged by GC.

19 July 1986

- Sheldon, R. A., In: *Aspects of homogeneous catalysis*, (ed.) R. Ugo, D. Reidel, Dordrecht, 1981, Vol. 4, p. 3.
- Gould, E. S., Hiatt, R. R. and Irwin, K. C., *J. Am. Chem. Soc.*, 1968, **90**, 4573.
- Su, C. C., Reed, J. W. and Gould, E. S., *Inorg. Chem.*, 1973, **12**, 337.
- Powell, M. F., Pai, E. F. and Bruce, T. C., *J. Am. Chem. Soc.*, 1984, **106**, 3277.

- Schroder, M., *Chem. Rev.*, 1980, **80**, 187.
- Van Rheenan, V., Kelly, R. C. and Cha, D. Y., *Tetrahedron Lett.*, 1976, **29**, 1973.
- Corey, E. J., Danheiser, R. L., Chandrasekaran, S. and Siret, P., *J. Am. Chem. Soc.*, 1978, **100**, 803.
- Vijayasri, K., Rajaram, J. and Kuriacose, J. C., *Curr. Sci.*, 1985, **54**, 1279.
- Brooks, R. T. and Sternglanz, P. A., *Anal. Chem.*, 1959, **31**, 561.
- Vijayasri, K., Rajaram, J. and Kuriacose, J. C., *Inorg. Chim. Acta*, 1986, **117**, 133.

SALINITY STRESS RESPONSE OF PLANTS AND CALLI IN WHEAT

A. MALHOTRA, R. S. RANA, D. R. SHARMA* and J. B. CHOWDHURY*

Central Soil Salinity Research Institute, Karnal 132 001, India.

* Haryana Agricultural University, Hissar 125 004, India.

FOLLOWING reports¹⁻³ of several fold intra-specific heritable differences in adaptation to saline environment, many investigators have advocated the use of tissue culture technique for identifying salt-tolerant genotypes for generating new genetic variability for this purpose⁴⁻⁶. This approach towards developing more salt-resistant crop varieties is supported by observations in several nonhalophytes revealing sizable inter-specific differences at the cellular level in respect of salt tolerance⁷. In addition, halophytes have developed more successful adaptive strategies, based on certain anatomical and morphological features, to live with excessive salt concentrations^{8,9}. In this context, the present investigation on plants and calli of two wheat genotypes, vars HD 4502 and C 306, was undertaken to study their comparative response to salinity stress.

Plants were grown in 20 kg capacity glazed porcelein pots with four repeats, each having five plants. Saline soil grade ($\text{ECe } 7.0 \text{ dS m}^{-1}$) was prepared following the procedure described in the US Salinity Laboratory Handbook No. 60 using NaCl. Salinity level was maintained by flushing and saturating the soil with saline water of 7.0 dS m^{-1} conductivity. Controls were raised in non-saline soil under comparable conditions. Performance of var