Olefin epoxidation catalyzed by dioxotungsten(VI) Schiff base complexes

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Received 2 January 1998; revised 24 August 1998

The epoxidation of olefins is catalyzed by dioxotungsten(VI) complexes using tert-butyl hydroperoxide (TBHP) as the oxidant. Competitive epoxidation of olefins follows the order: cyclohexene > cycloheptene > norbornene. Norbornene gives exoepoxide only. The studies on the effect of surfactants (Triton-X-100, SLS and CTAB) show that addition of surfactant retards the epoxide yield. Results suggest that the olefin is coordinated to metal center in the rate determining step.

The oxidation of hydrocarbons using transition metal complexes is of industrial and biological significance. A number of complexes of the metals Fe, Mn, Cr, Ru, Mo, V, etc., with the ligands porphyrins, macrocycles and Schiff bases have been studied. The metal catalysts are of interest as they afford high selectivity towards epoxide formation. The tungsten compounds are useful catalysts in oxidation of organic compounds. Keeping this in view, we report here epoxidation of olefins using tert-butylhydroperoxide as the oxidant. These studies have helped us in understanding the mechanism of the dioxotungsten(VI) catalyzed epoxidation which has not been studied so far.

Experimental
The reagents, aldehydes and amines used were of high purity and solvents were used after purification.

The elemental analysis was carried out using a CARLOE-RBA elemental analyzer. The conductance data were recorded in dimethylformamide (10⁻³ M) using a Digital conductivity bridge having a diptype cell. The IR spectra in nujol mull were recorded on a Perkin-Elmer-883-IR spectrophotometer. The UV-visible spectra of the complexes in dichloromethane were recorded using CARL-ZIES spectrophotometer. The cyclic voltammetric studies were carried out in dichloromethane (10⁻³ M) using a BAS-CV-27 cyclic voltameter with glassy carbon (GC) as working electrode, Pt-wire as auxiliary electrode and saturated Ag/AgCl electrode as reference. Freshly prepared tetracyethylammonium perchlorate was used as the supporting electrolyte. Magnetic measurements were carried out on a "Susceptibility and low field Hysteresis apparatus". Analytical gas Chromatography was done on a NUCON-AMIL-5700 series gas chromatograph fitted with a Shimadzu CR-3A data processor.

Synthesis
The dioxotungsten(VI) complexes were synthesized using tridentate and tetradentate Schiff base ligands, viz., bis(salicylaldehyde)ethylenediamine (H₂SALEN), bis(salicylaldehyde)-o-phenylenediamine (H₂SALPHEN), bis(salicylaldehyde)propylenediamine (H₂SALPREN), bis(salicylaldehyde)anthranilic acid (H₂SAC), bis(salicylaldehyde)-o-aminophenol (H₂SAP), bis(2-hydroxy-1-naphthaldehyde)-1,2-di-aminopropane (H₂HYDTRIEN), bis(2-hydroxy-1-naphthaldehyde)-1,3-diaminopropane (H₂HYDPN) and bis(2-hydroxyacetophenone)ethylenediamine (H₂HAPPEN) (0.01 mol) in acetone (5 ml) and reacting the ligand with tungsten hexachloride in acetone (0.1 ml) and reacting the ligand with tungsten hexachloride (0.01 mol) in acetone (10 ml). The contents were refluxed for 2-3 h and fine crystals were obtained by cooling the solution overnight. The crystals were filtered and dried.

Epoxidation of cyclohexene
The epoxidation of cyclohexene was carried out in a three-necked round-bottom flask by taking catalyst (10 mg), olefin (0.0015 mol), TBHP (0.0002 mol) and benzene (10 ml). Dodecane (0.1 ml) was used as the internal standard. The contents were stirred at 80°C for 9 h. The products were analyzed by gas chromatographic technique at 120°C.

Competitive epoxidation of cyclic olefins
The competitive epoxidation of cyclo-olefins, viz., cyclohexene, cycloheptene and norbornene was...
studied by taking cyclohexene (0.0015 mol), other cyclic olefin (0.0015 mol), catalyst (20 mg) and TBHP (0.0004 mol) in benzene (10 ml).

Effect of additives
The effect of the surfactants sodium lauryl sulphate (SLS), cetyltrimethyl ammonium bromide (CTAB) and Triton-X-100, on the epoxidation of cyclohexene and norbornene was studied by adding 50 mg of the additive to the epoxidation system.

Results and discussion
Elemental analysis (C,H,N) (Table 1) values are in close agreement with the values calculated for the molecular formulae assigned to these complexes. A representative structure is given above (I):

The molar conductance values show that these complexes behave as non-electrolytes. The IR spectra of [WO₄(SALEN)] showed no absorption in the region 3500-3200 cm⁻¹ indicating thereby that phenolic group is involved in coordination. The absorption bands in the region 1610-1590 are assigned to the stretching vibrations of unsaturated >C=N< and >C=C< groups. The νC-O of hydroxy group is shifted to higher frequency (1210 to 1220 cm⁻¹) suggesting the involvement of phenolic hydroxyl group in coordination. An IR band at 980 cm⁻¹ due to O=W=O was observed. The complexes [WO₄(SALPREN)], [WO₄(SALPHEN)], [WO₄(SAP)], [WO₄(SAC)], [WO₄(HYDTRIEN)], [WO₄(HAPPEN)] and [WO₄(HYDPEN)] show characteristics similar to those of [WO₄(SALEN)].

Thus the infrared studies support the structures assigned to these complexes.

The results of magnetic susceptibility for the complexes under investigation reveal that all the complexes are diamagnetic showing thereby that all the electrons are paired.

The visible spectra of the complexes show bands in the regions 205-275 and 315-375 nm which are assigned to n→n* and n→π* transitions respectively.

The metal complexes are electroactive at glassy carbon electrode showing irreversible reduction (Fig. 1). The coulometric data suggest that the reduction is a one-electron transfer process.

The electrode process can be written as follow:

\[ [W^{VI}(L)O_2]^{2+} \rightarrow [W^{V}(L)O_2]^{-} \]
Oxidation of alkenes

The results of cyclohexene epoxidation (Table 1) show that tungsten complexes on epoxidation give cyclohexene oxide as the main product with cyclohexenol and cyclohexenone as the byproducts. The formation of cyclohexenol and cyclohexenone suggests that homolytic decomposition of tert-butylhydroperoxide takes place.

Norbomene on epoxidation gave only exo epoxide. The absence of endoepoxide and norcamphor suggests that during epoxidation either coordination of olefin to metal center is taking place in the rate determining step with the formation of oxometallacycle intermediate, or the two carbon-oxygen bonds are being formed at a rapid rate giving no room for C–C bond rotation. The formation of endoepoxide as a result of bond rotation has been suggested in cytochrome P-450 catalyzed reactions and also in Cr – Mn – and Fe-porphyrin catalyzed epoxidation.

Competitive epoxidation of norbornene and cyclohexene exhibits that cyclohexene undergoes epoxidation faster than norbornene. This suggests that coordination of olefin to the metal center takes place in the rate determining step. The relative ratio of cyclic-olefins epoxidation shows the order: cyclohexene (1) > cycloheptene (0.7) > norbornene (0.5).

The step was proposed to be the epoxide formation of an intermediate oxometallacycle [4]. The result shows that the competitive coordination of olefin to metal center takes place resulting in the formation of oxometallacycle which breaks down in the rate determining step to give epoxide. This is probably the low competitive coordination of norbornene compared to cyclohexene. This means that the better coordinating olefin exerts an inhibitory effect on the coordination and therefore the reactivity of the incoming coordinating olefins.

The effect of non-ionic surfactant Triton-X-100 anionic surfactant sodium lauryl sulphate and cationic surfactant cetyltrimethylammonium bromide suggests that surfactant addition retards the epoxide yield (0.017, 0.029 & 0.027 mmol respectively) while the yield of cyclohexenol and cyclohexenone is slightly increasing. The addition of these surfactants led to the formation of a new product, cyclohexenyl peroxide (0.119, 0.080 & 0.060 mmol respectively) at the expense of epoxide.

On the basis of aforementioned studies olefin epoxidation mechanism depicted in Scheme 1 can be suggested. For homolytic decomposition the above scheme (Scheme 2) can be suggested.

On comparison with the catalytic action of cis-dioxomolybdenum(VI) complexes, it was found that with dioxo tungsten(VI) complexes cyclohex-endo and cyclohexenone are formed while in the case of cis-dioxomolybdenum complexes only epoxide is formed.

Acknowledgement

The authors are thankful to the CSIR, New Delhi for financial assistance.
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