Catalytic Epoxidation of Alkenes by Sterically Crowded Ruthenium Complexes

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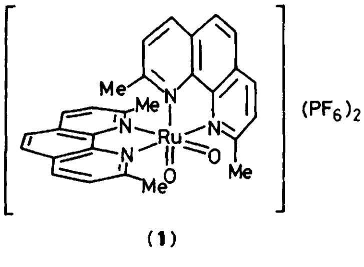
Treatment of $[Ru^{II}(2,9\text{-dimethyl-1,10-phenanthroline})_2(H_2O)_2]^{2+}$ with Ce^{IV} resulted in the formation of the dioxo-Ru^{VI} complex which was found to be an efficient catalyst for the oxidation of alkenes.

High-valent oxo-ruthenium compounds have attracted a good deal of interest in recent years as potential catalysts for the oxidation of water in photochemical water-splitting reactions.[1] Of particular interest are ruthenium complexes containing polypyridyl ligands whose structure provides a means of both stabilizing higher oxidation states and imparting stability to the complex. Though these materials have been suggested as catalysts for the oxidation of organic substrates,[2] the catalytic oxidation of alkenes or alkanes by O_2 has not been reported until recently. Groves *et al.*[3] have shown that dioxo(tetramesitylporphyrinato)ruthenium(VI), $[Ru^{VI}(O)_2(tmp)]$, is a catalyst precursor for the aerobic epoxidation of alkenes at ambient temperature and pressure.

In a continuing investigation of the catalytic activation of molecular oxygen,[4] we were intrigued by the recent report of Collin and Sauvage[5] characterizing a series of mononuclear ruthenium(II) complexes of sterically hindered diimine chelates. Of particular interest was the diaquo complex of bis(2,9-dimethyl-1,10-phenanthroline)ruthenium(II), $[Ru(dmp)_2(H_2O)_2]^{2+}$, owing to the availability of a +6 oxidation state as demonstrated by electrochemical studies. We report here that a high-valent ruthenium(VI) complex, tentatively formulated as $[Ru(O)_2(dmp)_2](PF_6)_2$ (**1**) is a catalyst precursor for the efficient oxidation of alkenes by dioxygen. High selectivity in the conversion of norbornene to its epoxide is observed. The dmp ligand is commercially available and the complexes are much simpler to prepare and purify than the dioxo(tetramesitylporphinato)ruthenium(VI) complex recently reported to be an epoxidation catalyst.[6] We found that addition of excess of Ce^{IV} to $[Ru(dmp)(H_2O)_2]^{2+}$ resulted in the formation of (**1**). Comparison of the i.r.



(**1**)

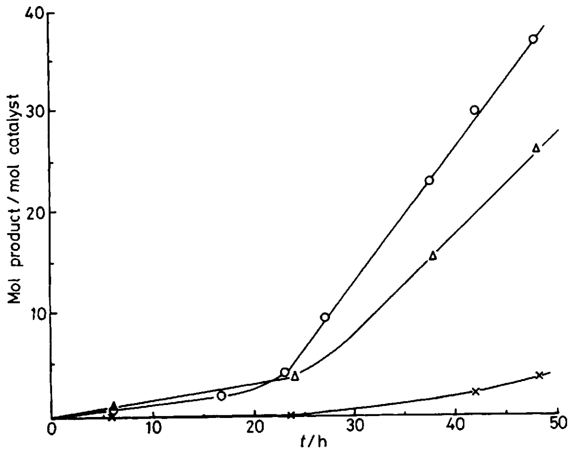


Figure 1. Activity curve for the epoxidation of norbornene catalysed by oxo-ruthenium complexes: ○, reaction using (**1**); ×, addition of (**1**) after 24 h; △, $[Ru^{IV}(dmp)_2(O)(H_2O)](PF_6)_2$.

spectrum of the complex before and after oxidation indicated the formation of a dioxo complex. The ν(Ru–O) band at 787 cm^{-1} and possible overlapping bands at 839 cm^{-1} suggest an O–Ru–O angle of about 90°. These results are consistent with the Ru^{VI} formalism reported for similar complexes, including *trans*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine)[7] and *trans*-$[Ru^{VI}(O)_2(tmp)]$, in which only one ν(Ru–O) stretch was observed at ~850 cm^{-1}. Thus, we tentatively assign this compound as $[Ru(O)_2(dmp)_2](PF_6)_2$, a formulation consistent with the elemental analyses. Attempts to grow crystals suitable for *X*-ray analysis are underway, as are ^{17}O experiments to aid in the i.r. interpretation.

The corresponding Ru^{IV} complex of (**1**), where the two available co-ordination sites are an oxo and aquo function, was also synthesized. The i.r. spectrum of the Ru^{IV} complex exhibits a single ν(Ru–O) stretch at 792 cm^{-1}, comparable to its position in similar oxo-Ru^{IV} complexes.[8] Elemental analyses have the proper C, H, N ratios but indicate the presence of a slight impurity. Attempts are underway to purify the complex and grow suitable crystals for *X*-ray analysis. The complex was used in its impure state for catalytic studies, since we believe the impurity has no effect on the catalytic activity of the system.

Starting with either the ruthenium-(IV) or -(VI) complex of dmp, efficient catalytic oxidation of norbornene, cyclohexene, and *trans*-β-methylstyrene occurs. In a typical experiment, a 100-fold excess of the alkene substrate was added to compound (**1**) in acetonitrile (50 ml; 0.5 mM) with stirring at 55 °C under ~40 lb in^{-2} O_2 pressure as described previously.[4] Samples were withdrawn periodically and monitored by gas chromatography (g.c.), and Fourier-transform i.r. and u.v.–visible spectroscopy. Of the three substrates studied, norbornene proved to be the most selective and active system. While only 4 equiv. of epoxide were formed in a 24 h period, 37 equiv. were observed after 48 h. In Figure 1 product formation as a function of time indicates the catalytic nature of the reaction and demonstrates an induction period prior to rapid product formation. Since the reaction products are not characteristic of a radical-chain process (*vide infra*), the induction period suggests that the active catalyst is formed during this period. A shift in the visible band at 416 nm as the reaction proceeded is consistent with this formulation. After 24 h, the band was red-shifted to a maximum of 450 nm and this corresponds to the beginning of the most active catalyst period. Between 48 and 96 h, the band gradually blue-shifted to 412 nm with a corresponding decrease in intensity and activity.

To determine the exact nature of the induction period for the norbornene system, two oxidation reactions were carried out simultaneously. In (i), all three components, *i.e.*, catalyst, substrate, and solvent were present, while in (ii) only the catalyst and solvent were present. After 24 h, 4 equiv. of epoxide had formed in experiment (i). Addition of norbornene at this point to experiment (ii) did not lead to immediate epoxidation (see Figure 1). An induction period comparable to that observed in (i) occurred, suggesting that the substrate is necessary for the formation of the 'active' catalytic species.

The remaining two substrates studied, cyclohexene and *trans*-β-methylstyrene, lacked the selectivity observed in the norbornene system. Following oxidation of cyclohexene, three products were observed: cyclohexene epoxide, cyclohex-2-enol, and cyclohex-2-one in a ratio of 1:3:9. Unlike the norbornene system, products were observed at a much faster rate. After 48 h, all catalytic activity had stopped and a yellow precipitate had formed. This was not observed for any of the other systems studied. The lack of selectivity for cyclohexene may be due to competing reactions involving an alternative pathway for product formation by attack at the allylic hydrogen.

To determine the stereoselectivity of epoxide formation, *trans*-β-methylstyrene was examined. After 24 h the cleavage product, benzaldehyde (2 equiv.), was the only detectable product based on g.c. results. This reaction continued for the next 24 h, with the detection of 5 additional equivalents of benzaldehyde. However, if the reaction was monitored during a week, both acetaldehyde and the *trans*-epoxide were observed. Balavoine *et al.*[9] reported that epoxides are converted into cleavage products in a ruthenium-catalysed periodate oxidation. Thus, cleavage of methylstyrene may involve initial formation of epoxide followed by cleavage or an alternative oxidation pathway.

The similarity in the stereochemical selectivity of the *trans*-β-methylstyrene oxidation to that reported by Groves[3] leads us to speculate that the mechanism for our catalyst is similar.

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