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HOMOGENEOUS CATALYSIS BY TRANSITION METAL COMPLEXES I. THE HOMOGENEOUS CYCLOHEXENE OXIDATION CATALYSED BY LOW VALENT TERTIARY PHOSPHINE–TRANSITION METAL COMPLEXES*

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SUMMARY

The oxidation of cyclohexene catalysed by low oxidation state phosphine–transition metal complexes has been studied at 65° and 1 atm of oxygen. The process is a radical reaction but no marked oxygen activation promoted by coordination on the transition metal is usually involved, and the effective action of transition metal complexes is related to their interaction with preformed cyclohexene hydroperoxide to form radicals. Only in few cases is oxygen activation probably involved.

INTRODUCTION

A great deal of interest has been devoted in the last few years to the activation of small molecules in the homogeneous phase by transition metal complexes[1]. The isolation and characterisation of 1/1 oxygen adducts of low valent phosphine complexes[2] have given rise to a hope of obtaining, through coordination, a more active form of oxygen. X-ray analysis of some oxygen adducts of related iridium and rhodium complexes[3] has, in fact, shown that the oxygen–oxygen distance is lengthened by coordination and that the amount of the increase is dependent on such factors as *d*-electron configuration of the metal and nature of the ligands. In order to explain this, the electronic structure of coordinated oxygen has been likened to some electronically excited states of molecular oxygen[4] or more simply, to some anionic species as O_2^{2-}, O_2^- formed by charge transfer to the metal[5].

It is thus to be expected that, mainly in reversible adducts, the reactivity of coordinated oxygen might be similar to that of singlet oxygen[6] or of the peroxide ion[7]. Preliminary results on oxidation of organic substrates using such oxygen adducts as catalysts have been reported[8–11], and this prompts us to report now some of the studies carried out in our laboratories on cyclohexene oxidation catalysed by these compounds.

* Part of this paper has been presented at the Chemical Society Meeting on Oxygen, Hydrogen and Nitrogen as ligands, Leeds, April (1968).