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Oxidative cleavage of styrene with oxygen catalysed by phosphinoruthenium(II) complexes

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Abstract

Highly selective oxidative cleavage of styrene by dioxygen has been achieved in mild conditions and in the presence of catalytic amounts of $[RuCl(DPP)_2]ClO_4$ or *trans*-$[RuCl_2(DPP)_2]$ (DPP = 1,3-bis(diphenylphosphino)propane).

Introduction

The oxidation of organic compounds by molecular oxygen catalysed by transition-metal complexes is attracting considerable attention from both synthetic and mechanistic viewpoints, although so far only a limited number of ruthenium complexes have been shown to promote the oxygen-oxidation of organic substrates, such as alkenes, alcohols or thioethers [1].

Recently we reported that stable five-coordinate phosphinocomplexes of ruthenium(II) and osmium(II) of the type $[MCl(LL)_2]ClO_4$ (LL = 1,3-bis(diphenylphosphino)propane, DPP, or 1-diphenylphosphino-2-(2′-pyridyl)ethane, PPY), can function as effective catalysts for the oxidation by single-oxygen oxidants (iodosobenzene, hypochlorite) of a variety of substrates, including alkenes [2a] and alkanes [2b]. We now report that the above ruthenium(II) derivatives also catalyze the aerobic oxidative cleavage of styrene at room pressure and temperature and without the need of a coreductant. Cleavage of carbon–carbon double bonds is usually carried out by use of stoichiometric reagents such as high-valent metal oxides and particularly ruthenium tetroxide, which almost invariably give carbonyl compounds directly [3]. Use of efficient non-enzymatic systems that promote the oxidative cleavage of alkenes with molecular oxygen is relatively rare [4], the results presented below may serve to demonstrate the merits of this approach.

Results and discussion

Styrene (1 mmol), in the presence of 4 μmol of $[RuCl(DPP)_2]ClO_4$ in aerobic dichloromethane solution (1 ml) was found to give benzaldehyde slowly (less than 1

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turnover/h) in quantitative yields ($> 99\%$), without any apparent loss of catalytic activity during several days. No other oxidation products (epoxide, allyllic alcohols, carbonylic compounds) could be detected by GLC. The complex *trans*-$[RuCl_2(DPP)_2]$ behaves very similarly, except that the activity is practically lost within hours. Other alkenes (stilbenes, β-methylstyrene, norbornene, 1-octene) were recovered unchanged when their oxidation under the same conditions was attempted, and related osmium(II) derivatives, e.g. $[OsCl(DPP)_2]ClO_4$, were found to be ineffective even with styrene.

In the absence of oxygen, the reaction fails to produce any oxidised product, indicating that dioxygen is necessary for the oxidative cleavage of styrene, which probably proceeds as in eq. 1. The high volatility of formaldehyde precluded its quantitative determination by GLC.

$$PhCH{=}CH_2 + O_2 \rightarrow PhCHO + HCHO \qquad (1)$$

When styrene was used under an inert atmosphere in the presence of a terminal oxidant (iodosylbenzene) and of catalytic amounts of $[RuCl(DPP)_2]ClO_4$, oxidation of the substrate again took place, but with formation of both benzaldehyde and styrene oxide (in a molar ratio around 2/1). When the same procedure was carried out aerobically, a larger quantity of benzaldehyde was formed, the amount of which somewhat exceeds the amount of the oxidant consumed (measured by the iodobenzene formed), whereas the presence of air had little effect on the production of styrene oxide, clearly indicating that dioxygen plays no direct role in the formation of this product. Labelling experiments with $^{18}O_2$ confirmed that the oxygen atom in the formed benzaldehyde was derived predominantly from dioxygen and not from the terminal oxidant.

In order to rule out possible activation by perchlorate ion the hexafluorophosphate salt of the ruthenium(II) complex was also used, instead of the perchlorate. Both complexes proved to be effective in the catalytic oxidative cleavage of styrene, and no differences in activity and selectivity were observed.

The metal-catalysed double-bond cleavage can formally be regarded as a double decomposition by oxygen, analogous to the process proposed for formation of formaldehyde from ethylene and oxygen on heterogeneous catalysts [4c]. In the present case, a plausible non-radical mechanism involves the activation of a molecule of dioxygen by the coordinatively unsaturated $[RuCl(DPP)_2]^+$ cation. However, as there is no evidence for the complexation of dioxygen either to *trans*-$[RuCl_2(DPP)_2]$ or to $[RuCl(DPP)_2]ClO_4$, it seems unlikely that the present autoxidation involves oxygen activation. On the other hand we note that with the present ruthenium catalysts epoxidation occurs only in the presence of a terminal oxidant: since in this case convincing evidence of an oxo-metal species has been obtained [2a], such oxo-metal intermediate may be dismissed in the case of the oxidative cleavage with oxygen.

Complete suppression (or substantial inhibition) of the catalytic activity is observed when the aerobic oxidation is conducted in the presence of free-radical traps, such as 2,6-di-t-butyl-4-methylphenol or 1,3-dinitrobenzene (in a 20% molar ratio to the catalyst). This and the fact that significant and erratic induction times (up to 5 h) are always observed at the onset of the oxidations, strongly point to a homolytic origin for the oxidation products, in a route involving the formation of styrene radicals, followed either by trapping by the radical scavengers or further oxidation. Significantly, anaerobic oxidation of styrene by iodosylbenzene in the presence of the same metal complexes is not affected by the presence of chain stopping reagents [2a].

The mechanism can reasonably be assumed to be similar to that recently proposed by Hecht for the closely related oxygen-oxidation of *cis*-stilbene by Fe-bleomycin [4b,6], which enables formation of an alkene cation radical reactive intermediate via an one-electron transfer to the metal in an oxidised state. It is relevant to note that the conventional oxidative cleavage of alkenes by RuO_4, which involves a cyclic ruthenium(IV) diester intermediate, is also thought to proceed via a radical alkene cation-perruthenium transition state [3].

In the above formulation an outer-sphere oxidation of the ruthenium(II) complex with molecular oxygen can be envisaged, either involving direct two-electron transfer from the metal, to form a ruthenium(IV) complex and peroxide, or an one-electron transfer to give ruthenium(III) and superoxide (eq. 2), which could disproportionate to yield peroxide [7]. The high-valent metal complex could now generate the radical cation (eq. 3), which can be oxidised by a dioxygen species to the carbonylic derivatives (eq. 4). It should be noted that oxidation rates are not affected by oxygen pressure (0.1–1 atm).

$$Ru^{II} + O_2 \rightarrow Ru^{IV} + O_2^{II-}(Ru^{III} + O_2^{I-}) \qquad (2)$$

$$Ru^{IV}(Ru^{III}) + PhCH{=}CH_2 \rightarrow Ru^{II} + PhCHCH_2^+ \qquad (3)$$

$$PhCHCH_2^+ + (O_2 + e) \rightarrow \rightarrow PhCHO + HCHO \qquad (4)$$

A kinetic investigation of this system involving use of initial reaction rates was carried out. As the styrene concentration was increased, with the concentration of catalyst kept constant there was a proportionate increase in the rate of formation of benzaldehyde for the styrene concentration range 0.3–2.0 *M* (Fig. 1). At lower concentrations, the degree of conversion of styrene was too small for initial reaction rate data to be significant. The effect of varying the concentration of $[RuCl(DPP)_2]ClO_4$ on the yield of benzaldehyde in the oxidation of styrene is shown in Fig. 2. As the initial catalyst concentration is increased, the rate increases until a maximum is reached at about 13 m*M* (normal reaction conditions). Upon further increase in the catalyst concentration, the rate drops markedly becoming practically zero at 30 m*M* concentration and above.

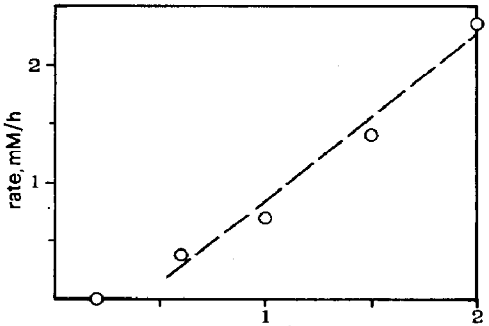

Fig. 1. Rate of benzaldehyde formation, m*M*/h, vs. styrene concentration, (*M*) in dichloromethane using $[RuCl(DPP)_2]PF_6$ 4 m*M*, at 22° C in air (at atmospheric pressure).

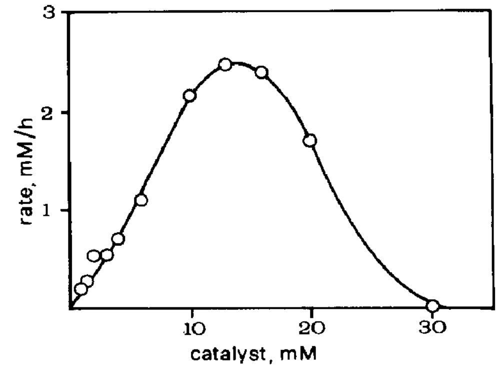

Fig. 2. Catalyst concentration study: rate of benzaldehyde formation mM/h, vs. $[RuCl(DPP)_2]PF_6$ concentration (mM) in dichloromethane and styrene 1 M, at 22° C in air (at atmospheric pressure).

We cannot yet provide a firmly based explanation of the loss of activity of this catalytic system, although it is apparent that at high concentrations the catalysts themselves act as substrates that effectively compete with styrene for the active metal intermediates. The formation of stable and inert peroxo-bridged ruthenium(III) complexes, reminiscent of iron(II) porphyrin chemistry [8], must also be tentatively considered as responsible for the inactivation of the catalysts (eq. 5).

$$2Ru^{II} + O_2 \rightarrow Ru^{III}OORu^{III} \qquad (5)$$

Nevertheless, the largely predominant metallorganic species during the oxidation reaction, both at lower and higher catalyst concentrations, were always the $[RuCl(DPP)_2]ClO_4$ or *trans*-$[RuCl_2(DPP)_2]$ complexes, as demonstrated by ^{31}P NMR spectroscopy.

Experimental

Materials. Styrene was purified by chromatography on alumina and stored at −20° C. Iodosylbenzene was purchased from K&K Laboratoriums 1,3-bis(diphenylphosphino)propane (DPP) was purchased from Strem Chemicals. The complexes $[RuCl(DPP)_2]Y$ ($Y = ClO_4$, PF_6) were prepared, as previously described [5], by refluxing ethanolic suspensions of the corresponding *trans*-$[RuCl_2(DPP)_2]$ in the presence of an excess of $NaClO_4$ or NH_4PF_6.

Instrumentation. NMR spectra were recorded on a JEOL FX 90 Q FT spectrometer. Organic analyses were carried out with a DANI 3800 gas chromatograph equipped with FID, using a 2 m Ucon LB 550 on Chromosorb W-AW 60–80 mesh column (2 mm i.d.) or a 30 m SE-30 capillary column (0.25 mm i.d.). The identity of each product was confirmed by examination of the fragmentation pattern in the mass spectra obtained with a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV.

Procedure for the catalytic oxidations. 1 ml of a dichloromethane solution containing 0.05–2.1 mmol of olefin, 0.5–30 mmol of catalyst and a gas-chromatographic standard (n-decane, 5 mM) were stirred magnetically in a 10 ml vial, and GLC analyses were performed on aliquots withdrawn at appropriate times with a microsyringe. The reactions were carried out at 22° C either under an inert atmosphere or oxygen, at 1 atm. Reaction rates were determined for early stages of the reaction (up to 10 turnovers), and were reproducible to within 10–15%.

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