Phosphino Complexes of Rhodium as Catalysts for the Aerobic and Anaerobic Oxidation of Hydrocarbons

MARIO BRESSAN and ANTONINO MORVILLO

Dipartimento di Chimica Inorganica, Università di Padova, via Marzolo 1, 35131 Padua (Italy)

Rhodium-based catalytic systems have been described in the recent literature, which are capable of oxygenating alkenes [1–6] and alkanes [7] in the presence of dioxygen, hydrogen peroxide or t-butyl hydroperoxide. We previously reported that [Rh-(diphosphine)$_2$]$^+$ complexes are able to catalyze the aerobic oxidation of alkenes with various activities and selectivities [8]. Now, as an extension of that investigation, we have found that the same phosphino complexes are also active in the catalytic oxygenation of alkenes and alkanes with single-oxygen oxidants, such as hypochlorites. The relationship in terms of catalytic behavior of these rhodium derivatives to the closely related diphosphino complexes of ruthenium-(II) [Ru(diphosphine)$_2$Cl]$^+$ is an important consideration [9].

In a typical experiment, the substrate (1×10^{-3} mol) and the catalyst [Rh(DPE)$_2$]BF$_4$ [DPE = 1,2-bis(diphenylphosphino)ethane] (2×10^{-6} mol) were dissolved in CH$_2$Cl$_2$ (1 ml) and stirred with 1 ml of an aqueous solution of 1 M LiClO at room temperature. GLC analyses were performed on aliquots withdrawn with an hypodermic syringe. The identity of each product was confirmed by comparison of the mass spectral cracking patterns. The catalytic system maintains the initial activity for a limited number of turnovers (at best *c.* 150 cycles), until the organic layer bleaches, due to complete collapse of the metal complex. During both alkane- and alkene-oxidations with hypochlorite, moderate amounts (less than 20%) of chloro derivatives were also formed. The fact that other oxidants, like KHSO$_5$ or PhIO, do not lead to the formation of chloro derivatives indicates that hypochlorous acid, and not the chlorinated solvent, is responsible for the chlorination [10].

[Rh(DPE)$_2$]BF$_4$ catalyzes oxygen transfers from hypochlorite to alkenes and to cycloalkanes, but not to linear-chain alkanes (Table 1). Tertiary CH groups of adamantane are converted into tertiary alcohols, and methylene groups of adamantane and cyclohexane into ketones, with no evidence of the formation of secondary alcohols. The large ratio of the tertiary position oxidations to the secondary, found for adamantane oxidation, implies a free-radical path, where hydrogen abstraction occurs in preference on

TABLE 1. [Rh(DPE)$_2$]BF$_4$-catalyzed oxidation of hydrocarbons

Substrate major products	Catalytic activity [a]	
	LiClO [b]	O$_2$ [c]
1-Octene	0	0.3
2-octanone		90%
oct-3-en-2-one		10%
2-Octene	0.04	0.01
oct-3-en-2-one	70%	
octene-2,3-dioxide	30%	
2- and 3-octanone		75%
1- and 4-methoxy-oct-2-ene		25%
Styrene	3.8	0.4
styrene oxide	65%	
benzaldehyde	25%	
phenylacetaldehyde	10%	
acetophenone		>95%
Cyclohexene	1.2	0.5
cyclohexene oxide	85%	
cyclohexen-2-ol	15%	
2-methoxycyclohexene		80%
cyclohexanone		10%
Adamantane [d]	1.7	0
1-adamantanol	90%	
adamantanone	10%	
Cyclohexane	0.5	0
cyclohexanone	>95%	

[a]Initial rate, turnovers per hour. [b]Catalyst, 2 mM, and substrate, 1 M, in CH$_2$Cl$_2$; LiClO, 1 M, in H$_2$O; 20 °C. [c]Catalyst, 50 mM, and substrate, 1.25 M, with O$_2$ (1 atm) in CH$_3$OH and in the presence of CH$_3$SO$_3$H, 50 mM, at 50 °C. [d]0.5 M.

the tertiary carbons. The present rhodium/hypochlorite combination represents one of the few examples of rhodium-based catalysts capable of preferentially converting alkenes into epoxides, although other oxidation pathways, i.e. allylic attack and oxidative cleavage, often simultaneously operate (Table 1).

In the presence of aqueous hypochlorite, the orange dichloromethane solutions of [Rh(DPE)$_2$]BF$_4$ immediately turn yellow with formation of minor amounts (*c.* 30%) of diphosphine dioxide, as evidenced by the appearance in the ^{31}P NMR spectra of the characteristic single resonance at 31.4 ppm. The diagnostic doublet of [Rh(DPE)$_2$]BF$_4$ at 57.6 ppm ($J_{Rh-P} = 133$ Hz) disappears and is replaced by a deceptively simple spectral pattern, consisting of two couples of signals of equal intensity ($J_{P-P} = 12$ Hz), centered at 38.6 and 36.2 ppm, which clearly indicates

non-equivalence of the phosphorus atoms of the diphosphine and is tentatively attributed to an ABX $[P_1P_2Rh]$ spin system. This spectral pattern remains unchanged at lower temperatures. The observed large upfield shift strongly suggests that the formed species is a rhodium(III) and not a rhodium(I) derivative [11]. A yellow and still catalytically active product could be isolated in the solid state, the analytical elemental data of which, although consistent with a 1:1 diphosphine:rhodium ratio, were erratic and did not allow any convincing formulation. No $\nu(Rh=O)$ absorptions were detected in the 700–800 cm^{-1} region of the IR spectra.

Other simple diphosphino complexes of rhodium-(III), i.e. $[Rh(DPE)(SO_4)]BF_4$ [8b] and $[RhCl_2-(DPE)_2]BF_4$, catalyze the same hypochlorite oxidations, with comparable rates and selectivities, whereas rhodium trichloride, as well as the related iridium(I) derivative $[Ir(DPE)_2]BF_4$, are completely inactive. It is concluded that the catalytically active species in the hypochlorite oxidations might be complexed species of rhodium(III).

The mechanism through which $[Rh(DPE)_2]BF_4$ mediates the oxidation of the hydrocarbons in the presence of single-oxygen oxidants might reasonably be different from that of the oxidations with dioxygen, previously examined in detail [8a, c, d], where rhodium(I) derivatives are the active species. Different chemioselectivities were indeed observed for a representative choice of hydrocarbons, which are listed in Table 1. Alkanes are not affected by the oxygen oxidations, but undergo ready oxygenation in the presence of hypochlorite. The aerobic oxidation of styrene and of other terminal alkenes selectively leads to the corresponding methyl ketones, whereas a mixture of styrene oxide, benzaldehyde and phenylacetaldehyde is obtained when the oxidation of styrene is carried out in the presence of LiClO, 1-octene being recovered unchanged. Also, cyclohexene oxidation leads to different products if carried out aerobically (allylic attack) or in the presence of hypochlorite (epoxidation). Other single-oxygen oxidants, like PhIO and $KHSO_5$, exhibit chemioselectivities quite similar to those observed with LiClO, but with definitely lower conversions.

In the oxygen oxidations based on rhodium, dioxygen adducts of rhodium(I), often unstable at room temperature [12], have been repeatedly proposed as the catalytically active species, capable of reacting with the alkenes to give peroxo-metallacyclic intermediates [1]. Moreover, a co-reductant is often necessary, in order to scavenge the second oxygen atom and to close the catalytic cycle; whether or not a rhodium(III)–oxo derivative is responsible for the second oxygen transfer is still controversial, and other pathways have indeed been proposed [4]. In the case of the present $[Rh(diphosphine)_2]^+$ complexes, primary and secondary alcohols can be used as co-reductants, making the oxidation of the alkenes viable in these oxidizable solvents, but not in other media like dichloromethane.

The mechanism of the hypochlorite oxidations should involve either oxo–rhodium derivatives in high oxidation state (III or, less likely, V), acting as oxygen-transfer agents, or simply rhodium(III) complexes, capable of directly oxidizing the hydrocarbons in the presence of water via a Wacker-like mechanism. The combined evidence is, however, conflicting and does not allow one to distinguish between the two mechanisms. The oxo–rhodium pathway is strongly supported by the formation during the hypochlorite oxidation of styrene of minor but significant amounts of phenylacetaldehyde, which typically arise from a rearrangement of metal–oxo–carbocation intermediates (phenonium migration), formed either by reaction of metal–oxo species with the alkene [13] or by a metal–oxo-mediated isomerization of the epoxide [14]. The presence of oxo species, however, could not be confirmed by ^{18}O-incorporation experiments and no labeled norbornene oxide was produced during the catalytic PhIO oxidation of norbornene in the presence of $H_2^{18}O$, whereas oxo–metal species are expected to undergo fast oxygen-atom exchange with water [15].

References

1 H. Mimoun, M. M. Perez Machirant and I. Seree de Roch, *J. Am. Chem. Soc., 100* (1978) 5437.
2 M. Faraj, J. Martin, C. Martin, J. M. Bregeault and J. Mercier, *J. Mol. Catal., 31* (1985) 57.
3 P. Mueller and H. Idmounaz, *J. Organomet. Chem., 345* (1988) 187.
4 R. S. Drago, A. Zuzich and E. D. Nyberg, *J. Am. Chem. Soc., 107* (1985) 2898.
5 G. Read, *J. Mol. Catal., 44* (1988) 15.
6 H. Boenemann, W. Nunez and D. M. M. Rohe, *Helv. Chim. Acta, 66* (1983) 177.
7 L. W. Fine, M. Grayson and V. H. Suggs, *J. Organomet. Chem., 22* (1970) 219.
8 (a) A. Morvillo and M. Bressan, *J. Mol. Catal., 37* (1986) 63; (b) *Inorg. Chim. Acta, 121* (1986) 219; (c) M. Bressan, F. Morandini, A. Morvillo and P. Rigo, *J. Organomet. Chem., 280* (1985) 139; (d) M. Bressan, F. Morandini and P. Rigo, *J. Organomet. Chem., 247* (1983) C8.
9 M. Bressan and A. Morvillo, *J. Chem. Soc., Chem. Commun.,* (1989) 421; (1988) 650; *Inorg. Chem., 28* (1989) 950.

10 H. E. Fannoni, S. Khrisna, D. G. Kuhn and G. A. Hamilton, *J. Am. Chem. Soc., 105* (1983) 7672.

11 P. E. Garrou, *Chem. Rev., 81* (1981) 229.

12 B. R. James and D. Mahajan, *Can. J. Chem., 58* (1980) 996.

13 T. C. Bruice, *Aldrichim. Acta, 21* (1988) 87.

14 J. M. Garrison and T. C. Bruice, *J. Am. Chem. Soc., 111* (1989) 191; T. J. Collin, S. Ozaki and T. G. Richmond, *J. Chem. Soc., Chem. Commun.,* (1987) 803.

15 K. Srinivasan, P. Michaud and J. K. Kochi, *J. Am. Chem. Soc., 108* (1986) 2309.