Journal of Organometallic Chemistry, 276 (1984) C23—C26
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

HOMOGENEOUS OXIDATION OF 1-OCTENE BY t-BUTYL HYDROPEROXIDE CATALYZED BY RHODIUM(III) SPECIES

MAHMOUD FARAJ, JEAN-MARIE BRÉGEAULT*, JACQUES MARTIN and CLAUDINE MARTIN

Université Pierre et Marie Curie, Laboratoire de Cinétique Chimique, 1 rue Guy de la Brosse, 75005 Paris (France)

(Received July 18th, 1984)

Summary

Chlororhodium(III) complexes catalyze the oxidation of oct-1-ene by t-BuOOH in R^1R^2CHOH, to yield products of dioxygen oxidation: i.e. the methyl ketone resulting from olefin oxidation, the acetal or ketone formed by solvent cooxidation, and isomerized olefins.

Introduction

A new class of stable alkylperoxidic palladium complexes with the formula $[RCO_2Pd(OO\text{-}t\text{-}Bu)]_4$ has been recently synthesized [1]; the complexes transfer oxygen to terminal olefins, to form methyl ketones. Related palladium-catalyzed ketonization of terminal olefins by alkyl hydroperoxides has been demonstrated [2,3].

Treatment of $[(Ph_3P)_2PtO_2]$ with benzoyl chloride in the presence of an olefin gave the corresponding epoxides [4]; a reactive acyl(peroxi)platinum intermediate was identified at low temperatures. Following that work, several related contributions appeared [5—7]. Ketonization of olefins by "PtOO-t-Bu" species has also been demonstrated [5,6].

Rhodium and iridium complexes are expected to catalyse the decomposition of alkyl hydroperoxides to radicals $RO^•$ and $RO_2^•$ [8—12]. However, treatment of the residue from the reaction of t-butyl hydroperoxide with $[IrCl(CO)L_2]$ (L = PPh_3; $AsPh_3$ or PPh_2Me) gave at least two products; a yellow complex was identified as the bis-t-butylperoxy oxidation adduct [11—13]. An investigation of the rhodium(II) acetate-catalyzed oxidation of olefins in which α,β-unsaturated ketones (enones) were formed as the major products from cyclic olefins was recently reported [14].

0022-328X/84/$03.00

In order to improve the understanding of the catalysis cycle for Mimoun's system ("$RhCl_3 \cdot 3H_2O$"/$Cu(ClO_4)_2 \cdot 4HMPA$) [15], which is effective in the oxidation of 1-alkenes to methyl ketones by dioxygen in alcoholic media, we decided to investigate the reactions of some new precursors [16]. It was also important to study the reactions of rhodium(III) precursors with other oxidizing agents. We present below some preliminary results on the activation of t-butyl hydroperoxide by rhodium precursors for the oxidation of oct-1-ene to octan-2-one.

Results and discussion

For a typical run at 25°C the glass reactor was charged with a catalyst precursor, e.g. 13.45 mg "$RhCl_3 \cdot 3H_2O$" (0.05 mmol), 1.4 cm^3 EtOH, and 0.6 cm^3 oct-1-ene (3.82 mmol). Pure nitrogen was introduced, then 0.55 cm^3 t-BuOOH (70% aqueous solution; 3.82 mmol) was added through a serum cap. After vigorous stirring for 24 h, GLC analysis showed the formation of octan-2-one in 37% yield based on t-BuOOH (or oct-1-ene) (Table 1, run 1). This implies that other processes can compete.

TABLE 1

OXIDATION OF OCT-1-ENE CATALYZED BY RHODIUM(III) SPECIES

Run[d]	T (°C)	t-BuOOH/alkene (mmol/mmol)	Time (h)	Precursors[e]	Yield of octan-2-one (%)	Yield of octan-2-one mmol/mmol Rh	(Internal olefins) × 100/ Σ octenes
1	25	1 (3.82/3.82)	24	1	37[a]	28	
2	25	2 (7.64/3.82)	24	1	43[a]	32	
3	60	(1/6.35)	4	2 + 3LiCl	74[b]	15	91
4	60	(1/6.35)	4	2 + 2$Cu(BF_4)_2$ + 3LiCl	90[b]	21	11
5	60	1 (3.82/3.82)	4	3	23[a]	18	
6	60	1 (3.82/3.82)	4	3 + 2HCl	41[a]	30	
				3 + 1$BiCl_3$			34
7	60	1 (3.82/3.82)	4	3 + 2LiCl	24[a]	19	25
8[c]	60	1 (3.82/3.82)	4	3 + 2HCl	17	13	

[a] (Octan-2-one/oct-1-ene) × 100. [b] (Octan-2-one/t-BuOOH) × 100. [c] Hexan-2-ol (solvent); mmol hexan-2-one 1.22; [d] EtOH: 1.4 cm^3 (solvent) runs 1—7. [e] 1: "$RhCl_3 \cdot 3H_2O$" $\simeq 0.02$ mol l^{-1}; 2: $[Rh(H_2O)_6](ClO_4)_3 \simeq 0.02$ mol l^{-1}; 3: $[Rh(C_2H_4)_2Cl]_2 \simeq 0.02$ mol l^{-1}.

Increasing the temperature up to 60°C resulted in a faster oxidation of oct-1-ene, as can be seen from Fig. 1. Going to temperatures above 60°C has little or no effect on the initial rate. This behaviour reflects the complexity of the reaction mechanism.

The reaction may be carried out in alcoholic solvents (with primary or secondary alcohols, e.g. ethanol, butan-1-ol, hexan-1-ol, hexan-2-ol). Solvents such as t-butyl alcohol, dichloroethane, ethyl acetate, DMF, and butanone, were found to be strong inhibitors of the reaction. The complexity of the solvent dependence is illustrated by the following rate sequence: ethanol ≃ butan-1-ol > methanol > hexan-1-ol > hexan-2-ol. Coordination of the olefin to the metallic centre must be a key step, and this is strongly inhibited by competing σ-donor solvents.

When "$RhCl_3 \cdot 3H_2O$" was used as precursor at 60°C (oct-1-ene/Rh $\simeq$ 127 in EtOH as solvent (1.4 cm^3) and 70% t-BuOOH (1 mmol) as oxidant [t-BuOOH/oct-1-ene 1/6.35; oct-1-ene 1 cm^3], octan-2-one was formed selectively, and the overall yield after 4 h corresponded closely (86%) to the t-BuOOH consumption. Octan-3- and -4-one were not detected, and no octanal was identified. Table 1 shows that the use of an excess of t-BuOOH (t-BuOOH/oct-1-ene $\simeq$ 2) does not give complete conversion of the olefin, and that it is more convenient to use lower ratios.

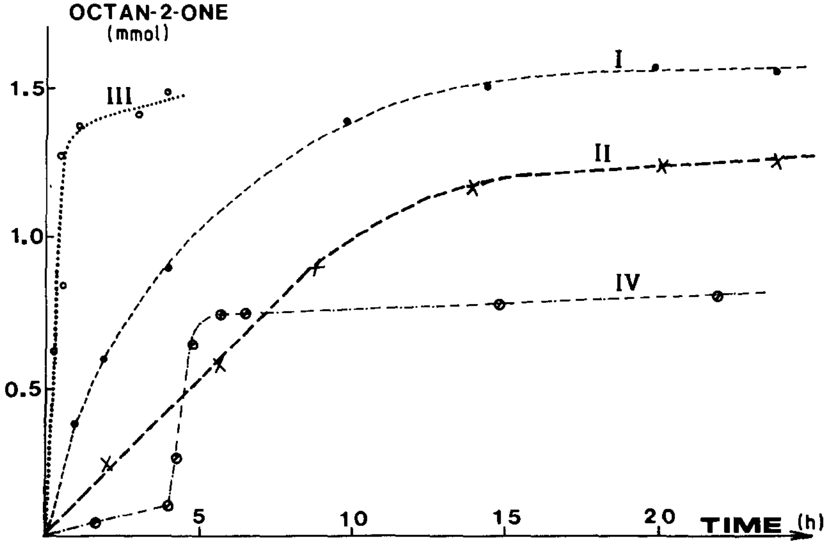

Fig. 1. Oxidation of oct-1-ene: 3.82 mmol; t-BuOOH: 3.82 mmol; solvent: EtOH (1.4 cm^3); Rh: 0.02 mol l^{-1}; olefin/Rh = 75. Curve I: $[Rh(\mu\text{-}CF_3COO)(CO)_2]_2$ initially treated with t-BuOOH; temperature: 25°C; yield: 40%. Curve II: 1: temperature 25°C; yield 33%. Curve III: 1; temperature 60°C; yield 38%. Curve IV: 2 + LiCl: 0.06 mol l^{-1} after 4 h; yield 21%; temperature 60°C.

The influence of the nature of the rhodium catalysts on the oxidation of oct-1-ene by t-BuOOH is shown in Table 1 (temperature: 60°C). Trivalent rhodium complexes such as "$RhCl_3 \cdot 3H_2O$", $[HRhCl_2[P(C_6H_5)_2(n\text{-}Bu)]_3]$, or systems such as $[Rh(H_2O)_6](ClO_4)_3$ + 3LiCl, or $[Rh(H_2O)_6](ClO_4)_3$ + $2Cu(BF_4)_2$ + 3LiCl (runs 3 and 4), were also effective as catalyst precursors, but monovalent rhodium precursors such as $[RhCl(C_2H_4)_2]_2$ and $[RhCl(CO)_2]_2$ were less efficient. Rhodium complexes bearing strongly coordinating anions such as trifluoro- (tfacac) and hexafluoro-acetylacetonate (hfacac), namely $[Rh(tfacac)(CO)_2]$ and $[Rh(hfacac)(CO)_2]$, were found to be almost inactive. The introduction of two or three Cl ligands per rhodium atom (by addition of LiCl, HCl, or $BiCl_3$, etc.) leads to the activation of the catalyst precursor (Table 1: runs 5 and 6 and Fig. 1), suggesting that exchange at the rhodium centre is necessary; it therefore seems likely that the precursors are "$Rh^{III}Cl_x$" species. The maximum turnover of the catalyst in the oxygenations is currently about 35. Extensive double bond migration in the recovered octene was demonstrated by capillary GLC, *cis*- and *trans*-oct-2-ene were mainly formed, and so we suggest that "$HRhCl_xL_y$" species form one of the key types of intermediates in the catalytic system, as in the "Rh/Cu/Li" system [16], which is one of the best precursors for O_2 activation in EtOH. It appears that introduction of Cu^{2+} reduces the extent of isomerization (Table 1: runs 3 and 4).

All the GLC essays show that regardless of the catalyst precursors considered, there is another, competitive, reaction taking place alongside 1-alkene ketonization and isomerization. It is difficult to exclude a process involving oxidation of the primary or secondary alcohol solvent used to enhance the olefin oxidation (Table 1, run 8).

The presence of water has little effect on the reaction, and its inhibiting effect is less than that of t-BuOH (vide infra). Addition of non-coordinating strong acids such as (HCl, p-$CH_3C_6H_4SO_3H$, acid/Rh $\simeq$ 2) resulted in better conversion of the olefin (Table 1, runs 5 and 6).

In a typical oxidation with a stoichiometric or smaller amount of t-BuOOH, oxidation of oct-1-ene slows substantially after 35 turnovers. The deactivation of the catalyst (demonstrated by the decrease in rate) is accompanied by a change of colour (orange red to yellow). It appears that the decline in catalytic activities is mainly due to formation of t-BuOH which coordinates to the metal. The extent of the auto-retardation must be related to the ratio of the equilibrium constants for the formation of catalyst-hydroperoxide and catalyst-alcohol complexes.

The reactivities of several different linear olefins towards t-BuOOH in the presence of rhodium precursors were also examined. Only terminal olefins are transformed to methyl ketones.

A likely explanation of the results is that chloride ions (or CF_3COO^-) effectively stabilize the coordination of the oxidizing group (e.g. OH or OO-t-Bu, etc.) and of the 1-alkene:

$$HRhCl_xL_y + \text{t-BuOOH} \rightarrow HORhCl_xL_y + \text{t-BuOH} \quad (L = HOR) \qquad (1)$$

In this case the active species must be a hydroxy complex. An alternative process is:

$$HRhCl_xL_y + \text{t-BuOOH} \rightarrow HRhCl_{x-1}L_y(\text{OO-t-Bu}) + H^+ + Cl^- \qquad (2)$$

So far, attempts to isolate alkylhydroperoxidic rhodium(III) species have failed.

References

1 H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer and R. Weiss, J. Am. Chem. Soc., 102 (1980) 1047.
2 P.G. Field and D.A. Lock, U.S. Patent 3 891 711 (to Burmah Oil Company) 1975.
3 H. Mimoun, R. Charpentier, French Demande 7 900 828, 1979.
4 M.J.Y. Chen and J.K. Kochi, J. Chem. Soc., Chem. Comm., (1977) 204.
5 J.M. Brégeault and H. Mimoun, Nouv. J. Chim., 5 (1981) 287.
6 G. Strukul, R. Ros and R.A. Michelin, Inorg. Chem., 21 (1982) 495.
7 Y. Tatsuno and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 5832.
8 V.P. Kurkov, J.Z. Pasky and J.B. Lavigne, J. Am. Chem. Soc., 90 (1968) 4743.
9 L.W. Fine, M. Grayson and V.H. Suggs, J. Organomet. Chem., 22 (1970) 219.
10 A. Fusi, R. Ugo, F. Fox, A. Pasini and S. Cenini, J. Organomet. Chem., 26 (1971) 417.
11 B.L. Booth, R.N. Haszeldine and G.R.H. Neuss, J. Chem. Soc., Chem. Comm., (1972) 1074.
12 B.L. Booth, R.N. Haszeldine and G.R.H. Neuss, J. Chem. Soc., Perkin Trans. I, (1975) 209.
13 I.J. Harvie and F.J. McQuillin, J. Chem. Soc., Chem. Comm., (1976) 369.
14 S. Uemura and S.R. Patil, Chem. Lett., (1982) 1743.
15 H. Mimoun, M. Mercedes Perez Machirant and I. Sérée de Roch, J. Am. Chem. Soc., 100 (1978) 5437.
16 M. Faraj, J. Martin, C. Martin, J.M. Brégeault and J. Mercier, J. Mol. Cat., to be published.