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A possible molecular pathway for the catalytic oxidation of secondary alcohols to ketones with hydrogen peroxide using platinum(II) complexes as catalysts

Roberto Zennaro, Francesco Pinna, Giorgio Strukul*
Department of Chemistry, University of Venice, Dorsoduro 2137, 30123 Venice (Italy)

and **Henri Arzoumanian**
Ecole Nationale Supérieure de Synthèses, de Procédés et d'Ingénieurie Chimique d'Aix-Marseille, URA du CNRS 1410, Université d'Aix-Marseille, 13397 Marseilles (France)

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Abstract

Attempts to accomplish the oxidation of secondary alcohols to ketones using hydrogen peroxide as oxidants and [(dppe)Pt(CF_3)(CH_2Cl_2)] ClO_4 as catalyst are reported. The β-hydride elimination from an alkoxy complex was shown to produce the corresponding ketone and (dppe)Pt(CF_3)H. Oxidation of the Pt–H bond in this complex with H_2O_2 or (dppe)Pt(CF_3)(OOH) yielded (dppe)Pt(CF_3)(OH), thereby revealing the possibility of a heterolytic catalytic pathway. Attempts to carry out the catalytic oxidation of a variety of alcohols produced appreciable amounts of ketones, but the reaction was recognized, with one significant exception, to be essentially homolytic in nature.

Introduction

Late transition metal alkoxy complexes are interesting compounds that possess fairly wide reactivity and are potentially relevant to homogeneous catalysis [1]. One of the most interesting reactions of this class of complexes is the β-hydride elimination, which has been only occasionally reported, especially for synthetic purposes in the preparation of metal hydrides [2], although its reverse reaction is widespread in catalytic hydrogenation processes. Associated with β-hydride elimination from alkoxy complexes is the formation of organic carbonyl compounds, which have been clearly identified in the case of certain Pt(II), Rh(III) and Ir(I) complexes [3] (reaction (1)).

(1)

This process may constitute a good basis for a catalytic system aimed at the conversion of secondary alcohols into ketones, provided that a suitable

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*Author to whom correspondence should be addressed.

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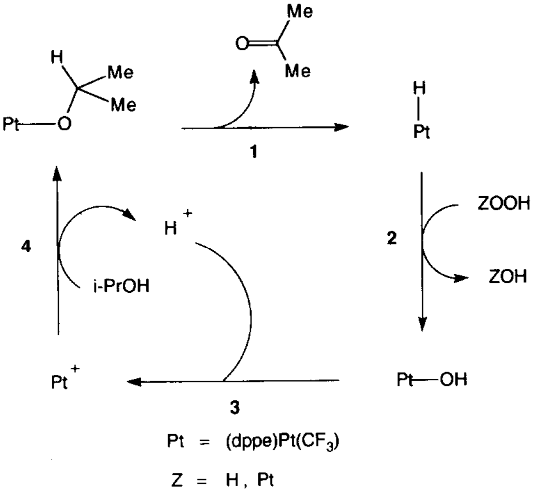
oxidant is found which is capable of removing the hydride ligand and regenerating the starting materials, leading to metal–alkoxy formation. This has been often accomplished by hydride transfer to an unsaturated molecule (olefins or ketones) thereby giving rise to a second (and in principle unnecessary) organic coproduct [4]. To avoid this, an alternative might be the oxidation of the hydride to water. In this note we wish to report our attempts to set up the molecular steps leading to this end, and to carry out catalytically the resulting oxidation of alcohols to ketones.

Results and discussion

For this study we directed our attention toward platinum(II) alkoxy complexes because they are by far the most stable and widespread complexes of this class [1]. The chemistry investigated is summarized in Scheme 1, which outlines the possible catalytic cycle.



Scheme 1.

We first tested the feasibility of reaction (1) by synthesizing (dppe)Pt(CF_3)(OPr^i) (see Experimental section for spectroscopic characterization), starting from (dppe)Pt(CF_3)Cl and Na(OPr^i), and then reacting it at room temperature in isopropanol. The reaction was carried out in isopropanol under N_2 in a Schlenk tube, and monitored by IR analysis by periodically removing small aliquots. As the reaction proceeded the solid isolated showed a decrease in the $\nu(O–Pr^i)$ band at 1180 cm^{-1} and an increase in a new band at 2030 cm^{-1}. After 10 days quantitative formation of acetone in the liquid phase was revealed by GLC. Removal of the solvent left a white solid that was recognized to be pure (dppe)Pt(CF_3)H by its spectroscopic features (IR (nujol): 2030 cm^{-1}; ^{19}F NMR (CD_2Cl_2): δ ($CFCl_3$) -10.61 ppm (dt);

^3J(FH) 14.5, ^3J(FP-*cis* 14.5, ^3J(FP-*trans*) 57.5, ^2J(FPt) 757 Hz) and by comparison with an authentic sample [5].

Using the same experimental conditions, similar results were also obtained starting from [(dppe)Pt(CF_3)(CH_2Cl_2] ClO_4 and reacting it with i-PrOH, *i.e.* coupling reactions (4) and (1). However, in this case, the ^{19}F NMR spectrum of the solid mixture isolated from solution showed that only ~40% of the starting compound had reacted. Finally, no reaction was observed when starting from (dppe)Pt(CF_3)(OH).

Since reaction (3) was repeatedly observed in our studies of the catalytic properties of these Pt(II) complexes [6, 7], the gap remaining to close the catalytic cycle shown in Scheme 1 is reaction (2).

To oxidize the hydride ligand we first tested (dppe)Pt(CF_3)(OOH) [8]. This and other homologous species were recognized to be the actual oxidants in the catalytic epoxidation of olefins with (P–P)Pt(CF_3)X complexes (P–P = various diphosphines; X = solvent, –OH) using hydrogen peroxide as primary oxidant [6]. Hence, equimolar amounts (0.03 mmol) of the Pt–H and Pt–OOH species were dissolved in CD_2Cl_2 and the progress of the reaction was monitored by ^{19}F NMR spectroscopy. Thirty min after mixing, in addition to (dppe)Pt(CF_3)H and (dppe)Pt(CF_3(OOH) (δ($CFCl_3$) -28.33 ppm (dd); ^3J(FP-*cis*) 11.1, ^3J(FP-*trans*) 60.1, ^2J(FPt) 553 Hz) the spectrum also showed the presence of a small amount of a third species (δ)$CFCl_3$) -28.53 ppm (dd); ^3J(FP-*cis*) 9.2, ^3J(FP-*trans*) 55.1, ^2J(FPt) 591 Hz) which was recognized to be (dppe)Pt(CF_3)(OH) [9]. The reaction proceeded slowly and after 3 days ~30-35% of the starting complexes had converted into Pt–OH.

Better results were obtained when Pt–H (0.03 mmol) dissolved in CD_2Cl_2 was reacted with excess 35% H_2O_2 (0.2 mmol). Again, ^{19}F NMR spectra showed the rapid formation of (dppe)Pt(CF_3)(OOH) (arising from reaction of Pt–OH and excess H_2O_2 [8]) and the reaction was virtually complete in ~3 h.

The above results suggest that the catalytic cycle of Scheme 1 could indeed occur, and its chemistry may constitute an alternative route for the oxidation of alcohols to ketones using H_2O_2 as oxidant. In fact, while no examples of the use of Group VIII metals have been reported to our knowledge, prior work in this field has dealt only with peroxo complexes of Mo(VI), W(VI) and V(V) that can be formed by reaction with hydrogen peroxide [10].

The use of [(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4 as catalyst for the oxidation of a variety of alcohols with hydrogen peroxide was tested at 75–83 °C. This choice is due to the slow β-hydride elimination process, as reported above for reactions (4) and (1). The results obtained are reported in Table 1. The selectivity observed was in most cases > 98% with a few exceptions, *i.e.* run 4 where the cyclohexanone produced is partly converted into caprolactone through Baeyer–Villiger type oxidation [11] or run 9 where the solvent DMSO was partly oxidized to dimethylsulfone. As shown, best results were obtained when using a two-phase system consisting of DCE/H_2O, while monophasic mixtures as in runs 2, 5, 6 and 8 gave lower amounts

TABLE 1

Catalytic oxidation of alcohols with hydrogen peroxide using [(dppe)M($CF_3(CH_2Cl_2)$)] ClO_4 as catalyst; M = Pd, Pt[a]

Run	M	Substrate	Time (h)	Temp (°C)	Solvent	Product (mmol)
1	Pt	2-hexanol	96	75	DCE	1.32
2	Pt	2-hexanol	96	75	pyridine	0.14
3	Pt	2-octanol	28	75	DCE	0.49
4	Pt	cyclohexanol	70	75	DCE	0.40[b]
5	Pt	cyclohexanol	96	75	pyridine	0.27
6	Pt	cyclohexanol	48	75	cyclohexanol	0.09
7	Pt	2-propanol	19	25	DCE	0.09
8	Pt	2-butanol	22	75	[c]	0.03
9	Pt	2-butanol	23	70	DMSO	1.40[d]
10	Pt	menthol	22	83	DCE	0.06
11	Pt	benzyl alcohol	25	83	DCE	0.74
12	Pt	cyclopentanol	23	83	DCE	0.67
13	Pd	2-propanol	6	25	DCE	0.05
14	Pd	2-propanol	7	25	2-propanol	0.15
15	Pd	2-butanol	8	25	DCE	0.05
16	Pd	2-butanol	6	25	2-butanol	0.12
17	Pd	2-butanol	2	54	2-butanol	0.45

[a] Experimental conditions: metal 0.04 mmol, alcohol 4 mmol, solvent 2.5 ml, 30% H_2O_2 4 mmol, N_2 1 atm.

[b] Cyclohexanone partly (25%) oxidized to caprolactone.

[c] 2-Butanol/THF 2/1 (vol) used as solvent.

[d] Dimethylsulfone (0.07 mmol) also formed.

of product. This is particularly surprising in the case of run 6, in which the alcohol itself was used as solvent. The use of pyridine as solvent gave unexpected results since it is conceivable that pyridine should ease the deprotonation of the alcohol [10a] (reaction (4)). Blank reactions carried out in the absence of catalyst under identical conditions showed that a spontaneous oxidation can occur to an extent <10% of the amounts of products indicated in Table 1.

The homologous Pd complex (dppe)Pd($CF_3(CH_2Cl_2)$)]ClO_4 was also tested as catalyst, since it is known that Pd species are more effective in promoting β-hydride elimination. This species can operate at 25 °C, while it decomposes at high temperatures. The results obtained, reported in Table 1, indicate a faster reaction, but the overall yields are again modest.

The use of relatively high temperatures lead to partial decomposition of the oxidant. We observed by random checks in Table 1 that the amount of H_2O_2 consumed at different times was always 2–3times the amount of product formed. This suggests that hydroxy or hydroperoxy radicals may be present in the working catalytic system and have some influence on product formation. Therefore, we tested the oxidation of cyclopentanol in the presence of radical scavangers (di-t-butyl-*p*-cresol or DTBPC) and radical

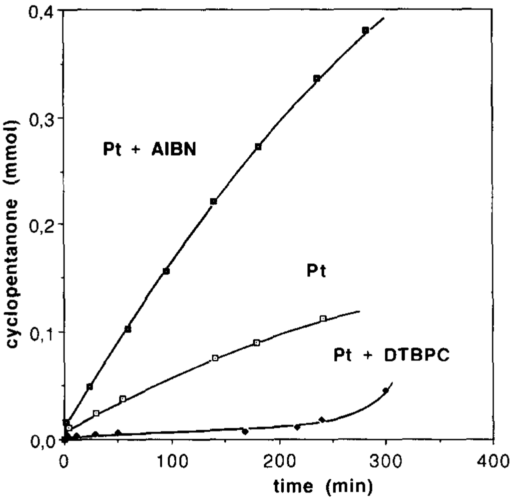


Fig. 1. Effect of the addition of a 10-fold excess of AIBN or DTBPC on the oxidation of cyclopentanol with hydrogen peroxide using [(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4 as catalyst. Experimental conditions as in run 12, Table 1.

initiators (azo-bis-(isobutyro)nitrile or AIBN). A summary of the results obtained in a typical reaction with Pt as catalyst using the same experimental conditions of Table 1 is reported in Fig. 1. It is seen that the reaction is strongly retarded by an excess of DTBPC and the activity is increased by AIBN. Similar results were obtained with Pd and 2-butanol at room temperature. These observations strongly support the idea that, under the experimental conditions of Fig. 1, the reaction is of a mostly radical nature. The only exception is the oxidation of isopropanol carried out at room temperature with the Pt complex as catalyst, in which in fact no effects were observed with either DTBPC or AIBN. This observation suggests that a heterolytic pathway as depicted in Scheme 1 is indeed viable for Pt, although, due to the slow β-hydride elimination step from this class of Pt(II) complexes, rather limited in scope, at least for the moment.

Experimental

Apparatus

IR spectra were taken on a Perkin-Elmer 683 spectrophotometer in Nujol mulls using CsI plates. ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT 80A spectrometer operating in the FT mode, using as external references $CFCl_3$ and 85% H_3PO_4, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator.

Identification of products was made with GLC by comparison with authentic samples.

Materials

Solvents were dried and purified according to standard methods. Alcohols were purified by passing through neutral alumina prior to use. Hydrogen peroxide (30% from Fluka), DBPC, AIBN (both from Fluka) and the oxidation reaction products were commercial products and used without purification.

The following compounds were prepared according to literature procedures: $(dppe)Pd(CF_3)(CH_2Cl_2)]ClO_4$ [8], $(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4$ [9], $(dppe)Pt(CF_3)(OH)$ [9], $(dppe)Pt(CF_3)Cl$ [9], $(dppe)Pt(CF_3(OOH)$ [8], $(dppe)Pt(CF_3)H$ [5].

Preparation of (dppe)Pt(CF$_3$)(O-Pr^i)

This complex was prepared under dry N_2 using conventional Schlenk and syringe techniques. The complex $(dppe)Pt(CF_3)Cl$ (0.800 g, 1.15 mmol) was suspended in 60 ml dry degassed benzene. To the mixture, kept on an ice bath, a solution (1.2 M in isopropanol) of sodium isopropylate (5.75 mmol) was added dropwise with stirring. The mixture was reacted for 6 h and allowed to warm slowly to room temperature. The resulting solution was brought to dryness *in vacuo* and extracted with CH_2Cl_2. The filtrate was concentrated and heptane was added. The white solid obtained was filtered, washed with Et_2O, dried, and recrystallized from CH_2Cl_2/Et_2O. Yield 72%. Anal. (%) Calcd. for $C_{30}H_{31}F_3OP_2Pt$: C, 49.93; H, 4.33%. Found: C, 50.21; H, 4.05% IR (cm^{-1}): 1180 s (ν O–Pr^i). ^1H NMR (CD_2Cl_2, 27 °C)*: δ 2.72 (d, CH_3); $^3J(HH)$ 2.4 Hz. ^{19}F NMR (CD_2Cl_2, 27 °C): δ −27.92 (dd); ^3J(FP-*cis*) 10.0, ^3J(FP-*trans*) 59.1, ^2J(FPt)555 Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 27 °C): δ 39.43 (dq, P *trans* CF_3); ^3J(PF)59.1, ^2J(PP)4.9, ^1J(PPt)1980 Hz; δ 31.40 (dq, P *cis* CF_3); ^3J(PF)9.9, ^2J(PP)4.9, ^1J(PPt)3895 Hz.

Catalytic reactions

These were carried out in a 25 ml round-bottomed flask equipped with a reflux condenser, a stopcock for vacuum/N_2 operations and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature was maintained with an external oil bath equipped with a Vertex thermometer. Stirring was performed by a Tefloncoated bar driven externally by a magnetic stirrer. The concentration of the commercial H_2O_2 solution was checked iodometrically prior to use.

The following general procedure was followed:

The catalyst (0.04 mmol) was placed solid in the reactor which was evacuated and filled with N_2. Purified, N_2-saturated solvent (2.5 ml) followed by the

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*The proton NMR spectrum of this complex clearly shows the doublet corresponding to 6 protons of the two methyl groups of the isopropoxy ligand, while we could not locate the signal corresponding to the central proton, which should consist of a septet with further splitting [8] by coupling with the two different phosphorus atoms (for a total of 28 lines) flanked by Pt satellites.

alcohol substrate (4.0 mmol) were added under N_2 flow. After heating at the required temperature under stirring, a 30% H_2O_2 solution (4.0 mmol) was injected through the septum and time was started. All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the catalyst with LiCl did not show any differences in randomly selected analyses. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector.

Acknowledgements

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