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Lewis acidic complexes of platinum(II): a mechanistic study of the Baeyer–Villiger oxidation of methylcyclohexanone with hydrogen peroxide catalyzed by $[(\text{triphosPO})\text{Pt}]^{2+}$ species

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Abstract

A kinetic study of the Baeyer–Villiger epoxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})\text{Pt}(\text{CH}_2\text{Cl}_2)]^{2+}$ is reported based on initial rate analysis. The mechanism suggested involves coordination of the ketone to the coordinatively unsaturated complex, followed by nucleophilic attack of free hydrogen peroxide. The importance of the Lewis acid character of the metal center is crucial in promoting the activation of the substrate as well as its ability to facilitate the leaving of the otherwise bad OH^- leaving group from the intermediate *quasi*-peroxymetallacycle.

Keywords: Platinum; Lewis acids; Homogeneous catalysis; Oxidation; Peroxides

1. Introduction

The idea of using electron-rich metal centers like Pd(II) and Pt(II) as Lewis acid catalysts is a relatively recent one [1]. Indeed, the common view about these species is to consider them more as bases rather than acids. However, it has been observed that the Lewis acidity of these systems can be actually exploited, provided that at least one positive charge is present on the complex. In the past few years, the number of applications of these systems in homogeneous catalysis has been increasing [1]. Despite a long lasting involvement in homogeneous catalytic oxidation with Pt(II) complexes, it was only relatively recently [1a] that we realized the importance of Lewis acidity in the promotion of such reactions. This was clearly elucidated very recently [2] by comparing the behavior of complexes significantly differing in this property.

We have studied [2] a class of cationic complexes of Pt(II) of the type $[(\text{P–P–P})\text{PtX}]^{n+}$ and $[(\text{P–P–O})\text{PtX}]^{n+}$ (P–P–P = triphos; P–P–O = triphosPO; X = solvent, OH, OOH; $n = 1, 2$) and have found that they are considerably Lewis acidic. This property was found crucial for their selectivity properties as they preferentially promote the Baeyer–Villiger oxidation of ketones versus the epoxidation of olefins in substrates containing both functional groups (see in Scheme 1 the case of dihydrocarvone). In competitive experiments carried out either with olefins and ketones in the same batch or in the presence of unsaturated ketones, their selectivity towards the oxidation of the carbonyl group was found to be complete [2].

The Baeyer–Villiger oxidation of ketones is widespread in organic synthesis [3] but quite elusive catalytically [4] as the properties necessary for a catalyst to be active are unclear. Hence, having established a clear correlation with the Lewis acidity of the metal complex can be very important for the development of new, more effective and selective catalytic systems.

On this basis, we thought of interest to corroborate the above observations, based only on reactivity studies, with a mechanistic investigation that helps in clarifying the exact role of the metal. For this reason, we report here a kinetic analysis of the oxidation of methylcyclohexanone, taken as prototype substrate, with 35% hydrogen peroxide using $[(\text{P–P–O})\text{Pt}(\text{acetone})](\text{BF}_4)_2$ as catalyst, i.e. the complex that proved most active in the oxidation reaction.

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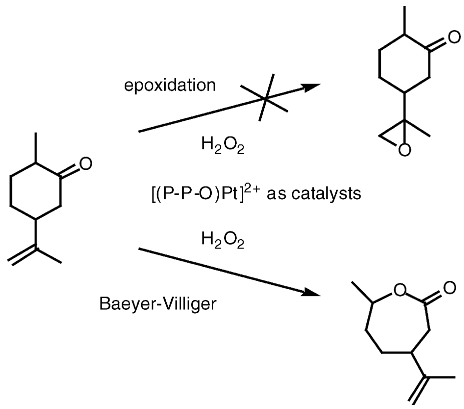
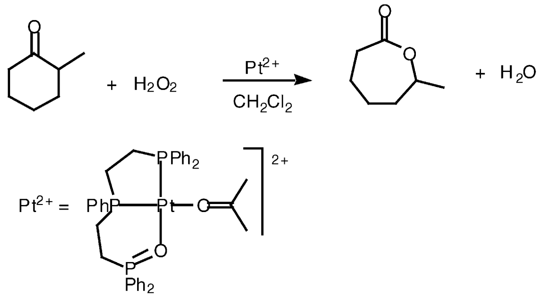


Scheme 1.



Scheme 2.

2. Results and discussion

The reaction studied is shown in Scheme 2 and it is two-phase (H_2O/CH_2Cl_2). This was chosen because a screening of the best reaction conditions, already performed previously [2], indicated that the reaction can be conveniently carried out at room temperature with easily detectable reaction rates. In the present work, all experiments were carried out at 20 °C, a temperature at which side reactions can be minimized. A typical reaction profile showing the formation of 2-heptalactone versus time is reported in Fig. 1. No other products are formed during the course of the reaction. As can be seen, the initial rate remains constant for about 1 h and can be determined with reasonable accuracy. The initial rate was analyzed as a function of the concentrations of the reaction different reactants. Due to the possible effect of H^+, all reactions were carried out at pH 1.5 by buffering with $KHSO_4/K_2SO_4$.

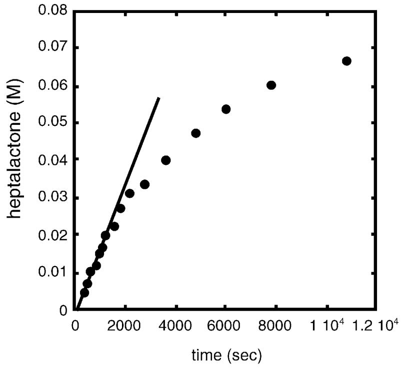


Fig. 1. A typical lactone concentration vs. time progress in the Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})Pt(CH_2Cl_2)]^{2+}$. Experimental conditions: $[Pt]_T$ 4.42 × 10^{-3} M, [methylcyclohexanone] 0.367 M, $[H_2O_2]_{org}$ 15.5 × 10^{-2} M.

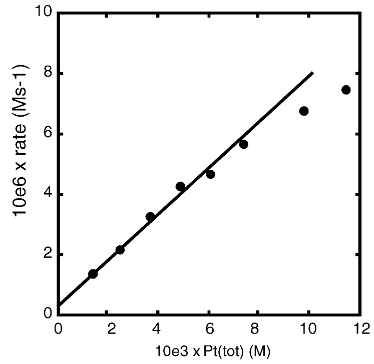


Fig. 2. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})Pt(CH_2Cl_2)]^{2+}$. Effect of the total Pt concentration. [2-Me-cy-one] 0.366 M; $[H_2O_2]_{org}$ 1.52 × 10^{-2} M; T 25 °C; N_2 1 bar.

An analysis of the effects of the concentrations of the total amount of Pt complex added, methylcyclohexanone and hydrogen peroxide is reported in Figs. 2–4. Being the system biphasic, the concentration of H_2O_2 given in the figures refers to the organic phase. It was already found [5] that the partition coefficient of hydrogen peroxide in H_2O/CH_2Cl_2 is 534/1. Therefore, the H_2O_2 concentration in the organic phase was changed by changing the concentration of the water solution, although the total amount of hydrogen peroxide used was in a 1/1 ratio with respect to the methylcyclohexanone substrate.

As can be seen from Fig. 2, the effect of total Pt concentration is first order with a negligible intercept in agreement with the observation that in the absence of

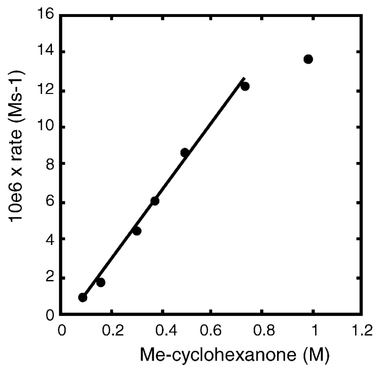


Fig. 3. Baeyer–Villiger oxidation of methylcyclohexanone with 35% hydrogen peroxide catalyzed by $[(\text{triphosPO})Pt(CH_2Cl_2)]^{2+}$. Effect of the concentration of ketone. Pt_T 4.35 × 10^{-3} M; $[H_2O_2]_{org}$ 1.52 × 10^{-2} M; T 25 °C; N_2 1 bar.