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Oxidation of Benzyl Alcohols by Monomeric Iron Phthalocyanine Complexes: Substituents' Effect on Their Catalytic Performance

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Abstract

Iron phthalocyanines tetra substituted with either electron-donating n-hexyloxy or electron-withdrawing n-hexylsulfonyl substituents were prepared and tested as oxidation catalysts for benzyl alcohol, 4-bromobenzyl alcohol, 4-methylbenzyl alcohol and 4-*tert*-butylbenzyl alcohol. Oxidation reactions were performed at room temperature in acetonitrile, acetone, ethanol, toluene, and the best result was obtained in acetonitrile. Oxidation of alcohols using *tert*-butyl hydroperoxide as an oxidant in the presence of these iron(II) phthalocyanines resulted in the production of corresponding benzaldehyde and benzoic acid. When comparing the substituent effect, the hexylsulfonyl electron-withdrawing substituted phthalocyanine complex exhibited better catalytic performance in acetonitrile for all benzylic alcohol derivatives. It showed that electron-withdrawing substituted iron(II) phthalocyanine tends to produce benzaldehydes, while electron-donating substituted iron(II) phthalocyanine produced benzoic acid. This kind of catalytic system is suitable for the oxidation of benzylic alcohols to produce benzaldehyde and benzoic acid derivatives.

**Keywords:** Oxidation, Benzyl alcohol, Iron phthalocyanine, Catalyst

1. Introduction

Oxidation reactions are amongst the most important in synthetic chemistry and offer a significant methodology for the modification of chemical substances [1]. Numerous oxidation reactions have been employed for the improvement in organic synthesis and industrial applications. Aldehydes and other carbonyl group compounds are very important organic intermediates in the production of medicine, fragrance, flavors and dyes [2]. Therefore, the selective oxidation of alcohols by transition metal catalysts and various catalytic systems have been broadly studied and to obtain the corresponding carbonyl compound to alcohol is a main goal [3]. Iron is a versatile metal center, cheap, nontoxic and possesses several stable oxidation states which makes it interesting for chemical applications [4]. So many iron compounds, such as iron(III) nitrate [5], iron(III) dodecyl sulfonate [6], and iron(III) tosylate [7] have been used as catalysts for the oxidation of alcohols into corresponding carbonyl compounds. Phthalocyanine complexes (Pcs) are aromatic compounds that have excellent properties such as thermal, chemical and light stability. The chemical and electronic structure of these molecules can be tailored by either metal insertion or covalent peripheral and non-peripheral substitutions [8]. Metal phthalocyanines (MPcs) have been used in many areas, including commercial pigments [9], photodynamic therapy [10], gas sensing materials [11, 12], information storage, computer disk writing, and catalysis [13]. MPcs complexes are structurally similar to porphyrin complexes that perform aerobic oxidation, reduction and transport of dioxygen destruction of peroxide in nature. Pcs are amongst the preferred catalysts because of their similar structural analogy with porphyrin and their possible preparation on a large scale as well as their chemical and thermal stability [14]. MPcs are most important compounds for catalytic oxidation reactions, which have been used for the oxidation of epoxidation of alkenes [15], olefins, aromatic, benzylic, and so many other complexes [16]. Different types of monomeric iron phthalocyanine were used in alcohol oxidation reactions and some substituent effect on the conversion, yield and selectivity has been investigated [17].

To further investigate these effects, two different MPcs substituted with hexyloxy electron-donating and hexylsulfonyl electron-withdrawing groups were used (**Scheme 1**) and their catalytic activities were examined. Linear hexyl groups were selected to enhance solubility

in organic solvents. Oxidation of benzyl alcohol was selected as a model oxidation reaction.
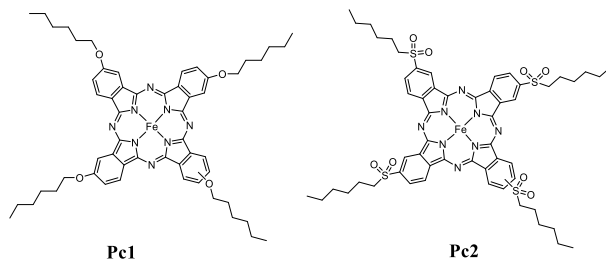
Scheme 1: Molecular structure of iron (II) tetra-(hexyloxy)phthalocyanine (**Pc1**) and iron (II) tetra-(hexylsulfonyl)phthalocyanine (**Pc2**).

2. Materials and Methods

Iron (II) tetra-(hexyloxy)phthalocyanine (**Pc1**) and iron (II) tetra-(hexylsulfonyl)phthalocyanine (**Pc2**) were prepared according to literature methods [18, 19]. Benzyl alcohol, 4-bromobenzyl alcohol, 4-methylbenzyl alcohol, 4-*tert*-butylbenzyl alcohol, ethanol, acetone, toluene, acetonitrile and *tert*-butyl hydroperoxide (TBHP, 70% in water) were purchased from Aldrich and used as received. All oxidation reactions were performed under ambient conditions. The oxidation products were monitored by an Agilent Technologies 7820A GC system.

2.1. General procedure for oxidation of alcohols

Oxidation reactions were performed in 10 mL flasks. Alcohol (0.125 mmol, 1 eqv.) and catalyst (2.5 µmol, 0.02 eqv.) were stirred in solvent (4 mL). After the solution became homogeneous, the reaction was initiated by adding 70 % TBHP solution (12.5 mmol, 100 eqv.). The oxidation reactions were carried out at room temperature and under air for 1 hour. The oxidation product yields were determined by GC.

The calculation of conversion and selectivity were defined according to the following equations:

$$\text{Conversion (\%)} = 100 - \frac{\text{Peak area of alcohol}}{\text{Peak area of (alcohol+all products)}} \, x100 \quad \textbf{(1)}$$

Equation (1). Conversion calculation

$$\text{Selectivity to BzA (\%)} = 100 - \frac{\text{Peak area of benzaldeyhde}}{\text{Peak area of all products}} x100 \quad \textbf{(2)}$$

Equation (2). Selectivity to BzA calculation.

$$\text{Selectivity to BA (\%)} = 100 - \frac{\text{Peak area of benzoic acid}}{\text{Peak area of all products}} x100 \quad \textbf{(3)}$$

Equation (3). Selectivity to BA calculation.

3. Results and Discussion
3.1. Optimization of oxidation reaction conditions

Optimum reaction conditions (substrate/catalyst ratio, reaction temperature and use of the TBHP as an oxidant) were adjusted to our previous works with *N*-bridged diiron phthalocyanines bearing eight *t*-butyl groups that highly provide solubility in organic solvents used as oxidation catalysts [20]. Since monomeric and dimeric phthalocyanines have different chemical structures, the solubility of these complexes could be different and affect conversion in oxidation reactions. To find first the solvent effect, oxidation reactions were performed in ethanol, toluene, acetone and acetonitrile at room temperature for one hour. Oxidation of benzyl alcohol (**BnOH**) was selected as a model reaction by using **Pc2**.

Products were identified using gas chromatography (GC) by comparison with corresponding standard compounds. As seen in **Fig. 1**, two product formations were clearly observed on GC spectra. These products are benzaldehyde (**BzA**) and benzoic acid (**BA**) (**Scheme 2**).
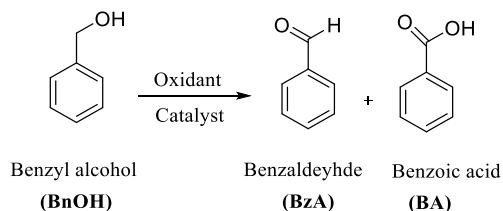
Scheme 2. Catalytic oxidation products of benzyl alcohol, catalyzed by **Pc2**.

As seen in GC spectra (**Fig.1**), conversion of **BnOH** to **BzA** and **BA** were observed in all solvents. As a depicted in **Fig.2**, highest conversion (100%) was observed in

acetonitrile and a slightly lower conversion (84%) was obtained in acetone. In terms of product selectivity, **BzA** formation was predominant in ethanol (65%) and toluene (61%), while reaction performed in acetone (79%) and acetonitrile (54%) induced the formation of **BA** as a main product. The reaction in acetonitrile supported poorly one product formation that was 46 % **BzA** and 54 % **BA**, nonetheless it was most effective solvent in terms of **BnOH** conversion.
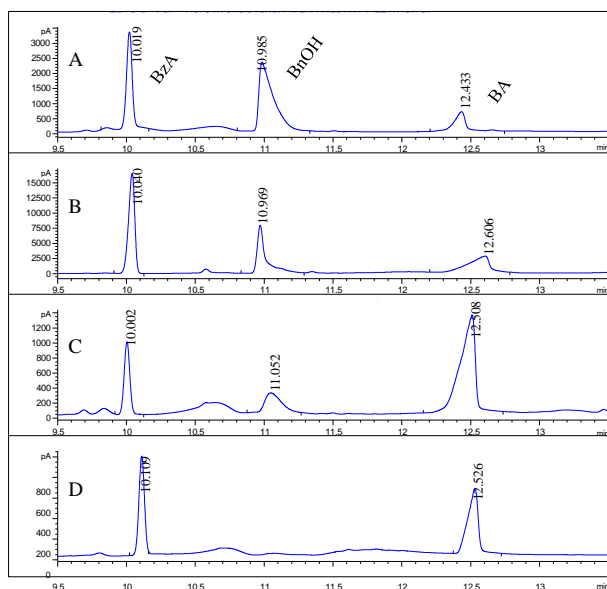

Figure 1: Solvent effect on the conversion of benzyl alcohol in ethanol A, toluene B, acetone C and acetonitrile D, catalyzed by **Pc2**.
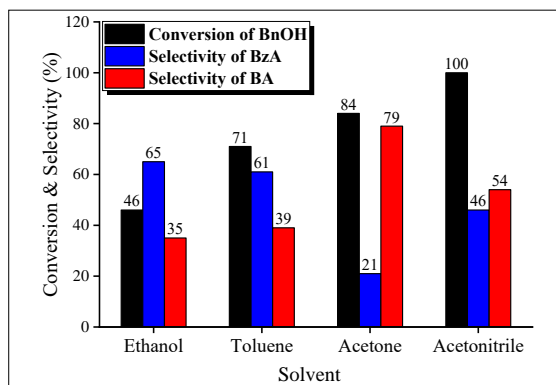

Figure 2: Solvent effect on the selectivity of benzyl alcohol, catalyzed by phthalocyanine **Pc2**.

3.2. Oxidation of alcohols with Pc1 and Pc2.

The catalytic performance of the phthalocyanines complexes were investigated with four different benzylic alcohols. As shown in **Fig.3**, the oxidation products all of the benzylic alcohols are corresponding benzaldehydes and benzoic acids. The catalytic activity of the SO_2R electron-withdrawing groups substituted iron phthalocyanine **Pc2** was higher than OR electron-

donating groups substituted iron phthalocyanine **Pc1** in the oxidation of all alcohols. In terms of the selectivity, **Pc2** exhibited better selectivity to benzaldehyde in acetonitrile. The performed benzyl alcohol oxidation here was compared with the reports on FePc derivatives catalyzed reactions regarding temperature, reaction time and conversion **Table 1**. It can be seen that in spite of good selectivity to benzaldehyde and with higher benzyl alcohol conversion previously studied FePc catalysts, they need slightly high reaction temperature and time [21-23]. Although chitosan aerogel FePc catalyst milder reaction conditions and had selectivity to benzaldehyde at 100%, it exhibited 40% benzyl alcohol conversion [24]. In the meantime, catalysts **Pc1** and **Pc2** exhibited high conversion of benzyl alcohol and its derivatives at room temperature. When the two catalysts were compared with each other, the **Pc2** exhibited the higher benzyl alcohol conversion than the **Pc1**.
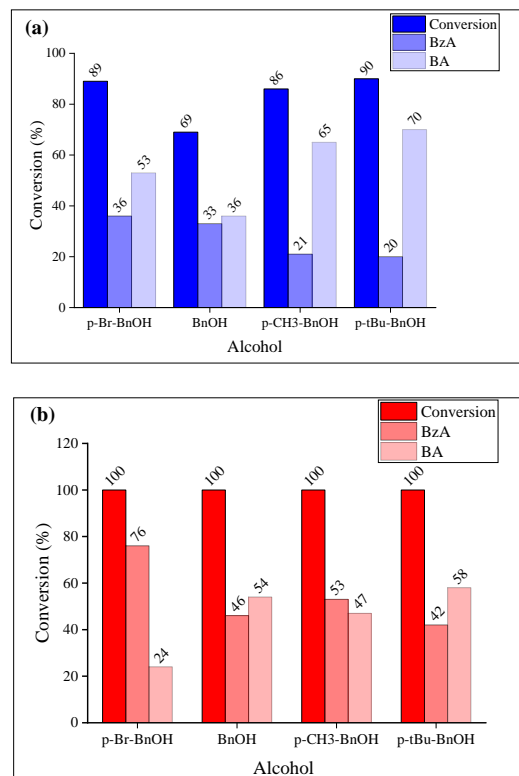

Figure 3: Oxidation of benzyl alcohols, catalyzed by **Pc1** (**a**) and **Pc2** (**b**).

3.3. Proposed catalytic mechanism

The catalytic activity of the phthalocyanine complexes depends on the iron atom at the macrocycle center that tends to produce radical intermediates with TBHP [23]. A possible mechanism of these oxidation reactions is based on progress on the radical intermediates as shown in **Scheme 3**. Firstly, the reaction is initiated interaction between the iron atom in the phthalocyanine cavity and *tert*-butyl hydroperoxide can give rise to active a higher state Fe(III)Pc-OH and *tert*-butoxy radical species [24].

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Then, Fe(III)Pc-OH can activated by the reaction with *tert*-butoxy radical to which can produce further a higher state of active Fe(IV)Pc=O complex. In the next step, Fe(IV)Pc=O can absorbs a radical hydrogen from alcohol and come back to Fe(III)Pc-OH state. Complex Fe(III)Pc-OH can take a hydrogen from radical benzaldehyde intermediate and benzaldehyde formation can occur in the last step [14, 20].

Table 1. Comparison of catalyst performance of previously reported some FePc catalysts for BA oxidation.

Catalyst	Oxidant	Rxn temp. (°C)	Rxn time (h)	Conversion (%)	Ref
Tetra-substituted FePc	TBHP	70	3	94	[21]
Polyfluoro substituted FePc	TBHP	50	3	89	[22]
Fluoro substituted FePc	TBHP	90	3	90	[22, 23]
Chitosan aerogel FePc	H_2O_2	25	24	40	[14, 24]
Pc1	TBHP	25	1	69	
Pc2	TBHP	25	1	100	
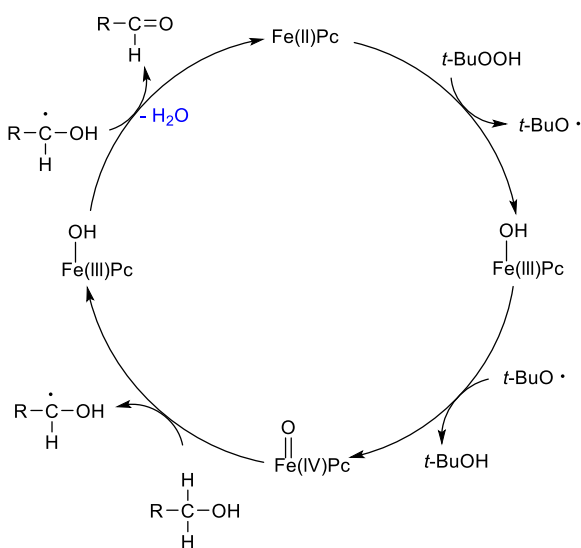
Scheme 3. The proposed mechanism for the oxidation of alcohols by TBHP in the presence of iron phthalocyanine catalyst.

4. Conclusion

Sulfonyl substituted **Pc2** was selected for the model reaction and tested for alcohol oxidation reactions in four different solvents. Among these solvents, acetonitrile was shown to be most adequate for alcohol oxidation reactions. The catalytic activities of **Pc1** and **Pc2** were then tested for oxidation of benzylic alcohols in acetonitrile. The oxidation products of both iron phthalocyanine catalysts were benzaldehyde and benzoic acid as expected. Compared to the substituent effect of phthalocyanine complexes, **Pc2** containing electron-withdrawing groups showed better catalytic performance than **Pc1** containing electron-donating groups in all benzylic alcohol derivatives. In general, phthalocyanine complexes are useable catalysts for benzyl alcohol oxidation because of their room temperature condition,

good substrate conversion and easily obtainable materials.

Author's Contribution

Zeynel Şahin: Drafted and wrote the manuscript, performed the experiment and result analysis.

Ethics

There are no ethical issues after the publication of this manuscript.

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