



Editor's Choice paper

## Selective oxidation of glycerol catalyzed by iron complexes

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## ABSTRACT

Iron complexes with the polydentate ligand bis(2-pyridinylmethyl)amine (BPA) were employed as catalysts for the oxidation of glycerol using hydrogen peroxide as oxidant. The only observed reaction products were dihydroxyacetone (DHA) and formic acid. Although the overall conversion was in all cases lower than 50%, by accurate choice of the experimental conditions selectivities in DHA up to 100% were obtained.

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### 1. Introduction

The attention of both academic and industrial world towards the conversion of biomass to fuels and chemicals has enormously increased in the last decade, within a common effort to develop effective alternatives to fossil-based carbon sources. Biofuels, that is, biomass-derived fuels, are presently employed as substitutes and/or additives to petroleum-derived fuels. Biofuel production has been long considered with some concern, due to competition of first generation biofuels for edible crops as well as land use (the fuel vs. food dilemma); however the recently developed biofuel manufacturing procedures from non-edible crops mostly cultivated on poor soil, from algal lipids, from animal or waste fats (second/third generation biofuels) appear to be ethically acceptable [1].

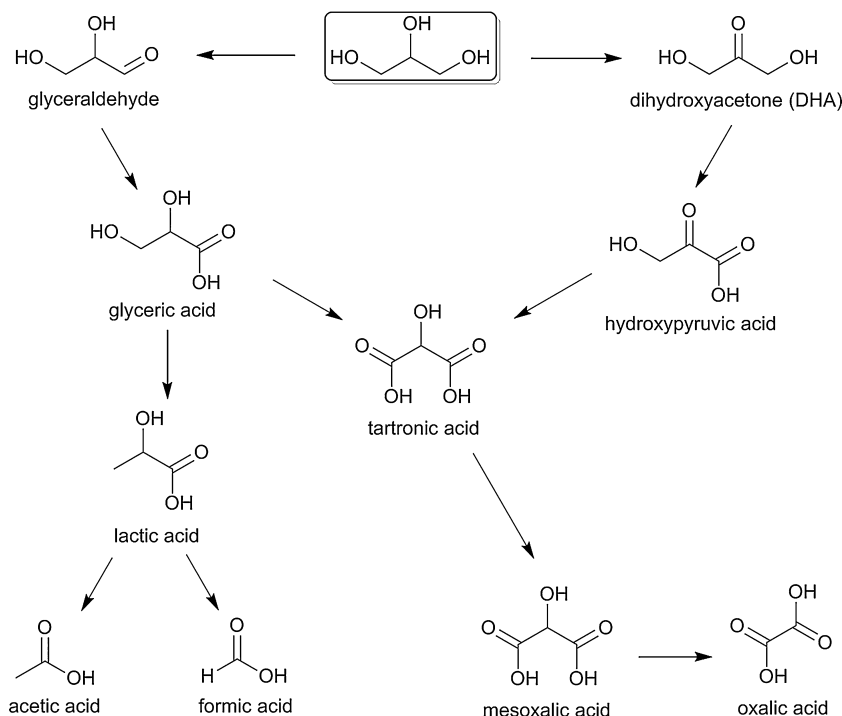
Even if at present the reasons for increasing substitution of petrol-derived diesel with biodiesel lie more on political rather than economical ground, any way for lowering biomass-derived fuel prices would translate into enhancement of its use. A major route for lowering biodiesel cost is the valorization of glycerol, the byproduct of industrial biodiesel production by transesterification of biomass-derived triglycerides with methanol: at present a large surplus of glycerol is annually produced, which makes it one of the most attractive platform chemicals of the near future. In recent years many efforts have been employed to develop efficient catalytic routes for glycerol valorization, such as reforming

to hydrogen and carbon monoxide, hydrogenolysis to 1,2 or 1,3-propanediol, dehydration to acrolein, oxidation etc. [2]; however, only very few of these processes are presently used for industrial production [3]. Glycerol catalytic oxidation is one of the non-commercialized routes so far, in spite of its apparent simplicity as well as the commercial relevance of most of the possible reaction products (see Scheme 1): in fact, due to the high functionality of glycerol its selective oxidation has proved to be a hard task to achieve. Dihydroxyacetone (DHA) is the glycerol oxidation product with highest commercial value due to its employment in cosmetics; its industrial production makes use of a fermentation process, whereas no catalytic procedure is presently employed on an industrial scale [3,4]. Various heterogeneous catalysts have been reported to promote glycerol oxidation, however most of these systems produce highly oxygenated compounds such as glyceric acid and its derivatives, whereas only a limited number of heterogeneous catalysts, mostly based on Pd, Pt and Au, produce significant amounts of DHA [2a,3,5].

Recently our group [6] as well as other scientists [7,8] published interesting results on catalytic glycerol oxidation to DHA using iridium or palladium-based catalysts: however, the catalytic reactions so far reported are unsuitable for industrial application, due to the high cost of the transition-metal catalysts employed. The development of new processes for glycerol oxidation based on less expensive, more abundant and preferably environmentally safe metals is therefore highly desirable.

Homogeneous iron-based catalysts are attracting rapidly increasing interest as convenient substitutes for the expensive, less available and often toxic precious metals counterparts [9]. Recently

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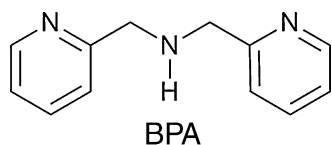
**Scheme 1.** Products obtained by glycerol oxidation.

developed processes catalyzed by iron catalysts include reduction of C=C, C≡C or C=O bonds [10] as well as asymmetric hydrogenation [11], hydrocarbon oxidation and olefin epoxidation [12].

With regard to reduction and oxidation reactions, mechanistic studies have contributed to shed light upon catalytically active iron species [13]. Interestingly, several papers have appeared in the last three or four years, reporting alcohol oxidation catalyzed by iron complexes [14]. Even though none of these papers deals with glycerol oxidation, the properties of some iron catalysts here described appeared very interesting for our purposes. From a perusal of the results reported in these papers, the use of polydentate ligands in association with iron appears to be highly effective in enhancing both catalytic activity and selectivity; years ago this type of association was successfully employed in our lab, in the course of studies regarding iron derivatives with polydentate P,N ligands as hydrogen-transfer catalysts [15].

Two papers by Bauer and coworkers published in 2013 attracted our interest [16]: they describe the oxidation of alcohols catalyzed by iron complexes with bis-picolylamine ligands. Such catalysts display a remarkable selectivity towards secondary OH groups in comparison to primary hydroxyls: notably, the authors also report the oxidation of diols to the corresponding ketoalcohols [16b]. These iron-based complexes appeared to be the perfect candidates as catalysts for glycerol oxidation to DHA.

Here we describe our results in the oxidation of glycerol catalyzed by iron complexes in association to the tridentate ligand bis(2-pyridinylmethyl)amine (BPA) (see Fig. 1). To the best of our knowledge, the data here reported represent the first example of selective oxidation of glycerol to DHA promoted by an iron catalyst.



**Fig. 1.** bis(2-pyridinylmethyl)amine (BPA).

## 2. Experimental

### 2.1. General

Some reactions and manipulations (where indicated) were performed under argon atmosphere, using standard Schlenk tube techniques. The GC standard naphthalene was recrystallized from ethanol. All the other chemicals were reagent grade and were used as received from the commercial suppliers.

### 2.2. Instrumental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded either on a Varian 500 spectrometer operating at 500 MHz and 125.68 MHz, respectively, or on a Jeol EX400 spectrometer operating at 400 MHz and 100.4 MHz, respectively; chemical shifts were measured relative to the residual solvent signal. Assignments were verified by COSY and HSQC spectra.

Electrospray mass spectra were obtained by an ion-trap instrument (ESI-MS Bruker Esquire 4000) equipped with an electrospray ion source. The instrument performed with 10.0 psi nebulizer pressure, end-plate offset  $-500$  V, capillary 4000 V and capillary exit at 113.3 V. The drying gas ( $\text{N}_2$ ) flow was  $5 \text{ L min}^{-1}$  and the spectral range was from  $m/z = 100$  to 1200.

The chemical yields of the catalytic reactions were determined by GC on an Agilent 6850 instrument with helium as carrier gas and a TCD detector. Reaction mixture diluted 1:1.5 in methanol was injected at  $100^\circ\text{C}$  through the cool on-column injector in a Rtx<sup>®</sup>-Wax Restek capillary column (30 m length, 0.32 mm ID, 0.5  $\mu\text{m}$  df) protected by a Restek Hydroguard<sup>®</sup> FS precolumn (5 m length, 0.53 mm ID).

### 2.3. Synthesis of the iron catalyst

Compound  $[\text{Fe}(\text{BPA})_2(\text{OTf})_2]$  was prepared according to the reported procedure [16a].

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