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Selective oxidation of glycerol catalyzed by iron complexes

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Highlights

- We describe a green process for glycerol oxidation catalyzed by iron complexes.
- Glycerol can be selectively oxidized to dihydroxyacetone.
- The catalytic reactions are carried out at r.t. with hydrogen peroxide as oxidant.
- It is the first example of iron-catalyzed glycerol oxidation to dihydroxyacetone.

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.

Keywords

Iron catalysts; Glycerol valorization; Selective oxidation; Dihydroxyacetone.

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, i.e. 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 annualy 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 oxigenated componds such as glyceric acid and its derivatives, whereas only a limited number of heterogeneous catalysts, mostly based on Pd, Pt and Au, produce significative 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 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 higly 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].



Scheme 1. Products obtained by glycerol oxidation.

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 corrresponding 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(2pyridinylmethyl)amine (BPA) (see Figure 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.



BPA Figure 1. bis(2-pyridinylmethyl)amine (BPA).

2. Experimental section

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

¹H and ¹³C 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 instrumet performed with 10.0 psi nebulizer pressure, end-plate offset -500V, capillary 4000V and capillary exit at 113.3V. The drying gas (N₂) flow was 5 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 °C through the cool on-column injector in a Rtx[®]-Wax Restek capillary column (30 m length, 0.32 mm ID, 0.5 μ m df) protected by a Restek Hydroguard[®] FS precolumn (5 m length, 0.53 mm ID).

2.3. Synthesis of the iron catayst

Compound [Fe(BPA)₂(OTf)₂] was prepared according to the reported procedure [16a].

2.4. Procedure for catalytic reactions

In a typical catalytic reaction, 3.54 mg (0.010 mmol) of Fe(OTf)₂ were dissolved in 0.35 ml of MeCN; to that solution, $5.4 \mu l (0.030 \text{ mmol})$ of BPA and, after 5 min, 0.35 ml of 1.0 M glycerol solution in water (0.35 glycerol mmol) were added through a microsyringe leading to a deep orange solution. Then H₂O₂ (100 μ l, 30 wt % in H₂O 0.98 mmol) was slowly added dropwise via microsyringe under vigorous stirring until addition was complete.

In case of reactions carried out under argon, the $Fe(OTf)_2$ and BPA solution was deaerated by bubbling argon through a needle for 10 min. After addition of the glycerol solution, the reaction vessel was closed with a serum cap and hydrogen peroxide was added by a micro-syringe; then the vessel was heated under vigorous stirring to the chosen reaction temperature in a thermostatted oil bath. After the desired reaction time, the catalytic reaction was stopped by cooling the Schlenk tube to -18°C and letting air in under stirring.

2.5. Analysis of the reaction mixtures

Qualitative analysis was accomplished by NMR; the data were compared with those of authentic samples obtained by conventional routes or by commercial suppliers. Quantitative evaluation of product distributions was performed by GC with naphthalene as the internal standard, using response factors previously determined by the analysis of standard solutions; the quantitative analysis thus performed allowed a reproducibility within $\pm 1\%$.

3. Results

3.1. Oxidation of glycerol promoted by iron catalysts

The iron complex $[Fe(BPA)_2(OTf)_2]$ was employed as alcohol oxidation catalyst by Bauer et al. [16b], using either H₂O₂ or *t*-BuOOH as oxidant. Interestingly, other similar polydentate ligands used by the same Authors gave rise to iron compounds which were either less active or inactive in promoting alcohol oxidation.

We chose to use the same iron species as catalyst for our initial tests on glycerol oxidation; hydrogen peroxide was selected as oxidant, a mixture H_2O/CH_3CN as reaction medium.

 $[Fe(BPA)_2(OTf)_2]$ proved to be an active catalyst for glycerol oxidation: after 90 min at r.t. an overall conversion of 46% was measured, with formation of two products, i.e. DHA and HCOOH (selectivity of 53 and 47%, respectively, Table 1 entry 1). Table 1

Oxidation of glycerol with H2O2 promoted by iron catalysts^a

Entry	catalyst	BPA(tot) /Fe	Conv. ^b (%)	DHA Sel. (%)	HCOOH Sel. (%)
1	[Fe(BPA) ₂ (OTf) ₂]	2	46	53	47
2	$Fe(OTf)_2 + BPA$	2	47	49	51
3	Fe(OTf) ₃ + BPA	2	45	65	35
4	Fe(OTf) ₂	0	45	2	98
5	Fe(OTf) ₃	0	18	21	79
6	$Fe(OTf)_2 + BPA$	3	26	80	20
7	Fe(OTf) ₃ + BPA	3	27	78	22
8	$FeCl_2 + BPA$	3	33	34	66
9	Fe ₃ (CO) ₁₂ + BPA	3	5	62	38
10	[Fe(BPA) ₂ (OTf) ₂] + BPA	3	19	81	19

^a Experimental conditions: $[Fe]=1.0x10^{-2}$ M; [glycerol]/[Fe]=35; $[H_2O_2]/[glycerol] = 2.8$; H_2O_2 30 % w/w; solvent MeCN: $H_2O=2:1$; T=25 °C; t=90 min; ^b Calculated as % of glycerol reacted.

In other words, formation of the desired product DHA was accompanied by that of formic acid, one of the common glycerol overoxidation products. Interestingly, in the final reaction mixture glyceraldehyde, which in the majority of glycerol oxidation reactions is formed together with DHA, was present only in traces, and other possible overoxidation products were not detected. When the same reaction was repeated by using a catalyst prepared "in situ" from $Fe(OTf)_2$ and 2 equivalents of BPA similar results were obtained (Table 1 entry 2); on the other hand, substitution of the Fe(II) with the corresponding Fe(III) precursor, i.e. $Fe(OTf)_3$,

also produced a mixture of DHA and formic acid, although with the Fe(III) precursor the selectivity in DHA was moderately improved (Table 1 entry 3).

It was appropriate to verify the catalytic activity of the iron triflates in the absence of BPA: both $Fe(OTf)_2$ and $Fe(OTf)_3$ showed some activity in glycerol oxidation, the Fe(II) species being more active than the Fe(III) salt, but both proved to be selective towards formic acid formation (Table 1 entries 4 and 5); therefore, the ligand BPA appeared to play a key role in promoting the formation of DHA.

Such hypothesis was confirmed by repeating the reactions performed with the catalysts prepared "in situ" in the presence of a higher ligand/Fe ratio: comparison in Table 1 of entries 6 and 7 (relative to BPA/Fe = 3) with 2 and 3 (BPA/Fe = 2), respectively, shows an improvement in DHA selectivity by increasing the BPA/Fe ratio, although at the expenses of the overall conversion.

Other iron salts were tested as catalyst precursors in association with BPA: $FeCl_2$ was less active and selective, whereas $Fe_3(CO)_{12}$ proved to be poorly catalytically active (Table 1 entries 8 and 9). In the absence of an iron compound, reaction of glycerol with H_2O_2 produced only traces of the oxidation products.

Finally, the reaction in which the preformed catalyst $[Fe(BPA)_2(OTf)_2]$ was employed (Table 1 entry 1) was repeated in the presence of added free BPA: the results (Table 1 entry 10) show a positive effect on the selectivity (81% in DHA) although accompanied by a decrease in glycerol conversion; in fact, the composition of the final reaction mixture appears to be the same as that obtained using the catalytic system prepared "in situ" with the same BPA/Fe overall ratio (compare in Table 1 entries 6 and 10).

3.2. Optimization of experimental conditions for oxidation of glycerol to DHA

Our studies proceeded with an investigation on the effect of various parameters on activity and selectivity of the catalytic reactions. Our goal was to maximize formation of the desired product DHA. For these reactions we employed the catalytic system prepared "in situ" from $Fe(OTf)_2$ and 3 equivalents of BPA; in all cases the only detected products were mixtures of DHA and formic acid, in some cases together with traces of glyceraldehyde.

We first examined the effect on the catalytic reaction of molar substrate/catalyst ratio (see Table 2 entries 1, 2). Rather surprisingly, the conversion slightly improved by increasing the substrate concentration, but on the other hand the same variation dramatically affected the selectivity, which changed from a DHA/formic acid ratio of 4:1 to 1:3 with sub/Fe of 35 and 100, respectively.

On the other hand, an increase of iron loading (*i.e.* substrate/iron molar ratio 20 or lower) failed to produce higher reaction yields, as both conversion and selectivity were very similar to those obtained at substrate/iron=35.

Also the choice of reaction temperature influenced both conversion and selectivity of glycerol oxidation (Table 1 entries 1, 3, 4). In comparison to the standard reaction at r.t. (entry 1), an increase of temperature produced higher conversion but lower yield of DHA (entry 4); on the contrary, when the reaction was performed in an ice bath the conversion was only slightly affected, whereas the selectivity increased from 80 to 97% (entry 3).

With regard to the reaction medium, an acetonitrile/water mixture appeared to be a good choice; no significant effect was observed by changing the relative amount of the two solvents, the best results were obtained with a CH_3CN/H_2O volume ratio of 2:1. Further tests with other solvents were not attempted, on one hand because of the restricted choice due to limited glycerol solubility, on the other because use of solvents classified as "undesirable" from the environmental point of view [17] was not considered.

Also the initial choice of H_2O_2 as oxidant proved to be appropriate: *t*-BuOOH was also tested in our reactions, but it turned out to be a worse oxidant for glycerol, especially from the point of view of overall conversion (compare entries 1 and 5 in Table 2). **Table 2**

Oxidation of glycerol with H₂O₂ catalyzed by Fe(OTf)₂ + BPA^a

Entry	T (°C)	t (min)	H ₂ O ₂ /glycerol	glycerol/Fe	$\mathrm{H_2O_2}$ % (w/w)	Conv. (%) ^b	DHA Sel. (%)	HCOOH Sel. (%)
1	25	90	2.8	35	30	26	80	20
2	25	90	2.8	100	30	32	27	73
3	0	90	2.8	35	30	23	97	3
4	40	90	2.8	35	30	30	68	32
5°	25	90	2.8 ^d	35	70 ^e	6	80	20
6	25	90	2.0	35	30	21	86	14
7	25	90	1.5	35	30	17	100	-0
8	25	90	2.8	35	10	25	93	7
9	25	15	2.8	35	30	20	83	17
$10^{\rm f}$	25	15	2.8	35	30	19	98	2
$11^{\rm f}$	25	90	2.8	35	30	24	92	8

^a Experimental conditions: $[Fe] = 1.0x10^{-2} \text{ M}; [BPA]/[Fe] = 3;$ solvent MeCN:H₂O (2:1); ^b calculated as % of glycerol reacted; ^c reaction carried out with *t*-BuOOH as oxidant; ^d *t*-BuOOH/glycerol; ^e *t*-BuOOH % (w/w); ^f reactions carried out under an argon atmosphere.

Other important parameters which are known to affect catalytic oxidations are hydrogen peroxide concentration and $H_2O_2/substrate$ ratio. We examined the effect of both factors on our catalytic reactions. The hydrogen peroxide/glycerol molar ratio was varied from 2.8 to 2.0 and 1.5. The data reported in Table 2 (entries 1, 6, 7) show an evident effect on both reaction conversion and selectivity: the former decreased and the latter increased by decreasing the excess of hydrogen peroxide employed: notably, at $H_2O_2/glycerol = 1.5$ formation of formic acid was completely suppressed, with a resulting selectivity in DHA of 100%.

Also the concentration of the hydrogen peroxide solution proved to significantly influence the catalytic reaction: by lowering the concentration of aqueous H_2O_2 from 30% to 10% a positive effect was obtained on both conversion and selectivity, the latter raising to a value of 93% in DHA (Table 2 entries 1 and 8). Since the efficiency of H_2O_2 as oxidant can be affected by the pH of the medium [14b,18], we performed the same reaction of Table 2 Entry 1, but replacing water with a buffer solution at pH=1: in the acidic solution apparently a different catalyst was formed (pale yellow instead of deep purple solution) which proved to be poorly selective towards DHA formation (about 65% of formic acid obtained).

With regard to reaction time, it proved useless to carry out the catalytic reactions at longer reaction times in order to increase the conversion: as a matter of fact most of glycerol consumption occurred in the first 15 minutes, whereas at longer reaction times the conversion increase was not substantial (compare entries 9 and 1 in Table 2).

Finally, it was of interest to examine the effect of performing the catalytic reaction with the exclusion of air, i.e. under an argon atmosphere. The effect of oxygen on iron-catalyzed oxidations can be various, ranging from possible oxidation of the iron species to concurrent catalytic reactions which make use of oxygen as oxidating agent. Interestingly, in our case the catalytic oxidation of glycerol carried out under argon proved to be more selective than the corresponding reactions in air, with selectivities in DHA up to 98% (in Table 2, compare entries 9 and 1 with 10 and 11, respectively). Moreover, for the reactions performed in inert atmosphere the trend of conversion vs. reaction time was the same as that observed in the presence of air (see Table 2 entries 10, 11). At this point, the effect of the parameters on reaction conversion and selectivity was rather clear: in order to obtain high selectivities in DHA the reactions must be carried out with low substrate/iron ratio, at room temperature or lower, using a moderate excess of H_2O_2 as 10% solution, preferably under an argon atmosphere. Various other catalytic reactions were then performed, with the aim of increasing the conversion without significative loss in selectivity: unfortunately, all the attemped combinations of parameters, although in most cases leading to very high selectivities, failed to raise the overall conversions.

3.3. Attempted oxidation of a glycerol acetal

An alternative possible route for enhancing the selectivity of glycerol oxidation might make use of a glycerol acetal as starting material. We recently reported a selective procedure for glycerol acetalization to five and six-membered cyclic acetals and ketals [19]: these molecules are potentially useful substrates for selective transformations of the single non-protected hydroxyl group. Replacement of glycerol with one of these derivatives in oxidation reactions might in principle give a double advantage: on one hand, no competition between primary and secondary OH groups would be possible; on the other, the acetal is expected to be less subject to overoxidation and subsequent decomposition.

We therefore carried out a number of reactions using the six-membered cyclic acetal 2-phenyl-[1,3]-dioxan-5-ol (Figure 2) as starting material and the catalyst prepared "in situ" from $Fe(OTf)_2$ and three equivalents of BPA. Unfortunately, analysis of the final reaction mixtures only revealed the presence of an isomeric mixture of five and six-membered acetals as well as the deacetalization products glycerol and benzaldehyde, whereas DHA was only detected in traces. In fact, attempts in our previous work to substitute glycerol with one of its acetals had been frustrated by either low reactivity of the substrate, or by its decomposition [20].

Figure 2. cis, trans-1,3-O-benzylideneglycerol.

3.4. ESI-MS data

In order to obtain some insight on the nature of the iron species formed in solution we carried out a series of ESI-MS measurements. The spectra of an acetonitrile solution containing $Fe(OTf)_2$ and 3 equivalents of BPA showed in positive ion mode signals at m/z 603, 404, 254 which were assigned to $[Fe(BPA)_2(OTf)]^+$, $[Fe(BPA)(OTf)]^+$ and $[Fe(BPA)]^+$, respectively. The presence of free BPA ligand was revealed by the peak at m/z 200 [M+H]. When the same solution was treated with aqueous glycerol solution reproducing the same concentration and molar ratio used in the catalytic reactions, the MS spectra contained, aside the peaks formerly observed, only few minor signals of very low intensity, none of which could be related to iron-glycerol adducts.

Other spectra of reaction mixtures (Table 1 entries 6 and 10, see Supplementary Information) were also performed in search for signals related to either peroxo or oxygen containing adducts of the type $[Fe(BPA)(glycerol)(OTf)]^+$, however such peaks were never observed. In fact, as the evolution of the catalytic reactions under investigation rapidly leads to formation of inactive species, the MS spectra of reaction mixtures probably show signals mainly – if not only – related to inactive iron complexes.

4. Discussion

The capability of iron of promoting alcohol – including glycerol – oxidation is no recent discovery. The first report on iron-catalyzed glycerol oxidation by hydrogen peroxide dates back to 1899 [21]; other studies on alcohol and/or glycerol oxidation in the presence of iron salts followed in the last century [22] and appeared also recently [23]. A common feature of the iron-promoted glycerol oxidation so far reported was the formation of mixtures of oxidation products of doubtful usefulness.

Therefore, if on one hand the capability of iron to promote glycerol oxidation has long been known, on the other appropriate control on the catalyst selectivity must be applied, in order to make it suitable for the selective production of glycerol oxigenates. In this respect, the recent studies published on selective alcohol oxidation (see Introduction) represent a promising starting point, as they demonstrate that iron atoms can be tamed into active and selective catalytic sites by association with the suitable ligands and reaction conditions.

The present attractiveness of iron-based catalysts is due on one hand to low price and availability of this metal, on the other by the increasing awareness of the scientific community of the environmental issues: from this point of view, the properties of iron in terms of low toxicity and environmental safety make it an excellent choice for the development of green processes. Moreover, the interest towards iron-based catalysts is enhanced by the desire of mimicking natural iron-containing enzymes [24].

The catalytic reactions here described fit well into our current interest for the development of catalytic processes in coherence with the Green Chemistry principles [25]. All the experimental conditions employed are environmentally benign: catalyst, reaction medium and temperature, oxidating agent (H_2O_2 , which only gives water as byproduct). The catalytic reaction itself is highly atomeconomical, which favorably compares with some industrial processes for the production of glycerol oxigenates that make use of stoichiometric reagents [5].

In the Results section we have described the application of the catalytic system iron/BPA to the oxidation of glycerol. A first comment on the results is related to the reaction selectivity: of the various possible products only DHA and formic acid are formed, in variable amounts which depend on the experimental parameters. Formic acid is a rather common product of glycerol oxidative degradation [26]; in our case, as DHA is the glycerol oxidation product of highest commercial value, our efforts have been directed towards its selective formation.

Apparently, the catalytic system under investigation is composed of at least two active species, each one promoting formation of one of the two products. Preferred oxidation of the secondary hydroxyl group of glycerol leads to formation of DHA; it is reasonable to assume that this reaction is promoted by an iron catalyst with at least one coordinated BPA ligand, as we can gather from a comparison of the results obtained with and without added BPA, reported in Table 1. DHA thus formed is not subsequently oxidized in significative amount, as confirmed by the results obtained in catalytic reactions in which glycerol was replaced by DHA: in standard catalytic conditions only minor amounts of formic acid (<8% of the original DHA) were detected.

At variance, formic acid is probably formed via initial oxidation of a primary hydroxyl group of glycerol to give glyceraldehyde (See Scheme 2), which is subsequently oxidized to formic acid (in fact, glyceraldehyde is known to be less stable to oxidation than DHA): this reaction is promoted by a different catalyst, probably having no BPA coordinated to iron. As a matter of fact, formation of formic acid is also observed when no BPA is added to Fe(II) or Fe(III) triflate. The latter reaction is disfavoured in the presence of excess BPA, as well as at low temperature and low concentration of H_2O_2 : that is the reason why in these experimental conditions the selectivity in DHA is high. A beneficial effect on selectivity is also observed when oxygen is excluded from the reaction mixture: these findings might be interpreted in terms of oxygen playing some role either in glyceraldehyde oxidation or in possible reactions with the catalyst to give less selective iron species.



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Scheme 2. Production of DHA and formic acid via oxidation of secondary and primary hydroxyl groups, respectively.

With regard to the mechanism of the iron-catalyzed alcohol oxidation, previous studies proposed various mechanistic pathways [16a, 27]. There is a common agreement about initial reaction of the iron compound with the peroxide to give a species containing the Fe-O-O-R mojety (R = H or alkyl): this iron complex is not catalytically active, but it can generate the active catalyst (or catalysts). It has been proposed that the fate of the iron-peroxo intermediate can undergo at least two different decomposition routes, namely homolytic and heterolytic reactions. The former route produces radical species which promote oxidation reactions with radical mechanism, typically poorly selective. At variance, the heterolytic decomposition probably forms high valent iron-oxo species, the catalytic activity and selectivity of which are strongly influenced by the nature of the other ligands coordinated to iron; the role of high valent iron-oxo species in oxidation catalysis has been the object of both experimental and theoretical studies [13a, 28].

Evidence in favour of substrate coordination is uncommon for iron catalyzed alcohol oxidation [14b], on the contrary most studies propose catalytic mechanisms which exclude alcohol coordination to the iron centre [16a, 29]. In the present case, ESI-MS spectra of solutions containing the iron salt, BPA and glycerol did not provide evidence for coordination of glycerol to the metal; on the other hand, in the MS spectra of catalytic mixtures no peaks could be assigned to iron-BPA oxo or peroxo complexes.

Finally, our findings relative to the nature of the iron precursor, i.e. the similar results obtained using Fe(II) and Fe(III) triflates, are compatible with formation of Fe(IV) or Fe(V) oxo species, indipendently from the initial iron oxidation state. The worse catalytic results observed when using $FeCl_2$ as precursor can be explained in terms of formation of dimeric inactive or less active species, as previously proposed [30].

5. Conclusions

The results here reported describe the properties of iron complexes with the polydentate ligand BPA as effective catalysts for the oxidation of glycerol. In all the catalytic reactions only two products were detected, namely dihydroxyacetone and formic acid; such products appear to be obtained by two different pathways, promoted by different catalytic species. By tuning the experimental conditions, although conversions exceeding 50% were never obtained, complete suppression of the reaction leading to formic acid was achieved: in these conditions DHA was formed with up to 100 % selectivity. To the best of our knowledge, this study represents the first example of iron-catalyzed selective oxidation of glycerol to DHA; moreover, the catalytic reaction here described is a remarkable example of green process, from the point of view of metal, oxidant, reaction medium as well as of the experimental conditions employed.

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Figure Caption list

Scheme 1. Products obtained by glycerol oxidation.

Figure 1. bis(2-pyridinylmethyl)amine (BPA).

Figure 2. cis, trans-1,3-O-benzylideneglycerol.

Scheme 2. Production of DHA and formic acid via oxidation of secondary and primary hydroxyl groups, respectively.

Selective oxidation of glycerol catalyzed by iron complexes

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