transfer rate. The energy-transfer rate is further determined by the so-called spectral overlap of the antenna and the lanthanide ion, that is, how well the donating and receiving energy levels match. The energy-transfer rate in $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ will be even slower than in $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$, because the antenna triplet state ($E_T = 17\,400\ cm^{-1}$)[16] matches the $Nd^{III}\ {}^4G_{5/2}$ state at $17\,100\ cm^{-1}$, whereas the overlap with the only Yb^{III} energy level, the ${}^2F_{5/2}$ state which is at $10\,240\ cm^{-1}$, is much smaller.

Deoxygenated $[D_6]$DMSO solutions of the ferrocene-functionalized (Nd)**2** and (Yb)**2** complexes (10^{-4} M) exhibit the typical linelike lanthanide emission upon excitation of the ferrocene antenna at 320 nm.[17] At room temperature, sensitized emission at 1060 and 1330 nm (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and ${}^4I_{13/2}$ transitions, respectively) is observed for (Nd)**2**, and at 980 nm (${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) for (Yb)**2** (see Figure 3). The excitation spectra of (Nd)**2** and (Yb)**2** (not shown), closely follow the absorption spectrum of the ferrocene antenna and confirm unambiguously that excitation takes place through the antenna. Upon excitation at 337 nm the lanthanide luminescence decay curves could be fitted mono-exponentially with lifetimes of 2.0 ± 0.2 µs for (Nd)**2** and 18.8 ± 0.8 µs for (Yb)**2**.

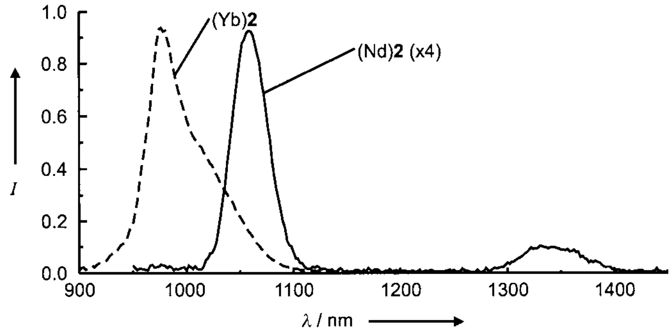

Figure 3. Emission spectra of (Yb)**2** and (Nd)**2** in $[D_6]$DMSO (10^{-4} M) upon excitation at 320 nm. The spectra have been corrected for the absorbance of the samples.

In conclusion, the transition metal complexes $[Ru(bpy)_3]^{2+}$ and ferrocene are able to sensitize both Nd^{III} and Yb^{III}. Moreover, these sensitizers enable excitation with visible light. The luminescent nature of the $[Ru(bpy)_3]^{2+}\,{}^3$MLCT state has allowed a direct study of the sensitization process. It has been established for the $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ complex that the energy transfer takes place in a "classical way" through the antenna triplet state with a rate of $1.1 \times 10^6\ s^{-1}$. The sensitization process of $[(Yb_2\text{-}Ru)\mathbf{1}]^{2+}$ follows the same pathway, although the energy transfer rate is lower ($\leq 10^5\ s^{-1}$).

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[14] Comparison of the antenna luminescence spectrum of $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ with the standard $[Ru(bpy)_3]^{2+}$ complex in DMSO shows that the emission maximum of $[(Nd_2\text{-}Ru)\mathbf{1}]^{2+}$ has shifted to the red: from 634 nm to 666 nm. The amide groups stabilize the ^{3}MLCT state, and probably the excited electron is localized on the amide-functionalized bpy ligand.

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[17] Excitation in the weaker ferrocene absorption band at 440 nm ($\varepsilon = 200\ M^{-1}\,cm^{-1}$) also resulted in sensitized lanthanide luminescence.

A Novel Iron-Based Catalyst for the Biphasic Oxidation of Benzene to Phenol with Hydrogen Peroxide

Daniele Bianchi,* Rossella Bortolo, Roberto Tassinari, Marco Ricci, and Rodolfo Vignola*

Direct oxidation of benzene to phenol is an important reaction in organic chemistry. Often, however, its selectivity is rather poor since phenol is more reactive toward oxidation than benzene itself, and substantial formation of over-oxygenated by-products (catechol, hydroquinone, benzoquinones, and tars) also occurs.[1]

Similar over-oxidation problems are efficiently solved in biological systems by segregating catalysts and products into

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[*] Dr. D. Bianchi, Dr. R. Bortolo, R. Tassinari, Dr. M. Ricci
EniChem S.p.A.-Centro Ricerche Novara "Istituto G. Donegani"
Via Fauser 4, 28100 Novara (Italy)
Fax: (+390) 321-447425
E-mail: daniele.bianchi@enichem.it

Dr. R. Vignola
EniTecnologie
Via Ramarini 32, 00016 Monterotondo (Italy)
Fax: (+390) 6-90673243
E-mail: rvignola@enitecnologie.eni.it

different environments. The active sites of several oxygenases are deeply buried in hydrophobic pockets[2] where lipophilic substrates are readily oxidized, while the more hydrophilic reaction products are promptly released into the surrounding aqueous environment. Likewise, the cellular membranes have important functions as selective barriers around the cell that allow the import of components and the export of products.[3]

In the course of industrial research aimed at developing a new process for the one-step production of phenol, we wondered whether a biphasic system could mimic these important features of biological systems. Here we report on a new method for the selective biphasic oxidation of benzene to phenol with hydrogen peroxide as oxidant, an iron complex as catalyst, and trifluoroacetic acid as cocatalyst.

The first aspect that we investigated was the solvent system. The importance of this component is well illustrated by the history of hydrocarbon oxidation with hydrogen peroxide. For example, water is the solvent in the Fenton system,[4] while pyridine is characteristic of the Gif chemistry widely studied by Barton et al. in the last ten years.[5] We found that the use of an aqueous/organic reaction medium dramatically affects the selectivity of the reaction. Screening was carried out with $FeSO_4$ (a conventional Fenton catalyst) and a series of organic solvent/water mixtures as reaction media.

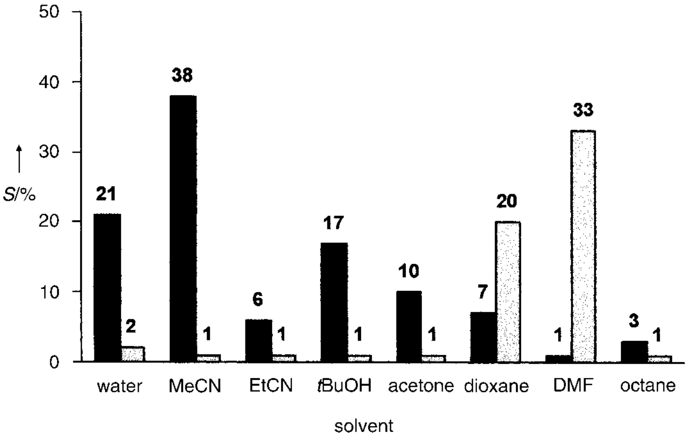

Figure 1. Effect of the reaction medium on the oxidation of benzene. The reaction was carried out under the conditions described in the Experimental Section with $FeSO_4$ as catalyst in absence of ligands. The composition of the reaction medium was water/solvent/benzene 45/45/10 (v/v/v). Black bar: Fraction of H_2O_2 oxidizing benzene to phenol; gray bar: fraction of H_2O_2 oxidizing benzene to dioxygenated products (hydroquinone, catechol, and 1,4-benzoquinone). The concentration of overoxidation products (tars) was not determined. S = selectivity based on H_2O_2.

As shown in Figure 1, a remarkable enhancement of selectivity was obtained with the biphasic system water/acetonitrile (1/1) in the presence of benzene. In this medium the concentration of benzene in the aqueous phase increased from 0.18 % (solubility of benzene in water)[6] to 0.76 %, and the phenol was largely extracted (85 %) into the organic phase. Thus, the biphasic process minimizes over-oxidation by reducing the contact between phenol and the catalyst, which is soluble in the aqueous phase. This hypothesis was confirmed on comparing the benzene/phenol molar ratios in the aqueous phase of water/benzene and water/acetonitrile/benzene reaction mixtures, which were 0.25 and 3.7, respectively. Such enhancement is not possible in the case of solvents that are too hydrophobic, such as *n*-octane, which quantitatively extract benzene from the aqueous phase, or with those that are too hydrophilic, such as dimethylformamide (DMF), which do not form a two-phase system.

The identification of a more efficient and selective catalyst, which is an essential requirement for industrial application, was the second key aspect of the study. After testing a series of bidentate N,N, N,O and O,O ligands for iron (Table 1), 5-carboxy-2-methylpyrazine-*N*-oxide (**1**; entry 15) was selected as the most efficient catalyst precursor. The nature of the ligand plays a crucial role in determining both the catalyst reactivity and selectivity. In general, complexes with N,N ligands (entries 2–5) were almost inactive, those with O,O ligands (entries 6–8) displayed good activity but poor selectivity, and those with N,O ligands,

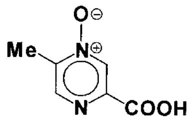

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Table 1. Oxidation of benzene: selection of the ligand for iron.[a]

Entry	Ligand	H_2O_2 conversion [%]	Selectivity on H_2O_2[b] [%]	Selectivity on C_6H_6[c] [%]
1	none	77	38	33
2	2,2′-bipyridine	6	< 1	n.d.
3	1,10-phenanthroline	6	< 1	n.d.
4	2,6-di(2-pyridyl)pyridine	0	0	–
5	2,3-di(2-pyridyl)pyrazine	4	< 1	n.d.
6	1,2-dihydroxybenzene	100	44	60
7	1,2-dihydroxynaphthalene	100	25	n.d.
8	1,2-dihydroxynaphthalene-4-sulfonic acid	100	3	n.d.
9	8-hydroxyquinoline	0	0	–
10	pyridine-2-carboxylic acid	13	15	n.d.
11	pyridine-2,6-dicarboxylic acid	2	< 1	–
12	quinoline-2-carboxylic acid	90	33	n.d.
13	pyrazinecarboxylic acid	78	70	81
14	pyrazine-2,3-dicarboxylic acid	90	52	78
15	5-carboxy-2-methylpyrazine-*N*-oxide (**1**)	94	78	85

[a] Screening was carried out under the reaction conditions described in the Experimental Section with a molar ratio Fe/ligand/CF_3COOH of 1/4/1. The reaction medium was water/acetonitrile/benzene (5/5/1). [b] Selectivity based on H_2O_2: (moles of phenol produced) × 100/(moles of converted hydrogen peroxide). [c] Selectivity based on benzene: (moles of phenol produced) × 100/(moles of converted benzene). n.d.: not determined.

especially the pyrazinecarboxylic acid derivatives (entries 13–15), gave the best results.

The cocatalyst was selected from a series of acids, including acetic, phosphoric, sulfuric, *p*-toluenesulfonic, and trifluoroacetic acids. The latter gave the best results and increased the phenol selectivity (based on H_2O_2) from 68 (in the absence of any acid cocatalyst) to 78%. Conversely, complete inhibition of the catalytic activity occurred with phosphoric acid.

With $FeSO_4$, ligand **1**, and trifluoroacetic acid, in the selected water/acetonitrile/benzene biphasic system, under optimized reaction conditions (a further increase in selectivity was obtained by lowering the temperature from 50 to 35 °C), we achieved a benzene conversion of 8.6% with selectivities of 97% (based on benzene) and 88% (based on H_2O_2). These values are higher than those reported for other iron-based catalysts such as the Fenton [7] and Gif systems.[8] In the former case, high selectivities based on H_2O_2 (up to 83%) were only obtained at low benzene conversion (<1%). In the latter, a series of iron complexes with pyridine-2-carboxylic acid derivatives were reported to be completely ineffective in the oxidation of benzene under Gif reaction conditions.

It is also noteworthy that in the biphasic system, only a negligible amount (<1%) of biphenyl was detected among the secondary products, whereas in the classical Fenton oxidation, this compound is formed by radical dimerization of hydroxycyclohexadienyl radicals in a yield of 8–39%.[9]

This different reactivity and selectivity was confirmed in the oxidation of toluene. In the biphasic system, this reaction afforded a mixture of hydroxylation products (*o*- and *p*-cresol) and benzylic oxidation products (benzylic alcohol, benzaldehyde, benzoic acid) in 76 and 23% overall yield, respectively (see Experimental Section). Conversely, under Fenton conditions, the reported product distribution was: hydroxylation 4%, benzylic oxidation 56%, and radical dimerization to bibenzyl 30%.[9]

The catalyst system is also effective in the oxidation of alkanes, including a substrate as poorly reactive as methane, which is mainly converted (70 °C, 5 Mpa) to formic acid (46% based on hydrogen peroxide); in this case, a biphasic system is not expected to form.

In conclusion, a new iron-based homogeneous catalyst for the oxidation of benzene to phenol with 97% selectivity was discovered. An attractive feature of the process is the operation in a biphasic system, with the quantitative distribution of the catalyst in the aqueous phase, that can be separated and reused in several consecutive cycles as a "working solution" without any appreciable loss of activity. In the light of these promising results, the development of a continuous process, more suitable for industrial application, is presently under investigation.

Experimental Section

1 was synthesised according to a literature procedure.[10] All other chemicals (Aldrich) were used as purchased.

Solvent screening: $FeSO_4 \cdot 7H_2O$ (0.06 mmol) and CF_3COOH (0.06 mmol) were dissolved in water (8 mL), and the solution added to a mixture of an organic solvent (acetonitrile, propionitrile, *tert*-butyl alcohol, acetone, dioxane, dimethylformamide, or *n*-octane; 8 mL) and benzene (1.6 mL, 18 mmol). The resulting biphasic system was stirred at 50 °C, and an aqueous solution of hydrogen peroxide (30% w/w, 1.8 mmol) was added stepwise over 1 h. At the end of the reaction, the hydrogen peroxide concentration in the aqueous phase was determined by titration with potassium permanganate, and the concentration of oxidation products in the aqueous and organic phases was determined by HPLC analysis.

Catalyst screening: $FeSO_4 \cdot 7H_2O$ (0.06 mmol), CF_3COOH (0.06 mmol), and one of the ligands listed in Table 1 (0.24 mmol) were dissolved in water (8 mL), and the reaction mixture was stirred for 1 h at 25 °C. The resulting solution was added to a mixture of acetonitrile (8 mL) and benzene (1.6 mL, 18 mmol). The reactions were carried out as described for solvent screening.

Optimized conditions for benzene oxidation: $FeSO_4 \cdot 7H_2O$ (0.4 mmol), CF_3COOH (0.4 mmol), and **1** (0.4 mmol) were dissolved in water (109 mL), and the reaction mixture was stirred for 1 h at 25 °C. The resulting solution was added to a mixture of acetonitrile (109 mL) and benzene (22 mL, 248 mmol). The resulting biphasic system was stirred at 800 rpm at 35 °C, and an aqueous solution of hydrogen peroxide (30% w/w, 24 mmol) was progressively added with a peristaltic pump over 4 h. At the end of the reaction, the concentrations of hydrogen peroxide and of the oxidation product were measured as described above. Hydrogen peroxide and benzene conversions were 95 and 8.4%, respectively, with selectivities to phenol of 88 and 97% based on hydrogen peroxide and benzene, respectively. The molar product distribution was: phenol 97.1, hydroquinone 0.5, catechol 0.6, 1,4-benzoquinone 0.1, biphenyl 0.1, and tars 1.5%.

Toluene oxidation: The reaction was carried out as described above for benzene, with water (109 mL), acetonitrile (109 mL), $FeSO_4 \cdot 7H_2O$ (0.4 mmol), CF_3COOH (0.4 mmol), **1** (0.4 mmol), toluene (240 mmol), and hydrogen peroxide (30% w/w; 24 mmol). After 4 h at 50 °C the hydrogen peroxide and toluene conversions were 60 and 3.1%, respectively. The molar product distribution was: *o*-cresol 44, *p*-cresol 32, 2-methyl-1,4-benzoquinone 1, benzyl alcohol 5, benzaldehyde 15, and benzoic acid 3%.

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