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Sulfonamide-substituted iron phthalocyanine: design, solubility range, stability and oxidation of olefins[†]

Ümit İşci,* Celal Caner, Yunus Zorlu, Ayşe Gül Gürek, Fabienne Dumoulin and Vefa Ahsen*

4-*tert*-Butylbenzenesulfonamide was used as a substituent of tetra peripherally substituted Fe(II) phthalocyanine, taking into account several parameters crucial for the design of potential oxidation catalysts such as solubility and stability. The resulting phthalocyanine exhibits a remarkable stability under oxidative conditions. The main product of the oxidation of cyclohexene using H₂O₂ as the oxidant is the allylic ketone, 2-cyclohexen-1-one. Styrene oxidation led mainly to the formation of benzaldehyde.

The oxidation of cycloalkenes is of considerable interest in industrial organic synthesis, because derivatives containing an oxygen substituent in the ring are crucial intermediates in the synthesis of fine chemicals. Many reports have been published concerning the oxidation of cyclohexene using different oxidants in various solvents.^{1–6} Allylic oxidations of olefins are in general focusing on the use of transition metal salt-based catalysts.^{7,8}

Environmental preoccupations of our modern world, together with economic factors are the key considerations to be taken into account when designing potential catalysts: their synthesis must be cheap, short and high yielding. Besides, their catalytic efficiency must be elevated, which implies the best possible stability to maximize the turnover. To be versatile, their solubility must cover a wide range of solvents.

When appropriately metallated, phthalocyanines have catalytic properties, in most of the cases for oxidation reactions.^{9,10} So far, iron phthalocyanines have proven to be particularly relevant, due to the availability of the metal as opposed to precious transition metals (ruthenium, rhodium, platinum, *etc.*), and their heme-like biomimetic action mechanism. The design of phthalocyanines for catalytic applications must be carefully achieved, taking into account the considerations

listed above, especially regarding the choice of the substituents, which must be chemically resistant to the oxidation conditions. This is why *tert*-butyl substituted phthalocyanines, which are easily prepared from a commercially available phthalonitrile, are widely used, either for $Fe(\pi)$ phthalocyanines or for their dimeric N-bridged derivatives.^{11,12} Since then, such dimeric iron phthalocyanines bearing electron-withdrawing sulfonyl substituents have been identified as particularly interesting, thanks to the stability conferred by this type of substituents already oxidized.^{13,14}

Aiming at enlarging the scope of possible catalysts, we were interested in sulfonamide-substituted iron phthalocyanines and designed the targeted phthalocyanine **1** represented in Fig. 1.

Substitution patterns including or based on sulfonamide function are scarcely used for phthalocyanines: tetrasulfophthalocyanines were amidified by octylamine,¹⁵ and tetrasulfonamide Co(II) phthalocyanine was used for the catalytic



Fig. 1 Structure of targeted phthalocyanine 1.

Department of Chemistry, Gebze Institute of Technology, PO Box 141, Gebze, 41400 Kocaeli, Turkey. E-mail: u.isci@gyte.edu.tr, ahsen@gyte.edu.tr;

Fax: +90 262 605 3005; Tel: +90 262 605 3092

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Scheme 1 Preparation of phthalonitrile 4 and of targeted phthalocyanine 1.

oxidative sweetening of LPG.¹⁶ Amidified tetrasulfo phthalocyanines proved to be as well good NO_x sensors, thanks to the possible intermolecular interactions with nitrogen dioxide.¹⁷ Cavaleiro *et al.* introduced sulfonamide functions on aromatic substituents of the phthalocyanine ring,¹⁸ and evidenced the high non-linear transmission properties of these derivatives.¹⁹

As far as we could find out, no substituent linked to the phthalocyanine ring *via* the nitrogen atom of the sulfonamide function exists, when the interests are obvious: the simple synthesis of the corresponding phthalonitrile from the commercially available 4-aminophthalonitrile **2** (as well easily accessible on a large scale by the quantitative reduction of 4-nitrophthalonitrile) and from a substituted chlorosulfonyl benzene (Scheme 1), here 4-*tert*-butylbenzene-1-sulfonyl chloride **3**. Phthalonitrile **4** was indeed readily obtained, and suitable crystals of **4** were grown by recrystallization from ethanol at room temperature by slow evaporation. Its structure and geometries were established by single-crystal X-ray structure analysis.

The ORTEP molecular structure with atomic numbering scheme is represented in Fig. 2. The compound crystallizes in the orthorhombic space group $Pca2_1$. The structure shows that the C1 \equiv N1 and C2 \equiv N2 bond lengths are 1.141(3) Å and 1.143(3) Å, respectively, and are similar to values reported in the literature.²⁰ The C9–C14 ring is nearly orthogonal to the phthalonitrile aromatic ring (C3–C8) with an angle of 86.98(9)°. The NH group forms a linear intermolecular N–H…N hydrogen bonding interaction with a N…N distance of 3.062(3) Å.

Phthalonitrile 4 was converted into the corresponding targeted phthalocyanine 1 in the presence of FeCl_2 in refluxing ethylene glycol, which are the routine conditions for preparing



Fig. 2 ORTEP molecular structure of 4. Displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary radii.



Fig. 3 UV-vis spectra of 1 in acetone (blue), tetrahydrofuran (red), dimethylsulfoxide (black), chloroform (pink), dimethylformamide (green) and acetonitrile (yellow).

Fe(II) phthalocyanines,²¹ and are allowed to obtain 1 in a 32% yield particularly good for Fe(II) phthalocyanines.²¹

Phthalocyanine **1** exhibits a wide range of solubility, as evidenced by the UV-vis spectra recorded in different solvents of various polarities, namely acetone, tetrahydrofuran, dimethylsulfoxide, chloroform, dimethylformamide and aceto-nitrile (Fig. 3).

The split in the UV-Vis spectra near 640 nm comes from the aggregation species, as reported on related derivatives.²²

The stability of a potential oxidation catalyst is crucial and hydrogen peroxide was used to evaluate the stability of **1** in acetonitrile. With a 1000-fold excess of the oxidant (Fig. 4), UV-vis spectra was recorded at regular intervals over 2 hours, and then overnight. Phthalocyanine **1** proved to be as stable as the N-bridged dimeric derivatives, which are the most stable reported iron phthalocyanines, and the most powerful oxidation catalysts.²³ During the titration of phthalocyanine **1** with H_2O_2 , some spectral changes were observed. When a diminution of the Q band intensity would reveal a degradation of the phthalocyanine,²⁴ the increased absorbance between



Fig. 4 UV-vis spectra of 1 in acetonitrile in the presence of a 1000-fold excess of H_2O_2 , recorded over two hours and overnight. Inset: plot of the Q band max vs. time.



Scheme 2 Cyclohexene oxidation products

400 and 600 nm over 24 h can be interpreted as the result of the metal-oxidation by H_2O_2 into its iron-oxo form, without significant transformation of the phthalocyanine macrocycle,²⁵ the apparition of the shoulder after 24 h suggesting the formation of the μ -oxo dimeric species.²³

Iron phthalocyanine complex **1** was tested in the catalysis of cyclohexene oxidation. The reactions were performed at 25 °C in acetonitrile. The oxidation of cyclohexene afforded full conversion after 2 h, and three products (cyclohexene-one, cyclohexene-ol, cyclohexene oxide, Scheme 2)



Scheme 3 Oxidation of styrene by 1.

were clearly identified using GC-MS, in respective yields of 40, 8 and 6%. The excellent predominance of allylic oxidation (88.9% of all the oxidation products) must be noted to acknowledge the potential of this new catalyst, the largely predominant allylic oxidation product being the enone (cyclohex-2-en-1-one, 74.1% of all the oxidation products).

To enlarge the scope of the study, the oxidation of cyclohexene by **1** was tested in different solvent systems (Table 1). DMF appeared to have a limiting effect on the cyclohexene conversion. Compared to acetonitrile, conversion in acetone and dichloromethane is slower, but the oxidation products are formed in similar proportions.

In dichloromethane (entry 3), the yield of cyclohexene-1-ol increased, while the lowest yield in cyclohexene oxide is observed. While the yield of cyclohexene oxide increased in acetone (entry 2) and acetonitrile (entry 1), the cyclohexene oxide yield decreased in the other solvents (entries 3 and 4).

Styrene was also studied as another oxidation substrate (Scheme 3) in acetonitrile, with 60% conversion after 3 h. Styrene was converted into benzaldehyde (38%), the main oxidation product, and styrene oxide (22%).

To conclude, this work, based on the rational design of a phthalocyanine to be a potential new oxidation catalyst, demonstrated the relevance of sulfonamide substitution pattern, as it provides a wide range of solubilities, and exhibits excellent stability under oxidative conditions. Catalytic oxidation experiments of olefins were conducted using the environmentally friendly oxidant H_2O_2 . The main oxidation products of cyclohexene are allylic oxidation products under different conditions. Benzaldehyde was the main product of styrene oxidation.

These results prompted us to carry out more oxidation investigations and the activity of phthalocyanine **1** in the oxidation of several pollutants is currently being investigated. Furthermore, other sulfonamide substituents are also being tested.

Table 1 Solvent effect in the allylic oxidation of cyclohexene with H₂O₂ catalysed by 1

Entry	Solvent	Time (h)	Conversion (%)	ON^a (%)	$OL^{a}(\%)$	$E^{a}(\%)$	TON ^b
		()			()	()	
1	CH ₃ CN	2	100	40	8	6	108
2	CH ₃ COCH ₃	3.5	95	43	8	5	112
3	CH_2Cl_2	3.5	80	41	10	1	104
4	DMF	3	45	13	2	2	34

^a ON: 2-cyclohexen-1-one, OL: 2-cyclohexen-1-ol, E: cyclohexene oxide. ^b TON: mmol product/mmol catalyst.

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