

Epoxidation of the Commercially Relevant Divinylbenzene with [*tetrakis*-(Pentafluorophenyl)porphyrinato]iron(III) Chloride and Its Derivatives

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Supporting Information

ABSTRACT: Fluorinated Fe-porphyrins, especially [*tetrakis*(pentafluorophenyl)porphyrinato]iron(III) chloride (*tetrakis*(pentafluorophenyl)porphyrinato = TPFPP) (TPFPP)FeCl (**Fepor-2a**), were found to be highly efficient for catalyzing the double epoxidation of divinylbenzene (DVB) to divinylbenzene dioxide (DVBDO), a novel component of epoxy resin formulation. The electronic properties of the catalysts are highly dependent on the substituents on the phenyl groups of these metalloporphyrins. The electron-rich fluorinated Fe-porphyrins are more selective toward epoxidation but are more vulnerable toward decomposition in H₂O₂. On the other hand, the electron deficient Fe-porphyrins are more stable, yet more Lewis acidic, which facilitates the formation of byproducts such as epoxide ring opening and overoxidation.

poxy resins are materials of great industrial importance, as they are commonly used in paintings, coatings and electronic packagings. Conventional epoxy resin formulation usually involves diglycidyl ether of bisphenol A or bisphenol F, with this synthesis resulting in high viscosity and large coefficients for thermal expansion (CTEs), as well as high chlorine content.^{1,2} For some applications, however, these characteristics are undesirable. For example, high viscosity results in low heat resistance for epoxy thermosets,³ which is disadvantageous in applications like modeling or electronic coating.⁴ High thermal expansion (represented by the coefficient of thermal expansion $(CTE))^5$ is not desirable for electronic laminates to have good resistance to thermal fatigue.⁶ The chlorine content arising from the coupling of bisphenol A and epichlorohydrin renders the epoxy resins corrosive, a problematic property for applications involving electronic devices.¹ Thus, new types of epoxy resin formulations that circumvent these problems are desirable. Epoxy resin formulation using divinylbenzene dioxide (DVBDO in Figure 1) results in a material possessing low viscosity (20 cP),⁷ high heat resistance,³ low CTE loading,¹ high filler loading, high glass transition (T_{σ}) values, and very low to no extractable ionic contamination.⁸ These properties contribute to the application of DVBDO in various products such as electronic packaging materials, composites, or other industrial materials. Therefore, developing a highly efficient process to synthesize DVBDO is of substantial industrial value.

Epoxidation of divinylbenzene (DVB) is the key step for the synthesis of divinylbenzene dioxide (DVBDO). However, to date, there are only limited examples that provide DVBDO with both high yield and high turnover number. For approaches that use environmentally benign oxidants such as H₂O₂, to the best of our knowledge, only two peer-reviewed reports are available,^{9,10} both of which suffered from low yield and low selectivity. Dow Chemical Company patented several processes for the double epoxidation of DVB: they have demonstrated that catalysts like methyltrioxorhenium,11 phosphotungstic acid,¹¹ and the Fe(III)-pyridinedicarboxylate complex¹² are efficient for the double epoxidation of DVB, and that oxidants like peroxyacetimidic acid¹³ show very good selectivity for the formation of DVBDO. However, some of these catalysts have drawbacks such as low selectivity, low turnover number, using high cost noble metal, and stoichiometric formation of organic byproducts.¹³ Other oxidant such as *m*-CPBA and *tert*butylhydroperoxide have also been studied;^{14,15} however, these oxidants generate stoichiometric amount of organic byproduct. We have recently discovered that a Mn-porphyrincontaining porous organic polymer (Mn-PPOP) is a very selective heterogeneous catalyst for the double-epoxidation of DVB to DVBDO using 2-(tert-butylsulfonyl)iodosylbenzene.^{16,17} Unfortunately, 2-(tert-butylsulfonyl)iodosylbenzene is synthesized from a highly toxic starting material thiophenol via a route entailing several steps. Most importantly, the epoxidation reaction generates 2-(tertbutylsulfonyl)iodobenzene as a stoichiometric byproduct, making the process unsuitable at an industrial scale. Clearly desirable for large-scale production of DVBDO would be a

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Figure 1. Structure of DVBDO (mixture of meta and para isomers) and metalloporphyrins in the present study.

catalyst that can use a clean oxidant like H_2O_2 . The range of biomimetic catalysts featuring heme-type enzymes, and our previous experience with metalloporphyrin-catalyzed epoxidation chemistry, suggested that Fe-porphyrin complexes might well prove effective as double-epoxidation catalysts.

Synthetic Fe-porphyrins and phthalocyanine have been extensively studied due, in part, to their structural similarity to the natural enzyme P450.^{18–22} Uniquely effective catalytic activity for H_2O_2 -based epoxidation of alkenes to epoxides has been demonstrated for fluorinated metalloporphyrins such as **Fepor-2a**; see Figure 1.^{23–25} However, styrenic alkenes have only rarely been studied in this context.²⁶ To our knowledge, only one example of catalysis of such a process by **Fepor-2a** has been reported,²⁷ and the question of byproduct formation was not addressed in the report. The reactivity of styrene species typically differs from that of cyclooctene and cyclohexene. Styrenic alkenes are more inert toward oxidation due to the double bond conjugation with the benzene ring. Furthermore, once the styrene-derived epoxide is formed, it is more susceptible to overoxidation (e.g., to thermally stable benzaldehyde) than are many other epoxides (Scheme 1).





These differences often result in low yields and poor selectivity.²⁸ Thus, for styrenic alkenes it is difficult to make good predictive analogies based on the reactivity of simpler molecules like cyclohexene; this is especially true for divinylbenzene due to the double possibility for side reactions (where these side reactions may include epoxide rearrangement, ring opening, or overoxidation).

Herein, we report that **Fepor-2a** catalyzes in selective fashion the double oxidation of DVB to DVBDO with a high turnover number (TON > 600) using H_2O_2 as the oxidant. We also report on how the electronic properties of catalyst substituents alter reaction selectivity and catalyst stability.

Stephenson and Bell have reported an interesting and relevant example of **Fepor-2a**-catalyzed epoxidation of a styrenic alkene;²⁷ unfortunately, the substrate conversion and yield based on styrene were low (<20%) and the issues of catalyst stability and the byproduct formation were not addressed. Given the structural and electronic similarity of styrene to DVB, our study uses styrene as a model substrate. The yield of the desired epoxide was 80% (Figure 2). Analysis of byproducts indicated that the main product-loss reactions were epoxide ring-opening by MeOH (11%), epoxide overoxidation to benzaldehyde (5%), and epoxide rearrangement (3%). It is important to point out that oxidative degradation of the porphyrin itself is often an issue for metalloporphyrin-



Figure 2. Time profile of the Fepor-2a catalyzed epoxidation of styrene by H_2O_2 .

catalyzed oxidation reactions. Consistent with its electron deficient nature, and as evidenced by an unchanged electronic absorption spectrum (Figure 3), Fepor-2a was stable throughout the reaction.



Figure 3. UV–vis spectra of Fepor-2a (in methanol) and of the catalyst-containing reaction after completion of epoxidation of 100 equiv of styrene; H_2O_2 was 160 equiv relative to Fepor-2a.

The redox potential of the iron center, as well as the oxidation strength of the catalyst in an oxygen-transfer sense, can be tuned by varying the porphyrin substituents.^{24,29} The latter can also be tuned by changing the identity of the metal. Additional effects might be expected based on replacement/ removal of the initially present chloride ligand. By changing the chemical identity of the axial ligand, the peripheral substituents, and the metal center (Table 1), we studied four metal-

Table 1. Epoxidation of Styrene Using Fluorinated Metalloporphyrins and Non-Fluorinated Metalloporphyrins

Entries	Porphyrins	Conversion * (%)	Vield* (%)	OMe O⊢ Yield* (%)	CHO Yield* (%)	CHO Yield* (%)
1	Fepor-1	0	0	0	0	0
2	Mnpor-2	0	0	0	0	0
3	Fepor-2a	95	80	11	3	4
4	Fepor-2a + AgNO ₃	98	81	8	4	2

^{*}Conversion and yield are based on NMR integration. Reaction conditions: porphyrins (0.003 M), styrene (0.3 M), H_2O_2 (0.48 M), DCM/MeOH = 1/3, reaction temperature = rt.

loporphyrins. The cationic (TPFPP)Fe⁺ (formed in situ by addition of $AgNO_3$, extraction of chloride, and precipitation of AgCl) catalyzed the reaction with a slightly faster rate than (TPFPP)FeCl but similar selectivity and yield (Table 1, Entry 4).

Unfortunately, upon completion of the reaction, or shortly after, the reaction solution lost its color, indicating catalyst decomposition. The fluorine-free compound **Fepor-1** did not catalyze epoxide formation, a finding we consider further below. Replacing Fe with Mn leaves **por-2** completely unreactive for the epoxidation of styrene (Table 1 Entry 2).

To understand in a quantitative way how **Fepor** ring substituents influence catalytic activity and selectivity, we examined candidate epoxidation reaction mechanisms using quantum chemical calculations.

We adopted the most general and complete mechanism proposed in the literature to date by Bell and co-workers.²⁴ Two parallel steps emanating from a common intermediate were proposed to be rate-determining as shown in Figure 4. The O–O bond of the coordinated hydrogen peroxide undergoes either homolysis (Reaction 2) to produce a



Figure 4. Two rate-determining and competing steps in iron porphyrin-catalyzed olefin epoxidation are proposed to account for the selectivity toward epoxide.

catalytically inactive one-electron oxidized iron(IV) porphyrin species, or heterolysis (Reaction 1) to form a catalytically active two-electron oxidized iron(IV) π -radical cation species.^{26,30} The competition between these two steps is purported to account for the catalytic selectivity toward olefin epoxidation or hydrogen peroxide decomposition. Herein, we report the energy barriers and rate ratios for these two reactions for two Fe-porphyrins, **Fepor-1** and **Fepor-2a**, as shown in Table 2.

Table 2. Rate-Determining Barriers of Reaction 1 andReaction 2 for Two Iron Porphyrin Catalysts*

	Fepor-1	Fepor-2a
E_{a1}	10.54	4.46
E_{a2}	12.16	22.30
r_{1}/r_{2}	$A_1 e^{-\frac{E_{a_1}^1}{RT}} c_{MeOH} / A_2 e^{-\frac{E_{a_2}^1}{RT}}$	$A_3 e^{-\frac{E_{a1}^{2a}}{RT}} c_{MeOH} \Big/_{A_2} e^{-\frac{E_{a2}^{2a}}{RT}}$
$(r_1/r_2)^{2a}/(r_1/r_2)^1$	$e^{\frac{E_{a1}^{1}-E_{a1}^{2a}}{RT}} / e^{\frac{E_{a2}^{1}-T}{RT}}$	$r_{az}^{2a} = 7.75 \times 10^{11}$

^{*}All energies are in kcal·mol⁻¹, relative to isolated reactants including ZPE. Calculations are done in the gas phase. Computational details can be found in Supporting Information.

For catalyst **Fepor-1**, the energy barrier of reaction 1 is close to that of reaction 2, whereas for **Fepor-2a**, the energy barrier of reaction 1 is about 18 kcal/mol lower than that of reaction 2. To directly assess the competition between these two reactions, it is necessary to calculate the ratio of reaction rates, r_1/r_2 , because the molecularity of these two reactions is different. We adopted the Arrhenius equation and made two assumptions: (1) the activation energies can be approximated by the zeropoint corrected energy barriers, and (2) the two catalysts share the same pre-exponential factors for reaction 1 and reaction 2, A_1 , and A_2 , respectively. The last row of Table 2 shows that the ratio of r_1/r_2 for the two catalysts, that is, **Fepor-2a** to **Fepor-1**, is extremely large, indicating that **Fepor-2a** has a much higher selectivity toward reaction 1 compared with **Fepor-1**. Thus, the computational results are in excellent accord with the

Scheme 2. Epoxidation of DVB by (TPFPP)FeCl using H_2O_2



	Table 3.	Epoxidation	of DVB	Using	Functionalized	Fluorinated	Fe-Port	ohyrins*
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entries	porphyrins	total alkene conversion/DVB conversion (%)	DVBDO yield based on DVB (%)	DVBMO yield based on DVB (%)	EVBO yield based on EVB (%)	RO yield based on alkene (%)
1	Fepor-2a	98/100 (14 h)	75	5	52	12
2	Fepor-2b	48/31 (9 h)	3	28	26	0
3	Fepor-2c	69/88 (10 h)	38	43	74	0
4	Fepor-2d	99/99 (12 h)	35	3	21	35
5	Fepor-2e	100/100 (10 h)	63	0	62	20
6	Fepor-2a + AgNO ₃	73/97 (6 h)	29	43	66	6

^{*}Conversion and yield are based on NMR integration. Reaction conditions: porphyrins (0.003 M), DVB (0.3 M), H_2O_2 (0.078 equiv was added every 20 min until the reaction was completed or the color of the reaction mixture turned redish, see Supporting Information about the exact amount of H_2O_2 in each experiment), DCM/MeOH = 1/3, reaction temperature = rt.

experimental observations, in which **Fepor-2a** has a much higher epoxide yield than **Fepor-1** does. Our calculations suggest that the origin of this difference is the significantly increased tendency of **Fepor-2a** for epoxidation, leading the core catalysis to the preferred epoxide product.

These results suggest why **Fepor-2a** shows higher selectivity and reactivity than does **Fepor-1**. Preliminary results from calculations using a solvent model reveal the same trend. Further theoretical study on this mechanism is underway.

Returning to experimental studies, when we examined the epoxidation of divinylbenzene, using **Fepor-2a**, the reaction worked smoothly under the conditions identified above as the optimal for the epoxidation of styrene. The desired product, DVBDO, was formed in 77% yield, with a small amount of partially oxidized divinylbenzene monoxide (DVBMO) remaining (Scheme 2). Also observed was a 55% yield for ethylvinylbenzene oxide (EVBO), a product arising from the presence of ethylvinylbenzene (EVB) in the starting material.³¹ As with styrene, no catalyst decomposition was observed. It should be pointed out that only 3.2 equiv (per DVB) of H₂O₂ were used, meaning that little excess H₂O₂ remained. This may be a significant advantage for the large-scale production of DVBDO, as it decreases the need for recovery or intentional degradation of peroxide at the reaction conclusion.

To understand the significance of fluorine substituents to the catalytic behavior of **Fepor-2a**, the 4-position of the *meso*-

phenyl group on the Fe-porphyrin was functionalized with other heteroatoms to give four additional Fe-porphyrins (Figure 1). Evaluation of the set of five Fepor-2 as DVB epoxidation catalysts showed that electron-withdrawing groups stabilized the catalyst and electron-donating groups destabilized it. Thus, Fepor-2b and Fepor-2c decomposed before alkene conversion was complete (Table 3, Entries 2-3). In contrast, for Fepor-2d and Fepor-2e,³² no degradation of the porphyrin core was observed (Entries 4 and 5). Compared to Fepor-2a, Fepor-2e should be less withdrawing; however, a slight electron donating conjugation effect of the fluorine lone pair electrons may compromise the strong inductive effect of fluorine. The ethyl ester version Fepor-2e extends the conjugation of the iron-porphyrin which also makes the Fe-center electron deficient. Overall, the Lewis acidity of the iron center of Fepor-2a and Fepor-2e might be similar. However, we observe more overoxidized benzaldehyde derivative byproduct and other unidentified byproduct from Fepor-2e. In entry 6, Fepor-2a plus AgNO₃ is also selective toward epoxidation; however, the reaction did not reach 100% double bond conversion due to the relatively faster $\mathrm{H_2O_2}$ addition which decomposed the catalyst (Table 1, Entry 4).

Substituent composition also significantly affects reaction selectivity. Versions of Fepor-2 featuring electron-withdrawing functionalities at the 4-position of substituent rings yielded significant amounts of ring-opened product, whereas those

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featuring electron-donating functionalities did not. The ringopened products presumably derive from Lewis-acid catalyzed attack of the initially formed epoxide products. Electron withdrawing substituents, of course, will increase the Lewis acidity of the catalyst's iron center. Introducing electrondonating functionalities at the 4 position suppresses undesirable ring-opening activity but at the expense of incomplete epoxidation.³³ However, although it is more tedious and costly to synthesize **Fepor-2e**, no partially oxidized DVBMO is formed, which makes it a potential catalyst candidate for further exploration because it is easier to separate ring opening and overoxidized aldehyde byproduct than DVBMO from an industrial operation perspective. Product distributions as a function of catalyst identity are summarized in Table 3 and graphically illustrated in Figure 5.



Figure 5. Product distribution chart for functionalized Fe-porphyrincatalyzed epoxidation of DVB.

Fepor-2a, the fully phenyl-fluorinated version of the catalyst, seems to provide the best overall performance in terms of selective double epoxidation of DVB. As such, this catalyst was the focus of efforts to optimize reaction conditions for both turnover number and selectivity. Removing dichloromethane or replacing MeOH with *i*-PrOH resulted in greater byproduct formation and smaller turnover numbers. Increasing the alkene concentration led to faster catalyst decomposition. However, lowering the reaction temperature to 0 °C minimized formation of the most significant byproduct (the MeOH ring-opened product) and increased the reaction turnover number (>600) as well as the yield of DVBDO (80%) (Figure 6). It is also pleasing that at 0 °C, only 1.8 equiv (relative to alkene) of H₂O₂ are needed to fully convert the starting material.

In conclusion, we find that **Fepor-2a** catalyzes the double epoxidation of DVB to DVBDO with good selectivity and a high turnover number. Changes in the chemical identity of the substituents of **Fepor-2** alter its catalytic behavior dramatically. In the oxidizing environment, electron donating groups engender catalyst decomposition; electron withdrawing groups make the catalyst more robust but also more Lewis acidic, which leads to more byproduct formation. For good catalyst performance, the choice of reaction conditions is critical. An optimal result was obtained when the reaction was performed at 0 °C (turnover number > 600 and quantitative H₂O₂ consumption).



Figure 6. Time profile of the epoxidation of DVB at 0 $^\circ C$ with turnover number >600.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of the fluorinated Fe-porphyrins, and procedures for catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(31) Commercial available DVB is a mixture of 80% DVB and 20% ethyl vinylbenzene (EVB), both DVB and EVB are also mixtures of *meta* and *para* isomers with a raito approximately 2 to 1.

(32) Fe-porphyrin in Entry 5 may be oxidized into aldehyde or acid in the reaction conditions, the conjugation effect of these functional groups makes this Fe-porphyrin electron deficient.

(33) The idea for incorporating bromine, alkyne and carboxylate is that they could be further incorporated into porous organic polymers or metal organic framworks so that an heterogeneous catalyst for this reaction can be synthesized.