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Research Note

Epoxidation of styrene with cobalt-hydroxyapatite and oxygen in dimethylformamide: A green technology?

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Abstract

The role of amide-type solvents, particularly DMF, was studied in the epoxidation of styrene over Co^{2+}-exchanged hydroxyapatite. Even under relatively mild conditions, DMF is autoxidized with molecular oxygen to N-(hydroperoxymethyl)-N-methylformamide, which acts as an oxygen-transfer agent in the epoxidation of styrene, thereby producing N-formyl-N-methylformamide in considerable amounts. In addition, the drastic effect of reactor operation mode (open and closed systems) on the catalyst performance reveals the formation of another, volatile byproduct from DMF that inhibits the reaction in closed reactors (autoclaves).

Keywords: Epoxidation; Hydroxyapatite; Aerobic; Styrene; Dimethylformamide; Solvent effect; Sacrificial solvent

1. Introduction

Catalytic epoxidation of olefins with oxygen as the terminal oxidant is a field of great interest due to the versatility of epoxides as synthetic intermediates [1]. In most cases, a sacrificial compound (usually aldehydes) are added as oxygen acceptors to achieve reasonable yields and selectivities; however, from environmental and economic standpoints, this approach has no real advantage compared with the use of a chemical oxidant, such as H_2O_2. Only a few heterogeneous catalysts are active with molecular oxygen alone under mild conditions in the liquid phase [2–6]. The solvent plays a crucial role in these reactions; based on the usual solvent parameters, its influence is difficult to rationalize [3,7–9]. There are increasing indications in the literature that some preferred solvents cannot be considered to be inert in oxidation reactions, because they are involved, either directly or indirectly, in the reaction route [10,11]. Note that even the oxygenation of aliphatic and aromatic hydrocarbon solvents during epoxidation has been detected [12].

Here we discuss a special solvent effect in the epoxidation of styrene with Co^{2+}-exchanged hydroxyapatite (CoHAp). Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp]-based materials have recently found applications as solid, recyclable catalysts. The Ca^{2+} ions in the lattice can be exchanged with other, catalytically active cations, resulting in interesting materials analogous to heterogenized homogeneous catalysts. CoHAp has been applied as a catalyst in the oxidative dehydrogenation of 2-butanol, ethane, and propane in the gas (vapor) phase [13,14]. We show that in the epoxidation of styrene with CoHAp in dimethylformamide (DMF), a widely used excellent medium for epoxidation reactions with molecular oxygen, the solvent plays the role of a "sacrificial" auxiliary.

2. Experimental

Styrene (>99.5%, Fluka) was freshly distilled before use. The solvents DMF, N,N-dimethylacetamide, N,N-dibuthylformamide, N,N-diethylformamide, 1,4-dioxane, and 1,2-dichloroethane were dried over molecular sieve 4 Å. The catalyst Co^{2+}-hydroxyapatite (CoHAp) was prepared as we described previously [15]. 1.0 g HAp, calcined at 500 °C (BET surface area, 81 $m^2\,g^{-1}$; micropore area, 10.3 $m^2\,g^{-1}$; average pore diameter, 20 nm), was shaken with 75 mL of a 67 mM aqueous solution of $CoCl_2$ for 20 min. The solid (CoHAp) was filtered off, washed with deionized water, and dried for 6 h at 80 °C. The XRD patterns showed only diffraction peaks due to HAp.

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The catalyst contained 2 wt% Co and the (Ca + Co)/P ratio was 1.60 (by ICP-OES), lower than the Ca/P ratio in stoichiometric HAp (1.67). For more information on the characterization of CoHAp, see Refs. [13–15] (e.g., the BET surface area did not change significantly with the introduction of Co).

Epoxidation of styrene was carried out in a 100-mL glass reactor in the presence of oxygen, at atmospheric pressure. The slurry containing 100 mg of CoHAp (Co, 0.034 mmol) and 1 mmol of anisole (internal standard) in 10 mL of solvent was stirred for 5 min under oxygen at room temperature. The reactor was placed in a preheated oil bath; after 5 min, styrene was added to start the reaction. Two different reactor operation modes were applied. In the "open" system, oxygen was flown through the reactor and the cooling system at a flow rate of ca 10 $cm^3 min^{-1}$. In the closed operation mode, the reactor was flushed with oxygen and than closed with a balloon filled with O_2. The selectivity and conversion were determined by gas chromatography (GC) analysis (Thermo Quest Trace 2000, equipped with an HP-5 capillary column and a flame ionization detector), and the response factors related to anisole as internal standard were determined for styrene and the products. The products were identified with authentic samples. *N*-formyl-*N*-methylformamide (FMF) resulting from the autoxidation of DMF was identified by GC-mass spectroscopy (MS) analysis (m/z: 87, 73, 59, 42, 30, 15). The response factor of DMF to anisole was used for quantification of FMF. The GC-MS analysis was performed with an HP 6890 equipped with an HP-5MS capillary column and a mass selective detector HP-5973. The reaction rate was characterized by the average TOF at high conversion (TOF = [mol(converted styrene)/mol(Co)]/h).

3. Results and discussion

3.1. Epoxidation with CoHAp

Cobalt-exchanged hydroxyapatite proved to be an active and reasonably selective catalyst for the epoxidation of styrene with molecular oxygen, as illustrated in Fig. 1. The reactions were carried out in a commonly used "open" reactor; that is, oxygen was bubbled into the liquid, and the excess was removed from the reactor via a cooling system. Analysis of the liquid phase revealed formation of styrene oxide and benzaldehyde as the main products, along with minor quantities of phenyl glycol, benzoic acid, phenylacetaldehyde, and nonvolatile (probably polymeric) species. After 2 h of reaction, the epoxide selectivity was 62% at 83% styrene conversion (see supporting information). The selectivity to styrene oxide remained almost unchanged with conversion, but the selectivity to benzaldehyde decreased slowly (from 28 to 20%), parallel with benzoic acid formation. This selectivity is similar to those obtained with Co–NaX and Co-MCM-41 catalysts at significantly lower conversion (and also in DMF solvent), the first example related to the cobalt-catalyzed heterogeneous aerobic epoxidation of styrene that does not involve a co-reductant [8]. The catalytic activity of CoHAp, characterized by the average TOF (48 h^{-1}), is comparable to or even better than those of Co–NaX and Co-MCM-41. The reactions with HAp and without catalyst are shown in the supporting information. The autoxidation of styrene under the reaction conditions is significant; after 2 h of reaction, the conversion of styrene was 77% with 41% styrene oxide selectivity and 66% total selectivity to oxygenated nonpolymeric products. HAp acts in the reaction as an inhibitor, diminishing the conversion to 24% and the styrene oxide selectivity to 16%, whereas with Co (CoHAp), both the rate and selectivity of styrene oxide formation increase (49% styrene oxide selectivity and 88% total selectivity at 91% styrene conversion).

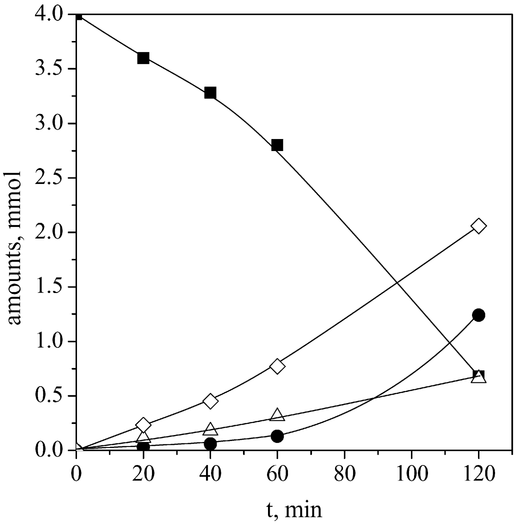


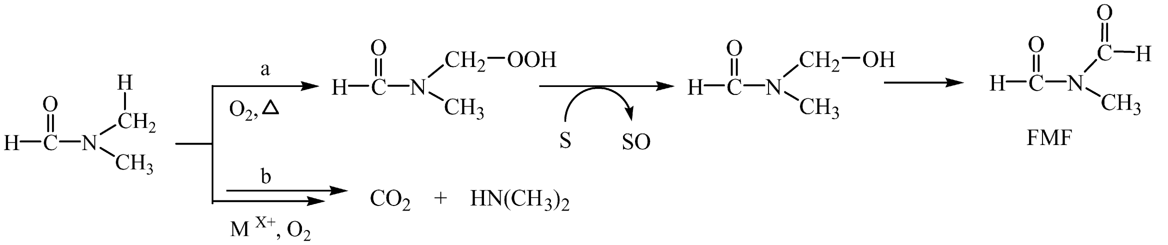
Fig. 1. Formation of styrene (■), styrene oxide (◇), benzaldehyde (△), and *N*-formyl-*N*-methylformamide (FMF) (●) during epoxidation of styrene with CoHAp and molecular oxygen. Conditions: "open" reactor, 100 mg CoHAp (Co: 0.034 mmol), 4 mmol styrene, 10 ml DMF, 383 K, 1 bar.

Table 1
The role of solvent in the epoxidation of styrene with CoHAp (100 mg CoHAp, 3.5 mmol styrene, 10 ml solvent, 1 bar O_2, 120 min, open system)

Solvent	T (K)	Styrene conversion (%)	Epoxide yield (%)
N,*N*-Dimethylformamide (DMF)	373	91	49
N,*N*-Dimethylacetamide (DMA)	373	100	7
N,*N*-Diethylformamide (DEtF)	373	59	11
N,*N*-Dibuthylformamide (DBF)	373	77	19
N,*N*-Dimethylformamide (DMF)	353	71	35
3-Pentanone	353	17	7
1,4-Dioxane	353	77	6

3.2. Solvent effect

Both the epoxide selectivity and the effect of reaction conditions on the catalyst performance were similar to those reported previously for other solid catalysts [3,7,8]. For example, increasing the temperature from 353 to 383 K raised the epoxide selectivity from 35 to 62% under the conditions specified in Fig. 1 and Table 1 (also see supporting information). As seen from Fig. 1 and the supporting information, benzaldehyde and styrene oxide, the two main products, form in parallel during the reaction, but the consecutive route via styrene oxide is also feasible [16]. Introducing other metal ions (i.e., Fe^{3+}, Ru^{3+}, and Ni^{2+}) into HAp was less promising; these catalysts were



Scheme 1. Autoxidation of DMF: (a) thermal oxidation of DMF and epoxidation of styrene (S) in DMF; (b) metal ion-catalyzed oxidation of DMF.

less active and selective than Co^{2+}. It is also known that epoxidations with molecular oxygen run well only in some selected solvents, especially alkyl amides [3,7,8]. The solvent played a crucial role in the epoxidation of styrene, as shown in Table 1. Better than 10% epoxide yield was obtained only in alkyl formamides, and even within this class, DMF seems to be outstanding. On the other end of the list, no reaction was detectable in several solvents, such as 1,2-dichloroethane, hexane, ethyl acetate, and *tert*-butyl alcohol. No correlation between the epoxide yield and the typical characteristics of the solvents (polarity, acidity, or basicity) could be found. It is very probable that the outstanding yields in DMF indicate a special role of the solvent in the epoxidation process. Similar unusual solvent effects have been noted in several oxidation reactions [3,7–10,16]. Tang and coworkers suggested that the tetrahedrally coordinated Co^{2+} sites, including DMF as a ligand, play an important role in the activation of oxygen, but they did not investigate the role of solvent as a co-reductant.

It seems to be a reasonable assumption that the unusual solvent effect in epoxidations with molecular oxygen may be traced to the high reactivity of DMF (and other alkyl amides) with oxygen. A closer supervision of the product distribution revealed an oxidation product of DMF, *N*-formyl-*N*-methylformamide (FMF) (Scheme 1 [17]). Formation of FMF ran parallel with the conversion of styrene and formation of styrene oxide (Fig. 1), suggesting that DMF may be an active component in the oxidative transformation of styrene. Note that several products were formed from the other three alkylamide-type solvents during styrene epoxidation, indicating that these solvents are also not stable under the reaction conditions. The autoxidation of *N*-alkyl-amides and *N*,*N*-dialkyl-amides was investigated by Sagar and coworkers in the 1960s [17–19]; they found that oxidation of these compounds resulted in formation of hydroperoxides, which decomposed to *N*-acyl-amides and *N*-formyl-amides.

In what follows, we focus only on the “fate” of DMF during styrene epoxidation. The experiments were aimed at clarifying whether DMF is a co-reductant of oxygen that plays an important role in epoxidation or whether its autoxidation is a side reaction that does not influence epoxidation.

3.3. “Sacrificial” solvent?

The aerobic epoxidation of alkenes with a “sacrificial” aldehyde is a well-investigated field of oxidation chemistry [20,21]. Beside aldehydes, nitriles and amides also have been reported to be useful additives in the epoxidation of alkenes with H_2O_2 [22–24]. Alper and coworkers found a positive influence of *N*-methylpyrrolidinone in the cobalt-catalyzed oxidation of cyclohexene and suggested that *N*-methylpyrrolidinone acted as an initiator in oxidation and promoted the reaction as a dipolar aprotic solvent [25]. Further, DMF can be used as a reactant in a wide variety of catalytic reactions, including hydrogenations, hydroformylations, carbonylations, and syn-gas reactions [11].

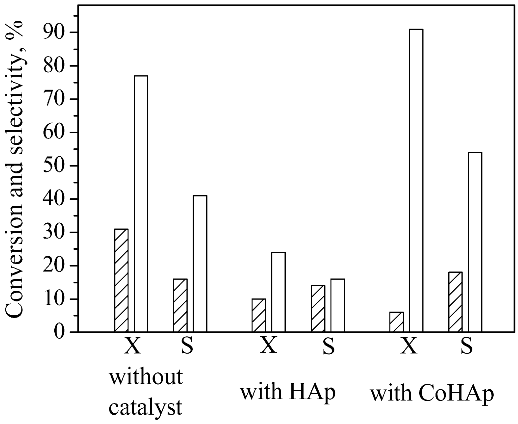


Fig. 2. Epoxidation of styrene without catalyst, with HAp, and with CoHAp. Dashed columns: closed system, empty columns: open system. X: styrene conversion, S: epoxide selectivity. Conditions: 100 mg HAp or CoHAp, 3.5 mmol styrene, 10 ml DMF, 373 K, 1 bar, 2 h, open reactor.

To investigate the role of DMF in the epoxidation of styrene with oxygen, we repeated the reaction in the absence of catalyst and with Co-free HAp (Fig. 2, open reactor system). Stirring styrene in DMF with oxygen yielded 32% epoxide in 2 h. Compared with this unexpectedly high value, the positive effect of CoHAp on rate and selectivity seems to be moderate. The main effect on selectivity was to reduce the amount of nonvolatile products (from 34 to 12% of the converted styrene). In fact, a comparison of the reactions in the presence of HAp with and without Co indicates a considerable catalytic effect of the metal; both the rate and the epoxide selectivity were multiplied. Obviously, HAp should be considered an inhibitor of styrene oxidation.

A comparison of the data in Fig. 2 and Table 2 obtained in the open reactor reveals that formation of FMF, the autoxidation product of DMF (Scheme 1), correlates with styrene conversion and epoxide selectivity. On the other hand, FMF was not detectable when styrene was not present in the reaction mixture, suggesting a synergism between the oxidation of styrene and DMF. Inhibition of the oxidation of DMF and

Table 2
Formation of *N*-formyl-*N*-methylformamide (FMF) during epoxidation of styrene in open and closed reactors. For conditions, see caption of Fig. 2

Catalyst	FMF (mmol)	
	Closed system	Open system
No	0.05	0.45
HAp	0	0.03
CoHAp	0	1.3

styrene through addition of hydroquinone proved a free-radical mechanism whether or not the catalyst was present.

The thermal autoxidation of *N*-alkyl- and *N*,*N*-dialkylamides proceeds via a radical chain mechanism [17–19]. Homolysis of the alkyl C–H bond adjacent to the amide nitrogen is followed by oxidation of the generated radical to such products as acyl amides (Scheme 1, a). Formation of FMF, the autoxidation product of DMF, can be explained in terms of a peroxy-radical mechanism. The peroxy-radicals may propagate a chain reaction by abstracting hydrogen from a further molecule. The intermediate *N*-(hydroperoxymethyl)-*N*-methylformamide can act as an oxygen-transfer agent in the epoxidation of styrene, accompanied by the formation of FMF (Scheme 1, a). Drago and coworkers reported the application of an *N*-alkylamide hydroperoxide in catalytic oxidation [26]. In our experiments, FMF was detected only in the presence of styrene, and the amount of FMF was related to the amount of styrene oxide. We can conclude that in the epoxidation of styrene in DMF, the solvent acts as the co-reductant of molecular oxygen.

3.4. Open and closed reactors

Beside the chemical nature of the solvent, the most influential parameter of styrene epoxidation was the reactor operation mode. Liquid-phase epoxidations are commonly carried out in open laboratory reactors, in which oxygen or air flows through the glass reactor and a cooling system. This type of reactor was used in all epoxidation reactions of styrene in DMF presented until now. Testing of some closed reactors (autoclaves) at 1–5 bar revealed strikingly different catalyst performance. For a better comparison, here we present only data obtained in the same reactor used as an "open system," but the reactor was closed with a balloon after flushing with oxygen. As shown in Fig. 2, the conversion and epoxide selectivity decreased dramatically in the closed reactor. The drop in conversion by a factor of 15 was strongest in the presence of CoHAp; that is, in the closed reactor system both HAp and CoHAp acted as inhibitors. Parallel to the slower formation of styrene oxide, the rate of FMF formation also decreased (Table 2). The decreased formation of FMF was most pronounced in the case of CoHAp. These changes indicate that the closed reactor has radical scavengers that inhibit the formation of FMF, and thereby the epoxidation of styrene, and that these radical scavengers are promoted in the presence of CoHAp.

The results in Table 2 seem to be in good agreement with the known metal ion-catalyzed autoxidation of DMF, leading to CO_2 and dimethylamine (Scheme 1, b) [27]. Thus, in the presence of CoHAp, the autoxidation of DMF to gaseous byproducts should be more pronounced. Franco and coworkers studied the electroreduction of CO_2 in DMF on gold [28]. In the absence of CO_2, the electrolysis produced radicals by the electrochemical reduction of DMF, whereas the radicals were not detected in the presence of CO_2. This observation might explain why the epoxidation of styrene was inhibited in the closed system (Fig. 2), where CO_2 originating from the oxidative decomposition of the solvent cannot leave the reactor. However, control experiments did not confirm this hypothesis. Replacement of a mixture of Ar and O_2 with a mixture of CO_2 and O_2 as an oxidizing agent barely affected the reaction rate. Further investigation is needed to identify the volatile byproduct inhibiting the reaction in the closed system.

4. Conclusion

The present study demonstrates that DMF, as well as some other amides (Table 1), are not inert solvents in the epoxidation of styrene with molecular oxygen. DMF interacts with oxygen, styrene, and the cobalt-containing catalyst according to a complex reaction network (Scheme 1), resulting in the formation of various products, such as *N*-formyl-*N*-methylformamide, CO_2, and dimethylamine (Scheme 1). DMF should be considered a "sacrificial" solvent that functions as a co-reductant in the epoxidation reaction, and its transformation leads to considerable amounts of byproducts. Thus, the atom-efficiency of epoxidation with molecular oxygen in DMF and other amide solvents is poor, and the method is far from a "green" technology.

Despite all limitations of epoxidation in amide-type solvents, this work provides the first evidence that Co^{2+}-exchanged hydroxyapatite can be successfully used as a solid epoxidation catalyst.

Supporting information

The online version of this article contains additional supplementary information.

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