Revisiting the Mukaiyama-type epoxidation for the conversion of styrene into styrene carbonate in the presence of O 2 and CO 2

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Abstract

Since its first report in the early 1990s, Mukaiyama-type aerobic epoxidation involving the presence of an aldehyde as an electron donor is considered as an interesting oxidation reaction. Among the various metal catalysts efficient for this process, salen-type complexes have many advantages: i) cheap Schiff-base ligands can be easily synthesized and functionalized, ii) their metal complexes are described with most transition metals from the periodic table and iii) these compounds are also efficient for the catalytic formation of cyclic carbonates from epoxides and CO_2, which makes them ideal candidates for the oxidative carboxylation of alkenes. The present work aimed at revisiting the aerobic oxidation of styrene using Cr(III) and Mn(III) salen complexes in the presence of isobutyraldehyde with the idea to further use these complexes (without any work-up), as co-catalysts for the formation of styrene carbonate under CO_2 pressure. However, contrary to what is often described in the literature, the present study showed that the introduction of a metal catalyst is not necessary for the epoxidation of styrene at 80°C in benzonitrile. In our hands, yields of c.a. 15% of styrene carbonate were obtained from styrene using O_2 (3.5 bar) and CO_2 (11 bar) as reagents in the presence of isobutyraldehyde (2.5 eq), tetrabutylammonium bromide (c.a. 2 mol%) and the Cr(III) salen complex (c.a. 1 mol%). Apparently, the oxidation of Cr(III) to Cr(VI) species in the presence of O_2 and isobutyraldehyde is detrimental to the kinetics of the tetrabutylammonium bromide-catalyzed cycloaddition of CO_2 to styrene oxide.

1. Introduction

The use of O_2 in synthetic epoxidation reactions is an important challenge since only one epoxide, ethylene oxide, is produced at industrial scale with this oxidant, through a heterogeneous silver-catalyzed, gas phase epoxidation process. In spite of the versatility and importance of olefin epoxides, no other olefins has been commercially epoxidized using only molecular oxygen as the oxidant, with the exception of the production of 3,4-epoxy-1-butene on a semi-factory scale by Eastman Chemical Company.[1] Indeed, for kinetic reasons, molecular oxygen is not reactive enough under relatively mild conditions. This is explained by the triplet ground state of molecular oxygen since, according to Wigner rule,[2] reactions occurring between triplet molecules and singlet molecules such as alkenes are kinetically unfavorable.[3] Different approaches can be implemented for the activation of O_2 and alkenes such as the use of heat, catalysis, electrocatalysis or photocatalysis.[4] The high-energy spin forbidden pathways can be bypassed, for example, by a more kinetically favorable free radical mechanism in which *in-situ* formed peroxyl radicals act as the active oxidant instead of O_2. This often results in serious complications as unwanted oxidation side-reactions are more likely to occur, leading to the formation of mixtures of by-products that lower the yield of epoxide. The most commonly used strategy to overcome the lack of reactivity of O_2 is the utilization of co-substrates (co-reductants) capable of providing additional electrons to the system. Indeed, Nature provides many examples of enzyme assisted oxidation reactions using O_2 that are of great inspiration for chemists.[5] In monooxygenases for instance,[6] the cleavage of the O=O bond and the transfer of one of the two oxygen atoms of O_2 to the substrate systematically goes through a bi-electronic reduction of the two oxygen atoms to their (-I) oxidation state with the assistance of catalysts and external electron sources such as NADH, or NADPH. By analogy, chemists have used numerous sacrificial reagents such as inorganic compounds (Zn, BH_4^-, H_2…)[7,8] or organic molecules (alcohol, aldehydes…)[9] or the assistance of electrodes. Several metal complexes are able to catalyze the aerobic epoxidation of olefins in the presence of aldehydes. This process in known as the Mukaiyama-type alkene epoxidation reaction.[10]

Original Mukaiyama-type catalytic systems based on the use of O_2 and an aldehyde for epoxidation were first described in the early 1990[ies] with bis(1,3-diketonato)Ni(II) complexes and a selection of simple aldehydes offering interesting applications, such as, in the regioselective epoxidation of steroids.[11,12] Aldehydes bearing a secondary or tertiary carbon next to the carbonyl moiety (such as isobutyraldehyde (IBA) and pivalaldehyde (PA)) provided the best results. Very quickly, many works described analogous systems based on the utilization

of complexes including a large range of first row transition metals[13] such as manganese(III),[14] cobalt(II),[15] iron(III)[16] and copper(II).[17] Among all these, chiral Mn(III) salen derivatives rapidly emerged as promising catalytically active species for unfunctionalized olefins.[18] According to the authors, the chiral manganese(III) salen complexes coupled with O_2 and an aldehyde (typically pivalaldehyde in 3-fold excess) might work like monooxygenase enzymes. However, the nature of the active oxygen specie(s) and the mechanism of the reaction is still the subject of debate (See usual mechanism proposals in Figure S1).[19] The survey of the literature shows that manganese salen complexes are interesting epoxidation catalysts that can be used with a large scope of alkenes. They are easy to synthesize, some of them are commercially available (such as the Jacobsen catalyst used in the present work) and their substituents can be tuned to optimize their catalytic performances or to allow asymmetric versions of reactions (see **Figure 1** for a series of representative examples).[20]
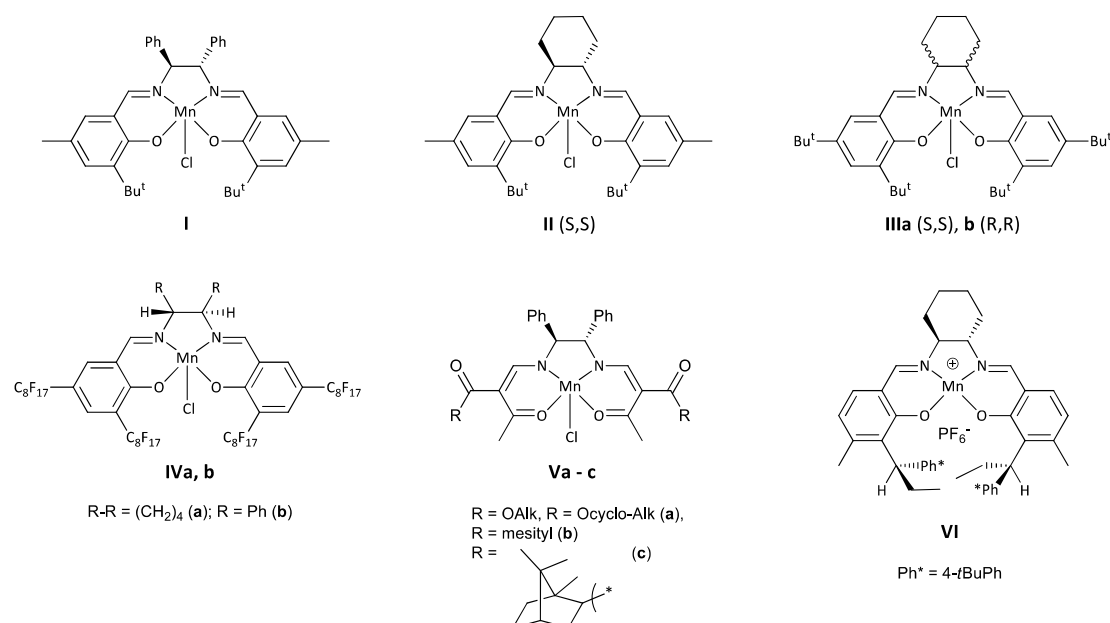
Figure 1: A selection of manganese(III) complexes used in Mukaiyama-type asymmetric aerobic alkene epoxidation[20]

The present study is a preliminary work targeting the oxidative carboxylation of styrene to get styrene carbonate. The idea is to develop a simple catalytic system able to perform the aerobic epoxidation of styrene and the cycloaddition of CO_2 onto styrene oxide under a single set of conditions in the presence of {M-Salen} complexes useful for both steps (**Figure 2**).[21]

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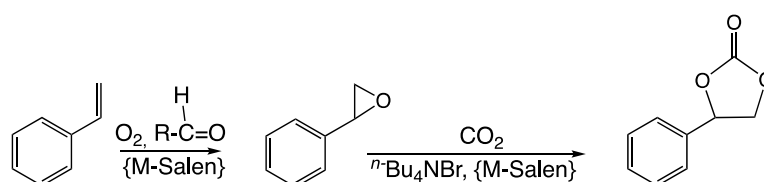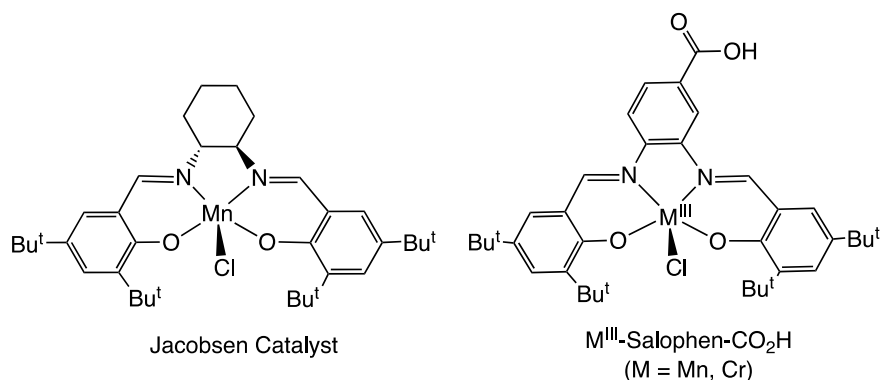
Figure 2. *Two-steps formation of styrene carbonate from styrene through oxidative carboxylation using O_2 and CO_2 (top). Structure of the different catalysts tested (bottom).*

Catalysts for the cycloaddition step often involve quaternary ammonium salts, but usually, relatively high temperatures and/or pressures are required that is why further work was done by our group, amongst others, in order to lower the conditions of the cycloaddition reaction.[22,23,24] With benzonitrile as the solvent and 1.7 mol% of tetrabutylammonium bromide as the main catalyst, we recently reported good results for the conversion of styrene oxide into styrene carbonate in mild conditions (and relatively short reaction times) using either 0.9 mol% of Cr^{III}-salophen-CO_2H (up to 90% yield of styrene carbonate after 7 h at 80°C)[23] or Mn^{III}-salophen-CO_2H (100% of styrene carbonate after 3 h at 120°C with) as co-catalyst (Figure 2).[22] Indeed, earlier studies of our group showed that oxidative carboxylation of styrene carried out at 120°C in the presence of the Jacobsen catalyst, isobutyraldehyde and a quaternary ammonium chloride in the presence of O_2 and CO_2 in benzonitrile did not give styrene carbonate, but plenty of side-products as the result of the autoxidation of the aldehyde favored by the combination of a high reaction temperature and the use of a chloride salt instead of a bromide one. [25]

In this manuscript, we focused our attention on the Mukaiyama-type aerobic epoxidation as an individual step using the above-mentioned Mn^{III}-salophen-CO_2H and Cr^{III}-salophen-CO_2H complexes as well as the Jacobsen catalyst (Figure 2) in order to explore oxidation conditions compatible with those implemented for the CO_2 cycloaddition. Styrene being the most common used model substrate to test the different catalysts for CO_2 cycloaddition, we decided here to focus our attention on its epoxidation by the Mukaiyama process. First results dealing with the oxidative carboxylation of styrene in the presence of O_2 and CO_2 assisted by Cr^{III}-salophen-CO_2H, tetrabutylammonium bromide and isobutyraldehyde will be presented.

2. Experimental Section

Materials and methods. Solvents and other reagents were obtained from various commercial sources and used as received. The Jacobsen catalyst ((R,R)-(−)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride) was purchased from Sigma-Aldrich. Other {M-Salophen} complexes were synthesized as previously described.[22,23] For the characterization of the complexes, high-resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse of Sorbonne Université. IR spectra were obtained from KBr pellets on a *Jasco FT/IR-4100* spectrometer or by Attenuated Total Reflection Infra-Red spectroscopy, using a *Tensor R27 FTIR* equipped with a ZnSe crystal with resolution better than 1 cm^{-1}. Gas chromatography (GC) analyses were performed on a Shimadzu NEXIS-GC-2030 AF instrument equipped with a split/splitless (SPL) injector, a flame ionization detector and a GC Capillary Column SH-Rxi-5MS (ID: 0.25 mm; film thickness: 0.25 μm; Length: 30 m) using He as a vector gas (1.5 mL min^{-1}) and the following temperature conditions: ramp from 70 to 250°C at 10°C min^{-1}, then an isotherm at 250°C during 10 min.

Protocol for a typical catalytic epoxidation test. Styrene (1 mL, 8.7 mmol), the [M(salen)] catalyst (72.4 µmol), isobutyraldehyde (IBA, 2 mL, 22 mmol), the GC internal standard (*p*-xylene, 1 mL, 8 mmol) and benzonitrile (solvent, 20 mL) were mixed in a round-bottom flask connected to a condenser at room temperature. Then, the mixture was heated at 80°C before introducing 16 mL/min of dioxygen through the solution. The reaction medium was stirred at 80°C for 3 h and the O$_2$ flow kept constant throughout the experiment. It is important to note here that, even at room temperature, IBA is easily carried away by the flow of oxygen and that it is necessary to have an efficient cooling system.

Protocols for the one-pot oxidative carboxylation of styrene.

Orthogonal catalysis approach: Styrene (0.70 mL, 5.6 mmol), isobutyraldehyde (1.33 mL, 15 mmol), n-Bu$_4$NBr (31.1 mg, 96.2 µmol), Cr^{III}-salophen-CO$_2$H (48.3 µmol), the GC internal standard (p-xylene, 0.66 mL, 5.3 mmol) and 13.5 mL of benzonitrile were mixed in a Teflon pot, further introduced in a stainless-steel autoclave equipped with a magnetic stirrer and an electric heater. The autoclave was then purged with O$_2$, pressurized with 3.5 bar of O$_2$ and 11 bar of CO$_2$ before heating it at 80°C. The reaction mixture was stirred for 3 or 23 h.

One-pot catalysis approach: Styrene (0.70 mL, 5.6 mmol), isobutyraldehyde (1.33 mL, 15 mmol), the GC internal standard (p-xylene, 0.66 mL, 5.3 mmol) and 13.5 mL of benzonitrile were mixed in a Teflon pot, further introduced in a stainless-steel autoclave equipped with a

magnetic stirrer and an electric heater. The autoclave was then purged with O_2, pressurized with 3.5 bar of O_2 and heated at 80°C. After 3 h at 80°C, the autoclave was cooled down to room temperature, the oxygen evacuated. Later, n-Bu$_4$NBr (31.1 mg, 96.2 µmol) and Cr^{III}-salophen-CO_2H (48.3 µmol) were added. The autoclave was then purged and pressurized with 11 bar of CO_2 and heated at 80°C for 20 h. At the end of the experiments, the autoclave was cooled down to room temperature.

After each catalytic test, the resulting solutions were analyzed by gas chromatography after dilution (samples of 25 µL diluted in 10 mL of CH_2Cl_2). Styrene, styrene oxide, benzaldehyde, styrene glycol and styrene carbonate amounts were determined from the integration of their respective GC areas relatively to p-xylene (internal standard).
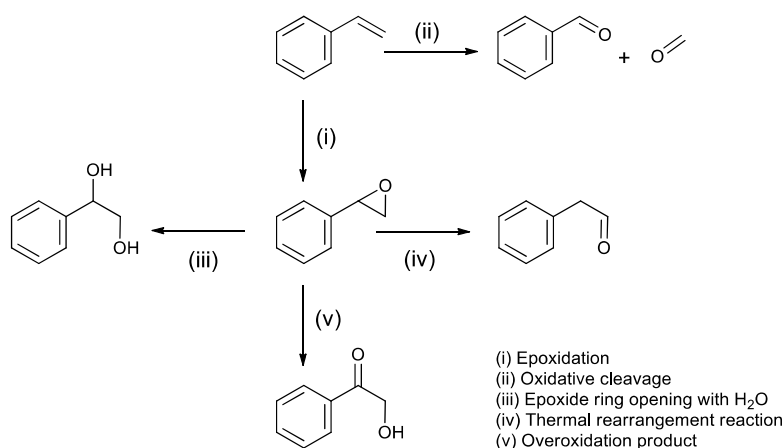
3. Results and Discussion

3.1. Epoxidation tests

As reported in our previous work, optimized reaction conditions for the cycloaddition of CO_2 onto styrene oxide assisted by tetra-*n*-butylammonium bromide and the Jacobsen catalyst required the use of 1 mol% of Mn(III) complex and 2 mol% of bromide in benzonitrile.[22] Later, we showed that the Jacobsen catalyst had an optimum catalytic activity at 120°C, keeping interesting performances at 80°C[23]. Starting from styrene, our goal here was thus to work also with 1 mol% of the Mn(III) catalyst and 2.5 equivalents of isobutyraldehyde in a temperature range compatible with cycloaddition. In all cases, the catalytic tests were performed under a 16 mL.min^{-1} oxygen flow. The temperatures investigated were 50, 60 and 80°C as we know that higher values (*e.g.* > 100°C) are not acceptable for the one-pot transformation of styrene into styrene carbonate with O_2 and CO_2 in the presence of isobutyraldehyde.[25] The commercially available Jacobsen catalyst as well as two other complexes, Salophen-tBu-Mn[22] and Salophen-tBu-Cr[23] (Figure 3) were studied. The first is interesting since it should allow relevant comparisons with the literature while the two others, bearing a carboxylic group, are adapted for amide bonding targeting later applications in anchored homogeneous catalysis (Figure 3).[22,23]
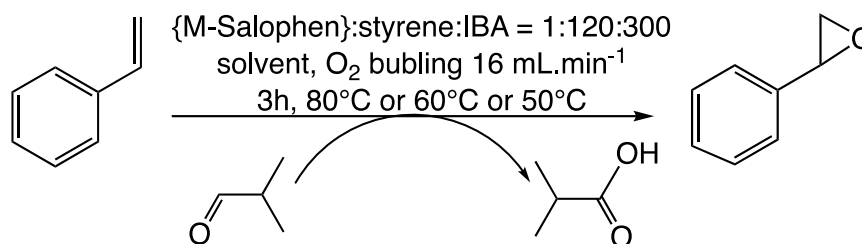
Figure 3. Experimental conditions for the Mukaiyama-type epoxidation of styrene used in this work.

**Preliminary study involving the Jacobsen Catalyst**

Styrene conversion in the presence of the Jacobsen catalyst was almost complete after 3 h. However, the maximum yield in styrene oxide was only 62%. Two side-products, benzaldehyde (17%) resulting from the oxidative cleavage of the C=C bond and styrene glycol (10%) could be detected by Gas Chromatography (GC). Styrene glycol was probably obtained from the hydrolysis of part of the styrene oxide formed, even if its direct formation from styrene cannot be excluded (**Figure 4**).

(i) Epoxidation
(ii) Oxidative cleavage
(iii) Epoxide ring opening with H_2O
(iv) Thermal rearrangement reaction
(v) Overoxidation product

Figure 4. Main products obtained from styrene in the Mukaiyama conditions

It is noteworthy that lowering the temperature to 60°C, then 50°C led to very similar results in terms of styrene conversion and styrene oxide selectivity, the yield increasing up to 67% at 60°C (**Figure 5**).[26]
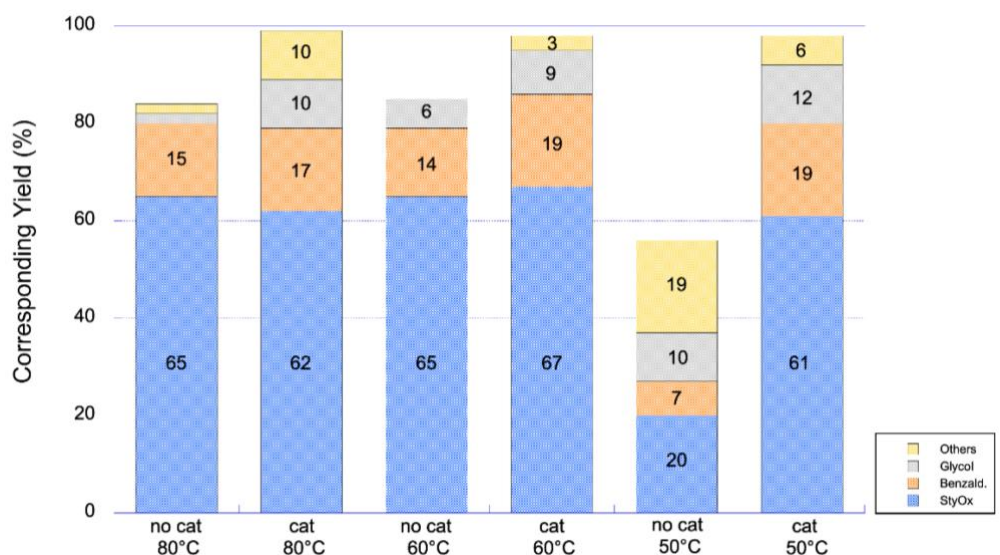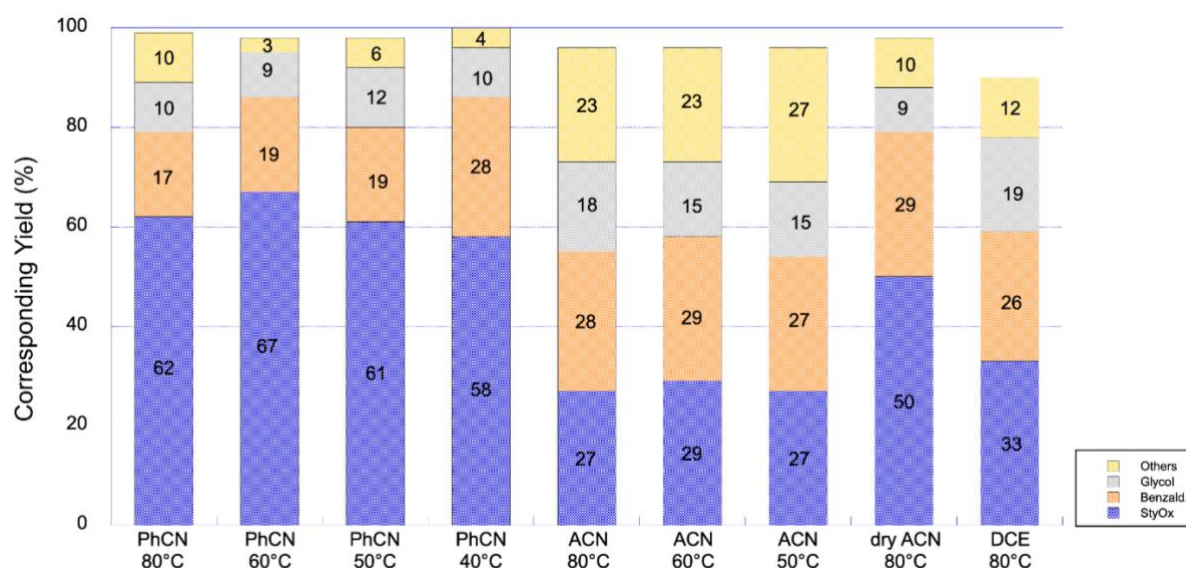
Figure 5. *Influence of the temperature and of the Jacobsen complex in the aerobic epoxidation of styrene (0.35 M) with 1 mol% Mn or no Mn, 2.5 eq IBA (vs. styrene), 16 mL.min⁻¹ O₂ in PhCN (20 mL) for 3 h. Styrene, styrene glycol, benzaldehyde and styrene oxide were quantified by GC. The sum of the different yields, including other compounds, corresponds to styrene conversion (same for Fig. 6 and 7).*

Blank tests were carried out systematically in the absence of the Jacobsen catalyst, thus showing that the conversion of styrene remained quite high with 84% at 60°C and 80°C. Most importantly, at 80°C in our case, the yields of styrene oxide and benzaldehyde were found to be similar to those obtained in the presence of the Jacobsen catalyst (respectively, 65% and 15 % at 80°C, instead of 62% and 17%). However, it is noteworthy that styrene conversion is lower in the absence of the catalyst. Such decrease seems to be related to the reduced amounts of styrene glycol and other co-products formed. The positive role of the manganese(III) catalyst in styrene conversion and styrene oxide yield was obvious at 50°C. Indeed, without catalyst at this temperature, the styrene conversion dropped to 56%, and more importantly, the yield of styrene oxide was only 20% (**Figure 5)** compared to 61% in the presence of the Jacobsen catalyst. The contribution of the catalyst thus seems particularly significant when the reaction occurs at the lowest temperatures.

Often, blank tests were not performed in other reported works and, if done, they generally led to zero conversion of the substrate.[13,27,29] However, it has to be noted that at least Kanada and co-workers[28] then Lassila *et al*[29] observed very good yields of epoxides (sometimes quantitative) after 3 h with a large range of olefins (such as cyclooctene, 1-methylcyclohexene or the two isomers of 2-octene…) in 1,2-dichloroethane in mild conditions (40°C or room temperature), and in the presence of 3 equivalent of IBA or PA only (no metal). Although styrene was not part of the scope of the tested substrates, a yield of 70% was observed for *p*-chlorostyrene oxide after 6 h. Epoxidation in those cases, appears to proceed via a mechanism

related to aldehyde autoxidation, via the formation of an acylperoxy radical obtained by reaction of IBA with O_2.

The aforementioned results obtained in the absence of any catalyst led us to investigate the role of benzonitrile (PhCN) itself. It has to be reminded that, in their early works, Mukaiyama and co-workers, used halogenated solvents,[11] but later, acetonitrile was introduced due to its more sustainable properties and its resistance to oxidants. A series of tests with the Jacobsen catalyst was carried out here between 50 and 80°C with PhCN, but also acetonitrile (ACN) and 1,2-dichloroethane (DCE) at 80°C (**Figure 6**). All experiments were performed during 3 h.


Figure 6. *Influence of the solvent (20 mL) and of the temperature in the aerobic epoxidation of styrene (0.35 M) with 1 mol% Mn, 2.5 eq IBA (vs. styrene), 16 mL.min^{-1} O_2 for 3 h.*

Even if styrene conversions remained quite important with ACN (96% for all temperatures), the distribution of the products was found to be significantly different from that obtained with benzonitrile. Hence, the styrene oxide yields (up to 29 % at 60°C) were about 2.3 times lower than in benzonitrile. On the contrary, greater proportions of benzaldehyde (*c.a.* 1.5 times more), styrene glycol (*c.a.* 1.2 at 50°C to 1.8 times more at 80°C) and important amounts of other compounds (up to 27% at 50°C) were observed in ACN. The higher affinity of ACN towards water led us to hypothesize that the higher yields of glycol obtained in that solvent could be related to its higher water content compared to benzonitrile. An experiment was thus conducted at 80°C using freshly distilled ACN and dried glassware. Consistently, the yield of styrene glycol decreased (another source of water to consider is molecular oxygen) and the yield of styrene oxide dramatically increased from 27 to 50%. In parallel, water did not have

any influence on the yield of the oxidative cleavage of the styrene double bond, since the amount of benzaldehyde remained constant (27-29%) upon drying ACN. Finally, in order to compare with the early publications, an experiment was also performed in (non-distilled) 1,2-dichloroethane (DCE) at 80°C, leading to a product distribution very similar to that obtained with non-distilled ACN, confirming the poor interest of this family of solvents in this particular reaction. Nitrile solvents with low water contents definitely favor the styrene epoxidation vs. its C=C cleavage, thus emphasizing the possible role of the -C≡N function in the epoxidation process. Indeed, it is known, that nitriles can form adducts with reduced forms of oxygen, such as hydrogen peroxide, to give peroxycarboximidic species capable of alkene activation.[30] In the present case, the differences in the respective yields of styrene oxide and benzaldehyde in acetonitrile and benzonitrile could be due to the different abilities of their adducts with molecular oxygen to transfer one oxygen atom to styrene or to differences in their formation rates. Drying acetonitrile would help to form more peroxycarboximidic species at the expense of water adducts, explaining the increase of the styrene oxide yield.

Other experiments were conducted with different amounts of sacrificial reducing aldehyde (0, 1, 2.5 or 5 molar equivalent(s) of IBA versus styrene) at 80°C in the absence or presence of the Jacobsen catalyst (see **Figure 7**).
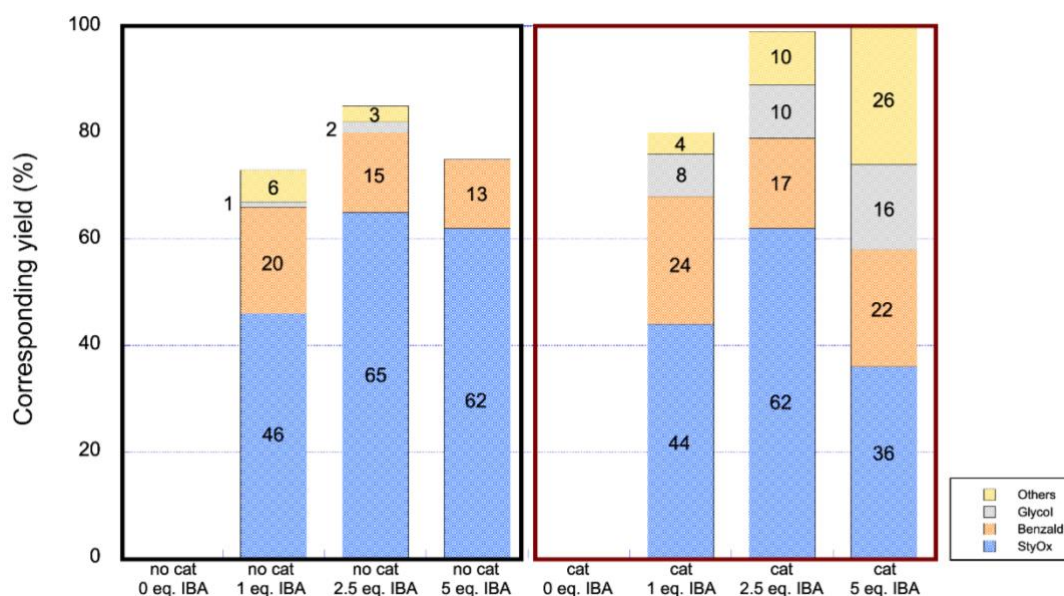
Figure 7*. Influence of the amount of sacrificial aldehyde (0-5 eq vs. styrene) in the aerobic epoxidation of styrene (0.35 M) with 1 mol% Mn or without Mn, 16 mL.min^{-1} O$_2$ in benzonitrile (20 mL) at 80°C for 3 h.*

In the absence of sacrificial aldehyde, no reaction occurred at all whether with (**figure 7**, right) or without catalyst (**figure 7**, left), thus showing the essential role of the aldehyde in

this process. In both conditions (*i.e.* with or without catalyst), best results, in terms of epoxide yield, were observed for 2.5 equivalents of IBA added. The yields of styrene oxide were respectively 62% with Jacobsen catalyst and 65 % without.

Use of other catalysts

In this work, two other Salophen complexes bearing Mn(III) and Cr(III) centers ([(N,N'-bis(3,5-di-tert-butylsalicylidene)-1-carboxy-3,4-phenylene-diamine)chloromanganese-/chrome(III)], identified therein as M^{III}-salophen-CO_2H, with M = Mn and Cr, see **figure 3**, bottom right) were also tested in the epoxidation of styrene at 80°C in benzonitrile with 2.5 equivalents of IBA. As a reminder, both Cr^{III}-salophen-CO_2H and Mn^{III}-salophen-CO_2H turned out to be efficient catalysts in our hands for the CO_2 cycloaddition reaction onto styrene oxide.[21,22]

Concerning Mn^{III}-salophen-CO_2H, for short, no significant differences could be evidenced with the Jacobsen catalyst, meaning that the replacement of the cyclohexyl moiety by a more rigid benzoic acid one has no strong influence on the catalytic properties of Mn(III). Another set of experiments was carried out with Cr^{III}-salophen-CO_2H and compared with those involving the Jacobsen catalyst (**Table 1**).

**Table 1:** *Influence of the catalyst on the aerobic epoxidation of styrene.*

Catalyst	Styrene Conversion %	Yield (%)			
		Styrene oxide	Benzaldehyde	Styrene glycol	Others
Jacobsen complex	99	62	17	10	10
Cr^{III}-salophen-CO_2H	95	48	19	20	8

Styrene (0.35 M) with 1 mol% metal complex, 2.5 eq of IBA (vs. styrene), 16 mL.min⁻¹ O_2 in benzonitrile at 80°C for 3 h.

After 3 h, Cr^{III}-salophen-CO_2H led also to a very good styrene conversion (95%) but the styrene oxide yield (48%) was lower in comparison with the two Mn complexes. Approximately, the amount of benzaldehyde formed remained equivalent for the 3 complexes. The lower styrene oxide selectivity with Cr^{III}-salophen-CO_2H can be correlated with a higher amount of styrene glycol, from 10% for the Mn(III) species up to 20% for Cr(III). Thus, it appeared that Cr(III) promotes more oxirane ring cleavage by hydrolysis compared to Mn(III). Such behavior is not very surprising. Indeed, Cr(III) is known to behave as a stronger Lewis acid site than Mn(III).

Some groups have extensively reported the ability of Cr(III) for epoxide ring opening, including in the frame of CO_2 cycloaddition.[31]

We then paid attention to the behaviour of the metal complexes during the reaction. It was thus observed that contacting the Mn(III) catalysts with IBA in the presence of O_2 resulted in a rapid color change even at 50°C. Nothing occurred in the absence of O_2 and/or IBA. EPR spectroscopy has been used earlier by Talsi, Kholdeeva and co-workers in the case of the Jacobsen catalyst.[32] Both groups attributed such evolution to a rapid oxidation of the initial Mn(III) complex mostly into an unstable Mn^{IV}-salen compound. According to these authors, the *in-situ* formed Mn^{IV}-salen intermediate would be responsible for the formation of benzaldehyde, while a Mn^{III}-salophen-acylperoxo complex obtained in parallel would be at the origin of the epoxide. In the case of the Cr^{III}-salophen-CO_2H complex, we also observed a similar rapid color change and, after 3 h, the renewal of styrene and/or IBA no longer resulted in styrene conversion. The color evolution of the Cr(III) complex was followed by UV/visible spectroscopy (**Figure 8**).
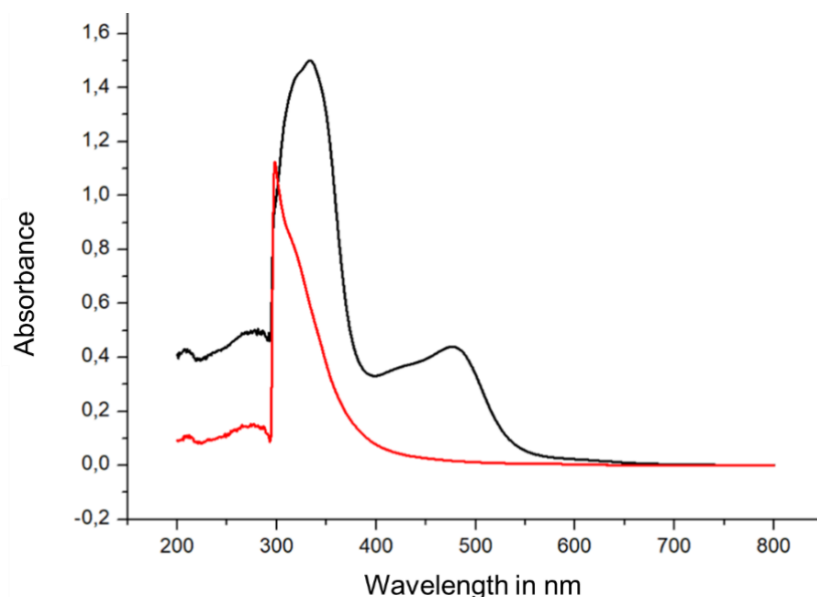
Figure 8. *UV/visible spectra of the initial solution of Cr^{III}-salophen-CO_2H in benzonitrile in the presence of IBA and styrene before (in black) and after (in red) O_2 bubbling. The reaction mixtures were diluted to reach c.a. 10^{-4} M Cr.*

An intense band attributed to a metal to ligand charge transfer ($\varepsilon = 4800$ l.mol^{-1}.cm^{-1}) could be observed in the visible region (maximum at 480 nm) of the spectrum of the initial Cr^{III}-salophen-CO_2H. Interestingly, this band rapidly disappeared in the presence of IBA and dioxygen (**Figure 8**). No other electronic transitions could be observed in the visible part of the spectrum recorded at the end of the reaction, which seems to be in favor of the presence of a

majority of Cr(VI) centers with d^0 configuration. The resulting yellow light coloration of this solution would be due to the tail of the higher energy and intense absorption bands. The diamagnetism of the crude reaction mixture could also be confirmed indirectly by recording its ^{1}H NMR spectrum.

3.2. One-pot oxidative carboxylation of styrene using CO_2 and O_2

In the first part of this work, using 0.9 mol% of M^{III} Salen and 2.5 eq of IBA vs. styrene, we have shown that Salen complexes are not essential for the conversion of styrene in its aerobic IBA-assisted epoxidation at 80°C in benzonitrile. It was also shown that Mn^{III} Salen complexes are not detrimental to the epoxide yield in these conditions while Cr^{III}-salophen-CO_2H leads to more epoxide ring opening as the result of its higher Lewis acidity compared to Mn^{III}. The ability of Cr^{III}-salophen-CO_2H to activate epoxides[33] and our previous results on the cycloaddition of CO_2 onto styrene oxide using Cr^{III}-salophen-CO_2H[23] and tetrabutylammonium bromide, also carried out in benzonitrile at 80°C, under 11 bar of CO_2, led us to choose the Cr^{III} complex (0.9 mol%) for the study of the oxidative carboxylation of styrene by O_2 and CO_2 in the presence of IBA (2.5 eq. vs. styrene) and tetrabutylammonium bromide (1.7 mol%). Ideally, an orthogonal catalysis approach should be preferred, i.e. an approach where Cr^{III}-salophen-CO_2H, ^{n}-Bu_4NBr and IBA are introduced at the beginning with O_2 and CO_2 (**Table 2**). However, the sequential execution of the two steps (use of O_2, Cr^{III}-salophen-CO_2H and IBA for the epoxidation, then removal of O_2 and addition of ^{n}-Bu_4NBr and CO_2 for the cycloaddition) which corresponds to one-pot catalysis should not be excluded because of possible interferences between the two reactions. In the present work, the O_2 and CO_2 pressures will be adjusted to 3.5 and 11 bar (RT), respectively.

Before working on the orthogonal catalysis protocol with pressurized O_2 and CO_2, the aerobic styrene epoxidation had to be tested with IBA only (no Cr^{III}-salophen-CO_2H) under 3.5 bar of O_2 (Table 2, entry 1), thus affording, after 3 h reaction, 98% conversion of styrene with a 44% yield of styrene oxide vs. 48% under O_2 flux (Table 1).

Table 2: Attempts of oxidative carboxylation of styrene under a single set of conditions (orthogonal catalysis)

Conditions	**1**	**2**	**3**	**4**
t (h)	3	3	3	23
M-Salen	-	Cr^{III}-salophen-CO_2H	Cr^{III}-salophen-CO_2H	Cr^{III}-salophen-CO_2H
QAS	-	-	^{n}-Bu$_4$NBr	^{n}-Bu$_4$NBr
P_{O2} (bar)	3.5	3.5	3.5	3.5
P_{CO2} (bar)	-	11	11	11
Products		Yields (%)		
Styrene oxide	44	42	40	25
Benzaldehyde	13	14	13	10
Styrene glycol	10	24	20	16
Styrene carbonate	-	-	3	14
Others	31	18	24	34

Styrene (0.35 M) with 0.9 mol% Cr^{III}-salophen-CO_2H except for entry 1, 1.7 mol% ^{n}-Bu$_4$NBr (except for entry 1 and 2), 2.5 eq of IBA (vs. styrene) under 3.5 bar of O_2 and 11 bar of CO_2 (except for entry 1) in benzonitrile at 80°C.

The yields of the other main products, benzaldehyde and styrene glycol, are displayed in **Table 2**. Avoiding the formation of benzaldehyde and styrene glycol was not possible as shown in the first part of this work. Regarding the other reaction products, these may arise from a set of side reactions involving O_2 and/or indirectly IBA. Indeed, part of these secondary products may be obtained by the reaction of styrene oxide with isobutyric acid formed by the oxidation of the sacrificial aldehyde. Epoxides are known to react with carboxylic acids to form 1,2-diol mono-esters, especially in the presence of ionic liquids involving bromides.[34] However, using GC-MS analysis, we have not been able to detect the addition product of isobutyric acid onto styrene oxide.

Using IBA and Cr^{III}-salophen-CO_2H together with O_2 and CO_2 (**Table 2**, entry 2) did not change significantly the styrene oxide and benzaldehyde yields (42% and 14%, respectively instead of 48% and 13% without CO_2 and Cr^{III}-salophen-CO_2H) but the styrene glycol yield increased from 10 to 24% as observed in **Table 1** upon the replacement of Mn^{III}-salophen-CO_2H by Cr^{III}-salophen-CO_2H. As expected no styrene carbonate was formed in the absence of ^{n}-Bu$_4$NBr. Finally, the experiment was conducted in the presence of IBA, tetrabutylammonium bromide and Cr^{III}-salophen-CO_2H with O_2 and CO_2 (**Table 2**, entries 3 and 4). Some styrene carbonate was detected after 3 h (3%, **Table 2**, entry 3), the yield reaching a maximum of 14% after 24 h (**Table 2**, entry 4). As expected, a consequent decrease of the styrene oxide yield, from 40 to 25%, could be observed in parallel. It therefore appears that styrene oxide was not fully converted into styrene carbonate, even after 24 h.

To conclude this series of experiments, we confirmed the ability of the ^{n}-Bu$_4$NBr/ Cr^{III}-salophen-CO_2H catalytic system to induce, with IBA, the production of styrene carbonate from

styrene in the presence of O_2 and CO_2 with a single set of reaction conditions. However, after 23 h, the yield of styrene carbonate was lower (14%) than expected from the results obtained when the epoxidation and CO_2 cycloaddition reactions were considered separately. In the alternative one-pot catalysis approach, styrene epoxidation was conducted first with IBA under 3.5 bar of O_2 during 3 h at 80°C. After cooling, molecular oxygen was evacuated, then ^{n}-Bu$_4$NBr and Cr^{III}-salophen-CO_2H were introduced before adjusting the CO_2 pressure to 11 bar (RT) and the reaction temperature to 80°C. The duration of the second step was 20 h. In these conditions, styrene was totally consumed in less than 3 h and the yield of styrene carbonate was 16% with 15% of benzaldehyde, 15% of styrene glycol and 17% of styrene oxide which is not significantly different from the results obtained in the orthogonal catalysis protocol.

4. Conclusion

Having in mind the direct conversion of styrene into styrene carbonate in the presence of O_2 and CO_2, the present study aimed at finding aerobic epoxidation conditions compatible with the cycloaddition of CO_2 onto styrene oxide that was performed earlier at 80°C, in our hands, using benzonitrile as a solvent, tetrabutylammonium bromide as a catalyst and a Cr^{III} Salophen as a Lewis acid.[23] A detailed investigation of the conditions required for the aerobic styrene epoxidation was carried out based on the work initiated by Mukaiyama and co-authors in 1991. With isobutyraldehyde as a sacrificial reductant, we showed that a complete conversion of styrene could be reached within 3 h at 60°C, thus affording a maximum yield of styrene oxide of 61% under a controlled flow of dioxygen (16 mL.min^{-1} in our reactor configuration). However, significant amounts of undesired by-products were obtained, including benzaldehyde resulting from the oxidative cleavage of the styrene double bond. Finally, it was demonstrated that the optimum epoxide yield required a styrene: IBA molar ratio of 2.5. Benzonitrile was also found to be a very interesting solvent as it allows a higher yield of styrene oxide at the expense of styrene glycol and benzaldehyde. Blank experiments showed that the aldehyde is required and not the metal complex to get optimum styrene oxide yield at 60 and 80°C, *i.e.* the temperature used for the CO_2 cycloaddition in hour hands. Below 60°C, the presence of the metal complex is necessary for both the conversion of styrene and the selective formation of styrene oxide.

Finally, the overall transformation allowing the formation of styrene carbonate from styrene with O_2 and CO_2 as reactants in the presence of IBA, tetrabutylammonium bromide and

the chromium complex, chosen for its ability to activate epoxides, was studied at 80°C in benzonitrile. In the present conditions, using either an orthogonal or a one-pot catalysis approach, the maximum yield of styrene carbonate reached about 14-16% after 23 h. These results may appear at first sight to be quite low, but a significant improvement was obtained when compared to our previous work carried out in benzonitrile at 120°C with IBA[25], the Jacobsen catalyst and a chlorinated quaternary ammonium salt where no styrene carbonate was produced at all. By-products are responsible for the low amount of styrene carbonate, but not only. The in-situ oxidation of chromium (III), which is not required for epoxidation at 80°C, to chromium (VI) species with less Lewis acidity, as evidenced in the study of the epoxidation step, could be at the origin of the slowing down of the CO_2 cycloaddition and the accumulation of styrene oxide. Adding an excess of a reducing agent, such as hydrazine, reduced Cr(VI) back into Cr(III) but with no positive impact on the styrene carbonate yield. Therefore, Salen complexes bearing non-redox centers (unmodified in the presence of O_2 and IBA) but still being good Lewis acids should be preferred for the overall reaction at 80°C to optimize the yield of styrene carbonate.

5. Acknowledgements

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