

# Experimental and Theoretical Insight into the Mechanism of CO<sub>2</sub> Cycloaddition to Epoxides Catalyzed by Ammonium Ferrates

Nicola Panza,<sup>a</sup> Raffaella Soave,<sup>b</sup> Fausto Cargnoni,<sup>b</sup> Mario Italo Trioni<sup>b</sup> and Alessandro Caselli<sup>\*a,b</sup>

<sup>a</sup>Department of Chemistry, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy. E-mail: [alessandro.caselli@unimi.it](mailto:alessandro.caselli@unimi.it); phone: +39 02 50314372. <sup>b</sup>CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche “G. Natta”, via Golgi 19, 20133, Milano, Italy.

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## ABSTRACT:

Soluble tetrabutylammonium ferrates, [TBA][FeX<sub>3</sub>Y] (TBA = "Bu<sub>4</sub>N) were synthesized by treating ferric salts (FeX<sub>3</sub>) with tetrabutylammonium halides. Their activity as a stand-alone catalyst in CO<sub>2</sub> cycloaddition reactions to epoxides was assessed under solvent free and quite mild reaction conditions (CO<sub>2</sub> pressures between 0.4 and 0.8 MPa) and TOF up to 428 h<sup>-1</sup> (T = 150 °C) were observed. Good yields of cyclic organic carbonates were obtained, especially with terminal epoxides, without the need of any Lewis base as co-catalyst, with a broad reaction scope. A scale-up reaction on 5 mL of styrene oxide was performed and the robustness of the catalyst was proved up to three recycles in the case of propylene oxide (TON = 594). To shed light on the reaction mechanism, an extensive set of theoretical calculations has been carried out. Iron salts almost annihilate the barrier for the epoxide ring opening and stabilize the first reaction intermediate. Along the same reaction path, chloride proved to be more effective as nucleophile than bromide, and preferentially attacks on the more hindered carbon atom. On the other hand, when no Lewis acid (LA) is present, the rate determining step of the reaction becomes the ring opening of the epoxide. A tight correlation with experimental results was observed.

## 1. Introduction

The exponential increase of carbon dioxide (CO<sub>2</sub>) emission in the atmosphere,<sup>[1]</sup> as the terminal product of all the carbon-based processes for energy production (*i.e.* burning fossil fuels), has become an alarming problem which threatens the whole environment.<sup>[2,3]</sup> To control the atmospheric CO<sub>2</sub> concentration, amongst other methods, two plausible ways of transforming the energy production from fossil fuel to sustainable processes have been envisaged: (i) the reduction of CO<sub>2</sub> into carbon-neutral fuels and

chemicals<sup>[4,5]</sup> and (ii) non-reductive couplings to yield high-value added products.<sup>[6-9]</sup> If CO<sub>2</sub> can indeed be transformed into a variety of other molecules, the conversion process should always necessitate less energy than that offered by the target product, in line with the 4<sup>th</sup> principle of circular chemistry: “*Energy efficiency should be maximised*”.<sup>[10]</sup> However, the activation and utilization of CO<sub>2</sub> molecule, which is the most oxidized form of carbon and thus thermodynamically stable and kinetically inert, is in most cases still a challenge. Consequently, to limit the use of harsh reaction conditions, catalyst design is a critical aspect to lower the energetics requirements in order to achieve a close to neutral carbon cycle.

The coupling of CO<sub>2</sub> with high free energy substrates such as epoxides to generate polycarbonates and/or cyclic carbonates represents one of the few processes that has been industrialized until now.<sup>[11,12]</sup> Since the first report by Inoue *et al.* in 1969,<sup>[13]</sup> this field has witnessed an impressive boost in the last decades. In the most commonly employed catalytic systems, a Lewis base is needed for the nucleophilic attack that yields to the ring opening of the epoxide. In general, the nucleophiles of choice are represented by organic halide salts, and the attack is favored by the presence of a Lewis acid (LA) to activate the epoxide either in an *intermolecular* or in an *intramolecular* fashion. Following this, the ring-opened product can undergo either CO<sub>2</sub> insertion to form a carbonate or repetitive epoxide insertion to lead to polyether formation.<sup>[11]</sup> In most cases, once the carbonate is formed by CO<sub>2</sub> insertion, especially for non-hindered epoxides, a fast backbiting of the intermediate leads to the formation of cyclic carbonates, which have great relevance in industrial processes. The five membered cyclic carbonates obtained by CO<sub>2</sub> cycloaddition with epoxides are biodegradable liquids with low toxicity<sup>[14]</sup> and are mainly employed as aprotic polar solvents,<sup>[11]</sup> electrolytes in secondary batteries, intermediates in fine chemical synthesis and monomers for polycarbonate based polymers.<sup>[15-18]</sup> The appropriate choice of the catalyst is thus fundamental in order to control the selectivity of the process and several homogeneous and heterogeneous catalytic systems have been developed in the last decades.<sup>[19-23]</sup> The former, in general, possess higher activities, but lack of recyclability. Homogeneous catalysts that consist of ionic nucleophile (Lewis bases), typically organic halides, such as quaternary ammonium,<sup>[24-26]</sup> bis(triphenylphosphine)iminium salts<sup>[27]</sup> and ionic liquids<sup>[28]</sup> in the absence of a LA, gave preferentially cyclic carbonates, since the ring closure becomes the most favorable step after the formation of the carbonate intermediate. However, they generally suffer from quite high reaction temperatures and CO<sub>2</sub> pressure to achieve good conversions, intensive work up procedures for the isolation of the product (cyclic carbonates have high boiling points)<sup>[29]</sup> and lack of reutilization of the catalytic system due to degradation.<sup>[30]</sup> The presence of a Lewis acid appears to be fundamental in order to activate the epoxide

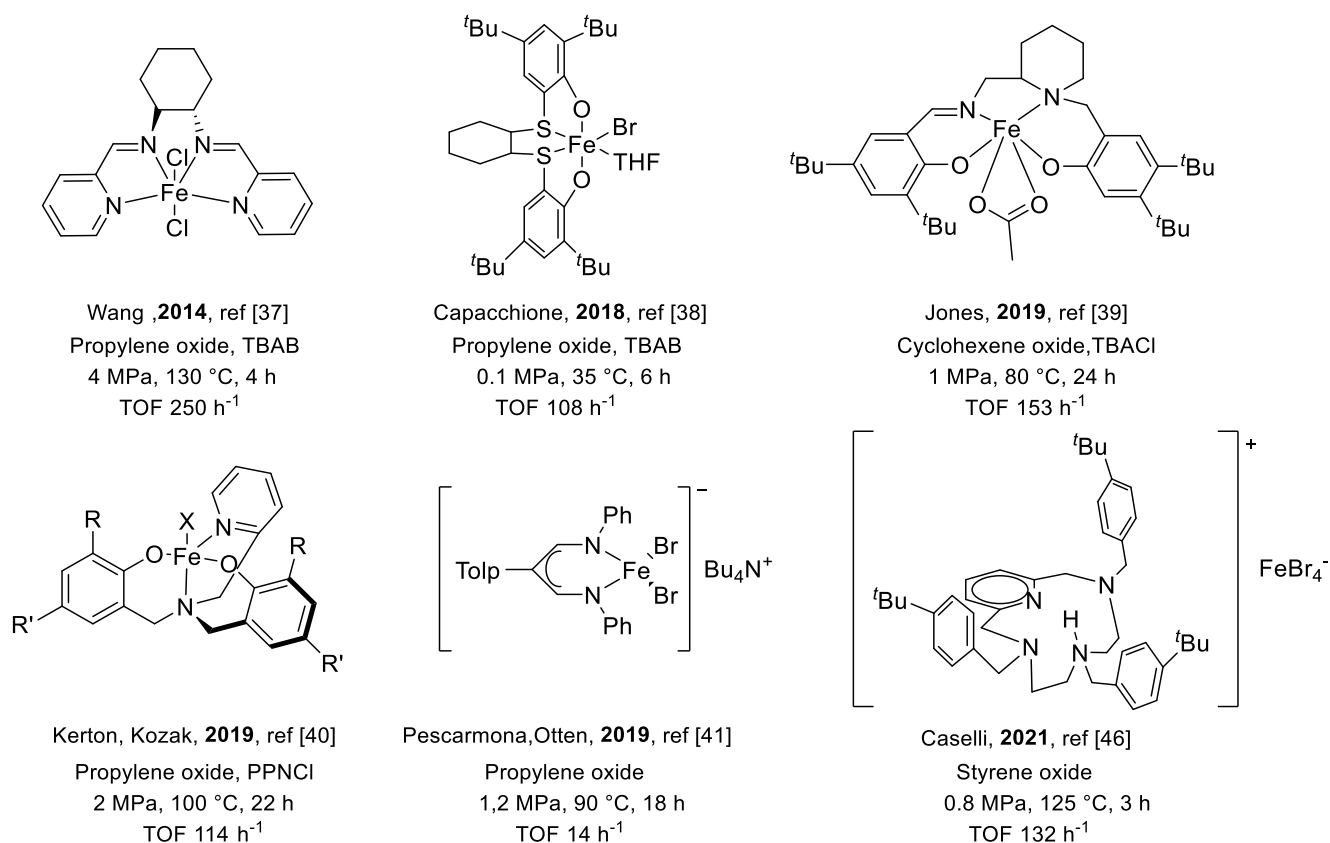
towards the attack of the nucleophilic Lewis base.<sup>[7]</sup> These two active species can be embedded in a single bifunctional catalyst or in a binary system of two separate components.

In either case, the class of LAs that has been most exploited consists of metal complexes, with very high activities but whose selectivity towards cyclic or polymeric carbonates is strongly correlated to the nature of both the attacking nucleophile and the metal.

In this respect, the careful design of bifunctional metal-based complexes is a crucial point towards the development of active and selective catalysts, even at very low catalyst loading. Recent research efforts focused on the development of metal complexes (either as bifunctional or binary catalytic systems) based on earth-abundant, non-toxic metals such as aluminium<sup>[31]</sup> and iron.<sup>[32]</sup> Due to its natural abundance together with its high chemical reactivity, iron in particular is considered one of the most promising metals for homogeneous catalysis.<sup>[33]</sup> Since the first patent reported by Marquis and Sanderson in 1994 on the use of a chloroferric phthalocyanine as catalyst for the synthesis of propylene carbonate,<sup>[34]</sup> quite a few iron complexes active as catalysts in the chemical fixation of CO<sub>2</sub> with epoxides have been reported (Figure 1).<sup>[32,35–41]</sup>

In our ongoing studies of pyridine containing macrocyclic ligands (Pc-L),<sup>[42]</sup> we have recently disclosed that a well-defined [Zn(II)Br(Pc-L)]Br complex is an efficient catalyst even at 0.5 mol% loading and under reasonably mild reaction conditions (0.8 MPa of CO<sub>2</sub> at 125 °C).<sup>[43]</sup> We have also shown that ferric complexes of Pc-L act as homogeneous catalysts for selective oxidation reactions,<sup>[44,45]</sup> and that a new “ferrate” species obtained by reaction between a protonated Pc-L ligand and FeBr<sub>3</sub> is a competent stand-alone catalyst for the cyclic carbonates production from CO<sub>2</sub> and epoxides without the addition of any external nucleophile.<sup>[46]</sup> Given the high activity of the “ferrate” anion, we became interested in exploiting the reactivity of tetrabutylammonium ferrates, [TBA][FeX<sub>3</sub>Y] (TBA = <sup>n</sup>Bu<sub>4</sub>N),<sup>[47]</sup> that can be easily obtained from low cost chemicals such as ammonium halides and ferric salts,<sup>[48,49]</sup> as stand-alone catalysts in the CO<sub>2</sub> cycloaddition to epoxides. It was found that the obtained [TBA][FeX<sub>3</sub>Y] complexes exhibit good catalytic activity under quite mild reaction conditions with a remarkable selectivity in the cyclic carbonate products.

In this work, the effect of different experimental factors (reaction temperature, CO<sub>2</sub> pressure, type of nucleophile and recycling of the catalyst) on the reaction cycle together with DFT results about the possible reaction mechanisms are presented.



**Figure 1.** Selected examples of reported iron-based homogeneous catalytic systems for the cycloaddition of CO<sub>2</sub> to epoxides.

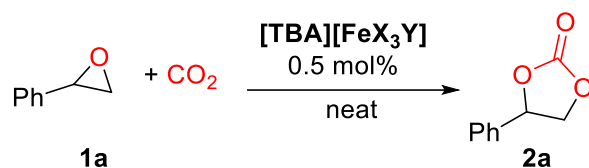
## 2. Results

A series of tetrahalogenoferrate(III) salts, [TBA][FeX<sub>3</sub>Y], was prepared by mixing an ethanolic solution of the appropriate ferric salt with a stoichiometric quantity of tetrabutylammonium halide. A precipitate was obtained and filtered off and recrystallized by ethanol at -20 °C. The ammonium ferrate salts were obtained in good yields (see Supporting Information, Table S1) and were characterized by ESI-MS analysis, showing the formation of both the [FeX<sub>3</sub>Y]<sup>-</sup> anion and the ammonium cation. Elemental analyses confirmed the purity of the material obtained.

The catalytic activity of the four different tetrahalogenoferrates(III) stabilized with TBA was tested using styrene oxide (SO) as benchmark substrate under solvent free reaction conditions. Obtained results are reported in Table 1. All the ferrate salts proved to be active in this transformation at 100 °C in 0.5 mol% catalyst loading with high conversion values up to >99% in the case of [TBA][FeBr<sub>3</sub>Cl] in 4 hours of reaction time (Table 1, entry 3). As it can be seen graphically from Figure 2, the best balance between conversion of the starting epoxide and selectivity towards styrene carbonate was obtained when using [TBA][FeCl<sub>3</sub>Br] as catalyst (Table 1, entry 2). This result is particularly important to us since this ferrate

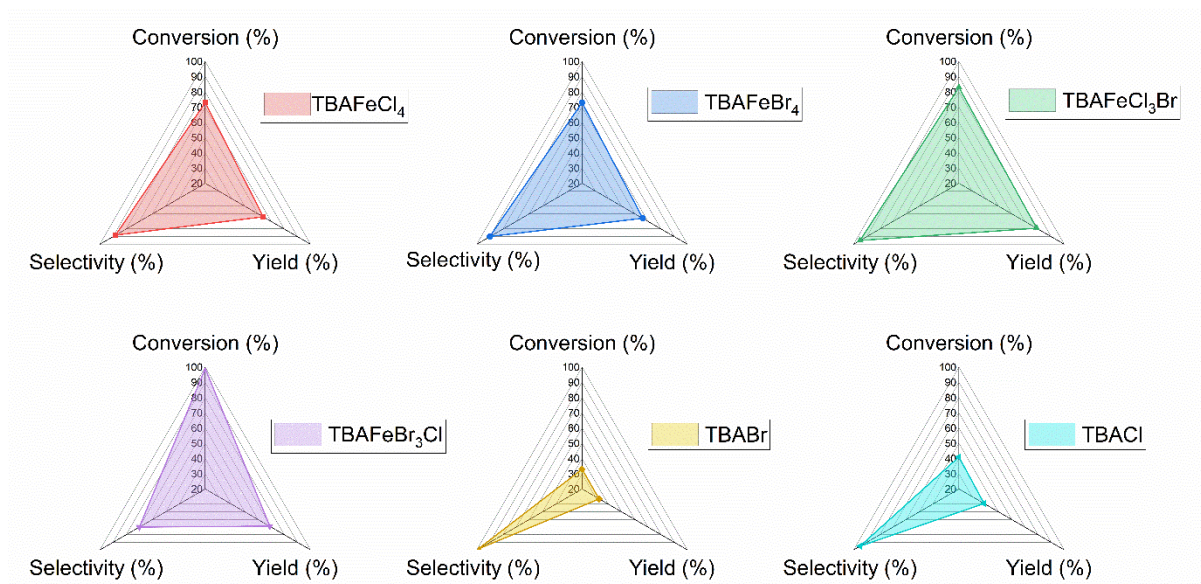
salt is the result of the combination of the cheapest iron salt (ferric chloride hexahydrate) and ammonium halide (tetrabutylammonium bromide) among all those used. On the other hand, homoleptic chloride and bromide ferrates gave almost identical results, with quite good selectivities (compare entries 1 and 4, Table 1). It is important to note that the activity of simple ammonium halides in the same reaction conditions is not negligible (Table 1, entries 5 and 6), but the rate of the reaction is almost halved in comparison with the novel ferrate compounds, proving the beneficial role of iron (*vide infra*). **TBACl** gave a slightly better conversion, while **TBABr** resulted in a complete selectivity in favor of the cyclic carbonate.

**Table 1:** Cycloaddition of CO<sub>2</sub> to styrene oxide catalyzed by the tetrahalogenoferrates(III) salts.<sup>[a]</sup>



Entry	Cat. 0.5 mol%	Con. <b>1a</b> %	Sel. <b>2a</b> %	TOF <sup>[b]</sup> (h <sup>-1</sup> )
1	[TBA][FeCl <sub>4</sub> ]	73	88	36
2	[TBA][FeCl <sub>3</sub> Br]	83	95	42
3	[TBA][FeBr <sub>3</sub> Cl]	99	70	49
4	[TBA][FeBr <sub>4</sub> ]	73	88	36
5	TBACl	41	95	21
6	TBABr	33	>99	17

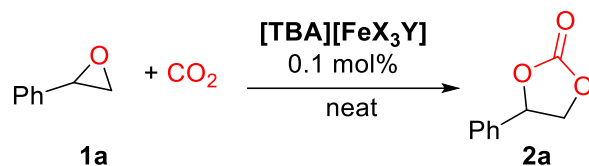
<sup>[a]</sup> Reaction conditions: styrene oxide (SO) 2.19 mmol; cat. 0.5 mol%; P = 0.8 MPa; T = 100 °C; t = 4 h. Conversion and selectivity determined by <sup>1</sup>H NMR using mesitylene as the internal standard. <sup>[b]</sup> Turnover frequency (mol<sub>1a(converted)}</sub> · mol<sub>cat</sub><sup>-1</sup> · reaction time<sup>-1</sup>).



**Figure 2.** Graphic representation of conversion, yield and selectivity for all the tested ferrates under the reaction conditions reported in Table 1 in the cycloaddition of CO<sub>2</sub> to styrene oxide.

### 2.1. Effect of the catalyst loading

When lowering the catalyst loading to 0.1 mol% at 100 °C, still notable catalytic activities were observed with TOF ranging from 80 h<sup>-1</sup> with [TBA][FeCl<sub>4</sub>] (Table 2, entry 1) to 95 h<sup>-1</sup> when using [TBA][FeBr<sub>4</sub>] (Table 2, entry 3).<sup>§</sup> However, in 4 h of reaction time, only poor conversion were obtained, with a significant decrease in the observed selectivity. Increasing the temperature to 125 °C improved the catalysts activity with observed TOF up to 184 h<sup>-1</sup> (Table 2, entry 6). Again, the best selectivity was observed with the mixed ferrate [TBA][FeCl<sub>3</sub>Br] (94%, Table 2, entry 5). A further increase on the reaction temperature (T = 150 °C) led to an almost quantitative conversion of the starting epoxide in just 4 h of reaction time and with 0.1 mol% of catalyst for all the tested ferrates, (Table 2, compare entries 8-10). In these conditions, if the reaction is stopped after two hours, an 86% conversion of the starting epoxide is observed with 0.1 mol% loading of [TBA][FeBr<sub>4</sub>], with the remarkable TOF of 428 h<sup>-1</sup> (Table 2, entry 13). Again, the best selectivity is observed for the mixed salt [TBA][FeCl<sub>3</sub>Br] (96%, Table 2, entry 12). It should be however pointed out that under those reaction conditions (T = 150 °C and P of CO<sub>2</sub> = 0.8 MPa) also the simple quaternary ammonium salts TBACl and TBABr are quite competent catalysts, with the former giving an overall conversion of 56% and the latter an impressive selectivity of 99% (Table 2, entries 14 and 15). However, the TOF observed when employing the ferrate catalysts are higher, confirming the role played by the ferric salt as LA (see later for a discussion on the reaction mechanism).

**Table 2:** Effect of lower catalyst loading and higher temperatures.<sup>[a]</sup>

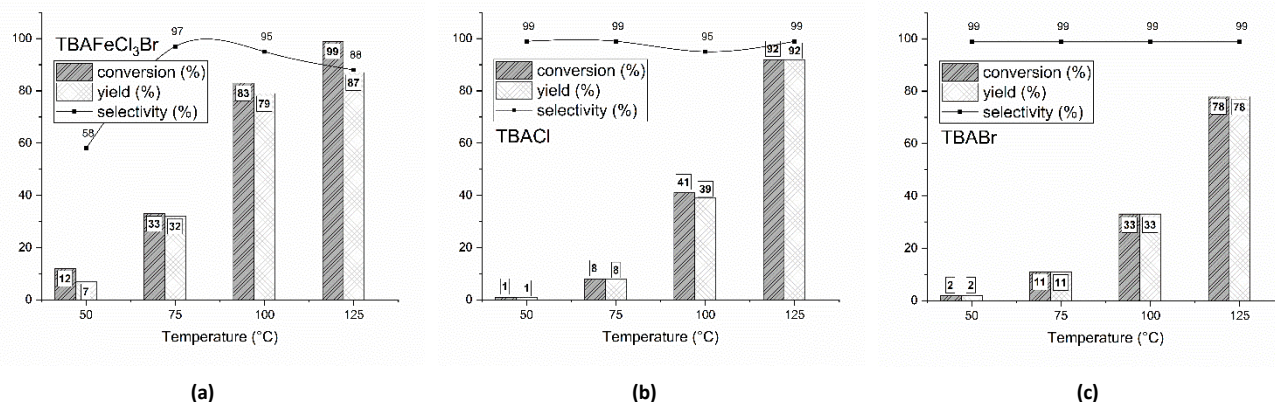
Entry	Cat. 0.1mol%	T (°C)	Con. <b>1a</b> %	Sel. <b>2a</b> %	TOF <sup>[b]</sup> (h <sup>-1</sup> )
1	[TBA][FeCl <sub>4</sub> ]	100	32	60	80
2	[TBA][FeCl <sub>3</sub> Br]	100	35	74	87
3	[TBA][FeBr <sub>4</sub> ]	100	38	76	95
4	[TBA][FeCl <sub>4</sub> ]	125	53	91	132
5	[TBA][FeCl <sub>3</sub> Br]	125	66	94	164
6	[TBA][FeBr <sub>4</sub> ]	125	74	81	184
7	TBABr	125	50	84	125
8	[TBA][FeCl <sub>4</sub> ]	150	94	83	234
9	[TBA][FeCl <sub>3</sub> Br]	150	95	83	237
10	[TBA][FeBr <sub>4</sub> ]	150	91	81	227
11 <sup>[c]</sup>	[TBA][FeCl <sub>4</sub> ]	150	75	87	374
12 <sup>[c]</sup>	[TBA][FeCl <sub>3</sub> Br]	150	67	96	319
13 <sup>[c]</sup>	[TBA][FeBr <sub>4</sub> ]	150	86	84	428
14 <sup>[c]</sup>	TBACl	150	56	86	279
15 <sup>[c]</sup>	TBABr	150	39	>99	194

<sup>[a]</sup> Reaction conditions: styrene oxide (SO) 2.19 mmol; P = 0.8 MPa; t = 4 h. Conversion and selectivity determined by <sup>1</sup>H NMR using mesitylene as the internal standard. <sup>[b]</sup> Turnover frequency (mol<sub>1a(converted)}</sub> · mol<sub>cat</sub><sup>-1</sup> · reaction time<sup>-1</sup>). <sup>[c]</sup> t = 2 h.

## 2.2. Effect of the temperature

The temperature dependence of the catalyst was investigated in the case of [TBA][FeCl<sub>3</sub>Br] and the respective ammonium halides TBABr and TBACl in the reaction of SO with CO<sub>2</sub>, at a 0.5 mol% loading and at 0.8 MPa. All the reactions were performed in neat SO, **1a** (250 μL), and stopped after 4 h (Figure 3). The mixed ferrate catalyst [TBA][FeCl<sub>3</sub>Br] outperform both ammonium quaternary salts at low temperatures, but this difference in activity becomes less important at 125 °C.

This is in agreement with the role played by the ferric salt as LA in activating the epoxide towards the nucleophilic attack of the halide. At higher temperatures, this effect becomes less important. At 125 °C all these compounds proved to be active in this transformation with complete conversion obtained in the case of the ferrate salt. The higher selectivity of simple ammonium halides compared to the ferrate compound might be traced to the presence of iron that might be responsible for secondary non-negligible reaction paths. The decrease of the temperature down to 100 °C resulted in a clear difference between the ferrate compound and the ammonium halides: the activity of the latter is indeed almost halved, while [TBA][FeCl<sub>3</sub>Br] maintains good values of conversion (83%) of the substrate and high selectivity (95%).



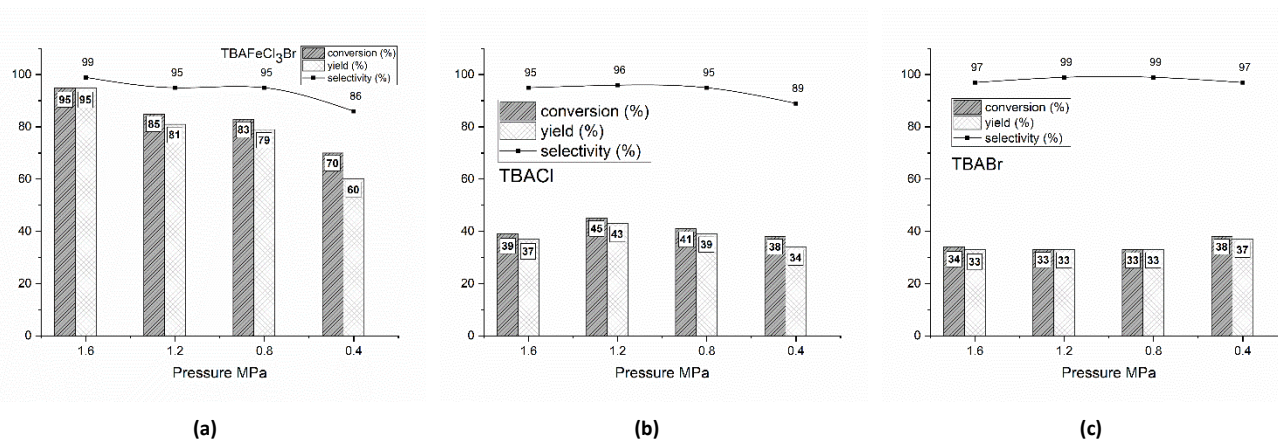
**Figure 3.** Conversions, yields and selectivities of **2a** at different temperatures (50, 75, 100, 125 °C) with [TBA][FeCl<sub>3</sub>Br] (a), TBACl (b) and TBABr (c). Reaction conditions: cat = 0.5 mol%; styrene oxide (SO) 2.19 mmol; P = 0.8 MPa; t = 4 h. Conversion and selectivity determined by <sup>1</sup>H NMR using mesitylene as the internal standard.

The difference between the presence or absence of iron is even more striking at lower temperatures: at 75 °C the ferrate compound still maintains moderate activity (33% conversion, 97% selectivity) while simple ammonium salts failed to react. Interestingly, even at 50 °C, a 12% conversion of the starting epoxide is observed when using 0.5 mol% of [TBA][FeCl<sub>3</sub>Br], paving the way for a possible application of this catalyst even at room temperature.

### 2.3. Effect of the CO<sub>2</sub> pressure

Next, we monitored the dependence of the model reaction under otherwise identical conditions (T = 100 °C at 0.5 mol% catalyst loading) on the applied CO<sub>2</sub> pressure, with the aim to reduce minimize the need for special glassware in this transformation (Figure 4). In this case both [TBA][FeCl<sub>3</sub>Br] and the ammonium halides proved to be only slightly influenced by the pressure of CO<sub>2</sub> employed. In the case of ammonium halides, the activity remains constant between 1.6 and 0.4 MPa CO<sub>2</sub> pressure but always lower compared with the ferrate compound. The latter suffers of a minor decrease of activity when moving to lower pressure but even at 0.4 MPa of CO<sub>2</sub> pressure a 70% conversion in just 4 h of reaction time was observed. With the aim to observe if there was a stronger effect of CO<sub>2</sub> concentration at lower conversions, we have repeated the reactions at shorter reaction times (1 h) at both 0.4 and 1.6 MPa CO<sub>2</sub> pressure under otherwise identical conditions (see Supporting Information). Again, [TBA][FeCl<sub>3</sub>Br] outperforms the simple TBACl and TBABr salts, even if at low conversion a stronger effect of CO<sub>2</sub> pressure is observed for the former and the yield of **2a** is more than doubled at higher pressures (33% yield of **2a** at 1.6 MPa to be compared with 13% at 0.4 MPa).




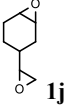
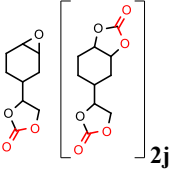






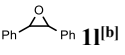
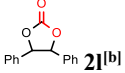

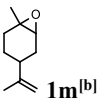
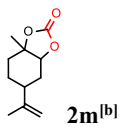
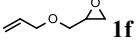
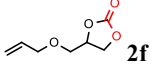
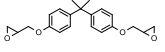
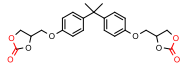
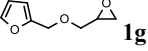
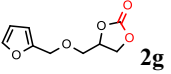
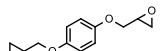
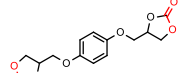
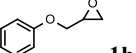
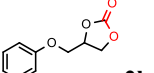




**Figure 4.** Conversions, yields and selectivities of **2a** at different CO<sub>2</sub> pressures (1.6, 1.2, 0.8 and 0.4 MPa) with [TBA][FeCl<sub>3</sub>Br] (a), TBACl (b) and TBABr (c). Reaction conditions: cat = 0.5 mol%; styrene oxide (SO) 2.19 mmol; T = 100 °C; t = 4 h. Conversion and selectivity determined by <sup>1</sup>H NMR using mesitylene as the internal standard.

#### 2.4. Reaction scope

With the best catalyst and the optimal reaction conditions in hand (Table 1, entry 2), we explored scope and limitations of the catalytic system. We choose these conditions to reduce the reaction time while maintaining a high conversion and good selectivity towards the desired cyclic carbonate. Results are summarized in Table 3. In general, our complex performs well in this transformation for most of the epoxides, with a remarkable higher activity in the case of terminal ones. The activated substrate (+-) epichlorohydrin was almost quantitatively converted (97%) in the corresponding cyclic carbonate **2b** (99% selectivity). Alkyl substituted epoxides, **1c-e**, were transformed with high selectivities (up to 99%) to the desired cyclic carbonates **2c-e**, although we noticed a small decrease in the conversion of the substrates while increasing the alkyl chain, that can be explained by a poorer solubility of the catalyst in the less polar reaction media. Moreover, the very low boiling point of the epoxide, especially in the case of **1c**, can lead to a small weight loss in the preparation and venting of the autoclave. Different glycidyl ethers **1f-h** were also tested: a quantitative selectivity for the cyclic carbonate products, **2f-h**, was obtained in all cases. Phenyl glycidyl ether, **1h**, was proved to be even more reactive, with complete conversion and selectivity to **2h**. We were pleased to see that the catalyst was active also in the activation of more sterically demanding epoxides such as cyclohexene oxide, **1i**. The latter is largely studied as a model compound as internal epoxide<sup>[50]</sup> and it is usually considered poorly reactive, with the consequent need of harsh reaction conditions or high catalyst loading to reach a satisfactory conversion. In our case, under the same reaction conditions employed for terminal epoxides and increasing the catalyst loading just to 1 mol%, we obtained a high conversion of cyclohexene oxide (68%) with full

**Table 3.** Scope of the cycloaddition of CO<sub>2</sub> to different epoxides catalyzed by [TBA][FeCl<sub>3</sub>Br]. Results expressed as conversion and selectivity to the cyclic carbonate.<sup>[a]</sup>

Substrate	Product	Conv. (%)	Sel. (%)	TOF (h <sup>-1</sup> )	substrate	product	Conv. (%)	Sel. (%)	TOF (h <sup>-1</sup> )
		97	99	49			73	92 [8]	37
		92	99	46			50	33	25
		75	87	38			11	27	6
		76	99	38			0	0	-
		84	99	42			78	94	39
		75	99	38			36	89	18
		99	99	50			68	99	34

<sup>[a]</sup> Reaction conditions: epoxide 250  $\mu$ L; [TBA][FeCl<sub>3</sub>Br] = 0.5 mol%; T = 100  $^{\circ}$ C; P = 0.8 MPa; reaction time = 4 h; neat. Results expressed as conversion and selectivity, determined by <sup>1</sup>H NMR using mesitylene as the internal standard. TOF = mol<sub>I</sub>(converted) · mol<sub>cat</sub><sup>-1</sup> · reaction time<sup>-1</sup>. <sup>[b]</sup> Catalyst loading increased to 1 mol%. <sup>[c]</sup> 250  $\mu$ L propylene carbonate (PC) as solvent.

selectivity to the cyclic product and no formation of any polymeric by-product. In a competing experiment of the reactivity of terminal and internal epoxides, we studied the reactivity of 4-vinylcyclohexene dioxide, **1j**, observing a good conversion of the substrate (73%) with an almost complete selectivity in favor of the terminal cyclic carbonate, **2j** (92%), and the formation of only 6% of the di-carbonate product **2j'** (8% selectivity).

More hindered substrates, as expected, gave less satisfactory results. In the case of 1,2-epoxy-1-methylpropane, **1k**, a deceiving conversion of only 50% was observed, but with a very poor selectivity in favor of the cyclic carbonate. However, no other by-products were observed: this might be due to the high volatility of the substrate, thus resulting in an overestimation of the conversion value. In the case of *t*-stilbene oxide, **1l**, and limonene oxide, **1m**, no satisfactory results were obtained. Finally, terminal diepoxides were tested as substrates for their possible application as non-isocyanate polyurethane monomers:<sup>[51]</sup> the *bis*-carbonate of (bisphenol-A)diglycidyl ether (BADGE), **2n**, was obtained in 73% yield (94% selectivity) using only 1 mol% catalyst. Under the same reaction conditions, 1,4-(bisbenzyloxy)diglycidyl ether was converted in the *bis*-carbonate product **2o** with a 32% yield and 89% selectivity. In both cases, propylene carbonate was successfully employed as solvent, as previously reported by our group.<sup>[46]</sup>

### 2.5. Scale up of the reaction and catalyst recycle.

A 20-fold scale-up reaction (5 mL of epoxide) was performed to evaluate the activity of our catalytic system in such conditions, using SO **1a** as the substrate and [TBA][FeBr<sub>3</sub>Cl] as the catalyst (0.5 mol%). The latter proved to be active even in these conditions with a minimum decrease in conversion (74%) maintaining the same selectivity for the cyclic product **2a** (95%). Pure styrene carbonate (SC) (4.19 g, 58% yield) could be isolated by simple treatment in *n*-hexane followed by filtration from the cold solution (-20 °C). To evaluate the robustness of the catalyst, the recyclability of the system was tested in the case of the synthesis of propylene carbonate (PC), under the optimized reaction conditions, by simply adding fresh **1c** (PO) three times (total volume 0.750 mL) and restoring the catalytic cycle charging again the reaction vessel under CO<sub>2</sub> pressure. We choose this reaction, since we have observed that the formed PC is a suitable solvent for the ferrate catalyst (*Vide supra*). Results of three catalytic cycles are summarized in the Supporting Information (Table S5). In the three consecutive runs, we observed only a minimal drop in the PC yield (from 99% to 96%) that might be also due to the increased solvent volume or even to a higher dilution of the catalyst. In any case, a remarkable TON of 594 was achieved.

## 3. Discussion

The mechanism for the formation of cyclic carbonates by the cycloaddition of CO<sub>2</sub> to epoxides was examined from both an experimental and a theoretical point of view. As mentioned previously and known from the literature,<sup>[52]</sup> simple ammonium salts are competent catalysts, but harsh reaction conditions are needed. The presence of a LA is known to facilitate the attack of the nucleophile to the epoxide, lowering the transition state (TS) energy by means of the coordination of the metal to the oxygen atom of the

epoxide. In the case of the ferrate salts  $[\text{FeX}_4]^-$ , we must consider that we have the concomitant presence of both the nucleophile,  $\text{X}^-$ , and the LA as  $\text{FeX}_3$ , that may trigger the ring opening of the epoxide. This kind of equilibrium between “ate” and free ferric salt in the case of  $[\text{FeBr}_4]^-$  has been already predicted by Capacchione and co-workers<sup>[53]</sup> and recently disclosed by Hein *et al.* in the case of indium bromide.<sup>[54]</sup> The existence of such an equilibrium might indeed trigger the nucleophilic attack of a free halide to the epoxide without the need of any external nucleophile and, at the same time, would guarantee the presence of a Lewis acid in the solution as  $\text{FeX}_3$ , thus activating the epoxide. We<sup>[46]</sup> and others<sup>[41]</sup> have indeed already shown that ferrate salts may act as single-component catalysts, without the need of any additional nucleophile. In 2019, Gual, Cano and co-workers reported that an imidazolium based iron containing ionic liquid  $[\text{BMIm}][\text{Fe}(\text{NO})_2\text{Cl}_2]$  is a competent catalyst for the  $\text{CO}_2$  cycloaddition to epoxides and showed by mechanistic studies that (i) a bifunctional catalyst is formed in situ by partial dissociation in solution to give  $[\text{BMIm}][\text{Cl}]$  and (ii) the Cl atom acts as the real nucleophile.<sup>[55]</sup> North and co-workers have proposed a similar mechanism in the cyclic carbonate formation promoted by a Cr(salophen) complex in the presence of TBABr.<sup>[56]</sup>

In view of our experimental results (Table 1), we were intrigued to understand the real nature of the attacking nucleophile. In the commonly accepted mechanism for the  $\text{CO}_2$  cycloaddition to epoxides, the energetic span of the catalytic cycle depends on the nucleophilicity of the halide and on its leaving group ability.<sup>[41]</sup> Since the reaction has been performed in neat epoxide, an aprotic media,  $\text{Cl}^-$  should be considered a better nucleophile, but its leaving group ability is worse than that of  $\text{Br}^-$ . Moreover, the halide lability from the ferrate salt should also be considered. Interestingly, we experimentally observed that the mixed ferrate salts,  $[\text{TBA}][\text{FeBr}_3\text{Cl}]$  and  $[\text{TBA}][\text{FeCl}_3\text{Br}]$ , are the most active catalysts with respect to the homoleptic ones (see Table 1). We reasoned that this might be traced to the better nucleophilicity of  $\text{Cl}^-$  and the better leaving group capability of  $\text{Br}^-$ .

When using  $[\text{TBA}][\text{FeBr}_3\text{Cl}]$  as catalyst, the scramble of the halides in solution to form  $[\text{TBA}][\text{FeCl}_4]$  and  $[\text{TBA}][\text{FeCl}_2\text{Br}_2]$  is not negligible and must be taken into account, as evidenced by the presence of  $[\text{FeCl}_4]^-$  detected by ESI(-)-spectroscopy. For this reason, we performed some reactions to investigate the influence of external nucleophiles to  $[\text{TBA}][\text{FeCl}_4]$  by adding catalytic quantities of TBABr or TBACl (see Supporting Information). As expected, the addition of the chloride salt did not affect the reaction, while the addition of TBABr slightly improved the conversion. In addition, the optically pure (*S*)-styrene oxide was employed as substrate in the cyclic carbonate formation promoted by  $[\text{TBA}][\text{FeCl}_3\text{Br}]$  (see Supporting Information). Enantiomerically pure (*S*)-styrene carbonate was

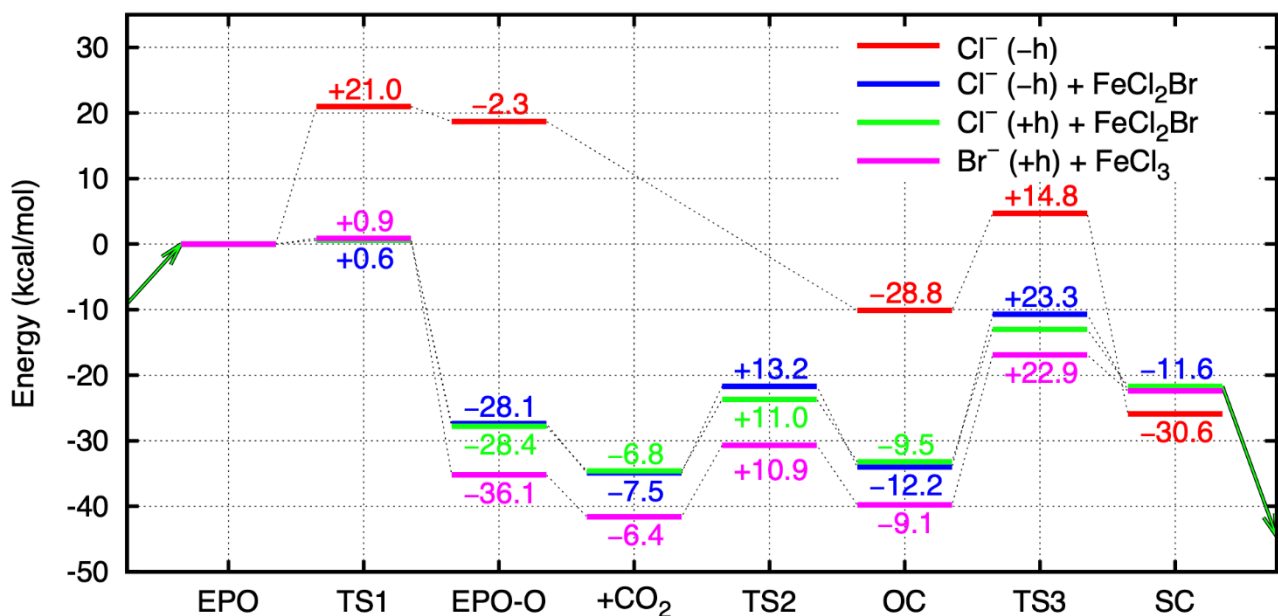
obtained, clearly showing that the reaction proceeds with retention of configuration, most probably through a double S<sub>N</sub>2 attack at the less hindered β C-atom of the SO.<sup>[55]</sup>

To shed light on the mechanism of the reaction under investigation we performed an extensive set of theoretical calculations. Since this system presents many degrees of freedom and a large set of possible reaction paths and intermolecular conformations has to be considered, we adopted a multi scale approach to span adequately its phase space. We selected a semiempirical algorithm as implemented in the xTB code<sup>[57]</sup> to perform a thorough screening of possible reactive channels, intramolecular and intermolecular conformations. The most relevant ones have been then optimized at DFT level, using semiempirical geometries of reaction intermediates, TSs and intermolecular complexes as starting guess.

As [TBA][FeCl<sub>3</sub>Br] is an ionic compound, upon dissolution in SO it likely undergoes dissociation to [FeCl<sub>3</sub>Br]<sup>-</sup> plus [TBA]<sup>+</sup>. The ferrate anion might further dissociate in FeCl<sub>2</sub>Br plus Cl<sup>-</sup> or FeCl<sub>3</sub> plus Br<sup>-</sup>. The [FeCl<sub>3</sub>Br]<sup>-</sup> species preferentially sticks to the epoxide ring facing a carbon atom. Forcing its approach to carbon, the epoxide ring opens by breaking the C-C bond. The activation barrier for this process is larger than 30 kcal/mol, indicating that this is not a viable reactive channel at the temperatures spanned in our experiments. This result is consistent with the observation that no reaction product derived from a C-C bond breaking has been detected. Alternatively, further dissociation of the ferrate anion upon solvation requires just 9 and 15 kcal/mol considering the release of a chloride or a bromide anion, respectively. Neglecting the contribution of entropy along the dissociation process we can affirm that, at the experimental conditions described in previous sections, the concentration of the chloride anion is about two orders of magnitude smaller than the concentration of ferrate, while the molarity of bromide is four orders of magnitude smaller. The chloride anion and the corresponding LA can therefore be considered as viable reactants, while bromide is almost absent in the reaction environment. Considering these species - and carbon dioxide as well - acting in the reaction process, the formation of the cyclic carbonate can be schematized as occurring in three consecutive steps, in agreement with literature results: (a) chloride (or bromide) forms a bond with a carbon atom of the epoxide ring, which opens by breaking a C-O bond in a concerted mechanism; (b) the C atom of carbon dioxide binds to the oxygen atom of the former epoxide thus forming an open carbonate species; (c) the carbonate closes the ring and the formation of a C-O bond induces simultaneous breaking of the carbon - halide bond. These steps have been studied both with and without the iron-based LA, and the possible role of carbon dioxide as weak LA has been considered as well. Data are collected in Table 4, and the relevant steps of the reaction mechanism have been pictorially rendered in Figure 5. Figure 6 reports geometries of relevant structures along the most favorable process. The overall view of theoretical results can be summarized as follows:

- Step (a) and (c), *i.e.* epoxide ring opening and carbonate ring closure, occur via energy activated transition states.
- Step (b) occurs with no activation barrier when no LA is present in the reaction environment. Conversely, in presence of an iron based Lewis acid, the incorporation of CO<sub>2</sub> in the open epoxide has an energy barrier, but in no case this becomes the rate determining step of the reaction.
- Depending on the reaction path considered, after its formation the carbonate might rearrange its conformation before ring closure. This process requires an activation energy of just few kcal/mol and in no case becomes relevant in the kinetics of the overall reaction.
- When no LA is present the rate determining step of the reaction is the epoxide ring opening. Conversely, when the iron atom of the LA interacts with the oxygen of the epoxide, the rate determining step becomes the carbonate ring closure.
- Strong Lewis acids such as FeCl<sub>2</sub>Br or FeCl<sub>3</sub> almost annihilate the barrier of epoxide ring opening and, quite importantly, largely stabilize the first reaction intermediate, which, when no LA is present, is very close in energy to the TS and is likely to evolve back to the reactants instead of the products.
- Carbon dioxide as weak LA is much less effective than FeCl<sub>2</sub>Br and FeCl<sub>3</sub> in lowering the energy barrier for the epoxide ring opening, which remains the rate determining step of the reaction.
- The most favorable reaction path occurs when the epoxide ring is activated by FeCl<sub>2</sub>Br and a chloride anion attacks the more hindered carbon. The chloride anion acts in a slightly more effective way with respect to bromide along this same reaction path.

Coming into a more quantitative analysis, our simulations proved that the reaction occurs much more favorably when a Lewis acid activates the epoxide ring. The key feature is that the barrier for the epoxide ring opening drops down to less than 1 kcal/mol, and the first reaction intermediate (the open epoxide species) is largely stabilized, residing more than 20 kcal/mol below the TS. To incorporate carbon dioxide in the epoxide requires then a barrier slightly larger than 10 kcal/mol, much smaller than the rate determining step of the reaction. The closure of the carbonate ring in presence of FeCl<sub>2</sub>Br requires an activation energy of 20.2 kcal/mol when a chloride anion attacks the more hindered carbon atom. Indeed, this value is only slightly smaller than the height of the rate determining step when no LA is present, *i.e.* 21.0 kcal/mol. This barrier corresponds to epoxide ring opening after the attack of Cl<sup>-</sup> to the less hindered carbon.



**Figure 5.** Schematic energy profiles for the relevant steps of the reaction under investigation. **EPO**: complex between the epoxide, the halide and the Lewis acid, if present; **TS1**: transition state for epoxide ring opening; **EPO-O**: open epoxide species; **+CO<sub>2</sub>**: complex between the open epoxide and carbon dioxide; **TS2**: transition state for the incorporation of CO<sub>2</sub> into the epoxide; **OC**: open carbonate species; **TS3**: transition state for epoxide ring closure; **SC**: complex between the cyclic carbonate species, the Lewis Acid and the halide. The energy of **EPO** is set to zero in all systems; data reported along the curves report the energy difference with respect to the previous step. In a single case (Cl<sup>-</sup> (+h) + FeCl<sub>2</sub>Br) we report the energy of the reactants with the undissociated ferrate anion (left arrow) and the products with the halide and the Lewis acid associated to form the ferrate anion (right arrow). For each curve we report the nature of the halide (Cl<sup>-</sup> or Br<sup>-</sup>), the carbon attacked by the halide (less hindered, -h, or more hindered, +h), and the presence of the Lewis acid.

**Table 4.** Barrier of the transition states of the main steps of the reaction under investigation. We refer to the caption of Figure 5 for the meaning of labels.

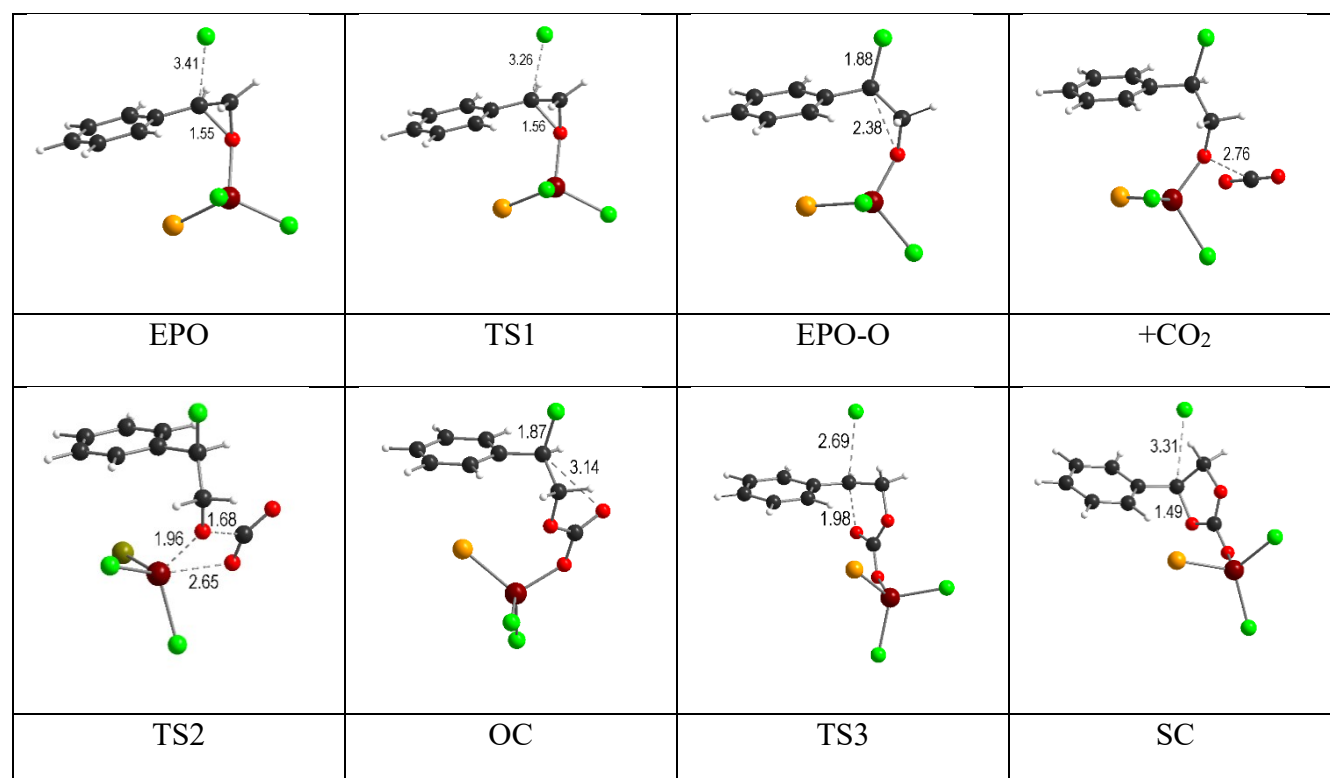
System	Epoxide opening	CO <sub>2</sub> incorporation	Carbonate closing
	(kcal/mol)	(kcal/mol)	(kcal/mol)
	TS1	TS2	TS3
Cl <sup>-</sup> (-h)	21.0	no barrier	14.8
Cl <sup>-</sup> (+h)	24.4	no barrier	10.7
Cl <sup>-</sup> + CO <sub>2</sub> <sup>[a]</sup> (-h)	18.3	no barrier	14.8
Cl <sup>-</sup> + CO <sub>2</sub> <sup>[a]</sup> (+h)	17.5	no barrier	10.7
Cl <sup>-</sup> + FeCl <sub>2</sub> Br (-h)	< 1	13.2	23.3
Cl <sup>-</sup> + FeCl <sub>2</sub> Br (+h)	< 1	11.0	20.2
Br <sup>-</sup> + FeCl <sub>3</sub> (+h)	< 1	10.9	22.9

<sup>[a]</sup> In these test cases a molecule of carbon dioxide is inserted close to the oxygen atom of the epoxide before opening of the ring, thus acting as a weak Lewis acid.

However, as discussed in more details in the Supporting Information section, epoxide conversion implies barriers in the range 20-25 kcal/mol, and – more importantly - the speed-up due to the presence of a LA is compatible with a barrier lowering of the rate determining step of about 1 kcal/mol. These outcomes strengthen the confidence that our theoretical calculations are adequate to provide a rationale for experimental evidences. The possibility that a second molecule of iron base catalyst comes into play into

the reaction mechanism is not considered in this study. According to the literature, Fe(III) might also assist the attack and the detachment of the halide species to and from carbon, determining a second order kinetics in the concentration of the metal.<sup>[38]</sup> We cannot rule out *a priori* this hypothesis, and a complete kinetic study is beyond the scope of the present work. Our results indicate that, at the conditions spanned by the experiments presented here, a monometallic mechanism is a viable possibility from a thermodynamic point of view.

As a further insight in the reaction mechanism, we considered carbon dioxide to behave as a weak Lewis acid and a reactant at the same time. From inspection of Table 4, we can see that CO<sub>2</sub> lowers the barrier of step (a) to just 17.5 kcal/mol when considering the presence of chloride anions, and generates the open carbonate intermediate in a concerted mechanism with epoxide ring opening. The barrier for carbonate ring closure is much smaller and measures 10.7 kcal/mol. Based just on these values, the above process should be the most favorable among the ones considered in this study, which contradicts the experimental evidence that the presence of a Lewis acid in the reaction environment is crucial for the reaction to occur at quite mild conditions.



**Figure 6.** Relevant geometries along the reaction path, referred to the case of Cl<sup>-</sup> attack on the more hindered carbon atom of the epoxide ring in presence of FeCl<sub>2</sub>Br as Lewis acid. The reaction proceeds from left to right, top to bottom. We refer the reader to the caption to Figure 5 for the meaning of labels.

A possible explanation, indeed verified by our simulations, is that the sticking of CO<sub>2</sub> to SO in the active site (*i.e.* with the carbon atom of CO<sub>2</sub> facing the oxygen of the epoxide ring, and the halide anion facing



a carbon atom of this same ring) is quite weak and competitive with several other conformations. In particular, many CO<sub>2</sub>-epoxide complexes lay in a very limited energy range (< 5 kcal/mol) but they are not relevant to the reaction process. In conclusion, while almost each molecule of a strong LA activates one epoxide ring, this is not the case for CO<sub>2</sub>, which is randomly distributed over a variety of non-reactive sites. We can conclude that, at the conditions spanned by our experiments, the rate determining step of the whole reaction process does not involve a carbon dioxide molecule, neither as a reactant to be incorporated in the open epoxide nor as a catalyst to activate epoxide ring opening.

#### **4. Conclusions**

We synthesized a series of ammonium “ferrate” salts, both homoleptic and mixed, which proved to be robust and active catalysts for the cycloaddition of CO<sub>2</sub> to epoxides without the addition of any additive or co-catalyst. The synthesis of the catalyst is straightforward, starting from cheap and commercially available iron(III) halide salts and quaternary ammonium salts. Quite mild reaction conditions were tolerated (0.4 MPa of CO<sub>2</sub> pressure and T below 100 °C). A TOF (up to 428 h<sup>-1</sup> at T = 150 °C) for the SO conversion to SC and a TON of 594 in the case of PC have been observed, which are remarkable when compared to the state of the art of the iron based homogeneous catalytic systems.<sup>[32]</sup> All the reactions, at least in case of liquid epoxide, can be performed without the use of solvent and without the need of any added co-catalyst. The scope of the reaction was investigated and the catalyst showed to be active on most of the substrates tested. Scale-up and catalyst recycle experiments were successful. To gain a deeper insight into the reaction mechanism and the role played by the combination of the Lewis acid (iron salt) and nucleophile (halide anion), theoretical calculations have been carried out. A very good correlation between the DFT calculations and the experimental outcomes has been observed. In view of these results, further studies are ongoing in our laboratories to diversify the ferrate complexes with the aim to achieve an easier recovery of the catalyst at the end of the reaction.

#### **5. Experimental section**

##### *5.1. General considerations*

All chemicals and solvents were commercially available and used as received except where specified. <sup>1</sup>H NMR analyses were performed with 400 MHz spectrometers at room temperature. The coupling constants (*J*) are expressed in hertz (Hz), and the chemical shifts ( $\delta$ ) in ppm. Catalytic tests were analyzed by <sup>1</sup>H NMR spectroscopy. Low resolution MS spectra were acquired with instruments equipped with ESI/ion trap sources. High resolution MS spectra were acquired on a Q-ToF SYNAPT G2-Si HDMS 8K instrument (Waters) equipped with a Zspray<sup>TM</sup> ESI source (Waters). The values are expressed as

mass-charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano.

### 5.2 Synthesis of ferrate salts, [TBA][FeX<sub>3</sub>Y]

All the ferrate salts were synthesized according to literature procedures<sup>[49]</sup> and their synthesis and characterization are reported in the Supporting Information.

### 5.3. General procedure for CO<sub>2</sub>/epoxide cycloaddition

A 250 mL stainless steel autoclave reactor was equipped with three 2.5 mL glass vials, containing the catalyst/epoxide mixture (0.25 mol% in 250  $\mu$ L of substrate) and, when required, 125  $\mu$ L of PC as co-solvent. The vials were equipped with magnetic stirring bars and sealed with specific caps. The autoclave was then charged with 0.5 MPa CO<sub>2</sub> and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa of CO<sub>2</sub> and placed in the heating bath for 4 h. The reactor was then cooled to RT and the CO<sub>2</sub> pressure released. To each vial, the appropriate amount of internal standard (mesitylene) and 0.3 mL of CDCl<sub>3</sub> were added. An aliquot of the resulting solution (100  $\mu$ L) was taken and diluted with 500  $\mu$ L of CDCl<sub>3</sub> to perform quantitative <sup>1</sup>H NMR analysis. Products were isolated by silica-gel chromatography (**5b** and **5k**) (hexane/AcOet 5:1) or directly collected by filtration as a pure solid from the reaction mixture (**5g**) (see Supporting Information).

### 5.4 Theoretical calculations

Theoretical calculations aimed at a better understanding of the reaction mechanism have been performed at two different theory levels.

First, we employed the semiempirical tight-binding based quantum chemistry (QC) method GFNn-xTB<sup>[57]</sup> in the framework of meta-dynamics (MTD), in order to explore the wide variety of possible reaction mechanisms. Within this approach, the total energy  $E_{\text{tot}}$  of the system is the sum of the total (electronic) tight-binding QC energy  $E_{\text{tot}}^{\text{el}}$ , the biasing root-mean-square deviation (RMSD)  $E_{\text{bias}}^{\text{RMSD}}$ , and an optional reactor wall cavitation potential  $E_{\text{bias}}^{\text{wall}}$ ,

$$E_{\text{tot}} = E_{\text{tot}}^{\text{el}} + E_{\text{bias}}^{\text{RMSD}} + E_{\text{bias}}^{\text{wall}} \quad (1)$$

A standard thermostat bath temperature of 27 °C has been mainly adopted in the molecular dynamics (MD) and MTD simulations, but during the chemical reaction space exploration it has been varied among -73 °C and 327 °C, to guess if unexpected reaction paths could be feasible by slightly heating the system. A MTD simulation, indeed, allows atom-selective heating and thereby efficient crossing of small/large chemical barriers depending on the strength of the bias.

As stated by the author,<sup>[57]</sup> due to the approximate character of this method, “the resulting structure ensembles require further refinement with more sophisticated approaches”. For this reason, the preliminary GFNn-xTB screening of the reaction paths has been followed by more rigorous first principles all electron DFT simulations, adopting the B3LYP hybrid functional<sup>[58,59]</sup> as implemented in the Gaussian 09 code.<sup>[60]</sup> As for the set of basis functions, we selected the 6-31++g(d,p) basis set, which ensures a reliable description of the valence shell electrons. This same DFT scheme proved successful in a recent investigation focused on the reactivity of organic compounds on an inorganic substrate.<sup>[61]</sup> The geometries of reactants, intermediates, transition states (TSs) and products were fully optimized.

The TS structures were searched through the Berny algorithm,<sup>[62]</sup> computing the force constants at every point.

The presence of solvent in the reaction environment has been taken into account through the Solvation Model based on Density (SMD) approach.<sup>[63]</sup> The solvent considered in our calculations is toluene, whose dielectric constant amounts to 2.38 and is close to that of SO.

Dispersion forces of the Grimme type<sup>[64]</sup> were included between the molecules involved in the reaction in order to account for van der Waals interactions. The D3 version of Grimme’s dispersion with the original D3 damping function has been selected.

The calculated reaction barriers (Figure 5 and Table 4) are reported in kcal/mol as total energy differences between adjacent compounds along the reaction coordinate.

From the computational point of view the role of the tetrabutylammonium cation in the CO<sub>2</sub> fixation process resulted to be trivial, the only effect of its presence being a rigid down-shift of the energy reaction graph. Therefore, it has been neglected in the final calculations.

### **CRedit authorship contribution statement**

**Nicola Panza:** Data curation, Writing - original draft, Visualization. **Fausto Cargoni, Raffaella Soave** and **Mario Italo Trioni:** DFT calculations, Conceptualization, Writing - review & editing. **Alessandro Caselli:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

### **Declaration of Competing Interest**

There are no conflicts to declare.

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### **Supporting Information**

Experimental details of the synthetic procedures and the catalytic reactions, HPLC and <sup>1</sup>H NMR data, and complete energy reaction paths from ab initio computations are given in the Supporting Information.

## References and notes

§ Only the results obtained with the homoleptic, [TBA][FeCl<sub>4</sub>] and [TBA][FeBr<sub>4</sub>], and with the most promising [TBA][FeCl<sub>3</sub>Br] mixed ferrates are reported; for more details refer to the Supporting Information.

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