Reconsidering TOF calculation in the transformation of epoxides and CO_2 into cyclic carbonates

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Abstract:

The combination of Lewis acids and Lewis bases, currently defined as catalysts and co-catalysts (or promoter) respectively, in the reaction between epoxides and CO_2 to give cyclic carbonates, is discussed, starting from examples in which the Lewis base was used in larger amount with respect to the Lewis acid. In these cases, turnover frequency (TOF) values have been usually calculated taking into account solely the amount of the Lewis acid employed. The occurrence of two distinct reaction pathways, one catalysed by the sole Lewis base and the other one catalysed by the Lewis acid/Lewis base couple, in which the Lewis acid alone does not play a catalytic role, should bring researchers to reconsider the TOF calculation based solely on the amount of Lewis acid, especially when the amount of the Lewis base used is much larger than the Lewis acid. In order to draw a more precise picture of how the use of a Lewis base/Lewis acid co-catalytic system affects the reaction course, we analytically examined a general mechanistic scheme able to model the overall process. For these cases, we propose a simple equation for a better estimation of TOF values and a normalization approach for a more consistent comparison between various catalytic systems.

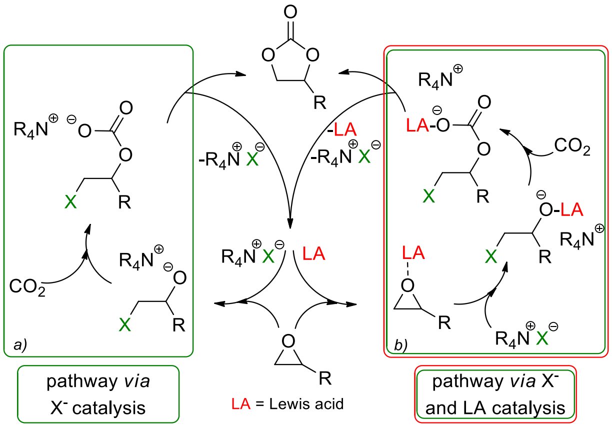
Keywords: CO_2 conversion; Catalysis; Cyclic carbonate; Epoxide; Heterogeneous catalysis

1. Introduction

The reaction between epoxides and carbon dioxide leading to either cyclic carbonates or polycarbonates has attracted, in recent years, a great interest, since both classes of products are commercially valuable. Cyclic carbonates are usually obtained under thermodynamic control, and have many applications such as chemical intermediates, solvents and electrolytes solvents for lithium ion batteries. Moreover, the interest toward using carbon dioxide as a sustainable building block for the chemical industry has pushed forward the scientific community in researches on this topic.[1]

Among the possible synthetic methodologies, two approaches have been largely employed: *a*) catalysis with halide salts, usually as ammonium salts $R_4N^+X^-$, (R_4N^+ = tetrabutylammonium, X^- = I^-, Br^- or Cl^-) or imidazolium or phosphonium salts, that act as good nucleophiles and good leaving groups and, *b*) catalysis with Lewis acids coupled with halogen anions (Scheme 1).

The first step of route *a* is the epoxide ring opening due to the nucleophilic attack by the Lewis base X^-. The corresponding alkoxide intermediate attacks as a nucleophile the CO_2 molecule to form a second intermediate species that undergoes ring closure to afford the cyclic carbonate, releasing the catalytic species. On the other hand, the first step of route *b* is the activation of the epoxide ring by coordination of the Lewis acid, which promotes the nucleophilic attack by the Lewis base (X^-) leading to the epoxide ring opening. The alkoxide intermediate acts as a nucleophile towards the CO_2 to form a further intermediate species, which ultimately undergoes ring closure to produce the cyclic carbonate by releasing the two co-catalytic species. Many studies have been carried out from a mechanistic point of view, both for metal-based catalysed or organocatalyzed reactions.[2]



Scheme 1. Pathways *a* and *b* for the transformation of epoxide and CO_2 to cyclic carbonate.

Since 2005, Arai *et al.* stated that the activity of ionic liquids, such as imidazolium salts, is greatly enhanced by the addition of Lewis acidic compounds of metal halides or metal complexes that have no or low activity by themselves.[3] When R_4NX alone is used as catalyst, the catalytic activity is measured as turnover number (TON) or TOF values related to the amount of such single catalytic species. When Lewis acid and R_4NX are used as catalyst and co-catalyst, respectively, as usually described in many papers, the catalytic activity is measured as TON or TOF values related only to the amount of the Lewis acid, even when the amount of R_4NX is much higher with respect to that of the Lewis acid. Moreover, in some cases, when the Lewis base/Lewis acid ratio was increased higher yields in the cyclic carbonate were obtained, but the TON and TOF values have been calculated only considering the amount of the Lewis acid. Such approaches lead, in some cases, to astonishing TON and TOF values. Now the question arises whether such values provide a sensible measure of the real catalytic activity.

Here we would like to start a discussion on the use of such values, in order to shed some light on this particular issue. For this purpose, and considering the huge amount of work published on the topic, we would like to comment some literature data, in which the Lewis base has been used in larger amount with respect to the Lewis acid (molar ratio Lewis base:Lewis acid ≥ 10:1). We have selected papers reporting conversions or yields data with or without calculated TOF values but, in every case we have highlighted the role of the so-called co-catalyst. The catalytic systems here discussed are based on simple Lewis acids or metal complexes, metal-organic frameworks, metal-based polymers, chosen without any particular criticism but with the sole intention to discuss the activity of binary catalytic systems formed by Lewis acid and Lewis base in the formation of cyclic carbonates. Reaction conditions of the reported examples are slightly different since reaction time, temperature and CO_2 pressure do not exactly match, but are similar enough to make some consideration.

2. Discussion

It is worth preliminarily stressing that the main aim of this paper is to discuss about the performances of some catalytic systems in terms of their TOF values. Indeed, the problem of "benchmarking" is a main issue in assessing the performances of any catalytic system.[4] In several cases, the reported claims of TON or TOF values could be misleading because they were calculated using an approach that could be, in our opinion, incorrect, especially when the nucleophilic catalyst (the usually so-called co-catalyst) is used in large amount with respect to the Lewis acid catalyst. In order to demonstrate our point of view, we have selected several papers depending on the nature of the catalytic system, *i.e.*: *a*) Lewis acid based on metal halides or metal complexes and ammonium or phosphonium halide salts, *b*) Lewis acid based on organometallic polymers and ammonium halide salts, *c*) Lewis acid based on MOFs and ammonium halide salts. Then, we have discussed these data by applying two simple expressions (equations 1 and 8, see later), which have been derived from a kinetic approach, aiming at demonstrating how in several cases the TOF calculation should be different, since the amount of halide salts has not been taken into account.

The use of simple Lewis acids such as $ZnCl_2$ dates back to 1986.[5] It was soon clear the synergistic catalytic activity by the combined use of $ZnCl_2$ and tetrabutylammonium iodide (TBAI). Starting from a 0.2:0.1 mol% ratio of $ZnCl_2$:TBAI to a 0.2:0.8 mol% ratio, the yield increased from 57% to 98%. The combined use of $ZnBr_2$ and 1-butyl-3-methylimidazolium chloride, gave a similar result, whereas no reaction occurred when only $ZnBr_2$ was used.[6] $ZnBr_2$ alone does not catalyse the reaction, but exhibited a significant catalytic activity when used in combination with hexabutylguanidinium bromide (HBGBr). When the molar ratio HBGBr:$ZnBr_2$ was 8:1 (HBGBr 0.24 mol%) a quantitative yield was obtained. On the other hand, HBGBr alone, at even lower amount (0.06 mol%), gave a 18% conversion. (Table 1, entry 1).[7] Phosphonium bromide $PPh_3C_6H_{13}Br$, in 0.12 mol%, gave a 15.4% yield of propylene carbonate. The addition of 0.012 mol% of $ZnCl_2$ gave a 84% yield that corresponds to a TOF of 6960 h^{-1} (Table 1, entry 2).[8] Under similar reaction conditions, Ph_4PI alone (0.086 mol%) catalysed the formation of propylene carbonate in 8.4% yield. Its combined use with $ZnBr_2$ (0.009 mol%) afforded the carbonate with a claimed TOF value of 7822 h^{-1} (Table 1, entry 3).[9]

In addition to simple zinc halides, zinc complexes have been widely used as Lewis acid.

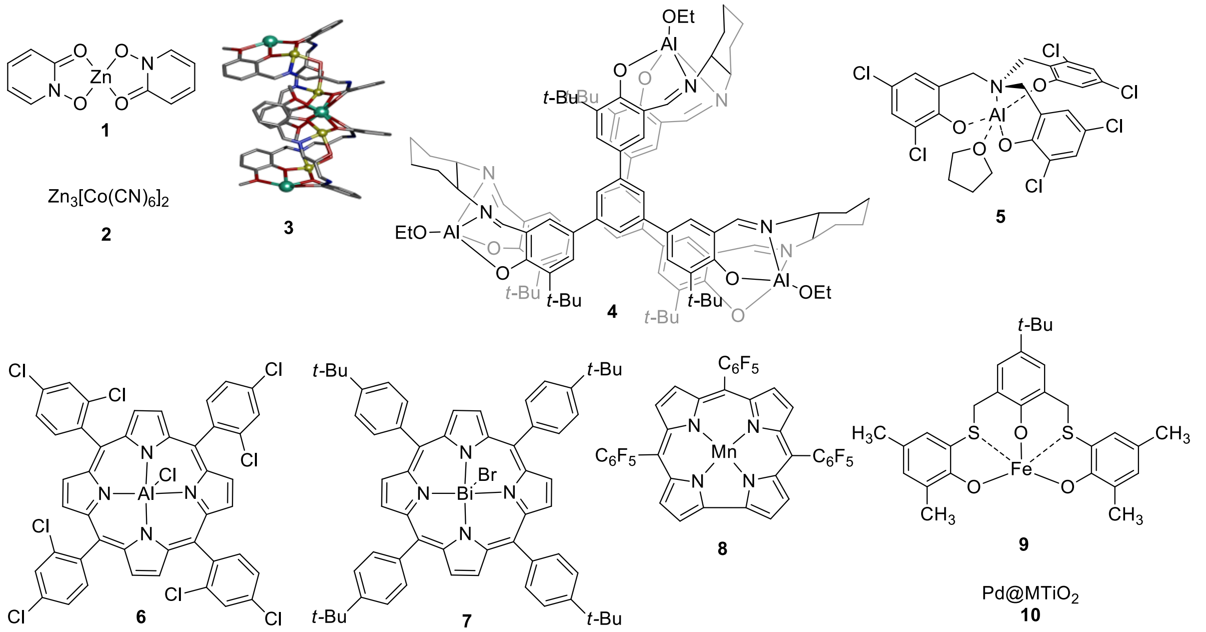


Figure 1. List of Lewis acids **1-10**.

The 2-hydroxypyridine *N*-oxide Zn(II) complex **1** was used in the presence of TBAI. Complex **1** was not catalytically active whereas a significant 34% yield was observed when TBAI was used as the sole catalyst. When both catalysts were used, in similar ratio (TBAI:**1** = 3.3:1) a 97% yield was obtained. However, lowering the amount of Lewis acid catalyst down to 0.0025 mol% and increasing the amount of TBAI up to 0.9 mol% (TBAI:**1** = 360:1), under harsher reaction conditions, a TOF value of 22000 h^{-1} was claimed (Table 1, entry 4).[10] However, under such reaction conditions, reaction using TBAI alone was not reported.

Another example of zinc-based Lewis acid was the double metal cyanide complex $Zn_3[Co(CN)_6]_2$ (**2**) which was used in the presence of an excess of tetrabutylammonium chloride (TBAC) (TBAC:**2** = 10.8). This catalytic system converted styrene oxide into styrene carbonate in 86% yield. The use of $Zn_3[Co(CN)_6]_2$ (**2**) did not afford the carbonate whereas a 14% yield was obtained using TBAC alone (Table 1, entry 5).[11]

Zn-based Lewis acid helicate **3** was used in combination with tetrabutylammonium bromide (TBAB). Reaction were carried out with TBAB:**3** = 30:1 or 200:1 (0.75:0.025 mol% or 0.5:0.0025 mol%, respectively). In both cases, the role of TBAB cannot be ruled out if we compare yields with those achieved using TBAB alone under the same conditions (Table 1, entry 6).[12] TBAB was used in 10 mol% togheter with an Al-based catalyst, Al(III)@cage **4** at 0.33 mol% (TBAB:**4** = 30.3) (Table 1, entry 7).[13] Such large amount of TBAB certainly gives a significant contribution to the overall yield. Indeed, a 58% yield of propylene carbonate was reached in the presence of 10 mol% of TBAB whereas TBAB, as the sole catalyst in 7.2 mol%, gave a 20.4% yield of propylene carbonate under similar conditions (see Table 2, entry 4).[14]

Another example of Al-based Lewis acid catalyst is the aluminium complex **5** which was used for the conversion of 1,2-epoxyhexane in the presence of TBAI. Under the adopted reaction conditions TBAI, as the sole catalyst at 0.05 mol% loading, led to 13% conversion after 2 h. The use of TBAI at 0.05 mol% and Al-complex **5** at different loadings (0.0025, 0.0010 and 0.0005 mol%) gave the carbonate in 38-24% yields. The calculated TOF values were based only on the amount of Al-complex **5**, giving a TOF value up to 24000 h^{-1} (TBAI:**5** = 100:1). The use of PPNI or PPNBr (PPN = bis-(triphenylphosphine)iminium) in a 100 fold excess with respect to **5**, gave higher yields that correspond to higher TOF values (Table 1, entry 8).[15] However, no yields were reported with PPNI or PPNBr alone under the same reaction conditions.

Aluminium porphyrin complex **6** in combination with bis-(triphenylphosphine)iminium chloride (PPNCl) was highly active. Under the adopted condition, PPNCl alone (0.24 mol%) gave only an 8.3% conversion whereas an almost quantitative conversion was obtained working in the presence of

0.002 mol% of **6** with a PPNCl:**6** molar ratio of 120:1. By keeping the same molar ratio and decreasing the amount of catalyst **6**, a high TOF value was reached (Table 1, entry 9).[16]

Table 1. Selected data related to the conversion of epoxides in the presence of Lewis acid based on metal halides or metal complexes.[a]

Entry	**Epox.**	**Lewis base (mol%)**	**Lewis acid (mol%)**	**LB:LA**[b]	**Yield or conv (%)**	**TOF (h^{-1})**	**Conditions (t, T, pCO_2)**	**Ref.**
1	PO	HBGBr (0.06)	-	-	18	-	1 h, 100 °C, 4 MPa	[7]
		HBGBr (0.24)	$ZnBr_2$ (0.03)	8.0	100	3571		
2	PO	$PPh_3C_6H_{13}Br$ (0.12)	-	-	15.4	-	1 h, 120 °C, 1.5 MPa	[8]
		$PPh_3C_6H_{13}Br$ (0.12)	$ZnCl_2$ (0.012)	10	84	6960		
3	PO	Ph_4PI (0.086)	-	-	8.4	-	1 h, 120 °C, 2.5 MPa	[9]
		Ph_4PI (0.086)	$ZnBr_2$ (0.009)	9.5	74.5	7822		
4	SO	TBAI (0.5)	-	-	34		12 h, 80 °C, 1 MPa	[10]
		TBAI (0.5)	**1** (0.15)	3.3	97			
	PO	TBAI (0.9)	**1** (0.0025)	360	55	22000	1 h, 120 °C, 3 MPa	
5	SO	TBAC (1.08)	-	-	14		6 h, 120 °C, 0.34 MPa	[11]
		TBAC (1.08)	**2** (0.1)	10.8	86	153		
6	SO	TBAB (0.75)	-	-	25	-	1 h, 120 °C, 10 bar	[12]
		TBAB (0.75)	**3** (0.025)	30	96	3840		
		TBAB (0.5)	-	-	19	-		
		TBAB (0.5)	**3** (0.0025)	200	67	26800		
7	PO	TBAB (10)	**4** (0.33)	30.3	58	n.r.	48 h, r.t., 1 atm	[13]
8	HO	TBAI (0.05)	-	-	13		2 h, 90 °C, 10 bar	[15]
		TBAI (0.05)	**5** (0.0025)	20	38	7600		
		TBAI (0.05)	**5** (0.0010)	50	33	16500		
		TBAI (0.05)	**5** (0.0005)	100	24	24000		
		PPNI (0.05)	**5** (0.0005)	100	29	29000		
		PPNBr (0.05)	**5** (0.0005)	100	36	36000		
9	PO	PPNCl (0.24)	-	-	8.3	-	0.5 h, 120 °C, 3.0 MPa	[16]
		PPNCl (0.24)	**6** (0.002)	120	96.4	96400		
		PPNCl (0.06)	**6** (0.0005)	120	46.3	185200		
10	PO	TBAI (2.4)	-	-	58.4	292	1 h, 90 °C, 2 MPa	[17]
		TBAI (2.4)	**7** (0.2)	12	92.9	465		
		TBAI (2.4)	**7** (0.001)	2400	37.9	37900		
11	SO	TBAB (2)	-	-	<15		4 h, 60 °C, 1 atm	[18]
		TBAB (2)	**8** (0.05)	40	60			
		TBAB (2)	**8** (0.05)	40	94 (Y)	235	8 h, 60 °C, 1 atm	
12	PO	TBAB (0.1)	-	-	5	-	1 h, 120 °C, 2 MPa	[19]
		TBAB (0.1)	**9** (0.01)	10	52	5200		
		TBAB (0.25)	-	-	10	-	1 h, 120 °C, 2 MPa	
		TBAB (0.25)	**9** (0.025)	10	82.6	3304		
		TBAB (0.25)	**9** (0.025)	10	>99	4000	1 h, 120 °C, 4 MPa	
13	ECH	TBAB (5)	-	-	22		2 h, 80 °C, 1 atm	[20]
		TBAB (5)	**10** (0.12)[c]	41.6	98	639.5		

[a] PO: propylene oxide; SO: styrene oxide; HO: 1,2-epoxyhexane; ECH: epichlorohydrin; n.r.: not reported. [b] LB:LA = Lewis base:Lewis acid molar ratio. [c] loading evaluated from the amount of **10** used (20 mg).

The bismuth (III) porphyrin complex **7** was used at 0.2 mol% loading in combination with TBAI at molar ratio TBAI:**7** = 12:1 to give propylene carbonate in 92.9% yield whereas TBAI alone gave a 58.4% yield. Catalyst **7** was used also at 0.001 mol% loading in the presence of TBAI (TBAI:**7** = 2400:1). The yield was 37.9% with a claimed TOF value of 37900 h^{-1} (Table 1, entry 10).[17]

The manganese(III)corrole **8** (0.05 mol%) with 2 mol% TBAB (TBAB:**8** = 40:1) exhibited good catalytic activity at atmospheric pressure of CO_2 giving a 60% conversion of styrene oxide. By doubling the reaction time, a 94% yield was obtained. Catalyst **8** was not active, whereas ca. 15% conversion was observed under such mild conditions with TBAB at 2 mol% (Table 1, entry 11).[18]

The dinuclear thioether-triphenolate iron(III) complex **9** was found to be a good catalyst for the conversion of PO to PC. A high TOF value (5200 h^{-1}; 52% conv.) was obtained in the presence of TBAB at 0.1 mol% (TBAB:**9** = 10:1). Without the iron(III) catalyst **9** the conversion was 5%. A similar contribution of TBAB was observed under more drastic conditions (Table 1, entry 12).[19]

Catalyst based on palladium nanoparticles embedded on mesoporous TiO_2 (Pd@MTiO_2, **10**) was not active, whereas the use of TBAB gave a 22% yield in the reaction of epichlorohydrin and CO_2. The combined use of Pd@MTiO_2 **10** and TBAB gave an almost quantitative yield (Table 1, entry 13).[20]

The use of polymeric Lewis acid catalysts in combination with ammonium halide salts as co-catalysts (Figure 2) has been also largely employed. The metalporphyrin-based microporous organic polymer HUST-1-Co **11** was used in the presence of a large excess of TBAB (TBAB:**11** = 232:1) to give high yield of propylene carbonate. The use of TBAB alone gave a 20.4% yield whereas a very low yield was observed with **11** alone (Table 2, entry 1).[21]

The aluminium porphyrin-based hyper-cross linked polymer **12** was used in 0.25 mol% loading in the presence of TBAB (2 mol%) under mild conditions (40 °C, 1.0 MPa) to give quantitative conversion of propylene oxide. Under such conditions, catalyst **12** or TBAB alone did not give conversion. However, under more drastic conditions (100 °C and 3.0 MPa; TBAB:**12** = 200:1) a TOF value of 14880 h^{-1} was reported. The contribution of TBAB under such high performing conditions, was not reported (entry 2).[22]

The contribution of TBAB was quite significant in the transformation of epichlorohydrin with cobalt porphyrin based porous organic polymer **13**. Indeed, in the presence of 7.2 mol% of the sole TBAB a 34% conversion was obtained, which increased up to 95.6% with the addition of the metal-based catalyst (TBAB:**13** = 33:1). In this case, even the Lewis acid catalyst alone gave the corresponding cyclic carbonate, although in low amount (entry 3).[23]

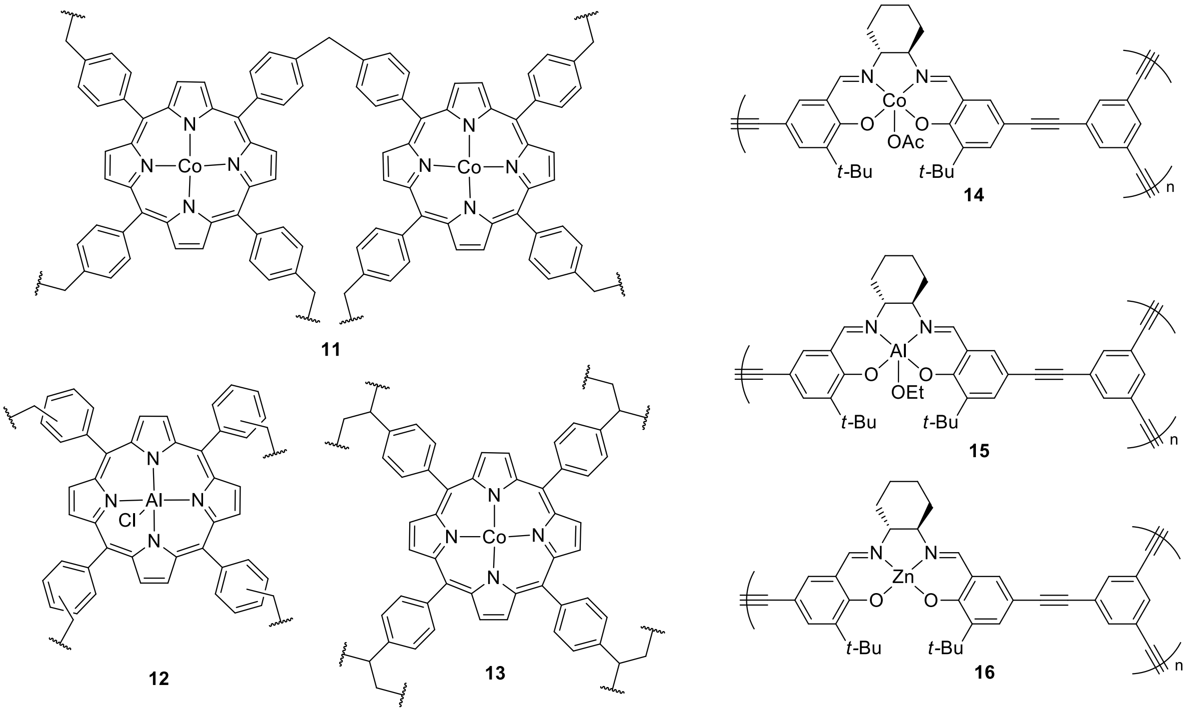


Figure 2. Polymeric Lewis acids **11-16**.

Cobalt and aluminium based conjugated microporous polymers **14** and **15**, when co-catalysed with TBAB (TBAB:**14** or **15** = 14.7), displayed high catalytic activity in the conversion of propylene oxide at atmospheric pressure and room temperature. The contribution of the sole TBAB was significant when the reactions were carried out both at 25 °C and at 100 °C (entry 4).[14]

Zinc-coordinated conjugated microporous polymer **16** was used at different loadings in the presence of an excess of TBAB. The role of TBAB, when used in 1.8, 1.25 and 0.9 mol%, was not neglegible. A TOF value of 11600 h^{-1} (29% yield) was reported when **16** was used in 0.0025 mol% in combination with 0.9 mol% of TBAB that, in turn, gave a significant 11.5% yield when used as the sole catalyst (TBAB:**16** = 360:1; entry 5).[24]

Table 2. Selected data related to the conversion of epoxides in the presence of Lewis acid based on organometallic polymers.[a]

Entry	Epoxide	Lewis base (mol%)	Lewis acid (mol%)	LB:LA[b]	Yield or conv (%)	TOF (h^{-1})	Conditions (t, T, pCO_2)	Ref.
1	PO	-	**11** (0.031)	-	4.5		30 h, r.t., 1 atm	[21]
		TBAB (7.2)	-	-	20.4			
		TBAB (7.2)	**11** (0.031)	232	94.6	103		
2	PO	TBAB (2)	**12** (0.25)	8	>99		1 h, 40 °C, 1.0 MPa	[22]
		TBAB (1)	**12** (0.005)	200		14880	1 h, 100 °C, 3 MPa	
3	ECH	-	**13** (0.217)	-	9.7		24 h, 29 °C, balloon	[23]
		TBAB (7.2)	-	-	34.0			
		TBAB (7.2)	**13** (0.217)	33	95.6	436		
4	PO	-	**14** (0.49)	-	6.7		48 h, 25 °C, 0.1 MPa	[14]
		TBAB (7.2)	-	-	20.4			
		TBAB (7.2)	**14** (0.49)	14.7	81.5	3.4		
		TBAB (7.2)	**15** (0.49)	14.7	78.2	3.3		
		TBAB (7.2)	-	-	31	4	1 h, 100 °C, 3 MPa	
		TBAB (7.2)	**14** (0.49)	14.7	98.1	201		
		TBAB (7.2)	**15** (0.49)	14.7	91.2	187		
5	PO	TBAB (1.8)	-	-	17.6	10	1 h, 120 °C, 3 MPa	[24]
		TBAB (1.8)	**16** (0.1)	18	74.8	748		
		TBAB (1.25)	-	-	14.1	11		
		TBAB (1.25)	**16** (0.0075)	167	38.1	5080		
		TBAB (0.9)	-	-	11.5	13		
		TBAB (0.9)	**16** (0.005)	180	35.7	7140		
		TBAB (0.9)	**16** (0.0025)	360	29	11600		

[a] PO: propylene oxide; SO: styrene oxide; ECH: epichlorohydrin. [b] LB:LA = Lewis base:Lewis acid molar ratio.

Metal-organic frameworks (MOFs) have been widely employed as catalysts for cyclic carbonate synthesis.[25] In Table 3 are reported some examples in which the Lewis base was used in larger amount with respect to the Lewis acid. The single-walled nickel-based organic nanotubes (Ni-TCPE1 **17** and Ni-TCPE2 **18**; Table 3, entry 1)[26] were inactive toward the formation of cyclic carbonate (at 0.05 mol%) whereas high yields were obtained when used in the presence of TBAB at 1.5 mol% (TBAB:**17** or **18** = 30:1). Conversion using the sole TBAB was not reported, but a comparison with another report[27] showed that, under the same reaction conditions, the conversion of styrene oxide with TBAB was significant (59%, see entry 2).

A 3D copper-phosphonate network, with the general formula $Cu_7(H1L)_2(TPT)_3(H_2O)_6$ (**19**) was tested in the formation of styrene carbonate which was obtained in very low yield in the absence of TBAB. In the presence of TBAB at 1.5 mol%, without catalyst **19**, a 59% yield was obtained, whereas a quantitative yield was reached with 0.01 mol% of **19** was added (TBAB:**19** = 150:1; entry 2).[27]

A phosphonate-based Zr-MOF **20** was used in 0.033 mol% with TBAB in 1 mol% to give a 95% conversion (TBAB:**20** = 30:1). The phosphonate-based Zr-MOF **20** was not active whereas, under the same conditions, TBAB gave a 50% conversion, which means that TBAB gave an important contribution to the 95% overall yield (entry 3).[28]

The MOF-based catalyst MMCF-2 **21** catalysed, under very mild conditions, conversion of propylene oxide into propylene carbonate in only 0.125 mol% in the presence of 7.2 mol% of TBAB (entry 4). No data were available about the catalytic activity of MMCF-2 **21** or TBAB alone.[29] On the other hand, comparison with data reported in Table 2, entry 4, or in ref. [12] shows that the sole contribution of TBAB can be significant.

The metal-metalloporphyrin framework MMPF-9 **22** and MMPF-18 **23** were used in the presence of a large amount of TBAB (7.2 and 10 mol%, entries 5-6).[29-30] The triazole-containing MOF **24** was also employed under mild conditions in only 0.2 mol% in the presence of a large amount of TBAB (10 mol%, entry 7).[31] In the latter cases (entries 4-7), because of the presence of large amount of TBAB (7.2-10 mol%, TBAB:Lewis acid = from 40:1 to 58:1), the contribution of TBAB alone cannot be considered negligible (11% yield at 7.2 mol% loading[12, 14]).

Table 3. Selected data related to the conversion of epoxides in the presence of Lewis acid based on MOFs.

Entry	Epoxide	Lewis base (mol%)	Lewis acid (mol%)	LB:LA[b]	Yield or conv (%)	TOF (h^{-1})	Conditions (t, T, pCO_2)	Ref.
1	SO	TBAB (1.5)	**17** (0.05)	30	>99	166.7	12 h, 100 °C, 1 MPa	[26]
		TBAB (1.5)	**18** (0.05)	30	86.2	143.3		
2	SO	-	**19** (0.01)	-	1.9		12 h, 100 °C, 1 MPa	[27]
		TBAB (1.5)	-	-	59			
		TBAB (1.5)	**19** (0.01)	150	>99	119		
3	SO	TBAB (1.0)	-	-	50		12 h, 100 °C, 1 MPa	[28]
		TBAB (1.0)	**20** (0.033)	30.3	95	238		
4	PO	TBAB (7.2)	**21** (0.125)	57.6	95.4	n.r.	48 h, r.t., 1 atm	[29]
5	PO	TBAB (7.2)	**22** (0.125)	57.6	87.4	15[a]	48 h, r.t., 1 atm	[29]
6	PO	TBAB (10)	**23** (0.25)	40	97	n.r.	48 h, r.t., 1 atm	[30]
7	PO	TBAB (10)	**24** (0.2)	50	96	200	48 h, r.t., 1 atm	[31]

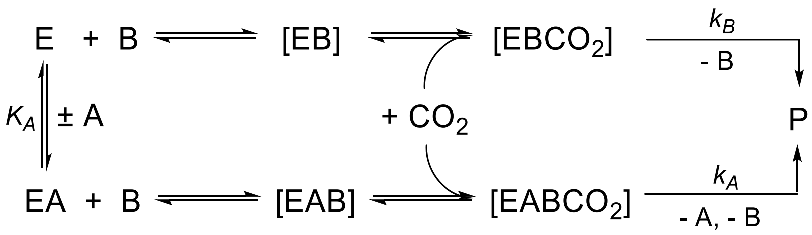
[a] TOF reported in ref. [1d]. [b] LB:LA = Lewis base:Lewis acid molar ratio.

These examples allow to positively assess that the formation of the product actually occurs by both pathways. Therefore, we may ask whether TOF values reported in literature are really representative of the true catalytic activity of the catalytic system, which is actually composed by both catalysts. The cases reported hereinabove claimed TOF values calculated only on the amount of the Lewis acid without taking into account the large amount of Lewis base that, by itself, catalysed the transformation into cyclic carbonates. We believe that TOF values calculated in this way may be misleading. Here we would like to demonstrate that in these cases a reasonably approximated value for the Lewis acid catalyst ($\mathrm{TOF}_{(A)}$) should be calculated by applying equation 1, i.e. by considering the reaction yields in the presence or absence of the Lewis acid catalyst (P_{AB} and P_B respectively) after a given reaction time *t*, and then dividing their difference by *t* and the analytical concentrations of the catalyst (A_0).

$$TOF_{(A)} \approx \frac{(P_{AB} - P_B)}{t \cdot A_0}$$

(equation 1)

Aiming at critically reconsidering and rationalizing the literature results summarized hereinabove, and then at justifying our choice of equation 1 as a reasonable way to define $\mathrm{TOF}_{(A)}$, the mechanistic aspects of the reaction should be preliminarily taken into account. This problem has been approached on some occasions from a computational viewpoint, in order to individuate the structures and relative stabilities of the possible complex reaction intermediates, and to draw the correct reaction coordinate[2c, 32] as well. On the other hand, studies on the reaction kinetics are scarce, due to the obvious experimental difficulties, and have mainly exploited the initial rates method.[33] Therefore, based on the suggestions from these works, we considered from an analytical viewpoint a reasonable mechanistic scheme able to model the process (Scheme 2):



(Scheme 2)

where E represents the epoxide substrate, B the Lewis base halide anion, A is the Lewis acid catalyst, P the cyclic carbonate product, which is actually formed *via* either a base-only catalysed or a co-catalysed pathway. The substrate and the catalysts can form three different adducts ([EA], [EB] and [EAB]), from which two further reactive intermediates with CO_2 can be obtained ([$EBCO_2$] and [$EABCO_2$]). The latter ones are the immediate precursors of the product P, through two different irreversible steps, the kinetic constants of which are indicated as k_B and k_A respectively. Finally, the formation of P implies the liberation of the catalyst(s), which can initiate a new catalytic cycle.

According to chemical kinetics principles, in order to deduce the rate law for scheme 2, we have to start from the kinetic equation in differential form relevant to the product P, which must be expressed as a function of its immediate precursors [$EBCO_2$] and [$EABCO_2$], i.e.:

$$v = \frac{d|P|}{dt} = -\frac{d|E|}{dt} = k_B[EBCO_2] + k_A[EABCO_2]$$

(equation 2)

Then, the concentrations of the precursor species should be written as a function of the concentration of the reactant E, the partial pressure of CO_2 (p_{CO2}) and the analytical concentrations of the co-catalyst (B_0) and the catalyst (A_0). Owing to the complexity of the mechanistic scheme examined, the latter task cannot be accomplished unless some suitable approximations and simplifications are introduced. The particular case $A_0 << B_0$, i.e. the assumption that all the concentrations of the species containing the catalyst A are negligible in comparison with the other species present in the system, is a good start point. Moreover, we also assumed that all the species in the system but gaseous CO_2 are present in a homogeneous phase. Then, we took into account three different possible scenarios, namely: *a*) all the pre-equilibria are fast with respect with the final steps leading to P; *b*) the association equilibria between the substrate E and the catalysts are fast, whereas the steady-state approximation should be applied to the precursors [EBCO$_2$] and [EABCO$_2$]; *c*) only the association equilibrium between E and the Lewis acid A is fast, and the steady-state approximation should be applied also to the adducts [EB] and [EAB].

The mathematical procedure to work out the three different cases is long and tedious (see note 1 in SI), though quite trivial. However, it is interesting to notice that, irrespective of the scenario considered, the same final equation is always obtained:

$$v = \frac{d|P|}{dt} = -\frac{d|E|}{dt} = \frac{k'_B p_{CO_2} B_0 |E|}{1 + K'_B|E|} + \frac{k'_A p_{CO_2} A_0 B_0 |E|}{1 + (K_A + K'_B + K'_A B_0)|E| + K_A K'_B |E|^2}$$

(equation 3)

where the constants k'_B, k'_A, K'_B and K'_A consist of complex combinations of the true kinetic and thermodynamic constants relevant to Scheme 2, depending on the particular case considered (see Supporting). Noticeably, constants K'_B and K'_A (and even k'_B and k'_A in the scenario *c*) result to be a function of p_{CO2}. Careful analysis of equation 2 discloses interesting consequences. If the Lewis acid catalyst is absent and only the halide ion catalyses the reaction, then equation 3 reduces to:

$$-\frac{d|E|}{dt} = \frac{k'_B p_{CO_2} B_0 |E|}{1 + K'_B|E|}$$

(equation 4)

The latter relationship strictly resembles the well-known Michaelis-Menten equation, the general solution of which has been discussed in detail elsewhere,[34] and corresponds to a peculiar mixed kinetic course, partly zero-th order and partly first order in E. In this case the reaction rate shows a simple linear dependence on B_0. The simultaneous presence of the Lewis acid makes the kinetic profile of the reaction more complicated, because the exact integration of equation 3 is quite hard to work out. The quadratic dependence on |E| in the denominator of the second term is peculiar, suggesting that in fact a very large concentration of E might suppress the co-catalysed pathway. This can be easily understood considering that under the latter conditions the halide ion is subtracted from the formation equilibrium of [EB], suppressing in turn the formation of the ternary complex [EAB]. However, it is very unlikely that such a condition might ever occur (see note 2 in SI); thus, equation 3 can be reasonably simplified as:

$$v = \frac{d|P|}{dt} = -\frac{d|E|}{dt} = \frac{k'_B p_{CO_2} B_0 |E|}{1 + K'_B |E|} + \frac{k'_A p_{CO_2} A_0 B_0 |E|}{1 + (K_A + K'_B + K'_A B_0)|E|}$$

(equation 5)

It is important to stress that, depending on the fate of the two denominators (i.e., from a mathematical standpoint, depending on whether $(K_A + K'_B + K'_A B_0)$|E| is negligible with respect to 1 or vice versa) equation 5 is consistent with diverse possible experimental trends, and might be reduced to either a first-order or a zero-th order expression in E, B_0 or p_{CO2}. In fact, because B_0 is present in the denominator of the second term of equations 3 and 5, then in the presence of the Lewis acid the reaction rate will no longer show a strict linear dependence on B_0. Similar considerations may be put forward for the CO_2 reagent, taking into account that p_{CO2} is sneakily concealed into the complex pseudo-constants of equations 3 and 5 (by contrast, the reaction rate should be always linearly dependent on A_0, see note 3 in SI).

According to a Reviewer's suggestion, we also considered the possibility that the Lewis base has a limited solubility (S_B) in the reaction system, in such a way that part of it forms a separated phase in equilibrium. In this case, it is not possible to consider a mass balance on B. However, this paradoxically leads to a significant simplification of the mathematical problem, because one can assume that the concentration of the free base in the reaction phase is kept constant to S_B. Hence, algebraic workout of the problem leads to the relationship:

$$v = \frac{d|P|}{dt} = -\frac{d|E|}{dt} = k'_B p_{CO_2} S_B |E| + \frac{k'_A p_{CO_2} A_0 S_B |E|}{1 + (K_A + K'_A S_B)|E|}$$

(equation 6)

with constants k'_B, k'_A and K'_A maintaining exactly the same meaning as in equation 3, irrespective of the possible scenario occurring. Noticeably, equation 6 is still valid even though A_0 is not negligible (or even comparable) with respect to S_B.

Comparison of equations 5 and 6 with equation 4 immediately shows that (at least whenever either the amount of Lewis acid is negligible with respect to the Lewis base, or the latter one has a solubility low enough to form a separated phase in equilibrium) the overall reaction outcome derives from two perfectly distinct kinetic contributions, one of which (the first term of the sum in the right-hand part of equations 4 and 5) corresponds to the yield of a reaction catalysed by the sole Lewis base and does not depend on the concentration of the Lewis acid. This implies, in our opinion, that for a correct and reliable evaluation of the catalytic performance of the double-catalyst system per se, it is mandatory to separate the two different contributions. This goal can be simply achieved by performing a blank experiment in the presence of the ammonium salt alone under the operational reaction conditions adopted, in order to ascertain the contribution of the Lewis-base-only catalysed pathway to the overall process. The point seems particularly important when a large amount of ammonium salt is used in comparison to the amount of Lewis acid. It is worth mentioning here that the problem of "turning over" definitions in catalysis has been recently addressed in a seminal paper by Kozuch and Martin.[35] In particular, it was pointed out how the concepts of TOF and TON have been regrettably confused (the second one being actually related to the durability of the catalyst), and that TOF should be defined or calculated in such a way to have the dimension of a frequency (i.e. s^{-1}, or at least an inverse of time). Moreover, authors outline that calculated TOF values are strictly dependent on the reaction conditions, reactants concentrations and extent of reaction progress included (ideally, TOF provides an estimation of the catalyst activity independent on the reactant only when the conditions for a zero-th order kinetics occur, which cannot be in general assumed). Therefore, they propose a definition of TOF as "*the derivative of the number of turnovers of the catalytic cycle with respect of the time per* *active site, [...] All the influencing conditions should be properly declared, such as the concentrations and temperature*". At the same time, in analogy with the concept of thermodynamic standard state, they proposed the introduction of a "standard" TOF (TOF°) according to the relationship: TOF = dN/dt = TOF°·[R]/c°, where [R] is the concentration of the reactant and c° is its concentration in the standard state. These concepts have risen an intense debate and the relevant theoretical issues have been object of criticism.[36] In particular, it has been complained that rate constants, rather than TOF values, provide a conceptually correct measure of catalytic efficiency. However, Kozuch's ideas constitute a good basis to discuss the case of double catalysis we are examining.

Now, keeping in mind our kinetic analysis discussed hereinabove, and the need to separate the contributions of the two different pathways to the overall reaction course, it is apparent that the contribution from the co-catalysed pathway can be simply defined as the difference between the reaction yields observed in the presence and in the absence of the Lewis acid catalyst. Therefore, we suggest that a sensible TOF value for the Lewis acid catalyst ($TOF_{(A)}$) should be rather defined based on the contribution of the co-catalysed pathway alone. Thus, according to Kozuch's approach, one could define $TOF_{(A)}$ as a difference of two derivatives (which in fact corresponds to the second term of equations 3 or 5):

$$TOF_{(A)} = \left[\left(\frac{d|P|}{dt}\right) - \left(\frac{d|P|}{dt}\right)_{A_0=0}\right] \cdot \frac{1}{A_0} = \frac{k'_A p_{CO_2} B_0 |E|}{1 + (K_A + K'_B + K'_A B_0)|E|}$$

(equation 7)

Such a definition seems particularly suitable whenever the initial reaction rates can be evaluated.[33] For practical purposes a reasonably approximated value for $TOF_{(A)}$ might be simply calculated by considering equation 1 that acts as a simplified version of equation 7. Indeed, equation 7 rigorously reduces to equation 1 whenever the kinetic course of the reaction is zero-th order in E (see note 4 in SI).

According to Kozuch's approach, $TOF_{(A)}$ values are strictly function of the operational conditions, in particular of the concentrations of the substrate and the halide Lewis base, and on the partial pressure of CO_2. All these conditions should be carefully reported, in order to get a useful value for comparison purposes. Therefore, in this way a strictly conditional TOF value for the Lewis acid is defined. On the other hand, by analogy with Kozuch's concept of standard TOF, we can also observe that a normalization of the TOF value defined above with respect to both the concentration of the Lewis base and the pressure of CO_2 makes perfectly sense. In other words, a more descriptive evaluation of the catalytic activity of the Lewis acid might be rather provided by a "normalized TOF" ($TOF^{N}_{(A)}$) defined as:

$$TOF^{N}{}_{(A)} = \frac{TOF_{(A)}}{\frac{B_0}{c^{\circ}{}_{B}} \cdot \frac{p_{CO_2}}{p^{\circ}{}_{CO_2}}}$$

(equation 8)

where c°_{B} and p°_{CO2} are the concentration of the Lewis base and the pressure of CO_2 in their standard states, which are introduced just in order to preserve dimensionality. According to the mathematical elaboration reported in the supporting information, although TOF is still a conditional value dependent on B_0, p_{CO2} and $|E|$, it provides a parameter which is more strictly related to the true kinetic and thermodynamic constants relevant to the reaction scheme.

By applying equation 1, we have calculated the $TOF_{(A)}$ and $TOF^{N}_{(A)}$ values for selected cases (Table 4) from previously discussed examples (Tables 1-3), in which the molar ratio Lewis base:Lewis acid ranged from *ca.* 10:1 up to 2400:1. Clearly, all the recalculated TOF values are lower than the reported ones, depending on the contribution of the Lewis base. For instance, in the case of catalyst **1** the corresponding $TOF_{(A)}$ value should be 17400 h^{-1} instead of the reported 22000 h^{-1} (Table 4, entry 2). In the case of catalyst **3** the corresponding $TOF_{(A)}$ value should be 19200 h^{-1} instead of the reported 26800 h^{-1} (Table 4, entry 5). Similarly, in the case of catalyst **5**, the corresponding $TOF_{(A)}$ value should be 11000 h^{-1} instead of the reported 24000 h^{-1} (Table 4, entry 8). The claimed TOF of 37900 h^{-1} (Table

4, entry 11) does not make sense since the yield with TBAB alone was higher than in the co-presence of the Lewis acid **6**. As another example, in the case of catalyst **16** the corresponding $\mathrm{TOF}_{(A)}$ value should be 7000 h^{-1} instead of the reported 11600 h^{-1} (Table 4, entry 17). In addition, normalization of $\mathrm{TOF}_{(A)}$ values by using equation 8 has been carried out. These values allow a more consistent comparison between various catalytic systems. As can be seen from Table 4, in some cases, under normalized conditions, catalysts with high TOF values can be regarded as less performing than catalysts displaying lower TOF values. In this sense, these values should not be used in an absolute way but in a comparative manner.

Table 4. $\mathrm{TOF}_{(A)}$ and $\mathrm{TOF}^{N}_{(A)}$ calculation for selected data.

Entry	Epox.	Lewis base (mol%)	Lewis acid (mol%)	LB:LA[b]	Yield or conv (%)	Yield or conv (%)[a]	TOF (h^{-1})	$\mathrm{TOF}_{(A)}$ (h^{-1})	$\mathrm{TOF}^{N}_{(A)}$ (10^3 h^{-1})	Ref.
1	PO	$PPh_3C_6H_{13}Br$ (0.12)	$ZnCl_2$ (0.012)	10	84	15.4	6960	5700	321	[8]
2	PO	TBAI (0.9)	**1** (0.0025)	360	55	11.5[c]	22000	17400	65.3	[10]
3	SO	TBAC (1.08)	**2** (0.1)	10.8	86	14	153	120	3.3	[11]
4	SO	TBAB (0.75)	**3** (0.025)	30	96	25	3840	2840	38.4	[12]
5	SO	TBAB (0.5)	**3** (0.0025)	200	67	19	26800	19200	389	[12]
6	HO	TBAI (0.05)	**5** (0.0025)	20	38	13	7600	5000	1013	[15]
7	HO	TBAI (0.05)	**5** (0.0010)	50	33	13	16500	10000	2030	[15]
8	HO	TBAI (0.05)	**5** (0.0005)	100	24	13	24000	11000	2230	[15]
9	PO	PPNCl (0.24)	**6** (0.002)	120	96.4	8.3	96400	88100	1240	[16]
10	PO	TBAI (2.4)	**7** (0.2)	12	92.9	58.4	465	173	35.6	[17]
11	PO	TBAI (2.4)	**7** (0.001)	2400	37.9	58.4	37900	--	--	[17]
12	PO	TBAB (0.25)	**9** (0.025)	10	82.6	10	3304	2904	58.8	[19]
13	PO	TBAB (7.2)	**14** (0.49)	14.7	98.1	31	201	137	1.93	[14]
14	PO	TBAB (7.2)	**15** (0.49)	14.7	91.2	31	187	123	1.73	[14]
15	PO	TBAB (1.25)	**16** (0.0075)	167	38.1	14.1	5080	3200	8.65	[24]
16	PO	TBAB (0.9)	**16** (0.005)	180	35.7	11.5	7140	4840	18.2	[24]
17	PO	TBAB (0.9)	**16** (0.0025)	360	29	11.5	11600	7000	26.3	[24]
18	SO	TBAB (1.5)	**17** (0.05)	30	>99	59[d]	166.7	68	0.46	[26]
19	SO	TBAB (1.5)	**18** (0.05)	30	86.2	59[d]	143.3	45	0.30	[26]
20	SO	TBAB (1.5)	**19** (0.01)	150	>99	59	119	49	0.33	[27]
21	SO	TBAB (1.0)	**20** (0.033)	30	95	50	238	114	1.15	[27]
22	PO	TBAB (7.2)	**22** (0.125)	57.6	87.4	20.4[e]	15	11	0.15	[29]

[a] Without Lewis acid. [b] LB:LA = Lewis base:Lewis acid molar ratio. [c] Yield obtained in the presence of TBAB (0.9 mol%) under identical reaction conditions.[24] [d] From ref. [27]. [e] Value based on the use of TBAB under identical condition.[14]

3. Conclusion

In summary, we have discussed the catalytic activity of binary catalytic systems formed by Lewis acid and Lewis base, such as R_4NX or phosphonium halide salts in the formation of cyclic carbonates in terms of TOF values which are calculated considering only the amount of the Lewis acid catalyst, even when the amount of Lewis base is used in large amount with respect of Lewis acid which, in turn, does not catalyse the reaction when used alone. Based on some literature data and on a kinetic discussion, we have showed that such assumption is not always correct especially when the amount of the Lewis base used is much more than the amount of Lewis acid. Indeed, two very well-known distinct reaction pathways may take place and, for this reason, a blank experiment with the Lewis base alone under the best reaction condition, must be reported in any case. These data will help in determining the real catalytic activity of the Lewis acid catalyst and the whole catalytic system constituted by Lewis acid and Lewis base catalysts. Equation 1 could be applied for an approximated estimation of the TOF value. Normalization of the TOF values may give a further indication of the catalytic activity for a better comparison between different catalytic systems.

Nevertheless, to have a complete picture of the usefulness of a catalytic system, other aspects must be taken into account such as reaction conditions, cost of the catalyst, productivity (as grams of cyclic carbonates per gram of catalyst), recoverability and reusability.

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SUPPORTING INFORMATION

Note 1.

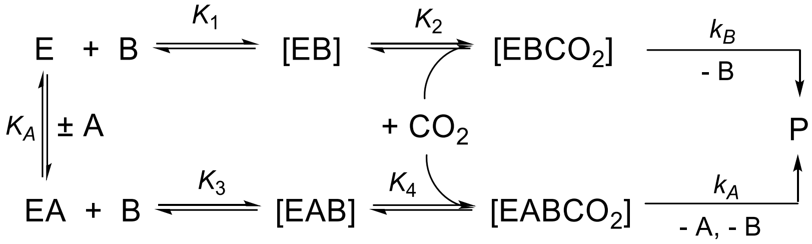
In order to derive equation 2 from Scheme 1 we must first consider the mass balances on the co-catalysts A and B, keeping into account the assumption $A_0 \ll B_0$, i.e.:

$A_0 = |A| + [EA] + [EAB] + [EABCO_2]$ and

$B_0 = |B| + [EB] + [EAB] + [EBCO_2] + [EABCO_2] \approx |B| + [EB] + [EBCO_2]$

At this point the problem splits for the three different scenarios.

a) All the equilibria are fast



Then, the following mass action conditions should be considered:

$[EA] = K_A|E||A|$;

$[EB] = K_1|E||B|$;

$[EBCO_2] = K_1K_2\, p_{CO2}|E||B|$;

$[EAB] = K_AK_3\, |E||A||B|$;

$[EABCO_2] = K_AK_3K_4\, p_{CO2}|E||A||B|$;

which inserted in the mass balances give:

$A_0 = |A| + K_A|E||A| + K_AK_3\, |E||A||B| + K_AK_1K_2\, p_{CO2}|E||A||B| =$

$= |A|\, (1 + K_A|E| + K_AK_3\, |E||B| + K_AK_3K_4\, p_{CO2}|E||B|)$ and

$B_0 = |B| + [EB] + [EBCO_2] = |B| + K_1|B||E| + K_1K_2\, p_{CO2}|B||E| =$

$= |B|\, (1 + K_1|E| + K_1K_2\, p_{CO2}|E|)$

Thus, with few algebraic passages one obtains:

$$|B| = \frac{B_0}{1 + K_1|E| + K_1K_2p_{CO_2}|E|}$$

$$|EBCO_2| = \frac{K_1K_2p_{CO_2}B_0|E|}{1 + K_1|E| + K_1K_2p_{CO_2}|E|}$$

$$|A| = \frac{A_0}{1 + K_A|E| + K_AK_3|E||B| + K_AK_3K_4p_{CO_2}|E||B|}$$

$$[EABCO_2] = \frac{K_AK_3K_4p_{CO_2}A_0|E||B|}{1 + K_A|E| + K_AK_3|E||B| + K_AK_3K_4p_{CO_2}|E||B|}$$

At this point, the expression for B must be inserted into the one for [EABCO$_2$], then the resulting expressions for [EBCO$_2$] and [EABCO$_2$] must be inserted in the differential kinetic expression given by equation 1. After the algebraic passages needed, one obtains an expression equivalent to equation 2, with the following conditions:

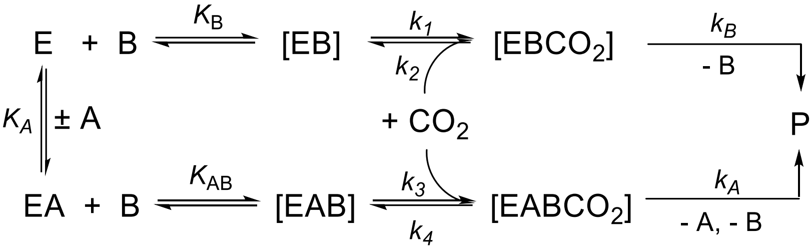
$k'_B = k_B K_1 K_2$

$K'_B = K_1 + K_1 K_2\, p_{CO2}$

$k'_A = k_A K_A K_3 K_4$

$K'_A = K_A K_3 K_4\, p_{CO2}$

b) Only the equilibria relevant to the formation of the substrate-catalyst(s) complexes are fast



The following mass action conditions should be considered:

[EA] = K_A|E||A|;

[EB] = K_1|E||B|;

[EAB] = $K_A K_{AB}$ |E||A||B|;

Moreover, on applying the steady-state approximation to [EBCO$_2$] and [EABCO$_2$] one obtains:

$$[EBCO_2] = \frac{k_1\, p_{CO_2}}{k_2 + k_B}[EB] = \frac{k_1 K_B\, p_{CO_2}}{k_2 + k_B}|E||B|$$

$$[EABCO_2] = \frac{k_3\, p_{CO_2}}{k_4 + k_A}[EAB] = \frac{k_3 K_A K_{AB}\, p_{CO_2}}{k_4 + k_A}|E||A||B|$$

Again, all these expressions must be inserted in the mass balances for A$_0$ and B$_0$:

$A_0 = |A| + K_A|E||A| + K_A K_{AB}\,|E||A||B| + \frac{k_3 K_B K_{AB}}{k_4 + k_A}\, p_{CO2}|E||A||B|$

$B_0 = |B| + [EB] + [EBCO_2] = |B| + K_B|B||E| + \frac{k_1 K_B}{k_2 + k_B}\, p_{CO2}|B||E| =$

$= |B|\,(1 + K_B|E| + \frac{k_1 K_B}{k_2 + k_B}\, p_{CO2}|E|)$

In analogy with the previous case, the expressions for the mass balances must be algebraically elaborated in such a way to obtain [EBCO$_2$] and [EABCO$_2$] as a function of A$_0$, B$_0$, |E| and p_{CO2}. Then, inserting them into equation 1, an expression equivalent to equation 2 is obtained, with the conditions:

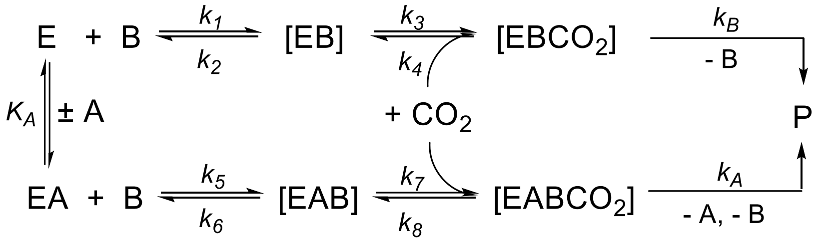
$$k'_\mathrm{B} = \frac{k_1 k_B K_B}{k_2+k_B}$$

$$K'_\mathrm{B} = \left(1 + \frac{k_1\, p_{CO_2}}{k_2+k_B}\right) K_B$$

$$k'_\mathrm{A} = \frac{k_3 k_A K_A K_{AB}}{k_4+k_A}$$

$$K'_\mathrm{A} = \left(1 + \frac{k_3\, p_{CO_2}}{k_4+k_A}\right) K_A K_{AB}$$

c) Only the association equilibrium between E and A is fast



The steady-state approximation must be applied to all the species but [EA]. Hence:

$[EA] = K_\mathrm{A}|E||A|$;

$k_1|E||B| + k_4[EBCO_2] = (k_2 + k_3)[EBCO_2]$

$k_3\, p_{CO2}[EB] = (k_4 + k_\mathrm{B})[EBCO_2]$

$k_5[EA]|B| + k_8[EABCO_2] = (k_6 + k_7)[EABCO_2]$

$k_7\, p_{CO2}[EAB] = (k_8 + k_\mathrm{A})[EABCO_2]$

Again, algebraic manipulation of these expressions and of the mass balances on A_0 and B_0, afford the expressions for $[EBCO_2]$ and $[EABCO_2]$, which inserted into equation 1 lead to an expression equivalent to equation 2, with the conditions:

$$k'_B = \frac{k_1 k_3 k_B}{k_2 k_4 + k_2 k_B + k_3 k_B\, p_{CO_2}}$$

$$K'_B = \frac{k_1\left(k_3 p_{CO_2} + k_4 + k_B\right)}{k_2 k_4 + k_2 k_B + k_3 k_B\, p_{CO_2}}$$

$$k'_A = \frac{k_5 k_7 k_A K_A}{k_6 k_8 + k_6 k_A + k_7 k_A\, p_{CO_2}}$$

$$K'_A = \frac{k_5 K_A\left(k_7 p_{CO_2} + k_8 + k_A\right)}{k_6 k_8 + k_6 k_A + k_7 k_A\, p_{CO_2}}$$

Note 2

Regarding the simplification of equation 3 into equation 5, from a mathematical standpoint one should try to assess that the following condition is verified:

$$1 + (K_A + K'_B + K'_A B_0)|E| \gg K_A K'_B |E|^2$$

which can be trivially transformed as:

$$|E| \ll 1/|E| + 1/K_A + 1/K'_B + K'_A B_0/K_A K'_B$$

Of course, this cannot be directly verified, because it is not possible to get a reliable independent estimation of the apparent constants K_A, K'_A and K'_B. However, the very fact that, in the few cases reported in literature, the reaction kinetic profile reduces to a simple first-order trend (or even a zero-th order one) positively implies that the previous hypotheses must be actually verified. Speculating *"per absurdum"*: even though the initial concentration E_0 of the epoxide were so large to provide an effective suppression of the co-catalyzed pathway (i.e., in mathematical terms, even if E_0 is larger or comparable with respect to the sum $[1/K_A + 1/K'_B + K'_A B_0/K_A K'_B]$), as long as the reaction proceeds the concentration of the epoxide itself must progressively decrease, up to a point when the suppression cannot be any longer effective. As a consequence, one must observe an increase of the apparent reaction rate as the reaction proceeds. This in turn should result in a kinetic behaviour somehow resembling that of an auto-catalytic reaction: in other words, the reaction kinetics could not be led back to a simple apparent first-order profile."

Note 3

The previous mathematical treatment can be easily extended, with few suitable adaptations, even to the case that the LA catalyst is constituted by an insoluble material. In the framework of the well-known Langmuir-Hinshelwood model, we can assume that the reaction rate linearly depends on the number of LA active sites, which in turn linearly depends on the amount material. Then, whatever the scenario considered, indicating the latter quantity again as A_0, the amount of the precursor complex [EA] will anyway present the same functional dependence on A_0 and $|E|$ as in the homogeneous case. Consequently, equation 2 remains valid.

Note 4

As a school hypothesis, we also analysed the possibility that the amount of A is comparable with the one of B (in turn not forming a separate phase). In this case, the approximations used to obtain equation 3 are no longer valid, because the concentrations of the intermediates containing both A and B are not negligible in the mass balance for B; therefore, even the first term of the sum in equations 3 and 5 must depend on A_0. However, one may qualitatively reason that, on increasing A_0, the formation of the binary complex [EB] decreases because of a mere mass action effect, which results in a partial suppression of the Lewis base-only catalysed pathway. Therefore, the "blank" experiment will overestimate this contribution. Thus, equations 7 or 1 will provide a lower limit value for true $TOF_{(A)}$, whereas calculation of TOF without keeping into account the "blank" experiment will still provide an upper limit.