# 8-Hydroxyquinolates of trivalent metals as new catalysts for the reaction of CO<sub>2</sub> with epoxides

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Tris-(8-hydroxyquinolates) of aluminum(III), chromium(III), and iron(III) in the presence of triphenylphosphine oxide efficiently catalyze the formation of alkylenecarbonates by the reaction of CO<sub>2</sub> with oxiranes, *viz.*, propylene oxide, but-2-ene oxides, and isobutylene oxide. The catalytic system is active at 140–170 °C and a CO<sub>2</sub> pressure of 15–100 atm.

Key words: cycloaddition, carbon dioxide, oxiranes, alkylenecarbonates, 8-hydroxy-quinolates.

A great interest in chemical use of  $CO_2$  is provoked by unfavorable climatic changes caused by carbon oxides and resulting in global warming.<sup>1</sup> Only few industrial processes based on carbon dioxide as synthon are known, although it is cheap, non-toxic, and accessible. One of such processes is the catalytic synthesis of cyclic carbonates by the cycloaddition of carbon dioxide to epoxides (Scheme 1).





R, R<sup>´</sup> = H, Alk, Ar; Cat. is catalyst

Cyclic carbonates are widely used as solvents and chemicals in syntheses of various substances, mainly gly-cols.<sup>2</sup>

The main problem in the synthesis of cyclocarbonates according to Scheme 1 is a necessity, as a rule, to use high temperatures (190–220 °C). As a result, carbonates and glycols are contaminated by pyrolysis products that can easily be determined from the absorption bands at 220, 275, and 350 nm in the UV spectra. These admixtures render glycols unsuitable for the production of polyalkyleneterephthalates and fibers.<sup>3</sup> The pyrolysis products are not formed below 180 °C. However, at these temperatures catalysts are most often inefficient. In addition, the majority of catalysts contain the Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup> anions, which contaminate cyclocarbonates and terephthalates that formed, and this is inadmissible for

environmental reasons.<sup>3</sup> These catalysts, some of which are used in industry, are onium compounds,<sup>2</sup> metal halides,<sup>3,4</sup> metal porphyrin and phthalocyanine complexes,<sup>5-7</sup> tin(IV) iodides,<sup>8,9</sup> and chromium(III) salen complexes.<sup>10</sup>

Therefore, the problem of searching for efficient catalysts, which would allow the synthesis of cyclocarbonates at temperatures <180 °C and simultaneously contain no halogen atoms, is urgent.

## **Results and Discussion**

We found that 8-hydroxyquinoline salts  $M(Ox)_3$  (OxH is 8-hydroxyquinoline, M = Al,  $Cr^{III}$ , Fe<sup>III</sup>) in the presence of triphenylphosphine oxide efficiently catalyze alkylenecarbonate formation from CO<sub>2</sub> and mono- and disubstituted olefin oxides. The experimental results are summarized in Tables 1 and 2.

Triphenylphosphine oxide is likely the most active cocatalyst. In the presence of hexamethapol,  $(Me_2N)_3P=O$ , and triethyl phosphate, the reaction occurs with much lower yields, whereas phosphoryl compounds themselves do not catalyze cycloaddition.

The iron and aluminum compounds are more active than the chromium complex in the reaction involving propylene oxide: under the same conditions, smaller amounts of them have to be introduced to achieve high yields. Chromium hydroxyquinolate turned out to be somewhat more active in the reactions of but-2-ene and isobutylene oxides with  $CO_2$ .

Tables 1 and 2 show that disubstituted carbonates are formed in lower yields and under more rigid conditions than propylene carbonate. In most cases, there is some optimum pressure under which the best yield is achieved.

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Entry	Cat. : PPh <sub>3</sub> (mol.%)	P <sub>CO₂</sub> ∕atm	Density $CO_2/g \text{ cm}^{-3}$	Yield of carbonate (%)		
Al(Ox) <sub>3</sub>						
1	0.52:5.2	256	0.42	27		
2	The same	90	0.13	57		
3	» »	35	0.045	85		
4	» »	18	0.023	92 (80) <sup>b</sup>		
5	» »	8	0.010	45		
Fe(Ox) <sub>3</sub>						
6	1.04 : 10.4	90	0.13	60		
7	1.04 : 10.4	35	0.045	98		
8	0.52:5.2	22	0.028	99		
9	0.25:2.5	22	0.028	60		
$Cr(Ox)_3$						
10	1.04 : 10.4	252	0.41	50		
11	The same	90	0.13	73		
12	» »	16	0.020	95		
13 <sup>c</sup>	» »	16	0.020	82		

**Table 1.** Reaction of propylene oxide with  $CO_2$  in the presence of different catalysts (Cat.)<sup>*a*</sup>

<sup>*a*</sup> Experimental conditions: 155 °C, reaction duration 5.5 h.

<sup>b</sup> The yield of propylenecarbonate obtained in the preparative experiment is indicated in parentheses.

<sup>c</sup> At 140 °C.

The optimum values are relatively low (*viz.*, from 15 to 100 atm). It is of interest that the reaction with supercritical CO<sub>2</sub> (see Table 1, entries 1, 2, 6, 10, and 11), produces much lower yields of propylene carbonate than that with of pre-critical CO<sub>2</sub>. This is probably explained by a decrease in the solubility of the catalyst in the reaction mixture with an increase in the density of CO<sub>2</sub>. Such an "antisolvent" effect<sup>11</sup> is well known for supercritical CO<sub>2</sub>. The preliminarily prepared mixture of epoxide, Ph<sub>3</sub>PO, and Al(Ox)<sub>3</sub> is intensely yellow, which indicates a high

**Table 2.** Reactions of but-2-ene and isobutylene oxides with  $CO_2^a$ 

Entry	Epoxide	P <sub>CO2</sub> /atm	Yield of carbonate (%)
14	But-2-ene oxide		
	(trans: cis = 60: 40)	100	58
15	The same	20	49
16 <sup>b</sup>	» »	20	26
17 <sup>c</sup>	» »	20	26
18	Isobutylene oxide	160	37
19	The same	100	41
20 <sup>b</sup>	» »	100	37
21 <sup>c</sup>	» »	100	46
22	» »	20	22

<sup>*a*</sup> Experimental conditions: 155 °C, reaction duration 5.5 h,  $Cr(Ox)_3$ : Ph<sub>3</sub>PO = 1.04 : 10.4 (mol.%).

<sup>b</sup> At 140 °C.

<sup>c</sup> At 170 °C.

**Table 3.** Stereoselectivity of the cycloaddition of  $CO_2$  to but-2-ene oxide\*

Entry	Ratio of <i>trans</i> - to <i>cis</i> -isomers			
	But-2-ene	Butylenecarbonate		
23	60:40	60:40		
24	97:3	91:9		
25	21:79	25:75		

\* Experimental conditions: 155 °C, reaction duration 5.5 h,  $Cr(Ox)_3$ :  $Ph_3PO = 1.04$ : 10.4 (mol.%).

concentration of  $Al(Ox)_3$  in a solution. This phenomenon is much less pronounced in reactions involving butene oxides.

To determine the stereoselectivity of cycloaddition catalyzed by metal hydroxyquinolates, we prepared samples of but-2-ene oxide enriched (compared to the equilibrium mixture) in one of the isomers. The results presented in Table 3 indicate a high stereoselectivity of this reaction.

8-Hydroxyquinoline salts are easily prepared, stable at temperatures <300 °C, and are used in quantitative gravimetric and spectroscopic analyses of metals.<sup>12</sup> The published data<sup>13–15</sup> indicate that the aluminum 8-hydroquinolate molecule has a quasi-octahedral configuration, and the oxygen and nitrogen atoms are in the vertices of the octahedron. The chromium and iron complexes probably have similar structures.

We found that the <sup>27</sup>Al NMR spectrum of the pure salt in CDCl<sub>3</sub> has a broad singlet at 26 ppm (line half-width is 1160 Hz), which is typical of hexacoordinate structures with five-membered cycles.<sup>16</sup> The addition of Ph<sub>3</sub>PO (10 mol. equiv.) does not change the chemical shift (line half-width is 1480 Hz), which indicates a symmetry loss.<sup>16</sup>

Analysis of our previous results<sup>17</sup> and literature data<sup>6,10</sup> suggests that the active catalyst should simultaneously possess the properties of both a weak acid (for the electrophilic activation of the oxirane ring) and a weak base (for the nucleophilic activation of  $CO_2$ ). We believe that the acidic part of the catalyst is the pentacoordinate aluminum atom formed by the reversible opening of the aminoalcohol fragment (Scheme 2).

## Scheme 2



The existence of this equilibrium (first described previously<sup>15</sup>) is confirmed by changes in the  $^{27}$ Al NMR spectra in the presence of Ph<sub>3</sub>PO, which indicate the appearance of a new ligand in the coordination sphere.

The alkoxy group (in this case, the phenoxy group) can play a role of a base activating the  $CO_2$  molecule.

A comparison with the previously described catalysts shows that we succeeded in finding the group of active catalytic systems based on 8-hydroxyquinolates of trivalent metals for the reaction of  $CO_2$  with epoxides. These catalytic systems catalyze the synthesis of cyclocarbonates at temperatures <180 °C, contain no halogens, and provide, to a great extent, retention of the configuration of substituents in the initial epoxides.

### Experimental

Reactions were carried out in a stainless steel 40-mL autoclave designed for a maximum working pressure of 600 atm and equipped with a pocket for a thermocouple and a D-60 tensometric sensor for precision pressure monitoring.

Aluminum hydroxyquinolate was synthesized by a previously described procedure.<sup>12</sup> The Fe<sup>III</sup> and Cr<sup>III</sup> hydroxyquinolates were prepared using a known method.<sup>18</sup> Propylene oxide (Merck) and Ph<sub>3</sub>PO (Chemapol) were used as received. But-2-ene and isobutylene oxides prepared as described previously<sup>19</sup> were distilled above CaH<sub>2</sub> before the reaction. But-2-ene oxide was enriched in *trans*- or *cis*-isomer sby the rectification of a mixture with a *trans*-isomer : *cis*-isomer ratio of 60 : 40.

<sup>1</sup>H NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 MHz) relatively to the Me<sub>4</sub>Si external standard, and <sup>27</sup>Al NMR spectra were recorded on a Bruker CXP-200 spectrometer using Al(NO<sub>3</sub>)<sub>3</sub> as external standard. IR spectra were obtained on a Bruker IFS-113 spectrometer.

In a typical experiment, propylene oxide (0.42 g, 7.2 mmol), aluminum hydroxyquinolate (0.017 g, 0.038 mmol), and Ph<sub>3</sub>PO (0.11 g, 0.38 mmol) were placed in an autoclave, which then was filled to a specified pressure with carbon dioxide preliminarily passed (as a liquid) through columns packed with SiO<sub>2</sub> and active carbon. The charged autoclave was heated in a furnace equipped with a device for automated temperature maintenance (Miniterm 300), and the temperature and pressure inside the autoclave were monitored during heating. After the end of the reaction, the autoclave was cooled, excess CO<sub>2</sub> was let out to the atmosphere, and the reaction mixture was diluted with the specified amount of acetone and analyzed by GLC on a column with SE-30. In experiments with supercritical CO<sub>2</sub>, the autoclave preliminarily charged with the epoxide and catalyst samples was heated to a temperature higher than the CO<sub>2</sub> critical temperature (usually 40-50 °C), after which it was charged with carbon dioxide using a high-pressure pump until the necessary density was achieved,<sup>20</sup> closed, and heated as described above.

In a preparation experiment, propylene carbonate was obtained after distillation in 80% yield (2.45 g) from propylene oxide (1.74 g, 30 mmol), aluminum hydroxyquinolate (71.8 mg, 0.156 mmol), and Ph<sub>3</sub>PO (433.7 mg, 1.56 mmol) at an initial CO<sub>2</sub> pressure of 50 atm and 20 °C. The <sup>1</sup>H NMR spectrum and retention time of the product (GLC, SE-30) coincided with the corresponding characteristics of the propylene carbonate sample (Merck). Isomeric butylenecarbonates were isolated by distillation, and their b.p. and NMR spectra corresponded to those described in the literature.<sup>21-23</sup>

The IR spectra of the reaction mixtures contained only an absorption band of monocarbonates (v(CO) =  $1798 - 1803 \text{ cm}^{-1}$ ).

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