Synthesis of Diphenyl Carbonate from CO_2, Phenoxide, and CCl_4 with $ZnCl_2$ as Catalyst

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Direct synthesis of diphenyl carbonate (DPC) from phenoxide, CO_2 and CCl_4 in one pot was realized with $ZnCl_2$ as catalyst. Trichloromethyl cation may act on potassium phenyl carbonate, which brings the carbonyl more easily attached on by the phenoxide. Onium salts promote the reaction greatly, especially with phenol and potassium carbonate instead of phenoxide as reactants. Moreover, the substituent on the aromatic ring has significant effects on the selectivity and yield of carbonate.

Diphenyl carbonate (DPC) is a key raw material for the production of aromatic polycarbonates. As yet, it can be obtained through the phosgenation of phenol,[1] oxidative carbonylation of phenol,[2] transesterification of dimethyl carbonate (DMC),[3] or dimethyl oxalate (DMO) with phenol.[4] All those methods have certain disadvantages, for example, the phosgenation process uses severely toxic phosgene as raw material,[5] oxidative carbonylation method needs noble metal catalyst and costly procedures, and transesterification demands intricate multistage procedures with a critical thermodynamic limitation,[6] which results in very low DPC yield and selectivity. It will be undoubtedly a much more economical option if DPC can be synthesized directly from phenol and CO_2.

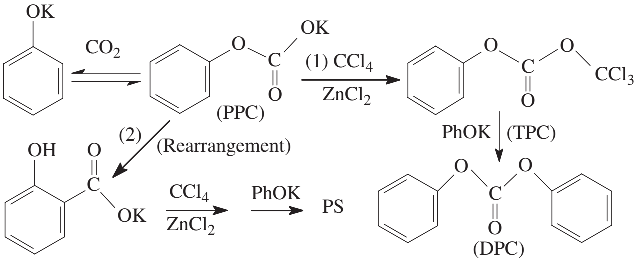
In this work, the direct synthesis of DPC from phenoxide, CO_2, and CCl_4 in one pot was realized with $ZnCl_2$ as catalyst. The effects of reaction temperature, promoter, and substituent attached to the aromatic ring on the carbonate yield were investigated.

The reaction results are summarized in Table 1. In the presence of an inert atmosphere N_2, no reaction was observed at 100 °C (Entry 1). With the introduction of CO_2, DPC is detected even at 80 °C (Entry 2). As the temperature is elevated to 100 °C, phenyl salicylate (PS) appears as the main by-product (Entry 3). It seems that with the increase of reaction temperature, the yields of both DPC and PS increase, but the selectivity to DPC decreases slightly. At 120 °C, the yields of DPC and PS come up to 3.6% and 4.6%, respectively (Entry 4).

Table 1. Synthesis of DPC form potassium phenoxide in liquid CCl_4 at different temperatures[a]

Entry	Temperature /°C	Catalyst	Yield/%[b] DPC	PS
In the presence of N_2 (1 MPa)				
1	100	$ZnCl_2$	—	—
In the presence of CO_2 (1 MPa)				
2	80	$ZnCl_2$	0.1	—
3	100	$ZnCl_2$	1.4	1.7
4	120	$ZnCl_2$	3.6	4.6

[a]Reaction conditions: PhOK 30 mmol, catalyst 2.0 g, CCl_4 40 mL, reaction duration 6 h. [b]Yield based on phenoxide was determined by GC analysis.



Scheme 1. The possible reaction mechanism.

According to the above described results, it is found that the presence of CO_2 is an important factor for synthesis DPC. One possible reaction process is started with the nucleophilic attack of the potassium phenoxide to CO_2 and it produces potassium phenyl carbonate (PPC).[7] During the reaction, trichloromethyl cation $CCl_3{}^{\delta+}$ is formed on the catalyst surface, which is similar to the destruction of carbon tetrachloride over lanthanide oxide-based catalyst.[8] Thus, potassium phenyl carbonate may either form trichloromethyl phenyl carbonate (TPC) through binding with $CCl_3{}^{\delta+}$ (Scheme 1, pathway 1) or be rearranged into salicylate[7] (Scheme 1, pathway 2). After transesterification with phenoxide, TPC changes into DPC, KCl, and phosgene. The phosgene, produces in situ during the reaction, reacts with phenoxide to produce another molecular DPC. In one word, one molecular CO_2 couples with one molecular CCl_4 to produce two molecular DPC.

$$4\mathrm{PhOK} + \mathrm{CCl_4} + \mathrm{CO_2} \xrightarrow{\mathrm{ZnCl_2}} 2\mathrm{DPC} + 4\mathrm{KCl}. \qquad (1)$$

Further tests proved that the yield and selectivity of DPC can be improved significantly by using the reactants of phenol + K_2CO_3 as a substitute for potassium phenoxide with certain co-catalysts like onium salts. As listed in Table 2, with potassium phenoxide as reactant, the main product is PS (Entries 1–5). With tetramethylammonium bromide (Me_4NBr) as co-catalyst, the formation of DPC and especially PS is suppressed in comparison with the reaction without co-catalyst (Entry 2). Using tetrabutylammonium bromide (Bu_4NBr) as co-catalyst, the yield of PS increases moderately and a small amount of phenyl *p*-hydroxybenzoate (PPB) is detected even at such a low temperature (Entry 3). With cetyltrimethylammonium bromide ($CeMe_3NBr$) as co-catalyst, DPC yield was also suppressed (Entry 4). These results suggested that onium salt with large organic group (Bu_4NBr) can enhance the conversion of phenoxide obviously, while the onium salt with small organic group (Me_4NBr) is facile to enhance the selectivity to DPC. This may be related to their difference in the steric hindrance. The reaction at 120 °C exhibits high selectivity to PS (Entry 5), which proved further that higher

Table 2. Effect of co-catalyst onium salts on the reaction behavior

Entry	Temperature /°C	Co-catalyst	Yield/%[c] DPC	PS
With PhOK as reactant[a]				
1	110	—	6.6	17.9
2	110	Me_4NBr	4.6	4.2
3	110	Bu_4NBr	6.2	21.1
4	110	$CeMe_3NBr$	3.6	15.3
5	120	Me_4NBr	2.9	23.0
With phenol + K_2CO_3 as reactants[b]				
6	120	—	15.8	2.9
7	120	Me_4NBr	14.1	3.7
8	120	Bu_4NBr	29.7	2.2
9	120	$CeMe_3NBr$	20.4	2.7

[a] Reaction conditions: PhOK 30 mmol, $ZnCl_2$ 2.0 g, co-catalyst 0.5 g, CCl_4 40 mL, CO_2 3.0 MPa, reaction duration 6 h. [b] Phenol 30 mmol and K_2CO_3 15 mmol was used instead of PhOK. [c] Yield based on phenoxide was determined by GC analysis.

temperature is favorable for the formation of PS. Using phenol + K_2CO_3 instead of PhOK as reactants, DPC turns out to be the main product. In this case, PhOK may be formed in situ during the reaction. DPC yield reaches 15.8% at 120 °C (Table 2, Entry 6). It further increases to 29.7% with Bu_4NBr as co-catalyst (Entry 8), while the selectivity to PS is kept at a low level (2.2%).

The carbonate yield also depends on the substituent attached to the aromatic ring of pheoxide as listed in Table 3. With methyl as the substituent, the conversion of R-PhOK as well as the yield of carbonate is much lower than those of reaction without substituent attached to the aromatic ring. This suggests that methyl substituent, especially at the *para*-position, is unfavorable for the carbonate formation (Entries 3–6). However, the steric hindrance due to the methyl substitution at the *ortho*-position may suppress the rearrangement of potassium *o*-methylphenyl carbonate (PPC) into salicylate, which results in the high carbonate selectivity (Entries 3 and 4).

With chlorine as substituent, either at *ortho*- or *para*-position, however, gives high selectivity to carbonate, because chlorine as an electron-withdrawing group makes the rearrangement of PPC more difficult. Like the methyl substituent, the steric hindrance of *o*-chlorine substituent can enhance the selectivity to DPC (Entries 7 and 8). Especially, with chlorine as a substituent at *para*-position (Entries 9 and 10), high yield of carbonate (45.6% at 120 °C) was obtained also with high selectivity (98.0%). These proved that electron-withdrawing group as substituent attached to the aromatic ring can enhance the formation of carbonate.

In summary, this work demonstrates that DPC can be obtained from phenoxide, CCl_4, and CO_2 in one pot with $ZnCl_2$ as catalyst. Onium salt with large organic group promotes the reaction greatly, especially with phenol and potassium carbonate as reactants. Moreover, the substituent attached to the aromatic ring on the carbonate yield has significant effects on the selectivity and yield of carbonate.

Table 3. Effects of substituents attached to the aromatic ring on the carbonate selectivity and yield[a]

Entry	R	Temperature /°C	Selectivity /%	Yield /%
1	H	100	87.0	5.0
2	H	120	63.0	7.0
3	*o*-Me	100	100	3.1
4	*o*-Me	120	86.0	3.3
5	*p*-Me	100	—	—
6	*p*-Me	120	40.0	1.8
7	*o*-Cl	100	100	5.7
8	*o*-Cl	120	100	6.2
9	*p*-Cl	100	100	20.5
10	*p*-Cl	120	98.0	45.6

[a] Reaction conditions: R-PhOK 30 mmol, $ZnCl_2$/MCM-41 (loading = 4 mmol/g) 1.0 g, CCl_4 40 mL, CO_2 1.0 MPa, reaction duration 6 h.

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