

Synthesis of diphenyl carbonate from phenol and carbon dioxide in carbon tetrachloride with zinc halides as catalyst

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Abstract

Synthesis of diphenyl carbonate (DPC) from phenol and CO₂ has been explored in CCl₄ with zinc halides as catalyst. DPC yield and selectivity are influenced by the catalyst usage, reaction temperature, CO₂ pressure and initial composition of reactants. The main byproduct is phenyl salicylate (PS). Zinc halides as Lewis acid exhibit high catalytic activity for DPC synthesis; ZnCl₂ gives higher DPC yield and selectivity than ZnBr₂ and ZnI₂. High DPC yield was obtained with ZnCl₂ as catalyst at 120 °C and 4.0 MPa. Based on the experimental observation, a possible reaction scheme has been proposed. The electronegativity of halogen ligand may determine the formation of DPC and PS; the Cl ligand in ZnCl₂ with strong electronegativity may favor the formation of DPC.

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1. Introduction

Diphenyl carbonate (DPC) is a key raw material for producing aromatic polycarbonates. It is still mainly synthesized by using severely toxic phosgene as a raw material. The phosgene route is definitely to be replaced by the environmentally benign routes due to the worldwide awareness of pollution hazards of phosgene [1]. At present, the main nonphosgene routes include the oxidative carbonylation of phenol [2–7] and transesterification of dimethyl carbonate (DMC) with phenol [8–11]. Although the raw materials are easily available for the oxidative carbonylation of phenol, its commercialization is hampered by the low DPC yield, use of noble metal catalysts and costly procedures [7]. Transesterification suffers from low DPC yield and selectivity even at an elevated temperature, because this two-step process is thermodynamically limited [11]. The transesterification of dimethyl oxalate (DMO) with phenol catalyzed by homogeneous [12,13] and heterogeneous [14,15] catalysts is another

approach to DPC synthesis; however, the attainable DPC yield in such a multistage process is still much lower than expectations. It will be undoubtedly attractive if DPC can be synthesized directly from phenol and CO₂ [16], because CO₂ is abundant and environmentally benign.

However, the direct synthesis of DPC from phenol and CO₂ proved to be difficult due to the inertness of CO₂. Phenyl carbonate (PhOCOO⁻) [17] could be produced from the reaction of CO₂ with phenoxide, and CCl₃⁺ could be formed from the decomposition of CCl₄ over Lewis acid catalysts [18,19]. It was then supposed that trichloromethyl phenyl carbonate can be formed from CO₂ and phenoxide in CCl₄ in the presence of Lewis acid catalysts, and DPC can be then obtained through transesterification of trichloromethyl phenyl carbonate with phenoxide. On this view, direct synthesis of DPC from phenoxide, CO₂ and CCl₄ in one pot was realized with ZnCl₂ as catalyst [20].

In this work, the synthesis of DPC from phenol and CO₂ was investigated in CCl₄ with zinc halides as catalyst. The effects of catalyst usage, reaction temperature, CO₂ pressure and initial composition of reactants on the DPC yield and selectivity were then examined. Based on the experimental observation, possible reaction scheme was proposed.

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2. Experimental

2.1. Materials and reaction procedures

Standard samples DPC and phenyl salicylate (PS) was purchased from Aldrich Chemical Co.; phenol, CCl_4 , and K_2CO_3 were obtained from Tianjin Tian-Da Chemical Corporation. Liquid CCl_4 was freshly distilled before use. CO_2 (99.95%) from Beijing Analytical Instrument Co. was used without further treatment. Anhydrous ZnCl_2 , ZnBr_2 and ZnI_2 were obtained from Tianjin Chemical Reagent Co. and were dehydrated before use [21].

All reactions were carried out in an autoclave of 250 mL that was flame-dried prior to use. Phenol, CCl_4 , K_2CO_3 and zinc halides were first placed in the autoclave, and then the autoclave was sealed and flushed with CO_2 to wash out air in it. Then it was pressurized to a certain pressure with CO_2 and heated to the reaction temperature. After the reaction lasted for a given time, the vessel was cooled down to room temperature and the resultants were then taken out and subjected to analysis.

A small amount of cetane was added to the reaction mixture as an internal standard to perform GC analysis. The products were identified by using GC–MS (HP 5972) by comparison with the authentic samples. Quantitative analysis was carried on a GC (Shimadzu GC-14B) with an FID and a DB-1 capillary column (60 m \times 0.25 mm \times 0.25 μm). DPC selectivity and yield were obtained on the basis of phenol conversion.

2.2. Phase equilibrium measurements

The phase changes of the reaction mixture were measured with a high-pressure view cell (15.00 mL) as described in the reference [22]. The pre-evacuated cell was first charged with a known mass of liquid mixture (phenol + CCl_4), and then it was pressurized with CO_2 and heated to the desired temperature (120 °C). The content in the cell was maintained at this temperature for 2 h to reach a phase equilibrium. Generally, both liquid and vapor phases were formed in the cell, and their volumes can be estimated by a scale on the view cell. Then, both the gas and liquid phases were sampled and their compositions were determined through GC analysis.

3. Results and discussion

3.1. Selection of catalysts

The effects of various zinc halides (ZnX_2 , X = Cl, Br and I) on the DPC synthesis are summarized in Table 1. The main products are DPC and PS in all cases. Zinc halides as Lewis acid exhibit certain catalytic activity for DPC synthesis; ZnCl_2 gives higher DPC yield and selectivity than ZnBr_2 and ZnI_2 . With ZnCl_2 as catalyst, the DPC yield and selectivity reached 19.1% and 80.2%, respectively; however, the DPC yield was much lower with ZnBr_2 or ZnI_2 as catalyst. Moreover, iodine substituted phenol was formed with ZnI_2 as catalyst.

The catalytic activity of zinc halides may be related to the electronegativity of halogen ligands. ZnCl_2 is a well known

Table 1

Phenol conversion and DPC yield in DPC synthesis with various zinc halides as catalyst^a

Catalyst	Phenol conversion (%)	DPC selectivity (%)	DPC yield (%)
ZnCl_2	23.8	80.2	19.1
ZnBr_2	9.3	70.7	6.2
ZnI_2	5.9	71.0	4.2

^a Reaction conditions: 15 mmol zinc halide, 30 mmol phenol, 15 mmol K_2CO_3 , 40 mL CCl_4 , and 3.0 MPa CO_2 were charged into the 250 mL autoclave; the reaction lasted for 6 h at 120 °C.

Lewis acid catalyst. It facilitates the dissociation of CCl_4 molecule into CCl_3^+ [18,19], which promotes the formation of intermediate trichloromethyl phenyl carbonate and thereafter DPC. Cl in ZnCl_2 with high electronegativity may favor the formation of stable CCl_3^+ and reaction intermediates; however, ZnBr_2 and ZnI_2 exhibit lower catalytic activity due to the low electronegativity of Br and I ligands. Moreover, ZnBr_2 and ZnI_2 are also less stable than ZnCl_2 under the reaction conditions.

3.2. Effects of CO_2 pressure on the reaction behavior

Through the visual observation, it was proved that the reaction mixture is separated to liquid and gas phases under the reaction conditions. At low pressure, CO_2 concentration in the liquid phase is very low, while the main content in the gas phase is CO_2 . The compositions in both the gas and liquid phases change with the increase in CO_2 pressure, as shown in Fig. 1.

With the increase in CO_2 pressure from 0.1 to 4.0 MPa, the CO_2 content in the liquid phase increased from 0.05 to 1.96 mol/L; the CCl_4 content in the gas phase increased from 0.01 to 0.84 mol/L. Because the amount of CO_2 dissolved in liquid CCl_4 is larger than the amount of CCl_4 released in gaseous CO_2 , the volume of liquid phase increases substantially with the pressure. The phenol concentration in the liquid phase is kept at a stable level (0.60–0.79 mol/L), although it varies slightly with the pressure due to the change in the liquid volume and its amount released to the gas phase.

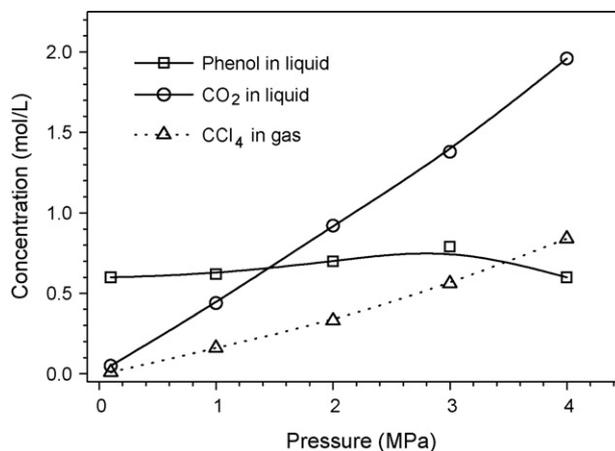


Fig. 1. Variation of phenol and CO_2 contents in liquid phase and CCl_4 content in gas phase with CO_2 pressure (2.4 mL CCl_4 and 1.8 mmol phenol was charged into a 15.0 mL view cell).

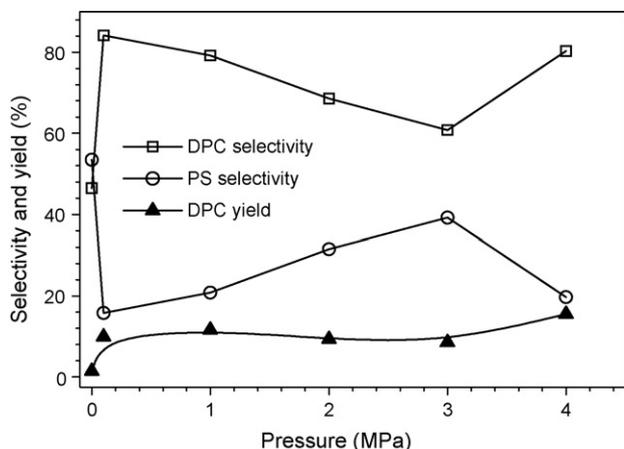


Fig. 2. Effects of CO₂ pressure on the DPC synthesis (reaction conditions: 15 mmol ZnCl₂, 30 mmol phenol, 15 mmol K₂CO₃, and 40 mL CCl₄ were charged into the 250 mL autoclave; reaction lasted for 6 h at 120 °C).

Because the reaction takes place mainly in the liquid phase, CO₂ pressure influences the reaction behavior significantly due to the change in the concentration of the reactants. As shown in Fig. 2, DPC is hardly obtained without charging CO₂ in the system except a certain amount of CO₂ that may be formed from the reaction of K₂CO₃ with phenol. Phenol conversion increases with the pressure due to the increase in CO₂ concentration. At 0.1 MPa, DPC yield and selectivity are 9.9% and 84.2%, respectively. However, DPC selectivity decreases with increasing CO₂ pressure from 0.1 to 3.0 MPa, exhibits a minimum at 3.0 MPa, and then increases again with the pressure; PS selectivity exhibits a maximum at 3.0 MPa. It is difficult to explain this phenomenon. Perhaps PS formation is more sensitive to the concentration of CO₂ in CCl₄. DPC selectivity is enhanced again at a pressure higher than 3.0 MPa; this is possibly accounted for by assuming that the properties of dense reaction mixture at high pressure may be in some way similar to those of supercritical fluid, which alters the reaction pathways.

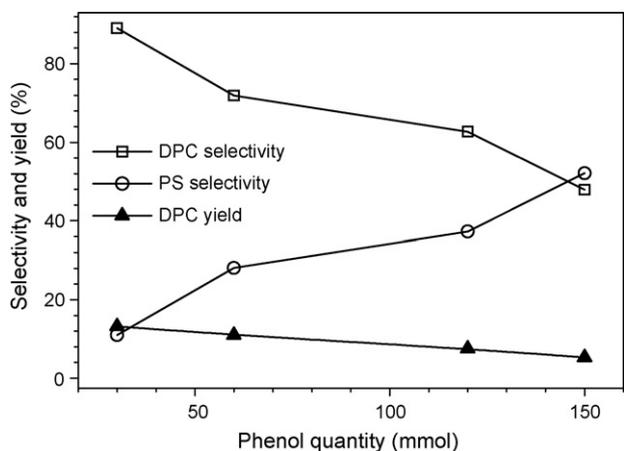


Fig. 3. Effects of the quantity of phenol added on the DPC synthesis (reaction conditions: 15 mmol ZnCl₂, 15 mmol K₂CO₃, 40 mL CCl₄, and 3.0 MPa CO₂ were charged into the 250 mL autoclave; reaction lasted for 6 h at 120 °C).

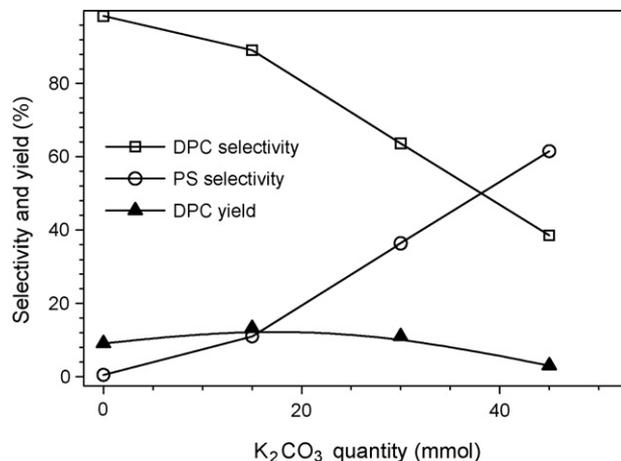


Fig. 4. Effects of the quantity of K₂CO₃ added on the DPC synthesis (reaction conditions: 15 mmol ZnCl₂, 30 mmol phenol, 40 mL CCl₄, and 3.0 MPa CO₂ were charged into the 250 mL autoclave; reaction lasted for 6 h at 120 °C).

3.3. Effects of phenol concentration on the reaction behavior

Phenol concentration in CCl₄ also exhibits significant influences on the reaction behavior. As shown in Fig. 3, with the increase in the quantity of phenol added to the autoclave, DPC selectivity decreases and PS selectivity increases significantly. It seems that high phenol concentration favors the formation of PS.

3.4. Effects of K₂CO₃ quantity on the reaction behavior

The effects of K₂CO₃ quantity added to the autoclave on the reaction are shown in Fig. 4. DPC selectivity decreases significantly with the increase in the K₂CO₃ quantity, while PS selectivity increases accordingly. This indicates that high concentration of K₂CO₃ (it means stronger alkalinity) facilitates the PS formation. DPC yield reaches a maximum of 13.2% with 15 mmol K₂CO₃ added to the reactor, which is corresponding to a K₂CO₃/phenol mole ratio of 0.5.

3.5. Effects of water quantity on the reaction behavior

The effects of water quantity added to the autoclave in DPC synthesis are shown in Fig. 5. DPC selectivity decreases from 99.5% to 73.0% with increasing water quantity added from 0 to 5.0 mL, while DPC yield reaches a maximum of 22.4% when 1.0 mL water is blended with 40 mL CCl₄. The decline in DPC selectivity may be due to the hydrolysis of DPC in the presence of water. However, proper amounts of water could enhance the dissolution of ZnCl₂ in the reacting mixture, which may promote the reaction. This suggests that DPC synthesis under current conditions is tolerant of certain amounts of water in the reaction system.

3.6. Effects of reaction temperature on the reaction behavior

As illustrated in Fig. 6, DPC selectivity decreases from 98.5% to 75.7% with the increase in temperature from 90 to 190 °C.

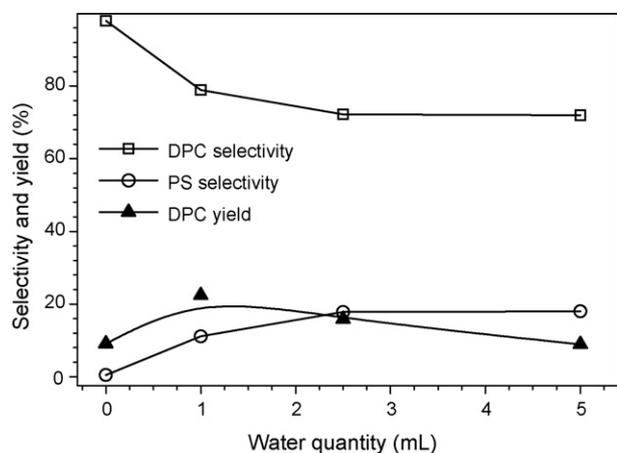


Fig. 5. Effects of the quantity of water added on the DPC synthesis (reaction conditions: 15 mmol ZnCl_2 , 30 mmol phenol, 15 mmol K_2CO_3 , 40 mL CCl_4 , and 3.0 MPa CO_2 were charged into the 250 mL autoclave; reaction lasted for 6 h at 120 °C).

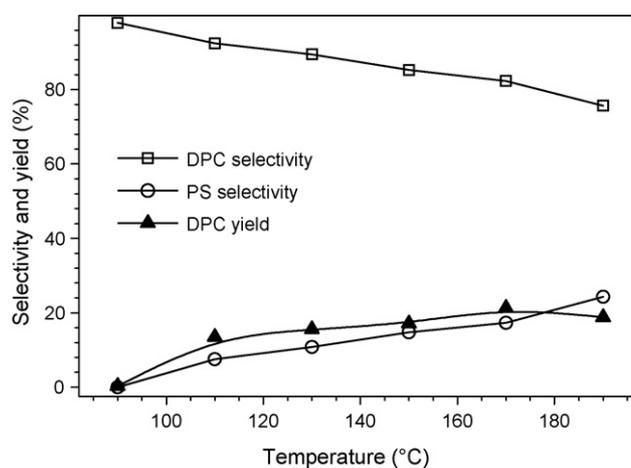


Fig. 6. Effects of reaction temperature on the DPC synthesis (reaction conditions: 15 mmol ZnCl_2 , 30 mmol phenol, 15 mmol K_2CO_3 , 40 mL CCl_4 , and 3.0 MPa CO_2 were charged into the 250 mL autoclave; reaction lasted for 6 h).

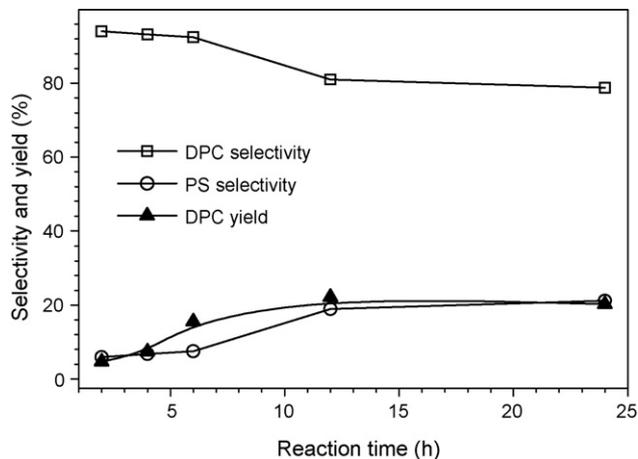


Fig. 7. Effects of reaction time on the DPC synthesis (reaction conditions: 120 °C; 15 mmol ZnCl_2 , 30 mmol phenol, 15 mmol K_2CO_3 , 40 mL CCl_4 , and 3.0 MPa CO_2 were charged into the 250 mL autoclave).

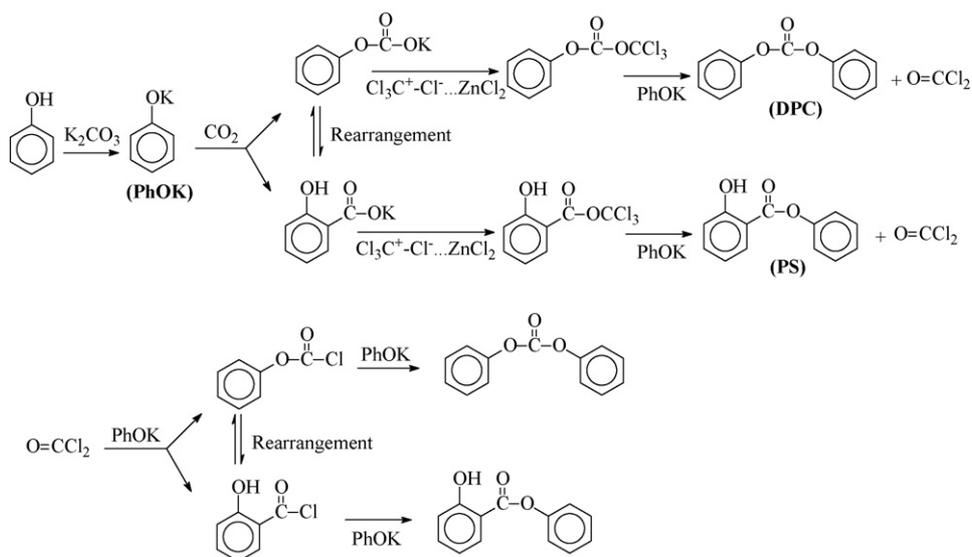
Below 90 °C, DPC yield is very low; it increases with elevating temperature from 90 to 120 °C. DPC yield hardly changes with further increasing temperature. Therefore, a temperature of 120 °C is appropriate for the DPC synthesis.

3.7. Effects of reaction time on the reaction behavior

The effects of reaction time on the DPC synthesis are depicted in Fig. 7. DPC selectivity is kept at a stable level for first 6 h, and then it decreased with the reaction time. In another way, DPC yield increases to 15.6% at 6 h and reached a maximum of 22.2% at 12 h. This suggests that a reaction time of 6–12 h is appropriate for the DPC synthesis.

3.8. Possible reaction scheme

Although the complicated characterizations are necessary to draw a detailed reaction mechanism for DPC synthesis



Scheme 1. Possible reaction pathways for the DPC synthesis from phenol and CO_2 in CCl_4 with ZnCl_2 as catalyst.

under current conditions, a rough reaction path is suggested in Scheme 1. In this reaction scheme, potassium phenoxide reacts with CO_2 , and potassium phenyl carbonate and potassium salicylate are then formed [17]. With the action of Lewis acid catalyst ZnCl_2 , CCl_3^+ is formed from CCl_4 decomposition. Then potassium phenyl carbonate interacts with CCl_3^+ to form the intermediate trichloromethyl phenyl carbonate (PhOCOOCCl_3), which further reacts with another potassium phenoxide to form DPC and phosgene-like intermediate through a transesterification process.

Potassium phenyl carbonate and potassium salicylate can be rearranged to each other with the action of ZnCl_2 catalyst. PS is thus formed in a similar way. The phosgene-like intermediate would further react with potassium phenoxide to form DPC and PS. The rate-determining step should be the reaction of PhOCOO^- with CCl_3^+ to form the intermediate PhOCOOCCl_3 , which made the carbonyl easily attached by phenoxide. The Cl ligand in ZnCl_2 with strong electronegativity is helpful in forming stable CCl_3^+ , and then favor the formation of DPC.

4. Conclusions

DPC can be synthesized from phenol and CO_2 in CCl_4 with zinc halides as catalyst. Its yield and selectivity are influenced by the catalyst usage, reaction temperature, CO_2 pressure and initial composition of reactants. The main byproduct is PS. Zinc halides as Lewis acid exhibit high catalytic activity for DPC synthesis; ZnCl_2 gives higher DPC yield and selectivity than ZnBr_2 and ZnI_2 . High DPC yield is obtained with ZnCl_2 as catalyst at 120°C and 4.0 MPa.

DPC may form via the intermediate trichloromethyl phenyl carbonate PhOCOOCCl_3 that is produced from the interaction of PhOCOO^- with CCl_3^+ . The electronegativity of the halogen ligand in zinc halides may determine their activity for the formation of DPC and PS. The Cl ligand in ZnCl_2 with strong electronegativity is helpful in forming stable CCl_3^+ , and thus favors the formation of DPC.

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