

PROCESS FOR THE PRODUCTION OF AROMATIC CARBONATES

BACKGROUND OF THE INVENTION

The present invention relates to the preparation of aromatic carbonates. More particularly, this invention relates to lower-cost methods for carbonylation of aromatic hydroxy compounds to produce diaryl carbonates.

Diaryl carbonates are valuable monomer precursors for the preparation of polycarbonates by melt transesterification. A particularly advantageous route for the synthesis of diaryl carbonates is the direct carbonylation of aryl compounds in the presence of carbon monoxide, oxygen, and a catalyst system. The catalyst system generally comprises a metal catalyst, a metal or organometallic co-catalyst, an organic co-catalyst, and other optional constituents. U.S. Patent No. 4,187,242 to A. J. Chalk, for example, discloses a catalyst system comprising a Group VIII B element (ruthenium, rhodium, palladium, osmium, iridium and platinum) or complexes thereof as a catalyst, and a metal co-catalyst selected from Group IIIA, IVA, VA, VIA, IB, IIB, VIB, or VII B metals, together with a base. U.S. Patent No. 4,201,721 discloses a catalyst system comprising palladium, a manganese or cobalt complex, a base and a desiccating agent.

The catalyst systems disclosed in U.S. Patent No. 5,142,086 to King, Jr. et al. and U.S. Patent No. 5,284,964 to E. J. Pressman, et al. comprise organic co-catalysts selected from aromatic ketones, aromatic polycyclic hydrocarbons, and aromatic amines. U.S. Patent Number 5,231,210 to Joyce et al. discloses use of a palladium catalyst in combination with an inorganic co-catalyst in the form of a cobalt pentadentate complex of aromatic amines, aliphatic amines, aromatic ethers, aromatic or aliphatic amine ethers, and Schiff bases, such as di-(salicylal)-3,3'-diamino-N-methyldipropylamine; a

quaternary ammonium or phosphonium halide; and quinones and aromatic diols formed by the reduction of quinones. U.S. Patent No. 5,498,789 to Takagi discloses a recent development in catalyst systems, wherein the system comprises palladium, at least one lead compound soluble in a liquid phase, at least one halide selected from quaternary ammonium halides and quaternary phosphonium halides, and optionally at least one copper compound. All of the foregoing patents and disclosures are incorporated by reference herein.

A presently preferred catalyst system requires a metal catalyst, an inorganic co-catalyst, an organic co-catalyst, and a halide source. The halide source is preferably present in significant concentration, on the order of one to five weight percent of the total reaction mixture. During the course of diaryl carbonate production halide may be consumed, for example in the formation of undesired halogenated aromatic byproducts. A conservative estimate places the cost of the halide source at greater than or equal to three dollars per pound. Under conditions of commercial production this represents a considerable expense, and complicates purification of products and disposal of by-products. Accordingly, defining conditions for the production of diaryl carbonates, which minimize halide source consumption, is clearly desirable.

SUMMARY OF THE INVENTION

The above-described and other disadvantages of the prior art are overcome or alleviated by the method described herein for the production of aromatic carbonates, comprising reacting an aromatic hydroxy compound, carbon monoxide, and oxygen in the presence of a catalyst system comprising at least one metal catalyst, at least one halide source, and at least one inorganic co-catalyst, wherein optimization of the molar ratio of inorganic co-catalyst to metal catalyst in the initial reaction mixture results in reduced halide source consumption.

DETAILED DESCRIPTION OF THE INVENTION

Aromatic hydroxy compounds suitable for use in the practice of the invention include monocyclic, polycyclic or fused polycyclic aromatic monohydroxy or polyhydroxy compounds having from 6 to 30, and preferably from 6 to 15 carbon atoms. Illustrative aromatic compounds include, but are not limited to, phenol, cresol, xylenol, resorcinol, hydroquinone, naphthol, catechol, cumenol, the various isomers of dihydroxynaphthalene, bis(4-hydroxyphenyl)propane-2,2, α,α' -bis(4-hydroxyphenyl)p-diisopropylbenzene, and bisphenol A. Aromatic organic monohydroxy compounds are particularly preferred, with phenol being the most preferred.

Other essential reagents in the method of this invention are oxygen and carbon monoxide, which react with the phenol to form the desired diaryl carbonate. The carbon monoxide may be high-purity carbon monoxide or carbon monoxide diluted with another gas such as nitrogen, argon, carbon dioxide or hydrogen, which have no negative effects on the reaction. The oxygen used in the present invention may be high purity oxygen, air, or oxygen diluted with another gas such as nitrogen, argon, carbon dioxide or hydrogen, which have no negative effects on the reaction. Gas is preferably supplied to the reaction mixture in proportions of about 2 to about 50 mole percent oxygen, with the balance being carbon monoxide. The gases may be introduced separately or as a mixture, to a total pressure in the range from about 1 to about 500, preferably about 10 to about 250 atmospheres.

The catalyst system comprises at least one metal catalyst. A preferred metal catalyst comprises a palladium source. Examples of suitable palladium sources include palladium or palladium compounds such as palladium black; supported palladium such as palladium/carbon,

palladium/alumina, palladium/silica and the like; inorganic palladium salts such as palladium chloride, palladium halide, palladium iodide, palladium sulfate, palladium nitrate and the like; and organic palladium salts such as palladium acetate, palladium oxalate and the like. Palladium (II) acetylacetonate, $(\text{Pd}(\text{acac})_2)$, palladium complexes such as $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, and others known in the art, or a mixture of palladium and a compound which can produce the above complexes in the reaction system may also be used. Palladium/carbon, palladium acetate, and $\text{Pd}(\text{acac})_2$ are preferred. An effective amount of the palladium catalyst is, for example, an amount sufficient to provide about 1 mole (gram-atom) of palladium per 100 to 10,000,000 and preferably per 1000 to 1,000,000 equivalents of aromatic hydroxy compound.

At least one inorganic co-catalyst is also present in the catalyst system. Preferred inorganic co-catalysts include divalent or trivalent manganese halide or carboxylate salts, or amine, diketone, or carbon monoxide complexes; or cobalt (II) halide or carboxylate salts, or amine, diketone, or carbon monoxide complexes, e.g., cobalt chloride and cobalt acetate. Also useful are cobalt (II) salts complexed with a pentadentate ligand selected from the group consisting of aromatic amines such as bipyridines, pyridines, terpyridines, quinolines, isoquinolines, and biquinolines; aliphatic amines such as ethylene diamine and tetraalkylethylenediamine; aromatic ethers, such as crown ethers; aliphatic ethers; aromatic or aliphatic amine ethers such as cryptands; and Schiff bases, such as di-(salicylal)-3,3'-diamino-N-methyldipropylamine.

An effective amount of inorganic co-catalyst is that amount sufficient to provide from about 0.1 to about 5.0, preferably from about 0.25 to about 1.5, and most preferably from about 0.5 to about 1.0 mole of metal per mole of palladium. Without being bound by theory, it is hypothesized that optimal quantities of inorganic co-catalyst prevent or at least decrease

formation of halogenated aromatic byproducts, thereby lowering the required quantity of halide source for the reaction.

At least one organic co-catalyst is also present in the catalyst system. Organic co-catalysts include, for example, quinones and aromatic diols formed by the reduction of said quinones, or a mixture thereof. 1,4-Benzoquinone and hydroquinone have been found to be effective, as well as compounds such as 1,2-quinone and catechol, anthraquinone, 9,10-dihydroxy anthracene, and phenanthraquinone. Aromatic organic amines are preferred, for example terpyridines, phenanthrolines, and quinolines such as 2,2':6',2''-terpyridine, 2,2':6',2''-4-thiomethylterpyridine, 2,2':6',2''-terpyridine-N-oxide, 1,10-phenanthrolines, 2,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline. An effective amount of inorganic co-catalyst is an amount sufficient to provide from about 0.1 to about 3.0, and preferably from about 0.3 to about 1.0 mole of organic co-catalyst per mole of palladium.

At least one halide source is also present in the catalyst system. The halide source in the present invention is preferably a quaternary ammonium halide or quaternary phosphonium halide represented by the following formula:



wherein R^1 to R^4 each indicate an alkyl or aryl group having a carbon number of 1 to 10, R^1 to R^4 may be the same as or different from each other, and X indicates a halide, preferably chlorine or bromine. Other halide sources include hexasubstituted guanidinium halides, such as hexaalkyl guanidinium halides, hexaaryl guanidinium halides, and hexasubstituted guanidinium halides containing mixtures of alkyl and aryl substituents each substituent group independently having a carbon number of 1 to 22; for example

hexaalkylguanidinium chlorides or bromides. Preferred halides include tetra-
n-butylammonium bromide, tetraphenylphosphonium bromide, and
hexaethylguanidinium bromide. Mixtures of the aforementioned halide
sources are also suitable for use in the invention. An effective amount of the
5 halide source is in the range from about 5 to about 150, and preferably from
about 20 to about 50 moles per mole of palladium.

At least one desiccant may optionally be present in the reaction
system. A preferred desiccant is a non-reactive material such as a molecular
sieve. 3-Angstrom (A) molecular sieves are presently preferred. The presence
10 of a desiccant is particularly advantageous over long reaction times, for
example in continuous reaction processes, in order to prevent degradation of
the diaryl carbonate product.

An inert solvent such as hexane, heptane, cyclohexane, benzene,
toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether,
15 diphenyl ether, tetrahydrofuran, or dioxane can be used. When an aromatic
hydroxy compound as a raw material is used as a reaction solvent, an
additional solvent need not be used, although mixtures of solvents are also
suitable for use in the present invention.

Reaction is effected in a reactor in which the above-described
20 aromatic hydroxy compound and catalyst system are charged under pressure
of carbon monoxide and oxygen and heating. Reaction temperatures in the
range of about 60 to about 150 °C are typical. In order for the reaction to be as
rapid as possible, it is preferred to substantially maintain the total gas
pressure and partial pressure of carbon monoxide and oxygen until
25 conversion of the aromatic hydroxy compound is complete, as disclosed in
U.S. Patent No. 5,284,964 to Pressman et al., incorporated herein by reference.
For example, to produce diphenyl carbonate, the catalyst system is stirred in
neat phenol at about 100 to about 200 °C while a gaseous carbon monoxide

and oxygen mixture of constant composition is introduced at elevated pressure (up to about 1600 pounds per square inch).

The diaryl carbonates produced by the method of this invention may be isolated by conventional techniques. It is often preferred to form and thermally crack an adduct of the diaryl carbonate with the aromatic hydroxy compound, as is described in U.S. Patent Nos. 5,239,106 and 5,312,955.

The method is further illustrated by the following non-limiting Examples.

The Examples in the Table below are based on reaction mixtures having 60-62 grams of phenol and a catalyst system comprising sufficient palladium in the form of $\text{Pd}(\text{acac})_2$ to provide approximately 500 parts per million (ppm) palladium as indicated in the Table below, 2,2':6',2''-terpyridine (0.33 equivalents per equivalent of palladium), hexaethylguanidinium bromide (10 equivalents per equivalent of palladium), cobalt di-(salicylal)-3,3'-diamino-N-methyldipropylamine as specified in the Table below, and a desiccant (38 - 42 grams of 1/16 inch 3A molecular sieves) in a perforated Teflon basket mounted on a stir shaft. The reactions were conducted under 9.1% oxygen in carbon monoxide at 600 pounds per square inch and under a total gas feed of 330 milliliters per minute for the times indicated, and then a sample was removed for analysis by high pressure liquid chromatography (HPLC) for yield of diphenyl carbonate (DPC) and ppm of brominated phenol produced.

TABLE 1:

Run No.	CoSMDP T ¹	Pd (ppm)	Hours	Yield DPC (wt %)	Pd Turn-overs ²	Reaction Rate ³	BrPhOH Produced (ppm)	Cost Ratio ⁴
A	0	500	2	0.7	7	0.02	3029	6.93
B	0.25	500	1.5	31	305	0.96	1886	0.10
C	0.5	511	2	39	384	0.92	677	0.03
D	1	524	2	42	394	0.97	346	0.01
E	2	499	2	35	349	0.82	300	0.01

¹ Cobalt di-(salicylal)-3,3'-diamino-N-methyldipropylamine : Equivalents per equivalent of palladium

² Moles of palladium charged per mole of diphenyl carbonate produced per hour

³ Moles of DPC produced per liter-hour

⁴ Cost of bromine source per pound of DPC produced, assuming a cost of approximately \$9.00 (U.S.) per pound for hexaethylguanidinium bromide.

The "cost ratio" (cost of bromine source per pound of DPC produced) is calculated by determining the amount of brominated phenol produced as a reaction by-product. Since each mole of brominated phenol represents a mole of bromine source that is consumed (without concomitant production of DPC product), the cost ratio indicates how much bromine source is wastefully consumed. The above Table indicates that bromide source consumption is reduced by the addition of increasing quantities of inorganic co-catalyst cobalt di-(salicylal)-3,3'-diamino-N-methyldipropylamine to the initial reaction mixture.

The method of the present invention effectively and dramatically reduces the consumption of halide source in the direct

carbonylation of aromatic hydroxy compounds to produce diaryl carbonates by increasing the level of inorganic co-catalysts. This reduction in halide source and aromatic hydroxy compound loss results in lower catalyst system and raw materials-related operating costs, which allows for enhanced efficiency in product purification. This translates directly into reduced installed investment costs.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.



WHAT IS CLAIMED IS:

1. A method for the production of aromatic carbonates, comprising:

5 reacting an aromatic hydroxy compound, carbon monoxide, and oxygen in the presence of a catalyst system comprising

at least one metal catalyst;

at least one halide source; and

at least one inorganic co-catalyst, wherein optimization of the molar ratio of inorganic co-catalyst to metal catalyst reduces consumption of
10 the halide source.

2. The method of claim 1, wherein the at least one halide source is a hexaalkyl guanidinium halide; or a quaternary ammonium halide or quaternary phosphonium halide represented by the following formula:



15 wherein R^1 to R^4 each indicate an alkyl or aryl group having a carbon number of 1 to 10, R^1 to R^4 may be the same as or different from each other, and X indicates chlorine or bromine.

3. The method of claim 1, wherein the halide source is selected from the group consisting of tetra-n-butylammonium bromide, tetraphenylphosphonium bromide and hexaethylguanidinium bromide.
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4. The method of claim 1, wherein the at least one inorganic co-catalyst is selected from the group consisting of lead compounds, divalent manganese halide salts, divalent manganese carboxylate salts, trivalent manganese halide salts, trivalent manganese carboxylate salts, divalent



manganese amine, diketone, or carbon monoxide complexes, trivalent manganese amine, diketone, or carbon monoxide complexes, cobalt (II) halide salts, cobalt (II) carboxylate salts, cobalt (II) amine, diketone, or carbon monoxide complexes, cobalt (II) chloride, cobalt (II) acetate, cobalt (II) salts
5 complexed with a pentadentate ligands selected from the group consisting of aromatic amines, bipyridines, pyridines, terpyridines, quinolines, isoquinolines, biquinolines, aliphatic amines, ethylene diamine, tetralkylethylenediamine, aromatic ethers, crown ethers, aliphatic ethers, aromatic amine ethers, aliphatic amine ethers, cryptands, Schiff bases, and di-
10 (salicylal)-3,3'-diamino-N-methyldipropylamine.

5. The method of claim 1 wherein the amount of the at least one inorganic co-catalyst is from about 0.1 to about 3 equivalents per equivalent of metal catalyst.

6. The method of claim 1 wherein the amount of the at least one
15 inorganic co-catalyst is from about 0.25 to about 3 equivalents per equivalent of metal catalyst.

7. The method of claim 1 wherein the amount of the at least one inorganic co-catalyst is from about 0.5 to about 1 equivalent per equivalent of metal catalyst.

20 8. The method of claim 1, wherein said aromatic hydroxy compound is selected from the group consisting of monocyclic aromatic monohydroxy compounds, polycyclic aromatic monohydroxy compounds, fused polycyclic aromatic monohydroxy compounds, monocyclic aromatic polyhydroxy compounds, polycyclic aromatic polyhydroxy compounds,
25 fused polycyclic aromatic polyhydroxy compounds, phenol, cresol, xylenol, resorcinol, hydroquinone, naphthol, catechol, cumenol, isomers of



dihydroxynaphthalene, bis(4-hydroxyphenyl)propane-2,2, α,α' -bis(4-hydroxyphenyl)p-diisopropylbenzene, and bisphenol A.

9. The method of claim 1, wherein said aromatic hydroxy compound is phenol.

5 10. The method of claim 1, wherein said at least one metal catalyst is at least one member selected from the group consisting of palladium black; supported palladium, palladium/carbon, palladium/alumina, palladium/silica, inorganic palladium salts, palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate, organic
10 palladium salts, palladium acetate, palladium oxalate, palladium (II) acetylacetonate, $(\text{Pd}(\text{acac})_2)$, palladium complexes, $\text{PdCl}_2(\text{PhCN})_2$, and $\text{PdCl}_2(\text{PPh}_3)_2$.

11. The method of claim 1, further comprising at least one organic co-catalyst selected from the group consisting of quinones, 1,4-benzoquinone,
15 hydroquinone, 1,2-quinone, catechol, anthraquinone, 9,10-dihydroxy anthracene, phenanthraquinone, aromatic organic amines, terpyridines, phenanthrolines, quinolines, 2,2':6',2''-terpyridine, 2,2':6',2''-4-thiomethylterpyridine, 2,2':6',2''-4-terpyridine-N-oxide, 1,10-phenanthrolines, 2,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline,
20 and 3,4,7,8-tetramethyl-1,10-phenanthroline.

12. The method of claim 1, further comprising a desiccant.

13. The method of claim 11, wherein said at least one metal catalyst is palladium acetate, said at least one halide source is tetrabutylammonium bromide, said at least one inorganic co-catalyst is cobalt di-(salicylal)-3',3'-
25 diamino-N-methyldipropylamine, said at least one organic co-catalyst is 2,2':6',2''-terpyridine,



14. The method of claim 13, further comprising 3-Angstrom molecular sieves.

15. A method for the production of aromatic carbonates, comprising:

5 reacting phenol, carbon monoxide, and oxygen in the presence of a catalyst system comprising

 a palladium catalyst;

 hexaethylguanidinium bromide; and

 an inorganic co-catalyst in a quantity in the range from about
10 0.25 to about 1 equivalent per equivalent of palladium.