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(72) Inventeurs/Inventors:
ARNOLDY, PETER, NL;
KREMERS, ANTOON PAUL MICHAEL, NL

(73) Propriétaire/Owner:
SHELL CANADA LIMITED, CA

(74) Agent: SMART & BIGGAR

(54) Titre : PROCEDE DE CARBONYLATION UTILISANT UN CATALYSEUR AU PHOSPHINE DE PALLADIUM
(54) Title: CARBONYLATION PROCESS USING PALLADIUM PHOSPHINE CATALYST

(57) Abrégé/Abstract:

The invention relates to a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reaction with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid, which reaction is carried out in the presence of a free radical inhibitor.

A B S T R A C T

CARBONYLATION PROCESS USING PALLADIUM PHOSPHINE CATALYST

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CARBONYLATION PROCESS USING PALLADIUM PHOSPHINE CATALYST

This invention relates to a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reaction with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid.

Such processes provide a versatile tool for the economic production of various chemicals starting from readily available unsaturated hydrocarbon feedstock. The carbonylation reaction may be represented by the equation:

$$\mathrm{A + CO + BOH} \xrightarrow[\text{catalyst}]{\text{carbonylation}} \mathrm{H\text{-}A\text{-}CO\text{-}OB}$$

where A represent the unsaturated hydrocarbon compound and BOH represents the hydroxy compound, such as water alcohols and carboxylic acids Generally, olefinic precursors provide saturated products, whereas acetylenic precursors provide olefinic products; multiple carbonylations such as producing saturated products from acetylenic precursors not being excluded. Depending on the nature of the hydroxy compound BOH, various functionalized products, including carboxylic acids, esters, and anhydrides can be obtained.

Recently, it was found that very suitable catalysts are constituted by catalytic systems comprising cationic palladium, a phosphine ligand, and a protonic acid. These catalyst systems allow the carbonylation reaction to proceed at high rate under mild conditions in respect of temperature and carbon monoxide pressure. By dedicated choice of the type of phosphine and the nature of the protonic acid, extremely high selectivities to specific desired product could be obtained. For further details of specific carbonylation reactions thus catalyzed reference is made to published European Patent Application Serial Nos. EP - 106379,

EP-186228, EP-190473, EP-271144, EP-282142, EP-386833, EP-386834, EP-441446, and EP-441447. The low temperatures of these carbonylation reactions are particularly advantageous in that the usual problem of polymerization as side reaction in preparations and/or purifications involving vinylic precursors or products does not occur to an appreciable extent.

Generally, these catalyst systems should comprise a rather high ratio of moles of phosphine to gram atoms of palladium for securing high conversions at low palladium concentration. The high phosphine content disadvantageously attributes to the waste streams and the economics of the above processes, in particularly when using ingenuously substituted phosphines for specific selective processes. It would be desirable to reduce the phosphine/palladium ratio without affecting the performance of these catalyst systems.

The use of inhibitors in other carbonylation reactions and/or preparation processes for methyl methacrylate (MMA) has been reported. However, in such cases the inhibitor was added for its well-known function of inhibiting polymerization reactions of vinylic compounds, since the processes were carried out at temperatures of about 100 °C or much higher. So, US-4,447,640 discloses the preparation of MMA by carbonylation of 1,2-dihaloalkanes in the presence of a supported palladium catalyst and an inhibitor at temperatures in the range of 150-300 °C. The specification mentions that homogeneous catalysts comprising a group VIII metal salt in conjunction with a triorganic phosphine can also be used, without providing further detail. The alleged effects of inhibitor addition as elucidated in column 4, lines 7-37, are prevention of polymerization of the MMA product and increase of the active life of the catalyst by prevention of fouling of the catalyst through deposit of carbon thereon. The latter problem would clearly seem to be confined to heterogeneous catalysts. US-4,480,116 discloses the preparation of MMA by acid hydrolysis of acetone cyanohydrin in the presence of 50-3000 ppm of specific inhibitors, particularly during the work up procedures. Again, the alleged effect is prevention of polymerization of MMA product, whereas this publication is silent on any effect on the life of the catalyst. In Example 22 of EP-A-386833, the carbonylation of 3-butynol is carried out in the presence of hydroquinone for preventing polymerization of the methylenolacton product formed. US-4,416,823 discloses the dimeric hydroesterification of 1,3-alkadienes in the presence of a palladium/phosphine/thiol stabilized complex catalyst at preferred temperatures in the range of 80-120 °C. Preferably, the reaction is conducted in the presence of a vinyl polymerization inhibitor to avoid an increased incremental loss of 1,3-butadiene to polymeric byproducts. None of these publications give any hint to the reduction of a phosphine/palladium ratio in general carbonylation reactions, let alone the type of carbonylation reaction of the present invention.

For solving the problem indicated above, the invention provides a process as indicated in the preamble of this specification, which process is characterized in that the reaction is carried out in the presence of a free radical inhibitor.

According to one aspect of the present invention, there is provided a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reacting the olefinically or acetylenically unsaturated hydrocarbon compound with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid, characterised in that the reaction is carried out in the presence of a free radical inhibitor selected from the group consisting of aromatic hydroxyl compounds, aromatic keto compounds, benzoquinones, naphthoquinones, phenazines, phenoxazines and phenothiazines.

According to another aspect of the present invention, there is provided use of a free radical inhibitor selected from the group consisting of aromatic hydroxyl compounds, aromatic keto compounds, benzoquinones, naphthoquinones, phenazines, phenoxazines and phenothiazines in a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reacting the olefinically or acetylenically unsaturated hydrocarbon compound with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid for the effect of reducing the rate of consumption of the phosphine.

It is now believed that some phosphine was inactivated during the previously described carbonylation reaction and that the high ratio of phosphine to palladium in the catalyst system was required for maintaining a sufficient supply of available phosphine during the entire course of the carbonylation reaction. So, differently stated, the invention proposes the use of a free radical inhibitor in a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reaction with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid for reducing the rate of consumption of the phosphine.

It was surprisingly found, that in the present carbonylation reaction the free radical inhibitor provides a beneficial effect different from its usual effect of inhibiting vinylic polymerization. As a consequence, catalytic systems having a lower phosphine/palladium ratio than used heretobefore, can be used without negative influence to the catalyst life, and therefore the degree of conversion, in the carbonylation process conducted under the same conditions. Accordingly, the invention provides a reduction of costs of phosphine ligands and a reduction of the disposal of the phosphine content of the waste stream of the known process.

The concentration of the free radical inhibitor may vary within wide limits depending on factors such as the duration of the carbonylation, the concentration of trace oxygen, the catalyst concentration and the temperature. For economically attractive carbonylation reactions, the concentration of the free radical inhibitor is preferably in the range of 0.0005 - 1% by weight, more preferably in the range of 0.001 - 0.1% by weight, based on the total of reaction components. It is an additional advantage of the present invention, that these inhibitor concentrations also will very effectively inhibit any polymerization reaction. At normal process temperatures of about 50 °C, this side effect is thought advantageous in theory, but of secondary significance in practice.

Free radical inhibitors, sometimes referred to as polymerization inhibitors, suitable for use in the present process are well-known from polymerization technology, and any such free radical inhibitor can be used in the present process. Representative suitable free radical inhibitors include aromatic hydroxyl compounds, aromatic keto compounds, benzo- and naphthoquinones, phenazines, phenoxazines and phenothiazines. Preferred free radical inhibitors are selected from the group of substituted phenols, including such phenols substituted with further hydroxy groups, for instance hydroquinone. The phenols may carry any further inert substituent, in particular alkyl groups such as methyl and tert.-butyl, and include hydroxylated condensed aromatic ring systems, such as naphthol.

Representative specific free radical inhibitors non-limitatively include monohydric phenols, such as 4-methyl-2,6-di-tert.-butylphenol ("butylated methylphenol"), 2,4-dimethyl-6-tert.-butylphenol, beta-naphthol, p-methoxyphenol ("methylhydroquinone"); dihydric phenols, such as hydroquinones, naphthohydroquinones, catechols, for instance p-tert.butylcatechol, and trihydric phenols, such as pyrogallol.

Due to the presence of the free radical inhibitor, the catalytic system used in the present process is effective at lower initial phosphine proportion. Accordingly, catalyst systems are advantageous, which comprise, at the start of the reaction, a ratio of moles of phosphine to gram atoms of palladium in the range of from 2.5 to 50, preferably of from 5 to 30. Higher phosphine proportions do not disturb the reaction, but attenuate the economic benefits achieved by the invention.

The proportion of the protonic acid in the catalyst system related to the initial proportion of phosphine, is suitably in the range of from 0.5 to 10. It has been found that the use of an acid/phosphine ratio around one is beneficial to the rate of phosphine consumption, and accordingly it is preferred that the ratio of moles of protonic acid to moles of phosphine is in the range of from 0.7 to 1.5.

The olefinically or acetylenically unsaturated compounds to be carbonylated, the suitable sources of cationic palladium, phosphine and protonic acid, the reaction conditions and further experimental details are extensively described in the published European patent applications mentioned at page 1, line 27 to page 2, line 2.

In summary, olefinically unsaturated hydrocarbons include alkenes, in particular 1-alkenes, having generally 2-20 carbon atoms, which may be straight or branched and may comprise a plurality of double bonds, for example ethene, propene, 1-butene, 2-butene, the isomeric pentenes, hexenes, octenes, and 1,5-cyclooctadiene. Acetylenically unsaturated compounds include alkynes, in particular 1-alkynes, which may be straight or branched unsubstituted and may comprise a plurality of triple bonds or further double bonds, for example ethyne, propyne, and 1-butyne. Suitable hydroxy compounds include water, alcohols, and carboxylic acids, which may be aliphatic, cycloaliphatic or aromatic, preferably contain not more than 20 carbon atoms, and may have more than one hydroxy function. Examples of suitable alcohols include methanol, ethanol, propanol, isobutanol, tert.butanol, stearyl alcohol, phenol, ethylene glycol and glycerol. Examples of suitable carboxylic acids include acetic acid and propionic acid.

Suitable palladium sources include palladium compounds such as salts, for example palladium acetate, and complexes, for example tetrakis-triphenylphosphinepalladium and bis-triphenylphosphine-palladium acetate, but also metallic palladium which is solubilized by the acid component of the catalyst system. Suitable phosphines generally include triorganic phosphines, of which the organic substituents independently of each other may be aliphatic, cycloaliphatic, aromatic or heterocyclic and contain 1-10 carbon atoms, for example triphenylphosphine, ethyldiphenylphosphine, dicyclohexylphenylphosphine, 2-pyridyldiphenylphosphine, bis(6-methyl-2-pyridyl)phenylphosphine, tri-p-chlorophenylphosphine and tri-p-methoxyphenylphosphine. Preferred phosphines comprise at least one optionally substituted 2-pyridyl group. Suitable protonic acids preferably have a non-coordinating or weakly coordinating anion. Generally, such acids are strong acids having a pKa below 4.5, more particularly below 2 (measured at 18 °C in aqueous solution), and include sulphuric acid, sulphonic acids, phosphonic acid and certain carboxylic acids. In the present context, the protonic acid may be generated by interaction of a Lewis acid, such as BF_3, with a proton donor, such as HF, or may be generated in situ. It may also be an acidic ion exchange resin.

The process is conveniently effected in the liquid phase. A separate solvent is not essential. Solvents for optional use in the process include aromatic hydrocarbons, esters, ethers and sulphones. At the preferred concentrations, the free radical inhibitor will readily dissolve in the liquid reaction medium. The present process is conveniently carried out at a temperature in the range of from 10 to 130 °C. Preferred temperatures are in the range of from 30 to 90 °C. Convenient pressures are in the range of from 100 to 10,000 kPa. The molar ratio between the olefinically or acetylenically unsaturated hydrocarbon compound and the hydroxy compound is not critical, and may vary within a range of 0.01 to 100:1. The quantity of the catalyst system is not critical, and the quantity of palladium may conveniently be in the range of 10^{-7} to 10^{-1} of gram atom palladium per mole of unsaturated compound.

The carbon monoxide required for the process according to the invention may be used in a practically pure form or diluted with an inert gas, for example nitrogen. Also hydrogen may be present, if it is substantially inert in the particular carbonylation reaction.

The catalyst systems used in the present process may be prepared by any convenient method. Thus they may be prepared by combining a separate palladium compound, the phosphine and the protonic acid. Alternatively, they may be prepared by combining a palladium compound and an acid addition salt of the phosphine. Alternatively, they may be prepared from a palladium compound which is a complex of palladium with the phosphine, and the protonic acid. The free radical inhibitor may be introduced into the reaction by any convenient method. It may, for example, be admixed with the catalyst system, or it may be incorporated into one of the precursor feeds.

By way of example, the invention will be demonstrated by reference to the carbonylation of an acetylenically unsaturated compound, more particularly the preparation of an alkyl methacrylate by reaction of propyne with carbon monoxide and an alkanol. Such a process is described in more detail in EP-271144, and uses a catalyst system that can be formed from a palladium compound, a protonic acid and an organic phosphine of the general formula $PR_1R_2R_3$, wherein one, two or each of R_1, R_2 and R_3 represent a heterocyclic 5 or 6 atom ring comprising at least nitrogen as hetero atom, which ring is optionally substituted and/or may form part of a larger condensed ring structure that is optionally substituted, and any remaining group R_1, R_2 or R_3 represents an optionally substituted hydrocarbyl group.

At the beginning of the reaction, the liquid carrier mainly comprises methanol besides liquified propyne if the reaction is conducted at increased pressure. In the course of the reaction methanol is replaced by methyl methacrylate product further acting as the liquid carrier or solvent for the reaction mixture. In a continuously conducted process, part of the reaction feed consist of a recycled methyl methacrylate/methanol azeotrope stream, and accordingly in each stage of the reaction methyl methacrylate is present.

Example A

Representative stability tests were carried out by preparing solutions of the indicated molar amounts of the catalyst components in mixtures of methyl methacrylate (MMA) and methanol (MeOH) at the indicated weight ratios or in MeOH only. Palladium acetate (PdAc) was used as source of palladium, diphenyl 2-pyridyl phosphine as the ligand and methane sulphonic acid as the acid component of the catalyst system. In tests Nos. 1-3, 5, 6 and 8, furthermore the indicated amount of the indicated type of free radical inhibitor was added. Tests Nos, 4 and 7 are for reference purposes. The solutions were stored for 24 hours under a gaseous medium and at a temperature as indicated. Thereupon, the solutions were analysed on their content of phosphinoxide relative to the total of phosphorus compounds, phosphine and phosphinoxide. The initial oxide content of the phosphine sample used in these experiments was 2.4 %mol.

The results of the tests are mentioned below. It is seen that the presence of a free radical inhibitor increases the life time of the catalyst system. The effect is particularly pronounced, if the reaction solvent comprises MMA even under a nitrogen atmosphere, due to presence of trace amounts of dissolved oxygen.

Example B

In this Example the results of carbonylation experiments as a function of the amount of oxygen fed via the catalyst solution is given.

Carbonylation experiments were carried out in a CSTR (continuously fed, stirred tank reactor). A 300 ml Hastelloy autoclave was employed, which autoclave was equipped with a heating mantle and cooling spiral, to control the temperature, and with a hollow-shaft stirrer to improve CO mass transport.

Catalyst components as defined in Example A and free radical inhibitor (methylhydroquinone) were dissolved in the MeOH feed at ambient temperature and pressure (18 ppmw Pd/MeOH, Pd/ligand/acid/-inhibitor molar ratio of 1:20:15:40). The gas atmosphere was varied (air or inerts, i.e., N_2 or Ar). Propyne was fed via syringe pumps.

At the start of the experiment, the reactor was filled with catalyst/MeOH solution, heated to 45 °C, and pressurized with CO up to 1,100 kPa. Subsequently, catalyst/MeOH solution, propyne, and CO were fed continuously to the reactor (propyne/CO/MeOH molar ratio 1:1.25:1.9) at 1,100 kPa and 45 °C. The liquid reactor content was kept constant by a level control system at 220 ml. Steady states were obtained at different residence times by varying the feeding rates. Activity and selectivity data were derived from gas-liquid chromatographic analysis of the continuously withdrawn product stream. Selectivity to MMA was 99.2% in all cases, the major by-product (0.8%) being methyl crotonate.

propyne feed	treatment of catalyst solution	propyne conversion (%) at residence time:	
		1.6 h	4.4 h
A	mild stripping with inert gas	78	98
A	air saturation	63	80
B	mild stripping with inert gas	69	88
B	severe stripping with inert gas	79	90

Differences in performance were caused by ligand oxidation by oxygen. Different feeds of propyne were used, one being purified both by topping and tailing ("A"), and one being purified by topping only ("B", containing heavier trace impurities). From the above results it can be concluded that, for a given propyne feed of a certain purity, the performance is affected by the presence of oxygen and thus by ligand oxidation.

Test	(No.)	1	2	3	4	5	6	7	8
MMA	(%wt)	46.8	48.6	49.3	50.2	47.4	48.8	-	-
MeOH	(%wt)	53.2	51.4	50.7	49.8	52.6	51.2	100	100
medium		N_2	N_2	N_2	N_2	N_2	N_2	air	air
Pd	(mmol/kg)	0.23	0.12	0.11	0.11	0.12	0.11	0.21	0.23
ligand	(mmol/kg)	2.41	1.20	1.16	1.16	1.23	1.11	2.84	2.92
acid	(mmol/kg)	5.06	2.38	2.40	2.28	2.44	2.24	1.31	1.22
H/L	(mol/mol)	2.1	2.0	2.1	2.0	2.0	2.0	0.46	0.42
L/Pd	(mol/mol)	10	10	10	10	10	10	14	13
inhibitor									
	type*	HQ	HQ	MEHQ	-	HQ	BMP	-	MEHQ
	(mmol/kg)	4.94	4.68	9.02	-	0.97	2.25	-	3.01
temp.	(°C)	45	45	45	45	45	45	20	20
oxide**									
t=20 hr	(%mol)	13.1	10.4	14.5	90.0	21.7	15.3	16.5	6.8

* HQ = hydroquinone; MEHQ = methylhydroquinone; BMP = butylated methylphenol.

** molar proportion of phosphinoxide relative to total P compounds present; initial oxide content of ligand: 2.4 %mol.

CLAIMS:

1. A process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reacting the olefinically or acetylenically unsaturated hydrocarbon compound with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid, characterised in that the reaction is carried out in the presence of a free radical inhibitor selected from the group consisting of aromatic hydroxyl compounds, aromatic keto compounds, benzoquinones, naphthoquinones, phenazines, phenoxazines and phenothiazines.

2. A process as claimed in claim 1, wherein the concentration of the free radical inhibitor is in the range of 0.0005 - 1 % by weight based on the total weight of the reaction components.

3. A process as claimed in claim 1, wherein the concentration of the free radical inhibitor is in the range of 0.001 - 0.1 % by weight based on the total weight of the reaction components.

4. A process as claimed in any one of claims 1 to 3, wherein the free radical inhibitor is a substituted phenol.

5. A process as claimed in any one of claims 1 to 4, wherein the phosphine and the palladium are present in an initial ratio of 2.5 to 50 moles of phosphine to gram atoms of palladium.

6. A process as claimed in any one of claims 1 to 4, wherein the phosphine and the palladium are present in an initial ratio of 5 to 30 moles of phosphine to gram atoms of palladium.

7. A process as claimed in any one of claims 1 to 6, wherein the protonic acid and the phosphine are present in an initial ratio of 0.5 to 10 moles of protonic acid to moles of phosphine.

8. A process as claimed in any one of claims 1 to 6, wherein the protonic acid and the phosphine are present in an initial ratio of 0.7 to 1.5 moles of protonic acid to moles of phosphine.

9. A process as claimed in any one of claims 1 to 8, wherein an acetylenically unsaturated compound is carbonylated.

10. A process as claimed in any one of claims 1 to 8, wherein propyne is reacted with carbon monoxide and an alkanol to form an alkyl methacrylate.

11. Use of a free radical inhibitor selected from the group consisting of aromatic hydroxyl compounds, aromatic keto compounds, benzoquinones, naphthoquinones, phenazines, phenoxazines and phenothiazines in a process for the carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound by reacting the olefinically or acetylenically unsaturated hydrocarbon compound with carbon monoxide and a hydroxy compound in the presence of a catalyst system comprising a source of cationic palladium, a source of phosphine and a protonic acid for the effect of reducing the rate of consumption of the phosphine.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS