Claims

1. A process for the production of an ethylenically unsaturated carboxylic acid ester, preferably an α,ß ethylenically unsaturated carboxylic acid ester, by the reaction of formaldehyde or a suitable source thereof with a carboxylic acid ester in the presence of a basic metal methyl carbonate co-reactant, wherein the process produces a second basic metal salt, wherein the process includes the step of contacting the second basic metal salt with:

a) carbon dioxide (CO_2) and optionally, methanol, and/or

b) dimethyl carbonate,

to regenerate the basic metal methyl carbonate co-reactant, and wherein the formaldehyde or suitable source thereof is added to the reactor, containing a liquid phase comprising the carboxylic acid ester together with the dissolved basic metal salt, at a rate which maintains the carboxylic acid ester in a molar excess compared to the said formaldehyde or suitable source thereof in the liquid phase.

2. A process according to claim 1, wherein at least some of the carbon dioxide (CO_2) is by-product carbon dioxide (CO_2).

3. A process according to claim 1 or 2, wherein, when carbon dioxide (CO_2) is used, the step of contacting the second basic metal salt with carbon dioxide (CO_2) is carried out in the presence of methanol.

4. A process according to claim 3, wherein at least some of the methanol is by-product methanol.

5. A process according to any preceding claim, wherein the process is a continuous process.

6. A process according to any preceding claim, wherein the reaction takes place with the reactants and co-reactant dissolved in the liquid phase.

7. A process according to any preceding claim, wherein the basic metal methyl carbonate co-reactant is a group I or a group II metal methyl carbonate.

8. A process according to claim 7, wherein the basic metal methyl carbonate co-reactant is caesium methyl carbonate.

9. A process according to any preceding claim wherein the second basic metal salt is a metal carboxylate of the following formula:

R^3-CH_2-COOM

wherein M is a metal of the basic metal methyl carbonate co-reactant and R^3 is hydrogen or a C_1 to C_4-alkyl group, preferably a methyl group or is a metal carboxylate of the following formula:

CH_2=C(R^4)(COOM)

wherein M is a metal of the basic metal methyl carbonate co-reactant and R^4 is hydrogen or a C_1 to C_4-alkyl group, preferably a methyl group.

10. A process according to claim 9, wherein the second basic metal salt is a group I or group II metal salt.

11. A process according to claim 10, wherein the second basic metal salt is a group I or group II metal propionate and/or methacrylate.

12. A process according to claim 10 or 11, wherein the second basic metal salt is caesium propionate and/or caesium methacrylate.

13. A process according to any preceding claim, wherein the step of contacting the second basic metal salt with a) carbon dioxide (CO_2) and optionally, methanol, and/or b) dimethyl carbonate is carried out at a temperature below about 250°C.

14. A process according to any preceding claim, wherein the step of contacting the second basic metal salt with a) carbon dioxide (CO_2) and optionally, methanol, and/or b) dimethyl carbonate is carried out at a pressure of between about atmospheric pressure and 2000psi.

15. A process according to any preceding claim, wherein the suitable source of formaldehyde is selected from formalin (formaldehyde, methanol, water), low molecular weight

polyformaldehyde (paraformaldehyde), gaseous formaldehyde, formaldehyde hemiacetal (alcoform), trioxane or anhydrous formaldehyde, or formaldehyde from a distillative drying process, or other sources of formaldehyde where the level of water is <30%, more preferably, <20% by weight of the level of formaldehyde.

16. A process according to claim 15, wherein the formaldehyde from the distillative drying process is a formaldehyde-containing product obtained by a process comprising distilling a formaldehyde solution in the presence of a water entraining compound, such as methyl propionate, such that the formaldehyde containing product is recovered as a complex with methanol and also typically includes the water entraining compound, most suitably methyl propionate.

17. A process according to any proceeding claim, wherein the process further comprises one or more solvents.

18. A process according to claim 17, wherein the solvent is wholly or substantially aprotic.

19. A process according to claim 18, wherein the solvent is an aprotic protophilic solvent or an aprotic photophobic solvent, more preferably, an aprotic protophilic solvent.

20. A process according to claim 19, wherein the solvent is selected from dimethyl formamide, diethyl formamide, dimethylacetamide(DMAc), diethylacetamide, 1-methyl-2-pyrrolidinone, hexamethylphosphoric triamide, pyridine, tetramethyl urea, dimethylsulfoxide, acetonitrile, propionitrile, benzonitrile, acetone, 2-butanone, 3-pentanone, acetophenone, nitromethane, nitrobenzene, tetrahydrothiophene 1,1-dioxide (sulfolane), diethyl ether, diisopropyl ether, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, diglyme, benzene, cyclohexane, xylene or toluene.

21. A process according to any preceding claim, wherein the carboxylic acid ester reactant is of the following formula:

$R^3-CH_2-COOR^4$,

wherein R^4 is an alkyl group, preferably a C_1 to C_4-alkyl group, more preferably, a methyl group, and R^3 is hydrogen or a C_1 to C_4-alkyl group, preferably a methyl group.

22. A process according to any preceding claims, wherein the process includes an initial step of reacting formaldehyde or a suitable source thereof with a carboxylic acid ester in the presence of a first basic metal salt co-reactant prior to the process according to any one of claims 1-21.

23. A process according to claim 22, wherein the first basic metal salt co-reactant is a group I or a group II metal salt.

24. A process according to claim 23, wherein the first basic metal salt co-reactant is selected from group I or group II metal oxides, hydroxides, carbonates, hydrogen carbonates, methyl carbonates, alkoxides, such as methoxides and t-butoxides, fluorides and phosphates.

25. A process according to claim 24, wherein the first basic metal salt co-reactant is selected from potassium oxide, caesium oxide, sodium oxide, rubidium oxide, barium oxide, potassium hydroxide, caesium hydroxide, sodium hydroxide, rubidium hydroxide, barium hydroxide, potassium phosphate, caesium phosphate, sodium phosphate, rubidium phosphate, barium phosphate, sodium methoxide, potassium methoxide, rubidium methoxide, sodium t-butoxide, potassium t-butoxide, rubidium t-butoxide, caesium t-butoxide, sodium fluoride, potassium fluoride, rubidium fluoride, caesium fluoride, potassium carbonate, caesium carbonate, sodium carbonate, rubidium carbonate, barium carbonate, potassium hydrogen carbonate, sodium hydrogen carbonate, rubidium hydrogen carbonate, caesium hydrogen carbonate, and barium hydrogen carbonate.

26. A process according to any preceding claim, wherein the process further comprises a dehydration step.

27. A process according to claim 26, wherein the dehydration step is performed after the step of contacting the second basic metal salt with a) carbon dioxide (CO_2) and optionally, methanol, and/or b) dimethyl carbonate.

28. A process according to claim 26, wherein the dehydration step may is performed before the step of contacting the second basic metal salt with a) carbon dioxide (CO_2) and optionally, methanol, and/or b) dimethyl carbonate.

29. A process according to claim 26, 27 or 28, wherein the dehydration step is performed by dissolving the liquid phase in methanol followed by passing the resultant solution through a molecular sieve or by flash distillation of the liquid phase.

30. A process according to any preceding claim wherein the carboxylic acid ester is non-cyclic.

31. Use of a) carbon dioxide (CO_2) and optionally, methanol, and/or b) dimethyl carbonate, to regenerate a basic metal methyl carbonate co-reactant from a second basic metal salt which has been produced during a process for the production of an ethylenically unsaturated carboxylic ester, preferably an α,ß ethylenically unsaturated carboxylic acid ester, by the reaction of formaldehyde or a suitable source thereof with a carboxylic acid ester in the presence of a basic metal methyl carbonate co-reactant, wherein the formaldehyde or suitable source thereof is added to the reactor, containing a liquid phase comprising the carboxylic acid ester together with the dissolved basic metal salt, at a rate which maintains the carboxylic acid ester in a molar excess compared to the said formaldehyde or suitable source thereof in the liquid phase.