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(54) CARBON DIOXIDE ASSISTED HYDROLYSIS OF AMINOPHOSPHONATES
KOHLENDIOXID-ASSISTIERTE HYDROLYSE VON AMINOPHOSPHONATEN
HYDROLYSE D'AMINOPHOSPHONATES AU DIOXYDE DE CARBONE

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(72) Inventors:
• JOHNSON, Todd, J.
  Booneville, MO 65233 (US)
• MILLER, William, H.
  Glendale, MO 63122 (US)

(74) Representative: Bosch, Henry A. et al
Monsanto Services International S.A.,
Patent Department,
Avenue de Tervuren 270/272,
Letter Box No. 21
1150 Brussels (BE)

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BACKGROUND OF THE INVENTION

[0001] This invention relates to processes for preparing aminophosphonic acids.

[0002] This invention relates to a process for preparing aminophosphonic acids, such as N-phosphonomethylglycine, known also by its common name glyphosate. Glyphosate is a highly effective and commercially important phytotoxicant useful in controlling a large variety of weeds and crops. It is applied to the foliage of a very broad spectrum of perennial and annual grasses and broad-leaved plants to achieve the desired control. Industrial uses include control of weeds along roadsides, waterways, transmission lines, in storage areas, and in other nonagricultural areas. Usually glyphosate is formulated into herbicidal compositions in the form of its various salts which retain the anionic form of glyphosate in solution, preferably in water.

[0003] Amine phosphonomethylation to produce an aminophosphonic acid using formaldehyde and di- or trialkylphosphites has been shown in the literature, e.g., U.S. Patent No. 5,041,628; Polish Patent Nos. 136,276 and 159,424. Such phosphonomethylation produces aminophosphonate esters that must be hydrolyzed to obtain the desired aminophosphonic acid. Prior approaches to hydrolyzing the esters have used an acid such as hydrochloric acid, or a base such as sodium hydroxide. A common problem with these types of hydrolysis is that under basic conditions N-alkylation of aminophosphonate often occurs. When hydrochloric acid is used for hydrolysis, alkyl chloride formation also occurs. The formation of such by-products decreases the yield of the desired aminophosphonic acid and requires more extensive separation of the aminophosphonic acid from the resulting reaction mixture.

[0004] An economically and technically better method for hydrolyzing aminophosphonate esters that proceeds with high conversion and selectivity to aminophosphonic acid and avoids by-product formation is therefore desirable.

SUMMARY OF THE INVENTION

[0005] This invention relates to a process for preparing aminophosphonic acids which comprises contacting in an aqueous medium an aminophosphonate ester with a base in the presence of a hydrolysis facilitator selected from the group consisting of CO₂, CS₂ and COS. This invention also relates to a process for preparing aminophosphonic acids which comprises contacting an amine, trialkylphosphite, alkali metal hydroxide and formaldehyde to produce a reaction mixture, and hydrolyzing the reaction mixture in the presence of a hydrolysis facilitator and base. In one embodiment, alcohol that is produced during hydrolysis is removed using pressurized carbon dioxide at a suitable flow rate.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0006] The invention relates to a process for preparing aminophosphonic acids represented by the formula

\[
\begin{align*}
\text{O} & \\
\text{N} & \\
\text{R} & \\
\text{H} & \\
\text{H} & \\
\end{align*}
\]

wherein \( n \) is 1 to about 3 and \( R \) is hydrogen, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 to 12 carbon atoms, carboxylate salt or ester, or hydroxyethyl, comprising contacting in an aqueous medium an aminophosphonate ester with a base in the presence of a hydrolysis facilitator selected from the group consisting of CO₂, CS₂ and COS. Typically, at least 0.5 equivalents of base is added. Alternatively, the aminophosphonate ester can first be made by contacting an amine represented by the formula RNH₂ wherein \( R \) is as described in the formula above, trialkylphosphate wherein the alkyl group contains 1 to 6 carbon atoms, alkali metal hydroxide and formaldehyde.

[0007] Aminophosphonate esters suitable in the processes of the present invention have the general formula:

\[
\begin{align*}
\text{R}^1\text{O} & \\
\text{P} & \\
\text{(CH}_2\text{n}) & \\
\text{R} & \\
\end{align*}
\]

wherein \( R \) is hydrogen, \( C_{1-6} \) alkyl, \( C_{6-12} \) aryl, a substituted aryl, \( (C_{6-12})\text{aryl}(C_{1-6})\text{alkyl} \), \( -(CH}_2\text{m})\text{OR}^2 \), \( R^1 \) and \( R^2 \) are independently hydrogen, \( C_{1-6} \) alkyl, \( C_{6-12} \) aryl, \( (C_{6-12})\text{aryl}(C_{1-6})\text{alkyl} \), or a salt forming cation such as Na⁺, K⁺, \( [(C_{1-6})\text{alkyl}]\text{NH}_3^+ \), \( [(C_{1-6})\text{alkyl}]_2\text{NH}_2^+ \) or \( [(C_{1-6})\text{alkyl}]_3\text{NH}^+ \); \( R^3 \) is hydrogen, \( C_{1-6} \) alkyl, \( C_{6-12} \) aryl, \( (C_{6-12})\text{aryl}(C_{1-6})\text{alkyl} \), a substituted aryl, or a salt forming cation such as Na⁺, K⁺, \( [(C_{1-6})\text{alkyl}]\text{NH}_3^+ \), \( [(C_{1-6})\text{alkyl}]_2\text{NH}_2^+ \) or \( [(C_{1-6})\text{alkyl}]_3\text{NH}^+ \); \( n \) is between 1 and 6; and \( m \) is between 2 and 6. Preferably, the aminophosphonate ester is the mono- or diethyl ester of glyphosate, or the mono- or dimethylester of glyphosate.

[0008] Bases useful in the processes of the present invention are suitably alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide; alkaline earth metal hydroxides, such as calcium hydroxide; and tertiary amines, such as triethylamine. Preferably the base is sodium hydroxide. Generally, the number of equivalents of base...
added will be in the range of 0.5 to 3.0 equivalents, preferably 1.5 to 2.0 equivalents.  

[0009] The production of aminophosphonic acids from aminophosphate esters is conducted in the presence of a hydrolysis facilitator selected from the group consisting of CO₂, CS₂ and COS. Preferably, CO₂ is used as the hydrolysis facilitator. When CO₂ is the hydrolysis facilitator, the CO₂ is desirably pressurized to between 6.9 • 10⁵ and 3.4 • 10⁶ Pa (between 10 and 500 psi), and more preferably pressurized to between 1.0 • 10⁶ and 2.8 • 10⁶ Pa (between 150 and 400 psi).

[0010] The production of aminophosphonic acids from aminophosphonate esters is conducted at a suitable temperature which can vary over a wide range. The reaction temperature will generally be within the range of 75 °C to 120 °C, preferably about 100 °C. The hydrolysis reaction is conducted for a suitable time which can vary over a wide range depending on various parameters, e.g. the reaction temperature. Generally, the reaction time will be within the range of the time necessary for the phosphonate esters to be hydrolyzed to about 6 hours, preferably 1 hour to 4 hours. The production of aminophosphonic acids is also conducted at a suitable pH, which is generally in the range of 5 to 14, preferably at a pH of 7 to 10.

[0011] The production of aminophosphonic acids from aminophosphonate esters may be conducted while removing alcohol that is produced in the reaction. Preferably, the alcohol removal is conducted by introducing pressurized CO₂ at a suitable flow rate. The flow rate is generally between 0.1 and 1000 mL/min, preferably between 100 and 200 mL/min. The pressure of the CO₂ is preferably about 2.8 • 10⁶ Pa (400 psi).

[0012] As previously mentioned, the aminophosphonate ester can first be made by contacting an amine, trialkylphosphite, base and formaldehyde. The formaldehyde can be employed according to the invention as paraformaldehyde or as an aqueous solution of formaldehyde. Aqueous formaldehyde is commercially available as 37-50% by weight aqueous solutions which may contain methanol, ethanol, or n-butanol. The amount of formaldehyde utilized in the processes of the invention can be expressed as a molar ratio of formaldehyde starting material to phosphite starting material. Broadly, the molar ratio of formaldehyde to phosphite is 1:1 to 5:1, preferably 1:1 to 2:1, and most preferably 1:1 to 1.5:1.  

[0013] Trialkylphosphites, useful in the processes of the invention, are commercially available. Trialkylphosphites can be represented by the formula P(OR)₃ wherein R is an alkyl group. The alkyl groups of the trialkylphosphites are linear or branched alkyl groups having 1 to 6 carbon atoms and are optionally substituted with -OH groups. Trialkylphosphites are preferred over dialkylphosphites because of unexpectedly improved yields achievable with the trialkylphosphites.

[0014] Amines useful in the processes of the present invention can be represented by the formula RNH₂, wherein R is hydrogen, alkyl, aryl, carboxylate salt or ester, or hydroxyethyl. The preferred amine is glycine. Many amines useful in the processes of the present invention are commercially available. The amount of amine utilized in the processes of the invention can be expressed as a molar ratio of amine starting material to phosphite starting material. Broadly, the molar ratio of amine to phosphite is 1:1 to 5:1, and preferably 1:1 to 2.5:1.

[0015] The reaction of amine, phosphite and formaldehyde is conducted at a suitable temperature which can vary over a wide range. The reaction temperature will generally be within the range of 20 °C to 110 °C, preferably 40 °C to 75 °C. The reaction of amine, phosphite and formaldehyde is conducted for a suitable time which can vary over a wide range depending on various parameters, e.g. the reaction temperature.

[0016] The reaction of amine, phosphite and formaldehyde can optionally be conducted in the presence of an alcohol solvent wherein the alcohol is represented by the formula R'(OH)ₘ wherein R' is an alkyl group having 1 to 6 carbon atoms and m is 1 to 3. The alkyl group, R', can be linear or branched and preferably is the same alkyl group as that utilized in the trialkylphosphite starting material. Examples of suitable alcohols include, but are not limited to, methanol, ethanol, isopropanol, n-butanol and mixtures thereof.

[0017] The reactions of the present invention can optionally be carried out in an aqueous or aqueous-alcoholic medium. Preferably, the alcohol used is ethanol or methanol. The reaction mixture produced by contacting formaldehyde, amine and phosphite can optionally be diluted with water prior to hydrolysis. After the hydrolysis reaction is completed, the aminophosphonic acid can be recovered by any conventional method known to those skilled in the art.

[0018] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice.

EXAMPLE 1

[0019] This example illustrates the production of glyphosate from glycine and triethylphosphite following carbon dioxide assisted hydrolysis of the resulting reaction mixture.

[0020] Glycine (15.5 g, 200 mmol), 50% sodium hydroxide (12.0 g, 150 mmol) and 6.0 g of water were mixed to form a solution. 37% Formaldehyde (8.52 g, 105 mmol) and 10 mL of ethanol were added. The temperature was adjusted to 50 °C. Triethylphosphite (16.62 g, 50 mmol) was added over 30-45 minutes with the temperature being maintained at 50 °C. After the addition, the reaction was maintained at 50 °C for an additional 45 minutes to complete the phosphonomethyl-
The reaction mixture was next saturated with gaseous carbon dioxide which modified the pH of the solution to between 7 and 8, caused excess glycine to precipitate, and initiated a substantial amount of hydrolysis. The glycine can optionally be removed. The reaction mixture was then placed under carbon dioxide pressure at 1.4 x 10^6 Pa (200 psi) and heated to 100-120 °C to complete the hydrolysis, which took about 2-4 hours.

**EXAMPLE 2**

An autoclave was charged with a solution containing the di- and monoethylester of glyphosate (0.405 mol), NaOH (0.250 mol), water and ethanol. The pH of this solution was 7.6. Then 400 psi CO_2 (static) was established and the solution was heated to 100 °C. After 18 h, the conversion of the aminophosphonate esters to aminophosphonic acids was 100%. The chemical yield of glyphosate was 74% (0.370 mol). The selectivity for the conversion of the aminophosphonate esters to glyphosate and N-ethylglyphosate was 92% and 8%, respectively.

**EXAMPLE 3**

An autoclave was charged with a solution containing the di- and monoethylester of glyphosate (0.34 mol), NaOH (0.250 mol), water and ethanol. The pH of this solution was then adjusted to 5.6 with trifluoroacetic acid. The 2.8 x 10^6 Pa (400 psi) CO_2 (static) was established and the solution was heated to 100 °C. After 5.5 h, the conversion of the aminophosphonate esters to aminophosphonic acids was 81% (0.405 mol). The selectivity for the conversion of the aminophosphonate esters to glyphosate was 81%, while no N-ethylglyphosate was detected.

**EXAMPLE 4**

This example exemplifies the effect of pH on the selectivity and yield of the CO_2 assisted hydrolysis of glyphosate esters.

**EXAMPLE 5**

This example illustrates the removal of excess glycine prior to complete CO_2 assisted hydrolysis of glyphosate esters. This example also illustrates the dilution of the reaction mixture with water to avoid precipitation with no apparent effect on the rate or selectivity of the hydrolysis.

**EXAMPLE 6**

This example illustrates a process where base (NaOH) was added prior to the introduction of CO_2.

A 50 mL autoclave was charged with a 20 g portion of an alkaloida stream, as defined in U.S. Patent No. 4,486,359 incorporated herein by reference, which had 66% of the phosphorous as dimethylester of glyphosate and 10.4% other. Then 2.8 x 10^6 Pa (400 psi) CO_2 was established over the solution. After 5 h, the solution contained 91.7% glyphosate, 14.4% monoethylester of glyphosate and 6.9% other for a 102% conversion to glyphosate based on the di- and monoethylester of glyphosate. Based on the original charge of P(OEt)_3, a 93% chemical yield of glyphosate was realized after CO_2 hydrolysis.
tained 80% glyphosate, and 20% N-methylglycophosate. There was no mono- or dimethylester of glyphosate present in the final stream.

**EXAMPLE 7**

[0034] This example illustrates a process where additional base was not added prior to the introduction of CO₂.

[0035] A 50 mL autoclave was charged with a 20 g portion of an alkaloida stream which had 66% of the phosphorous as dimethylester of glyphosate. An additional 20 g of water was added to this solution. Then 2.8 x 10⁶ Pa (400 psi) CO₂ was established and the solution was heated to 100 °C. After 5 hours at 100 °C, an aliquot was removed for analysis. Based on the original amount of dimethylester of glyphosate, the sample contained 90% monomethylester of glyphosate, 8% glyphosate, and 2% N-methylglycophosate. There was no dimethylester of glyphosate present in the final stream.

**COMPARATIVE EXAMPLE 1**

[0036] This example illustrates a process where additional NaOH was added, but CO₂ was not introduced to the system.

[0037] A 50 mL autoclave was charged with a 20 g portion of an alkaloida stream which had 66% of the phosphorous as dimethylester of glyphosate. An additional 20 g of water was added to this stream and its pH was adjusted to 10 with NaOH. Then the solution was heated to 100 °C. After 5 hours at 100 °C, an aliquot was removed for analysis. Based on the original amount of dimethylester of glyphosate, the sample contained 100% monomethylester of glyphosate.

**Claims**

1. A process for producing an aminophosphonic acid comprising contacting in an aqueous medium an aminophosphonate ester with base in the presence of a hydrolysis facilitator selected from the group consisting of CO₂, CS₂ and COS.

2. The process of claim 1 wherein the aminophosphonic acid has the formula

   ![Chemical Structure]

   wherein n is 1 to 3 and R is hydrogen, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 to 12 carbon atoms, carboxylate salt or ester, or hydroxyethyl.

3. The process of claim 1 wherein the molar ratio of base to aminophosphonate ester is at least 1:2.

4. The process of claim 1 wherein the base is an alkali metal hydroxide.

5. The process of claim 4 wherein the alkali metal hydroxide is sodium hydroxide.

6. The process of claim 1 wherein the base is an alkaline earth metal hydroxide.

7. The process of claim 1 wherein the base is a tertiary amine.

8. The process of claim 1 wherein the hydrolysis facilitator is CO₂.

9. The process of claim 8 wherein the pressure of the CO₂ is between 6.9 x 10⁴ and 3.4 x 10⁶ Pa (between 10 and 500 psi).

10. The process of claim 8 wherein the pressure of the CO₂ is between 1.0 x 10⁶ and 2.8 x 10⁶ Pa (between 150 and 400 psi).

11. The process of claim 1 further comprising introducing a flow of pressurized CO₂.

12. The process of claim 11 wherein the flow rate of CO₂ is between 100 and 200 mL/min.

13. The process of claim 1 wherein the contacting is carried out at a pH between 7 and 10.

14. The process of claim 1 wherein the contacting is carried out at a temperature between 75 °C and 120 °C.

15. The process of claim 1 wherein the aminophosphonate ester is glyphosate monoethylester, glyphosate diethylester, or a combination thereof.

16. The process of claim 1 wherein the contacting is conducted in an aqueous-alcoholic medium.

17. A process for producing an aminophosphonic acid comprising the steps of:

   contacting an amine, trialkylyphosphite, base and formaldehyde to produce a first reaction mixture, and hydrolyzing said first reaction mixture in the presence of a hydrolysis facilitator selected from the group consisting of CO₂, CS₂ and
COS to produce a second reaction mixture comprising aminophosphonic acid and alcohol.

18. The process of claim 17 wherein the aminophosphonic acid has the formula

\[
\text{HO-P-(CH}_2\text{)}_n\text{N-R}
\]

wherein \( n \) is 1 to 3 and \( R \) is hydrogen, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 to 12 carbon atoms, carboxylate salt or ester, or hydroxyethyl.

19. The process of claim 17 wherein the amine has the formula \( \text{RNH}_2 \) wherein \( R \) is hydrogen, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 to 12 carbon atoms, carboxylate salt or ester, or hydroxyethyl.

20. The process of claim 17 wherein the molar ratio of base to aminophosphonate ester is at least 1:2.

21. The process of claim 17 wherein the base is an alkali metal hydroxide.

22. The process of claim 21 wherein the alkali metal hydroxide is sodium hydroxide.

23. The process of claim 17 wherein the base is an alkaline earth metal hydroxide.

24. The process of claim 17 wherein the base is a tertiary amine.

25. The process of claim 17 wherein the hydrolysis facilitator is \( \text{CO}_2 \).

26. The process of claim 25 wherein the pressure of the \( \text{CO}_2 \) is between \( 6.9 \times 10^4 \, \text{Pa} \) and \( 3.4 \times 10^6 \, \text{Pa} \) (between 10 and 500 psi).

27. The process of claim 25 wherein the pressure of the \( \text{CO}_2 \) is between \( 1.0 \times 10^6 \) and \( 2.8 \times 10^6 \, \text{Pa} \) (between 150 and 400 psi).

28. The process of claim 17 further comprising removing the alcohol during the hydrolysis.

29. The process of claim 28 wherein the removing comprises introducing a flow of pressurized \( \text{CO}_2 \).

30. The process of claim 25 wherein the flow rate of \( \text{CO}_2 \) is between 100 and 200 mL/min.

31. The process of claim 17 wherein the hydrolysis is carried out at a \( \text{pH} \) between 7 and 10.

32. The process of claim 17 wherein the hydrolysis is carried out at a temperature between \( 75 \, ^\circ \text{C} \) and \( 120 \, ^\circ \text{C} \).

33. The process of claim 17 further comprising diluting the first reaction mixture with water prior to the hydrolysis.

34. The process of claim 17 wherein the amine is glycine.

35. The process of claim 17 wherein the trialkylphosphite is triethylphosphite.

Patentansprüche

1. Verfahren zur Herstellung einer Aminophosphonsäure, umfassend das Kontaktieren in einem wässrigen Medium eines Aminophosphonatohnesters mit Base in Gegenwart eines Hydrolyse-Fördermittels, gewählt aus der Gruppe, bestehend aus \( \text{CO}_2, \text{CS}_2 \) und \( \text{COS} \).

2. Verfahren nach Anspruch 1, wobei die Aminophosphonsäure die Formel besitzt

\[
\text{HO-P-(CH}_2\text{)}_n\text{N-R}
\]

worin \( n \) 1 bis 3 ist, und \( R \) Wasserstoff, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 12 Kohlenstoffatomen, Carboxylatsalz oder -ester oder Hydroxyethyl ist.

3. Verfahren nach Anspruch 1, wobei das Molverhältnis von Base zu Aminophosphonatester mindestens 1:2 beträgt.

4. Verfahren nach Anspruch 1, wobei die Base ein Alkalimetallhydroxid ist.

5. Verfahren nach Anspruch 4, wobei das Alkalimetallhydroxid Natriumhydroxid ist.

6. Verfahren nach Anspruch 1, wobei die Base ein Erdalkalimetallhydroxid ist.
7. Verfahren nach Anspruch 1, wobei die Base ein tertäres Amin ist.

8. Verfahren nach Anspruch 1, wobei das Hydrolyse-Fördermittel CO$_2$ ist.

9. Verfahren nach Anspruch 8, wobei der Druck von CO$_2$ zwischen $6.9 \times 10^4$ und $3.4 \times 10^6$ Pa (zwischen 10 und 500 psi) beträgt.

10. Verfahren nach Anspruch 8, wobei der Druck von CO$_2$ zwischen $1.0 \times 10^6$ und $2.8 \times 10^6$ Pa (zwischen 150 und 400 psi) beträgt.

11. Verfahren nach Anspruch 1, umfassend weiterhin die Einführung eines Stroms an verdichtetem CO$_2$.

12. Verfahren nach Anspruch 11, wobei die Strömungsrate des CO$_2$ zwischen 100 und 200 ml/min liegt.

13. Verfahren nach Anspruch 1, wobei das Kontaktieren bei einem pH zwischen 7 und 10 durchgeführt wird.

14. Verfahren nach Anspruch 1, wobei das Kontaktieren bei einer Temperatur zwischen 75°C und 120°C durchgeführt wird.

15. Verfahren nach Anspruch 1, wobei der Aminophosphonatester Glyphosatmonoethylester, Glyphosate-diiethylester oder eine Kombination hiervon ist.

16. Verfahren nach Anspruch 1, wobei das Kontaktieren in einem wässrig-alkoholischen Medium durchgeführt wird.

17. Verfahren zur Herstellung einer Aminophosphonsäure, umfassend die Schritte:

Kontaktieren eines Amins, Trialkylphosphit, Base und Formaldehyd zur Bildung einer ersten Reaktionsmischung, und Hydrolysieren der ersten Reaktionsmischung in Gegenwart eines Hydrolyse-Fördermittels, gewählt aus der Gruppe, bestehend aus CO$_2$, CS$_2$ und COS, zur Herstellung einer zweiten Reaktionsmischung, umfassend Aminophosphonsäure und Alkohol.

18. Verfahren nach Anspruch 17, wobei die Aminophosphonsäure die Formel besitzt

\[ \text{HO-P-(CH}_n\text{H)}_2\text{N-R} \]

worin $n$ 1 bis 3 ist, und R Wasserstoff, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 12 Kohlenstoffatomen, Carbonylatsalz oder -ester oder Hydroxyethyl ist.

19. Verfahren nach Anspruch 17, wobei das Amin die Formel RNH$_2$ besitzt, worin R Wasserstoff, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 12 Kohlenstoffatomen, Carbonylatsalz oder -ester oder Hydroxyethyl ist.

20. Verfahren nach Anspruch 17, wobei das molare Verhältnis von Base zu Aminophosphonatmindestens 1:2 beträgt.

21. Verfahren nach Anspruch 17, wobei die Base ein Alkalimetallhydroxid ist.

22. Verfahren nach Anspruch 21, wobei das Alkalimetallhydroxid Natriumhydroxid ist.

23. Verfahren nach Anspruch 17, wobei die Base ein Erdalkalimetallhydroxid ist.

24. Verfahren nach Anspruch 17, wobei die Base ein tertäres Amin ist.

25. Verfahren nach Anspruch 17, wobei das Hydrolyse-Fördermittel CO$_2$ ist.

26. Verfahren nach Anspruch 25, wobei der Druck von CO$_2$ zwischen $6.9 \times 10^4$ und $3.4 \times 10^6$ Pa (zwischen 10 und 500 psi) beträgt.

27. Verfahren nach Anspruch 25, wobei der Druck von CO$_2$ zwischen $1.0 \times 10^6$ und $2.8 \times 10^6$ Pa (zwischen 150 und 400 psi) beträgt.

28. Verfahren nach Anspruch 17, umfassend weiterhin das Entfernen des Alkohols während der Hydrolyse.

29. Verfahren nach Anspruch 28, wobei das Entfernen des Alkohols während der Hydrolyse umfasst.

30. Verfahren nach Anspruch 25, wobei die Strömungsrate von CO$_2$ zwischen 100 und 200 ml/min liegt.
31. Verfahren nach Anspruch 17, wobei die Hydrolyse bei einem pH zwischen 7 und 10 durchgeführt wird.

32. Verfahren nach Anspruch 17, wobei die Hydrolyse bei einer Temperatur zwischen 75°C und 120°C durchgeführt wird.

33. Verfahren nach Anspruch 17, umfassend weiterhin das Verdünnen der ersten Reaktionsmischung mit Wasser vor der Hydrolyse.

34. Verfahren nach Anspruch 17, wobei das Amin Glycin ist.

35. Verfahren nach Anspruch 17, wobei das Trialkylphosphit Triethylphosphit ist.

Revenifications

1. Procédé de production d’un acide aminophosphonique comprenant l’étape consistant à mettre en contact, dans un milieu aqueux, un ester aminophosphonate avec une base en présence d’un agent facilitant l’hydrolyse choisi dans le groupe constitué de CO₂, CS₂ et COS.

2. Procédé selon la revendication 1, dans lequel l’acide aminophosphonique répond à la formule

\[
\begin{align*}
\text{O} & \\
\text{HO} & \\
\text{P} & \\
\text{(CH}_2\text{)}_n & \\
\text{N} & \\
\text{R} & \\
\text{HO} & 
\end{align*}
\]

dans laquelle n vaut de 1 à 4 et R représente un atome d’hydrogène, un groupe alkyle contenant 1 à 6 atomes de carbone, un groupe aryle contenant 6 à 12 atomes de carbone, un sel ou ester carboxylate, ou un groupe hydroxyéthyle.

3. Procédé selon la revendication 1, dans lequel le rapport molaire de la base à l’ester aminophosphonate vaut au moins 1:2.

4. Procédé selon la revendication 1, dans lequel la base est un hydroxyde de métal alcalin.

5. Procédé selon la revendication 4, dans lequel l’hydroxyde de métal alcalin est l’hydroxyde de sodium.

6. Procédé selon la revendication 1, dans lequel la base est une hydroxyde de métal alcalino-terreux.

7. Procédé selon la revendication 1, dans lequel la base est une amine tertiaire.

8. Procédé selon la revendication 1, dans lequel l’agent facilitant l’hydrolyse est CO₂.

9. Procédé selon la revendication 8, dans lequel la pression du CO₂ est comprise entre 6,9 × 10⁴ et 3,4 × 10⁶ Pa (entre 10 et 500 psi).

10. Procédé selon la revendication 8, dans lequel la pression de CO₂ est comprise entre 1,0 × 10⁶ et 2,8 × 10⁶ Pa (entre 150 et 400 psi).

11. Procédé selon la revendication 1, comprenant en outre l’étape consistant à introduire un courant de CO₂ sous pression.

12. Procédé selon la revendication 11, dans lequel le débit de CO₂ est compris entre 100 et 200 ml/min.

13. Procédé selon la revendication 1, dans lequel on effectue l’étape de mise en contact à un pH compris entre 7 et 10.

14. Procédé selon la revendication 1, dans lequel on effectue l’étape de mise en contact à une température comprise entre 75 °C et 120 °C.

15. Procédé selon la revendication 1, dans lequel l’estér aminophosphonate est l’estér monoéthylique de glyphosate, l’estér diéthylique de glyphosate ou une combinaison de ceux-ci.

16. Procédé selon la revendication 1, dans lequel on effectue l’étape de mise en contact dans un milieu alcoolique aqueux.

17. Procédé de production d’un acide aminophosphonique comprenant les étapes consistant à :

mettre en contact une amine, un phosphite de trialkyle, une base et du formaldéhyde pour produire un premier mélange de réaction, et hydrolyser ledit premier mélange de réaction en présence d’un agent facilitant l’hydrolyse choisi dans le groupe constitué par CO₂, CS₂ et COS pour produire un second mélange de réaction comprenant un acide aminophosphonique et un alcool.

18. Procédé selon la revendication 17, dans lequel l’acide aminophosphonique répond à la formule...
dans laquelle n vaut de 1 à 3 et R représente un atome d’hydrogène, un groupe alkyle contenant 1 à 6 atomes de carbone, un groupe aryle contenant 6 à 12 atomes de carbone, un sel ou ester carboxylate, ou un groupe hydroxyéthyle.

19. Procédé selon la revendication 17, dans lequel l’amine a pour formule RNH₂ dans laquelle R représente un atome d’hydrogène, un groupe alkyle contenant 1 à 6 atomes de carbone, un groupe aryle contenant 6 à 12 atomes de carbone, un sel ou ester carboxylate, ou un groupe hydroxyéthyle.

20. Procédé selon la revendication 17, dans lequel le rapport molaire de la base à l’ester aminophosphonate vaut au moins 1:2.

21. Procédé selon la revendication 17, dans lequel la base est un hydroxyde de métal alcalin.

22. Procédé selon la revendication 21, dans lequel l’hydroxyde de métal alcalin est l’hydroxyde de sodium.

23. Procédé selon la revendication 17, dans lequel la base est une hydroxyde de métal alcalino-terreux.

24. Procédé selon la revendication 17, dans lequel la base est une amine tertiaire.

25. Procédé selon la revendication 17, dans lequel l’agent facilitant l’hydrolyse est CO₂.

26. Procédé selon la revendication 25, dans lequel la pression du CO₂ est comprise entre 6,9 \times 10⁴ Pa et 3,4 \times 10⁶ Pa (entre 10 et 500 psi).

27. Procédé selon la revendication 25, dans lequel la pression de CO₂ est comprise entre 1,0 \times 10⁵ et 2,8 \times 10⁶ Pa (entre 150 et 400 psi).

28. Procédé selon la revendication 17, comprenant en outre l’étape consistant à enlever l’alcool pendant l’hydrolyse.

29. Procédé selon la revendication 28, dans lequel l’étape d’élimination comprend l’étape consistant à introduire un courant de CO₂ sous pression.

30. Procédé selon la revendication 25, dans lequel le