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(54) Title: REUSABLE FRIEDEL-CRAFTS CATALYSTS, THEIR USE, AND THEIR REGENERATION

(57) Abstract: Described is an improved process in which a Friedel-Crafts reaction is carried out in a reaction zone using a Friedel-Crafts catalyst. The improvement includes introducing anhydrous sodium tetrachloroferrate into the reaction zone as a Friedel-Crafts catalyst component. The anhydrous sodium tetrachloroferrate is a recyclable Friedel-Crafts catalyst. An especially efficacious catalyst system is formed *in situ* when the anhydrous sodium tetrachloroferrate is used in an acylation reaction in which an acylating agent, preferably acetyl chloride or acetic anhydride, or a combination of them, is employed.

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**REUSABLE FRIEDEL-CRAFTS CATALYSTS, THEIR USE,
AND THEIR REGENERATION**

BACKGROUND

[0001] Friedel-Crafts catalysts are widely used in a variety of Friedel-Crafts reactions such as acylation, alkylation, and sulfonylation. Unfortunately, many common Friedel-Crafts catalysts, such as aluminum chloride and ferric chloride, are not reusable and are thus converted into other chemical forms or discharged into the environment.

[0002] It would be of considerable advantage if new, reusable Friedel-Crafts catalysts could be provided for Friedel-Crafts reactions, especially if such catalysts are efficient, economical, and susceptible to facile regeneration for effective reuse.

[0003] The purpose of this invention is to provide Friedel-Crafts catalysts that have these advantageous properties and characteristics.

BRIEF SUMMARY OF THE INVENTION

[0004] It has been found that sodium tetrachloroferrate (NaFeCl_4) is an efficient and recyclable Friedel-Crafts catalyst, as for example in the acylation of aromatic compounds. It retains most of its catalytic activity even after aqueous workup. Pursuant to this invention, lithium tetrachloroferrate (LiFeCl_4) has also been found effective as a Friedel-Crafts catalyst in an acylation reaction.

[0005] As is well known in the art, Friedel-Crafts reactions are substitution reactions in which a hydrogen atom on an aromatic ring is replaced by a functional group or an alkyl group. In accordance with this invention, lithium tetrachloroferrate and especially sodium tetrachloroferrate are used as a Friedel-Crafts catalyst component in Friedel-Crafts reactions whereby various types of aromatic compounds are formed, including without limitation ketones, aldehydes, indanones, sulfones, carboxylic acids, amides, and esters, as well as alkylated and thioalkylated aromatic compounds, and brominated aromatics including carbonyl and sulfonyl compounds which require stoichiometric amounts of Lewis acid for the bromination. As used herein, a "Friedel-Crafts catalyst component" is a molecule that, when used in conducting a Friedel-Crafts reaction, may form *in situ* one or more active complexes or other catalytic species that facilitate the desired reaction. In other words, LiFeCl_4 or NaFeCl_4 is typically charged to the reactor as one of the components but it need not remain as

such when other components are present and/or reaction begins to take place. In fact, in one embodiment of this invention there is provided as a new composition, an equimolar complex between an acylating agent and sodium tetrachloroferrate, including for example a complex of this type where the acylating agent forming the complex is acetic anhydride or acetyl chloride, or is a mixture of complexes in which (i) one complex is an equimolar complex between acetic anhydride and sodium tetrachloroferrate and in which (ii) another complex is an equimolar complex between acetyl chloride and sodium tetrachloroferrate.

[0006] These and other embodiments of this invention will be still further apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Fig. 1 shows infrared absorbance spectra comparing the spectrum of an equimolar complex of acetyl chloride (the upper spectrum) with that of 98% pure acetyl chloride (the lower spectrum).

[0008] Fig. 2 shows infrared absorbance spectra comparing the spectrum of an equimolar complex of acetic anhydride (the upper spectrum) with that of over 99% pure acetic anhydride (the lower spectrum).

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0009] As can be appreciated from the above, this invention in one of its embodiments provides a substantial improvement in the conduct of chemical reactions that involve replacement of a hydrogen atom on the ring of an aromatic reactant by a functional group, and in which reaction a Friedel-Crafts catalyst is used. The improvement comprises introducing anhydrous sodium tetrachloroferrate into the reaction zone as a Friedel-Crafts catalyst component. Methods for producing anhydrous alkali metal tetrachloroferrate are known and reported in the literature. See for example, U.S. Pat. No. 3,729,543 to Wendell E. Dunn, Jr., EP 1,198,417 published April 2002, and Cerisier et al., *European Journal of Solid State and Inorganic Chemistry*, 1988, 25(1), 35-52.

[0010] Friedel-Crafts reactions are well known to those of ordinary skill in the art, and are reported in the literature. See for example Roberts and Khalaf, *Friedel-Crafts Alkylation Chemistry*, Marcel Dekker, NY, 1984; Olah, *Friedel-Crafts and Related Reactions*, Wiley, NY, 1963-1965; Olah, *Friedel-Crafts Chemistry*, Wiley, NY, 1973.

[0011] Anhydrous sodium tetrachloroferrate exists in the solid state at ordinary room temperatures. Friedel-Crafts reactions are typically conducted under anhydrous conditions, and thus it is desirable to introduce anhydrous sodium tetrachloroferrate into the reaction zone in molten liquid form, in the form of finely-divided solids, or in both such forms. In this invention, it is possible to introduce the anhydrous sodium tetrachloroferrate and/or anhydrous lithium tetrachloroferrate into the reaction zone before, during and/or after the introduction of the other reaction components. Preferably, anhydrous sodium tetrachloroferrate is introduced into the reaction zone in molten liquid form during and/or after the introduction of at least an aromatic hydrocarbon reactant and/or another liquid reaction component, or a solvent or diluent, and the resultant mixture is agitated so that the sodium tetrachloroferrate is well dispersed throughout the mixture.

[0012] To take advantage of the reusable characteristics of sodium tetrachloroferrate as a Friedel-Crafts catalyst component, after completion of the reaction in which the sodium tetrachloroferrate has been used as the catalyst component and a reaction mixture (reaction mass) has been formed, the following workup procedure is preferably employed. The reaction mixture is subjected to hydrolytic conditions so that an aqueous phase and an organic phase are formed, these liquid phases are separated from each other, typically by a liquid-liquid separation procedure such as decantation or draining, and then all water including water of hydration is removed from the aqueous phase to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component. A preferred way of removing all water including water of hydration is a procedure which comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c) passing anhydrous hydrogen chloride into or through the mixture from (b), to thereby regenerate said anhydrous sodium tetrachloroferrate. In some cases, solids may also be present in the resultant mixture from (a), and such solids typically are melted during the conduct of (b). If desired, this water removal operation can be conducted at reduced pressure. Depending on the pressure at which this operation is conducted, a suitable temperature can be in the range of about 150°C to about 300°C, and preferably is in the range of about 230°C to about 270°C. The temperature and pressure at which the operation is conducted should be such as to ensure removal of the water of hydration.

[0013] To ensure that the iron remains in the trivalent state, a gaseous oxidant can be passed into or through the liquid melt after the anhydrous hydrogen chloride has been passed into or through said liquid. In this way any divalent iron is oxidized to the trivalent state. Suitable gaseous oxidants include chlorine, oxygen, or air, any of which can be diluted with an inert gas such as nitrogen, argon, or the like. This operation can be performed at any temperature at which the anhydrous sodium tetrachloroferrate remains in the liquid (molten) state or in solution (*e.g.*, from about 20°C to about 300°C and preferably at temperatures in the range of about 120°C to about 270°C).

[0014] Preferably the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into the reaction zone as a Friedel-Crafts catalyst component. This enables the Friedel-Crafts reaction to be performed on a continuous basis, with the periodic inclusion of fresh anhydrous sodium tetrachloroferrate when and as needed.

[0015] Combinations of the foregoing operations are desirably employed. For example, the anhydrous sodium tetrachloroferrate is introduced into the reaction zone in molten liquid form after the introduction into the reaction zone of aromatic hydrocarbon reactant or inert liquid solvent, and after the reaction is completed and a reaction mixture has been formed, a procedure comprising the following steps is used:

- a) the reaction mixture is subjected to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed,
- b) these liquid phases are separated from each other, and
- c) all water including water of hydration is removed from the aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component. The removal of such water is preferably carried out by a procedure which comprises (1) distilling off distillable free water from the aqueous phase, (2) heating the resultant mixture to remove water of hydration, and (3) passing anhydrous hydrogen chloride into or through the mixture from (2) while raising the temperature of the mixture high enough so that water of hydration is removed from the mixture to thereby regenerate anhydrous sodium tetrachloroferrate. Passing a gaseous oxidant into or through the mixture after the anhydrous hydrogen chloride treatment is also desirable, as noted above.

Thereafter in a preferred mode of operation the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into the reaction zone as a Friedel-Crafts catalyst component.

[0016] In preferred embodiments of this invention a Friedel-Crafts acylation process is carried out. Such reactions involve introducing into a reaction zone at least an aromatic reactant having a position on the aromatic ring to be acylated, an acylating agent, and a Friedel-Crafts catalyst component, and effecting reaction the acylation in the reaction zone. The reaction is performed under inert, anhydrous reaction conditions. Pursuant to this invention, the Friedel-Crafts catalyst component introduced into the reaction zone is anhydrous sodium tetrachloroferrate or anhydrous lithium tetrachloroferrate, or both of them, to serve as Friedel-Crafts catalyst component(s). Since the Friedel-Crafts catalyst component and the reaction agent, such as the acylating agent, the alkylating agent, the sulfonylating agent, and the like, react mole per mole, preferably at least an equimolar amount of the Friedel-Crafts catalyst component, as compared to the reaction agent, is added to the reaction zone. Preferably substantially equimolar amounts of the Friedel-Crafts catalyst component and the reaction agent are added to the reaction zone. Because of its superior activity, use of anhydrous sodium tetrachloroferrate as the Friedel-Crafts catalyst component is preferred. The reaction is conducted in a liquid phase which typically is an excess of the aromatic reactant when a liquid, or an inert solvent, to dissolve reactants that are in the solid state.

[0017] The anhydrous sodium tetrachloroferrate is preferably introduced into the acylation reaction zone in molten liquid form, but can be added as solids, for example as a slurry in one of the reactants or in a solvent. In either case, the anhydrous sodium tetrachloroferrate is preferably introduced into the reaction zone (i) during and/or after the introduction into the reaction zone of at least a portion of the aromatic reactant to be acylated and before commencing the introduction of the acylating agent into the reaction zone. After the reaction is completed and a reaction mixture has been formed, the workup and regeneration procedures as described above, and preferably also the recycle procedure as described above, are conducted.

[0018] Another embodiment of this invention is a process of regenerating anhydrous sodium tetrachloroferrate catalyst from an aqueous phase containing hydrated sodium tetrachloroferrate catalyst. This process comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c)

passing anhydrous hydrogen chloride into or through the mixture from (b) to thereby regenerate said anhydrous sodium tetrachloroferrate. Here again it is desirable, though usually not necessary, to pass a gaseous oxidant (*e.g.*, chlorine, oxygen, air, or the like) into or through the liquid melt after the anhydrous hydrogen chloride has been passed into or through the mixture.

[0019] Acylation processes in which an aromatic ketone is produced form still additional embodiments of this invention. The process comprises introducing into a reaction zone components comprised of (i) an acylatable aromatic compound, (ii) anhydrous sodium tetrachloroferrate or anhydrous lithium tetrachloroferrate, or both of them, and (iii) an acylating agent, and employing reaction conditions in said reaction zone that effect reaction such that an aromatic ketone is formed. Preferably (i), (ii), and (iii) are introduced into the reaction zone in the order named. Component (i) is preferably an acylatable mononuclear aromatic compound, an acylatable binuclear non-fused ring aromatic compound, or an acylatable binuclear fused ring aromatic compound. Preferred acylating agents are carboxylic acid anhydrides and acyl halides, especially acetic anhydride or acetyl chloride, or both of them. In the acylation of isobutylbenzene to form isobutylacetophenone, which is an intermediate for the production of ibuprofen, it is preferred to use a combination of acetic anhydride and acetyl chloride.

[0020] A still further embodiment of this invention is the provision as a new composition, of an equimolar complex between an acylating agent and sodium tetrachloroferrate, including for example a complex of this type where the acylating agent forming the complex is acetic anhydride or acetyl chloride, or is a mixture of complexes in which (i) one complex is an equimolar complex between acetic anhydride and sodium tetrachloroferrate and in which (ii) another complex is an equimolar complex between acetyl chloride and sodium tetrachloroferrate. These complexes can be formed by interaction between sodium tetrachloroferrate and an acylating agent such as an acyl chloride or bromide such as acetyl chloride or an acid anhydride such as acetic anhydride or propionic anhydride. Such complexes can be preformed by interaction between sodium tetrachloroferrate and one or more acylating agents typically in an inert organic solvent (*e.g.*, dichloromethane) with the application of heat if necessary, and used in an acylation reaction. Alternatively, they can be formed, and typically will be formed, *in situ* when conducting an acylation reaction. Figs. 1 and 2 provide infrared absorbance spectra of complexes of sodium tetrachloroferrate with

acetyl chloride and acetic anhydride, respectively. The lower portions of these figures give the infrared absorbance spectra of acetyl chloride and acetic anhydride, respectively, for comparison.

[0021] The following Examples are presented for purposes of illustration. They are not intended to limit the invention to only the operations described therein.

EXAMPLE 1

Acetylation of Isobutylbenzene: Preparation of Acetophenones

[0022] To a mixture of 10 mmol of NaFeCl₄ and 0.8g (10 mmol) of acetyl chloride in 8 mL of dichloromethane, 2.68g (20 mmol) of 4-isobutylbenzene (IBB) was added in drops with stirring under nitrogen. After completing the addition of IBB, the mixture was stirred for 30 minutes. The reaction mixture was then treated with 20 mL of water and extracted with 30 mL of ether. Analysis of the ether phase by GC showed 48.7% IBB, 0.60/a 3-isobutylacetophenone (m-IBAP), 46.9% 4-isobutylacetophenone (p-IBAP) and 2.3% diisobutylphenylethylene (DBPE).

EXAMPLE 2

Benzoylation of IBB: Preparation of Benzophenones

[0023] To a stirred slurry of 50 mmol of NaFeCl₄ in 13.4g (100 mmol) of IBB, a solution of 7.0g (50 mmol) of benzoyl chloride in 15g of dichloromethane was added dropwise under nitrogen. After the addition, the mixture was stirred at room temperature overnight. The mixture was treated with about 50 mL of water and 50 mL of ether. Ether phase was separated and analyzed by GC, NMR and GC/MS. The products were identified by GC/MS as the expected o-isobutylbenzophenone, m-isobutylbenzophenone and p-isobutylbenzophenone in the ratio of 0.8:0.4:98.8. NMR analysis showed the ratio of unreacted IBB to the products as 1:1 indicating quantitative conversion of benzoyl chloride.

EXAMPLE 3

Sulfonylation of IBB: Preparation of Sulfones

[0024] To a stirred slurry of 50 mmol of NaFeCl₄ in 13.4g (100 mmol) of IBB, 9.6g (50 mmol) of p-toluenesulfonyl chloride was added in small portions and heated to 70°C. After

stirring at 70 °C for 2.5 hours, the mixture was treated with 50 mL of water and 50 mL of ether. Ether phase was separated and analyzed by NMR, GC and GC/MS. NMR found the ratio of unreacted IBB to products as 1:1 indicating quantitative formation of the isomeric sulfones. GC/MS identified the products as the o-, m-, and p-isomers of the expected sulfone in the ratio of 15.2:6.2:78.6.

[0025] In the following sets of Examples 4-7 and 8-10, IBB was subjected to acetylation and NaFeCl₄ was recycled multiple times. It was found that high activity was maintained after such recycling. In fact, in these examples the activity with acetyl chloride was 74-83% compared to virgin catalyst. The activity with acetic anhydride was 99-100% compared to virgin catalyst.

EXAMPLE 4

Acetylation of IBB Using Acetyl Chloride and Virgin NaFeCl₄

[0026] NaCl (Aldrich, 45.6g) and FeCl₃ (Aldrich, 127g) were mixed and heated to 150 °C to form NaFeCl₄. The material was cooled to ambient temperature and the solids were ground to powder (olive colored) under N₂. A portion of the NaFeCl₄ (75g) was mixed with commercially produced IBB (90g) and acetyl chloride (AcCl; 27g) was added dropwise at 10-16 °C over 40 minutes. The reaction was allowed to ride at 5-10 °C for an additional 60 minutes. The reaction mixture was maintained at 5-10 °C for one hour and GC analysis showed 42% IBAP, 55% IBB, 3% DBPE.

EXAMPLE 5

Regeneration of NaFeCl₄ in Water: Recycle of the NaFeCl₄ in Acetylation

[0027] FeCl₃ (Aldrich, 135g) and NaCl (Aldrich, 49g) were mixed with aqueous HCl (2.7%, 229g). The mixture was heated to 110-120 °C and condensate was removed (150 g) by flash distillation. Dodecane (Aldrich 300g) was added and the resulting mixture was heated and the dodecane and water were removed at from 90 to 155 °C under 25-50 mmHg. The remaining solids (166 g) were ground by mortar and pestle under N₂.

[0028] A portion of the recovered NaFeCl₄ (61g) was mixed with commercially produced IBB (75g) and cooled to 5-10 °C. Commercially produced AcCl (22g) was added over 40

minutes at 5-10°C. The reaction mixture was stirred for an additional hour at 5-10°C. GC analysis showed 35% IBAP, 62% IBB, and 2% DBPE. The reaction mixture was added to ice water (260g) and the aqueous and organic layers were separated by decantation.

EXAMPLE 6

2nd Regeneration of NaFeCl₄ in Water: Recycle of the NaFeCl₄ in Acetylation

[0029] Hydrolysis solution from Example 5 and from two additional runs similar to Example 5 were combined and the water was removed by flash distillation at ambient temperature ranging from 100-130°C and at 20 mmHg over the range of from 70-200°C. The material was maintained at 200°C for 40 minutes. The remaining solids were ground via mortar and pestle under N₂.

[0030] A portion of the recovered NaFeCl₄ (49.4 g) and commercially produced IBB (60.4 g) were mixed and cooled to 5-10°C. To this was added commercially produced AcCl (17.5 g) over 30 minutes at 5-10°C. The reaction mixture was stirred at 10°C for an additional hour. GC analysis showed 33.5% IBAB, 61% IBB, and 3% DBPE. The above mixture was hydrolyzed with ice water (350g).

EXAMPLE 7

3rd Regeneration of NaFeCl₄ in Water: Recycle of the NaFeCl₄ in Acetylation

[0031] Hydrolysis solution from Example 6 was heated and the water was removed by flash distillation at ambient temperature ranging from 100-130°C and at ca. 2.67 kPa (20 mmHg), ranging from 70-200°C. The material was maintained at 200°C for 40 minutes. The remaining solids were ground via mortar and pestle under N₂.

[0032] The regenerated NaFeCl₄ (40g) was mixed with commercially produced IBB (49g) at 5-10°C and commercially produced AcCl (14.2g) was added over 30 minutes while maintaining a reaction temperature of 8-11°C. The reaction was stirred at 5-10°C for an additional hour. GC analysis showed 31% IBAP, 64.7% IBB, and 3% DBPE.

EXAMPLE 8*Acetylation of IBB Using Acetic Anhydride and Virgin NaFeCl₄*

[0033] NaFeCl₄ (319g) was prepared as in Example 4 except that it was heated to 220 °C for 2 hr. The NaFeCl₄ was mixed with commercially produced IBB (197g) and commercially produced acetic anhydride (Ac₂O; 97g) was added over 40 minutes at 25-30 °C. The reactor temperature was increased to 45 °C and maintained at that temperature for a total of 300 minutes. GC analysis showed 62.6% p-IBAP, 1.26% m-IBAP, and 35.6% IBB.

[0034] The reaction mixture was quenched with 800g of H₂O, 300g of hexanes, and 170g of 37% aqueous HCl and the layers were separated by decantation. The aqueous phase was washed with hexanes (203g).

EXAMPLE 9*Regeneration of NaFeCl₄ from Example 8: Recycle of the NaFeCl₄ in Acetylation*

[0035] The aqueous solution from Example 8 (1704 g) was heated and the water removed by flash distillation at ambient pressure from 106 to 112 °C. The remaining water was removed at ca. 13.33 kPa (100 mmHg) from 70-220 °C while bubbling anhydrous HCl (380 g) into the solution. The reaction was then heated to 250-280 °C under atmospheric pressure while bubbling anhydrous HCl (50g) into the solution.

[0036] The regenerated NaFeCl₄ (295g) was ground and mixed with commercially produced IBB (180.6g). Commercially produced Ac₂O (89.3g) was added over one hour increasing the reactor temperature from 25 to 45 °C. The reaction temperature was maintained at 45 °C for an additional 420 minutes. GC results showed 62.9% p-IBAP, 1.2% m-IBAP and 35.6% IBB.

[0037] The reaction mixture was quenched with 1090 H₂O, the layers were separated by decantation, and the aqueous phase was washed with hexanes (180 g).

EXAMPLE 10*2nd Regeneration of NaFeCl₄ from Example 8: Recycle of the NaFeCl₄ in Acetylation*

[0038] The aqueous solution in Example 9 (1424 g) and HCl (aqueous, 37%, 133g) were mixed and the water was removed by flash distillation at ambient pressure from 105 to

112 °C. The remaining water was removed at ca. 13.33 kPa (100 mmHg) from 70-220 °C while bubbling anhydrous HCl (250 g) into the solution. The reaction was then heated to 250-280 °C under atmospheric pressure while bubbling anhydrous HCl (150g) into the solution. The solids were ground (283g).

[0039] A portion of the regenerated NaFeCl₄ (265g) was mixed with commercially produced IBB (166g) and commercially produced Ac₂O (82.4g) were added over 86 minutes increasing the reactor temperature from 23 to 45 °C. The reaction was maintained at 45 °C for an additional 390 minutes at which time GC analysis showed 62.4% pIBAP, 1.26% m-IBAP, and 36.2% IBB.

[0040] In order to illustrate the superiority of anhydrous sodium tetrachloroferrate as a Friedel-Crafts catalyst as compared to a mixture of ferric chloride and sodium chloride, comparative experiments were carried out under substantially identical reaction conditions. These experiments are set forth in Example 11.

EXAMPLE 11

Part A - Use of Anhydrous Sodium Tetrachloroferrate as Friedel-Crafts Catalyst Component

[0041] To a slurry of 14.4 g (64 mmol) of NaFeCl₄ in 13.4 g (100 mmol) of 4-isobutylbenzene at 40 °C was added dropwise over a period of 1 hour while stirring the resultant mixture, a solution of 3.5 g (34 mmol) of acetic anhydride and 1.3 g (17 mmol) of acetyl chloride in 5 mL of dichloromethane. After the addition, stirring of the mixture at 40 °C was continued for 4 hours. The reaction mixture was then worked up by treating with about 50 g of ice and extracting the mixture with 50 mL of ether. The ether phase was analyzed by GC.

Part B -Use of Anhydrous Ferric Chloride and Sodium Chloride as Friedel-Crafts Catalyst Component

[0042] To a slurry of 3.8 g (65 mmol) of NaCl and 10.6 g (65 mmol) of anhydrous FeCl₃ in 13.4 g (100 mmol) of 4-isobutylbenzene was added dropwise over a period of 1 hour while stirring the resultant mixture, a solution of 3.5 g (34 mmol) of acetic anhydride and 1.3 g (17 mmol) of acetyl chloride in 5 mL of dichloromethane. After the addition, stirring of the

mixture at 40°C was continued for 4 hours. The reaction mixture was then worked up by treating with about 50 g of ice and extracting the mixture with 50 mL of ether. The ether phase was analyzed by GC.

Part C – Results

[0043] The results of the experiments of Part A and Part B are summarized in the Table.

TABLE

Components Formed	Part A Product Mixture	Part B Product Mixture
Isobutylbenzene	50.29%	51.20%
Chlorinated Isobutylbenzene	none detected	2.47%
m-IBAP	0.89%	0.74%
p-IBAP	48.69%	38.4%
Heavies	none detected	ca. 7%

[0044] It can be seen from the data in the Table that the process of this invention (Part A) gave a substantially superior result as compared to use of a catalyst system of the prior art (Part B).

[0045] Components referred to herein by chemical name or formula, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component or a solvent). Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense (*e.g.*, "comprises" or "is"), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0046] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting the description to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0047] Each and every patent or publication referred to in any portion of this specification is incorporated into this disclosure by reference, as if set forth herein.

[0048] This invention is susceptible to considerable variation within the spirit and scope of the appended claims.

CLAIMS

1. A process in which a Friedel-Crafts reaction is carried out in a reaction zone, the process comprising introducing anhydrous lithium tetrachloroferrate, anhydrous sodium tetrachloroferrate, or both, into the reaction zone.
2. A process according to claim 1 wherein the anhydrous sodium tetrachloroferrate is introduced into the reaction zone in molten liquid form, in the form of finely-divided solids, or in both such forms.
3. A process according to claim 2 wherein the anhydrous sodium tetrachloroferrate is introduced into the reaction zone in molten liquid form.
4. A process according to claim 1 wherein the anhydrous sodium tetrachloroferrate is introduced into the reaction zone during and/or after introduction into the reaction zone of an aromatic hydrocarbon solvent.
5. A process according to claim 1 wherein the Friedel-Crafts reaction comprises an acylation process in which an acylation reaction is carried out in the reaction zone and in which one of the reactants introduced into the reaction zone is an aromatic reactant to be acylated and another of the reactants introduced into the reaction zone is an acylating agent.
6. In a process in which a Friedel-Crafts reaction is carried out in a reaction zone using a Friedel-Crafts catalyst, the improvement which comprises introducing anhydrous lithium tetrachloroferrate, sodium tetrachloroferrate, or both of them into said reaction zone as a Friedel-Crafts catalyst component.
7. The improvement of Claim 6 wherein anhydrous sodium tetrachloroferrate is introduced into said reaction zone, and is introduced in molten liquid form, in the form of finely-divided solids, or in both such forms.
8. The improvement of Claim 7 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form.
9. The improvement of Claim 6 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone during and/or after the introduction into said reaction zone of aromatic hydrocarbon reactant.
10. The improvement of Claim 7 wherein after the reaction is completed and a reaction mixture has been formed, (i) subjecting the reaction mixture to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed, (ii) separating these liquid phases from each other, and (iii) removing all water including water of hydration from the

aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component.

11. The improvement of Claim 10 wherein (iii) is conducted by a procedure which comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c) passing anhydrous hydrogen chloride into or through the mixture from (b) to thereby regenerate said anhydrous sodium tetrachloroferrate.

12. The improvement of Claim 11 further comprising passing a gaseous oxidant into or through said mixture (i) before said anhydrous hydrogen chloride has been passed into or through said mixture, or (ii) at the same time said anhydrous hydrogen chloride is being passed into or through said mixture, or both of (i) and (ii).

13. The improvement of Claim 12 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

14. The improvement of Claim 11 wherein the temperature to which said mixture is raised is in the range of about 150°C to about 300°C at which water of hydration is removed from said mixture.

15. The improvement of Claim 11 wherein the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into said reaction zone as a Friedel-Crafts catalyst component.

16. The improvement of Claim 7 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form after the introduction into said reaction zone of aromatic hydrocarbon reactant; and wherein after the reaction is completed and a reaction mixture has been formed, conducting a procedure which comprises (i) subjecting the reaction mixture to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed, (ii) separating these liquid phases from each other, and (iii) removing all water including water of hydration from the aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component.

17. The improvement of Claim 16 wherein (iii) is conducted by a procedure which comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c) passing anhydrous hydrogen

chloride into or through mixture from (b) to thereby regenerate said anhydrous sodium tetrachloroferrate.

18. The improvement of Claim 17 further comprising passing a gaseous oxidant into or through said mixture (i) before said anhydrous hydrogen chloride has been passed into or through said mixture, or (ii) at the same time said anhydrous hydrogen chloride is being passed into or through said mixture, or both of (i) and (ii).

19. The improvement of Claim 18 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

20. The improvement of Claim 17 wherein the temperature to which said mixture is raised is in the range of about 150 to about 300 °C at which water of hydration is removed from said mixture.

21. The improvement of Claim 17 wherein the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into said reaction zone as a Friedel-Crafts catalyst component.

22. In a Friedel-Crafts acylation process in which an acylation reaction is carried out in a reaction zone using a Friedel-Crafts catalyst and in which one of the reactants introduced into the reaction zone is an aromatic reactant to be acylated, and another of the reactants introduced into the reaction zone is an acylating agent, the improvement which comprises introducing anhydrous sodium tetrachloroferrate into said reaction zone as a Friedel-Crafts catalyst component.

23. The improvement of Claim 22 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form.

24. The improvement of Claim 22 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in the form of finely-divided solids.

25. The improvement of Claim 22 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone (i) during and/or after the introduction into said reaction zone of at least a portion of said aromatic hydrocarbon reactant and before commencing the introduction of said acylating agent into said reaction zone.

26. The improvement of Claim 22 wherein after the reaction is completed and a reaction mixture has been formed, conducting a procedure which comprises (i) subjecting the reaction mixture to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed, (ii) separating these liquid phases from each other, and (iii) removing all water

including water of hydration from the aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component.

27. The improvement of Claim 26 wherein (iii) is conducted by a procedure which comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c) passing anhydrous hydrogen chloride into or through mixture from (b) to thereby regenerate said anhydrous sodium tetrachloroferrate.

28. The improvement of Claim 27 further comprising passing a gaseous oxidant into or through said mixture after said anhydrous hydrogen chloride has been passed into or through said mixture.

29. The improvement of Claim 28 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

30. The improvement of Claim 27 wherein the temperature to which said mixture is raised is in the range of about 150 to about 300 °C at which water of hydration is removed from said mixture.

31. The improvement of Claim 27 wherein the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into said reaction zone as a Friedel-Crafts catalyst component.

32. The improvement of Claim 27 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form after the introduction into said reaction zone of aromatic hydrocarbon reactant; and wherein after the reaction is completed and a reaction mixture has been formed, conducting a procedure which comprises (i) subjecting the reaction mixture to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed, (ii) separating these liquid phases from each other, and (iii) removing all water including water of hydration from the aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component.

33. The improvement of Claim 32 wherein (iii) is conducted by a procedure which comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove the water of hydration, and (c) passing anhydrous hydrogen chloride into or through mixture from (b) to thereby regenerate said anhydrous sodium tetrachloroferrate.

34. The improvement of Claim 33 further comprising passing a gaseous oxidant into or through said mixture after said anhydrous hydrogen chloride has been passed into or through said mixture.

35. The improvement of Claim 34 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

36. The improvement of Claim 33 wherein the temperature to which said mixture is raised is in the range of about 150 to about 300°C at which water of hydration is removed from said mixture.

37. The improvement of Claim 33 wherein the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into said reaction zone as a Friedel-Crafts catalyst component.

38. A process of regenerating anhydrous sodium tetrachloroferrate catalyst from an aqueous phase containing hydrated sodium tetrachloroferrate catalyst, which process comprises (a) distilling off distillable free water from the aqueous phase, (b) heating the resultant mixture to remove water of hydration, and (c) passing anhydrous hydrogen chloride into or through mixture from (b) to thereby regenerate anhydrous sodium tetrachloroferrate.

39. The improvement of Claim 38 further comprising passing a gaseous oxidant into or through said mixture after said anhydrous hydrogen chloride has been passed into or through said mixture.

40. The improvement of Claim 39 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

41. A process as in Claim 38 wherein the temperature to which said mixture is raised is in the range of about 150 to about 300°C at which water of hydration is removed from said mixture.

42. A process of producing an aromatic ketone, which process comprises introducing into a reaction zone components comprised of (i) an acylatable aromatic compound, (ii) anhydrous sodium tetrachloroferrate or anhydrous lithium tetrachloroferrate, or both of them, and (iii) an acylating agent, and employing reaction conditions in said reaction zone that effect reaction such that an aromatic ketone is formed.

43. A process as in Claim 42 wherein (i), (ii), and (iii) are introduced into said reaction zone in the order named.

44. A process as in Claim 42 wherein (ii) is anhydrous lithium tetrachloroferrate.

45. A process as in Claim 42 wherein (ii) is anhydrous sodium tetrachloroferrate.
46. A process as in Claim 45 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form, in the form of finely-divided solids, or in both such forms.
47. A process as in Claim 46 wherein the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form.
48. A process as in Claim 42 wherein (i) is an acylatable mononuclear aromatic compound, an acylatable binuclear non-fused ring aromatic compound, or an acylatable binuclear fused ring aromatic compound.
49. A process as in Claim 42 wherein (iii) is acetic anhydride, acetyl chloride, or both of them.
50. A process as in Claim 42 wherein (i) is an acylatable mononuclear aromatic compound, an acylatable binuclear non-fused ring aromatic compound, or an acylatable binuclear fused ring aromatic compound; wherein (ii) is anhydrous sodium tetrachloroferrate; wherein (i), (ii), and (iii) are introduced into said reaction zone in the order named; and wherein an inert solvent is also introduced into said reaction zone.
51. A process as in Claim 50 wherein (iii) is acetic anhydride, acetyl chloride, or both of them.
52. A process as in Claim 51 wherein (i) is an acylatable mononuclear aromatic compound and (iii) is both acetic anhydride and acetyl chloride.
53. A process as in Claim 52 wherein the acylatable mononuclear aromatic compound is isobutylbenzene and the anhydrous sodium tetrachloroferrate is introduced into said reaction zone in molten liquid form.
54. A process as in Claim 53 wherein the acetic anhydride and acetyl chloride are introduced into the reaction zone in amounts corresponding to a mole ratio in which more than 50 mole % is acetic anhydride.
55. A process as in Claim 54 wherein after said reaction is completed and a reaction mixture has been formed, conducting a procedure which comprises (a) subjecting the reaction mixture to hydrolytic conditions so that an aqueous phase and a liquid organic phase are formed, (b) separating these liquid phases from each other, and (c) removing all water including water of hydration from the aqueous phase, to thereby regenerate anhydrous sodium tetrachloroferrate suitable for reuse as a Friedel-Crafts catalyst component.

56. A process as in Claim 55 wherein (c) is conducted by a procedure which comprises (1) distilling off distillable free water from the aqueous phase, (2) heating the resultant mixture to remove the water of hydration, and (3) passing anhydrous hydrogen chloride into or through mixture from (2) to thereby regenerate said anhydrous sodium tetrachloroferrate.

57. The improvement of Claim 56 further comprising passing a gaseous oxidant into or through said mixture after said anhydrous hydrogen chloride has been passed into or through said mixture.

58. The improvement of Claim 57 wherein said gaseous oxidant comprises chlorine, oxygen, or air.

59. A process as in Claim 56 wherein the temperature to which said mixture is raised is in the range of about 150 to about 300 °C at which water of hydration is removed from said mixture.

60. A process as in Claim 59 wherein the regenerated anhydrous sodium tetrachloroferrate while in the form of a liquid is introduced into said reaction zone as at least a portion of (ii).

61. An equimolar complex between an acylating agent and sodium tetrachloroferrate.

62. A complex of Claim 61 wherein the acylating agent forming the complex is acetic anhydride.

63. A complex of Claim 61 wherein the acylating agent forming the complex is acetyl chloride.

64. A mixture of complexes in which (i) one complex is an equimolar complex between acidic anhydride and sodium tetrachloroferrate and in which (ii) another complex is an equimolar complex between acetyl chloride and sodium tetrachloroferrate.

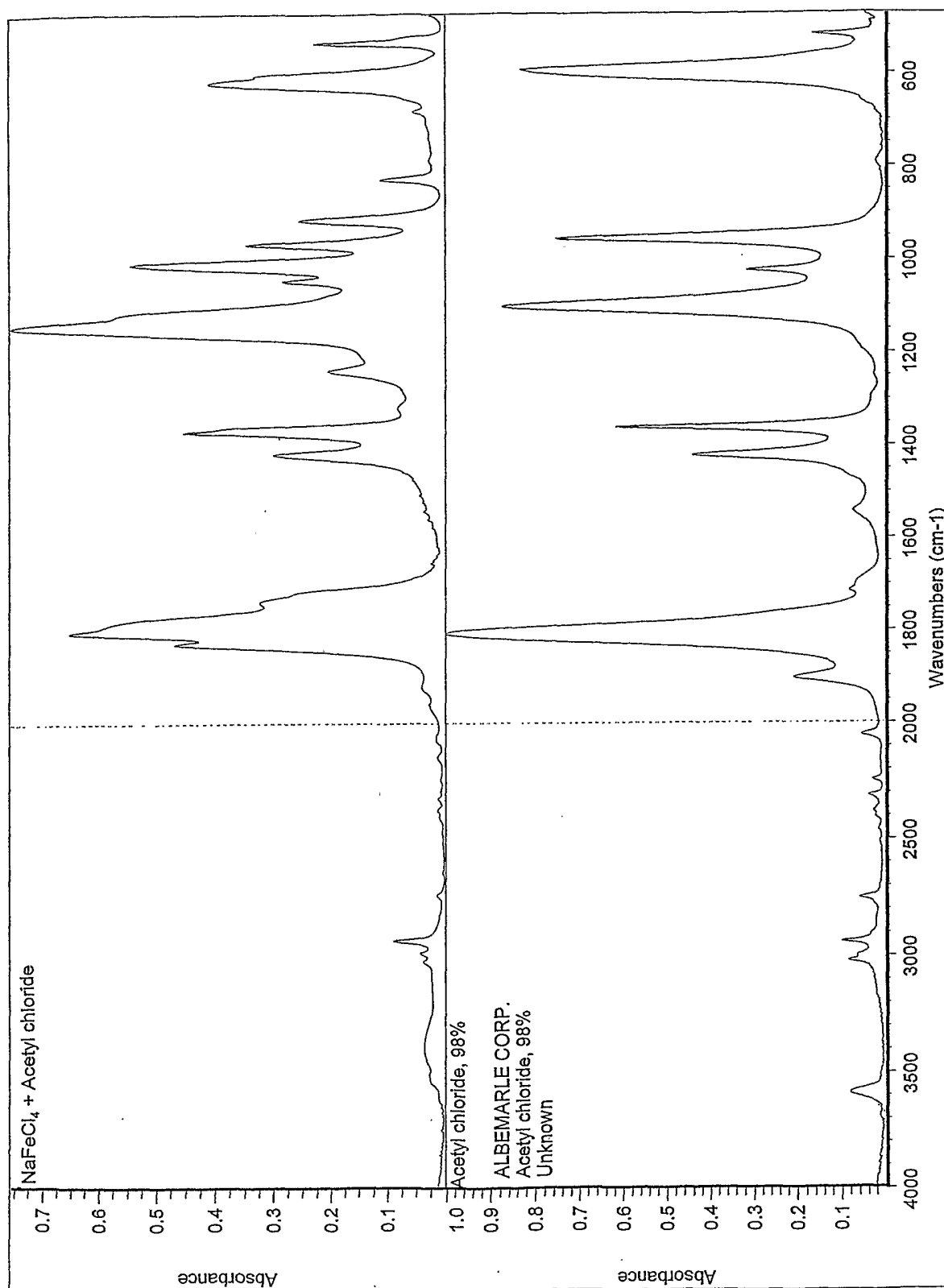


FIG. 1

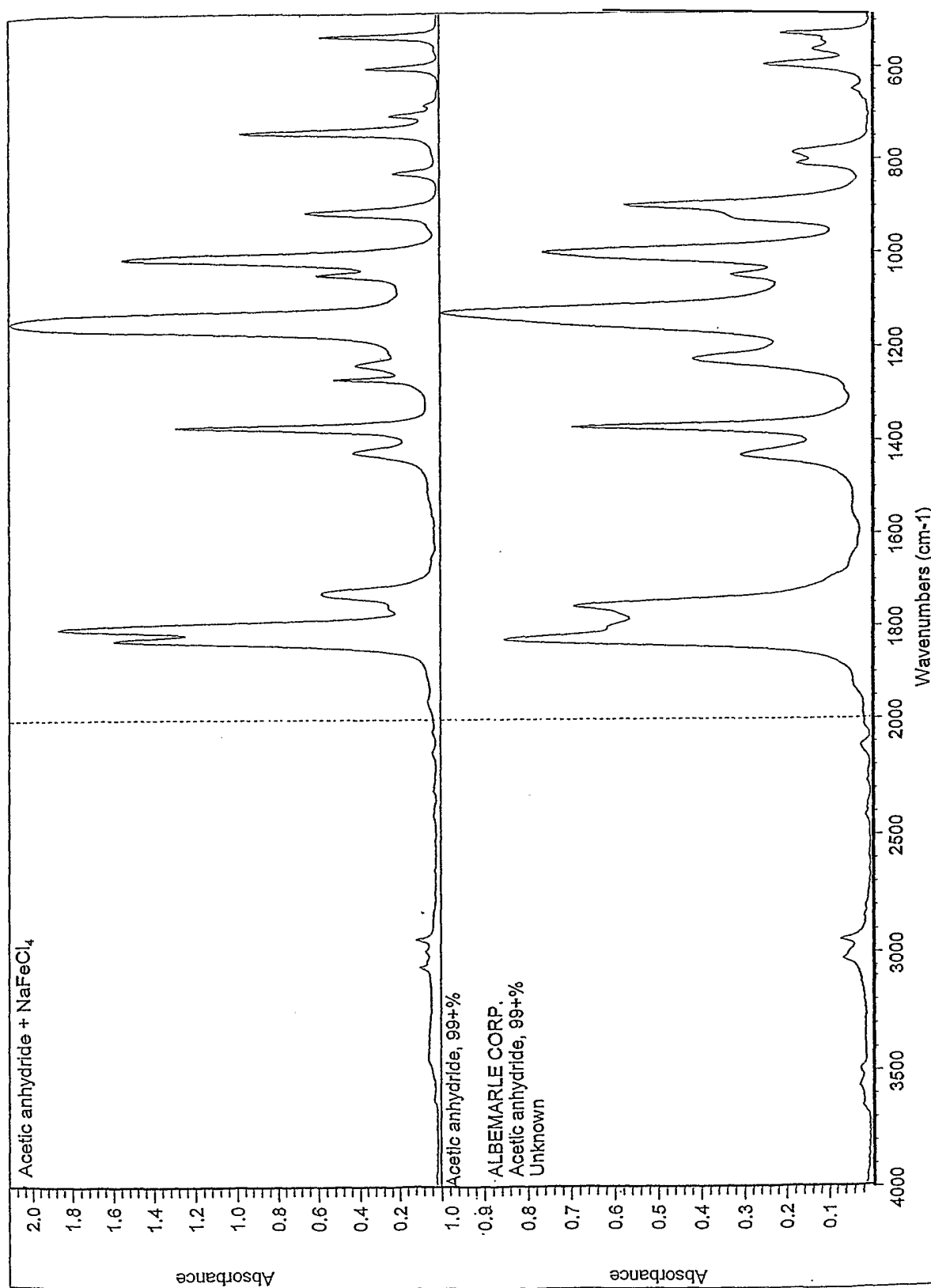


FIG. 2

INTERNATIONAL SEARCH REPORT

National Application No

US2004/027136

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G49/00 C07C45/46 B01J27/128 B01J27/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 872 174 A (BELLIS ET AL) 18 March 1975 (1975-03-18) column 4, line 28 - line 47; claims 1,3; example 4	38-41
Y	EP 0 493 023 A (NESTE OY; KEMIRA OY) 1 July 1992 (1992-07-01) page 2, line 14 - line 46; claims	38-41
Y	US 3 729 543 A (DUNN W, AU) 24 April 1973 (1973-04-24) cited in the application claims; example 4	38-41
A	EP 0 325 784 A (BASF AKTIENGESellschaft) 2 August 1989 (1989-08-02) examples claims 1,6; example 3	42-60
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

28 April 2005

Date of mailing of the international search report

06/05/2005

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ARATA K ET AL: "Friedel-Crafts acylation of toluene catalyzed by solid superacids" APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 197, no. 2, 1 May 2000 (2000-05-01), pages 213-219, XP004272315 ISSN: 0926-860X -----	

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Information on patent family members

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US2004/027136

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