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PROCESS FOR THE PREPARATION OF ALKYL TIN CHLORIDES

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This invention relates to the manufacture of organotin compounds and more particularly to alkyltin chlorides in which the alkyl radical contains at least three carbon atoms.

The present commercial method for preparing butyltin chlorides and other similar alkyltin halides is the Grignard process, i. e. reacting stannic chloride with butyl magnesium chloride to form tetrabutyltin, followed by reaction with additional stannic chloride to form the desired butyltin chlorides. The Grignard process has serious disadvantages and limitations in that the reaction is difficult to control on a large scale and is both laborious and time consuming. In addition, the process uses ether as a solvent, which material is difficult to handle and recover and increases the overall cost of manufacture of the butyltin chlorides.

It is believed that butyltin chlorides and other similar alkyl compounds containing at least 3 carbon atoms per organic radical have never been produced directly from tin or its alloys (J. Appl. Chem., June 4, 1954, p. 301). The use of tin alloys, e. g. sodium-tin alloys, produces primarily tetraalkyltins, when employed with methyl and ethyl chloride, rather than the desired alkyl tin chlorides (U. S. 1,639,947).

It is accordingly an object of this invention to provide an improved process for the manufacture of alkyltin chlorides in which the alkyl group contains at least three carbon atoms. Another object is to provide a process which will produce these compounds directly from metallic tin. Another object is to provide a process of the above type which gives a high conversion of tin to the desired alkyltin chlorides. Other objects and advantages of the present invention will become apparent as the description proceeds.

It has now been found that alkyltin chlorides can be produced in exceptional yield directly from tin and an alkyl chloride in which the alkyl group contains at least three carbon atoms if the tin is employed in the form of an alloy with sodium and the reaction is carried out at a temperature of at least 140° C. and under pressure conditions in which the alkyl chloride is maintained in a liquid state. Under these conditions, essentially complete reaction is effected, and a large fraction, generally above 50 percent, of the product is alkyltin chlorides. The remaining product is tetraalkyltin which can also be converted to the desired alkyltin chlorides, if desired, such as by reaction with stannic chloride. This process, in addition to unexpectedly producing the desired chloride compound, also results in exceptional and unexpectedly high tin conversions to the desired product.

More particularly, the present process comprises reacting an alloy of tin and sodium in granular or other reactive form with an alkyl chloride in a pressure reactor and at a temperature above about 140° C., preferably above about 160° C. The pressure of the reaction is generally controlled to contain the alkyl chloride in a liquid state. A high degree of agitation of the reactants is desired throughout the reaction. In general, the re-

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action requires from 2 to 20 hours to obtain complete or maximum conversion of the reactants, although only up to about 12 hours is normally necessary.

As pointed out above, the temperature of the reaction must be maintained above about 140° C. and preferably above about 160° C. While higher temperatures are suitable, up to the decomposition temperature of the product, they generally are unnecessary since the product distribution and the rate of reaction are surprisingly not materially effected by temperature changes. Accordingly, temperatures below about 200° C. are preferred. Temperatures of at least 140° C. appear to be very critical to effect reaction of the tin and alkyl chloride, but higher temperatures have no particular beneficial effect. With the lower alkyl chlorides, e. g. butyl chloride, reflux temperatures at atmospheric pressure do not effect any appreciable reaction.

The process can be carried out using a wide variety of alkyl chlorides having at least three carbon atoms. Typical examples of these alkyl chlorides are the monochlorides of propane, butane, pentane, hexane, heptane, octane, nonane and other hydrocarbons up to about 18 carbon atoms. In addition to the n-alkyl chlorides, the isomers of these compounds are also suitable, such as the secondary monochlorides and certain of the branched homologs.

The sodium-tin alloys can be made with varying concentrations of sodium, generally containing from 5 to 50 percent. Normally, it is preferred to employ one of the integral atomic ratios, including Na₄Sn, Na₂Sn, Na₄Sn₃, NaSn and NaSn₂. The preferred alloys contain between 10 and 30 percent by weight of sodium. The NaSn alloy is very desirable.

In some cases, it is desired to employ ternary alloys in which part of the sodium is replaced by another alkali or an alkaline earth metal. Suitable third components are lithium, potassium, barium, strontium and calcium. The third component can be employed up to about 25 percent of the sodium and preferably is used in a quantity between about 5 and 15 percent of the solution.

The use of a catalyst along with sodium-lead alloys is permissible and frequently desired. For this purpose, a relatively small quantity of a metal of group I of the periodic table, such as copper and silver, a metal of group II of the periodic table such as zinc, magnesium, mercury, and cadmium, or a metal of group III such as aluminum, can be used to increase the reactivity of the sodium-tin alloys. Normally, it is desired to use between 0.1 percent and 15 percent of the catalyst, based upon the total weight of the sodium-tin alloy. A more preferred concentration is up to about 5 percent.

The particle size of the alloy is not critical but in general should have an average diameter of not greater than about one-quarter inch. Normally, the smaller particles tend to react better. It is preferred to use a rather reactive alloy, that is, one made by a quick cooling technique. Suitable methods of solidifying the alloy are drum flaking, bed casting and the like. In some cases, particularly with the lower melting alloy compositions, it is desirable to quench the molten alloy directly in the alkyl chloride either prior to the reaction or directly within the reaction zone.

The reactants should be agitated during formation of the alkyltin chlorides. It is preferred to employ a rather vigorous agitation although the degree of agitation does not materially affect the yield or product distribution.

The reaction of this invention is highly exothermic and therefore suitable cooling should be provided to prevent an undue rise in temperature during the reaction, such as would effect decomposition of the reactants or the desired product. It is sometimes desirable to use a continuous reflux in the condenser to dissipate the heat of reaction,

In certain cases, it is preferred to add the alloy to the reaction mixture in small quantities, such as at spaced time intervals throughout the reaction, so as to minimize the heat load on the reactor. The alkyl chloride can also be added to the alloy and, when so operating, the reaction rate can be controlled by its rate of addition.

The alkyl chloride is generally employed in a substantial stoichiometric excess to the quantity of alloy. The larger quantities of alkyl chloride normally require somewhat higher temperature and/or longer reaction times to effect completion of the reaction. In general, the alkyl chloride is used in a total concentration of $\frac{1}{2}$ to 12 moles per mole of alloy, although it is preferred to use from $1\frac{1}{2}$ to 5 moles per mole of alloy.

After the reaction is complete, the liquid product containing the desired alkyltin chloride is separated from the solids by any suitable method, such as decantation, filtration, or centrifugation. Preferably, the solids are washed with a corresponding alkyl chloride or any other suitable organic solvent. Solvents are then removed from the solution so obtained, such as by distillation, leaving the desired alkyltin chloride product as a distillation bottoms or high boiling fraction. If desired, the product can be further purified by distillation, generally at reduced pressure, or can be fractionated to separate pure components.

Either the crude alkyltin chlorides, obtained by removal of solvent, or the purified components can thereafter be reacted with appropriate quantities of stannic chloride to produce higher chlorinated derivatives, the quantity of stannic chloride depending upon the product distribution and the particular alkyltin chlorides desired.

The tin can be recovered from the solids of the reaction product, following separation of the liquid alkyltin chloride product, in any suitable way. A preferred mode of operation comprises washing the solids with water to remove soluble salts, particularly sodium chloride, zinc chloride or other alkali or alkaline earth metal salts when such metals are used with the sodium tin alloy employed in the process. The washed solids are then contacted with a suitable reactant to condition the surface of the alloy or to agglomerate the same in order to prevent oxidation of the tin and to reduce the smelting temperature necessary for its ultimate recovery. The reactants suitable for this purpose are either a dilute basic or acidic solution. Typical basic solutions are aqueous sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate and other basic salts. These solutions can be employed in concentrations up to about 10 to 15 percent of alkali, a particularly effective range being 1 to 7 percent. Acidic reactants suitable for this purpose are the various mineral acids, including hydrochloric acid, sulfuric acid and phosphoric acid. Certain organic acids such as acetic acid have also been found suitable. Solutions of acidic salts can also be employed. In general aqueous acidic solutions are employed in a concentration of $\frac{1}{2}$ –5 percent, preferably 1–2½ percent. The quantity of reactant solution suitable for this purpose is not critical. Quantities from $\frac{1}{2}$ to 10 parts of reactant solution per part of solids has been found suitable.

Following the surface treatment, the solids can be again washed with water, if desired, to remove any additional quantities of water soluble impurities. Thereafter, the washed solids are then dried and smelted in a suitable melt pot. Any slag recovered in this process can also be reprocessed to recover its tin values.

By the above recovery process, 95–99 percent of the unreacted tin can normally be recovered for reuse in alloying with sodium for further reaction with alkyl chlorides in accordance with this invention.

The following examples illustrate the desirable features of the present invention but are not intended in any way to limit the scope of the same. In these examples, all quantities are given in parts by weight.

Example I

Into a closed pressure reactor were charged 52.2 parts of granulated monosodium tin alloy and 69.1 parts of n-butyl chloride. The reactor was closed and was agitated at a temperature of 145° to 155° C. for a period of 9¾ hours. The reactor was cooled and, upon filtering the slurry and washing the solids with benzene, there was obtained a light yellow product solution. On removal of benzene and excess butyl chloride by distillation, 37.2 parts of butyltin product were obtained. The product was composed of 14 weight percent tributyltin chloride and 86 weight percent tetrabutyltin, corresponding to a 30.9 weight percent tin conversion. The product distribution and yield were determined by chlorine and tin analyses.

Example II

Example I was repeated except a ternary alloy was employed consisting of monosodium tin and having about 8 weight percent of the sodium replaced by potassium. 46.4 parts of the alloy were employed with 60.2 parts of n-butyl chloride and the mixture was heated for four hours at 160° to 165° C. The product (24.6 parts) contained 53 weight percent of tributyltin chloride and 47 weight percent of tetrabutyltin, determined by chlorine and tin analyses.

Example III

A mixture of 48.6 parts of monosodium tin alloy (containing 2 percent zinc) and 62.2 parts n-butyl chloride was heated in an autoclave at a temperature of 160°–165° C. for four hours. Vigorous agitation was maintained during the reaction period. The reaction mixture was filtered and the solids washed well with n-butyl chloride to insure separation of all butyltin product.

The product solution was distilled and there was obtained, after removal of n-butyl chloride and small quantities of byproduct n-octane, 37.7 parts of butyltin compounds. The product, representing a 34.9 percent conversion of tin to butyltin compounds, was composed of 87 weight percent tributyltin chloride and 13 weight percent tetrabutyltin as determined by fractional distillation and by chlorine and tin analyses.

Solids from the reaction, composed of tin, zinc chloride and sodium chloride were washed well with water to remove sodium and zinc chlorides. This was followed by washing with a small quantity of dilute sodium hydroxide to agglomerate the finely divided tin particles and then with more water. The moist metal residue was added to a melt pot, heated gently at first until dry, and then heated at a higher temperature until molten, whereupon it was poured into molds. In this manner, 95–99 percent of the by-product tin was recovered for reuse.

Example IV

Example III was repeated except that the ratio of butyl chloride to sodium tin alloy was increased. In this example, 26 parts of monosodium tin alloy (containing 2 percent zinc) and 50 parts n-butyl chloride were heated at a temperature of 159°–161° C. for 12 hours. 15.8 parts of product were obtained containing 83 weight percent tributyltin chloride and 17 weight percent tetrabutyltin, based on chlorine analysis. In this example, 22.5 percent of the tin was converted to alkylated product.

Example V

The following example illustrates the method by which the product mixtures of this invention consisting of tetraalkyltin and trialkyltin chloride can be converted to dialkyltin dichloride by reaction with stannic chloride.

A mixture of 25 parts of butyltin chloride product (consisting of 92.5 weight percent tributyltin chloride and 7.5 weight percent tetrabutyltin) and 9–26 parts of anhydrous stannic chloride was heated under a dry, inert atmosphere at 200°–207° C. for one hour. The molten product from the reaction was distilled and there was obtained 32 parts

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of dibutyltin dichloride boiling at 140°–143° C. (10 mm. Hg pressure) and having a solidification temperature of 38.5° C. Yield in the reaction was 89.7 percent.

Similar results were obtained when other alkyltin products of this invention were heated with stannic chloride. Depending on the amount of stannic chloride which was used, the product obtained was substantially trialkyltin chloride, dialkyltin dichloride, or alkyltin trichloride.

Example VI

To an autoclave were added 43.2 parts of monosodium tin alloy (containing 2 percent zinc) and 46.8 parts of n-propyl chloride. The sealed autoclave was agitated and heated at 140°–145° C. for four hours. Separation of the product as in Example III yielded 16 parts of n-propyl tin compounds, comprising an 18.2 percent conversion of tin to propyltin product. The product mixture was composed of 67.5 weight percent tripropyltin chloride and 32.5 weight percent tetrapropyltin.

Unreacted tin was recovered from the solids as described in Example III.

Example VII

A reaction carried out with 45 parts monosodium tin alloy (containing 2 percent zinc) and 66.4 parts n-amyl chloride by the procedure described in Example III (heating four hours at 162° C.) yielded 31.8 parts of amyl tin compounds. Tin conversion was 27.2 percent and the mixture contained 95.3 weight percent triamyl tin chloride and 4.7 weight percent tetraamyl tin.

Unreacted tin was recovered from the solids by the procedure outlined in Example III.

Example VIII

The following example illustrates the critical temperature requirements for the process of this invention. This example was carried out at a temperature below 140° C. and resulted in essentially no tetrabutyltin or butyltin chlorides.

When 38.6 parts of monosodium tin (with 2 percent zinc added) were heated with 49.8 parts n-butyl chloride in a pressure autoclave for 8 hours at 94° C., distillation of the product solution did not yield any butyltin compound but the entire solution distilled in the range of benzene and butyl chloride.

Similar results were obtained using essentially the same reactants when carrying out tests at temperatures varying

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from room temperature up to 130° C. In these tests, large quantities of unreacted sodium and only minor quantities, if any, of the desired organotin products were obtained.

When the above examples are repeated using higher alkyl chlorides such as octyl chloride, decyl chloride, tetradecyl chloride, and octadecyl chloride, similar results are obtained. Also, highly desirable alkyltin chloride products are obtained using other sodium tin alloys, such as Na₄Sn and Na₂Sn or ternary alloys containing magnesium, cadmium and aluminum. The latter third components are employed in concentrations of 2–25 weight percent with similar results.

The alkyltin chlorides made by this invention are highly desirable for use as intermediates in making stabilizers for plastics, such as vinyl chloride, and are also useful as intermediates in the production of other valuable chemicals.

We claim:

1. In the process for producing alkyl tin halides by reacting a sodium-tin alloy with an alkyl halide, the improvement by which the alkyl halide is the chloride of an alkyl group having at least three and no more than eighteen carbons, and the reaction is carried out at a temperature at least as high as 140° C. but below the decomposition temperature of the desired product and at a pressure sufficient to maintain the alkyl chloride in a liquid state.

2. The combination of claim 1 in which the alkyl chloride is n-butyl chloride, and the reaction temperature is between 160 and 200° C.

3. The combination of claim 1 further defined in that the alkyl chloride is n-butyl chloride.

4. The combination of claim 1 further defined in that the temperature is between 160° and 200° C.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 40, for "solution" read -- sodium --.

Signed and sealed this 6th day of January 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents