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PROCESS FOR THE PRODUCTION OF COMPLEX ALUMINUM ALKYL COMPOUNDS AND, IF DESIRED, THE RECOVERY OF HIGHER ALPHA OLEFINS THEREFROM

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This invention relates to a process for the production of complex aluminum alkyl compounds and, if desired, the recovery of higher alpha olefins therefrom.

It is known that ethylene can be added to aluminum alkyls. In this reaction, the ethylene is incorporated in the aluminum compound, which results in the formation of aluminum alkyl compounds having higher alkyl radicals than those of the starting compound. This addition of ethylene to aluminum alkyl compounds having lower alkyl groups, e.g. ethyl, propyl or butyl, to form higher aluminum alkyl compounds is referred to as the growth reaction. Several possibilities are available to carry out this growth reaction. According to an earlier suggestion, it is effected at relatively low temperatures of about 90 to about 120° C. and preferably under pressure, the reaction rate being relatively low in this case so that an extended reaction time is required for an adequate growth. It may, therefore, be preferable to operate according to a later proposal (U.S. patent application No. 72,056, now Patent No. 3,207,771). According to this later process, higher temperatures ranging particularly between 120° and 200° C. are used. To avoid undesirable side reactions at these elevated temperatures, the residence time of the reaction mixture in the reaction space is reduced, residence times from 1 to 20 minutes being preferably used. This process may also be carried out continuously. In this case, flow velocities of the ethylene stream of 1 to 50 m./minute through the reactor are maintained with the reaction space having a diameter up to 3 centimeters and a very great length relative to this diameter. The ethylene stream is preferably recycled and the growth product separated after the passage through the reaction space.

Other variations of this growth reaction (U.S. applications Nos. 792,598, 795,901, 13,715, now Patent Nos. 3,066,162, 3,013,043, 3,074,987, respectively) involve reacting a mixture of different aluminum alkyl compounds. These mixtures contain compounds of the AlR_2X type or the corresponding complex salts of these aluminum compounds with potassium chloride or potassium bromide on the one hand and always some additional free aluminum trialkyl on the other. In case of this variant of the process, the additional amount present of free aluminum trialkyl first undergoes the growth reaction and then exchanges for the compounds of the AlR_2X type so that these finally also participate in the growth.

Furthermore, as is known, alpha olefins having more than 3 carbon atoms can be produced by displacing from aluminum alkyl compounds having higher alkyl groups said higher alkyl groups under the action of ethylene or other lower alpha olefins such as propylene or alpha butylene, which results in the formation of the corresponding alpha olefins. This reaction is referred to as the displacement reaction and is generally carried out under reaction conditions different from those of the growth reaction to re-form aluminum triethyl, tripropyl or the like.

It is also possible to carry out the growth and displacement in the form of a cyclic process in such a manner that always the lower aluminum alkyl compound obtained

by displacement is again charged to the growth reaction so that the aluminum compound is recycled while higher alpha olefins are simultaneously formed from ethylene. If, in this case, aluminum alkyl compounds having an alkyl radical of an even carbon number (ethyl, butyl and so on) are the starting material, even-numbered higher alpha olefins are obtained. If, however, the growth reaction is started with an aluminum alkyl compounds which has an odd number of carbon atoms in the alkyl radical (particularly aluminum tripropyl), then it is possible to produce any alpha olefin of the odd-numbered series.

The invention relates to a new variation of such a growth reaction and of the displacement reaction described. In particular, it is possible in accordance with the invention to carry out the combination of growth and displacement under novel and simplified process conditions.

It is an object of this invention to provide a process for the production of complex aluminum alkyl compounds by treating aluminum alkyl complex compounds having lower alkyl radicals with ethylene at elevated temperatures thereby growing the lower alkyl radicals to form higher alkyl radicals and, if desired, subsequently recovering higher alpha olefins by displacing said higher alkyl radicals from the resultant complex compounds by means of lower olefins, the displacement being likewise effected at elevated temperatures and the process being characterized in that complex compounds of aluminum trialkyl with alkali azide, alkali cyanide and/or potassium fluoride are used as the starting material.

Thus, in accordance with the invention, complex compounds of aluminum trialkyls are used for the first time as the starting material in the growth and displacement reaction, which compounds have not been disclosed up to the present for use in this process.

A great number of complex compounds of aluminum trialkyl are known. The group of aluminum alkyl complexes selected in accordance with the invention is distinguished by the fact that the individual members, with respect to the growth and displacement reaction of the invention, show a behavior which is identical or at least very similar so that it is possible to carry out the process of the invention advantageously with any complex compound of the group described of aluminum alkyl compounds.

The process of the invention is based on the following conception:

All of the previous growth and displacement reactions start either from an aluminum trialkyl or from a reaction mixture which invariably contains a certain amount of additional free aluminum trialkyl together, as the case may be, with other aluminum alkyl or aluminum alkyl complex compounds. According to the problem to be solved by the invention, reaction mixtures which, under normal conditions, need not contain additional free aluminum trialkyl were to be used as the starting material. The process of the invention is rather distinguished by the fact that one of the aluminum complex compounds described or mixtures of such compounds can be charged as the sole aluminum compound to both the growth and the displacement reactions while nevertheless obtaining satisfactory conversion.

The uniform behavior of the aluminum alkyl complex compounds of the invention is probably due to the fact that all of these compounds described are thermally cleaved to a certain extent at the elevated reaction temperature of the growth or the displacement so that a limited amount of free aluminum trialkyl is formed. However, this free aluminum trialkyl is only present at the increased reaction temperatures. Upon cooling of the

reaction mixture, the aluminum alkyl complex which is stable at normal temperature is re-formed so that a reaction mixture free from uncomplexed aluminum trialkyl is present both before and after the performance of the reaction (growth and displacement). Thus, the essential conditions for the aluminum alkyl complexes to be charged to the process of the invention are as follows: The complex aluminum alkyl compounds should undergo sufficient thermal dissociation at the elevated reaction temperatures that the lower complex compounds can be smoothly converted with ethylene into the higher complex aluminum alkyl compounds during the growth while the higher alpha olefins are smoothly split off during the displacement. At the same time, the complex compounds should be stable at relatively high temperatures so that the non-dissociated complex compound is re-formed after the particular conversion. Furthermore, for reasons of process engineering, the complex compounds should have a melting point which is as low as possible. Finally, as will be discussed later, the process can be carried out with particularly great advantage if the lower complex aluminum alkyl are highly insoluble in unsaturated or saturated hydrocarbons. Any aluminum alkyl complex meeting with these requirements can be used advantageously in the process of the invention and it is just the group of compounds claimed which comply with these conditions.

The advantages which can be obtained by means of the new process are numerous. First of all, handling of the complex aluminum ethyl compounds used in accordance with the invention is less dangerous than that of the highly active and inflammable free aluminum triethyl. Furthermore, the compounds of the invention are slower to react than free aluminum trialkyl. Therefore, for example, higher reaction temperatures can generally be used in the growth reaction as compared with the use of free aluminum trialkyl. This suppresses undesirable side reactions while simultaneously increasing the reaction rate. The process of the invention further avoids accumulation of heat and superheating which may easily result in an undesirable course of the growth reaction. It is essential for the displacement reaction that no free aluminum trialkyl is contained in the reaction mixture. The resultant mixture, upon cooling, immediately separates into two layers, the lower layer comprising the complex aluminum alkyl compound and the supernatant layer comprising the higher alpha olefins produced. Thus, the invention eliminates the expensive operation of a distillation for the separation of alpha olefins and uncomplexed aluminum trialkyl. The process of the invention is quite particularly useful in cases where the boiling ranges of the free aluminum trialkyl and of the alpha olefins produced are so close together that these compounds cannot be separated by distillation. Up to the present, it was the processing of such a reaction mixture which was connected with greatest difficulties. In the process of the invention, the very important C_8 to C_{14} olefins, for example, can be separated in a simple manner, e.g. by decantation, from the aluminum complex compound serving as a reaction aid.

The azides used in the process of the invention are complex compounds of the type $MeN_3.xAlR_3$ wherein Me is an alkali metal and R is an alkyl radical. The azides which can be used are described, for example, in U.S. patent application No. 95,473, now abandoned. On principle, any alkali metal may be incorporated in the complex, however, the use of the corresponding lithium compounds is not preferred. These lithium aluminum alkyl complexes are relatively instable to the other corresponding azide complexes and are apt to explosion-like decomposition.

The cyanide complex compounds used in accordance with the invention are produced by reacting alkali cyanide with aluminum trialkyl. It has been found when using these cyanide complexes that so-called mixed complexes can be employed with particular advantage. A mixture of different alkali metals is present in these mixed complexes. A mixture of sodium and potassium complexes, particularly in a molar ratio of about 1:1, is preferably used. These mixed complexes are distinguished by a particularly favorable position of the melting point and by a particularly high reactivity in the growth and displacement reactions. Therefore, their use is particularly preferred in the process of the invention.

Finally, it is possible in accordance with the invention to start from complexes of the general formula $KF.xAlR_3$ wherein x is a number from 1 to 2. These complexes also comply with the requirements to be met for carrying out the reaction.

On principle, the process of the invention may, of course, also be carried out in the presence of additional free aluminum trialkyl. In doing so, advantages are still obtained over prior art processes. Nevertheless, it is particularly preferred in accordance with the invention as mentioned above, to operate in the absence of additional free aluminum trialkyl.

The growth reaction, corresponding to the previously described processes, is effected at elevated ethylene pressures, the pressures used being especially above 20 atmospheres and preferably above 50 atmospheres. There is substantially no upper limit to the pressure, it being possible, for example, to operate at 200 or more atmospheres of ethylene pressure. As to the reaction temperatures, there are definite optimum temperature ranges for the particular types of complex compounds used in accordance with the invention. It is preferred when working with alkali cyanides to operate in the temperature range of 140° to 200° C. and preferably in the range of 150–180° C. The corresponding ranges for the potassium fluoride complex compounds are 170–220° C. and 180–210° C. Relatively most sensitive are the azide complexes. These may split off nitrogen at excessively high reaction temperatures thereby impairing a cyclic process with repeated use of the azide complex. To eliminate this risk, it is preferred in accordance with the invention to use temperatures of between 90° and 150° C. and particularly between 100° and 120° C. when using these azide complexes.

As already mentioned, the complex compounds of the invention exhibit the advantage over the free aluminum triakyl that they are less apt to side reactions. Therefore, within the high temperature ranges mentioned above, the growth reaction is easier controlled than a corresponding reaction carried out with the use of free aluminum trialkyl. Thus, in accordance with the invention, the earlier form of growth may be applied while using longer reaction periods. However, it is also possible, for example, to use the more recent embodiment of the growth reaction described in U.S. patent application No. 72,056. In this case, the aluminum compound is, for example, recycled at the elevated reaction temperatures through a helically wound tubular reactor together with the ethylene stream.

It may be pointed out that, of course, the corresponding aluminum alkyl hydride or aluminum hydride complexes may be used in place of the aluminum trialkyl complexes in the first growth step in accordance with the invention. These are immediately converted together with the ethylene present into the corresponding aluminum triethyl complexes and then intervene in the reaction of the invention in the manner described above.

The displacement of the grown higher alpha olefins from the aluminum complex compound by means of lower olefins may be effected by any method described. Thus, for example, it is possible to operate in the presence of nickel catalysts corresponding to the process of German Patent No. 1,034,169. However, it is particularly preferred to use the purely thermal displacement according to Belgian Patent No. 594,803. In this case, the grown complex compound is treated with the lower olefin used as the displacing agent at temperatures of between 200°

and 340° C. and preferably between 280° and 320° C. and residence times of between 0.1 and 10 seconds and preferably of between 0.5 and 1 second, it being necessary to reduce the residence time of the reaction mixture in the reactor as the reaction temperature increases. In the displacement, it is again preferred to pass the reaction mixture through an elongated, e.g. helically wound tubular reactor and to recycle it until an adequate conversion has occurred. In this case, the higher alpha olefins formed can be immediately separated after the passage through the reactor and cooling of the reaction mixture. Preferred are relatively low olefin pressures in the displacement reaction. Thus, pressures of below about 15 atmospheres and particularly pressures of about 2 to about 10 atmospheres are preferably used. The preferred olefins for the displacement include ethylene, propylene, and butylene.

Example 1

220 gms. of a sodium cyanide-aluminum triethyl complex having the approximate composition

$$NaCn.1.5Al(C_2H_5)_3$$

were melted and sprayed by means of a mixing nozzle into an ethylene current in a tubular reactor having a diameter of 2 centimeters and heated to 180° C. The operating pressure was 200 atmospheres. The flow velocity was set at 5 meters/minute and the effluent from the reactor was recycled through a separator to the injection pump. After several cycles, the reactor was shut down and the product discharged. After degassing of the liquid growth product to remove lower olefins, a sample was subjected to alcoholysis. In doing so, a small amount of volatile hydrocarbons and a hydrocarbon layer was obtained which was analyzed after washing and drying. It contained little olefins and substantially consisted of even-numbered unbranched saturated hydrocarbons having a distribution which corresponded to an average chain length of $Al—(C_2H_4)_3—C_2H_5$. In the second stage, the homogeneous growth product was injected together with ethylene through a mixing member into a second tubular reactor of a type described in Belgian Patent No. 594,803. This reactor was heated to 300° C. and then operated at an ethylene pressure of 9 atmospheres and a residence time of 0.8 second. The displacement product leaving the reactor can be withdrawn at the liquid separator. It is then subjected to a flash distillation to remove the produced lower olefins up to and including C_6 and then flows to a continuous phase separator. The upper phase obtained therefrom consists of more than 97% of alpha olefins having an aluminum value of 0.1%. These olefins weighing about 300 gms. were subsequently separated into the individual fractions by distillation. The lower phase consisting of the $NaCN.1.5Al(C_2H_5)_3$ complex is passed into a washing vessel where it is freed from traces of olefins by means of hexane under an argon atmosphere. The lower phase resulting from this hexane washing step may directly be passed to the growth reactor.

Example 2

265 gms. of a lower sodium azide-aluminum triethyl complex having the approximate composition

$$NaN_3.1.7Al(C_2H_5)_3$$

are filled into a 1 liter autoclave and heated to 110° C. Ethylene is introduced from a stock bottle under a pressure of 90 atmospheres and the growth reaction is carried out under a constant ethylene pressure. After 5 hours, the supply of ethylene is discontinued and the autoclave pressure released. The amount of ethylene consumed in this time was 390 gms. The somewhat viscous growth product which is also liquid at room temperature is discharged and freed from dissolved lower olefins under a water jet vacuum at a bath temperature of 80° C. In doing so, 26 gms. of a liquid predominantly consisting of alpha unbranched olefins are condensed in the cooled receiver.

Part of the product is carefully hydrolyzed with dilute hydrochloric acid while cooling and the upper hydrocarbon layer is washed, dried and analyzed by gas chromatography which gives the following composition:

	Percent
Hexane	27.9
Octane	30.4
Decane	17.7
Dodecane	14.5
Tetradecane	6.9
Hexadecane	3.0

Another portion of the growth product is mixed with 0.01% by weight of nickel in the form of nickel acetyl acetonate and then filled into an autoclave. Ethylene is introduced until a pressure of 80 atmospheres is reached and the autoclave is shaken for several hours at room temperature without heating whereupon the pressure decreases rapidly. The product is subsequently removed from the autoclave after having blown off the ethylene and the upper layer of the two-phase mixture is immediately siphoned off. The hydrocarbons are analyzed after washing with dilute acid to remove traces of aluminum-organic compound. It is demonstrated by analysis that this upper layer consists of pure alpha olefins, the distribution corresponding to that of the saturated hydrocarbons from the hydrolysis. The lower phase consists of the lower aluminum triethyl complex of sodium azide.

Example 3

300 gms. of a mixed cyanide complex having the formula $MeCN.2Al(C_3H_7)_3$ wherein Me is 50% sodium and 50% potassium are injected with ethylene into a tubular reactor of the type described in U.S. patent application No. 72,056 and the growth reaction is effected at a temperature of 200° C., a flow velocity of 7 meters/minute and an ethylene pressure of 250 atm. The growth product obtained within one hour is subjected to the displacement reaction with propylene in a second reactor. The growth product is injected into the preheated reactor at an operating pressure of 9 atmospheres, the residence time being 0.6 second. The displacement product obtained separates into two layers after pressure release. The olefins up to and including C_{10} are removed by flash distillation. The remaining two-phase mixture is separated in a separator. The upper layer consists of odd-numbered alpha olefins having a degree of purity above 92% and an aluminum content below 0.3%. Only traces of non-terminal olefins can be detected. The lower layer is directly passed to the growth reactor without being further washed.

Example 4

286 gms. of a potassium fluoride complex having the formula $KF.1.9Al(C_2H_5)_3$ was melted and reacted with ethylene in the same apparatus as described in Examples 1 and 3. The ethylene pressure was 150 atmospheres, the gas flow velocity 18 meters/minute and the reaction temperature 240° C. After recycling for two hours, the reactor contents were removed. About 10% by weight of the total product could be distilled off as olefins of C_4 to C_{10}. The growth product was then treated with ethylene in a displacement reactor as mentioned in Example 1, the reaction temperature being 360° C., the residence time 0.4 second and the ethylene pressure 12 atmospheres. After removal from the reactor, the displacement product was freed from lower olefins by evacuation. The upper phase of the two-phase system was separated, washed with dilute acid to destroy traces of aluminum-organic compound, dried and subsequently fractionated into the different carbon number ranges. The purity of the olefins was above 95%. The lower layer contained only

traces of dissolved olefins. It was found by alcoholysis that the alkyl groups bonded to aluminum consisted of more than 92% ethyl groups and about 6% butyl groups. The complex was then returned to the growth reactor.

What is claimed is:

1. A process for the production of complex compounds which comprises reacting a complex of aluminum trialkyl with a member selected from the group consisting of alkali metal azide, alkali metal cyanide and potassium fluoride with ethylene at an elevated temperature under conditions conducive to chain growth of said ethylene on to said aluminum trialkyl complex and recovering the aluminum trialkyl complex compound having higher alkyl radicals thereby formed.

2. Process according to claim **1** wherein said aluminum trialkyl complex is a complex of aluminum trialkyl with alkali metal cyanide in which a mixture of different alkali metals is contained.

3. Process according to claim **2** wherein said complex contains a mixture of sodium and potassium.

4. Process according to claim **2** wherein said complex contains two different alkali metals in a molar ratio of 1:1.

5. Process according to claim **1** wherein said reaction is effected at an ethylene pressure of at least 20 atmospheres.

6. Process according to claim **5** wherein said reaction is effected at ethylene pressures above 50 atmospheres.

7. Process according to claim **1** wherein said reaction is effected at temperatures above 100° C.

8. Process according to claim **7** wherein said complex is a complex of an alkali metal cyanide with aluminum trialkyl and said reaction is effected at a temperature between 140 and 200° C.

9. Process according to claim **8** wherein said reaction is effected at a temperature of between 150 and 180° C.

10. Process according to claim **7** wherein said complex is a complex of potassium fluoride and aluminum trialkyl and said reaction is effected at a temperature between 170 and 220° C.

11. Process according to claim **10** wherein said reaction is effected between 180 and 210° C.

12. Process according to claim **1** wherein said complex compound is a complex of an alkali metal azide and aluminum trialkyl and said reaction is effected at a temperature between 90 and 150° C.

13. Process according to claim **12** wherein said reaction is effected at a temperature of between 100 and 120° C.

14. Process according to claim **1** wherein said reaction is effected using relatively short residence times.

15. Process according to claim **14** wherein said reaction is effected with a residence time of about 20 minutes.

16. A process for the production of olefins which comprises reacting a complex of aluminum trialkyl with a member selected from the group consisting of alkali metal azide, alkali metal cyanide and potassium fluoride with ethylene at an elevated temperature under conditions conducive to chain growth of said ethylene on to said aluminum trialkyl complex, thereafter reacting said aluminum trialkyl complex compound formed with a lower olefin at an elevated temperature under conditions conducive to displacement of said higher alkyl radicals by said lower olefin from said aluminum trialkyl complex compound and separating said higher olefin from said complex compound.

17. Process according to claim **16** wherein slightly elevated olefin pressures are used in said displacement reaction.

18. Process according to claim **17** wherein olefin pressures of below 15 atmospheres are used in said displacement reaction.

19. Process according to claim **16** wherein said displacement reaction is effected at a temperature of between 200 and 350° C. and a residence time of up to 10 seconds.

20. Process according to claim **19** wherein said displacement reaction is effected at a temperature of between 280 and 320° C. and with a residence time of 0.5 and 1 second.

21. Process according to claim **16** wherein the aluminum trialkyl complex formed in said displacement reaction is recycled to the growth reaction step.

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TOBIAS E. LEVOW, *Primary Examiner.*