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LIQUID AMMONIA PROCESS FOR FORMING HYDROCARBONLEAD COMPOUNDS

Alfred J. Kolka, Birmingham, and Ivar T. Krohn, Royal Oak, Mich., assignors to Ethyl Corporation, New York, N. Y., a corporation of Delaware

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This invention relates to the manufacture of alkyl and aryllead compounds.

The most important of the alkyllead compounds is tetraethyllead which is made commercially by reacting monosodium lead alloy with an ethylating agent such as ethyl chloride. This reaction is relatively slow, needing 2 to 6 hours for completion, requires a temperature between 60° C., and 85° C., and requires the use of the lead alloyed with a reducing metal such as sodium, the alloying operation being an expensive one. Furthermore, the yield of tetraethyllead is limited to about 22 per cent based on the lead charged.

It is an object of our invention to provide a process which does not require an alloy of lead, although such may be used, which has the advantage of using low temperature in its operation, and in which the reaction is complete within a relatively short time.

The above objects are accomplished by treating a solution of lead and an alkali or alkaline earth metal in liquid ammonia with an alkylating agent. Various alkali and alkaline earth metals which are soluble in liquid ammonia can be successfully employed among which are sodium, potassium, and calcium.

In a preferred embodiment of our invention, an alkali or an alkaline earth metal is first dissolved in liquid ammonia. Lead is then dissolved in the solution, followed by addition of the alkylating agent. While the use of free lead is preferred, because the alloying step is eliminated, any of the lead alloys previously used in this art such as sodium-lead, potassium-lead, and calcium-lead can be first dissolved in ammonia and then the alkylating agent added. Furthermore, temperatures of 25° C. and less can be used when alkylating such alloys, for example NaPb, and high yields are obtained whereas when such low temperatures are used in the present commercial process, substantially no yield is obtained.

Any of the alkylating or arylating agents heretofore used or described in the prior art can be used, among which are the alkyl and aryl halides, preferably the iodides, bromides and chlorides, the dialkyl sulfates and the trialkyl phosphates. In general the alkylating and arylating agents are esters of inorganic acids having the proper alkyl groups for making the desired alkyllead compound, and having an acid group which forms a salt with the alkali or alkaline earth metal. Among those which can be used in our invention are ethyl, propyl, butyl and

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phenyl, chlorides, iodides and bromides, diethylsulfate and triethylphosphate.

While tetraethyllead is the principal compound discussed herein because of its large commercial use, other alkyllead compounds such as tetramethyllead, tetrapropyllead, dimethyldiethyllead, methyltriethyllead, tetraphenyllead, diethyldiphenyllead are readily made by the process of this invention.

The preferred temperature used in conducting our process is between —35° C. and 60° C., and the preferred reaction time is between 1 and 60 minutes. In general, the higher the temperature the shorter the reaction time. It should be noted that with these conditions little yield would be obtained in the present commercial process. The pressure used in our process is not critical as long as it is sufficient to maintain the ammonia as a liquid.

At temperatures below about 25° C., the alkyllead product can be left in contact with the reducing metal until the reaction is complete, but at higher temperatures it is preferred to remove the alkyllead product as fast as it is formed in order to prevent its decomposition by the reducing metal. The alkyllead products are substantially insoluble in liquid ammonia and therefore readily separable therefrom by well-known means such as decanting, filtering, centrifuging and the like.

The relative amounts of reducing metal to lead is not critical but in general, little improvement is obtained when the molar ratio of reducing metal to lead exceeds 4. However, with certain reducing metals, higher ratios may be used to advantage in order to increase the solubility of the lead in the liquid ammonia.

The amount of liquid ammonia should be in excess to that required to dissolve the metals and in general is between 1 and 100 parts to 1 part of metal used by weight, and preferably between 2 and 25.

Our invention can best be understood by referring to the following working examples in which the parts are by weight:

Example I

Into a reaction vessel equipped with an agitator, a jacket for circulation of heating or cooling liquids, a reflux condenser, charging and discharging ports, liquid feed lines, and means for releasing the pressure were added 20 parts of small pieces of commercial pig lead, 3.8 parts of metallic sodium and 185 parts of liquid ammonia. The mixture was agitated at —33° C.

under atmospheric pressure until the sodium and lead were in solution. To this mixture were added 28.6 parts of ethyl iodide and a temperature of about —30° C. was maintained for 4 minutes by refluxing the ammonia. At the end of this period the reaction mass was removed and charged to a steam still wherein the tetraethyllead product was recovered. By this operation 7.5 parts of tetraethyllead product was recovered which amounted to about 95 per cent based on the lead reacted.

In examples similar to Example I, except that ethyl chloride, ethyl bromide and diethyl sulfate were substituted for ethyl iodide as the alkylating agent, similar high yields were obtained. Likewise, when the temperature was raised to 25° C., the pressure being 165 pounds absolute, high yields of tetraethyllead based on the reacted lead were obtained.

Example II

In another operation using the same equipment and the same procedure as for Example I, except that the temperature was maintained at 25° C. under 150 pounds absolute pressure approximately 19.8 parts of NaPb alloy were added to 86 parts of liquid ammonia. To this solution were added 40 parts of ethyl iodide and the reaction was conducted for 60 minutes. At the end of the reaction period the tetraethyllead product was recovered by steam distillation and the yield was 5.7 parts or 20.4 per cent based on the lead charged.

Good yields also were obtained when other alkylating agents such as ethyl bromide and ethyl chloride were substituted for the ethyl iodide in the above example. Likewise lower temperatures, that is below 0° C., and shorter time also resulted in good yields when a lead alloy was used. In like manner when higher sodium alloys are used, good yields are obtained. For example, when Na_9Pb_4 alloy was substituted for the NaPb alloy in Example II, a tetraethyllead yield of 11.7 per cent was obtained which yield heretofore has not been obtained. Similar good yields are obtained when lead alloys of other metals are used, such as calcium-lead and potassium-lead alloys. It should be pointed out that in a commercial operation conducted similar

to Example II, except that no liquid ammonia was used, the low temperature of 25° C. resulted in substantially no yield of tetraethyllead.

Other examples within the scope of the following claims will occur to those skilled in the art.

We claim:

1. The process of forming hydrocarbonlead compounds comprising dissolving, in a reaction medium comprising essentially liquid ammonia, lead and a reducing metal selected from the class consisting of alkali and alkaline earth metals and reacting the resulting solution with an alkylating or arylating agent having the proper hydrocarbon groups in question and having a negative radical which reacts with the reducing metal.

2. The process of forming alkyllead compounds comprising dissolving, in a reaction medium comprising essentially liquid ammonia, lead and a reducing metal selected from the class consisting of alkali and alkaline earth metals and reacting the resulting solution with an alkylating agent having the alkyl groups in question and having a negative radical which reacts with the reducing metal.

3. The process of claim 2 for making tetraethyllead in which the alkylating agent is ethyl chloride.

4. The process of claim 2 in which the lead is free metallic lead.

5. The process of claim 2 in which the lead is a sodium-lead alloy.

6. The process of making tetraethyllead comprising reacting ethyl chloride at a temperaure between —35° C. and 60° C. for time between 1 and 60 minutes with a solution of lead and sodium in a reaction medium comprising essentially liquid ammonia.

ALFRED J. KOLKA.
IVAR T. KROHN.

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