

ALUMINIUM ALCOHOLATES.¹

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We distinguish the alcoholates as being those chemical compounds in which the hydrogen atom of the hydroxal group in an alcohol is replaced by a metal. The name "alcoholate" has been applied in the past, and to some extent is applied at present, to certain compounds which result from the direct union of the alcohols with many inorganic salts and in which the alcohol seems to serve in the same capacity that water of crystallization does in crystals. In our work, however, it has been found more convenient to give to these substances the name "addition products" and to reserve the name "alcoholate" to those compounds alone which result from a direct attack upon the hydroxyl group of the alcohol itself.

The results of the work which has been done on this subject are to be found scattered throughout the chemical literature for the last thirty or forty years. Most of the more common alcoholates have been prepared, but in many cases not even analyses were made of them; for they are of so little stability, due to their hygroscopic nature, that they do not present a field of the greatest attraction to the chemist. Besides this we have to take into account that there has been found as yet but one class of alcoholates which can be purified by distillation. These are the aluminium alcoholates. They have been worked with only once, and that when Gladstone and Tribe prepared them about ten years ago by means of their aluminium-iodine reaction.²

¹ The work on the alcoholates as set forth in this paper, was done by Mr. Rolland Hastreiter and myself as thesis work in the University of Wisconsin under the direction of Dr. H. W. Hillyer, assistant professor of Organic Chemistry. Mr. Hastreiter's work was done on the methylete and propylete.

² J. Chem. Soc. 1881, (39) p. 1.; 1882, (41) p. 5; 1886, (49) p. 25.

Briefly told, this reaction consists in bringing aluminium and iodine together in the presence of absolute alcohol. Gladstone and Tribe worked with various alcohols, purified their products by distillation and made analyses of them which usually agreed within one or two per cent. of the theoretical proportions. In only one or two cases did they make melting or boiling point determinations.

While working with aluminium amalgam for the purpose of reducing organic compounds in neutral aqueous or alcoholic solutions, results were obtained which led to an investigation of the aluminium alcoholates which we found could be prepared by means of this amalgam. When metallic aluminium is treated with an aqueous solution of mercuric chloride it becomes amalgamated, and this amalgam possesses the property of decomposing water, thus liberating hydrogen, which, in its nascent state, forms a suitable means for carrying on reduction.¹ This amalgam can be used then as a means of dehydrating alcohol or of carrying on a reduction in an alcoholic solution if water is present or is added. If, however, we dissolve the mercuric chloride in the alcohol itself and place the aluminium in the solution, the metal not only becomes amalgamated but the alcohol itself is attacked in a way quite similar to that of the water — hydrogen being given off and the alcoholate being formed. During the reaction, which starts at once on bringing the aluminium into the solution, there is a considerable rise in temperature, sometimes to the boiling point of the alcohol; and in the case of some alcohols, the contents of our flask became quite gelatinous in the course of half an hour and finally solid. This is then distilled under diminished pressure and the product redistilled and fractionated, after which it is analysed.

During the whole process of the experiment the greatest care has to be taken to keep the substance out of contact with the air, as the slightest moisture will cause it to decompose with remarkable rapidity. Although mercuric chloride was used in our first experiments, it was found to be unsatisfactory because, on distillation, our product was certain to become contaminated by a small amount of mercury being carried over into the re

¹ Ber. d. chem. Ges. 28, 1895.

ceiver. Hence we made experiments to find a substitute which would prove more satisfactory. Good results were obtained in using platinic chloride and stannic chloride, and future work was carried on with fuming stannic chloride.

So far, experiments have been made with five different alcohols, and our results seem to indicate that the reaction is one which can be applied to the alcohols quite generally. The following are the results, briefly stated, which we have obtained by what we call our aluminium-stannic chloride reaction.

WITH ETHYL ALCOHOL.

We used 5 grams of chipped aluminium and 7 c. c. of fuming stannic chloride in 50 c. c. of absolute ethyl alcohol. The action began immediately, accompanied at first by a considerable rise in temperature, and continued at the temperature of the laboratory for three or four days, when the contents of the flask had become quite solid. This was then distilled *in vacuo* as follows. The apparatus was first exhausted to a pressure of from 12 to 25 mm. and the substance gradually heated until the boiling ethylate was just about to pass over into the receiver. During this first heating some alcohol always passed over, and it became necessary to substitute a clean, dry receiver in which to collect the distillate. After this had been done and the pressure again reduced, the distillation was recommenced and continued until signs of decomposition began to appear. The distillate thus obtained was then subjected to another distillation and fractionated, during which process its boiling point was taken. It was then analysed. The ethylate thus obtained was a pure white solid of a gummy consistency, boiling at 235° C. under a pressure of 23 mm. and melting at 135° C. It was only slightly soluble in absolute alcohol but more so in ether and benzene. Chloroform did not dissolve it. On analysis it gave

| | Theoretical. | Found. | |
|-----------------|--------------|--------|-------|
| | | I. | II. |
| Aluminium | 16.66 | 17.86 | 17.57 |

These results show that it corresponds more closely to the ethylate than to any other substance which might be formed, and they agree very well, considering its hygroscopic nature. In the beginning of the reaction there was always a deposition of spongy tin upon the aluminium, and it was found, in using small amounts of stannic chloride and allowing the reaction to take place more slowly, that the yield of the alcoholate was invariably larger.

WITH METHYL ALCOHOL.

In attempting to prepare the methylate by this reaction, Mr. Hastreiter obtained the same result as Gladstone and Tribe. Upon adding the usual amounts of stannic chloride to the alcohol and aluminium, a reaction began but soon ceased. A larger amount caused the action to continue, and finally a gelatinous mass resulted. On heating, however, under reduced pressure, no distillate could be obtained. From the reaction, however, and from other experiments which were made, he was led to believe that the methylate was formed, but that it decomposed on heating even *in vacuo*.

WITH PROPYL ALCOHOL.

Mr. Hastreiter succeeded without difficulty in preparing the aluminium propylate by this reaction; only it was found necessary to keep the temperature at that of the water bath during the reaction. On distillation the yield was large and of a delicate amber color when liquid but white and opaque when solid. It boiled at 255° C. under a pressure of 15 mm. and melted at 65° C. On analysis it gave

| | Theoretical. | Found. | |
|-----------------|--------------|--------|-------|
| | | I. | II. |
| Aluminium | 13.10 | 14.30 | 13.20 |

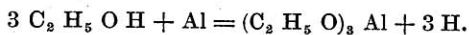
WITH ISOPROPYL ALCOHOL.

So far, experiments with isopropyl alcohol have been no more successful than those with methyl alcohol. An evolution of hydrogen takes place on the addition of the stannic chloride and continues, if the temperature is kept at that of the water bath, until a solid mass is formed; but no distillate can be obtained on heating under diminished pressure. Here, again, indications are that the isopropylate is formed but decomposes on heating.

WITH AMYL ALCOHOL.

With this alcohol it has been found that the amylate can readily be obtained. It is of a dark yellow color and boils at 291° C., under a pressure of 12 mm. No analysis has as yet been made of it.

The reaction involved in the formation of these alcoholates would seem at first thought to be very simple, since the product is a compound in which the aluminium has replaced, in each molecule of alcohol, one atom of hydrogen. This change in composition could be expressed, with common alcohol, by the equation



But this does not explain why it is necessary, for the progress of the reaction, to have present other things besides alcohol and metallic aluminium. By the initial reaction, when the stannic chloride is added, metallic tin is precipitated on the aluminium, and aluminium chloride is formed thus:



Both of these products seem to have an influence, as it is found that aluminium will not dissolve in alcohol in presence of tin alone and but slowly when aluminium chloride is present without the tin. The reaction is probably due to the action of the aluminium, or some compound of aluminium chloride with the alcohol, under the strain of the electric couple of which the tin and the aluminium are the negative and positive metals. The alcoholates so formed are themselves of considerable interest because they are one of a very small class of organo-metallic bodies containing oxygen which can be distilled, and because they

show how, through suitable means, such a stable group as the hydroxyl group of an alcohol may be attacked and torn apart.

Further work which is being done will no doubt bring to light other results of interest, and it is quite possible that the reaction may be turned to account in a commercial way as a means of purifying certain alcohols from traces of others which are more easily acted upon by the amalgam.

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