cent. boron, and was therefore again treated with nitric acid and the chlorate several times. A product was finally obtained which gave, on fusion and analysis, a boron content of 82.8 per cent., allowing for a small undissolved residue, which proved to be carbon.

Since some of this carbon was probably oxidized in the fusion, this result would be a little low. The theoretical boron content of $B_6C$ is 84.6 per cent. Therefore, this analysis together with the general properties of substance identify it with Joly's and Moissan's carbide. The conclusions reached by the foregoing are that Mühlhäuser actually obtained a mixture of the carbide with graphite, owing to the difficulty of separating the latter, but that he failed to obtain any large masses of the product because of the very high temperature necessary.

For the preparation of the carbide from boric oxide in considerable quantities a special form of electric furnace would have to be designed, so that means could be provided for the condensation of the boric oxide fumes—possibly this could be accomplished by using some sort of shaft furnace, whereby these fumes would be retained by the descending charge.

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## ALUMINUM PHENOLATE.

BY ALFRED N. COOK.

ALUMINUM phenolate was first prepared by Gladstone and Tribe[1] about twenty years ago, but no study was made of the compound except to distil it. While engaged in the study of phenyl ether and its preparation from aluminum phenolate it appeared to the author that a further study of the compound might be interesting and profitable.

*Preparation.*—The mode of operation found best in its preparation is to heat from 100 to 500 grams of phenol in a liter flask fitted with a return Liebig condenser. A simple air condenser is not sufficient in manufacturing a large quantity, since the escaping hydrogen keeps the tube hot and carries with it a large part of the phenol. In two or three instances in the earlier ex-

[1] J. Chem. Soc. 41, 7.

periments these escaping gases caught fire spontaneously on coming in contact with the air.

The aluminum is added gradually in the form of strips, very slowly at first or the action may be too violent and most of the phenol will escape uncondensed. When the action is well started the heat is removed as the heat of reaction is then sufficient. When the process is thus carried on as far as possible an excess of aluminum strips (which now does no harm) is added and a sharp heat is applied until hydrogen ceases to evolve. It is then poured out on a plate and allowed to cool and bottled up for future use.

A purer product can be obtained by starting with 100 grams than with a larger quantity, since it is subjected to the decomposing action of a high heat for a shorter time and the yield is better. The yield may be made practically quantitive by exercising due care in preventing the loss of phenol.

Gladstone and Tribe found that the action could be started by adding a little iodine, in which case the heat of the water-bath is sufficient, but I have found that 2 or 3 grams of powdered aluminum phenolate will do just as well. It requires a slightly higher heat, however, to start the reaction, probably due to the fact that aluminum phenolate is not dissolved by phenol at the temperature of the water-bath. Endeavors to start the reaction by means of aluminum chloride, and bromine were without success.

A platinum-aluminum couple with phenol as a battery fluid was tested and found to have an electromotive force of 0.1 volt at 54° C., and 0.35 volt at the boiling-point of phenol. The throw of the D'Arsonval galvanometer (which had an internal resistance of 240 ohms) was the same when used alone as when an external resistance of 130,000 ohms was introduced, showing an immense internal resistance.

From the above experiments it was thought that platinum strips might be used to start the reaction. Two experiments were carried out with success, but it required the application of a sharp heat for a few minutes.

Gladstone and Tribe state that aluminum alone is without action on phenol. While this is probably true of pure aluminum I have found that when commercial aluminum and pure phenol are heated sharply for two or three hours a violent reaction sets

up precisely the same as in the other methods. The action was probably produced by local action of a couple of aluminum and carbon, which occurs in aluminum as an impurity.

*Analysis.*—The analyses for aluminum all yielded high results, probably because the temperature required to complete the reaction of aluminum with phenol is also sufficient to change some of the aluminum phenolate into aluminum oxide and phenyl ether. It was noted that all solvents left a residue undissolved and also that the percentage of aluminum was highest in samples that had been most highly heated during their preparation. It was also observed that some samples, even those that had not been highly heated, had the odor of phenyl ether and when allowed to stand in contact with water for some time this odor was very much intensified.

The aluminum was determined by boiling the substance with water and igniting the resulting hydroxide and also by dissolving in hydrochloric acid and precipitating with ammonium hydroxide.

Calculated for $Al(OC_6H_5)_3$, 8.86 per cent. Found, 9.34 and 9.28 per cent.

In another sample which had been more highly heated at the close, in its preparation, there was found 9.94 per cent. of aluminum in each of two determinations.

*Properties.*—Aluminum phenolate is a translucent, brittle solid, and possesses a vitreous luster and a conchoidal fracture. When prepared as directed above, it varies from gray to nearly black, and sometimes has the appearance of dried glue. It has a tendency to become brown with age. It has a slight odor of phenyl ether mingled with that of phenol. When bottled up, crystals of phenol sublime and collect on the interior of the bottle in the course of a few weeks. If bottled tightly to exclude the air it may be kept unchanged for many months.

It melts at about 265° C. and when heated a little above the melting-point it begins to decompose as is explained further on. Its specific gravity is 1.23.

*Solubility.*—The substance is soluble in hot toluene and benzene from which there separates out a gelatinous mass on cooling, which on being dried and analyzed for aluminum yielded results far from that required by theory for aluminum phenolate. There was found 23.85 per cent. Calculated, 8.86 per cent.

It is also soluble in hot xylene but does not separate out on

cooling. On long contact with the air, however, there is gradually deposited a gelatinous mass.

The powdered substance is very readily soluble in methyl, ethyl and amyl alcohol, but not if these contain a little water. A sample of commercial "absolute alcohol" in stock would not dissolve it.

It is soluble in chloroform, carbon disulphide, aniline, carbon tetrachloride, acetone, etc. It is certain that aluminum phenolate reacts chemically with some of these solvents and apparently with all of them. In the case of all of them a very little water causes a large voluminous precipitate immediately, accompanied by the evolution of heat. It is also soluble in a strong solution of sodium phenolate in water. No method was found by which it could be purified.

*Action of Water.*—When several grams of powdered aluminum phenolate were added to a few cubic centimeters of water considerable heat was evolved. Two experiments were carried out in duplicate to determine the action of water. In the first the phenolate was boiled with water and there was formed $Al_2O_3.2H_2O$, as indicated by the weight of the dried product.

Calculated for $Al_2O_3.2H_2O$, 22.57 per cent. Found, 21.82 and 21.88 per cent.

In the second experiment the phenolate was allowed to remain in contact with cold water for two days when $Al(OH)_3$ was formed.

Calculated for $Al(OH)_3$, 25.39 per cent. Found, 24.30 and 24.29 per cent.

These results are as close as could be expected, considering the purity of the compound, but are sufficient to establish the character of the hydroxide formed. The first is the same hydroxide that is precipitated from a boiling solution of an aluminum salt with ammonium hydroxide, and the second is the same hydroxide that is precipitated from a cold solution of an aluminum salt with the same reagent.

*Action of the Air.*—When allowed to come in contact with the air for several weeks it loses its vitreous luster and conchoidal fracture and assumes a granular crystalline appearance. It is then moist and smells strongly of phenol, whereas when freshly prepared the odor is comparatively faint. Apparently the moisture of the air acts upon it, liberating phenol and forming aluminum hydroxide, $Al(OH)_3$.

When distilled it does not melt down as fresh aluminum pheno-late does, but remains in the granular form in which it was placed in the flask at the beginning. It did not run together in the least and at the close of the operation was poured from the flask as so much sand. From 123 grams of the substance there resulted 89 grams of distillate and 34 grams of powdery residue. It also distilled at a much lower temperature than fresh aluminum phenolate does. On redistilling the distillate about one-third came over in the neighborhood of 100°. This was apparently mostly water but had the characteristic odor of benzene. The temperature then rose rapidly to 179°. About two-thirds came over between 179–180°, the boiling-point of phenol. There were no higher boiling substances formed. The process of distillation evidently simply separated the mechanically held phenol and a little dissolved benzene, and decomposed the aluminum hydroxide, leaving aluminum oxide and other residue. Carbon dioxide does not act upon aluminum phenolate.

*Action of Bromine.*—Bromine was added to aluminum pheno-late in water until all action had ceased. There was immediately precipitated a light yellow compound which, by its melting-point, general properties and the analysis for bromine, was identified as tribromphenol.

When the strong bromine solution had cooled, a golden yellow, glistening compound, finely crystalline, separated out which, by its melting-point, general properties and analysis for bromine, was identified as tribromphenol bromide.

The action of bromine on aluminum phenolate is thus identical with its action on phenol but it acts more smoothly.

*Action of Nitric Acid.*—When treated with nitric acid aluminum phenolate yields orthonitrophenol, 1-2-4-dinitrophenol, and picric acid, the quantities of each produced depending on the concen-tration of the acid, the temperature at which it acts, and the time employed. It does not yield metanitrophenol as in the case of phenol, at least not in any considerable quantity. The action is also much milder than in the case of phenol.

Several experiments were carried out as follows: Fifty grams of aluminum phenolate were dissolved in 500 cc. of nitric acid (sp. gr. 1.21) at temperatures varying from —10 to 40°. Practically the same results were obtained each time. On an average there was obtained 20 grams of 2-4-dinitrophenol, 17 grams of nitro-

phenol, and 40 grams of a tarry residue. No picric acid was formed. The two nitrophenols were readily separated from one another and from the tarry residue by distilling under diminished pressure. The orthonitro compound boils at about 120° at 25 mm. pressure and the dinitro compound at 190°.

When aluminum phenolate is dissolved in nitric acid (sp. gr. 1.21) at 60° it is almost completely changed into 2-4-dinitrophenol. A small amount of picric acid is formed at the same time, but no orthonitrophenol. At 100° some dinitrophenol results, but there is formed mostly picric acid, the yield of which is increased on boiling. The dinitrophenol can be completely separated from the picric acid by distilling with steam but the process is long and tedious.

On dissolving aluminum phenolate in commercial nitric acid at the boiling temperature and heating for a short time it was completely transformed into picric acid, no dinitrophenol whatever resulting. If too strong an acid be used, or too great an excess, or if heat be applied too long the yield in picric acid is much reduced, owing to the complete oxidation of part of the compound. In my experiments a given amount of phenol yielded double its weight of picric acid and I think it would be possible to increase the yield still more. The calculated amount is 2.44 times the weight of phenol employed.

The picric acid is obtained in a very pure state. Without crystallization it melted at 120° and after one crystallization from alcohol it melted at 123°, which is the melting-point of the pure compound.

The barium salt of picric acid is described in the literature as containing five molecules of water of crystallization, but in preparing the salt three different times I obtained it with five molecules once, and three molecules twice. The two forms have the same appearance. In each case analyses were made for both barium and water and the results conformed closely to the theoretical.

The barium salt of 2-4-dinitrophenol is described as crystallizing from water with seven, six, and five molecules of water of crystallization. I prepared the yellow salt twice and analyzed it for both barium and water and in both instances it contained but four molecules. The results were in close agreement with the calculated.

The orange-red crystals which are described as containing five molecules of water were also analyzed for both barium and water and found to contain but four. The orange-red crystals on repeated recrystallization change gradually and finally completely into the yellow variety.

*Action of Alcohol.*—When commercial "absolute alcohol" was treated with powdered aluminum phenolate an action began at once and the temperature rose to a very perceptible degree and there was formed a gelatinous emulsion. The action was at first thought to be due to the presence of water in the alcohol, but some fresh absolute alcohol was prepared by means of calcium carbide from the commercial article (Eimer & Amend), and it was found that the aluminum phenolate dissolved in it very quickly with no perceptible evolution of heat. However, on adding a few cubic centimeters of water a bulky precipitate was thrown down and a marked evolution of heat took place.

The filtrate contained phenol as was shown by well-known tests, although the characteristic odor and caustic action were absent, on account of the presence of the alcohol. On distillation a residue of phenol remained. The precipitate was washed with alcohol and analyzed for aluminum with the following results:

Calculated for $Al(OC_2H_5)_3$: Al, 16.72 per cent. Found: Al, 17.47 and 17.26 per cent.

The alcohol radicle therefore simply takes the place of the phenol and the following equation would represent the reaction:

$$Al(OC_6H_5)_3 + 3HOC_2H_5 = Al(OC_2H_5)_3 + 3HOC_6H_5.$$
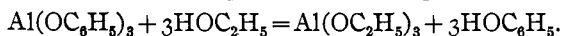
*Action of Ether.*—Powdered aluminum phenolate was treated with commercial ether, when there was obtained a flaky precipitate similar to that yielded by alcohol. Some absolute ether was prepared by means of sodium, from the commercial article. In this it quickly dissolved (with the exception of a small residue, probably $Al_2O_3$) with no evolution of heat. On adding a few cubic centimeters of water a bulky precipitate was formed immediately, accompanied by a marked evolution of heat. The precipitate was washed with ether and analyzed for aluminum and gave results in fair agreement with the requirement of theory for aluminum alcoholate, considering the conditions under which the compound was obtained. The filtrate was distilled and from it there was obtained a nearly quantitative yield of phenetol and

a small quantity of a high-boiling crystalline solid which was not examined. The following equation would represent the reaction:

$$3C_2H_5OC_2H_5Al(OC_6H_5)_3 = Al(OC_2H_5)_3 + 3C_2H_5OC_6H_5.$$
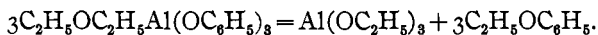
*Action of Other Reagents.*—Hydrochloric acid acts upon aluminum phenolate, liberating phenol and precipitating aluminum chloride. Sulphuric acid acts in an analogous manner. Hydrofluoric acid attacks it vigorously with the liberation of phenol. Acetic acid attacks it rather tardily and the weaker organic acids are without action upon it.

A solution of sodium hydroxide dissolves it, probably forming sodium aluminate and sodium phenolate. On adding a strong acid, phenol is liberated.

A strong solution of sodium hypochlorite dissolves it.

*Distillation.*—On being sharply heated aluminum phenolate melts and very soon begins to decompose. The products of distillation are a small quantity of benzene (which, however, may have resulted from the reducing action of the hydrogen during the process of manufacture and may have been simply held in solution in the solid aluminum phenolate), phenol, a varying amount of phenyl ether, depending upon the amount of heat employed, and some higher boiling substances not easily separated from one another and not identified.

The degree of heat should be as low as possible (and applied with a smoky flame) if it is desired to obtain as large a yield of phenyl ether as possible. There is also obtained by low heating a relatively larger amount of tarry residue. When a high degree of heat is employed the aluminum phenolate decomposes mostly into phenol and the higher boiling substances; much less phenyl ether is formed and there remains much less of the tarry residue. Some aluminum phenolate always passes over in the first distillation but is entirely decomposed during the second. On distilling *in vacuo* much more of the aluminum phenolate passes over unchanged, together with a larger amount of phenol and a very small amount of phenyl ether. From these results one would suspect that a larger yield of phenyl ether might be obtained by distilling under increased pressure, but the experiment was not tried on account of a lack of suitable apparatus.

By heating the flask as uniformly as possible during the whole operation and carrying the distillation as far as possible, a porous

residue remains which can quite readily be removed from the flask; otherwise, a hard asphalt-like residue remains which it is impossible to remove without sacrificing the flask.

As a method of preparing phenyl ether this is no doubt the best that has been employed up to the present unless it be the one recently proposed by Ullmann and Sponagel.[1] I have gone carefully over all of the other methods and find that this gives far the best yield. From 1227 grams of aluminum phenolate I obtained over 200 grams of phenyl ether boiling at 249–251°, by washing the first distillate with a solution of caustic soda to remove the phenol and fractionating the remainder. The caustic soda solution must be quite weak since phenyl ether is quite soluble in a strong solution of sodium phenolate. Having gone over the process a number of times I have calculated that about one-third of the aluminum phenolate is decomposed into aluminum oxide and phenyl ether probably according to the following equation:

$$2Al(OC_6H_5)_3 = Al_2O_3 + 3C_6H_5\text{—O—}C_6H_5.$$
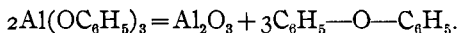
From the action of alcohol on aluminum phenolate it was thought that phenyl ether might be the result of the reaction of phenol, but equimolecular quantities of the two substances were heated for more than an hour and on extracting with ether and distilling, no phenyl ether was formed.

I am indebted to Mr. W. J. Morgan, of Iowa City, Ia., for some assistance in part of the work.

The action of aluminum phenolate on various organic compounds is now being studied in this laboratory and will be the subject of a future paper.

NOTE.—Since writing the above an endeavor was made to continue the study of the action of aluminum phenolate on organic compounds with some of the freshly prepared substance, but the solubility and the chemical action were found to be only very slight in every case. Aluminum phenolate was then prepared in a variety of ways from the same lot of chemicals in each case as was used several months ago, but all were without action. The substance used in that part of the research in connection with organic compounds was about a year old. Apparently some change takes place in aluminum phenolate with

[1] Ber. 38, 2211, 1905.

age. A quantity has been prepared and will be kept until a year hence when it is hoped that this study can be resumed.

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VERMILLION. S. DAK.
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## ON DIMETHYL 4-AMINOPHTHALATE AND CERTAIN OF ITS ACYL DERIVATIVES.

BY MARSTON TAYLOR BOGERT AND ROEMER REX RENSHAW.

As a sequel to the work on the nitro-*o*-phthalic acids recently conducted in this laboratory,[1] we have turned our attention to the aminophthalic acids also.

Very little information appears in the literature concerning 4-aminophthalic acid or its derivatives. It seemed of interest, therefore, to prepare a number of its derivatives and study their properties.

As the free 4-aminophthalic acid is not readily obtained pure, on account of its instability, we used its dimethyl ester as the starting point for our experiments. This was prepared from phthalic anhydride by nitrating, esterifying the mixture of nitro acids which result; separating the neutral ester of the 4-nitrophthalic acid, and then reducing the nitro acid with alcoholic hydrochloric acid and zinc dust. By this method, the amino ester was obtained in satisfactory yield and purity. Quite lately, Cohen and McCandlish[2] tried to reduce the nitrophthalic ester with hydrogen sulphide, but could get no pure product, the amino ester formed being invariably contaminated with a yellow, viscid oil, which they thought was probably a sulphur compound.

From the dimethyl ester, we prepared the following derivatives: hydrochloride; a dimolecular condensation product with formic acid; acetyl, propionyl, isobutyryl, benzoyl, *m*- and *p*-nitrobenzoyl, urethane, phenyluramino, ethoxalyl, oxalyl, phthalamic acid, succinamic acid, and the silver salts of both the latter; also 4-aminophthalanil.

[1] Bogert and Boroschek: This Journal, 23, 740 (1901); Bogert and Wright: Ibid. 27, 1310 (1905.)

[2] J. Chem. Soc. 88, 1269 (1905).