

THESIS

A STUDY OF THE CATALYTIC EFFECT OF ALUMINUM CHLORIDE IN THE CONDENSATION OF ACETIC ANHYDRIDE WITH BENZENE AND PHENOL

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A STUDY OF THE CATATYTIC REFECT OF ALUMINUM CHLORIDE IN THE CONDENSATION OF ACETIC ANHYDRIDE WITH BENZENE AND PHENOL

SUBMITTED TO THE FACULTY

of the

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by

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Introluction

Aluminum chloride as a calgifizer has been the subject of a great deal of research; the exact nature and mechanism of its reaction in this capacity is not definitely known, although many theories are advanced.

Friedel and Grafts (1) are responsible for this general method of condensing organic compounds, with aluminum chloride as a datalyst. The calalytic activities in Friedel and Grafts reaction of the anhydreus aluminum chloride may be explained by the production of a temporary combination between the chloride and the organic material $C_{c}R_{c}H + H|C|_{3} \rightarrow H|C| + H|C|_{C}C|_{c}$

the latter would then react with the halide

The regenerated aluminum chloride would react with the initial substance and the reaction would be repeated. This would, accordingly, necessitate the use of only a small amount of the catalyst. In some instances, however, it is found more practical to use larger amounts. On this account the catalytic action of aluminum chloride has been doubted. However, the use of larger quantities of the catalyst is due either to the slowness of the reaction or the desire to accelerate it by the production of a larger amount of the intermediate compound; in some cases the chloride compound formed is so stable that some of the

Gustavson (1) has succeeded in isolating an addition product of aluminum chloride with benzene - an orange colored oil $HICI_3 \cdot 3C \cdot HL$ which is decomposed by water. Also in the case of benzene and ethyl chloride

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The latter is stable and serves as a catalyst.

Huston and Friedmann (2) have given us an important application of the use of aluminum chloride as a catalyst in reactions where water is eliminated between an alcohol and a hydrocarbon. For example, benzyl alcohol and benzene give di-phenyl methane

C. H. CHLOH + C. H. -> C. H. - CHLC. H. + HLO

accompanied by other hydro-carbons. In the same way secondary aromatic alcohols yield tertiary hydro-carbons.

A mixture of methyl-phenyl-carbinol and five molecules of benzene kept at ten degrees in the presence of 5/10 molecules of aluminum chloride gives a 65⁻⁴ yield of di-phenyl ethane together with other products of the continued action of the aluminum chloride.

Colts CH(OH)CH2 + Colto - Colts CH2 Cults + 1420

Condensation of Adetic Anhydride and Eensene.

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In the present experiment the proportions used were scatic anhydride one mole, benzene five mole, aluminum chloride one mole/ The liquids were stirred by machine, with the gradual addition of the anhydride aluminum chloride. The temperature of the mixture rose rabidly but was kept below 60 degrees; hydrogen chloride was given off. After about half the aluminum chloride had been added, the temperature was more constant so that the rest could be added in larger portions/ At first the mixture was a golden yellow color. later turning bright green, and finally black. After all the aluminum chloride had been added . the process took about two and one-half hours - the vessel was covered an allowed to stand twenty-four hours. The substance was noured over cracked ice and allowed to decompose. The abqueous layer was then separated off and extracted with ether. The ethar was distilled off, the residue added to the oily nortion and distilled. Ao stonhesone was collected from assorbe 12020. After the soctophenone had been collected, the temperature rose rabidly to about 250°. In the first

In the first experiment the yield was about 10⁶ but in later experiments about a 30⁶ yield was obtained.

The acetophenone was purified by a redistillation, giving a golden yellow product. In order to prove that this product was agetophenone it was reduced to with zine amalgam in the following manner: (3):

200 gm/ of mossy 2ind stood in 400 cd of a 5⁴ solution of HgCl, for one hour; the solution was then poured off, 5- gm/ of an etophenone was added and enough HCl (1 part erude to 3 parts H₂O) so that the zind was just covered. The mixture was heated under a reflex conduser for 6 hours with the occasional addition of small portions of the diluted HCl to keep the evolution of the hydrogen lively; 500 cd of diluted HCl ware added in all.

The ageous portion was extracted with ether, and the other distilled off; the residue was added to the oily portion and distilled at 335° to 136° . The distillate was redistilled and dried. Yield was about 40° .

The production of acetophenone in this was has been noted by Friedel and Crafts in their study of phthalio and social anydrides (4).

Condensation of Acetic Anydride and Phenol.

Further experiments were made in the condensation of acetic anjydride with phenol. The proportions used were:

Acetic anhy iride one mole, Phenol one and one-tenth mole, aluminum chloride one mole.

25.4 gm. of anetic anhydride, 25.9 gm. of phenol suspended in 100 cc of carbon di-sul-phide, was stirred by machine with a gradual addition of 33.4 gm. of aluminum chloride. A muddy light brown percipitate was formed later becoming too thick to stir. After standing in a covered vessel for 24 hours, it was transferred to cracked ice and allowed to decompose/ A white puscipitate was formed upon decomposition. The adueous was extracted with other, the other distilled off, and the residue distilled - phenyl acetate distilling over 189° to 1°1°. Due to the fact that the carbon di-sulphide portion was not distilled, a yield of only 23 gm. was obtained.

The experiment was repeated using .4 mole of aluminum chloride, giving a yield of 31 gm.

The experiment was again repeated with .1 mole aluminum chloride, giving a theoretical yedd of 33 gm.

When repeated with no aluminum chloride a yield of 22 gm. was obtained.

The experiment was repeated with no aluminum chloride not allowing the substance to stand 24 hours, but pouring over cracked ice immediately after stirring. Yield 22 gn.

The experiment was repeated in the latter manner with ,1 mole of aluminum chloride/ Yield 20 gm.

In all experiments but the first, the carbon di-sulphide portion was added and distilled.

It is then evident that in order to allow the aluminum obforide to have its full catalytic effect, it is necessary to allow the mixture to stand 04 hours.

It is also evident that the action

between agetic anhydride and phenol will take place to a considerable degree without the aid of a catalytic agent, but a complete reaction will take place in the presence of .1 of a mole of aluminum chloride.

In an effort to prove that the product obtained was phonyl acetate and attempt was made to decompose it to sodium phonylate and sodium acetate. The substance was heated with 5% sodium hydroxide under a reflex condenser for seven hours to try to discolve the oily liquid. Wone of it discolved, showing that this condensation product is extremely stable.

Corrected for the error due to the length of the thermometer outside of the flash the boiling point of the substance was found to be 195.4° which is the boiling point of phenyl acetate.

Conclusion

- 1. Acstic anhydride will condense with benzene to give acetophenone in the presence of aluminum chloride.
- 2. Svidence is given to show that anhydrous aluminum chloride has a catalytic effect in the condensation of acetic anhydride and phenol.

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