[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

MIXED CATALYSTS IN THE FRIEDEL AND CRAFTS REACTION. THE YIELD OF BENZOPHENONE FROM BENZOYL CHLORIDE AND BENZENE USING FERRIC CHLORIDE–ALUMINUM CHLORIDE MIXTURES AS CATALYSTS

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Those who have used the Friedel and Crafts reaction to any extent are familiar with the fact that the yield of product may vary when different lots of the commercial grades of aluminum chloride are used. The usual explanation is that this variation is caused by exposure of the catalyst to moisture. Another possibility, however, is that the variation is due to a positive or negative acceleration of the main reaction or of side reactions, or the inauguration of side reactions by impurities. Ordinary aluminum is about 98 to 99% pure, the impurities being chiefly iron and silicon,[1] and hence aluminum chloride prepared from it would be expected to contain these same impurities. Aluminum chloride prepared from bauxite[2] would contain a considerably higher percentage of impurities than that made from aluminum.

In view of the well-known effect of impurities on many catalytic reactions, it seemed that an investigation of the effect of impurities in the catalyst on the yield of products from various Friedel and Crafts reactions would be desirable. Since ferric chloride alone is known to have considerable activity[3] and is also known to be an impurity of aluminum chloride, an investigation of the use of mixtures of ferric chloride with aluminum chloride was undertaken. Since we began this work, we have become aware of a publication along similar lines[4] and feel that it is desirable to publish our results in so far as they are complete at the present time.

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[1] The following analysis of three samples of aluminum is given by Calvet, *Compt. rend.*, **188**, 1111 (1929).

	Iron	Silicon	Copper	Aluminum by diff.
Aluminum prepared by Hoopes process	0.015	0.019	0.022	99.944
Pure aluminum	0.16	0.09	nil	99.75
Ordinary aluminum	0.46	0.36[a]	nil	99.18

[a] The value 0.036 is given but this must be a typographical error.

[2] McAfee, *Ind. Eng. Chem.*, 21, 670 (1929).

[3] Nencki and co-workers, *Ber.*, **30**, 1766, 1768 (1897); **32**, 2414, 2419 (1899).

[4] Boswell and McLaughlin, *Can. J. Res.*, **1**, 400 (1929); *C. A.*, **24**, 834 (1930). These investigators measured the amount of hydrogen chloride evolved in the reaction of benzene with chloroform. The catalysts used were aluminum chloride prepared from ordinary aluminum in various ways, ferric chloride, partially reduced ferric chloride and two mixtures of ferric chloride and aluminum chloride. Evidence is given for a maximum activity when an equimolecular mixture of ferric chloride and aluminum chloride is used.

After several preliminary experiments, it was decided to study first the reaction between benzoyl chloride and benzene. This reaction is not strictly catalytic since the optimum yields are obtained when one mole of aluminum chloride is used per mole of acid chloride. The reasons for studying this reaction, however, were that a comparison of the behavior of the catalysts could be based on the actual yield of the main product of the reaction, and that the results could be duplicated within an experimental error of 2 to 4%. Moreover, in this particular case the catalyst is completely in solution at the end of the reaction so that one is dealing essentially with a single phase system.

Pure aluminum chloride was obtained by the action of chlorine on aluminum having a purity of 99.95%.[5] The material obtained in this way was practically white as contrasted with the gray to deep yellow color encountered in the commercial grades of aluminum chloride. The anhydrous ferric chloride used was a commercial product that was resublimed in a current of nitrogen just before use. In each case where mixtures of aluminum chloride and ferric chloride were used, a homogeneous catalyst was obtained by fusing the mixture in a sealed tube. Actually it appears that the same results are obtained if a simple mixture of the powdered chlorides is used. The exact method of carrying out the reaction is given in the experimental part.

The first series of reactions was carried out to determine the effect of varying the molecular ratio of aluminum chloride to benzoyl chloride. Although it is generally recognized that, in the preparation of ketones, one mole of aluminum chloride is required for each mole of acid chloride,[6] no comprehensive data have been recorded on this point. The results obtained are plotted in Curve I, Fig. 1. According to the procedure used, there was a small amount of material obtained when benzene and benzoyl chloride alone were present, so that the curve does not pass exactly through the origin. As the amount of aluminum chloride is increased, the yield of benzophenone increases in direct proportion[7] until slightly over one mole of aluminum chloride is present. Further increases in the amount of aluminum chloride have no effect.

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[5] The authors are indebted to the Aluminum Company of America for supplying them with aluminum prepared by the Hoopes process and having this high degree of purity. Aluminum chloride was also prepared by passing carbon tetrachloride vapor over pure alumina heated to redness, but this method is much slower and more difficult. Moreover, the product obtained was not quite as pure as that made from pure aluminum.

[6] Rubidge and Qua, THIS JOURNAL, **36**, 732 (1914).

[7] Considerable trouble was experienced in obtaining concordant results when less than 0.5 mole of aluminum chloride was used. This was caused by the difficulty of removing completely the unreacted benzoyl chloride when it was present in considerable quantity, and was overcome by treating the benzene solution with an aqueous alcoholic solution of sodium hydroxide.

The second series was carried out on mixtures of aluminum chloride and ferric chloride. The total amount of mixed chlorides was kept constant at 1.1 moles and the composition varied from 100% ferric chloride to 100% aluminum chloride. The results are plotted in Curve II, Fig. 1, and indicate that in this reaction the use of mixtures gives results that are practically the mean between those obtained with pure aluminum chloride and pure ferric chloride.

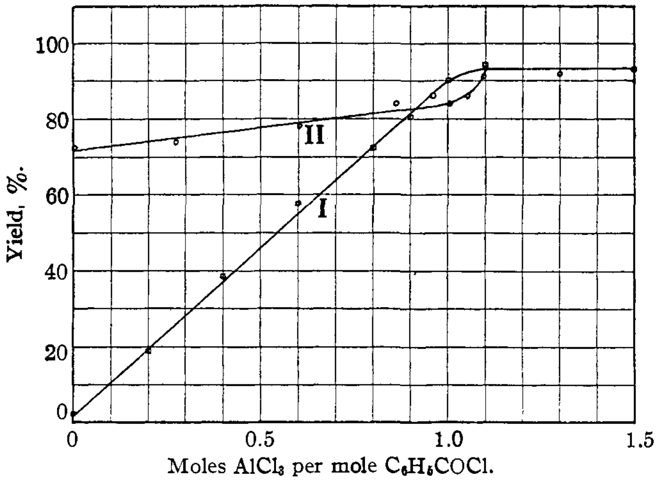

Fig. 1.—Curve I, variation of yield with amount of $AlCl_3$; Curve II, variation of yield using mixtures of $FeCl_3$ and $AlCl_3$, and keeping the total amount of catalyst at 1.1 moles per mole of C_6H_5COCl.

Apparently the lower yields when ferric chloride is present are caused by the acceleration or inauguration of a side reaction. Thus in all cases where ferric chloride is used, a by-product containing iron is formed which is insoluble in the reaction mixture. Further evidence of this detrimental effect is shown by Curve II, Fig. 2. In this series of reactions the amount of aluminum chloride was maintained constant at 1.1 moles, and additional ferric chloride added. In order to compare these results with those obtained when ferric chloride replaces aluminum chloride, the latter have been replotted as Curve I, Fig. 2. Curve II approximates Curve I at first but soon drops below it. A possible explanation of this fact is that when sufficient aluminum chloride is present to take care of all the needs of the main reaction, a greater amount of the ferric chloride is available for producing the side reaction. This explanation would also account for the initial rapid drop of Curve II, Fig. 1, with increasing amounts of ferric chloride. As long as ferric chloride replaces aluminum chloride that is in excess of one mole, the effect is very pronounced, but as the amount of aluminum chloride drops below one mole, the curve flattens out to a straight line whose slope is less because more of the ferric chloride is being used for the main reaction and less is available for producing the side reaction.

The yields of benzophenone are so high that no difference can be detected between the use of pure aluminum chloride and of resublimed commercial products. Some evidence has been obtained in another reaction, however, which indicates that the action of ferric chloride may be different in different types of the Friedel and Crafts reaction.

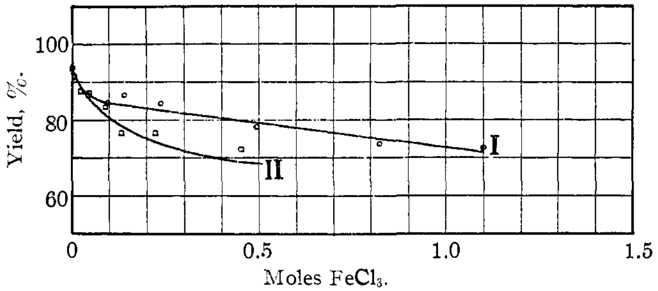

Fig. 2.—Curve I, same as Curve II, Fig. 1, replotted; Curve II, variation of yield using 1.1 moles $AlCl_3$ + varying amounts of $FeCl_3$.

Experimental

Reagents.—Pure anhydrous aluminum chloride was prepared in a suitable apparatus by passing chlorine over heated coils of aluminum sheet having a purity of 99.95%,[5] and was resublimed in an atmosphere of dry nitrogen just before use. The product obtained in this way was almost white, showing only the faintest yellow color in large crystals.

The anhydrous ferric chloride was a commercial C. P. grade and was resublimed in a current of dry nitrogen. Because of the rapid absorption of moisture from the atmosphere, it was necessary to work very rapidly with this material.

A commercial grade of benzoyl chloride was used which boiled at 196–198° and melted at −1 to 0°.

The benzene was dried by distillation and collected over a boiling range of less than 1°.

General Procedure.—Homogeneous mixtures of aluminum chloride and ferric chloride were prepared by placing the two salts in the desired proportions in a pyrex tube, sealing and heating in a bomb furnace until fused. The furnace was tilted at an angle so that the liquid collected in the lower end of the tube.

A 500-cc. three-necked, round-bottomed flask was fitted with a sealed mechanical stirrer, a dropping funnel and a reflux condenser carrying an exit tube for leading off the hydrogen chloride evolved during the reaction. The powdered catalyst was rapidly weighed and transferred to the flask, which contained 70 cc. of dry benzene. After starting the stirrer, 24 g. (0.17 mole) of benzoyl chloride was run in as rapidly as possible. After the reaction had slowed down somewhat, the mixture was refluxed with stirring for three and one-half hours, after which time the evolution of hydrogen chloride had stopped. After cooling, the contents of the flask was decomposed by pouring into 250 cc. of cold water, 10 cc. of concd. hydrochloric acid was added, and the two layers separated. The benzene layer was washed three times with 50-cc. portions of 10% hydrochloric acid and this followed by three washings with 50-cc. portions of 10% sodium hydroxide and a final washing with water. The various aqueous layers were washed successively with a 50-cc. portion of benzene and this was added to the main benzene solution. In the first four runs plotted in Curve I, Fig. 1, where a considerable excess of benzoyl chloride remained at the end of the reaction, it was necessary to modify the method of purifying the benzene solution. It was found that even hot dilute sodium hydroxide would remove the benzoyl chloride only very slowly. This difficulty was overcome by treating the benzene solution, after washing with hydrochloric acid, with 75 cc. of an aqueous alcoholic solution of sodium hydroxide prepared by adding an equal volume of 95% alcohol to a 12*N* solution of sodium hydroxide. It is essential that a decided excess of sodium hydroxide be present to prevent the formation of ethyl benzoate.

The purified benzene solution was dried over calcium chloride, the benzene distilled, and the residual oil heated *in vacuo* to 160° (thermometer in liquid) at 25-mm. pressure. The resulting crude benzophenone was weighed for yield.[8] The results are plotted in Figs. 1 and 2.

Summary

1. The yield of benzophenone prepared by the reaction of benzoyl chloride with benzene in the presence of mixtures of ferric chloride and aluminum chloride, has been found to be approximately the mean of that obtained using pure ferric chloride and pure aluminum chloride.

2. The ferric chloride has a detrimental action which is apparently due to the acceleration or inauguration of an unknown side reaction.

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THE MERCURATION OF BETA-RESORCYLIC ACID

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During the course of a study of the mercuration of resorcinol and some resorcinol derivatives,[1] it was decided to mercurate a carboxylic acid derivative of resorcinol. β-Resorcylic acid was selected for this work, because of the three carboxylic acid derivatives of resorcinol it is probably the easiest to prepare.

It has been found that β-resorcylic acid very readily forms monomercurated and dimercurated derivatives. The compounds produced are somewhat similar in properties to the corresponding mercurated alkyl resorcinols.[1] The reactions involved are also similar. The β-resorcylic acid derivatives, however, seem to form more stable compounds. For instance, they do not darken appreciably when exposed to sunlight. Also they are

[8] The yields were more readily duplicated using this procedure than by calculating the yield on the distilled product. On distillation practically the entire amount came over between 184 and 186° at 25 mm.

[1] Sandin, THIS JOURNAL, 51, 479 (1929).