

TARTARIC ACID FROM COAL TAR BENZENE

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During the hundred years which have elapsed since Wöhler's discovery of the synthesis of urea, one of the important duties of the chemist has been the preparation of naturally occurring substances by artificial means in order to furnish for our use a more abundant and often a purer product than nature provides. As is well known, many of these so called syntheses have become of great importance.

Tartaric acid is at present supplied as a by-product of wine making. The salts of tartaric acid occur in the juice of grapes to the extent of 0.3 to 1.7%. As the grapes ferment and the alcohol content of the juice rises, the potassium acid tartrate along with some calcium tartrate is precipitated. These salts are collected and are the source of free tartaric acid or its salts as at present furnished to industry. Their most important use at present is in the preparation of textiles for the reception of dyes.

It is the purpose of this paper to describe how tartaric acid may be prepared efficiently from the coal tar benzene, a cheap and abundant material.

The first stage is the process of Weiss and Downs, announced in 1920, for the oxidation of benzene to maleic anhydride. The oxidizing agent is air and the catalyst or oxygen carrier is an oxide of the rare element vanadium (V_2O_5). The process is a flameless combustion of benzene on the surface on the catalyst at about 400°C . Sixty percent of the heat of the entire combustion of benzene is liberated and must be conducted away. If the temperature rises, combustion of maleic anhydride, the desired product, occurs and the net yield is carbon dioxide and water. We may well admire the control of Messrs. Weiss and Downs of this "hair trigger" reaction. Their catalyst can be used repeatedly. The two other ingredients, benzene and air, are available at a low price.

The second stage in the preparation of tartaric acid from benzene has been more recently completed and it is to this part of the process that detailed attention is called.

Maleic anhydride may be dissolved in water to form maleic acid. If this acid is heated or exposed to light in the presence of a suitable catalyst, the atoms attached to the two inner carbon atoms rearrange themselves and fumaric acid results. Either maleic acid or fumaric acid can be oxidized in water solution to tartaric acid.

One of our cheapest oxidizing agents is sodium chlorate. In water solution it is rather inert, but in the present instance it acts effectively provided a small amount of osmium tetroxide is furnished as "go between" or oxygen carrier from chlorate to maleic or fumaric acid.

In 1913, Holman, Ehrhart and Schneider, in exploring the reactions of water solution of osmium tetroxide and various chlorates with a variety of substances, found that reagent would oxidize the acid salts of either fumaric or maleic acid to form tartrates. At the time of this discovery maleic acid was made from the very expensive malic acid of apples and was known only in the research laboratory so that the reaction was of little general interest. According to the Hofmann method upwards of 40 percent of the initial material was lost, partly as carbon dioxide which escapes from solution during the progress of the preparation.

Since the Weiss and Downs process of making maleic anhydride has made maleic acid easily available, interest in the possible production of tartaric acid from this source has been revived. Accordingly, at the University of Chicago, Mr. Nicolas Milas and myself began the study of this problem. It soon became apparent that the Hofmann method was promising of control, and now after intensive study of it we have been able to make such modifications that we may transform either maleic or fumaric acid to tartaric with a 97+% efficiency.

The basis of our success was, first, that we secured a simple and rapid test for finding out when the reaction was complete, so that the resulting tartaric acids were not unduly exposed to the oxidizing agent which must be used in excess of that actually consumed by the change. The test depends on the fact that though bromine attacks the salts of fumaric or maleic acid with great speed, it attacks the tartrates only very slowly. To secure a water solution containing only a trace of bromine and not hypo-

bromus acid in harmful amounts a mixture of bromine and excess potassium bromide was used. A neutral solution treated with this reagent became decolorized in less than five minutes if either fumarates or maleates were present.

The next important fact discovered was that the carrier must be reoxidized with great speed relative to its reaction with maleic acid or fumaric. If this is not done maleic acid will be burned to form carbon dioxide, water, etc., and a heavy loss of material occurs just as in the case of the Hofmann experiment. Now the acid molecules of maleic or of fumaric acid are inert toward oxidizing agents but their ions react swiftly. Hence to cut down the rate of the reaction we employed the acids themselves instead of the acid salts as was done by Hofmann. Undoubtedly the reaction is between the carrier and the ions of the acid, but since the ions are furnished in low concentration the sodium chlorate can reoxidize the carrier rapidly enough to avoid the above mentioned harmful effect.

The optimum temperature was found to be 50° , and the proportions of materials were 11.9 grams of sodium chlorate or the equivalent of other chlorates for 10g. of maleic acid and one tenth gram of osmium tetroxide in 150 cc. of solution. The catalyst was recovered by extraction with benzene. From this solution it can be reclaimed by various well known reactions. The refining of the tartaric acid in the product may then be carried out by any of the well known methods for the purification of organic acids. We used the barium salt-sulfuric acid method.

As has been stated, the product of the oxidation of maleic acid is meso tartaric acid, and the product of the oxidation of fumaric acid is the racemic acid. The tartaric acid of commerce is the dextro acid, which combined with the laevo acid makes racemic acid. The separation of racemic acid into these two acids was first made by Pasteur and since his time others have carried out the separation by several methods. However, none of these methods is suitable for large scale work. Fortunately this separation is not necessary for the synthetic acids, and their salts resemble the dextro acid closely in all important characteristics.