

much greater in time due to the catalytic influence of acetic aldehyde, the latter being formed by spontaneous decomposition of the peroxide.

Ether peroxide has been prepared in sufficient quantity to permit a study of its properties and decomposition products, and a structural formula has been assigned to it.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE BARRETT COMPANY]

PRELIMINARY STUDY ON THE FORMATION OF MALIC ACID

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Until comparatively recently very little maleic, fumaric and malic acids have been available to the chemist for investigation. The difficulty of obtaining even moderate quantities from natural sources discouraged work along these lines and a considerable portion of the data in the literature is inaccurate and misleading owing to the meagre quantities with which chemists had to deal. The authors^{1,2} described a method for the synthesis of maleic acid by the partial oxidation of benzene in the presence of a catalyst which has resulted in ample supplies of material becoming available. We desire here to present some results on the reactions of maleic, fumaric and malic acids in respect to the transformation of maleic acid to fumaric acid and malic acid and of fumaric acid to malic acid.

The earliest work on the transformation of fumaric acid to malic acid was carried on by F. Loydl³ who heated fumaric acid with dil. caustic soda solution at about 100° for 100 hours and in this way converted about 52% of the fumaric acid into malic acid. He states that the malic acid is deliquescent in a moist atmosphere, optically inactive and decomposes at 200° into water and fumaric acid without giving a trace of maleic acid.

E. Yungfleisch⁴ claims that malic acid with a small amount of water is converted almost completely to fumaric acid when heated in a sealed tube at 180°. As the proportion of water is not stated, the results are of questionable value. He further states that at 150° in the presence of a large excess of water fumaric acid is converted in part to malic acid which latter is identical with inactive malic acid.

A. Pictet⁵ repeated the latter part of Yungfleisch's work on the preparation of malic acid. He gives no experimental details of the reaction but describes the product as non-deliquescent and decomposing at 135°, giving maleic anhydride and water in the distillate and fumaric acid in the residue. He decided that he obtained a different product from that of Loydl,³ not realizing that the latter probably obtained an impure product by the method he employed, and concluded that there were probably two varieties of inactive malic acid corresponding to racemic and meso-tartaric acids.

¹ Weiss and Downs, *J. Ind. Eng. Chem.*, **12**, 228 (1920).

² U. S. pats. 1,318,631; 1,318,632; 1,318,633; 1,377,534.

³ Loydl, *Ann.*, **192**, 80 (1878).

⁴ Yungfleisch, *Bull. soc. chim.*, **30**, 147 (1878).

⁵ Pictet, *Ber.*, **14**, 2648 (1881).

H. J. Van't Hoff, Jr.⁶ followed the Loydl procedure using maleic acid but gives no details. He concludes that the malic acid obtained is the same as that he had previously obtained⁷ from monobromosuccinic acid.

Tanatar⁸ made the statement that maleic acid could be completely converted into fumaric acid by heating with water.

This statement was denied by Skraup⁹ who published a rather extended account of experimental work in this connection. He brought out the following facts. All acids to a greater or lesser degree aid the reaction of the change of maleic acid to fumaric acid. Maleic acid heated under pressure with water gives fumaric acid under conditions where malic acid is not converted into fumaric acid, thus allowing the conclusion that malic acid is not an intermediate product in the transition from maleic to fumaric acid. He shows that at the lower temperatures, starting with maleic acid, an equilibrium exists among all three acids, while at the higher temperatures only between malic and fumaric acids. He also repeated Loydl's experiments³ using both maleic and fumaric acids as raw materials, but slightly changed the procedure so as to insure a purer product. He obtained an inactive malic acid from each and showed that the behavior on heating both these acids as well as active malic acids was identical and different from that stated by Loydl. Heated rapidly to 200° the dry acids gave maleic and fumaric acids in about equal amounts, but heated slowly they formed fumaric acid to the extent of about nine times the quantity of maleic acid. Maleic acid heated alone at 130° gave fumaric acid and malic acid.

Tanatar¹⁰ replies to Skraup and states that a 10-30% aqueous solution of maleic acid heated in a sealed tube for 2 hours at 200-220° is practically entirely converted into fumaric acid, and under like conditions malic acid is left unchanged. Tanatar admits, however, that his experiments were only qualitative and that small quantities only were used, so that we can fairly conclude that his results are unreliable. The article is long and for the most part polemical.

A reply was made by Skraup¹¹ which is largely polemical in nature but gives the results of a few more experiments on heating maleic acid alone and in the presence of benzol. In the former case, all three acids were found in the reaction product and in the latter the same general results were obtained except that the greater portion of the unchanged maleic acid was isolated from the benzol solution as the anhydride.

Later Tanatar¹² replied again but the article is entirely polemical in nature.

In general, with regard to the literature we may say that in most cases the amounts of materials used were too small for accurate results and there is considerable doubt as to the purity of the substances employed. Therefore, our real knowledge of these reactions up to the present has been in many ways inaccurate and certainly incomplete.

Analytical Methods.—Since the determination of the equilibria of these three acids in water solution was dependent upon a knowledge of the composition of the water solutions, methods of analysis had to be developed.

It was early found that fumaric acid could easily be determined within

⁶ Van't Hoff, Jr., *Ber.*, **18**, 2713 (1885).

⁷ Ref. 6, p. 2170.

⁸ Tanatar, *J. Russ. Phys. Chem. Soc.*, **22**, 1, 310-312 (1890).

⁹ Skraup, *Monatsh.*, **12**, 107 (1891).

¹⁰ Tanatar, *Ann.*, **273**, 31-55 (1893).

¹¹ Skraup, *Monatsh.*, **14**, 501 (1893).

¹² Tanatar, *Ber.*, **27**, 1365 (1894).

a reasonable degree of accuracy when the temperature of the water solutions of malic acid was known, due to its slight solubility. The solubility of fumaric acid was determined to be 0.7 g. per 100 g. of water at 25°. All determinations of fumaric acid were therefore made at 25° and provided sufficient agitation and time to assure solution equilibrium.

Although considerable work has been done on the salts of malic and maleic acids, no satisfactory method of analysis has been developed to determine quantitatively these acids mixed in water solution.

It was, however, found that when the amount of maleic acid in solution was very small the bromine method, described below, was quite accurate.

Wislicenus¹³ reported that maleic acid in water solution is transformed into fumaric acid by the use of bromine and iodine but not by chlorine in the presence of light. In no case did the halogens attack the double bond. Since little information was available concerning the quantitative relations of this reaction, a study was undertaken to determine whether it was capable of development into a method for the quantitative estimation of maleic acid in the presence of malic acid.

During our investigation, different sources of light, that is, sunlight, an incandescent bulb and a Hanovia mercury vapor quartz light, were tried for this purpose. The speed of reaction under the effect of the last was by far the greatest and since it appeared that a long time of contact of the bromine and the acid resulted in the formation of by-products a quick acting test was desirable.

The method of procedure finally adopted was as follows.

The water solution of about 40% malic acid containing small amounts of maleic acid was saturated with fumaric acid by agitating at 25° in a thermostat. When this solution contained only malic and maleic acids, an excess of solid fumaric acid was added thereto. In the solutions taken from the bombs during the equilibrium experiments, there was always an excess of solid fumaric acid.

After saturation of the solution with fumaric acid had become complete, the undissolved fumaric acid was filtered off, care being taken to maintain the temperature of the solution at 25° by immersing the filtering apparatus in the thermostat.

The clear filtrate was placed in transparent fused quartz test-tubes of about 12 mm. in diameter and 15 cm. long. A very small amount of liquid bromine, that is, about 0.005 cc., was run in from a capillary tube and the quartz tube was placed under a Hanovia ultra-violet mercury vapor lamp at a distance therefrom of about 11 cm. The time of exposure was about 10 minutes, after which the liquid was decanted as completely as possible from the remaining liquid bromine at the bottom of the tube. The solution was placed in a dry bottle, iced externally until

¹³ Wislicenus, *Ber.*, 29, 1680 (1896).

seed crystals of fumaric acid separated and then the bottle was placed in the thermostat as before at 25°. It was found and checked by a number of observers that if the crystals of fumaric acid did not dissolve there was at least one part of maleic acid per thousand parts of malic acid in the original solution.

Since the object of this investigation was the study of the equilibrium at the higher temperatures, the conditions were such that there were only very small amounts of maleic acid in the resultant products. The test as described above is not quantitatively accurate for the estimation of all percentages of maleic acid, but was satisfactory for the purposes of the experiments described in the present paper.

Should the equilibria at lower temperatures be investigated, an accurate method for the analysis of malic-maleic acid mixtures in water solution would have to be developed.

Apparatus and Procedure for the Conversion Experiments

A water solution of the acid was placed in a thin-walled Pyrex glass tube having a length of 18–19 cm. and an external diameter of 3 cm. The glass tube was then inserted into a stout steel bomb which was about 30 cm. long and 5 cm. in diameter (external dimensions). The bore of the steel tube was just large enough so that the glass tube rested easily therein. A little water was placed between the glass tube and the steel bomb wall to insure good heat transference. A glass cap rested upon the open end of the glass tube to prevent the acid solution from becoming contaminated with iron rust. The bomb was closed by screwing a steel plug into the open end, an aluminum gasket being used to make a tight joint.

The steel bomb with its contents was then suspended in an upright position in an agitated oil-bath which had previously been heated to the desired temperature. After the bomb had been heated for the desired length of time, it was lifted from the oil-bath and, after the excess oil was removed from it, immersed in a vessel of cold water. When thoroughly cooled the bomb was opened and the glass tube removed.

The contents of the glass tube were then cooled to 25°, filtered with suction and the fumaric acid washed quickly with a small amount of cold water. It was found that when this washing was done sufficiently rapidly the amount of fumaric acid dissolved in the wash water was negligible. The washings and original filtrate were combined and titrated with standard caustic alkali solution. The fumaric acid which was filtered off was dried at 110° and weighed. Correction was finally made for the amount of fumaric acid dissolved in the malic acid solution by applying the solubility of fumaric acid (0.7 g. of acid in 100 g. of water at 25°) to the original amount of water taken.

The filtrate containing the malic acid, small amounts of fumaric acid and maleic acid, if any, was evaporated at a low temperature under a vacuum to 20 cc. volume and cooled to 25° to precipitate fumaric acid. Low temperature evaporation was used to prevent any further reverse conversion of malic acid to fumaric acid, as it had been shown that even heating a solution of malic acid below 100° gave no fumaric acid. The solution was then placed in a thermostat as directed under the test for maleic acid given above. Although this test is not quantitative for various amounts of maleic acid, it is evident that only very small errors could have arisen in this work as the amount of maleic acid was always below 0.5% of the total acids present.

A great many experiments have been made using various sizes of autoclaves, but since the results in general check those obtained in these small bombs, no description of them is considered of interest here. The only factor of importance in treating large volumes of solution which differed from the results given in this paper is that of the time of heating. Agitation of large volumes, particularly where solid fumaric acid is present, is needed to hasten the final equilibrium.

Preparation of Materials.—The maleic acid was prepared by dissolving in distilled water maleic anhydride which was made from high purity maleic acid by several redistillations under high vacuum. It was preserved ready for use in a stoppered bottle in a desiccator. It gave a solidifying point of 52.6°, and titrated as 99.1% pure maleic anhydride.

The inactive malic acid was carefully prepared by autoclaving maleic acid, followed by careful purification to remove fumaric acid. It contained no fumaric acid and no maleic acid as shown by the bromine test. It titrated 99.6% pure.

The fumaric acid was made by recrystallizing high purity fumaric acid several times from water and titrated 99.8% pure.

The *levo*-malic acid was a commercial¹⁴ product supposedly made from maple "sugar sand." It titrated 95.15% pure malic acid.

Experimental Results¹⁵

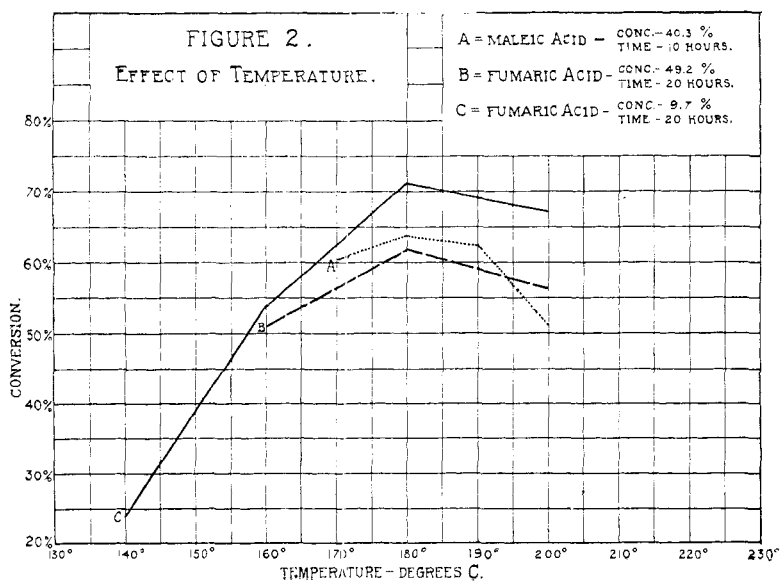
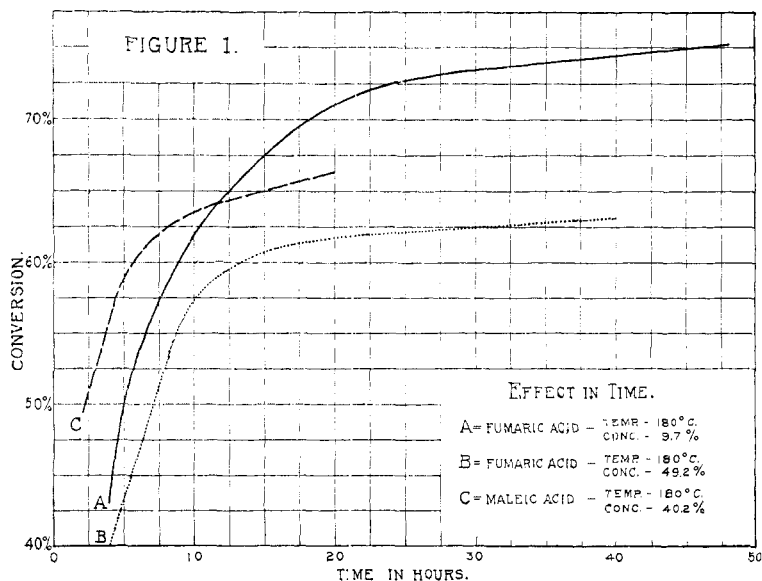
The main results are shown graphically in Figs. 1, 2 and 3 covering the effect of time, temperature and concentration on the equilibrium. The conversion is expressed as the percentage of either maleic or fumaric acid converted to malic acid. The results used in the curves are the average of two check determinations. When fumaric was used in the experiments, we were never able to detect maleic acid in the products. In the maleic series at the lower temperatures and times, maleic acid was

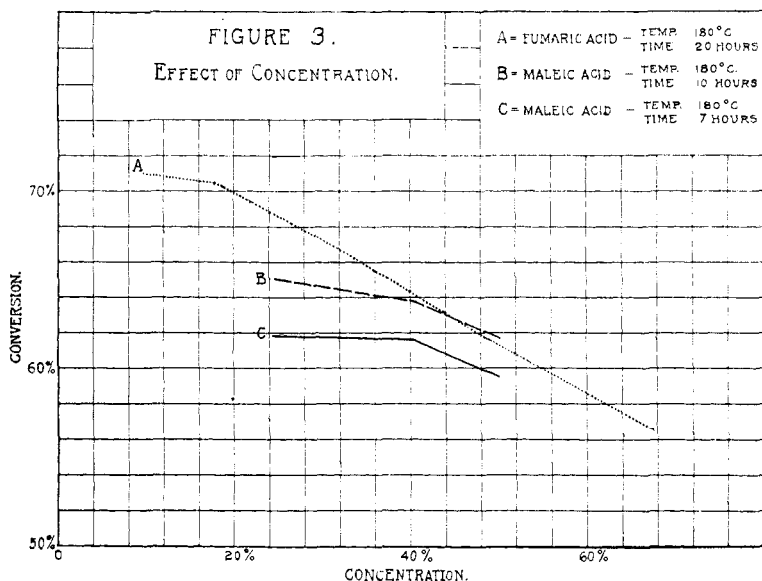
¹⁴ Eastman Kodak Company.

¹⁵ Much of the work on this problem was carried out by Messrs. F. Boettner, H. P. Corson and E. Wolesensky of The Barrett Company Research Laboratory staff.

found in the product but the amount never exceeded 0.5% of the acid used initially.

When maleic acid is used, we have a homogeneous system throughout but with fumaric acid without agitation the insolubility probably retards the reaction speed to a certain extent. However, it was proved that at





least at the conclusion of the heating period in our experiments we had a homogeneous system, that is, all products were in solution.

Some further tests were made heating inactive malic acid with water to see if approximately the same end-point were reached. At a concentration of 40% and a temperature of 180° after 7 hours 25.1% of malic acid had changed to fumaric; after 10 hours, 29.1% had changed. The reaction appears to approach the same end-point as when converting fumaric acid to malic acid.

A like test was carried out on the *levo*-malic acid obtained from maple sugar sand. Two runs were made at 180° for 10 hours at a 40% concentration and gave results of 26.4 and 27.2% conversion to fumaric acid. The residual malic acid was compared with the original by polariscope methods.

	300 mm. tube, 25°, 10% solutions	$[\alpha]_D^{22}$
Original malic.....	0.53°	1.8°
After pressure treatment.....	0.07°	0.24°
Ordinary inactive malic.....	0.02°	0.07°

It may be seen that here also we are approaching the same end-product.

There were also a few experiments in which maleic acid was heated alone, without the presence of a solvent. Four flasks containing maleic acid were heated in a glycerine-bath at 140°. In 5 minutes all the maleic acid was melted. Shortly afterward, fumaric acid crystals began to form in the molten mass and fall to the bottom.

Flask	Time Min.	Fumaric	Malic
		acid formed %	acid formed %
1	5	10	1
2	15	17	3.3
3	45	26	4.0
4	95	41	6.0

This seems to show that malic acid is not an intermediate product, for otherwise there would be a period where malic acid predominated in amount over the fumaric acid.

On the basis of the results obtained we at first attempted to calculate the physical-chemical equilibrium constants but soon found that the methods of manipulation and our lack of certain essential facts made it impossible to make such calculations with even an approximate degree of accuracy. We need only call attention to the fact that we did not have knowledge of the density of the final product at the temperatures and pressures used, and that due to the empty space in the bomb above the charge there was a certain amount of water volatilized from the solution during the operation, and as this was an indefinite volume no very accurate estimate of the molar concentration could be made.

Summary

1. We have shown that in water solution at the lowest temperatures investigated an equilibrium exists among maleic, malic and fumaric acids.
2. At the higher temperatures maleic acid substantially disappears and the equilibrium is between fumaric acid and inactive malic acid.
3. At the higher temperatures approximately the same end-point is reached whether one starts with maleic, fumaric, inactive malic or *levo*-malic acid.
4. An analytical method is described for the detection of small amounts of maleic acid in mixtures with fumaric and malic acid.
5. Malic acid solutions are practically unchanged by simple boiling at atmospheric pressure.
6. Malic acid does not appear to be necessarily an intermediate product in the transformation of maleic to fumaric acid.
7. An exact study of the equilibrium conditions among these acids would be of great scientific interest. We have pointed out certain manipulative and analytical difficulties which would have to be overcome before such accurate determinations could be made.

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