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Maleic Acid Production-Vapor Phase Oxidation of Crotonaldehyde Using Vanadium Pentoxide Catalysts[1]

BY W. L. FAITH AND A. M. SCHAIBLE[2]

The growing demand by industry for aliphatic acids and other oxygenated organic compounds has led to increased interest in catalytic oxidation processes. Many attempts to oxidize petroleum hydrocarbons to intermediate products have been made, but only a few have been successful.[3] More data on the catalytic oxidation of all types of simple organic compounds should lead eventually to a more successful attack on the partial oxidation of hydrocarbons.

The purpose of this study was to obtain data concerning the effect of various conditions on the yield of maleic acid obtained by the vapor phase oxidation of crotonaldehyde using vanadium pentoxide as the catalyst. The only reference to this reaction in the literature is a process patent by Drossbach.[4]

Oxidation Reactions of Crotonaldehyde

In the oxidation of crotonaldehyde, the first reaction that takes place is probably the oxidation of the aldehyde to crotonic acid. The next step, the oxidation of the crotonic acid, is the interesting part of the reaction studied. One ordinarily would suppose that the double bond of the crotonic acid would be the most labile part of the molecule, and therefore most susceptible to oxidation. This is true of the liquid phase oxidation of crotonic acid in which the chief oxidation products are acetic and oxalic acids.[5] In the vapor phase, using certain catalysts, the reaction differs in that the methyl group is oxidized leaving the double bond intact, thus producing maleic acid as the chief oxidation product. Actually, maleic anhydride is formed at the temperature at which the reaction is carried out.

From the industrial standpoint this reaction might become important, depending, of course, on the future cost of benzene and crotonaldehyde. From a research viewpoint, information on the oxidation of double bond compounds of this type should aid research on the oxidation of olefin hydrocarbons.

Method and Apparatus.—The apparatus was of the usual type employed for such studies. Both primary and secondary air for the reaction were passed through drying towers and flowmeters before contacting the crotonaldehyde to be oxidized. The primary air was mixed with crotonaldehyde in a carburetor held at a constant temperature, 109°F. (42.8°C.) for convenience. The air–aldehyde mixture was then passed through a heated tube (to prevent condensation) to a point just before entering the catalyst chamber where it was mixed with secondary air. The new air–aldehyde mixture then passed into the Pyrex catalyst chamber (length, 16 cm.; diameter, 2.5 cm.) where the reaction took place. The temperature of different parts of the catalyst mass was measured with a movable thermocouple inserted in a small Pyrex tube projecting into the center of the mass.

The products of reaction were led from the catalyst chamber to two Erlenmeyer flasks in series where the product, maleic anhydride, sublimed on the walls. Any acid (anhydride) which was not separated in this way was scrubbed from the gases in a third flask partially filled with water. The scrubbed gases were led through a flowmeter and thence to a sampling tube to furnish gas samples for carbon dioxide analysis.

Some polymerization of the aldehyde took place in the carburetor, but it did not markedly affect its volatility. It was necessary, however, to heat the tube carrying the primary air–aldehyde mixture to the catalyst chamber in order to prevent the aldehyde from condensing in this tube. Any liquid aldehyde in the tube polymerized rapidly. If, however, the aldehyde reached the catalyst chamber in the vapor phase, no polymerization was noticed.

Two different forms of vanadium pentoxide catalyst were used. One form was deposited on a carrier of granulated pumice (diameter, 1–3 mm.), the other form was deposited on aluminum balls (diameter, 2–3 mm.) made from turnings.

The catalysts were prepared from ammonium vanadate and oxalic acid in the usual manner.[6]

Analytical Methods

In the average run, 4 to 5 cc. of crotonaldehyde to be oxidized was introduced at a constant rate over a period of one and one-half to three hours. The exhaust gases were analyzed from time to time for carbon dioxide by means of an Orsat apparatus. Since none was detected in the early runs, a check was made on numerous runs by passing the exhaust gases through a barium hydroxide solution. No precipitate was noticed.

The solid product formed was dissolved in distilled water

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[1] The experimental work reported here is a part of Project No. 137 of the Kansas State College Engineering Experiment Station.

[2] Present address: Gulf Oil Corporation, Port Arthur, Texas.

[3] C. Ellis, "Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, pp. 850–931.

[4] Otto Drossbach, U. S. Patent 1,880,901 (Oct. 4, 1932).

[5] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, 1934, p. 361.

[6] L. F. Marek and D. Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chemical Catalog Co., New York, 1932.

and mixed with the scrubbing water in the third Erlenmeyer flask. Its maleic acid content was then determined by a modification of the barium maleate monohydrate method described by Milas and Walsh.[7] This method was found to be satisfactory because the only other acid formed, crotonic acid, did not precipitate as barium crotonate under the conditions employed. Check analyses on known mixtures were accurate within one per cent. The two variations from the published procedure were dilution with one-third more alcohol and separation of the precipitate by centrifugal force instead of filtration.

The purity of the barium maleate monohydrate was proved by the quantitative conversion to barium sulfate in the usual manner.

Anal. Calcd. for $C_4H_2O_4Ba{\cdot}H_2O$: Ba, 51.02. Found: Ba, 50.90, 51.23.

Further proof that the solid product was maleic acid was shown by its conversion to fumaric acid under the influence of light in the presence of bromine.

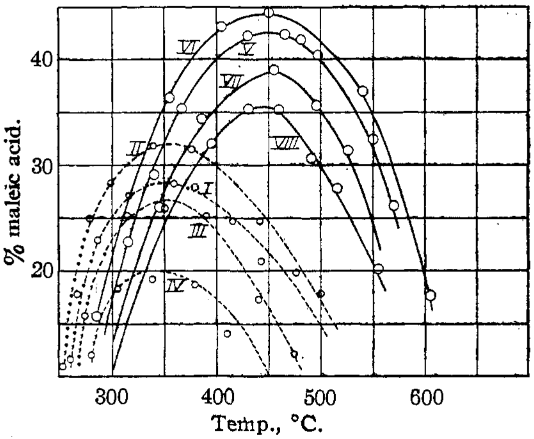

Fig. 1.—The effect of temperature on maleic acid conversion at various molar ratios of air to crotonaldehyde: ---, pumice carrier; —, aluminum carrier. Molar air-crotonaldehyde ratios (±10%): I, 180; II, 325; III, 115; IV, 72; V, 320; VI, 525; VII, 245; VIII, 165.

Effect of Air-Aldehyde Ratio

Results are plotted in Figs. 1 and 2. It may be seen that higher conversions were obtained with the catalyst deposited on the aluminum carrier than with that deposited on pumice. Using a molar air-aldehyde ratio of about 300, the maximum conversion to maleic acid was 42.2% with the former and 31.8% with the latter. The highest air-aldehyde ratio used was about 520 with the catalyst deposited on aluminum. Runs in this series resulted in the highest conversions obtained; the maximum conversion was 44.5% at 450°. In all cases, the conversions to maleic acid increased with increasing molar ratios of air to crotonaldehyde (Fig. 2).

Thermal Conductivity of Catalysts

The variation of conversion with catalyst temperature was not the same with both forms of the catalyst, because of unlike heat distribution. The exploring thermocouple showed that the catalyst deposited on aluminum turnings exhibited a more nearly even temperature distribution than the other. The temperatures shown in Figs. 1 and 2 are in each case the maximum temperature indicated by the thermocouple. Invariably, the maximum temperature of the catalyst deposited on aluminum occurred further forward in the catalyst chamber than it did in the case of the pumice catalyst.

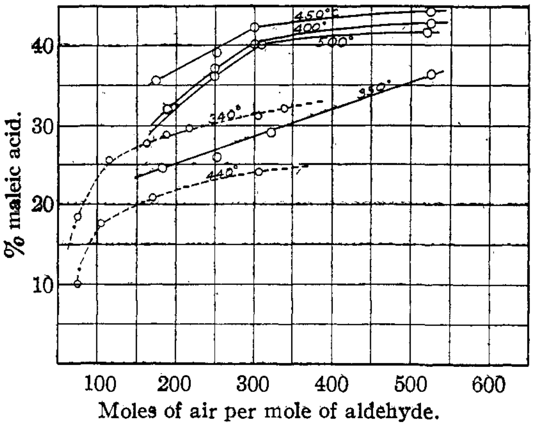

Fig. 2.—The effect of air-aldehyde ratio on maleic acid conversion at different temperatures: ---, pumice carrier; —, aluminum carrier.

The higher conversions obtained by use of the aluminum carrier are due probably to more rapid heat transfer from localized "hot spots" of reaction. When these high temperature regions of reaction build up on the surface of the catalyst deposited on pumice, the low thermal conductivity of the carrier effectively prevents transfer of this heat to other parts of the catalyst mass. The burden of heat removal is then left to the great excess of air passing over the catalyst. As a consequence, temperatures greater than the optimum for the reaction build up in localized regions, while the remainder of the catalyst mass may be far below the optimum temperature. This also accounts for the higher optimum temperature indicated by the pyrometer in the case of the aluminum carrier. A similar effect of the thermal conductivity of different forms of a catalyst has been reported previously by Faith and Keyes.[8]

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[7] N. A. Milas and W. L. Walsh, THIS JOURNAL, 57, 1389-1393 (1935).

[8] W. L. Faith and D. B. Keyes, *Ind. Eng. Chem.*, 23, 1250-1253 (1931).

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Summary

In a study of the catalytic vapor phase oxidation of crotonaldehyde to maleic acid a conversion of 44.2% was obtained.

Two forms of vanadium pentoxide catalyst were used, one deposited on aluminum balls as carriers, the other on pumice. The form of catalyst having the higher thermal conductivity, *i. e.*, that deposited on aluminum, yielded higher conversions.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

Studies on the Chemistry of the Fatty Acids. III. The Properties of Linoleic Acids Prepared by Debromination and by Low Temperature Crystallization, with a Proposed Method of Quantitative Estimation[1]

BY J. B. BROWN AND JEROME FRANKEL

In a previous report[2] procedures for the preparation of linoleic acid were described, based on fractional crystallization of the fatty acids of corn and cottonseed oils from several organic solvents. By a refinement of this method we have been able to prepare a relatively large amount of linoleic acid of better than 93% purity from corn oil. The question naturally arose as to whether this preparation was identical chemically with the so-called α-linoleic acid previously described in the literature by Rollett,[3] and others.[4]

The question is important because the only method previously successful in making the pure acid is that of Rollett which involves the classic bromination–debromination process and which necessarily introduces the question of tetrabromide and linoleic acid isomerism. Accordingly we have prepared some of the pure α-acid by Rollett's procedure, and have compared its properties with those of the acid prepared by crystallization. Although the latter naturally was more impure, we have found that so far as melting point, refractive index and tetrabromide number are concerned, there is little doubt that the two acids are identical.

When α-linoleic acid is brominated in petroleum ether it yields insoluble bromides equal to 90.6% of its original weight; the theoretical is 214%. Hence more than half of the resultant bromides are soluble. When the filtrate from these insoluble bromides is cooled to −70°, they partially precipitate as viscous oils. This formation of soluble bromides was originally noted by Rollett and is a general property of fatty acids with two or more double bonds. Ault and Brown,[5] working with arachidonic acid, took advantage of this fact in proposing a formula for quantitative estimation of arachidonic acid, based on a comparison of the octabromide number of the pure acid (prepared by bromination–debromination) with the octabromide number of a given fatty acid mixture. We wish to propose a similar formula for the estimation of linoleic acid, as follows

$$\text{Per cent. linoleic acid} = \text{T. N.} \times 100/90.6$$

where T. N. is the percentage yield of petroleum ether insoluble tetrabromides given by the fatty acid mixture under investigation and 90.6 is the tetrabromide number of a specimen of pure α-linoleic acid.

The yield of insoluble tetrabromides is naturally involved in the problems of *cis–trans* isomerism in the instance of the original acid and of optical isomerism as far as the products are concerned. It is reasonably certain that in our pure preparations we are dealing with a single *cis–trans* configuration,[6] probably *trans,trans*-9-10,12-13-octadecadienoic acid. Upon bromination, it is likely, though not proved, that at least two pairs of enantiomorphs result, one of which is quite insoluble and high melting; the other pair is very soluble and low melting. Apparently, they are formed in almost equal amount. If they were

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[1] Presented at the Fall Meeting of the American Chemical Society, 1937, Rochester, N. Y.

[2] Brown and Stoner, THIS JOURNAL, **59**, 3 (1937).

[3] Rollett, *Z. physiol. Chem.*, **62**, 410 (1909).

[4] Holde and Gentner, *Ber.*, **58**, 1067 (1925); Birosel, THIS JOURNAL, **59**, 689 (1937).

[5] Ault and Brown, *J. Biol. Chem.*, **109**, 615 (1934).

[6] Smith and West, *Philippine J. Sci.*, **32**, 297 (1927).