

of concentrations. The solubility curve for $(\text{NH}_4)_2\text{SeO}_4$ was not experimentally realizable.

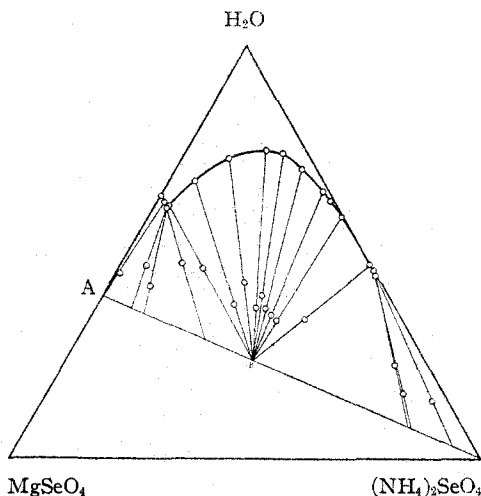


Fig. 1.—The isotherm at 30°: A represents $\text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$; B represents $\text{MgSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 \cdot 6\text{H}_2\text{O}$.

Weston⁵ investigated the corresponding sulfate system and found that the solubility curves of both $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ could not be realized. The selenate and sulfate systems are analogous in nearly every respect.

(5) Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

It should be noted that the solubilities given here for both magnesium selenate and for ammonium selenate do not agree with previous determinations.^{2,6} For the former, Meyer and Aulich give 31.2 wt. per cent. and for the latter, Tutton gives 57.9 wt. per cent. Tutton does not state his method for determining the solubility.

Approximate solubility determinations at 60° have been made. It was found that the same phases are present at that temperature as at 30°, the solubility of each phase increasing with increased temperature.

Acknowledgment.—Hydrogen peroxide used in the preparation of selenate salts was furnished by E. I. du Pont de Nemours and Company. This kindness is gratefully acknowledged.

Summary

1. The solubility relations in the system ammonium selenate–magnesium selenate–water have been determined at 30°.

2. The system is analogous to the corresponding sulfate system.

(6) A. E. H. Tutton, *ibid.*, **89**, 1071 (1906).

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Maleic Acid Production—Vapor Phase Oxidation of Five-Carbon Olefinic Acids¹

BY W. L. FAITH AND M. F. YANTZI

It has been shown that maleic acid may be produced by the catalytic oxidation of crotonic acid, or the corresponding aldehyde.^{2,3} The purpose of the present work was to study the catalytic vapor phase oxidation of several five-carbon olefinic acids under similar conditions. The major objective of the study was to determine whether the chief product of such oxidation would be maleic acid or a five-carbon unsaturated dicarboxylic acid.

Three acids were chosen for the work: 2-pentenoic acid, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$; 3-pentenoic acid, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{COOH}$; tiglic acid, $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COOH}$.

It was felt that the results of the study might

aid research on the catalytic vapor phase oxidation of olefin hydrocarbons.

Preparation of the Acids.—The 2-pentenoic acid was prepared by the method of Boxer and Linstead.⁴ The acid boiled at 103–111° under 19 mm. pressure.

The 3-pentenoic acid was prepared by the method of Linstead, Noble and Boorman.⁵ This acid boiled at 90–92° under 10 mm. pressure.

Tiglic acid was prepared by the method of Michael and Ross.⁶ The crystals melted at 64°.

Method and Apparatus.—The apparatus used for the oxidation of the 2- and 3-pentenoic acids was essentially the same as that previously described.³ In the oxidation of the tiglic acid, a preheater for the primary air was added to prevent deposition of tiglic acid crystals in the tube leading from the vaporizer to the catalyst chamber.

The bath surrounding the vaporizer was maintained at

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

(2) Otto Drossbach, U. S. Patent 1,880,991 (Oct. 4, 1932).

(3) W. L. Faith and A. M. Schaible, *THIS JOURNAL*, **60**, 52 (1938).

(4) S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740–751 (1931).

(5) R. P. Linstead, E. G. Noble and E. J. Boorman, *ibid.*, 557–561 (1933).

(6) A. Michael and J. Ross, *THIS JOURNAL*, **55**, 3684 (1933).

a constant temperature of 71.1° for the runs on the 2- and 3-pentenoic acids, and raised to 80.3° for those on tiglic acid. The catalyst, vanadium pentoxide deposited on a carrier of aluminum balls, also was prepared as before.

Analytical Methods

In most runs, 1 to 2 cc. of acid to be oxidized was introduced at a constant rate for a period of two hours.

Carbon dioxide was determined by passing a known portion of the exhaust gases through a gas-scrubbing bottle containing barium hydroxide solution for a period of twenty minutes during the run. The barium carbonate thus obtained was filtered, redissolved in hydrochloric acid and determined as barium sulfate in the usual manner.

The only acid product which formed in any quantity was maleic acid, and it was determined as the barium maleate monohydrate, using the same procedure as that described previously.³ Check analyses on known mixtures of 2-pentenoic acid and maleic acid were accurate within 2%.

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, 50.98. Found: Ba, 50.85, 50.86.

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

In the case of known mixtures of 3-pentenoic acid and maleic acid, check analyses were accurate within 1.5%. Again the purity was proved by conversion to barium sulfate.

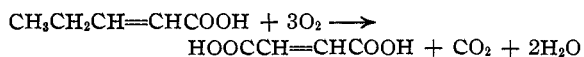
Anal. Calcd. for $C_4H_2O_4Ba \cdot H_2O$: Ba, 50.98. Found: Ba, 50.80, 50.81.

The acid was also converted to fumaric acid as above.

Check analyses on mixtures of maleic acid and tiglic acid were accurate within 2%, but since no maleic acid was found in the oxidation products of tiglic acid, a purity test was not made.

Aldehyde was determined by the neutral sodium sulfite method.⁷ Maleic acid was found to offer no interference under the conditions of this test.

Discussion and Results.—Typical results obtained by oxidation of the three acids are shown in Table I. The 2- and 3-pentenoic acids showed little difference in their oxidation characteristics. Maximum maleic acid conversions were obtained at 450° with both acids. In all cases more carbon dioxide was produced than could be accounted for by the reaction



With both acids, maleic acid conversions increased with increasing molar air-acid ratios. No maleic acid was found in the products of tiglic acid oxidation.

(7) P. C. R. Kingscott and K. S. G. Knight, "Methods of Quantitative Organic Analysis," Longmans, Green and Co., New York, N. Y., 1914, p. 245.

A mixture of aldehydes was found in the products of all runs. No single aldehyde was identified. Tests for malonic, acetic, oxalic, glutaconic and citraconic acids were negative. It should be noted that conversions to carbon dioxide in excess of that accompanying maleic acid formation varied considerably. Apparently total oxidation increases with the age of the catalyst, although no difference could be detected in maleic acid conversions.

TABLE I

RESULTS OF OXIDATION OF FIVE-CARBON OLEFINIC ACIDS

Catalyst temp., °C.	Molar air-acid ratio	A. 2-Pentenoic acid			
		Conversion to maleic acid and CO ₂ , %	Complete conv. to CO ₂ , %	"Other acid" ^a conv., %	Aldehyde conv. mole. %
300	1580	26.3	8.4	24.8	
350	1580	35.6	13.5	5.7	
400	1580	38.8	18.3	3.8	
450	1580	33.8	17.2	1.9	
500	1580	29.6	15.0	1.9	
450	1180	27.9	34.1		
450	1580	32.8	26.0	5.1	
450	1940	34.1	26.0	1.5	
450	3040	34.8	28.6	1.5	
		B. 3-Pentenoic acid			
300	1060	25.4	6.7	12.0	18.8
350	1060	38.2	7.7	4.7	15.3
400	1060	42.5	11.8	2.1	12.9
450	1060	35.4	13.2	0.0	11.8
500	1060	30.9	17.0	0.0	11.2
		C. Tiglic acid			
270	840	0.0		85.6	1.0
350	840	.0	16.4	72.6	10.0
400	840	.0	28.6	58.6	25.0
450	840	.0	35.5	38.6	33.0

^a Calculated in each case as the original acid.

Acknowledgment.—The authors wish to acknowledge the able assistance of H. F. Freeman who prepared the acids used in this investigation.

Summary

The catalytic vapor phase oxidation of 3 five-carbon olefinic acids was studied using a vanadium pentoxide catalyst.

2-Pentenoic acid was oxidized to maleic acid; a maximum conversion of 38.8% was obtained. 3-Pentenoic acid yielded maleic acid with a maximum conversion of 42.5%. Tiglic acid yielded only carbon dioxide and unidentified acids and aldehydes.