

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

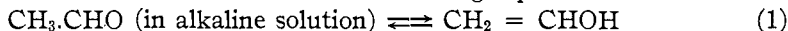
## THE INFLUENCE OF POTASSIUM HYDROXIDE ON THE FORMATION OF VINYL ALCOHOL FROM ACETALDEHYDE.

BY WILLIAM LLOYD EVANS AND CLOYD D. LOOKER.

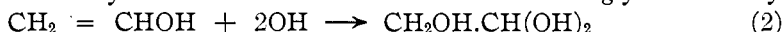
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When ethyl alcohol<sup>1</sup> and acetaldehyde<sup>2</sup> are oxidized by means of potassium permanganate in the presence of potassium hydroxide, acetic, oxalic and carbonic acids are obtained. The amount of the oxalic acid formed in the oxidation of these organic compounds has been found to be proportional to the concentration of the potassium hydroxide used and also to the temperature employed. In the absence of any added alkali no oxalic acid is formed with either ethyl alcohol or acetaldehyde.

Since acetates are unattacked by solutions of alkaline permanganate under the conditions surrounding these experiments, it was assumed with Nef,<sup>3</sup> Denis,<sup>4</sup> McLeod<sup>5</sup> and others that the intermediate formation of vinyl alcohol was necessary in order to offer a satisfactory explanation for the presence of oxalic acid and carbon dioxide; that is, the acetaldehyde is enolized in accordance with the following equation.



Then the vinyl alcohol so formed would be oxidized to glycollic aldehyde,



which is in turn itself oxidized to oxalic acid and carbon dioxide.<sup>6</sup> A consideration of these facts seems to show that the alkali present in these oxidations must affect the production of vinyl alcohol molecules from acetaldehyde.

Nef<sup>3</sup> found that basic mercuric vinylate  $((\text{CH}_2 = \text{CHO})_2\text{Hg}\cdot\text{HgO})$  was formed from an aqueous solution of acetaldehyde and sodium carbonate in the presence of freshly precipitated mercuric oxide. McLeod<sup>5</sup> has observed that no vinyl alcohol is present in an alkaline solution of acetaldehyde if the concentration of the alkali is less than 0.10%; *i. e.*, only acetic acid would be formed by the oxidation of acetaldehyde at alkali concentrations lower than this value. Furthermore, no oxalic acid or carbon dioxide would be formed under these conditions. From the work of Evans and Day<sup>7</sup> and Evans and Adkins<sup>8</sup> it has been shown that the maximum concentration of alkali at which ethyl alcohol and

<sup>1</sup> THIS JOURNAL, 38, 375 (1916); 41, 1267 (1919).

<sup>2</sup> *Ibid.*, 41, 1385 (1919).

<sup>3</sup> Nef, *Ann.*, 298, 315 (1897).

<sup>4</sup> Denis, *Am. Chem. J.*, 38, 568 (1907).

<sup>5</sup> McLeod, *ibid.*, 37, 25 (1907).

<sup>6</sup> THIS JOURNAL, 41, 1280, 1397 (1919).

<sup>7</sup> Evans and Day, *ibid.*, 41, 1282 (1919).

<sup>8</sup> Evans and Adkins, *ibid.*, 41, 1396 (1919).

acetaldehyde are oxidized quantitatively at any given temperature to acetic acid only may be easily calculated.

In view of the above facts, we thought it to be of considerable importance to ascertain the quantitative relationship which might exist between the concentration of the alkali used and the production of vinyl alcohol molecules in an aqueous solution of acetaldehyde.

### Experimental Part.

**Preparation of Acetaldehyde Solution.**—Acetaldehyde was prepared by a modification of the McLeod method<sup>5</sup>. The depolymerized paraldehyde was distilled into a series of small flasks through a 3-bulb Norton and Ott tube, the top bulb of which contained glass beads. The first flask, containing dil. sulfuric acid, was maintained above 40°; the second, between 27° and 40°; the third, between 22° and 27°; the fourth, containing anhydrous cupric sulfate and a calcium chloride tube, below 22°. The cupric sulfate remained almost unchanged in color. The acetaldehyde thus obtained was again distilled below 27° into a weighed amount of water until a sufficient quantity was obtained to make a 2-*M* solution.

**Apparatus and Manipulation.**—The experiment was carried out at 25°. The amount of standardized potassium hydroxide solution chosen

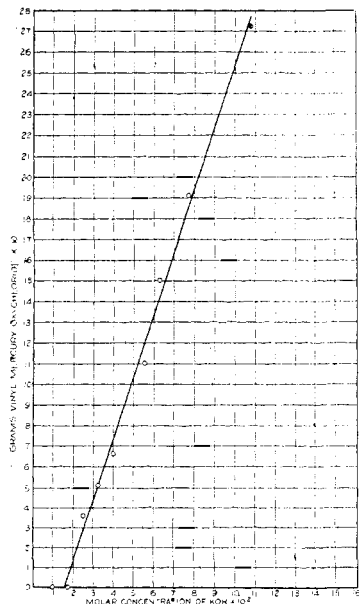


Fig. 1.

for a given experiment was diluted to 145 cc. To the potassium hydroxide solution was added 5 cc. of the acetaldehyde solution (2 *M*) and also 50 cc. of a mercuric chloride solution containing 0.3 g. more of the corrosive sublimate than was necessary to react with the alkali present. The reaction mixture was contained in a 250cc. round-bottom flask and was stirred for 30 minutes. Upon the addition of the mercuric chloride solution the yellow oxide of mercury which formed at first reacted immediately to give a white precipitate with the vinyl alcohol molecules present. This was quickly filtered through an alundum crucible, washed with water, alcohol and ether, then dried over phosphorus pentoxide for 24 hours in a vacuum desiccator. In some experiments the physical character of the precipitate caused much difficulty in filtration. When the white precipitate was unwashed it changed rapidly into a dark gray

color, this decomposition being accompanied by an evolution of acetaldehyde. After a period of 6 to 8 months, these dark precipitates contained many globules of bright, clean, metallic mercury.<sup>9</sup> However, after being treated as above, the white precipitate remained practically unchanged over a long period of time. The white precipitate obtained in our experiments has remained unchanged in color after two years.

**Character of the Precipitate.**—The white precipitate obtained in these experiments was found to be identical with that obtained by Polleck and Thummel<sup>10</sup> when they attempted to separate mercuric chloride by means of ethyl ether from basic mercuric chloride in potassium or sodium hydrogen carbonate solution. These investigators gave the following formula to their compound,  $\text{CH}_2=\text{CHOHgOHgHgCl}_2$ , and called it vinyl mercuryoxychloride. Our analyses showed 82.62% of mercury,<sup>9</sup> (calc. 82.34%).

Nef and Denis<sup>3,4</sup> obtained basic mercury vinylate,  $(\text{CH}_2=\text{CHO})_2\text{Hg.HgO}$  by a different procedure than that employed in these experiments.

**Results.**—The amounts of vinyl mercury oxychloride formed at the various concentrations of potassium hydroxide used in these experiments are shown in the following table.

TABLE I.

VINYL MERCURY OXYCHLORIDE FORMED.

KOH per 200 cc. G.	Molar concentrations of KOH $\times 10^2$ .	$\text{CH}_2=\text{CHOHgOHgHgCl}_2$ G.	Acetaldehyde equivalent $\times 10^4$ .
0.11	0.9804	0.000	0.000
0.20	1.7825	0.003	0.01806
0.28	2.4965	0.36	2.167
0.36	3.2085	0.51	3.071
0.45	4.0107	0.66	3.974
0.62	5.5259	1.10	6.623
0.70	6.2390	1.50	9.031
0.87	7.7540	1.91	11.500
1.20	10.6950	2.72	16.380

From the results of these experiments it is found that the vinyl alcohol production is primarily a function of the concentration of the potassium hydroxide used. Hence it would be expected that the yield of oxalic acid in the oxidation of ethyl alcohol and acetaldehyde by means of potassium permanganate and potassium hydroxide<sup>1,2</sup> would be proportional to the concentration of the alkali used. These results show that a concentration of about 1.40 g. of potassium hydroxide per liter is necessary before an appreciable amount of the white precipitate is obtained. From the experiments of Adkins and one of us<sup>8</sup> it was calculated that a concentration of 1.95 g. of potassium hydroxide per liter is the largest one that may be

<sup>9</sup> Compare *Ber.*, **22**, 2867 (1889).

<sup>10</sup> Polleck and Thummel, *ibid.*, **22**, 2863 (1889).

employed at 25° without oxalic acid being formed. Hence it is seen that considering the difficulty of handling the white compound of mercury there is a satisfactory concordance in the results of these different experiments.<sup>11</sup>

### Summary.

1. Vinyl mercury oxychloride is obtained when alkaline solutions of acetaldehyde are treated with mercuric chloride.

2. The yield of vinyl mercury oxychloride is proportional to the concentration of the alkali present, showing that the production of vinyl alcohol is likewise proportional to the concentration of the alkali.

3. Since the formation of vinyl alcohol is necessary to account for the presence of oxalic acid in the oxidation of ethyl alcohol and acetaldehyde, it follows from (2) that the yield of oxalic acid is also proportional to the concentration of the alkali used.

4. A concentration of about 1.40 g. of potassium hydroxide is necessary for the formation of vinyl alcohol at 25°. This result is in accord with those obtained on the oxidation of acetaldehyde.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY.]

## ADDITION REACTIONS OF PHOSPHORUS HALIDES. IV. THE ACTION OF THE TRICHLORIDE ON SATURATED ALDEHYDES AND KETONES.

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### Introduction.

The first paper of this series dealt with the action of phosphorus trichloride on benzaldehyde. The primary addition product formed by these two substances could be decomposed by the action of water or glacial acetic acid with the formation of an  $\alpha$ -hydroxyphosphonic acid. By the use of glacial acetic acid as a medium very good yields of this substance were obtained.<sup>1</sup> The results presented in this paper show that the reaction can be similarly employed for the preparation of hydroxyphosphonic acids from other aldehydes and ketones. The reaction as applied to ketones, however, is of somewhat limited scope. With certain ketones the yields are rather low (about 50%). Aromatic ketones such as benzophenone and benzil, either react only under very much modified conditions, or not at all. Camphor, also, has been found to be very unreactive.

<sup>11</sup> Compare THIS JOURNAL, 41, 1282 (1919); *Am. Chem. J.*, 37, 28 (1907).

<sup>1</sup> THIS JOURNAL, 42, 2337 (1920).