portant than the molecular weights. For *non-ideal* solutions, Equation 1 holds, and by the general methods of development above used, equations analogous to 2 could be obtained, although they would be much more complicated in general.[3] The separation of solutions (other than colloidal) by centrifuging has been little studied. Vibration was shown in the previous paper to be an important cause of difficulty in obtaining separations by an ordinary centrifuge.

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THE OXIDATION OF ACETOL WITH POTASSIUM PERMANGANATE[1]

BY WILLIAM LLOYD EVANS AND ORA L. HOOVER[2]

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The work presented in this paper is a continuation of a series of similar studies being made in this laboratory on the oxidation of organic compounds.[3] The main purposes of our investigation were the following: (1) to determine the influence of the initial concentration of the alkali upon the character and amounts of the reaction products formed; (2) to ascertain the influence of temperature on the character and the amounts of these products; (3) to learn, if possible, by means of exact quantitative data the course followed by the reactions involved in the oxidation of acetol by means of neutral and alkaline solutions of potassium permanganate. Previous investigations[4] on acetol have not been carried out under carefully controlled conditions and as a consequence the various results are not comparable, nor do they shed much light on the mechanism of the oxidation.

[3] Miller, *Trans. Am. Electrochem. Soc.*, **21**, 209 (1912), gives equations for the concentration distribution of a solute in a dilute solution under centrifugal force.

[4] National Research Fellow in Physical Chemistry.

[1] This paper was read at the New York meeting of the American Chemical Society in September, 1921.

[2] Du Pont Fellow.

[3] THIS JOURNAL, (a) **34,** 1087 (1912); (b) **35,** 54 (1913); (c) **38,** 375 (1916); (d) **41,** 1267, 1386 (1919).

[4] Linneman, *Ann.*, **134,** 174 (1865). Emmerling and Wagner, *ibid.*, **204,** 40 (1880). Perkin, *J. Chem. Soc.*, **59,** 793 (1891). Nef, *Ann.*, **335,** 269 (1904). Denis, *Am. Chem. J.*, **38,** 561 (1907).

Experimental Part

The acetol used in these experiments was prepared from monobromoacetone according to Nef's method. We established the stability of acetol in aqueous solution by periodically making molecular-weight determinations by the freezing-point method. Our values were found to be 71.6–71.8 (calc., 74). In the oxidations in which 1.789 g. of acetol was used, the solution contained 89.45 g. per liter; in those in which 1.699 g. was used, 40.26 g. per liter; in the experiments corresponding to Point 4 at 25° (Figs. 1 and 2), Points 1, 2, 3 and 4 at 50°, and all those at 75° and 100° the solution contained 60.057 g. per liter. The oxidations were carried out essentially as described previously by Day, Adkins and one of us.[3] Owing to the intense local heating occasioned by the interaction of acetol and the oxidizing agent, the aqueous solution of acetol was introduced at the rate of 0.06 g. per 6 minutes. After the acetol had been added in the desired amount the remaining permanganate was decomposed with a small excess of sodium hypophosphite solution. For reaction mixtures containing less than 0.5 g. of potassium hydroxide per liter, 10 cc. of a standard solution of potassium hydroxide was added after the permanganate had been decolorized. The air in the reaction flask was swept through an absorption train by aspirating 2.5 to 3 liters of air free from carbon dioxide through the apparatus in order to collect any carbon dioxide present. The filtrate from the hydrated oxide of manganese was analyzed for carbon dioxide, acetic and oxalic acids by previously

TABLE I

PARTIAL TABULATION OF THE ANALYSES OF REACTION MIXTURES

KOH N	Acetol G.	CO_2 G.	($C_2H_4O_2$) G.	($C_2H_2O_4$) G.	Carbon yield %
		Temperature 25°			
0.0000	1.6989	1.004	1.337	0.000	97.9
0.0040	1.6989	1.000	1.306	0.082	98.9
0.0080	1.6989	0.980	1.170	0.287	98.3
0.0160	1.2011	0.714	0.637	0.565	102.7
0.0349	1.7890	1.044	0.398	1.533	97.9
0.0699	1.7890	1.048	0.261	1.741	98.2
0.1399	1.7890	1.102	0.242	1.758	99.5
0.2797	1.7890	1.080	0.247	1.722	97.9
0.5595	1.7890	1.076	0.377	1.542	98.3
1.1189	1.7890	1.086	0.619	1.144	97.5
1.8183	1.7890	1.094	0.533	1.349	100.0
2.9373	1.7890	1.088	0.580	1.275	99.8
		Temperature 50°			
0.0000	1.2011	0.762	0.951	0.000	100.6
		Temperature 75°			
0.0000	1.8017	1.162	1.395	0.000	99.9
		Temperature 100°			
0.0000	1.2011	1.032	0.761	0.000	100.2

described methods.[3] Owing to the presence of phosphoric acid, the calcium oxalate was precipitated in an acetic acid solution. All reaction mixtures were examined for formic, lactic and pyruvic acids.[5] These acids were absent.

Data and Curves.—Typical results of the analyses of the different oxidation mixtures at 25° are shown in Table I. All of our results at 25°, 50°, 75° and 100°, showing the effect of the temperature and the concentration of the alkali on the amounts of carbon dioxide, acetic and oxalic acids produced from 0.1 mole of acetol, are given graphically in Figs. 1 and 2, respectively, all of the reacting materials being at the same concentration as those shown in Table I.

Theoretical Part

The oxidation of acetol to acetic acid, oxalic acid and carbon dioxide may be expressed by the following equations respectively.

$$CH_3{\cdot}CO{\cdot}CH_2OH + 3O \longrightarrow CH_3{\cdot}COOH + H_2O + CO_2 \quad (1)$$

$$CH_3{\cdot}CO{\cdot}CH_2OH + 6O \longrightarrow (COOH)_2 + 2H_2O + CO_2 \quad (2)$$

$$CH_3{\cdot}CO{\cdot}CH_2OH + 7O \longrightarrow 3CO_2 + 3H_2O \quad (3)$$

These reactions do not show the various steps through which the oxidation of acetol may proceed, nor do they indicate the quantity of various products to be expected under the different experimental conditions used. However, much light is shed on the nature of the changes taking place in these oxidations when the quantitative experimental results are studied in connection with these equations. The individual steps involved in each of the above reactions are better understood when one considers the several ways in which the acetol molecule may be both enolized and dissociated. These various ways may be represented by the following equations.

$$CH_3{\cdot}CO{\cdot}CH_2OH \rightleftarrows CH_3{\cdot}CHO + {>}CHOH \quad (4)$$

$$CH_3{\cdot}CO{\cdot}CH_2OH \rightleftarrows CH_3{\cdot}CO{\cdot}CH{<} + HOH \quad (5)$$

$$CH_3{\cdot}CO{\cdot}CH_2OH \rightleftarrows CH_3{\cdot}C(OH){=}CHOH \quad (6)$$

$$CH_3{\cdot}CO{\cdot}CH_2OH \rightleftarrows CH_2{=}C(OH){\cdot}CH_2OH \quad (7)$$

The application of these dissociation and enolization equations to Equations 1, 2 and 3 may be most easily treated under two general headings, namely, reactions taking place in neutral solution, and those taking place in alkaline solutions. These will be considered separately.

Neutral Solution.—Acetic acid and carbon dioxide were the sole oxidation products of acetol in neutral permanganate solutions. Our results show that an increase in temperature under these conditions is accompanied by an increase in the yield of carbon dioxide and a decrease in that of acetic acid (Figs. 1 and 2). At 50° and 75° the effect of temperature is not so marked, while at 100° it is very pronounced. At 25° acetic acid

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[5] Jones, *Am. Chem. J.*, **17**, 539 (1895). Denigès, *Bull. soc. chim.*, [4] **5**, 647 (1909). Simon, *Compt. rend.*, **125**, 534 (1897).

and carbon dioxide were obtained in practically equimolecular amounts. This is easily understood when one considers that in an aqueous solution acetol may exist in equilibrium with its products of dissociation as shown in Equation 4. That acetol does actually exist in this condition follows from the fact that Denis found that acetol may be oxidized quantitatively to acetic and formic acids in an aqueous solution either with silver oxide

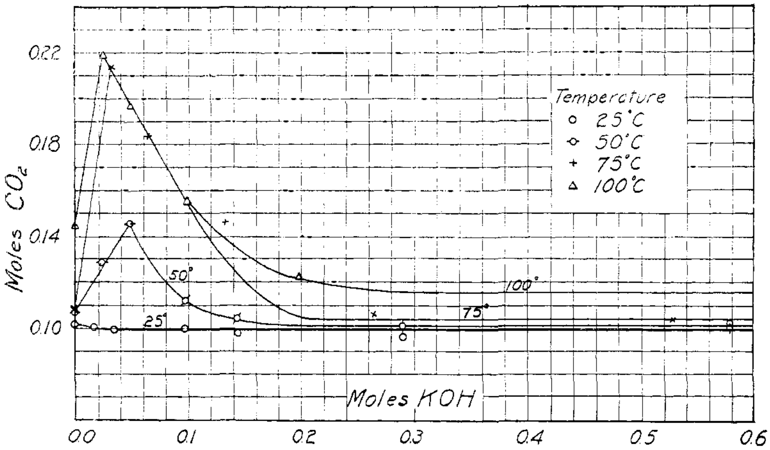

Fig. 1.—Effect of Temperature and Alkali on the Formation of Carbon Dioxide from 0.10 Mole of Acetol.

The solution contains 89.45 g. per liter in the experiments at 0.035 *N* KOH and higher concentrations.

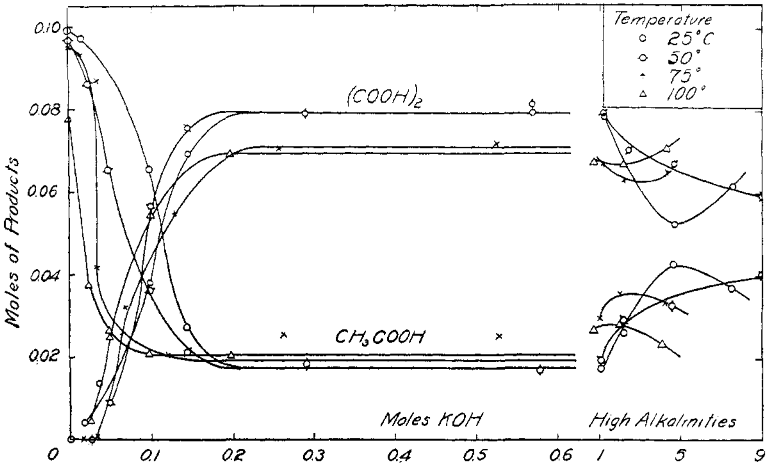

Fig. 2.—Effect of Temperature and Alkali on the Formation of Oxalic and Acetic Acids from 0.10 Mole of Acetol.

The solution contains 89.45 g. per liter in the experiments at 0.035 *N* KOH and higher concentrations.

alone or in the presence of alkalies. No trace of carbon dioxide was found. These changes in neutral permanganate solution at 25° may then be summarized in Equation 4. As is well known these products of dissociation are then easily oxidized to acetic acid and carbon dioxide, respectively, as shown in Equation 8.[6]

$$CH_3 \cdot CHO + {>}CHOH + 6OH \longrightarrow CH_3 \cdot COOH + CO_2 + 4H_2O \qquad (8)$$

All the areas for carbon dioxide above 0.10 mole in Fig. 1 represent carbon dioxide formed in excess of the equimolecular ratio, that is, more than one carbon atom equivalent of carbon dioxide. The deviation of the amounts of acetic acid and carbon dioxide formed at 50° and 75° from this equimolecular ratio is slight, while at 100° it is very marked. If the carbon dioxide equivalent to the acetic acid formed at 100° in accordance with Equation 1 be deducted from the total carbon dioxide yield (1.032 − 0.558 = 0.474 g.), and the acetol which is equivalent to this difference be calculated in accordance with Equation 3, then it can be shown that 22.15% (or 0.266 g.) of the total acetol (1.2011 g.) was oxidized in accordance with Equation 3; that is, acetol was in effect oxidized completely to carbon dioxide. Since no oxalic acid was formed under these conditions it is clear that the remainder of the acetol must have been oxidized to equimolecular amounts of acetic acid and carbon dioxide in accordance with Equation 1. In order to account for the carbon dioxide thus formed in accordance with Equation 3, one must consider the following facts. Denis[4] succeeded in obtaining pyruvic aldehyde by the oxidation of acetol by means of aqueous solutions of copper acetate.[7] She found that pyruvic aldehyde was converted to lactic acid through the benzilic acid rearrangement. This change took place incompletely and slowly in neutral aqueous solutions even on heating to 100° for 42 hours. Since the rate of rearrangement of pyruvic aldehyde into lactic acid in the absence of alkalies is so very slow, a possibility exists for a series of reactions taking place by which the aldehyde may be oxidized to carbon dioxide exclusively, or to acetic acid and carbon dioxide. In attempting to find a satisfactory explanation of this excessive carbon dioxide production, one is confronted with the very great difficulty that our knowledge of the properties of the possible intermediate compounds formed in the oxidation of acetol to carbon dioxide is very limited. In some cases the compounds themselves are unknown. However, the action of aqueous solutions of potassium permanganate on the products of dissociation of the theoretically possible intermediate compounds which can play a role in this oxidation is known. Therefore, one may be guided in the choice of the proper reaction mechanism in the oxidation of acetol

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[6] Nef, Ref. 4, pp. 250, 274. Denis, Ref. 4, p. 579. Evans, Ref. 7, p. 128. Evans and Morgan, Ref. 3b, p. 64.

[7] Evans, *Am. Chem. J.*, **35**, 121 (1906).

by a knowledge of these facts and by a consideration of the following possibilities. (1) The pyruvic aldehyde formed by the oxidation of acetol may be oxidized directly[8] to pyruvic acid. The pyruvic acid thus formed must exist in equilibrium with its enolic form (α-hydroxy-acrylic acid) in accordance with Equation 9.

$$CH_3\cdot CO\cdot COOH \rightleftarrows CH_2{=}C(OH)\cdot COOH \qquad (9)$$

(2) On the other hand, the pyruvic aldehyde may exist in equilibrium with its enolic form (α-hydroxy-acrylic aldehyde) in accordance with Equation 10.

$$CH_3\cdot CO\cdot CHO \rightleftarrows CH_2{=}C(OH)\cdot CHO \qquad (10)$$

These possibilities present several cases for our consideration. (A) The pyruvic acid formed by the oxidation of pyruvic aldehyde may dissociate in accordance with Equation 11.

$$CH_3\cdot CO\cdot COOH \longrightarrow CH_3\cdot COOH + {>}CO \qquad (11)$$

This reaction as a source of excessive carbon dioxide is excluded because the acetic acid and carbon dioxide formed by such a mechanism would be present in equimolecular amounts. Nor can it be urged that the pyruvic acid would first decompose into acetaldehyde and carbon dioxide because both acetaldehyde[3] at 25°, 50° and 75° and ethyl alcohol[3] at 100° are oxidized by neutral permanganate solutions to acetic acid exclusively. (B) If pyruvic aldehyde is dissociated in accordance with Equation 12 as rapidly as it is formed from the acetol then it is clear that acetic acid and

$$CH_3\cdot CO\cdot CHO \longrightarrow CH_3\cdot CHO + {>}CO \qquad (12)$$

carbon dioxide would be present as oxidation products in equimolecular amounts and for this reason this possibility is also excluded as one which will produce an excessive amount of carbon dioxide. This rigid exclusion of the possibilities shown in Equations 11 and 12 leaves only the enolic forms of both pyruvic acid and pyruvic aldehyde to be considered in seeking the correct solution of this problem.[9] (C) As shown in Equation 9, pyruvic acid is in equilibrium with its enolic form, α-hydroxy-acrylic acid. The hydroxy-acrylic acid so formed will be oxidized to hydroxy-pyruvic acid by aqueous solutions of potassium permanganate in the well-known manner in accordance with equation 13.[10]

$$CH_2{=}C(OH)\cdot COOH + 2OH \longrightarrow CH_2OH\cdot CO\cdot COOH + H_2O \qquad (13)$$

Hydroxy-pyruvic acid [11] is a compound similar to acetol in that it reduces both Fehling's solution and ammoniacal silver solution. This similarity in behavior is to be expected in view of the fact that both compounds contain the hydroxy-acetyl group bound to one other group. There are two

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[8] Compare Denis, Ref. 4, p. 575.

[9] Compare (a) Meyer, *Ber.*, **45**, 2847, 2852 (1912). (b) Witzemann, THIS JOURNAL, **39**, 2667 (1917).

[10] Compare Ref. 9b, p. 2665.

[11] Will, *Ber.*, **24**, 400, 3831 (1891).

ways in which hydroxy-pyruvic acid reacts in neutral permanganate solutions in order to produce the excessive carbon dioxide. Both of these lead one inevitably to the conclusion that the final intermediate compound in the oxidation of acetol to carbon dioxide through the hydroxy-pyruvic acid stage is glyoxylic acid. (1) Hydroxy-pyruvic acid is dissociated in accordance with Equation 14.

$$CH_2OH{\cdot}COOH + {>}CO \rightleftharpoons CH_2OH{\cdot}CO{\cdot}COOH \rightleftharpoons {>}CHOH + CHO{\cdot}COOH \quad (14)$$

The dissociation of hydroxy-pyruvic acid into glycolic acid and carbon monoxide is excluded as a possible step in the oxidation of acetol in neutral solution because glycolic acid is oxidized to oxalic acid and carbon dioxide.[3] Oxlaic acid was not present as a reaction product in our neutral solutions.[12] The dissociation in the direction yielding glyoxylic acid, similar to that of acetol in Equation 4, is in entire harmony with our experimental results, because these dissociation products are oxidized exclusively to carbon dioxide[3] and water. (2) The molecular hydroxy-pyruvic acid (Equation 14) is also oxidized at the primary alcohol group in the same manner as is acetol (Equation 5). The formyl-glyoxylic acid ($CHO{\cdot}CO{\cdot}COOH$) so formed will not undergo the benzilic acid rearrangement to form tartronic acid[13] but will be dissociated into glyoxylic acid and carbon monoxide,

$$CHO\text{-}CO\text{-}COOH \rightleftharpoons CHO{\cdot}COOH + {>}CO \quad (15)$$

both of which are oxidized completely to carbon dioxide. That mesoxalic acid is not a product of the reaction follows from the well-known fact that potassium mesoxalate is oxidized to equimolecular amounts of oxalic acid and carbon dioxide. However, when free mesoxalic acid is heated to 100° it decomposes with the evolution of one molecular equivalent of carbon dioxide.

From these considerations we conclude that pyruvic aldehyde, pyruvic acid, hydroxy-pyruvic acid, formyl-glyoxylic acid and glyoxylic acid are the successive steps in the oxidation of acetol to carbon dioxide exclusively (Equation 3). The formation of carbon dioxide in excess of one gram atom equivalent in the oxidation of lactic acid, pyruvic acid and propylene glycol observed earlier by Witzemann and one of us[14] is undoubtedly due to the intermediate formation of glyoxylic acid as shown by these equations. Furthermore, carbon dioxide is also obtained from the oxidation of glyoxylic acid, one of the dissociation products of hydroxy-pyruvic acid. (D) The enolic form of pyruvic aldehyde is also oxidized to hydroxy-pyruvic acid in accordance with the following equations; that is, hydroxy-

$$CH_2{=}C(OH){\cdot}CHO + 2OH \longrightarrow CH_2OH{\cdot}CO{\cdot}CHO + H_2O \quad (16)$$

$$CH_2OH{\cdot}CO{\cdot}CHO + 2OH \longrightarrow CHO{\cdot}CO{\cdot}COOH + H_2O \quad (17)$$

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[12] Cf. Ehrenfeld, *Z. anorg. Chem.*, **33**, 117 (1902).

[13] Denis, Ref. 4, p. 576.

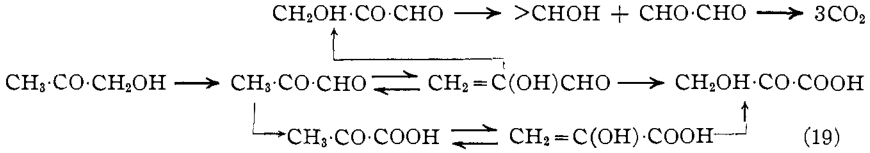
[14] Evans and Witzemann, This Journal, **34**, 1095 (1912).

pyruvic aldehyde may be oxidized to formyl-glyoxylic acid by the simultaneous oxidation of the primary alcohol and aldehyde groups to an aldehyde and carboxyl group respectively. Thus it is obvious that the enolic form of pyruvic aldehyde may also be a source of carbon dioxide.

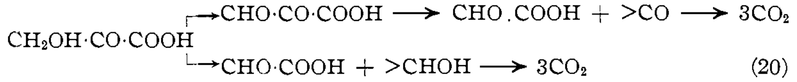
Hydroxy-pyruvic aldehyde may dissociate in the same manner as acetol (Equation 4) and hydroxy-pyruvic acid (Equation 14), thus,

$$CH_2OH{\cdot}CHO + {>}CO \rightleftharpoons CH_2OH{\cdot}CO{\cdot}CHO \rightleftharpoons {>}CHOH + CHO{\cdot}CHO \quad (18)$$

The dissociation of hydroxy-pyruvic aldehyde into glycolic aldehyde and carbon monoxide is excluded because glycolic aldehyde is oxidized to oxalic acid with neutral permanganate. On the other hand glyoxal yields carbon dioxide and water exclusively. In addition to the compounds mentioned in the preceding paragraphs as the various steps through which acetol is oxidized, hydroxy-pyruvic aldehyde must also be included as a product of the direct oxidation of pyruvic aldehyde. The relative amount of pyruvic aldehyde being converted to hydroxy-pyruvic aldehyde and into pyruvic acid by direct oxidation cannot be established by the results of our experiments. Finally, the reactions involved in the excessive carbon dioxide formation in the oxidation of acetol in neutral permanganate solutions may be summarized in the following equations.



$$\begin{tikzcd}
 & CH_2OH{\cdot}CO{\cdot}CHO \arrow[r] & {>}CHOH + CHO{\cdot}CHO \arrow[r] & 3CO_2 \\
CH_3{\cdot}CO{\cdot}CH_2OH \arrow[r] & CH_3{\cdot}CO{\cdot}CHO \arrow[r, shift left] \arrow[d] & CH_2{=}C(OH)CHO \arrow[l, shift left] \arrow[r] \arrow[ul] & CH_2OH{\cdot}CO{\cdot}COOH \\
 & CH_3{\cdot}CO{\cdot}COOH \arrow[r, shift left] & CH_2{=}C(OH){\cdot}COOH \arrow[l, shift left] \arrow[ur] &
\end{tikzcd} \quad (19)$$



$$\begin{tikzcd}
 & CHO{\cdot}CO{\cdot}COOH \arrow[r] & CHO.COOH + {>}CO \arrow[r] & 3CO_2 \\
CH_2OH{\cdot}CO{\cdot}COOH \arrow[ur] \arrow[dr] & & & \\
 & CHO{\cdot}COOH + {>}CHOH \arrow[r] & 3CO_2 &
\end{tikzcd} \quad (20)$$

Alkaline Solutions.—An increase in the concentration of the alkali used will tend to shift the equilibrium expressed by Equation 9 towards the enolic side, thereby increasing the concentration of the enolic compound. Our results are in complete harmony with this exceedingly important experimental fact, since an examination of Fig. 1 shows that the speed of the reactions producing carbon dioxide in accordance with Equation 3 is greatly accelerated by very small concentrations of potassium hydroxide. It is also clear that the speed of these reactions is increased with an increase in temperature. The results seem to indicate that there must be some point above 100° at which acetol is oxidized completely to carbon dioxide both in neutral solutions and in those of very small concentration of alkali. In Fig. 1 it is seen that an increase in the amount of carbon dioxide above the equimolecular ratio is accompanied by a decrease in the amount of acetic acid formed. The concentration of the alkali at the point of maximum production of carbon dioxide should be that at which the acetic acid production reaches a minimum value were it not for the fact that oxalic acid appears as one of the reaction products. The sources of these three reaction products will be taken up successively.

Acetic Acid.—The acetic acid obtained in the oxidation of acetol may be derived from three general reactions. (1) When the dissociation products indicated in Equation (4) are oxidized, acetic acid and carbon dioxide are obtained. (2) In harmony with Nef's views[15] to the effect that the metallic salts of the alcohols are dissociated at much lower temperatures than are the alcohols themselves, it is evident that an increase in the concentration of the alkali in these oxidations will tend to suppress the dissociation indicated by Equation 4 and to increase that indicated by Equation 21.

$$CH_3{\cdot}COCH_2OK \longrightarrow CH_3{\cdot}CO{\cdot}CH< + KOH \qquad (21)$$

The general effect of this reaction will be to produce a more rapid oxidation of acetol to pyruvic aldehyde in the manner indicated by Equations 21 and 22.

$$CH_3{\cdot}CO{\cdot}CH< + 2OH \longrightarrow CH_3{\cdot}CO{\cdot}CHO + H_2O \qquad (22)$$

In the presence of sufficient alkali the lactic acid formed by the rearrangement of the pyruvic aldehyde is then oxidized to pyruvic acid and this in turn is further oxidized almost entirely to oxalic acid and carbon dioxide.[16] However, in some earlier experiments, Witzemann and one of us[3] found that a small amount of acetic acid was always present as a reaction product when both lactic and pyruvic acids were oxidized with alkaline potassium permanganate. In view of these experimental facts, it is clear that pyruvic acid is one of the intermediate compounds which furnishes a part of the acetic acid obtained in the oxidation of acetol. Denis postulated the intermediate formation of acetol and pyruvic acid in the oxidation of acetone. On the basis of his own experiments and those of Fournier, and also on the basis of the mechanism of iodoform formation from acetone and acetaldehyde suggested by Pieroni and Tounioli, Witzemann points out that pyruvic acid is one of the intermediate compounds in the formation of acetic acid from acetone, acetol being the first intermediate compound. Within certain limits of alkalinity, our experimental results are in complete accord with the views of Denis and Witzemann in reference to the role played by pyruvic acid as a source of oxalic and acetic acids. The general method of experimental procedure used by both of these investigators was somewhat different from that employed by us.

Since acetic acid is present in largest amounts in solutions of smaller alkalinities, and since it is present as a reaction product in relatively smaller amounts at higher alkalinities, then from Fig. 2 it is evident that the acetic acid produced in accordance with Equation 4 must be formed in potassium hydroxide solutions ranging approximately from 0.0 to

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[15] Ref. 4, p. 312.

[16] Beilstein and Wiegand, *Ber.*, **17,** 840 (1884). Compare Fournier, *Bull. soc. chim.,* [4] **3,** 256 (1908).

0.2 *M*, while that obtained by the direct oxidation of pyruvic acid must be formed in potassium hydroxide solutions of about 0.2 to 0.6 *M*. (3) A totally unexpected result was obtained in the alkaline solutions ranging from about 1.0 to 9.0 *M*. Instead of the yield of acetic acid gradually diminishing it was found to reach a maximum again within these ranges of alkalinity (Fig. 2). This effect was influenced by the temperature, being greatest at 25° and least at 100°. This increase in the yield of acetic acid is easily understood from the equilibrium expressed by Equation 6. The enolized form of acetol is dissociated according to the following equation

$$CH_3{\cdot}C(OH){=}CHOH \rightleftarrows CH_3{\cdot}\underset{\wedge}{C}(OH) + {>}CHOH \qquad (23)$$

and these dissociation products are then oxidized to acetic acid and carbon dioxide. In consequence of this reaction, the decrease observed in the yields of oxalic acid was to have been expected. That the dissociation in Equation 23 actually takes place instead of an oxidation in accordance with Equation 24

$$CH_3{\cdot}C(OH)\underset{\wedge}{=}CHOH + 2OH \longrightarrow CH_3{\cdot}CO{\cdot}CHO + 2H_2O \qquad (24)$$

is rigidly established by the fact that such an oxidation would result in diminishing amounts of acetic acid owing to the formation of lactic acid from the pyruvic aldehyde formed.[14] This behavior of acetol is in harmony with the views of Kling[17] who showed that acetol in an aqueous alkaline solution showed the properties of a pseudo acid. He found that on adding an alkali the acetol was neutralized but became acid again thus showing a slow readjustment of the equilibrium. Kling assigned the following formula for the pseudo acid, $CH_3\overbrace{C(OH) - CH_2}^{O}$. In view of the general arrangement of groups and valence bonds about the carbon atom in a carboxyl group, we prefer $CH_3{\cdot}C(OH) = CHOH$, in which the oxygen atom is replaced by the divalent (CHOH) group. This latter view is also in harmony with the generally accepted opinion in reference to the consititution of the nitronic acids. Briefly summarizing, the sources of acetic acid in both neutral and alkaline solutions are those expressed by Equations 4, 5 and 6.

Oxalic Acid.—(1) It has been shown by several investigators[18] that acetaldehyde is converted into vinyl alcohol by potassium hydroxide solutions containing 1.4–1.9 g. of the base per liter. The glycolic aldehyde formed from vinyl alcohol is oxidized to oxalic acid and carbon dioxide under our experimental conditions. This source of oxalic acid

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[17] Kling, *Comp. rend.*, **140,** 1256(1905).

[18] Denis, Ref. 4, p. 568. McLeod, *Am. Chem. J.*, **37,** 23 (1907). Compare Nef, *Ann.*, **298,** 316 (1897). Compare Ref. 3 d, pp. 1280, 1397. THIS JOURNAL, **43,** 1925 (1921).

depends on acetol being dissociated in accordance with Equation 4. (2) As shown above, the oxalic acid obtained in the ranges of alkalinity from 0.2–0.6 *M* must result from the oxidation of pyruvic acid obtained from lactic acid. (3) In solutions containing 1.0–9.0 moles of alkali, oxalic acid was found to reach a new minimum (Fig. 2) and then rise toward a new maximum. In view of the new maximum in acetic acid, the new minimum in oxalic acid is easily explained. The new maximum in oxalic acid is understood from a consideration of the enolized form of acetol shown by Equation 7, that is, acetol is in equilibrium with α-hydroxy-allyl alcohol. This enolized form is then oxidized to dihydroxy acetone.

$$CH_2=C(OH)\cdot CH_2OH + 2OH \longrightarrow CH_2OH\cdot CO\cdot CH_2OH + H_2O \qquad (25)$$

We were unable to find any account in the literature of the action of this compound towards alkaline permanganate, but it is almost certain that it is oxidized in the same manner as glycerol, namely, to oxalic acid and carbon dioxide. In the analytical methods for the determination of glycerol by means of alkaline potassium permanganate a large excess of alkali is always used. Since the large concentration of alkali will tend to suppress the dissociation of dihydroxy-acetone shown in Equation 26.

$$CH_2OH\cdot CO\cdot CH_2OH \longrightarrow {>}CHOH + CHO\cdot CH_2OH \qquad (26)$$

It is obvious that the dihydroxy-acetone will be oxidized successively to mesoxalic aldehyde, mesoxalic acid, oxalic acid and carbon dioxide. This reaction must be accompanied by a corresponding decrease in the yield of acetic acid. Finally, the three general sources of oxalic acid are those indicated by Equations 4, 5 and 7.

Summary

1. Four general reactions (Equations 4, 5, 6, and 7) are involved in the oxidation of acetol in neutral or alkaline potassium permanganate solutions. The extent to which each reaction contributes in the general oxidation of acetol depends on the initial concentration of the alkali used.

2. Carbon dioxide and acetic acid are the sole oxidation products in neutral permanganate solutions at 25°, 50°, 75° and 100°. Oxalic acid is found in all alkaline solutions, save those in which the concentrations of the base are exceedingly small.

3. The carbon dioxide production at 50°, 75°, and 100° is in excess of one gram atom equivalent of carbon. Acetol is oxidized to give this excess of carbon dioxide through the following steps: pyruvic aldehyde (hydroxy-pyruvic aldehyde), pyruvic acid, hydroxy-pyruvic acid, formylglyoxylic acid and glyoxylic acid. The concentration of the alkali at the peaks of the carbon dioxide yields (Fig. 1) is approximately the same as that corresponding to the minimum yields for oxalic acid. The yield of carbon dioxide decreases as that of oxalic acid increases.

4. The general effect of the alkali is to increase the velocity of the oxi-

dation; to convert pyruvic aldehyde to lactic acid; to increase the enolization of pyruvic acid; to increase the enolization of the acetol (Equations 6 and 7); and to lower the dissociation point of acetol (Equation 21).

5. The acetic acid yields reach a second maximum and the oxalic acid a second minimum in solutions with an initial concentration of potassium hydroxide approximating 0.5 N. These points are also a function of the temperature.

6. The effect of temperature on the yield of oxidation products varies in different regions of alkalinity.

7. The sources of oxalic and acetic acids have been shown.

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THE 6-ALKYLOXYQUINALDINES

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The preparation of the 6-alkyloxyquinaldines involved the preparation of relatively large quantities of the various *p*-aminophenyl alkyl ethers. The problem can be attacked in two ways, namely, (1) the preparation of the *p*-nitrophenyl alkyl ethers and their subsequent reduction to the amino compounds, or (2) the preparation of the *p*-aceto-amino-phenyl alkyl ethers, and their hydrolysis by means of sulfuric acid.

We found that in some instances we obtained better yields by starting with the nitro compound, while in others it was advisable to proceed from the aceto-amino compound.

Several of the *p*-nitrophenyl alkyl ethers are described by Spiegel and Sabath[1] and Riess.[2] They were prepared by heating for 6 hours the potassium salt of *p*-nitrophenol in 16% alcoholic solution with the desired alkyl bromide or iodide in an autoclave at 170–180°.

We were able to prepare these ethers by boiling under a reflux condenser for 12 hours a solution of the potassium salt of *p*-nitrophenol in aqueous alcohol and the desired alkyl bromide or iodide. In a few cases the addition of the corresponding alcohol was necessary. The *p*-nitrophenyl butyl and *iso*-amyl and *p*-aminophenyl butyl and *iso*-amyl ethers have not been previously described.

Hinsberg[3] prepared *p*-aceto-aminophenyl-propyl ether and Jacobson[4]

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[1] Spiegel and Sabath, *Ber.*, **34,** 1937 (1901).

[2] Riess, *ibid.*, **3,** 780 (1870).

[3] Hinsberg, *Ann.*, **305,** 283 (1899).

[4] Jacobson, *ibid.*, **287,** 182 (1895).