These compounds are apparently identical with the isomers obtained by Polonowski in the condensation of glyoxal and ethyl aceto-acetate with zinc chloride.

4. All of these condensation products are easily oxidized.

ST. LOUIS, MISSOURI

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THE ACETONE-ISO-ACETONE EQUILIBRIUM

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Acetone is oxidized in either neutral or acid solutions of potassium permanganate to acetic acid and carbon dioxide. When the oxidation takes place in the presence of alkalies, the reaction products are acetic and oxalic acids, carbon dioxide and, under carefully controlled conditions, pyruvic acid.[1]

It has been shown by Sefton and one of us[2] that the yield of oxalic acid and carbon dioxide obtained through the oxidation of acetone at a given temperature with alkaline potassium permanganate increases with the concentration of the alkali used, while that of acetic acid diminishes. The reaction mechanism involved in the oxidation of acetone in alkaline solutions is best understood when one considers with Denis[3] and Witzemann[4] that one of the functions of the alkali in these reactions is that of forming the salt of iso-acetone as is shown by Reactions 1 and 2.

$$CH_3.CO.CH_3 \rightleftharpoons CH_3.C(OH){=}CH_2 \quad (1)$$

$$CH_3.C(OH){=}CH_2 + KOH \longrightarrow CH_3.C(OK){=}CH_2 + H_2O \quad (2)$$

That these compounds of acetone do exist has been pointed out by Freer[5] who succeeded in preparing sodium acetone in non-aqueous solvents. He also regenerated the acetone in large amounts when the sodium iso-acetone was treated with acids.

It is evident, therefore, that the next step in the oxidation of acetone in alkaline potassium permanganate solutions must be the conversion of a portion of the iso-acetone molecules to acetol, a compound which is then converted into carbon dioxide, acetic and oxalic acids.[6] When acetol is oxidized under conditions similar to those used for acetone, the same general results are obtained when one considers the influence exerted

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[1] Dumas and Stas, *Ann.*, **35**, 160 (1840). Gottlieb, *Ann.*, **52**, 130 (1844). Herz *Ann.*, 186, 258 (1877). Cochenhausen, *J. prakt. Chem.*, [2] **58**, 454 (1898). Fournier. *Bull. soc. chim.*, [4] **3**, 259 (1908).

[2] Evans and Sefton, THIS JOURNAL, **44**, 2276 (1922).

[3] Denis, *Am. Chem. J.*, **38**, 567 (1907).

[4] Witzemann, THIS JOURNAL, **39**, 2657 (1917); compare Ref. 2, p. 2281.

[5] Freer, *Am. Chem. J.*, **12**, 355 (1890); **13**, 320 (1891). Compare Bacon and Freer, *Philippine J. Sci.*, **2A**, 68 (1907). Denis, *Am. Chem. J.*, **38**, 367 (1907).

[6] Evans and Hoover, THIS JOURNAL, **44**, 1730 (1922).

by the concentration of the alkali upon the character and amounts of the final oxidation products. Since the yield of oxalic acid obtained by the oxidation of acetone at a given temperature depends upon the concentration of the alkali used, it follows that the extent to which iso-acetone molecules are formed must also be directly related to the concentration of the alkali. To obtain evidence for this point of view was the main purpose of the following experiments.

Experimental Part

The general experimental method followed in these experiments was similar to that used by Looker and one of us[7] in a study of the influence of potassium hydroxide in the formation of vinyl alcohol from acetaldehyde. The acetone used was purified by the well-known sodium iodide method. The product so obtained (b. p., 56.1–56.2°) was made up into a 2 *M* solution.

Apparatus and Manipulation.—The mercuric oxide obtained from 75 cc. of a saturated solution of mercuric chloride through precipitation by means of a slight excess of potassium hydroxide was carefully washed with water until it was alkali free. To this material, placed in a 250cc. flask and covered with 150 cc. of water, was added 10 cc. of the standard acetone solution. The amount of standardized potassium hydroxide solution chosen for each experiment was then added and the total reaction mixture was made up to a volume of 200 cc. The reaction flasks were agitated for 24 hours in a thermostat maintained at 25°. Before the addition of the alkali, the acetone and mercuric oxide showed no trace of a reaction, but after the lapse of approximately an hour after the alkali had been added the yellow mercuric oxide began to disappear and a white precipitate was slowly formed in its place. At the end of 24 hours the unchanged mercuric oxide in each case was removed by an aqueous solution of aceto-amide. The white precipitate was filtered into Gooch crucibles, washed well with water and dried at 75° in a vacuum oven.

Character of the White Precipitate.—The white precipitate formed in the experiments described above was found to be very stable, but when left in contact with mercuric oxide under water for too long a time, it was found to turn gray gradually. This white compound could not possibly be the mercury β-hydroxypropylene, $(CH_3.CO{=}CH_2)_2Hg$, referred to by Denis, since this formula corresponds to a mercury content of 63.88% of mercury. The compound obtained by us was found to contain 80.32% of mercury, an amount which corresponds to the basic mercury compound that may be represented by the formula $(CH_3.CO{=}CH_2)_2Hg.2HgO$, which gives a calculated mercury content of 80.47%. We found that the mercury content of the white compound obtained by us remained practically constant at the various concentrations of alkali used.

Reynolds[8] describes a compound to which he assigned the formula $2CH_3.CO.CH_3.3HgO$ which corresponds to a mercury content of 78.78%. Our compound did not decompose on simple heating to give acetone. However, when it was heated with acids the acetone was regenerated.

Results.—When the amounts of the basic mercuric iso-acetone are represented as functions of the molar concentrations of the potassium hydroxide used, we find, as shown in Fig. 1, that these amounts of the basic

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[7] Evans and Looker, This Journal, **43**, 1925 (1921).

[8] Reynolds, *Ber.*, **4**, 483 (1871).

mercuric iso-acetone increase with the concentration of alkali employed up to a concentration of about 3.69 × 10^{-2} M, when the curve becomes a straight line with almost constant values for basic mercuric iso-acetone obtained. This may be accounted for on the ground that the acetone and iso-acetone reach an equilibrium condition where increase of alkali causes relatively no more transformation of acetone to iso-acetone. The acetone equivalent to the basic mercuric iso-acetone formed at the equilibrium point is 26.5–27.0% of the weight of the acetone used. When the logarithmic values for the amounts of basic mercuric iso-acetone and those of the molar concentrations of the potassium hydroxide used are plotted as in Fig. 2, it was found that between concentrations of the potassium hydroxide corresponding to 0.2116 × 10^{-2} and 3.69 × 10^{-2} M almost all the points fall on a straight line, the amounts corresponding to the lowest concentrations of alkali used being a little low, probably due to experimental errors at these extremely small concentrations of alkali.

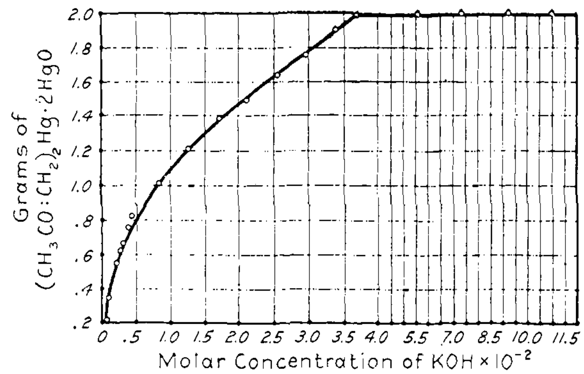

Fig. 1.

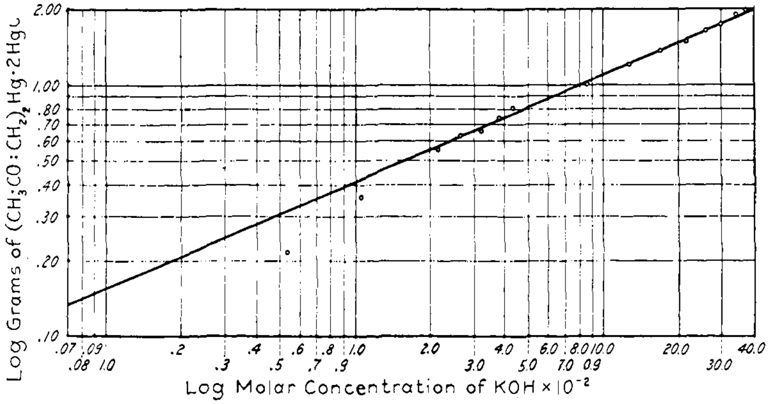

Fig. 2.

Summary of Discussion

1. Our results confirm the fact that acetone may be enolized in aqueous solutions, thus giving rise to the formation of iso-acetone which is in dynamic equilibrium with acetone, a relationship entirely analogous to the well-known behavior of ethyl aceto-acetate, malonic ester, acetaldehyde and many other compounds.

2. The effect of increasing the concentration of the alkali up to 3.69×10^{-2} M is one that gives rise to a corresponding increase in the concentration of iso-acetone molecules. The weight of the basic mercuric iso-acetone obtained at this concentration of alkali is equivalent to 26.5% of the original acetone used.

Beyond this concentration of alkali the acetone and iso-acetone are in equilibrium.

3. It is possible to determine quantitatively the relationship of iso-acetone concentration to the alkali concentration at the end of 24 hours at 25° through the formation of basic mercuric iso-acetone, $(CH_3.CO{=}CH_2)_2Hg.2HgO$, by adding freshly precipitated mercuric oxide to aqueous solutions of acetone containing various concentrations of potassium hydroxide.

4. The relationship between the amounts of basic mercuric iso-acetone obtained and the concentration of the alkali used between 0.2116×10^{-2} and 3.69×10^{-2} M potassium hydroxide solution was found to be logarithmic.

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4-META-NITROPHENYLSEMICARBAZIDE AND CERTAIN DERIVATIVES

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The following paper is a continuation of our study of the reaction between phenylsemicarbazide and ketones. The smooth character of the reaction between phenylsemicarbazide and the keto isomer of β-hydrojuglone, observed by Willstätter and Wheeler,[2] led to further studies with phenylsemicarbazide and substituted phenylsemicarbazides. Wheeler and Edwards[3] used phenylsemicarbazide to detect the keto form of tetrahydroxynaphthalene. Wheeler and Bost[4] prepared *p*-tolylsemicarbazide.

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[1] An abstract of a thesis submitted in June, 1925, to the Faculty of the University of North Carolina by T. T. Walker in candidacy for the degree of Master of Science.

[2] Willstätter and Wheeler, *Ber.*, **47**, 2800 (1914).

[3] Wheeler and Edwards, THIS JOURNAL, **38**, 390 (1916).

[4] Wheeler and Bost, *ibid.*, **46**, 2813 (1924).