dinitro derivative the sole product is the dinitrochloro-aniline formed by replacement of the chlorine atom *ortho* to the 2 nitro groups by an amino group. In the case of the *ortho-* and *para*-dinitro derivatives the main reaction is the replacement of 1 nitro group by an amino group to give the dichloro-aniline, while at the same time there is formed a comparatively small amount of dinitro-*p*-phenylenediamine by replacement of both chlorine atoms. The amounts of the diamines formed correspond to 27% of the 2,5-dinitro- and 8.5% of the 2,3-dinitro-1,4-dichlorobenzene.

3. The constitution of 2,3-dinitro-1,4-dichlorobenzene, melting at 101°, has been proved by reducing to the *p*-phenylenediamine and condensing this to quinoxaline.

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THE OXIDATION OF ISOPROPYL ALCOHOL WITH POTASSIUM PERMANGANATE[1]

BY WILLIAM LLOYD EVANS AND LILY BELL SEFTON

The work presented in this paper on the oxidation of *iso*propyl alcohol is a continuation of a series of studies made in this laboratory on the oxidation of certain organic compounds by means of potassium permanganate in the presence of potassium hydroxide.[2] The purposes of our investigation were as follows: (a) to determine by exact quantitative data the relationship of the initial alkalinity to the character and amounts of the products formed; (b) to determine the relationship of the temperature to the character and amounts of the oxidation products; (c) to ascertain the course followed by the reactions involved in the oxidation of *iso*propyl alcohol by means of alkaline permanganate.[2]

The literature shows that only a small amount of work has been done on the oxidation of *iso*propyl alcohol. When Berthelot[3] oxidized this substance by means of potassium chromate and sulfuric acid, acetone was the only oxidation product. He obtained the oxidation products of acetone when the reaction mixture was more concentrated. Remsen and Emerson[4] oxidized a series of alkyl side chain aromatic compounds and found that the *iso*propyl group was more easily oxidized by acid reagents than by alkaline ones. Hetper[5] oxidized *iso*propyl alcohol and acetone with potassium permanganate in both acid (phosphoric) and alkaline solution.

[1] Presented at the Chicago meeting of the American Chemical Society, September 1920.

[2] THIS JOURNAL, 34, 1086 (1912); 38, 375 (1916); 41, 1267, 1385 (1919).

[3] Berthelot, *Ann. chim. phys.*, 23, 212 (1872).

[4] Remsen and Emerson, *Am. Chem. J.*, 8, 262 (1887).

[5] Hetper, *Z. anal. Chem.*, 50, 355 (1911); 51, 417 (1912).

Experimental Part

Materials.—(a) The *iso*propyl alcohol was a commercial product.[6] A 3 *M* solution of it was made from the fraction boiling between 82° and 84°, density, 0.8004. By oxidizing a given sample and calculating the total carbon the strength of this fraction was found to be 93%. The density percentage tables for *iso*propyl alcohol published by Lebo[7] since the completion of our work show that such a mixture contains about 94% of the alcohol. (b) The potassium permanganate was found to have a purity of 99.75%. (c) All the water used in these oxidations was freed from carbon dioxide. (d) A commercial potassium hydroxide "purified by alcohol" was used. The carbon dioxide content of all our alkali solutions was determined with great frequency. (e) The phosphoric acid (85%) was examined for its volatile acid content.

Oxidation.—The equivalent of 30 g. of pure potassium permanganate was placed in a 2-liter flask, after which 1 liter of a potassium hydroxide solution was added. The initial alkalinity of the solutions varied from 0 to 85.12 g. of the base per liter. The flask was then placed in an electrically controlled thermostat, and its delivery tube was fitted to the tip of a buret containing the *iso*propyl alcohol solution. The lower end of the delivery tube was under the surface of the reaction mixture.

After the oxidizing mixture had reached the temperature of the thermostat, the *iso*propyl alcohol solution was added at the rate of 1 cc. every half hour until the color of the supernatant liquid showed that the endpoint was near. Then the solution was added drop by drop and at long intervals until only a faint color could be seen. If the pink color persisted overnight and could be discharged in the morning by the addition of 2 drops of the alcohol solution, the titration was considered successful. If the pink color disappeared overnight, we concluded that an excess of the alcohol had been added and the experiment was repeated. After the reaction was complete, the manganese dioxide was filtered in an atmosphere of air free from carbon dioxide.[2] The filtrate was made up to 2000 cc. and analyzed.

Analysis.—The acetic acid and carbon dioxide were determined by methods previously described by Day,[2] Adkins[2] and one of us. The oxalic acid was determined by treating 100 cc. of the reaction mixture with an excess of sulfuric acid (1:4); heating to 80°, and titrating with potassium permanganate in the usual manner. In order to make certain that no material except the oxalic acid was being attacked, every fifth sample was evaluated by treating an aliquot part of the filtrate with calcium acetate and then titrating the calcium oxalate by the usual methods. The results obtained by direct titration checked very closely in every case with those obtained by the precipitation method. The Robineau-Rollins Kebler method was used in the estimation of the acetone.

[6] Furnished by the Eastman Kodak Co.
[7] Lebo, THIS JOURNAL, **43**, 1005 (1921).

Data.—The data obtained in these experiments are shown in Table I. In Col. 1, are the numbers of the experiments; Col. 2 shows the grams of potassium hydroxide acid per liter; Col. 3, the weight of the *iso*propyl alcohol used; Cols. 4, 5, 6, and 7, the yields of oxalic acid, carbon dioxide, acetic acid, and acetone, respectively; Col. 8, the percentage recovery of

TABLE I

EXPERIMENTAL RESULTS

1	2	3	4	5	6	7	8
Expt.	KOH per liter G.	*Iso*propyl alcohol used G.	$C_2H_2O_4$ G.	CO_2 G.	$C_2H_4O_2$ G.	Acetone G.	*Iso*propyl alcohol recovered as carbon %
			At 25°				
1	0.00	2.615	1.744	1.864	1.224	0.120	99.29
2	0.50	2.481	2.054	1.793	0.897	0.077	97.92
3	1.06	2.421	2.520	1.705	0.591	0.055	97.93
4	2.12	2.418	2.734	1.696	0.450	0.039	97.45
5	3.18	2.326	2.871	1.628	0.350	0.014	97.77
6	5.32	2.276	2.867	1.595	0.339	...	99.12
7	10.64	2.297	2.877	1.612	0.300	...	97.75
8	21.28	2.313	2.890	1.600	0.312	...	97.12
9	85.12	2.238	2.877	1.588	0.345	...	101.70
			At 50°				
10	0.00	2.423	2.100	1.966	0.740	...	96.90
11	0.50	2.360	2.533	1.862	0.421	...	96.26
12	1.06	2.345	2.649	1.819	0.386	...	97.79
13	2.12	2.308	2.794	1.741	0.322	...	98.05
14	3.18	2.289	2.882	1.678	0.289	...	99.27
15	5.32	2.259	2.917	1.634	0.279	...	100.00
16	10.64	2.277	2.965	1.609	0.228	...	98.01
17	21.28	2.260	2.983	1.604	0.230	...	99.19
18	85.12	2.260	2.931	1.593	0.233	...	97.93
			At 75°				
19	0.00	2.224	1.977	2.196	0.271	...	92.47
20	0.50	2.192	2.415	1.932	0.164	...	95.27
21	1.06	2.192	2.620	1.840	0.156	...	97.29
22	2.12	2.177	2.737	1.728	0.149	...	97.86
23	3.18	2.167	2.782	1.658	0.144	...	97.31
24	5.32	2.164	2.832	1.645	0.146	...	98.69
25	10.64	2.164	2.836	1.653	0.143	...	98.69
26	21.28	2.160	2.839	1.630	0.148	...	98.45
27	85.12	2.164	2.838	1.640	0.144	...	98.53

the *iso*propyl alcohol calculated on the basis of the carbon content of the oxidation products. The molar distribution of the products obtained by such an oxidation of 0.1 mole of *iso*propyl alcohol at 25°, 50° and 75° with all the reacting materials at the same concentration as given in Table I is shown in Fig. 1. The effects of temperature and the concentration of

the alkali on the yields of carbon dioxide, acetic and oxalic acids are also shown in this drawing.
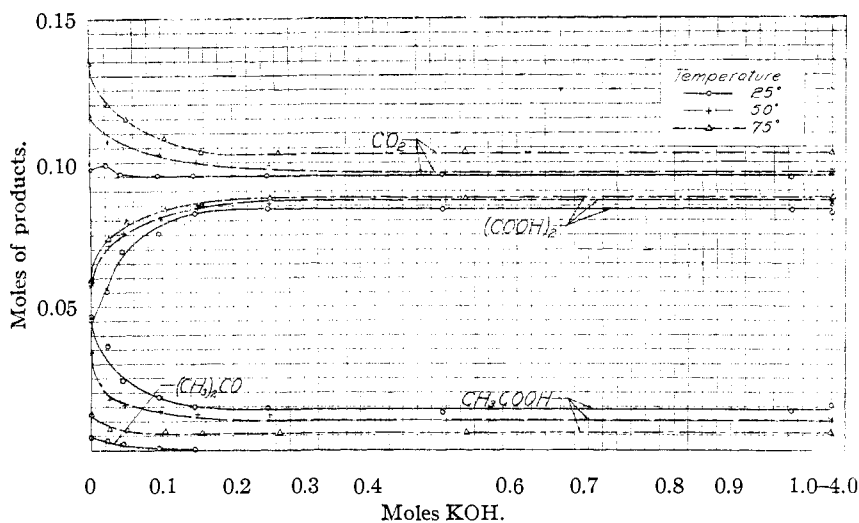

Fig. 1.—Effect of temperature and alkali on 0.10 mole of isopropyl alcohol.

Theoretical Part

In the oxidation of *iso*propyl alcohol to carbon dioxide, oxalic and acetic acids by means of alkaline potassium permanganate, acetone is the first product of the reaction. According to the well-known views of Nef, *iso*propyl alcohol may be dissociated in the following ways

a $CH_3CHOHCH_3 \longrightarrow CH_3.CH_2OH + > CH_2$

b $CH_3CHOHCH_3 \longrightarrow CH_3CHOHCH < + 2H$

c $CH_3CHOHCH_3 \longrightarrow > CHCHOHCH < + 4H$

d $CH_3CHOHCH_3 \longrightarrow CH_3CHO + CH_4$

e $CH_3CHOHCH_3 \longrightarrow CH_3\overset{V}{C}CH_3 + HOH$

Reaction a is excluded on the ground that ethyl alcohol is oxidized entirely to acetic acid in neutral solution of potassium permanganate.[2] If Reaction b took place, lactic aldehyde would be formed on oxidation and this in turn would rearrange to acetol, which is oxidized to acetic acid and carbon dioxide, oxalic acid being absent. A simultaneous oxidation of both methyl groups (Reaction c) would not account for the presence of acetic acid in the reaction products. A dissociation into acetaldehyde and methane (Reaction d) is also excluded, since acetaldehyde is oxidized exclusively to acetic acid.[2] If *iso*propyl alcohol is dissociated in accordance with Equation e, then acetone should be one of the reaction products, or the oxidation products of *iso*propyl alcohol should be the same as those of acetone. That *iso*propyl alcohol may be oxidized to acetone and to

the oxidation products of acetone is shown in Fig. 1. (See also Fig. 1 in the following paper.)

The effect of the alkali is to lower the dissociation point of the alcoholate formed and thereby increase the reactivity of the *iso*propyl alcohol in the formation of acetone.

$$CH_3CHOHCH_3 + KOH \longrightarrow CH_3CHOKCH_3 + H_2O;$$

$$CH_3CHOKCH_3 \longrightarrow CH_3\overset{\vee}{C}CH_3 + KOH$$
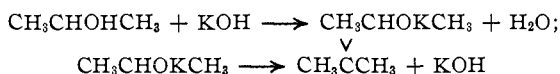
A comparison of the yields of oxalic acid obtained from equivalent amounts of *iso*propyl alcohol and acetone shows that that obtained from the former compound is the greater. That this is to be expected is due from a consideration of the following facts: (a) in order to enolize acetaldehyde into vinyl alcohol in sufficient amounts to yield oxalic acid with alkaline potassium permanganate, a concentration of at least 1.95, 1.30, and 0.85 g. per liter of the base is necessary at 25°, 50° and 75°, respectively; (b) when 2.615, 2.423 and 2.224 g. of *iso*propyl alcohol (Expts. 1, 10 and 19) are oxidized to acetone in accordance with the following equation

$$3CH_3CHOHCH_3 + 2KMnO_4 \longrightarrow 3CH_3COCH_3 + 2KOH + 2H_2O + 2MnO_2$$

1.65, 1.15 and 1.38 g. of potassium hydroxide per liter are obtained at 25°, 50° and 75°, respectively, as the first step in the reaction; (c) after the acetic and carbonic acids formed in these experiments are neutralized, there still remain 4.75, 5.69 and 5.84 g. of the base per liter at 25°, 50° and 75°, respectively. Hence, it is obvious that there will be a sufficient concentration of potassium hydroxide to bring about vinyl alcohol formation.

Results and Summary

Our results may be briefly summarized as follows.

1. *Iso*propyl alcohol is oxidized to carbon dioxide, oxalic and acetic acids at 25,° 50° and 75°.

2. In addition to these products, acetone is obtained in reaction mixtures of low alkalinity at 25° (see Fig. 1) in amounts capable of being measured, while it was found only in traces at 50°. No acetone was formed in samples of an alkalinity above 2.12 g. of potassium hydroxide per liter. The acetone production decreased with an increase in the concentration of the alkali. Witzemann,[8] in his work on the effect of variations in the available alkali on the yield of acetone in the oxidation of butyric acid with hydrogen peroxide, found that the yield of acetone falls as the alkalinity increases.

3. An examination of Fig. 1 shows that the production of oxalic and acetic acids increases and decreases, respectively, as the initial alkalinity increases from neutrality to concentrations approximating 0.1–0.2 N.

4. The general effect of temperature is to increase the yield of carbon

8 Witzemann, *J. Biol. Chem.*, **35**, 87 (1918).

dioxide in excess of one atom equivalent of carbon.   (See the following paper.)

5.   Oxalic acid is obtained in greater quantity from *iso*propyl alcohol in neutral solutions than from acetone, owing to the fact that in the first step of the reaction (acetone formation) no acids are formed to neutralize the potassium hydroxide obtained from the potassium permanganate. Furthermore, the course of the oxidation is such as to bring about a greater final concentration of alkali than in the oxidation of acetone alone.   Hence, vinyl alcohol formation takes place more readily.

COLUMBUS, OHIO

THE OXIDATION OF ACETONE WITH POTASSIUM PERMANGANATE[1]

BY WILLIAM LLOYD EVANS AND LILY BELL SEFTON

This paper is an account of a study made on the oxidation of acetone with neutral and alkaline potassium permanganate.   These experiments were carried out in conjunction with a similar investigation of the behavior of *iso*propyl alcohol under the same conditions.   It was of much interest to study the action of these two compounds in this manner since the action of a primary alcohol[2] and an aldehyde[3] towards these same reagents has been previously made in this laboratory.

The oxidation of acetone in aqueous solution has been made the object of much investigation by other workers.   Dumas and Stas,[4] Gottlieb,[5] and Herz,[6] oxidized it with chromic acid and obtained acetic acid and carbon dioxide as oxidation products.   The latter investigator also obtained formic acid as a reaction product when either silver oxide and bromine or potassium permanganate were used.   Pean de St. Gilles[7] discovered the solubility of potassium permanganate in acetone, an observation later confirmed by Franz Sachs.[8]   Cochenhausen,[9] Denis[10], Witzemann[11] and Four-

[1] Presented at the Chicago meeting of the American Chemical Society, September 1920.

[2] THIS JOURNAL, **38**, 375 (1916); **41**, 1267 (1919).

[3] *Ibid.*, **41**, 1385 (1919).

[4] Dumas and Stas, *Ann.*, **35**, 160 (1840).

[5] Gottlieb, *ibid.*, **52**, 130 (1844).

[6] Herz, *ibid.*, **186**, 258 (1877).

[7] St. Gilles, *Ann. chim. phys.*, [3] **55**, 396 (1859).

[8] Sachs, *Ber.*, **34**, 497 (1901).

[9] Cochenhausen, *J. prakt. Chem.*, **58**, 454 (1898).

[10] Denis, *Am. Chem. J.*, **38**, 572 (1907).

[11] Witzemann, THIS JOURNAL, **39**, 2657 (1917).