

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

5. Oxalic acid is obtained in greater quantity from *isopropyl* 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.

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

## THE OXIDATION OF ACETONE WITH POTASSIUM PERMANGANATE<sup>1</sup>

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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 *isopropyl* 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<sup>2</sup> and an aldehyde<sup>3</sup> 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,<sup>4</sup> Gottlieb,<sup>5</sup> and Herz,<sup>6</sup> 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<sup>7</sup> discovered the solubility of potassium permanganate in acetone, an observation later confirmed by Franz Sachs.<sup>8</sup> Cochenhausen,<sup>9</sup> Denis<sup>10</sup>, Witzemann<sup>11</sup> and Four-

<sup>1</sup> Presented at the Chicago meeting of the American Chemical Society, September 1920.

<sup>2</sup> THIS JOURNAL, **38**, 375 (1916); **41**, 1267 (1919).

<sup>3</sup> *Ibid.*, **41**, 1385 (1919).

<sup>4</sup> Dumas and Stas, *Ann.*, **35**, 160 (1840).

<sup>5</sup> Gottlieb, *ibid.*, **52**, 130 (1844).

<sup>6</sup> Herz, *ibid.*, **186**, 258 (1877).

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

<sup>8</sup> Sachs, *Ber.*, **34**, 497 (1901).

<sup>9</sup> Cochenhausen, *J. prakt. Chem.*, **58**, 454 (1898).

<sup>10</sup> Denis, *Am. Chem. J.*, **38**, 572 (1907).

<sup>11</sup> Witzemann, THIS JOURNAL, **39**, 2657 (1917).

nier<sup>12</sup> found that oxalic acid was also a reaction product when acetone was oxidized with alkaline potassium permanganate. Fournier found that acetone was oxidized in part to pyruvic acid by means of alkaline permanganate, the yield being inversely proportional to the temperature used and the time required for the reaction. Pyruvic acid was absent at temperatures above 20°. Witzemann investigated the role played by atmospheric oxygen and alkali in the oxidation of acetone with potassium permanganate. He concluded that the alkali enolizes the acetone and the pyruvic acid formed as an intermediate product, that it neutralizes the acids present, catalyzes the velocity of both the oxidation, and the absorption, of atmospheric oxygen.<sup>13</sup>

From this summary of the previous work done on the oxidation of acetone it is clear that the character of the reaction products must depend upon a number of factors, such as the nature of the oxidizing agent used, temperature, concentration of the reacting materials and the duration of the experiment. Most of the earlier work on this problem was qualitative in character. Our purpose, therefore, was to make a systematic and quantitative study of the oxidation of acetone for the following reasons: (a) to determine the character and amount of the products formed by the oxidation of acetone in the presence of varying concentrations of alkali; (b) to ascertain the influence of temperature on the character and the amounts of the products formed; (c) to learn the combined effect of (a) and (b); (d) to determine whether the oxidation products of acetone were the same as those of *isopropyl* alcohol; (e) to ascertain what light the results of such experiments might shed on the mechanism of the oxidation of acetone.

### Experimental Part

**Materials.**—The acetone used in these experiments was a commercial product.<sup>14</sup> It had been prepared from the bisulfite addition compound. The specimen used in making a 4 *M* solution for our experiments was found to contain 97.53% of acetone when examined by the Kebler<sup>15</sup> modification of the Robineau-Rollins method of analysis.

**Methods of Manipulation.**—The methods and conditions used in the oxidation of acetone were the same as those employed by us in the oxidation of *isopropyl* alcohol described in the preceding paper. In the low alkalinity oxidations at 50° and in all those at 25° it was found necessary to add an excess of acetone in order to reduce the permanganate completely. In the oxidation with neutral permanganate at 25°, this excess was nearly three times the amount actually oxidized. Four days were required for the complete reduction of the permanganate. In another experiment under the same conditions the excess of acetone was approximately equal

<sup>12</sup> Fournier, *Bull. soc. chim.*, [4] 3, 259 (1908).

<sup>13</sup> Ref. 11, p. 2671.

<sup>14</sup> Supplied by the Eastman Kodak Co.

<sup>15</sup> Kebler, *J. Ind. Eng. Chem.*, 10, 552 (1918).

to the amount oxidized, and the time required for complete reduction was 12 days. The unchanged acetone in the filtrate from the manganese dioxide was determined by the same methods as those used in our work on *isopropyl alcohol*.

**Results.**—Oxalic acid, carbon dioxide and acetic acid were found to be the sole reaction products, both in neutral and alkaline solution. No trace of pyruvic or formic acids was found, since these compounds themselves are oxidized rapidly under the conditions of these experiments, pyruvic acid to oxalic, acetic and carbonic acids, and formic acid to carbon dioxide. The analytical results are given in Table I. In Col. 1 are tabulated the numbers of grams per liter of potassium hydroxide used; Col. 2, the grams of acetone added to the oxidizing agent; Col. 3, the grams of

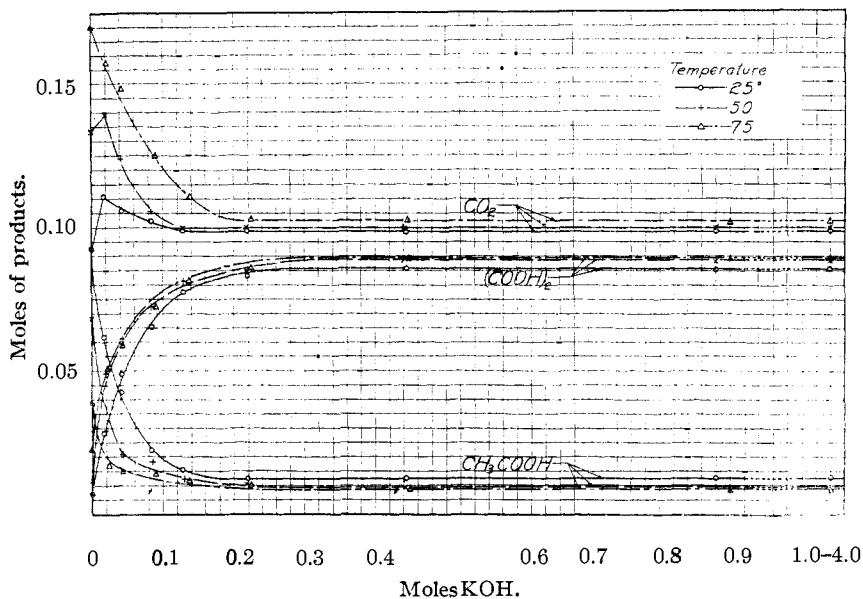
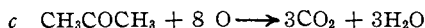
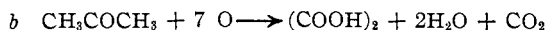
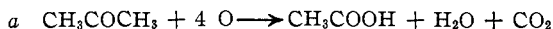


Fig. 1.—Effect of temperature and alkali on 0.10 mole of acetone.

unchanged acetone; Col. 4, the grams of oxidized acetone; Cols. 5, 6, 7, the yields of oxalic acid, carbon dioxide and acetic acid, respectively; Col. 8, the percentage recovery of acetone calculated from the carbon content of the oxidation products. The molar distribution of the products obtained by such an oxidation of 0.10 mole of acetone at 25°, 50°, and 75° with all the reacting materials at the same concentration as shown in Table I is shown in Fig. 1. The effect of temperature on the production of carbon dioxide, oxalic and acetic acids is also clearly seen in this drawing.

## Theoretical Part

The oxidation of acetone to acetic acid, oxalic acid and carbon dioxide may be expressed by the following equations, respectively.<sup>11</sup>



These reactions, as such, do not show the various stages through which the oxidation of acetone proceeds, nor do they indicate the quantity of

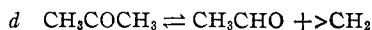
TABLE I  
OXIDATION OF ACETONE

Expt.	1 KOH per liter G.	2 Acetone added G.	3 Un- changed acetone G.	4 Acetone oxidized G.	5 (COOH) <sub>2</sub> G.	6 CO <sub>2</sub> G.	7 C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> G.	8 Acetone recovered as carbon %
At 25°								
1	0.00	12.340	9.067	3.273	0.371	2.292	3.156	98.03
2	0.50	5.718	2.522	3.196	1.397	2.685	2.046	97.43
3	1.06	4.607	1.916	2.691	2.026	2.156	1.192	96.89
4	2.12	3.137	0.596	2.541	2.572	1.976	0.817	99.20
5	3.18	2.832	0.285	2.547	3.074	1.916	0.416	97.12
6	5.32	2.631	0.121	2.510	3.258	1.885	0.330	98.64
7	10.64	2.561	0.081	2.480	3.312	1.855	0.331	100.20
8	21.28	2.561	0.054	2.507	3.325	1.880	0.329	99.74
9	85.12	2.531	0.031	2.500	3.329	1.872	0.336	100.13
At 50°								
10	0.00	3.470	0.428	3.042	0.565	3.075	2.156	98.67
11	0.50	2.220	0.592	2.628	2.004	0.761	0.783	98.00
12	1.06	2.794	0.251	2.543	2.427	2.393	0.545	97.34
13	2.12	3.470	0.925	2.545	2.866	2.049	0.469	97.50
14	3.18	2.961	0.434	2.527	3.196	1.910	0.330	97.58
15	5.32	2.535	0.000	2.535	3.342	1.915	0.291	98.66
16	10.64	2.487	0.000	2.487	3.419	1.871	0.241	99.72
17	21.28	2.494	0.000	2.494	3.388	1.900	0.238	99.42
18	85.12	2.487	0.000	2.487	3.410	1.897	0.242	100.80
At 75°								
19	0.00	2.644	0.0	2.644	0.910	3.400	1.064	97.92
20	0.50	2.463	0.0	2.463	1.892	2.925	0.429	97.33
21	1.06	2.465	0.0	2.465	2.242	2.759	0.382	99.23
22	2.12	2.457	0.0	2.457	2.752	2.322	0.363	99.98
23	3.18	2.461	0.0	2.461	3.132	2.068	0.308	100.90
24	5.32	2.463	0.0	2.463	3.299	1.928	0.273	100.50
25	10.64	2.463	0.0	2.463	3.394	1.918	0.210	100.40
26	21.28	2.452	0.0	2.452	3.393	1.896	0.205	100.30
27	85.12	2.457	0.0	2.457	3.388	1.909	0.204	100.10

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 our experimental results are studied in connection with these equations.

(1) *Neutral Solutions at 25°*.—That acetone is oxidized according to Equations *a* and *b* only follows from the fact that the acetone which is equivalent to the acetic and oxalic acids obtained (3.04 and 0.24 g., respectively) is 3.28 g., while that actually used was 3.273 g. According to the views of Nef,<sup>16</sup> acetone is dissociated into acetaldehyde and methylene,



these products of dissociation being subsequently oxidized to acetic acid and carbon dioxide. This interpretation of this reaction is in harmony with the fact that an aqueous solution of acetone at 100° may be oxidized with silver oxide to acetic and formic acids. These acids are also formed when acetol is acted upon by the same reagents and when acetone vapor is passed over heated quicklime.

The literature contains conflicting statements in reference to the stability of acetates towards alkaline potassium permanganate. In some recent experiments in this laboratory, Paul Hines and one of us<sup>17</sup> found that potassium acetate is oxidized to potassium oxalate very slowly over a long period of time under the conditions employed in these experiments. Hence, very small quantities of oxalic acid must be preceded by the intermediate formation of acetic acid. After the neutralization of the acids by the potassium hydroxide formed from the permanganate at 25°, there still remains 1.40 g. of the base. It has been shown by several investigators<sup>18</sup> that a concentration of 1.0 g. to 1.95 g. of potassium hydroxide per liter is necessary for the enolization of acetaldehyde to vinyl alcohol, which in turn is oxidized to oxalic acid. Hence it is clear that some of the acetaldehyde formed from the dissociation of acetone in accordance with Equation *d* is oxidized to oxalic acid.

(2) *Neutral Solutions at 50° and 75°*.—The carbon dioxide equivalent to the acetic and oxalic acids formed in neutral permanganate solutions at 50° (Expt. 10) is equal to 1.857 g. (1.581 g. and 0.276 g., respectively). Therefore, the carbon dioxide obtained by the complete oxidation of the acetone used is equal to 1.218 g. (3.075–1.857), or 39.59% of the total carbon dioxide was obtained in accordance with Equation *c*. From these facts it can be shown that 68.5% (2.08 g.) of the acetone was oxidized according to Equation *a*, 11.96% (0.364 g.) according to Equation *b*, and 17.6% (0.534 g.) according to Equation *c*. At 75° the carbon dioxide formed in neutral solution (Expt. 19) according to Equations *a* and *b* is equal to 35.9%, or 1.22 g. (0.78 and 0.44 g.) of the carbon dioxide obtained.

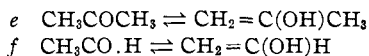
<sup>16</sup> Nef, *Ann.*, **318**, 191, 227 (1901); **335**, 276 (1904).

<sup>17</sup> Evans and Hines, *Science*, **54**, 527 (1921); *THIS JOURNAL*, **44**, 1543 (1922).

<sup>18</sup> Nef, *Ann.*, **298**, 316 (1897). McLeod, *Am. Chem. J.*, **37**, 23 (1907). Also see *THIS JOURNAL*, **41**, 1280, 1397, 1414 (1919); **43**, 1925 (1921).

Therefore, the carbon dioxide obtained according to Equation *c* is 64.1% (2.18 g. (3.4 - 1.22)) of the total. This amount of carbon dioxide is equivalent to 36.25% (0.95 g.) of the acetone used. Since 36.25% of the acetone is oxidized completely to carbon dioxide at 75°, 17.6% at 50°, and none at 25°, it is clear that the amount of carbon dioxide produced by Equation *c* is proportional to the temperature employed. From these results it can be shown graphically that acetone should be oxidized completely to carbon dioxide by means of alkaline permanganate at temperatures approximating 164°.

If acetone were oxidized in neutral permanganate solutions in accordance with Equations *a* and *b*, then the carbon dioxide formed would be equivalent to exactly  $\frac{1}{3}$  of the carbon content of the acetone used.<sup>19</sup> In order to account for this excess of carbon dioxide one must postulate the existence of *iso*-acetone molecules in aqueous solutions of acetone. The formation of *iso*-acetone molecules in an aqueous solution of acetone is similar to the formation of vinyl alcohol from acetaldehyde under similar conditions.



Freer<sup>20</sup> prepared sodium acetone in non-aqueous solvents and succeeded in regenerating acetone in large amounts by the use of acids.<sup>21</sup> In sodium acetone the metal is unquestionably bound to oxygen as in the sodium compounds of aceto-acetic and malonic ethyl esters. Hence the action of acids on sodium acetone must be that of forming *iso*-acetone which in turn comes to an equilibrium as indicated in Equation *e*. The *iso*-acetone molecules are then oxidized to acetol as pointed out by Denis and Witzemann. The following facts support the position of these investigators: the yield of carbon dioxide obtained by the oxidation of propylene glycol<sup>22</sup> and acetol<sup>23</sup> under these conditions is also greater than that equivalent to  $\frac{1}{3}$  of the carbon in these two compounds. In Witzemann's experiments the method of experimentation was different from that used by us. In the work of Hoover and one of us<sup>23</sup> on acetol it was shown that acetol is oxidized successively to pyruvic aldehyde, hydroxypyruvic aldehyde, and hydroxypyruvic acid, formylglyoxylic acid and carbon dioxide. Hydroxypyruvic aldehyde and hydroxypyruvic acid may then be dissociated into glyoxal and glyoxylic acid, respectively, which in turn are oxidized exclusively to carbon dioxide. This excess of carbon dioxide cannot be explained on the grounds of the complete oxidation of acetaldehyde and methylene into carbon dioxide because acetaldehyde is oxidized exclusively to acetic

<sup>19</sup> Compare Denis, *Am. Chem. J.*, **38**, 572 (1907).

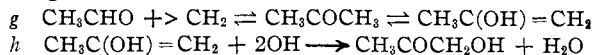
<sup>20</sup> Freer, *ibid.*, **12**, 255 (1890); **13**, 320 (1891).

<sup>21</sup> Compare Bacon and Freer, *Philippine J. Sci.*, **2**, Sec. A, 68 (1907); *Am. Chem. J.*, **38**, 367 (1907).

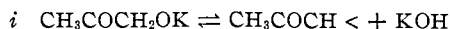
<sup>22</sup> *Science*, N. S., **44**, 527-528 (1921).

<sup>23</sup> Evans and Hoover, *THIS JOURNAL*, **44**, 1730 (1922).

acid in neutral solutions of potassium permanganate at 25°, 50° and 75°.<sup>24</sup> Finally, from the above consideration of our results it is clear that acetone is oxidized in neutral solution by two different general reactions as shown in Equations *g* and *h*.

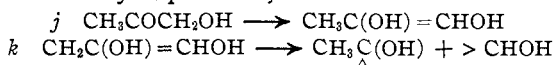


**Alkaline Solutions.**—It is a well-known fact that the enolization of many carbonyl-containing compounds such as acetaldehyde<sup>18</sup> is greatly enhanced by the addition of alkalis. Denis<sup>25</sup> has also shown that acetone is converted into *iso*-acetone in the presence of potassium hydroxide. Hence the general effect of increasing the concentration of the alkali in an aqueous solution of acetone would be to increase the number of *iso*-acetone molecules and to increase the reactivity of the intermediate acetol by lowering its dissociation point through salt formation in accordance with Equation *i*.<sup>26</sup>



From a consideration of Equation *g* it is clear that an increase in the concentration of the alkali will cause an increase in the concentration of the *iso*-acetone molecules and a consequent increase in that of acetol. This change will be accompanied by a corresponding decrease in the degree of dissociation of acetone into acetaldehyde and methylene.

That acetone is not oxidized exclusively in alkaline solutions through the intermediate formation of acetol follows from the work of Hoover and one of us<sup>23</sup> in which it was shown that at certain higher concentrations of alkali the yields of acetic and oxalic acids from acetol reached a certain maximum and minimum, respectively. This was explained on the ground that the acetol was enolized and the resulting compound was subsequently dissociated as shown by Equations *j* and *k*.



Such a change in the production curve of these acids should be expected in these experiments of high alkalinity, namely, 9, 18 and 27. These facts were not observed. The general effect of alkalis on the formation of oxalic and acetic acids in the oxidation of acetone is of the same general kind as that observed with acetaldehyde. Hence it is obvious that acetone is oxidized under the conditions of our experiments by more than one general reaction.

### Summary

1. Oxalic, acetic and carbonic acids are obtained by the oxidation of acetone with neutral and alkaline potassium permanganate at 25°, 50° and 75°.

<sup>24</sup> Evans and Adkins, *THIS JOURNAL*, 41, 1391 (1919).

<sup>25</sup> Ref. 10, p. 567.

<sup>26</sup> Nef, *Ann.*, 318, 138 (1901); *THIS JOURNAL*, 26, 1573 (1904).

2. The yield of oxalic acid increases with an increase in both the temperature employed and an increase in the concentration of the alkali, while that of acetic acid diminishes with a decrease in temperature and an increase in the concentration of the alkali.

3. The production of carbon dioxide increases with the temperature. In neutral permanganate solutions acetone should be oxidized completely to carbon dioxide at about 164°. Acetic acid and carbon dioxide arise from the oxidation of acetaldehyde and methylene, respectively. The presence of oxalic acid in neutral solutions is due to the very slow oxidation of acetic acid and the oxidation of vinyl alcohol.

4. Acetone in aqueous solution must exist in equilibrium with *iso*-acetone. An increase in the concentration of the alkali increases *iso*-acetone formation.

5. Our experiments also confirm the views of Denis and Witzemann that acetol is an intermediate product in the oxidation of acetone.

6. The maximum and minimum effect observed for acetic and oxalic acids, respectively, at higher concentration of alkali in the oxidation of acetol were not observed in our work.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

## THE PHYTOSTEROLS OF RAGWEED POLLEN

By FREDERICK W. HEYL

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In the unsaponifiable fraction of pollen fat from ragweed (*ambrosia artemesifolia*, L.) we have identified traces of a hydrocarbon, along with appreciable quantities of the higher homologs of the paraffin alcohol series. The presence of cetyl ( $C_{16}H_{34}O$ ) and octadecyl alcohol ( $C_{18}H_{38}O$ ) has been established.

The chief interest in this material, however, is found in the sterol alcohols. We have found the phytosterol fraction to be an optically active complex crystalline mixture which resists to a remarkable degree all efforts at separation by the regular methods of fractional crystallization. By persistent recrystallization of the acetates from acetic anhydride, one of these has been satisfactorily characterized. The regenerated phytosterol crystallizes in needles and melts at 147–149°. It agrees with the formula,  $C_{20}H_{34}O \cdot H_2O$ . To this we assign the name "ambrosterol." The corresponding acetate,  $C_{20}H_{32}O \cdot COCH_3$ , forms magnificent plates melting at 112–113°, and has a specific rotation of +27.7°.

Isomeric sterols of this composition have previously been isolated from quebracho,<sup>1</sup> cuprea bark<sup>2</sup> and cinchona bark,<sup>2</sup> Kô-sam seeds,<sup>3</sup> cascara

<sup>1</sup> Hesse, *Ann.*, **211**, 272 (1882).

<sup>2</sup> Hesse, *ibid.*, **228**, 291 (1885).

<sup>3</sup> Power and Lees, *Year Book Pharmacy*, **1903**, 503.