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# THE OXIDATION OF ACETALDEHYDE IN SOLUTION PART I.—THE CHEMISTRY OF THE INTERMEDIATE STAGES

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The uncatalyzed and trace-metal catalyzed oxidation of acetaldehyde in solution proceeds in two well-defined stages: (a) the oxidation of the aldehyde to peracetic acid; (b) the reaction of peracetic acid with acetaldehyde to give a peroxide X. The second stage has been confirmed by a separate study of the reactions between acetaldehyde and peracetic acid. The peroxide X is formed from equimolar amounts of aldehyde and peracid and the equilibrium constant of the reaction

#### acetaldehyde + peracetic acid $\rightleftharpoons$ peroxide X

has been measured. The nature and reactions of the peroxide X are discussed, and it is shown that it may be catalytically decomposed to acetic acid and acetic anhydride.

The oxidation of acetaldehyde by molecular oxygen occurs readily in the pure liquid and in solution at room temperature, and in the gaseous phase at higher temperatures. The nature of the peroxidic intermediates in the reaction, and the detailed mechanism of their formation and decomposition have been widely studied since the original observation by Liebig <sup>1</sup> in 1835 of the aerobic oxidation of aldehydes to the corresponding acids.

It was observed by Bach<sup>2</sup> that peroxidic compounds were the initial products of the autoxidation of aldehydes, and he suggested that these compounds reacted subsequently with the aldehyde to give the acid.

> <sup>1</sup> Liebig, Annalen, 1835, **14**, 139. <sup>2</sup> Bach, Compt. rend., 1897, **124**, 951.

Baeyer and Villager <sup>3</sup> suggested that peracids were formed, and showed that perbenzoic acid would oxidize benzaldehyde to benzoic acid.

$$R \cdot C_{H} + R \cdot C_{OOH} \longrightarrow 2R \cdot COOH$$
 . . (2)

Wieland 4, 5 believed that (2) occurred only in the presence of water and suggested that the aldehyde reacted via its hydrated form. In later investigations 5, 6 much doubt was expressed as to whether very pure aldehydes would oxidize or not in the presence of molecular oxygen. The existence of an induction period in the oxidation was noted by many workers and it was observed that reaction could be either readily induced by the addition of traces of iron, copper, cobalt or manganese salts,<sup>5, 6, 7</sup> or inhibited by the presence of inhibitors such as diphenylamine.<sup>8</sup> These observations indicated that the oxidation in solution was a chain reaction, which has been proved by Bodenstein and others 9 for the higher temperature oxidation of acetaldehyde in the gaseous phase and by Backstrom<sup>8, 10</sup> (benzaldehyde), and Bowen and Tietz<sup>11</sup> (acetaldehyde) for the photochemically initiated oxidation in the pure liquid state and in These different types of oxidation processes can be systematically solution. correlated if it is assumed that the various initiation processes give rise to free radicals which initiate a reaction chain. This view is now firmly established and there is wide agreement that the propagation reactions are of the type : 12

$$\begin{array}{l} \operatorname{Ac}^{\cdot} + \operatorname{O}_{2} \to \operatorname{AcOO}^{\cdot} \\ \operatorname{AcOO}^{\cdot} + \operatorname{AcH} \to \operatorname{AcOOH} + \operatorname{Ac}^{\cdot} \\ \left( \operatorname{Ac}^{\cdot} \equiv \operatorname{acetyl} \operatorname{radical}, \operatorname{CH}_{3} \subset \left\langle \begin{array}{c} \operatorname{O} \\ \end{array} \right\rangle \right). \end{array}$$

Opinion differs, however, as to the nature of the initiation and termination reactions. An important advance was made by Haber and Willstater <sup>13</sup> when they proposed that initiation by iron salts was due to an electron transfer reaction which may be represented by

 $AcH + Fe^{+++} \rightarrow Ac \cdot + H^+ + Fe^{++}$ .

Their scheme, however, did not explain the observed catalysis by ferrous ions. Most of the information relating to the heavy metal catalysis of the acetaldehyde oxidation is confined to the patent literature where claims are made for the effectiveness of single or mixed metal salts in producing acetic acid, peracetic acid or acetic anhydride respectively. The only detailed study of the thermal reaction in solution has been carried out by Kagan and Lubarsky<sup>14</sup> using solid manganese salts as They showed that the active catalyst was trivalent manganese catalysts.

<sup>3</sup> Baeyer and Villager, Ber., 1900, **33**, 1569. <sup>4</sup> Wieland, Ber., 1922, **45**, 2606; Ber., 1921, **54**, 2358.

<sup>5</sup> Wieland and Richter, Annalen, 1931, 486, 226; Annalen, 1932, 495, 284.

<sup>6</sup> Kuhn and Meyer, Naturwiss., 1928, 16, 1028.

<sup>7</sup> Meyer, J. Biol. Chem., 1933, 103, 25. Richter, Ber., 1931, 64, 1240. Oppen-heimer and Stern, Biological Oxidation (The Hague). Dufraisse and Horcleis, Compt. rend., 1930, 191, 1126.

<sup>8</sup> Moureu and Dufraisse, Chem. Rev., 1926, 3, 113.

<sup>8</sup> Moureu and Dufraisse, Chem. Rev., 1926, 3, 113.
<sup>9</sup> Bodenstein, S.B. Preuss. Akad. Wiss., 1931, 73. Hatcher, Steacie and Howland, Can. J. Res., 1932, 7, 149. Pease, J. Amer. Chem. Soc., 1933, 55, 2753.
<sup>10</sup> Backstrom, J. Amer. Chem. Soc., 1927, 48, 1460; Trans. Faraday Soc., 1928, 24, 601; Z. physik. Chem. B, 1934, 25, 99.
<sup>11</sup> Bowen and Tietz, J. Chem. Soc., 1930, 234.
<sup>12</sup> McDowell and Thomas, J. Chem. Soc., 1949, 2208, 2217; 1950, 1462.
<sup>13</sup> Haber and Willstater, Ber., 1931, 64, 2844.
<sup>14</sup> Kagan and Lubarsky, J. Physic. Chem., 1935, 39, 837.

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and made the important observation that the reaction between the intermediary peractic acid and acetaldehyde gave a peroxidic compound which was decomposed by the catalyst to give two molecules of acetic acid :

## $AcH + AcOOH \rightarrow peroxide \rightarrow 2AcOH.$

In the present investigation the kinetics and course of the cobalt ion catalyzed homogeneous oxidation by molecular oxygen have been studied using acetic acid as solvent for both the aldehyde and catalyst.

#### Experimental

**Materials.** OXYGEN was prepared by the thermal decomposition of potassium permanganate. Carbon dioxide was removed by potash and after drying over  $P_2O_5$ , the gas was stored over mercury in a gas reservoir.

COBALTOUS ACETATE: laboratory reagent cobaltous acetate was purified by twice fractionally crystallizing from aqueous acetic acid and dehydrated at 100° C *in vacuo* until the weight was constant. The anhydrous salt was stored in a desiccator over  $P_2O_5$ .

ACETIC ACID: A.R. glacial acetic acid was tested for freedom from peroxides and the water content (usually about 0 001 %) determined by the Karl Fischer method.<sup>15</sup> In view of the pronounced influence of water on the oxidation reaction the same sample of acid was used in many sets of comparative experiments.

ACETALDEHYDE was made by depolymerizing paraldehyde by heating with phosphoric acid. The paraldehyde was washed with 10 % sodium hydroxide and then with water containing a little dissolved sodium sulphate. It was dried over sodium sulphate and fractionally distilled. The depolymerization was carried out by heating with  $\frac{1}{2}$  % of 95 % phosphoric acid in the kettle of a 1 m. insulated fractionating column. The distillation was carried out in a stream of dry oxygen-free nitrogen and the middle fraction was collected in glacial acetic acid. The solution was stored in nitrogen and used within a few days.

PERACETIC ACID was prepared according to the method of Smits<sup>16</sup> by the reaction of concentrated hydrogen peroxide with acetic anhydride. Hydrogen peroxide solutions containing 75-85 % by weight of peroxide (estimated by permanganate) were used and sufficient acetic anhydride to ensure complete reaction of the water content to acetic acid was added to the initial reaction mixture.

The peracetic acid solution was fractionated at  $35^{\circ}$  C under reduced pressure and the distillate collected in a flask, cooled in a salt + ice bath. The acetic acid solutions used were about 4.5 M peracetic acid and contained very little acetyl peroxide (*ca.* o·I M).

**Procedure.**—MEASUREMENT OF OXVGEN ABSORPTION—.The oxygen absorbed was measured directly using a thermostated gas burette. The reaction vessel (roo mI.), which was pear-shaped in order to provide a large gas-liquid interface, was vigorously shaken during the experiment by attachment to a piston rod subjected to an up and down stroke of  $r\frac{1}{2}$  in. The vessel was immersed in a thermostat bath and all kinetic measurements were carried out at  $25^{\circ} \pm 0 \cdot r^{\circ}$ C. The vessel was attached by a short rubber tube to the gas burette. A side-arm to the vessel, fitted with ground-glass stopper, projected above the surface of the bath.

In carrying out an experiment, the vessel was fixed in position, and a measured amount of acetaldehyde + acetic acid solution run in from the storage burette. The vessel was then flushed out with oxygen, the catalyst solution added from a pipette, the stopper fixed in the side arm, and the shaker started immediately. The period of less than 1 min. between adding the catalyst and commencing the experiment was negligible in comparison with the time of reaction. The pressure of oxygen was maintained at 1 atm. by running mercury into the gas burette from a reservoir. Pairs of duplicate experiments were performed, one for the measurement of oxygen absorption, and the other for taking samples and estimating aldehyde and peroxides. Analytical Methods.—PEROXIDES were estimated by reaction with potas-

**Analytical Methods.**—PEROXIDES were estimated by reaction with potassium iodide. The methods used were designed to determine both the total peroxide concentration and the separate concentrations of hydrogen peroxide, peracetic acid and diacetyl peroxide.

<sup>15</sup> Fischer, Angew. Chem., 1935, 48, 394.
<sup>16</sup> Smits, Rec. trav. chim., 1930, 49, 675.

The method of D'Ans and Frey <sup>17</sup> for hydrogen peroxide and peracetic acid was used. Hydrogen peroxide may first be estimated by running the 1 ml. sample into ice-cold N H<sub>2</sub>SO<sub>4</sub> and titrating with potassium permanganate. As in no case was any hydrogen peroxide detected, this step was omitted. The peracetic acid was estimated by running the 1 ml. sample into a 5 % solution of potassium iodide in N H<sub>2</sub>SO<sub>4</sub>, and the liberated iodine titrated immediately with o·1 N sodium thiosulphate (Method 1).

Time		Peroxide Cono. (g. atom active O/litre)	
(min.)	Method 1	24	2b
10	0.025		0.025
20	0.020		0.020
30	0.072		0.073
40	0.092		0.092
55	0.112		0.113
70	0.131		0.122
5	0.022	0.060	0.057
10	0.001	0.110	o•c88
20	0.130	0.101	0.130
30	0.126	0.176	0.190
45	0.101	0.178	0.167

TABLE II

TABLE III

Time		Peroxide Concentration	
(min.)	I	24	3
6	0.037	0.040	0°C41
12	0.066	0.082	0.103
20	0.108	0.162	0.127
30	0.132	0.230	0.311
50	0.100	0.290	0.281
75	0.249	0.300	0.310

Several methods of total peroxide estimations were tried, including the following :---

- Method 2a.--I ml. of sample in 10 ml. glacial acetic acid containing I g. powdered potassium iodide. The liberated iodine was titrated after 15 min. standing.
- Method 2b.—As above, except  $\frac{1}{2}$  ml. saturated aqueous potassium iodide solution added to reaction flask instead of the solid.
- Method 3.—After Kagan and Lubarsky,<sup>14</sup> in which  $\frac{1}{2}$  ml. of the sample in glacial acetic acid was added to 50 ml. 5 % neutral aqueous potassium iodide and the liberated iodine estimated after standing 5 min.

Blank peroxide estimations in the same media were performed in all cases. Some total peroxide estimations taken from experimental runs obtained by the above methods are shown in the following Tables. (Tables II and III are results from oxidation experiments and Table IV from the separate acetaldehyde + peracetic acid reaction).

<sup>17</sup> D'Ans and Frey, Z. anorg. Chem., 1914, 84, 145.

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Method 2b gave results agreeing fairly closely with the peracetic acid estimation by method I, whereas the results from methods 2a and 3 were considerably higher than the peracetic acid estimation, but were in reasonable agreement with each other.

It was concluded that there were two peroxides present during the oxidation, one of which was peracetic acid, the method of estimation, method I, being generally accepted by other workers.

The other peroxide, here designated peroxide X, does not liberate iodine from potassium iodide in mineral acid solution, nor under the conditions of method 2b where the glacial acetic acid medium contains some water (5% saturated aqueous potassium iodide). Peroxide X does, however, rapidly liberate iodine in neutral aqueous potassium iodide (as found by Kagan and Lubarsky), and in glacial acetic acid containing less than oor % water (Method 2a).

glacial acetic acid containing less than o'or % water (Method 2a). Diacetyl peroxide would liberate iodine just as well in solution 2b as in 2a, but would only liberate iodine very slowly in neutral potassium iodide (Clover and Houghton <sup>16</sup>), and in mineral acid solution (D'Ans and Frey <sup>17</sup>). It is clear therefore that peroxide X is not diacetyl peroxide, and that diacetyl peroxide cannot be present in any appreciable quantity. Bowen and Tietz <sup>11</sup> have given results from which they conclude that diacetyl

Bowen and Tietz<sup>11</sup> have given results from which they conclude that diacetyl peroxide is the main peroxidic product in the photochemical oxidation of acetaldehyde in solution. As has already been pointed out by Lubarsky and Kagan,<sup>19</sup> however, the argument of Bowen and Lietz is not conclusive and the peroxide formed may be other than the diacetyl peroxide.

Time		Peroxide Co	ncentration	
(min.)	I	2b	2a	3
o <b>*</b>	0.193	0.192	<b>0·1</b> 89	0.190
8	0.125	0.124	0.12	0.177
30	0.100	0.108	0.124	0.121
80	0.096	0.093	0.112	0.130
150	0.072	0.081	0.096	0.105

TABLE IV

\* Before the addition of acetaldehyde.

Methods 1 and 2a were adopted for use for the estimations of peracetic acid and total peroxides respectively, these two methods having been checked by methods 2b and 3 respectively.

During the course of this work a cause of error in method I was discovered. In the presence of air the method gave higher results than in its absence, a difference that only occurred when the acetaldehyde concentration in the sample was high. It is probable that this effect is due to free radicals from the peroxide + iodide reaction initiating oxidation of acetaldehyde by oxygen in solution, giving further peroxide to react with the iodide. Although such errors were in general small in this work, and do not appreciably affect the results quoted, it is possible to obtain relatively large errors when estimating a low concentration of peracetic acid in the presence of high acetaldehyde concentration, using a large volume of solution saturated with atmospheric oxygen.

ACETALDEHYDE.—The volumetric method due to Ripper <sup>20</sup> was used, the aldehyde being added to excess bisulphite solution, the aldehyde + bisulphite compound allowed to form and the excess bisulphite titrated with N/IO iodine. The method was satisfactory for solutions of acetaldehyde in water, toluene and glacial acetic acid, concentration determinations by weighing and volumetric estimation being in close agreement (Table I). In acetic acid it was found that the complex formed slowly and that it was necessary to allow the solution to stand for 1 hr. A blank with the same quantities of bisulphite and acetic acid was treated in precisely the same manner.

<sup>18</sup> Clover and Houghton, Ann. Chem. J., 1904, **32**, 43.
 <sup>19</sup> Lubarsky and Kagan, Acta Physicochim., 1935, **2**, 665.

<sup>20</sup> Ripper, Monatsh., 1900, 21, 1079.

In the presence of peroxides it was essential to estimate and destroy the total peroxides before the aldehyde determination on account of the reaction between the peroxides and the bisulphite. In the subsequent aldehyde estimation it was found desirable to have at lease a three-fold excess of bisulphite and to allow the solution to stand 90 min. before titration with iodine. In these determinations the bisulphite was stabilized by 10 % ethyl alcohol as recom-mended by Joslyn and Comar<sup>21</sup> and Lazarri<sup>22</sup> to prevent atmospheric oxidation.

TABLE V.—Aldehyde Molarity in GLACIAL ACETIC ACID

By Weighing	By Titration
0·101	0·100
0·322	0·317
0·628	0·633

Experiments performed with iodine added initially to the acetic acid +aldehyde solution showed that there was no reaction of iodine with the aldehyde during the total peroxide determination. Estimation of acetaldehyde after peroxide estimation by method 2a (total peroxide) gave a higher value ([AcH]<sub>a</sub>) than the estimation ([AcH]) after method 2b (peracetic acid alone) had been used. If the peroxide X is an addition compound between acetaldehyde and per-

acetic acid (as it is later shown to be) then acetaldehyde may be regenerated when it reacts with hydrogen iodide, viz.,

AcH . ACOOH + 2HI  $\rightarrow$  AcH + ACOH + H<sub>2</sub>O + I<sub>2</sub>

 $[AcH]_{b}$  will then indicate the true aldehyde concentration, whereas  $[AcH]_{a}$  will indicate the true concentration plus that liberated by the above reaction. Thus  $[AcH]_a - [X]$  should be equal to  $[AcH]_b$ . The results in Table VI from autoxidation experiments show that agreement is satisfactory. Similar agreement was obtained for results of estimations during the isolated peracetic acid + acetaldehyde reaction. Acetaldehyde estimations after estimating total peroxides by method 3 agreed with  $[AcH]_a$ .  $[AcH]_b$  was taken as the true aldehyde concentration.

Expt Time	Time	ime	[AcH] <i>a</i>	[AcH] <sub>ð</sub>	$[AcH]_a-[X]$
No.	(mi <b>n.</b> )	[X]		Conc. in moles/litr	e
D18 D29 D30	10 45 10 10 35	0.017 0.025 0.053 0.030 0.045	0·227 0·087 0·465 0·295 0·170	0·207 0·060 0·410 0·270 0·120	0.210 0.062 0.412 0.265 0.125
		0.032	0.090	0.032	0.029

TABLE VI

#### Results

The analytical data from a typical experiment are shown in Fig. 1. The oxygen concentration is plotted in moles absorbed per litre of solution and the peroxides in g. atoms of active oxygen per litre (for peracetic acid this also corresponds to molarity). The difference between the total peroxide and peracetic acid, as is established later, was due to the formation of a second peroxide. The concentration of the latter passes through a maximum when about two-thirds of the aldehyde has reacted and falls off towards zero as the reaction approaches completion. Over the initial 5-10 min. of the reaction the total peroxide produced (in g. atoms of oxygen) is equivalent to the oxygen absorbed in moles. The subsequent falling off in the total peroxide concentration as compared with oxygen absorbed represents the loss of peroxides by secondary reactions.

As will be seen from Fig. 2 the uncatalyzed reaction followed a similar course in spite of its irreproducibility of reaction velocity.

<sup>21</sup> Joslyn and Comar, Ind. Eng. Chem. (Anal.), 1938, 10, 364.

STOICHIOMETRY.—It is evident from the analytical results (Fig. 1) that the plot of acetaldehyde reacted was at an equal distance above the oxygen curve as peracetic acid was below the oxygen plot, i.e.

or

$$[AcH]_0 - [AcH]_t - [O_2] = [O_2] - [AcOOH]$$
$$\frac{[AcH]_0 - [AcH]_t + [AcOOH]}{O_2} = 2 \cdot 0,$$

where

[AcH]<sub>0</sub> = aldebyde molarity at time o, [AcH]<sub>t</sub> = ,, ,, ,, t, [O<sub>2</sub>] = oxygen absorbed moles/l. solution, [AcOOH] = peracetic acid molarity.



FIG. 1.—Analytical results of a typical experiment [AcH] = 0.70 M,  $[CoAc_2] = 2 \times 10^{-5} \text{ M}$ ; oxygen absorbed as g. moles per litre, aldehyde as molarity and peroxides as g. atoms active oxygen per litre.



FIG. 2.—Analytical results for the uncatalyzed reaction. [AcH] = 0.733 M

The above relationship holds for both the catalyzed (Fig. 3) and uncatalyzed reaction (Fig. 4) and the mean slope of 11 different determinations was 1.98 (range 1.88-2.06).



This relationship would hold if peracetic acid were initially formed and subsequently (a) reacted in equimolar quantity with acetaldehyde (to give, either directly or via an addition compound, acetic acid or anhydride), or (b)



FIG. 4.-Stoichiometry of uncatalyzed reaction.

decomposed to give acetic acid and oxygen. The relationship would not hold if diacetyl peroxide were formed in appreciable amount, e.g.

 $AcOOH + AcOH \rightarrow AcOOAc + H_2O.$ 

Direct measurements of the cobalt catalyzed rate of decomposition of peracetic acid (see later) indicate that (b) did not take place to any appreciable extent.

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**Equilibrium :** aldehyde + peracetic acid  $\rightleftharpoons$  peroxide.—The general shape of the curves representing the concentration data indicated the possibility of an equilibrium between the peracetic acid and the aldehyde on one side, and the peroxide X on the other. This was confirmed by substituting the analytical concentration of the reactions and products in

$$K = \frac{[\text{AcH}][\text{AcOOH}]}{[X]}.$$

The plot of [AcH][AcOOH] against [X] passed through the origin and was linear for all experiments The value of K was 0.30 mole/l. at 25° C Stability of Peroxides.—In the initial stages all the oxygen absorbed

Stability of Peroxides.—In the initial stages all the oxygen absorbed appears as peroxides and if it is assumed that this holds throughout the reaction then the difference between the amount of oxygen absorbed and the total peroxide concentration represents the amount of peroxide decomposed into nonperoxidic products.

Independent experiments have shown that peracetic acid is stable in the absence of a catalyst. Cobalt acetate catalyzes its decomposition, the rate being

Cobaltous Acetate M	$k_4 \ (\min.^{-1})$
$0  2 \times 10^{-5}  4 \times 10^{-5}  8 \times 10^{-5}  12 \times 10^{-5}$	0.011 (mean of 2 expt.) 0.015 ,, 6 ,, 0.036 0.075 ,, 4 ,, 0.087

TABLE VII

approximately first order and proportional to catalyst concentration The catalyzed rate of decomposition is, however, very slow compared with the rate of disappearance of peroxides during the oxidation (The first order velocity constant in acetic acid solution with cobalt acetate  $1.3 \times 10^{-5}$  M was found to be ca.  $3.5 \times 10^{-5}$  min.<sup>-1</sup> at 25° C.)

Assuming therefore that the decomposition of peroxide X is the important process and that this obeys a first order law then

 $\frac{\mathrm{d}}{\mathrm{d}t}\left(\mathrm{O}_{2}-\mathrm{total \ peroxide}\right)=k_{4}[\mathrm{X}].$ 

The plot of the left-hand term against [X] was linear in both the catalyzed and uncatalyzed reactions and the values of  $k_4$  obtained are summarized in Table VII. It is clear that the cobalt catalyzes the decomposition of the peroxide X and this is confirmed by studies of the direct decomposition of X described later.

this is confirmed by studies of the direct decomposition of X described later. The Reaction of Acetaldehyde with Peracetic Acid.—The above results are in agreement with the reactions scheme

$$\begin{array}{c} \text{AcH} + \text{O}_2 \rightarrow \text{AcOOH} \\ \text{AcOOH} + \text{AcH} \rightleftharpoons \text{X} \\ \text{X} \rightarrow \text{products.} \end{array}$$

Peracetic acid first produced reacts in equimolar quantities with acetaldehyde giving the peroxide X, which exists in equilibrium with these reactants. Estimates have been made of the value of equilibrium constant, and also of the catalyzed and uncatalyzed rates of decomposition of peroxide X.

In order to confirm this scheme, peracetic acid, prepared separately by an unambiguous method, was allowed to react with acetaldehyde in acetic acid solution, and the course of the reaction followed. The experimental procedure was as used in the previous oxidation experiments. 25 ml acetic acid solutions were shaken with r ml. peracetic acid + acetic acid solution in the absence of oxygen. At convenient intervals samples were extracted from the reaction vessel for analysis of peroxides and aldehyde. The initial rate of loss of aldehyde and peracid was very fast, although the total peroxide concentration decreased throughout at a slow rate. Results for a typical experiment are shown in Fig. 5.

Molar Ratios Reacting.—The plot of acetaldehyde concentration against peracetic acid concentration was linear (Fig. 6) and of slope unity, showing the reaction occurred in equal molar quantities. In the initial stages almost all of the peracetic acid reacted appeared as peroxide X, showing that this compound is formed from equimolar amounts of the reactants.



FIG. 5.—Reaction between acetaldehyde and peracetic acid.

Equilibrium Constant.—The immediate rapid though incomplete reaction of the aldehyde and peracid (in the absence of catalyst) giving peroxide X indicates the existence of an equilibrium. This was confirmed by plotting [AcH] [AcOOH] against [X] when a linear relationship was obtained. The calculated values of  $K = \frac{[AcH][AcOOH]}{[X]}$  for four different concentrations are summarized in Table VIII.



FIG. 6.—Equilibrium : acetaldehyde + peracetic acid  $\rightleftharpoons$  peroxide X.

The average value,  $K = 0.27 \text{ mole/l.} (25^{\circ} \text{ C})$ , agrees closely with the previous value at the same temperature obtained from data from the autoxidation. Similar determinations in the presence of cobalt acetate  $(8 \times 10^{-5} \text{ M})$  gave K = 0.28 mole/l.

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Rate of Decomposition of Peroxides.—The slope of the total peroxide against time curves corresponds to the overall rate of decomposition of the peroxides. In the absence of a catalyst, peracetic acid is stable and thus in this case the slope gives the rate of decomposition of peroxide X. The plot of d(total peroxide)/dt against [X] was linear indicating that the decomposition obeyed a first order law, viz.  $-d[X]/dt = k_4[X]$  with a value  $k_4 = 0.015$  min.<sup>-1</sup>. This result is in reasonable agreement with that from measurements on the autoxidation.

In the presence of cobalt acetate  $(8 \times 10^{-5} \text{ M})$  the rate of decomposition of peroxides was approximately doubled  $(k'_4 = 0.031 \text{ min.}^{-1})$ . The effect of the catalyst was greater than can have been due to decomposition of peracetic acid, so it may be assumed that the catalyst accelerates the decomposition of peroxide

Expt. No.	[AcH] <sub>0</sub>	[AcOOH] <sub>0</sub>	K
	Mole/l.	Mole/l.	Mole/l.
Р1	0·210	0·194	0·29
Р3	0·360	0·183	0·26
Р4	0·376	0·257	0·25
Р6	0·400	0·260	0·27

TABLE VIII

X, as was found in the oxidation experiments. Some gas evolution was observed at a rate (on a molar basis) about 10 % of the rate of disappearance of total peroxide concentration. The observations are in agreement with the experiments with peroxide X. When 1 % water was added to the reaction mixture no influence on the value of K or  $k_4$  was observed. With 5 % added water  $k_4$  was increased to 0.020 and with 10 % to 0.032. Nature and Reactions of Peroxide.\*—The formation of an intermediate

Nature and Reactions of Peroxide.\*—The formation of an intermediate peroxidic compound by reaction of acetaldehyde and peracetic acid was first postulated by Wieland <sup>4</sup> who suggested the compound was hydroxyethyl acetyl peroxide



Kagan and Lubarsky <sup>14</sup> also assumed that the intermediate peroxide had the above structure. Compounds of this general structure are formed by the interaction between acetaldehyde and hydrogen peroxide, acetaldehyde and ethyl bydroperoxide and between tetralin hydroperoxide and formaldehyde. Losch,<sup>23</sup> an abstract of whose work has recently become available, claims to have obtained a crystalline peroxide by oxidation of acetaldehyde at low temperatures. This peroxide, m.p. 20-22° C, m.wt. 105 and containing 14-15% active oxygen is said to change at room temperature without loss of weight to acetic acid. With a catalyst of mixed copper and cobalt salts it gave up to 60% acetic anhydride. Losch suggests that peracetic acid, if formed, in an intermediate stage would react with acetic anhydride to give diacetyl peroxide. In the present work no acetyl peroxide was detected and this is in conformity with the above view that the peracetic acid reacts with the aldehyde to form peroxide X which as shown below undergoes a fairly slow transformation to the anhydride at room temperature. The above formulation of the addition product is similar to analogous addition reactions of aldehyde, viz.,

 $CH_{3}C H_{4} C H_{4$ 

\* The experimental work reported in this section was carried out by L. Raphael. <sup>23</sup> Losch, Summary in Arbeitsgemeinschaft Methoden der Organischen Chemie Taqund I ((Berlin, 1941), p. 23 (microfilmed by U.S. Library of Congress). An alternative structure for the addition compound would result if the peracetic acid tended to react via the  $O_2H$  anion, viz.,



by a reaction similar to the addition of benzoyl cyanide to benzaldehyde



Structure (II) would readily give acetic anhydride by loss of a molecule of water. It is difficult to see how (I) could give rise to the anhydride, without postulating a re-arrangement to (II).

#### TABLE IX

### (All concentrations expressed as g./l.)

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F4	Concentration	concentration P	Peroxide			Acetic Acid	Acetal- dehyde
Expt. No.	of Oxidation Product	Time	(calc. as AcH . AcOOH)	Acetic Acid	Acetal- dehyde	Calc. A Oxidation AcH . A	ssuming Product is AcOOH
I	2.15	10 min.	1.00	1.10	0.20		
		I hr.		1.30	0.40		
		3 hr.	0.22	1.08			
		20 nr.	0.0	1.84	0.41	1.22	0.22
2	13.2	10 min.	6.84	6.00	3.64		
	1	ı hr.	0.36	10.60	3.28		
		3 hr.	0.06	10.40	3.30	9.95	3.55
· ·	2.62	to min	7.22	1.20	0.66		
3	2.03	Thr	0:60	1.67	0.00		
		2 hr	0.30	2:00	0.66	1.02	0.70
		5 m.	020	2 00	0.00	192	0,0
4	9.6	10 min.	4:55		2.51		
•	-	30 min.	2.22		(1.88)		
		23 hr.	0.0	6.82	1.30	7.00	2.58
5	1.915	10 min.	0.01		0.20		
		30 min.	0.28		0.22		
		23 nr.	0.0	1.37	0.34	1.40	0.21
	1	1	1	l	1	4	1

A crystalline peroxide was isolated by carrying out the uncatalyzed oxidation of pure acetaldehyde at  $-30^{\circ}$  C. In a typical experiment 30 ml aldehyde absorbed 600 cm.<sup>3</sup> oxygen after 6 hr. shaking. On removing unreacted aldehyde by evacuation the temperature being maintained below o° C, a white crystalline solid separated which was unstable at room temperature. The dry product melted with decomposition at about 20° C which agrees with the result quoted by Losch and indicates that the same compound was being studied. It was decomposed by water to give acetic acid. Solutions in glacial acetic acid (200 g./l.) decomposed very vigorously with much evolution of heat on the

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addition of 1-2 ml. of a 1 % solution of cobaltous acetate. The acetic acid solution liberated iodine from neutral potassium iodide and showed the typical reactions of a peroxide. The above reactions were studied quantitatively with the object of determining the composition of the peroxide.

(i) REACTION WITH WATER.—The dry compound was rapidly weighed in a cooled vessel and its decomposition in water followed by estimating total peroxide, acetic acid and acetaldehyde. The results for a series of concentrations are summarized in Table IX, and it is seen that the peroxide completely decomposes into acetic acid and acetaldehyde, the decomposition being more rapid in the more concentrated solution. It is observed that as the peroxide (expressed in Table IX as AcH. AcOOH) disappears the acetic acid increases but the acetaldehyde concentration remains essentially constant. The apparent decrease in aldehyde concentration on standing may be attributed to oxidation. This result indicates that the acetaldehyde is not a primary product of the decomposition but was loosely attached to the peroxide, probably as aldehyde of crystallization and was immediately liberated in water. Other results discussed below substantiate this conclusion. If it is assumed that this peroxide corresponds to structure (AcH.  $AcO_2H$ )AcH, where the aldehyde outside the brackets is aldehyde of crystallization, and that reaction with water occurs

#### $(AcH \cdot AcO_2H)AcH + H_2O \rightarrow 2AcOH + AcH,$

then the amounts of acid and aldehyde which should be formed on reaction with water are summarized in the last two columns of Table IX. The close agreement with experiment is strong evidence for the correctness of the above assumption.

(ii) REACTION IN ACETIC ACID.—This decomposition was followed by dissolving a known weight of the oxidation product in glacial acetic acid and estimating peracetic acid, total peroxide and acetaldehyde, as previously described. Since the peroxide concentration was high, and as will be shown, an equilibrium exists in solution, all peracetic estimations were made at about 10° C when a good end point was obtained. The results are summarized in Table X.

Expt. No.	Conc. of Oxidation Product g./l.	Peracetic Acid mole/l.	Total Peroxide mole/l.	Aldehyde* mole/l.	κ (10 ± 2° C)
24 26 31 32 33 34 36 37 38 39	216  268 220 250 190  185 216	0.55 0.45 0.48 0.50 0.50 0.50 0.50 0.50 0.50	1.75 1.09 1.63 2.91 2.47 2.19 2.2 0.86 1.94 2.43	3.15 5.68 4.58 4.05 	0.83 0.67 0.66 0.69 

TABLE X

\* Aldehyde = free acetaldehyde + acetaldehyde liberated on estimating peroxide X.

It is apparent that in all cases the estimated free acetaldehyde concentration is approximately twice the total peroxide concentration. This is precisely what would be expected if the oxidation product were peroxide X with one additional mole of aldehyde of crystallization. Furthermore, as shown in the previous sections, peroxide X exists in equilibrium with peracetic acid and acetaldehyde and if the crystalline oxidation peroxide had the composition X. CH<sub>3</sub>CHO a similar equilibrium should occur. The values of the equilibrium constant K derived on this assumption

$$K = [AcH][AcOOH]/[X]$$

are summarized in the last column of Table X. In spite of the difficulty of exact determination of K owing to the ease with which the solid oxidation product loses aldehyde and the necessity for rapid titration of the peroxides with the consequent variation of several degrees in the temperature at which measurements are recorded, the above values indicate that an equilibrium exists in solution between the peroxide, peracetic acid and acetaldehyde.

These results and those discussed above, together with the results of the reaction with water, lead to the conclusion that the product of the uncatalyzed oxidation of pure acetaldehyde and of the cobalt catalyzed oxidation in dilute solution is the peroxide X formed by reaction of peracetic acid and acetaldehyde in equimolar amounts and that the peroxide crystallizes from aldehyde solution with I molecule of aldehyde of crystallization.

Catalytic Decomposition to Acetic Anhydride and Acetic Acid.—The oxidation was carried out using a 50 % solution in glacial acetic acid (25 ml.) containing I ml. I % cobaltous acetate solution in glacial acetic acid. The

Peroxide g.	Acetic Annydride g.	Acetic Acid g.
4.42		
5.38	<b>1</b> .6	4.9
6.14	2.0	5.4

TABLE XI

resulting solution was analyzed for acetic anhydride and acetic acid by the method of Smith and Bryant.<sup>24</sup> In a typical experiment with a solution which had absorbed 400 ml. oxygen, no acetic anhydride was detected at the end of the absorption but on standing over night the peroxide content had fallen to zero and 0.84 g. acetic anhydride and 3.96 g. acetic acid were formed. In similar experiments it was established that the disappearance of the intermediate per-oxide coincided with the formation of anhydride. The catalysis of this reaction by cobaltic ion was proved by preparing the solid peroxide and following the decomposition of solutions in glacial acetic acid. At room temperature the decomposition of solution containing 100-200 g./l. by 2 ml. 1 % cobaltous acetate solution was very vigorous, with much gas formation and evolution of heat. At higher temperatures the decomposition of the above result that acetic acid and acetic anhydride are formed by catalytic decomposition of the intermediate peroxide. It was observed that when all the peroxide had disappeared the catalysts reverts to the lower valency state. Table XI shows that acetic acid was the major product and this may be partly formed by hydrolysis of the anhydride since the anhydride is formed from the peroxide by loss of a molecule of water.

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<sup>24</sup> Smith and Bryant, J. Amer. Chem. Soc., 1936, 58, 2452.