

CCLXV.—*The Decomposition of Acetyl Peroxide and the Mechanism of Kolbe's Electrosynthesis.*

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THE earlier idea of Schall (*Z. Elektrochem.*, 1896, **3**, 83), that acid peroxides are formed as intermediate products at the anode during the electrolysis of fatty acids, has in recent years been taken up by Fichter (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; *J. Chim. phys.*, 1926, **23**, 493), who has extended the peroxide theory to electrochemical oxidation in general. It is the purpose of this paper to show that the experimental justification for this view is unsound and that there is no necessity to assume that acetyl peroxide is formed during the electrolysis of acetates.

Whatever view we adopt regarding the mechanism of Kolbe's reaction we must assume that free  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  radicals are present at some stage in the process. If we accept the discharged-ion theory, *i.e.*, that the  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  radicals result simply from the discharge of acetanions and not from a dehydration of acetic acid by oxygen (compare Fairweather and Walker, *J.*, 1926, 3111 \*), the question still arises: Do the  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  radicals unite to form acetyl peroxide which then decomposes into carbon dioxide and ethane; or do they decompose "unimolecularly," so to speak, into carbon dioxide and free  $\text{CH}_3$  radicals, which then unite to form ethane?

The first view may be tested, as Fichter suggested, by preparing the pure acetyl peroxide and causing it to decompose. The application of results of such experiments to the Kolbe reaction at the anode may, however, not be conclusive. For even assuming that acetyl peroxide decomposes on heating entirely into carbon dioxide and ethane, it does not follow that in the anode process, in which

\* The values of the anode potential in that paper are through a regrettable error in the calculation all 0.56 volt too high. This in no way affects the reasoning in the paper, which is concerned only with the relative values of the potentials.

these gases are obtained from discharged acetanions, the  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  radicals must have first united to form a peroxide. On the contrary, one may argue that acetyl peroxide, when heated, breaks up into two  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  groups, which then react as in the electrical process (compare Wieland and Fischer, *Annalen*, 1925, 446, 60). It will be seen, however, from the experimental part that a simple decomposition of acetyl peroxide according to the equation  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2 = \text{C}_2\text{H}_6 + 2\text{CO}_2$  does not take place.

Fichter (*Helv. Chim. Acta*, 1927, 10, 869) claims to have obtained direct evidence for the peroxide theory, since he has shown that in the electrolysis of a solution of potassium hexoate small quantities of hexoyl peroxide are formed when the temperature is kept very low. This experiment shows that when the conditions are made very favourable the discharged acyl radicals unite to a small extent to form the acid peroxide, but one is not justified in concluding that the Kolbe synthesis, which is the main reaction, has proceeded through the intermediate stage of peroxide. In fact, the difficulty of isolating from the electrochemical products any peroxide at temperatures at which these peroxides are by no means unstable cannot be reconciled with this view. A further difficulty arises when one considers that by electrolysing a solution of an acetate at about  $100^\circ$  considerable quantities of ethane are obtained, although acetyl peroxide decomposes well below this temperature (see experimental part). Also Gibson (*Proc. Roy. Soc. Edin.*, 1924, 44, 151) has shown that hexachloroethane is formed in the electrolysis of trichloroacetic acid, of which the peroxide is apparently incapable of existence.

The decomposition of acetyl peroxide, on which Fichter largely bases his theory, has really not been studied to any extent (for the previous literature on the subject, see Fichter, *Helv. Chim. Acta*, 1918, 1, 151). It was decided, therefore, to investigate the nature and composition of the gases obtained by the decomposition of acetyl peroxide under various conditions.

#### EXPERIMENTAL.

Acetyl peroxide was prepared from acetic anhydride and sodium peroxide by the method of Gambarjan (*Ber.*, 1909, 42, 4010). The ethereal solution of peroxide was dried over calcium chloride, the ether evaporated at the ordinary temperature, and the crystalline residue of peroxide washed with ether; it was then sufficiently pure, m. p.  $26.5^\circ$  (Nef gives  $30^\circ$ , and Colson  $27^\circ$ ). Analysis: A mixture of 0.1—0.2 g. of the peroxide, 50 c.c. of water, 10 c.c. of glacial acetic acid, and 10 c.c. of a 20% solution of potassium iodide was kept for 24 hours (the liberation of iodine takes place slowly;

compare Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 183) and the iodine was then titrated with *N*/10-thiosulphate. Independently prepared samples of the peroxide were found to contain 99.6, 99.8, and 99.4% of  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2$ .

In all the experiments that follow, the gases evolved were collected over mercury and analysed in the usual manner in a Bone and Wheeler apparatus containing mercury.

*Decomposition of Pure Acetyl Peroxide.*—When acetyl peroxide is heated gradually above its melting point the liquid commences to evolve gas at 60–70°, and at 80° the evolution proceeds briskly. The decomposition takes place gently without the violent explosion that occurs when the substance is heated rapidly. The composition of the gas (% vol.) evolved at 80° is:  $\text{CO}_2$ , 58.7, 61.0;  $\text{C}_2\text{H}_4$ , 1.1, 1.6;  $\text{O}_2$ , —, 2.3;  $\text{CO}$ , 1.6, 3.0;  $\text{CH}_4$ , 34.0, 28.8;  $\text{C}_2\text{H}_6$ , 4.6, 3.4.

The proportion of methane formed is greater than in the explosive decomposition of acetyl peroxide investigated by Fichter (*Helv. Chim. Acta*, 1918, **1**, 152), which did not lead to a simple disintegration according to the equation  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{OC}\cdot\text{CH}_3 = \text{C}_2\text{H}_6 + 2\text{CO}_2$ . He also found considerable quantities of methane and ascribed its formation to a sort of “cracking” process, due to the violence of the explosion and the high temperature of the decomposition, which he supposes does not occur in the slow molecule-by-molecule decomposition at the anode.

A further experiment, in which the decomposition was carried out quantitatively and as slowly as possible, showed that the absolute yield of ethane, calculated on the weight of peroxide used, is very small. In a small, weighed tube 0.0500 g. of acetyl peroxide was gently heated till decomposition commenced at 61°. The heating was continued, at 65–75°, for about 4 hours, 11.0 c.c. of gas (measured at 13° and 754 mm.) being collected. The residue weighed 0.0257 g., and the amount of undecomposed peroxide in it, estimated by liberation of iodine from potassium iodide, was 0.0170 g. The decomposed peroxide (0.0330 g.) therefore produced 10.4 c.c. of gas (reduced to N.T.P.) having the following percentage composition by volume:  $\text{CO}_2$ , 58.3;  $\text{O}_2$ , 0.2;  $\text{CO}$ , 0.9;  $\text{CH}_4$ , 38.6;  $\text{C}_2\text{H}_6$ , 1.9. This corresponds to 1.0 molecule of carbon dioxide, 0.65 molecule of methane, and 0.04 molecule of ethane from 1 molecule of peroxide. The formation of ethane is therefore certainly not the main reaction.

*Decomposition of Solutions of Acetyl Peroxide.*—When a solution (100 g.) of acetyl peroxide (14.4 g.) in water containing acetic acid (27.7 g., to increase the solubility) was gradually warmed, effervescence set in at about 75° and between 80° and 90° there was a brisk

evolution of gas. The gases evolved at about 80° were collected and analysed (expts. *a* and *b*).

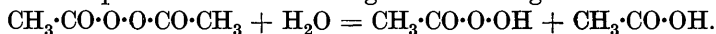
Acetyl peroxide dissolved in	CO <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> .	O <sub>2</sub> .	CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .
<i>a.</i> Aqueous acetic acid .....	76.0	1.2	3.1	1.4	16.0	2.3
<i>b.</i> " " " " .....	75.0	—	1.4	1.4	20.8	1.2
<i>c.</i> Ethyl alcohol .....	50.5	—	—	2.2	45.8	1.5
<i>d.</i> " " " " .....	51.0	—	—	1.7	45.6	1.7

Here again the amount of ethane formed is small compared with that of methane and there is relatively more carbon dioxide.

A solution of 0.15 g. of acetyl peroxide in 0.4 c.c. of alcohol was heated gradually in a water-bath. Gas evolution commenced at about 60°. The gas evolved between 60° and 70° was collected after passing through a cooled tube to condense any alcohol vapour; it consisted mainly of carbon dioxide and methane in nearly equal volumes, with only a very small amount of ethane (see expts. *c* and *d* in the table).

From these experiments, it is evident that the decomposition of acetyl peroxide does not take place to any large extent according to the equation  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2 = \text{C}_2\text{H}_6 + 2\text{CO}_2$ , and hence there is no reason to suppose that in the electrolysis of acetates, where the gases evolved at the anode are essentially carbon dioxide and ethane, acetyl peroxide has been formed at the anode. It must also be emphasised that methane is not present in the anode gases, although it appears to be one of the necessary products in the decomposition of acetyl peroxide. The only electrolytic formation of methane from acetates is recorded by Baur (*Z. Elektrochem.*, 1923, 29, 105), who used commutated direct current.

There is the possibility that the methane obtained in the above experiments from aqueous solutions of acetyl peroxide may have come from decomposition not of the peroxide itself but of the peracid which is got from it by hydrolysis. It has been shown by Clover and Richmond (*loc. cit.*, p. 184) that a solution of acetyl peroxide kept for 24 hours undergoes the change:



A solution of the peroxide which had been kept for a week liberated almost the whole of the required amount of iodine immediately after the addition of potassium iodide, showing that the change from peroxide to peracid was practically complete (since the former liberates iodine only very slowly). The solution of peracid was heated gradually and at about 40° gas evolution commenced. The gas evolved between 75° and 80° consisted mainly of oxygen with about 10% of carbon dioxide and no trace of ethane or methane. Hence the decomposition of the peroxide does not proceed through the peracid stage.

In the search for a method whereby acetyl peroxide might be decomposed at lower temperatures than those employed so far, the action of ultra-violet light on the peroxide was investigated: the peroxide decomposed, and larger quantities of ethane were obtained than by any of the previous methods. A solution of acetyl peroxide in aqueous acetic acid was placed in a quartz tube surrounded by a water-cooled quartz condenser and was exposed at a distance of 3 or 4 inches to the light of a mercury vapour lamp. A gas was slowly evolved and after 7 or 8 hours about 5 c.c. had collected. The composition of the gas is shown in the table (expts. *a* and *b*).

	Acetyl peroxide.	CO <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> .	O <sub>2</sub> .	CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .
<i>a.</i>	Dissolved in aqueous acetic acid	75.4	—	1.2	1.4	4.8	17.3
<i>b.</i>	„ „ „ „	68.5	—	1.4	1.3	11.8	17.1
<i>c.</i>	Solid .....	66.8	—	1.3	1.2	5.6	25.1
<i>d.</i>	„ .....	68.4	2.1	0.7	1.3	3.9	23.6
<i>e.</i>	„ .....	67.4	2.0	0.5	1.4	4.4	24.4

In experiments *c*, *d*, and *e*, solid acetyl peroxide was exposed to the ultra-violet light for about 3 hours. The amount of ethane formed was much greater than in the thermal decomposition. Even in this case, however, there is no reason to suppose that the main reaction consists in a simple breaking up of the acetyl peroxide into ethane and carbon dioxide.

#### *Conclusion.*

The results of the experiments described in this paper make it appear extremely unlikely that the formation of ethane and carbon dioxide at the anode in the electrolysis of acetates proceeds through the intermediate stage of acetyl peroxide. The view that the discharged acetate ions, which must necessarily be very unstable radicals, react together to give the above-mentioned products still affords the most satisfactory, although perhaps incomplete, explanation of Kolbe's electrosynthesis. In the interaction of these radicals some sort of momentary loose union may well take place prior to a more far-going disruption, but the assumption of the actual formation of the chemically known peroxide is unnecessary and also experimentally unsound. That a small portion of the acetate radicals might unite to form the more stable peroxide would not be surprising, and this possibility is not excluded.

The main arguments against the peroxide theory may be summed up as follows:

(1) The thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not indicate a reaction according to the equation  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2 = \text{C}_2\text{H}_6 + 2\text{CO}_2$ .

(2) Methane, which is not found in the anode gases during the

electrolysis of acetates, is always present among the decomposition products of acetyl peroxide, often in large amounts.

(3) Peroxides have not as yet been isolated by electrochemical means, even at low temperatures at which the peroxides are comparatively stable.

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