47. *The Decomposition of Acetyl Peroxide.*

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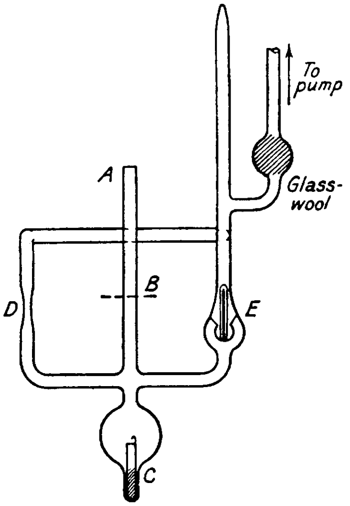
In the discussion of the anode reactions taking place during the electrolysis of organic acids or their salts, the theory of the intermediate formation of peroxides and per-acids has played a prominent part, largely due to the work of Fichter and his co-workers. This theory (known as the " peroxide theory ") is based mainly on the qualitative similarity between the products formed at the anode during the electrolysis of any given acid and the products of the thermal decomposition of the corresponding acyl peroxide or peracid. In many cases, however, the quantitative composition of the products is very different in the two processes. In particular, it has been shown (Walker, J., 1928, 2042) that the thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not consist mainly of a reaction according to the simple equation $(CH_3{\cdot}CO{\cdot}O)_2 = 2CO_2 + C_2H_6$ (1); methane is always formed, and the only circumstances in which the peroxide breaks up with any approach to the stoicheiometric proportions of equation (1) appears to be when it is exposed at the ordinary temperature to ultra-violet light; *e.g.*, in one such experiment a $CO_2 : C_2H_6$ ratio of 2·9 : 1 was obtained (Walker, *loc. cit.*, p. 2044). A more detailed investigation of this reaction is being undertaken.

As regards the thermal decomposition, however, it still seems to be assumed by supporters of the peroxide theory that if acetyl peroxide could be made to decompose at a sufficiently low temperature it would break up more nearly in accord with equation (1). On the other hand, comparison of the results of the explosive decomposition (Fichter and Krummenacher, *Helv. Chim. Acta*, 1918, **1**, 152) with those of the above-mentioned experiments, which were carried out at about 80°, suggested that less ethane would be formed at even lower temperatures. Since no experimental evidence was available, the nature of the gaseous products obtained by heating liquid acetyl peroxide at temperatures between 30° and 90° was investigated, and the above deduction confirmed.



EXPERIMENTAL.

The white crystalline peroxide, prepared by Gambarjan's method (*Ber.*, 1909, **42**, 4010), was recrystallised from ether. As the peroxide vapour readily attacks rubber and mercury, an all-glass apparatus was used (see fig.). After the peroxide, contained in a small glass tube, had been introduced through *A*, the apparatus was sealed off at *B*, evacuated through the Töpler pump, and the constriction *D* sealed, the bulb containing the peroxide being cooled with solid carbon dioxide during these operations.

The surrounding thermostat (not shown) was then slowly brought to the required temperature and maintained thereat (± 1·0°) until a sufficient quantity of gas (at least 10 c.c. measured at ordinary temperature and pressure) had been formed. The average rate of evolution of gas, in c.c. per hour, decreased rapidly at first, and then very slowly from about 14·0 at 90° to 0·2 at 30°. The bulb *C* was then cooled and, after the septum at *E* had been broken with the usual magnetic arrangement, the whole of the gas was collected through the Töpler pump. A portion of it was then transferred to a Bone and Wheeler apparatus, in which the carbon dioxide, oxygen, ethylene, and carbon monoxide were determined by absorption in the usual manner. The methane and ethane were determined by the fractional condensation method using liquid air (Walker and Shukla, J., 1931, 368) in order to confirm the presence of these two hydrocarbons independently of one another. The separated portions of the hydrocarbon residue gave *C*/*A* ratios on explosion very close to 2·00 and 1·25, *i.e.*, the theoretical values for these two gases respectively.

Results.—The composition of the gaseous products (in % by vol.) is shown in Table I. It will be seen that the amount of ethane becomes less with decreasing temperature, until it is only about 2% of the volume of methane formed.

TABLE I.

Temp.	30°.	45°.	55°.	70°.	80°.	90°.
CO_2, % by vol.	59·5	64·0	55·5	58·4	62·2	62·0
O_2 ,, ...	1·9	1·3	0·8	0·9	0·7	1·1
C_2H_4 ,, ...	0·5	0·4	0·3	0·1	0·7	0·1
CO ,, ...	1·9	1·1	1·6	1·0	1·0	0·8
C_2H_6 ,, ...	0·7	0·7	1·4	3·7	3·0	8·8
CH_4 ,, ...	35·4	32·3	40·0	35·9	32·2	27·1

A decomposition of the peroxide according to equation (1) is therefore not favoured by allowing the reaction to take place as slowly and at as low a temperature as possible. The results described in this and in the previous paper show that when acetyl peroxide is heated under a wide variety of conditions, both alone and in solution, methane and carbon dioxide are the main gaseous products. The formation, in the absence of solvent, of a considerable amount of a gum-like residue suggests a rather complex decomposition process in which polymerisation of simpler primary products occurs. In a few experiments upon the residue from the incompletely decomposed peroxide, no evidence was found for the formation of formaldehyde, peracetic acid, or acetic acid, which might accompany the methane according to Fichter and Panizzon's suggestion (*Helv. Chim. Acta*, 1932, **15**, 1007). Since, however, we have been concerned mainly with determining the effect of lower temperatures upon the formation of ethane, we have not attempted a complete investigation of the residue.

Discussion.—If acetyl peroxide is formed at the anode during the electrolysis of acetate solutions, then the conditions must be particularly favourable to the decomposition into $C_2H_6 + 2CO_2$, for in this case appreciable amounts of methane are formed only under very limited conditions of low current density and high concentration of acetate (cf. Shukla and Walker, *Trans. Faraday Soc.*, 1932, **28**, 457; also Fichter and Panizzon, *loc. cit.*). It does not appear likely that this is due to catalytic influence of the electrode surface, because Wieland and Pascual-Vila (*Annalen*, 1926, **446**, 60) found that the decomposition of acetyl peroxide in the presence of platinum under various conditions does not give ethane and carbon dioxide.

Finally, it is of interest to compare the gaseous products of the decomposition of acetyl peroxide with those of two other reactions in which the intermediate formation of this peroxide has been assumed, *viz.*, (i) the action of barium peroxide on acetic anhydride, and (ii) the oxidation of acetic acid with persulphates.

(i) This reaction was that actually used by Brodie (*Phil. Trans.*, 1863, **153**, 413) in his original preparation of acetyl peroxide, and for this purpose the temperature must be kept low. At higher temperatures a vigorous reaction takes place, and Schützenberger (*Compt. rend.*, 1868, **61**, 487) stated that a gas composed exactly of two volumes of carbon dioxide and one volume of a hydrocarbon having the character and composition of $2CH_3$ was evolved. This result has apparently never been confirmed, though often quoted as a method of preparing ethane (cf. Armstrong, *Nature*, 1934, **133**, 379). On the contrary the work of Darling (J., 1868, **21**, 500), of Fichter (*Z. Elektrochem.*, 1914, **20**, 473), and of Glasstone and Hickling (*Chem. and Ind.*, 1934, 512), in which barium peroxide and acetic anhydride were heated together under a variety of conditions, with and without the addition of water, shows that in every case little ethane and considerable quantities of methane are obtained. A comparison of the data of these investigators with the composition of the gas obtained by heating the peroxide alone (this paper and Walker, *loc. cit.*) shows that there is very close qualitative, and in some cases quantitative, resemblance in the gaseous products. To make the results more comparable, the gas compositions given in Table II are referred in each case to 100 vols. of methane, since in some cases the carbon dioxide was not determined and in others no ethane was found.

TABLE II.

Reaction.	Observers.	Composition (by vol.) of gaseous products (CH_4 = 100).		
Decomp. of $(AcO)_2$:		CH_4.	C_2H_6.	CO_2.
(*a*) liquid	W. & W.	100	2·0—32·5	139—229
(*b*) in aq. soln.	W.	100	5·8—14·4	360—475
BaO_2 and Ac_2O	D.	100	24·3	Not measured
	F.	100	16·5	255
	G. & H.	100	50·8	549
AcOH and $Na_2S_2O_8$	G.	100	0—30·5	Not measured
	F. & P.	100	0	489

W. & W. = Walker and Wild; W. = Walker; S. = Darling; F. = Fichter; G. & H. = Glasstone and Hickling; G. = Gordon; F. & P. = Fichter and Panizzon.

(ii) The reaction between acetic acid and sodium persulphate in aqueous solution has been investigated by Gordon (*J. Physical Chem.*, 1914, **18**, 55) and by Fichter and

Panizzon (*loc. cit.*, p. 996). The latter authors consider the first step in the reaction to be the oxidation of acetic acid to acetyl peroxide, and they attribute the fact that more methane than ethane is formed (see Table II) to hydrolysis of the peroxide to peracetic acid, since they assume that acetyl peroxide itself does not give methane as one of its primary decomposition products. In the light of the evidence now put forward, however, the products obtained in the oxidation of acetic acid appear to be such as are normally obtained from the decomposition of acetyl peroxide.

We conclude, therefore, that the reaction (1) is not the main process taking place when the peroxide is decomposed either directly or in reactions in which its intermediate formation appears likely.

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