238. *The Thermal and Photochemical Decomposition of Acetyl Peroxide.*

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IN recent years the thermal decomposition of a number of acyl peroxides of the type $(R \cdot CO \cdot O)_2$ (R = alkyl or aryl radical) has been investigated (Wieland and co-workers, *Annalen*, 1930, **480**, 157; 1934, **513**, 93; Fichter and Buess, *Helv. Chim. Acta*, 1935, **18**, 445; Erlenmeyer and Schoenauer, *ibid.*, 1936, **19**, 338). When peroxides of this class are heated, either in the pure state or in solution, decomposition takes place according to the scheme (I). This process is in general accompanied by reactions of types (2*a*) and

$$(R \cdot CO \cdot O)_2 \longrightarrow R_2 + CO_2 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

$$(R \cdot CO \cdot O)_2 + R'H \underset{\searrow}{\overset{\nearrow}{\rule{1.5cm}{0pt}}} \begin{array}{l} R \cdot CO \cdot OR' + RH + CO_2 \quad \cdot \quad \cdot \quad \cdot \quad (2a) \\ R \cdot CO \cdot OH + R'R + CO_2 \quad \cdot \quad \cdot \quad \cdot \quad (2b) \end{array}$$

(2*b*), where R'H may be a molecule of solvent, of peroxide, or of one of the decomposition products (cf. Gelissen and Hermans, *Ber.*, 1926, **59**, 662; this so-called RH scheme has been somewhat modified by Boeseken and Hermans, *Annalen*, 1935, **519**, 133; also Hermans, *Rec. trav. chim.*, 1935, **54**, 760). The whole decomposition process may, therefore, be very complex, and very little of the hydrocarbon R_2, which results from reaction (1), may appear amongst the final products.

The thermal decomposition of any particular acyl peroxide has usually been carried out in one of three ways : (*a*) Explosive decomposition, brought about by heating the peroxide in a steel bomb; (*b*) controlled decomposition, by gentle heating of the peroxide either alone or diluted with an inert material such as sand; (*c*) controlled decomposition of the peroxide in solution. Although a considerable amount of data has been accumulated regarding the nature of the products resulting from the thermal decomposition by these means of various acyl peroxides, very little is known about the mechanism of the decomposition process. The RH scheme (above) summarises in a convenient and comprehensive manner the different kinds of end-product of the thermal decomposition, but does not purport to represent the actual mechanism of the process. It has been applied almost entirely in discussing the behaviour of benzoyl and other aromatic peroxides. According to Hermans (*loc. cit.*, p. 767), aliphatic acyl peroxides decompose mainly according to reaction (1) but there does not exist much experimental evidence on the controlled decomposition of such peroxides (cf. Fichter, *Bull. Soc. chim.*, 1934, **1**, 1588).

Recently, we described some experiments on the decomposition of acetyl peroxide, $(CH_3 \cdot CO \cdot O)_2$ (J., 1935, 207; cf. also Walker, J., 1928, 2040). It was originally considered that the results might have some bearing on the mechanism of the Kolbe electrosynthesis of ethane from acetates, since there is a possibility of the formation and decomposition of acetyl peroxide in this process, but it is doubtful whether definite conclusions can be obtained in this direction (see later). The study of the decomposition of acetyl peroxide is of more direct interest in the general problem of the thermal decomposition of acyl peroxides, especially of aliphatic peroxides, for which the validity of the RH scheme is not certain. We hoped that conditions might be found under which the decomposition of acetyl peroxide could be controlled so as to approximate as nearly as possible to reactions of type (1) or (2) alone. In this paper some experiments on the thermal decomposition of acetyl peroxide in the vapour state and in solution are described. No data are on record regarding the decomposition of any acyl peroxides in the vapour state.

In the case of a few peroxides the photodecomposition produced by their exposure to ultra-violet light at the ordinary temperature has been investigated, and it appears that the products correspond more closely to a reaction of type (1) (cf. Walker, *loc. cit.*, p. 2044; Fichter and Schnider, *Helv. Chim. Acta*, 1930, **13**, 1428). The earlier experiments

with acetyl peroxide were performed on the solid substance. The results of irradiating the peroxide in the liquid and the dissolved state are now reported.

<div align="center">EXPERIMENTAL.</div>

1. *Thermal Decomposition of Acetyl Peroxide Vapour.*—The preparation of acetyl peroxide and the analysis of the gaseous products were carried out as previously described.

The decomposition of the peroxide vapour at 100° was performed in an all-glass apparatus (see Fig. 1). The solid peroxide, contained in a small tube, was introduced through A to the position shown at C, and surrounded by a freezing mixture. After being sealed off at B, the

<div align="center">FIG. 1.   FIG. 2.</div>
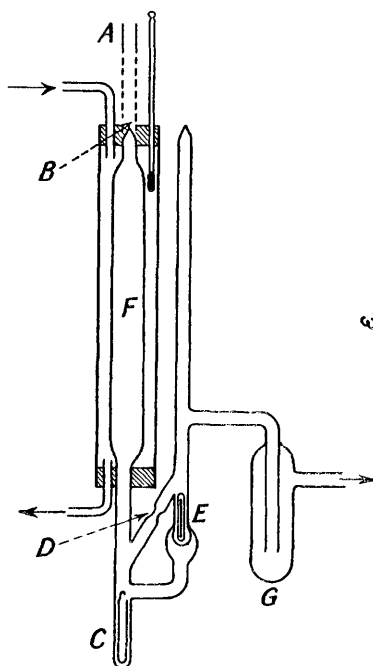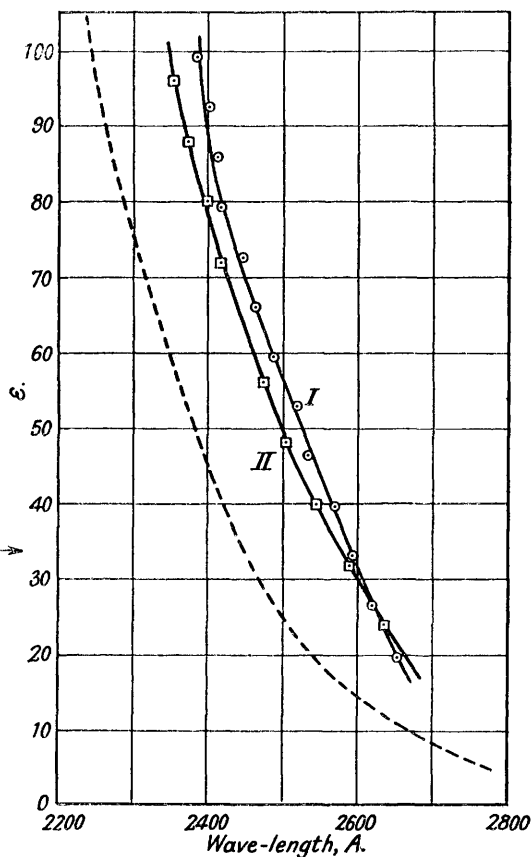
<div align="center">*Absorption of acetyl peroxide in* cyclohexane (I)
and in alcohol (II).</div>

whole apparatus was evacuated and then isolated from the pump by sealing at D. The peroxide in C was surrounded with a water-bath at 35°, and steam then passed through the jacket of the tube F containing peroxide vapour. The vapour pressure of liquid acetyl peroxide at 35° is of the order of a few mm. (owing to the slow decomposition of the liquid peroxide at this temperature, reliable measurements of the vapour pressure could not be made).

After sufficient time had elapsed, the heating was stopped, the tube C cooled with a freezing mixture, and the seal E broken with an electromagnet. The gaseous decomposition products were collected by means of a Töpler pump, the trap G, which was immersed in carbon dioxide–ether, preventing undecomposed peroxide vapour from entering the pump. In 6 hours 7·7 c.c. of gas (converted to N.T.P.) were collected. Similar results were obtained when the acetyl peroxide in C was kept solid at 18°, but owing to the lower vapour pressure of the solid, only 5·0 c.c. of gas were produced in $8\frac{1}{2}$ hours.

The results of the gas analysis were as follows :—

Decomposition of acetyl peroxide vapour at 100° from	Composition of gas, % by vol.						C_2H_6/CH_4.	CO_2/C_2H_6.
	CO_2.	O_2.	Unsat.	CO.	C_2H_6.	CH_4.		
(a) Liquid at 35°	64·7	0·9	1·4	2·4	24·9	5·3	4·7 : 1	2·4 : 1
(b) Solid at 18°	66·0	0·8	1·2	3·2	24·4	4·4	5·5 : 1	2·5 : 1

The thermal decomposition of acetyl peroxide vapour at 100° takes place very largely according to equation (1) (R = CH_3). The C_2H_6/CH_4 ratio is about 5 : 1, and may be compared with the value of 0·3 : 1, found in the decomposition of the pure liquid peroxide at 90°, which was the highest value obtained previously from the thermal decomposition under any conditions.

The ratio of CO_2/C_2H_6 approaches the value of 2 : 1 required stoicheiometrically (the values given in the last column of the table have been calculated on the assumption that 1 vol. of carbon dioxide is formed for 1 vol. of methane, which seems probable). The small amount of methane produced indicates that reactions of type (2a) occur to a slight extent even in the vapour phase.

2. *Thermal Decomposition of Acetyl Peroxide in Solution.*—With aromatic acyl peroxides it has been well established that the solvent almost invariably takes part in the decomposition process in solution (cf. Hermans, *loc. cit.*, p. 760). The previous work on acetyl peroxide showed that decomposition in presence of a solvent always gave very much more methane than ethane in the gaseous products. This suggests, on the basis of the RH scheme, that appreciable reaction of the type (2a) (R = CH_3) occurs. The whole reaction process in solution is, however, undoubtedly complex, and without a more complete investigation and identification of all the reaction products formed with any given solvent, it is not possible to discuss the detailed application of the RH scheme to the case of acetyl peroxide solutions. In spite of the complexity of the decomposition process, it is possible to determine the order of the reaction in solution with respect to the acetyl peroxide decomposed. If the RH scheme applies, one would expect the rate of decomposition of the peroxide in presence of a large excess of solvent to appear unimolecular, and this was found to be the case.

Experiments were made in which the amount of peroxide left in the solution after definite time intervals was determined by titration. Toluene was chosen as solvent, since it has a sufficiently high b.p., and the thermal decomposition of acetyl peroxide in this solvent gives practically no reaction of type (1). The volume composition of the gaseous products obtained when a solution of 0·5 g. of acetyl peroxide in 100 c.c. of toluene is heated at 80° is : CO_2, 44·6; O_2, 1·4; CO, 2·0; CH_4, 50·7; C_2H_6, 1·4% ; *i.e.*, almost entirely methane and carbon dioxide. At the ordinary temperature the solution of acetyl peroxide in toluene is quite stable. At 50° the rate of decomposition is too slow to allow of accurate measurements, but above 70° the decomposition becomes quite rapid, and the rate of reaction was measured at 80·0° and 87·3° ± 0·1°. Solutions of 1·25 g. of peroxide in 200 c.c. of toluene were used. The peroxide, dissolved in a small amount of toluene, was added to the main bulk of the solvent after it had attained the desired temperature. Portions of the solutions were removed at suitable intervals into cooled flasks, and the peroxide determined by titration of the iodine liberated from excess of potassium iodide with sodium thiosulphate solution in the usual manner. The results show that the reaction is of the first order with respect to the acetyl peroxide. In the following table the values of the percentage decomposition and of the unimolecular constant, k, at the different time intervals are recorded :

Temp.									
80·0°	t (mins.)	26	84	144	234	309	369		
	Decomp., %	8·8	30·6	46·7	65·3	75·2	79·0		
	$k \times 10^4$	(36·6)	43	44	45	45	42	Mean = 44	
87·3	t (mins.)	29	59	95	144	203	256		
	Decomp., %	24·2	47·6	65·5	80·1	88·6	92·3		
	$k \times 10^4$	(96)	110	112	112	107	100	Mean = 108	

The temperature coefficient of k is 3·3 for a rise of 10°, and the activation energy is 31 kg.-cals./mol.

3. *Photochemical Decomposition of Acetyl Peroxide.*—All the photodecomposition experiments were performed in a flat quartz cell fitted with a glass capillary delivery tube leading to a gas-collecting tube over mercury. The flat surface of the quartz cell (area about 12 cm.²) was exposed at 3—4 inches distance to the full light of a mercury vapour lamp of the horizontal

type, using a constant current of 2 amps. The cell was cooled by a jet of water flowing over it, the temperature being controlled to keep the peroxide solid or liquid as desired.

(a) *Solid acetyl peroxide.* In order to obtain data on the photodecomposition of the solid under conditions of exposure comparable with those for the decomposition of the liquid and dissolved peroxide, a few experiments were made in which the solid substance was irradiated at room temperature. About 30—40 c.c. of gas could be collected in $\frac{1}{2}$ hour. The mean composition of the gas from several experiments is given in the following table, and confirms the earlier results in which the percentages of ethane and methane had been determined by explosion of the total hydrocarbon residue. In the present experiments the presence of these two hydrocarbons was checked more directly by the method of fractional condensation and separate explosion.

After removal of the undecomposed peroxide by means of dilute acetic acid solution, an insoluble gum was left which smelt strongly of esters. It was not analysed further.

Composition of the Gaseous Products from the Photodecomposition of Acetyl Peroxide.

State of peroxide.	Temp.	Composition, % by vol.						
		CO_2.	O_2.	Unsat.	CO.	C_2H_6.	CH_4.	C_2H_6/CH_4.
Solid	16—18°	67·4	0·4	1·0	1·3	25·0	5·1	4·9
Liquid	30	61·5	—	—	1·8	17·5	19·5	0·90
Solution in *cyclo*hexane ...	16—18	59·7	0·9	0·9	1·3	8·4	28·9	0·29
Solution in alcohol	16—18	43·8	0·5	0·7	1·6	4·6	48·6	0·09

(b) *Liquid acetyl peroxide.* The peroxide in the quartz cell was kept liquid by running a stream of water at 30° over the outside of the cell. When the mercury lamp was switched on, sufficient gas was evolved in 1 hour. The mean composition is given in the table. Although less ethane is evolved than from the solid peroxide, the C_2H_6/CH_4 ratio is 45 times greater than in the thermal decomposition of the liquid peroxide at the same temperature, for which the ratio is about 0·02 (Walker and Wild, *loc. cit.*, p. 208).

(c) *Acetyl peroxide in* cyclohexane. Approximately 1% solutions of acetyl peroxide in pure *cyclo*hexane were irradiated in the water-cooled quartz cell at the ordinary temperature. A short induction period of about 2 minutes was always observed before gas evolution commenced, and slight gas evolution occurred after the lamp was switched off. Only the gas evolved during irradiation was collected. For every 0·1 g. of peroxide decomposed, about 38 c.c. of gaseous products were collected during 2 hours, the composition being shown in the table. Much less ethane is obtained than from the photodecomposition of the peroxide in the solid or the liquid state.

(d) *Acetyl peroxide in ethyl alcohol.* Absolute alcohol, redistilled over lime, was used. The evolution of gaseous products due to photodecomposition of the alcohol (cf. Berthelot and Gaudechon, *Compt. rend.*, 1911, **153**, 383) was negligible under the conditions of our experiments. With the solutions of the peroxide it was found that, after the light source was switched off, there was a considerable evolution of gas, which continued until all the peroxide had decomposed. In one case nearly a third of the total gas was obtained from this " dark " reaction. The composition of the main portion of the gas from a typical experiment is compared in the following table with that from the thermal decomposition of acetyl peroxide dissolved in alcohol (cf. Walker, *loc. cit.*, p. 2043) :

	Composition, % by vol.		
	CO_2.	C_2H_6.	CH_4.
During irradiation	46·2	5·1	45·4
" Dark " reaction	45·3	5·0	46·8
Thermal reaction	50·7	1·6	45·7

For comparison with the other data, the mean composition of the gas evolved during the irradiation in several experiments is included in the previous table. In this case, also, the amount of ethane formed is very small.

(e) *Absorption spectrum of acetyl peroxide in solution.* The absorption spectrum of acetyl peroxide dissolved in *cyclo*hexane and in ethyl alcohol was measured by means of a Hilger rotating-sector photometer and medium quartz spectrograph, with a tungsten-steel spark as light source. In Fig. 2 the wave-length (in A.) is plotted against the molecular extinction coefficient ε, defined by $\varepsilon cd = \log I_0/I$ ($d = 0·99$ cm., c is in g.-mols./litre, and I_0 and I are the intensities of the incident and the transmitted light, respectively). The solutions used contained about 0·015 g.-mol. of peroxide per litre. A cell containing pure solvent was placed in the variable light beam of the photometer.

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Acetyl peroxide has a continuous absorption band which commences at about 2800 A. and does not reach a maximum at the lowest wave-length investigated. As will be seen from Fig. 2, the absorption is very similar to that of hydrogen peroxide (broken curve, taken from Fergusson, Slotin, and Style, *Trans. Faraday Soc.*, 1936, **32**, 960). Both these substances contain the $-O-O-$ link, and one may attribute the ultra-violet band of acetyl peroxide to this part of the molecule (cf. also Lederle and Rieche, *Ber.*, 1929, **62**, 2578).

There is the possibility that in the photochemical decomposition of acetyl peroxide the primary process consists of a dissociation $(CH_3 \cdot CO \cdot O)_2 + h\nu \longrightarrow 2CH_3 \cdot CO \cdot O \cdot$, followed by a further fission of the acetate radicals into carbon dioxide and methyl radicals, which could combine together to form ethane or react with surrounding solvent molecules to give methane as one of the products. Further discussion of these suggestions would be too speculative, however, at this stage, since the experimental work has, so far, been concerned mainly with exploring the conditions of decomposition.

CONCLUSION AND SUMMARY.

Acetyl peroxide is readily decomposed under a variety of conditions either by heating to temperatures up to 100° or by exposure to ultra-violet light. Comparison of the gaseous products obtained by both methods shows that they are qualitatively similar but quantitatively different. In general, ethane is formed more readily in the photochemical decomposition, but even in this process more methane than ethane is usually produced. The whole process in either case is rather involved, and it is probable that in both types of decomposition at least two simultaneous or consecutive reactions are taking place.

Reference may be made to the question whether acetyl peroxide is formed and then decomposed at the anode in the electrolysis of acetate solutions (cf. Glasstone and Hickling, *J.*, 1936, 826; Fichter, *loc. cit.*; Höleman and Clusius, *Z. physikal. Chem.*, 1937, *B*, **35**, 261). The fact that acetyl peroxide can be made to decompose in a variety of ways to give a complex mixture of products makes it doubtful whether the results of such experiments have any direct bearing on the mechanism of the anodic process. It is uncertain whether any of the conditions of decomposition which we have described are at all comparable with the conditions existing at the surface of the anode during electrolysis. The observed similarity between the electrolytic products and those obtained from the decomposition of the peroxide under certain particular, but not necessarily comparable, conditions cannot, therefore, be used as evidence for the peroxide mechanism in the electrolytic oxidation, further discussion of which is beyond the scope of this paper.

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