446. *The Reaction between αα-Dimethylbenzyl Hydroperoxide and Ferrous Salts.*

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The reaction between ferrous ions and αα-dimethylbenzyl hydroperoxide has been studied in dilute acid aqueous solution in the absence of oxygen. Over a range of initial concentrations, 1·08 moles of ferrous ion are oxidised per mole of peroxide consumed; at high ferrous-ion concentrations, this ratio tends to 2. It is decreased by the presence of copper salts or methanol. The products of the reaction are acetophenone and 2-phenylpropan-2-ol. A mechanism is deduced from the experimental facts, and that for the reaction in the presence of oxygen is briefly considered.

THE reaction between hydrogen peroxide and ferrous ions has been studied in some detail (Barb *et al.*, *Trans. Faraday Soc.*, 1951, **47**, 462, 591), but comparatively little is known about the reactions of organic hydroperoxides with ferrous salts. The reaction between αα-dimethylbenzyl hydroperoxide and ferrous ions was investigated in 1948 in these laboratories by Dr. J. B. Williamson; the main features then discovered are in general agreement with recently published work (Kharasch *et al.*, *J. Org. Chem.*, 1950, **15**, 763; Hawkins, *J.*, 1950, 2169; Fordham and Williams, *J. Amer. Chem. Soc.*, 1950, **72**, 4465; 1951, **73**, 1634; Kolthoff and Medalia, *ibid.*, 1949, **71**, 3789). The present work is mainly concerned with the reaction in dilute acidified aqueous solution in the absence of oxygen.

In the Absence of Oxygen.—(a) *Overall consumption ratios in dilute solution.* The consumption ratio, R, is the number of moles of ferrous ion oxidised per mole of peroxide consumed. No systematic investigation of the variation of R with the ratio of the initial concentration of reactants has been reported.

A simple method of analysis has been used. As is well known, the ferric ions produced liberate iodine quantitatively from iodide. The following paper shows that the iron salts present catalyse the reaction between iodide and the peroxide to form iodine. The total amount of iodine liberated from added iodide is thus a measure of the sum of the ferric-ion and peroxide concentrations. If the iodide is added after reaction between the ferrous ions and peroxide has ceased, then the value of R for the overall reaction can easily be calculated from the iodine titration.

Typical results are shown in Fig. 1, in which the total iodine liberated is plotted against the ratio of the initial concentrations of reactants at constant initial peroxide concentration. The full line, calculated for $R = 1·08$, fits the experimental points over the whole of this range; *i.e.*, the value of R is constant and independent of the ratio of the initial concentrations over this range. The value of R appears to depend slightly on the acid concentration, as shown below :

		R	Ref.
0·01N-H_2SO_4,		1·02	Williamson (personal communication)
0·1	,,	1·08	Present work
1·0	,,	1·12	Williamson (personal communication)
1·5	,,	1·12, 1·15	Kolthoff and Medalia (*loc. cit.*)

The curve shown in Fig. 1 has been confirmed over a limited range ($[Fe^{2+}]_0/[RO_2H]_0 = 1—3$), the 2 : 2'-dipyridyl method (Jackson, *Ind. Eng. Chem. Anal.*, 1938, **10**, 302) being used to determine residual ferrous ion.

(b) *Overall consumption ratios with ferrous ions in great excess.* In these experiments, 25 ml. of the peroxide solution were added at a rate of 1 ml. every 30 sec. to a large excess of acidified ferrous sulphate solution, nitrogen being continuously bubbled through the mixture. The results obtained (Table 1) show that as the excess of ferrous ion over peroxide becomes large, the consumption ratio increases and tends to the limiting value of 2.

(c) *Variation in the consumption ratio throughout the reaction.* For conditions when the overall consumption ratio does not vary with the ratio of the initial concentrations, it is likely that $d[Fe^{2+}]/d[RO_2H]$ is constant throughout the reaction. An attempt was made

to confirm this by determining the variation of the concentration of each reactant with time. The reaction was stopped by rapidly extracting the peroxide with benzene, a method originally used by Kolthoff and Medalia. Difficulty was found, however, with

TABLE 1. *Consumption ratio when the ferrous ion is in great excess.*

$[Fe^{2+}]/[RO_2H]$ *	275	1375	2750	5500
R	1·10	1·52	1·75	1·90

* The peroxide concentration is calculated as that of the 1-ml. increment.

their procedure. (i) A determination of the partition coefficient of the peroxide between benzene and water over a range of concentrations showed that under the conditions of their experiments about 30% of the peroxide would remain in the aqueous phase; it was therefore necessary to increase the ratio of the volume of benzene to that of the aqueous phase. (ii) At the low concentrations of peroxide which had to be used, the iodide method of peroxide analysis (Kokatnur and Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432) gave high results on the benzene extracts from actual runs, although made-up solutions of the
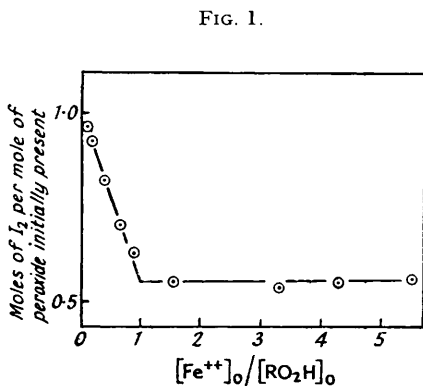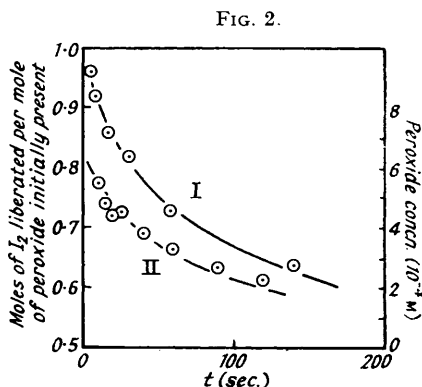

FIG. 1. *Graph of total iodine liberated against* $[Fe^{++}]_0/[RO_2H]_0$; $[RO_2H]_0$ *was* $1·65 \times 10^{-3}$M. *The line drawn is the theoretical line* $R = 1·08$.

FIG. 2. *Curve I (left-hand scale): Graph of iodine liberated against time;* $[RO_2H]_0$ *was* $1·65 \times 10^{-2}$M. *Curve II (right-hand scale): Graph of peroxide concentration against time. In both curves the line drawn is calculated from theory.*

peroxide in benzene gave exact results. The cause of this anomaly could not be found and a polarographic method of estimating the peroxide was developed. The results obtained for the peroxide analysis, shown in Fig. 2, are discussed later. (iii) The presence of organic substances in the aqueous phase caused the end-point of the titration of ferrous ions with ceric sulphate to drift. Also, at the beginning of reaction, the ferrous-ion determination was unsatisfactory owing to atmospheric oxidation. Reproducible results were difficult to obtain, and it was not possible to be certain that the consumption ratio did not tend to 2 initially. In order to settle this point a different procedure was used.

The iodide method used previously for measuring the overall consumption ratios was used. The reactants were mixed in a nitrogen atmosphere, and the iodide was added at a known time. If the value of R were 2, the total iodine liberated would be constant whatever the time of addition of iodide. Each mole of peroxide ($RO_2H \equiv I_2$) would produce 2 moles of ferric ions ($Fe^{3+} \equiv \frac{1}{2}I_2$). If, on the other hand, R is less than 2, the total iodine liberated will be less than that equivalent to the amount of peroxide originally present. The results of the experiments are shown in Fig. 2, from which it is clear that the total amount of iodine produced diminishes from the start of the reaction, so that R is less than 2 throughout the reaction.

(d) *Effect of added substances on the consumption ratio.* The effect of added methanol on the value of R is shown in Fig. 3, and it will be seen that comparatively large amounts decrease the value of R. At a given concentration of methanol, the value of R increases with increasing ferrous-ion concentration. Similar results were obtained on using ethanol

instead of methanol. The addition of 2-phenylpropan-2-ol to its limit of saturation in water did not affect the value of R in the absence of oxygen (in the presence of oxygen the value of R was increased slightly by the addition of the alcohol).

The value of the consumption ratio was apparently lower in the presence of added ferric salts, but this was traced to the presence of the copper impurity in the ferric salts used. Other impurities were cobalt and manganese, but these were found, in separate experiments, not to influence the value of the consumption ratio when added as manganous and cobaltous ions. " AnalaR " iron alum did not affect this ratio when added up to a ten-fold excess over the ferrous ion present, and separate experiments showed that addition of ammonium salts also did not affect it.

The variation in the value of R caused by the addition of copper ions is shown in Fig. 4. It is clear that in quite small amounts they cause an almost catalytic decomposition of the peroxide. The slope of the curve is so steep at low copper-ion concentrations that the point arises whether the consumption ratio of 1·08 found with ferrous salts alone is lower than the value 2 because of traces of copper salts in the reagents. This is considered to be unlikely because reproducible results are obtained with different batches of reagents.
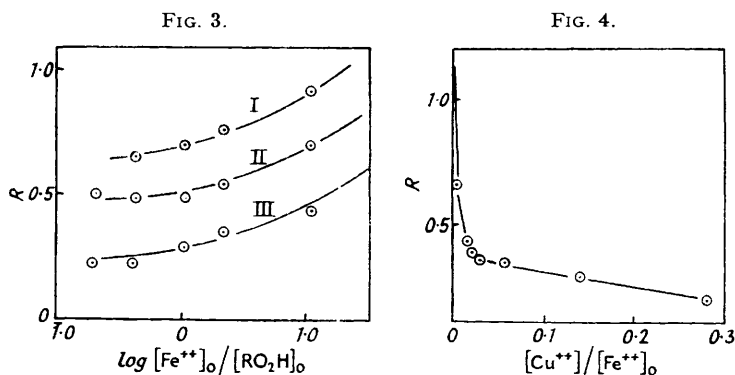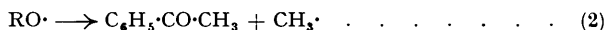

FIG. 3. *Variation of* R *with* log $[Fe^{++}]_0/[RO_2H]_0$ *at various methanol concentrations. These are, for curves I, II, and III respectively*: $[MeOH]/[RO_2H]_0 = 305, 770, 1540$. $[RO_2H]_0 = 1·65 \times 10^{-3}$M.

FIG. 4. *Variation of* R *with* $[Cu^{++}]/[Fe^{++}]_0$; $[Fe^{++}]_0$ *was* $3·6 \times 10^{-4}$M *and* $[RO_2H]_0$ $2·0 \times 10^{-4}$M. *Iron analysis by* 2 : 2'-*dipyridyl method.*

Mechanism of the Reaction.—The initial reaction between ferrous ions and the hydroperoxide is the production of RO· radicals $(R = CPhMe_2\cdot)$:

$$Fe^{2+} + RO_2H \longrightarrow Fe^{3+} + RO\cdot + OH^- \qquad \qquad (1)$$
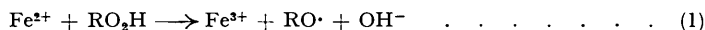
These decompose to form acetophenone :

$$RO\cdot \longrightarrow C_6H_5\cdot CO\cdot CH_3 + CH_3\cdot \qquad \qquad (2)$$

The consumption ratio of about 1 would be explained if the methyl radical reacted further without decomposing either ferrous ions or the hydroperoxide. This simple view is wrong, however, for it will be shown below that the decomposition of the peroxide is faster than that given by the expression $k_1[Fe^{2+}][RO_2H]$, and also that the product of the hydroperoxide decomposition is not entirely acetophenone, but includes 2-phenylpropan-2-ol, which would be produced by the reaction :

$$Fe^{2+} + RO\cdot \longrightarrow Fe^{3+} + RO^- \qquad \qquad (3)$$

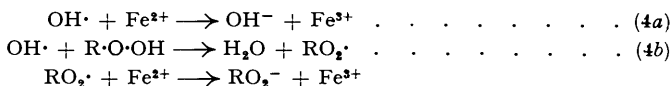$$H^+ + RO^- \longrightarrow ROH \qquad \qquad (fast) \ (3a)$$

A combination of reactions (1) and (3) would lead to the result that at high ferrous-ion concentrations the consumption ratio is 2, which is in fact the limiting value found in Table 1. It therefore seems that this reaction is significant at very high ferrous-ion concentrations. On the other hand, the fact that the consumption ratio is independent of the ratios of the initial concentrations of ferrous ion and peroxide over a wide range (as shown by Fig. 1) is taken to mean that reaction (3) is not significant under these conditions.

The constancy, at low ferrous concentrations, of the consumption ratio can only mean that the reaction which is in competition with reaction (2) for the RO· radical is one which does not involve ferrous ions or the peroxide, and we suggest

$$RO· + H_2O \longrightarrow ROH + OH· \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
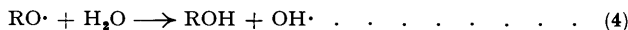
The OH· radical is removed by one of the following reactions :

$$OH· + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$
$$OH· + R·O·OH \longrightarrow H_2O + RO_2· \quad . \quad . \quad . \quad . \quad . \quad (4b)$$
$$RO_2· + Fe^{2+} \longrightarrow RO_2^- + Fe^{3+}$$

which are fast compared with reaction (4).

The fate of the methyl radical produced in reaction (2) must now be considered. The reaction $2CH_3· \longrightarrow C_2H_6$ will be significant at high concentrations; ethane was found by Hawkins (*loc. cit.*) and Kharasch *et al.* (*J. Org. Chem.*, 1950, **15**, 763). In the present experiments, it will not be significant, but Kharasch's finding (*loc. cit.*) of methanol as a major product indicates that the methyl radical reacts by

$$CH_3· + RO·OH \longrightarrow CH_3·OH + RO· \quad . \quad . \quad . \quad . \quad . \quad (5)$$
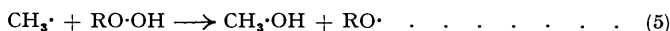
This type of reaction has been shown to take place in the thermal decomposition of αα-dimethylbenzyl hydroperoxide in cumene (Twigg, *Discuss. Faraday Soc.*, 1953, **14**, 240). Kharasch, Arimoto, and Nudenberg (*J. Org. Chem.*, 1951, **16**, 1556) have proposed, as an alternative to the reaction sequence represented by equations (2) and (5), the following :

$$CPhMe_2·O· + CPhMe_2·O·OH \longrightarrow C_6H_5·CO·CH_3 + CH_3·OH + CPhMe_2·O·$$
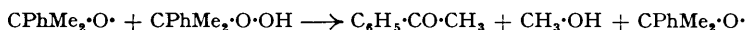
There is no evidence in favour of this reaction; in particular, the reaction is absent in the thermal decomposition of αα-dimethylbenzyl hydroperoxide. Although equivalent chemically, it is different kinetically from reactions (2) and (5); it would imply a dependence of the consumption ratio on the peroxide concentration, which has not been found.

By combination of equations (1)—(5), and assumption of a stationary concentration for the radicals, the consumption ratio R is calculated to be :

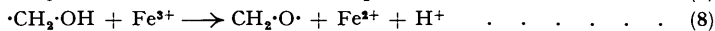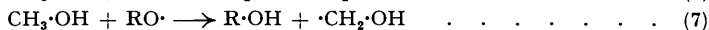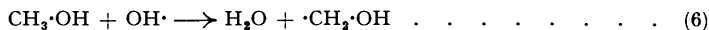$$R = \frac{d[Fe^{2+}]}{d[RO·OH]} = \frac{2}{1 + k_2/(k_3[Fe^{2+}] + k_4[H_2O])}$$

At low ferrous-ion concentrations, this expression is independent of ferrous and peroxide concentrations, and at sufficiently high ferrous concentrations it tends to the value of 2, as found experimentally.

Similarly, the rate of disappearance of peroxide is

$$- d[RO·OH]/dt = (2/R)k_1[Fe^{2+}][RO·OH]$$

In Fig. 2 the lines drawn represent the course of the reactions calculated by using $R = 1·08$, and $k_1 = 1·07 \times 10^{10} \exp\{-12,000/RT\}$ l. mole^{-1} sec.$^{-1}$ as given by Fordham and Williams (*loc. cit.*, 1951).

The effect of added methanol can be explained by the additional reactions

$$CH_3·OH + OH· \longrightarrow H_2O + ·CH_2·OH \quad . \quad . \quad . \quad . \quad . \quad (6)$$
$$CH_3·OH + RO· \longrightarrow R·OH + ·CH_2·OH \quad . \quad . \quad . \quad . \quad . \quad (7)$$
$$·CH_2·OH + Fe^{3+} \longrightarrow CH_2·O· + Fe^{2+} + H^+ \quad . \quad . \quad . \quad . \quad . \quad (8)$$
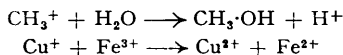
These equations, together with those above, give an expression for the consumption ratio that is in agreement with the results shown in Fig. 3.

The catalysis by copper has not been investigated in any detail, but the facts that it does not take place in the absence of ferrous ions and that the production of acetophenone is increased suggest that the copper catalyses the decomposition of the RO· radical to acetophenone, possibly by

$$CPhMe_2·O· + Cu^{2+} \longrightarrow Ph·CO·CH_3 + CH_3^+ + Cu^+ \quad . \quad . \quad . \quad . \quad (9)$$
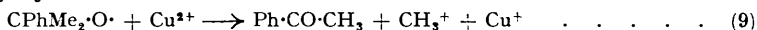
followed by the rapid reactions

$$CH_3^+ + H_2O \longrightarrow CH_3·OH + H^+$$
$$Cu^+ + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+}$$

Products of the Reaction.—Some results have been reported by Kharasch *et al.* and also by Hawkins (*locc. cit.*), who used high concentrations of reactants. Some difficulty has been found in the present work in recovering the products from the reaction carried out under controlled conditions. When the ferrous solution is added to a high concentration of peroxide under conditions where the rate of mixing is limiting, the consumption ratio is less than 1 and the proportion of hydroperoxide recovered as acetophenone is at least about 70%.

It has not been possible to recover the products from dilute solutions when the consumption ratio is 1·08. By increasing the concentrations to about 0·02M and adding the hydroperoxide solution rapidly to the ferrous solution, a consumption ratio of 1·20 was obtained. The acetophenone found was 39% of the hydroperoxide taken and the alcohol 26%, with 35% of the hydroperoxide unrecovered. In another experiment, by using a chemical method of estimating acetophenone, $33 \pm 10\%$ of the peroxide was recovered as acetophenone. For the reaction scheme proposed above for dilute solutions, the amount of hydroperoxide recovered as acetophenone should be 46%. The agreement with the above results is within the experimental error. When the peroxide solution is added slowly to a large excess of ferrous solution, the amount of acetophenone recovered was about 10% of the hydroperoxide taken. This is evidently due to reaction (3) becoming significant.
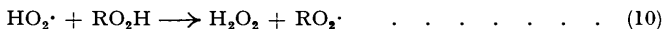
Owing to the experimental difficulties, the analysis of the products does not provide conclusive evidence for the reaction scheme proposed above, but it shows that a considerable amount of 2-phenylpropan-2-ol is produced by the reaction between ferrous ions and hydroperoxide.

The Reaction in the Presence of Oxygen.—Although most of the present experimental work has been confined to the study of the reaction in the absence of oxygen, it is possible to suggest a tentative mechanism for these conditions. The salient feature is that in the presence of oxygen the consumption ratio increases as the ferrous-ion concentration increases, and can exceed the value of 6 (Kolthoff and Medalia, *loc. cit.*; Fordham and Williams, *loc. cit.*, 1950). The latter authors' explanation involves the decomposition of the RO· radical to acetophenone and a methyl radical, followed by the oxidation of the latter to formic acid. At most, seven ferrous ions would be oxidised per methyl radical during this process, and the number would be less through removal of HO_2· radicals by reaction with ferric ions (Barb *et al.*, *loc. cit.*). Thus, in order to account for the very high consumption ratios found, most of the peroxide would have to be converted into acetophenone. Experiments have been carried out in which peroxide solution was slowly dropped into a solution of acidified ferrous sulphate through which oxygen was vigorously bubbled. Of the original peroxide, 13% was found as acetophenone, 67% as phenylpropan-2-ol and 20% was not recovered, while the consumption ratio was 4.
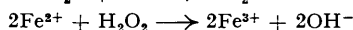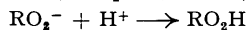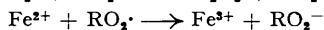
A possible explanation may be based on the equilibria suggested by Weiss (*Nature*, 1934, **135**, 648), *viz.*,

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{3+} + O_2^- \qquad H^+ + O_2^- \rightleftharpoons HO_2·$$
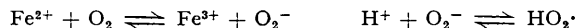
It is well known that if ferric ions are removed as fluoride complex, ferrous ions are rapidly oxidised by molecular oxygen. In the present case, it seems possible that the HO_2· radicals might react with one of the species present, *e.g.* :

$$HO_2· + RO_2H \longrightarrow H_2O_2 + RO_2· \qquad \qquad \qquad (10)$$

followed by

$$Fe^{2+} + RO_2· \longrightarrow Fe^{3+} + RO_2^-$$
$$RO_2^- + H^+ \longrightarrow RO_2H$$
$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

Reaction (10) is analogous to reaction (4*b*). A plausible explanation of the reaction in the presence of oxygen can therefore be made.

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

Materials.—Water distilled in Pyrex glass from alkaline permanganate was used. Analytical-grade reagents were used except for the reagent-grade ferric sulphate [Section (d)]. which contained as impurities : Co, 100; Cu, 2000; Mn, 3100; Pb, 650; Zn, 7·5 p.p.m. of the

salt. " AnalaR " iron alum contained 9 p.p.m. of Cu. These analyses were carried out by Mr. E. Archer. The αα-dimethylbenzyl hydroperoxide was prepared by oxidation of *iso*propylbenzene, and after extraction with light petroleum from the sodium salt was distilled in a molecular still before use. Its purity was 98% by the iodide method (Skellon and Wills, *Analyst*, 1948, **73**, 78).

Whenever appropriate, solutions and solvents were degassed by oxygen-free nitrogen before used. To obtain the results given in Fig. 1, 100 ml. of ferrous solution 0·1N in sulphuric acid were placed in a " Quickfit " B34 test-tube fitted with a wash-bottle head. 25 Ml. of 0·1% aqueous acidified hydroperoxide were then quickly added through a side-tube. When reaction had ceased, 5 ml. of potassium iodide solution (50% w/w) were added, and the liberated iodine was titrated with 0·05N-thiosulphate in a nitrogen atmosphere. The experiments on the variation in consumption ratio throughout the reaction were carried out similarly, except that the iodide was added at a known time after the reaction was started. Similar experiments were carried out for the other consumption ratio experiments. All experiments were carried out with the solution 0·1N in sulphuric acid.

The variation in the hydroperoxide concentration determined by the benzene-extraction method was carried out as follows. The reaction mixture was contained in a wide-necked flask kept in a thermostat at 25° and fitted with a stirrer. Side-arms were fitted through which nitrogen could be blown over the mixture and also benzene brought into the flask by applying nitrogen pressure to a separate vessel. A number of control experiments ensured that the rates of degassing and extraction were adequate. 100 Ml. of 0·1% hydroperoxide solution 0·1N in sulphuric acid were placed in the vessel and 5 ml. of ferrous sulphate solution were then added. At a noted time 100 ml. of benzene were blown into the vessel. After the contents of the vessel had been stirred vigorously for 5 sec., the two phases were separated. The ferrous-ion concentration in the aqueous phase was determined by titration with ceric sulphate. The benzene phase was evaporated in the presence of 25 ml. of 0·1N-sodium hydroxide (to retain the hydroperoxide as the sodium salt) by a stream of warm nitrogen. The solution was neutralised with acid and buffered by addition of solid potassium hydrogen phthalate. After being degassed with nitrogen, it was placed in a polarographic cell and the hydroperoxide estimated. αα-Dimethylbenzyl hydroperoxide has been found to give an irreversible wave with a maximum at −0·1 v (Godin and Wise, unpublished results).

In the experiments on the products, the solutions were mixed in a nitrogen atmosphere, and the products extracted with carbon tetrachloride. The resulting solution was concentrated, a 10-plate column being used to remove carbon tetrachloride, and the solutions were analysed by infra-red spectroscopy. No other products except acetophenone and the alcohol were found. In the chemical analyses the products were extracted in benzene, and the hydroxylamine method (Maltby and Primavesi, *Analyst*, 1949, **74**, 498) was used to determine acetophenone. The results of these experiments are summarised in Table 2.

TABLE 2. *Products of the reaction.*

[RO₂H] initially, 10⁻³ mole	[Fe²⁺] initially, 10⁻³ mole	Initial vol., ml.	R	Hydroperoxide recovered as :		
				COPhMe, %	CPhMe₂·OH %	Unrecovered, %
5	10 ᵃ	500	0·8	71	7	22
16	90 ᵃ	500	0·8	61	6	33
16 ᵃ	90	500	1·2	39	26	35
3 ᵃ	106	200	—	5	43	52
2 ᵃ	100	200	—	11 ᵈ	—	—
2 ᵃ	10	200	—	28 ᵈ	—	—
2 ᵇ	5 ᵇ	200	1·1	33 ᵈ	—	—
2 ᶜ	100	500	4	13	67	20

ᵃ This reactant was added to the bulk of the other reactant. ᵇ Both dropped into 200 ml. of water at same rate. ᶜ In oxygen atmosphere. ᵈ Analysis by hydroxylamine method.

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