445. *The Reaction between Organic Hydroperoxides and Iodide in the Presence of Iron Salts.*

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The reaction between iodide ions and organic hydroperoxides is catalysed by iron salts. With αα-dimethylbenzyl and *tert.*-butyl hydroperoxides, the mechanism involves the alternate oxidation and reduction of the iron :

$$Fe^{2+} + R{\cdot}O{\cdot}OH \longrightarrow Fe^{3+} + RO{\cdot} + OH^-$$
$$Fe_3{}^+ + I^- \longrightarrow (FeI)^{2+} \longrightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

For αα-dimethylbenzyl hydroperoxide, the results yield a value for the rate constant of the first reaction, which is in agreement with the known value.

Although the catalysis of the reaction between iodide ions and peroxides by tungstic or molybdic acid has long been known (Brode, *Z. physikal. Chem.*, 1901, **37**, 257), the mechanism has not apparently been investigated in terms of free radicals. In the present investigation, iron salts were used as a catalyst for the reaction of organic hydroperoxides with iodide. The iron solution was added to a mixture of peroxide, iodide, and acid through which a stream of nitrogen was passed. The liberated iodine was continuously titrated by addition of sodium thiosulphate from a burette. Preliminary experiments showed that the rate of disappearance of thiosulphate was unaffected by the rate of addition from the burette, even in moderately acid solutions. The reaction rate was the same in the dark, in diffuse daylight, or when a "Photoflood" lamp shone close to the reaction vessel. All experiments were therefore carried out in diffuse daylight.

Stoicheiometry and Products of Reaction.—In a large number of experiments under a variety of conditions it was found that the total amount of iodine liberated was given by $I_2 \equiv RO_2H$ within an accuracy of about 2% for αα-dimethylbenzyl and *tert.*-butyl hydroperoxides in the absence of oxygen. In the presence of oxygen, the amount of iodine liberated was considerably greater—roughly twice that equivalent to the hydroperoxide when the mixture was kept saturated with oxygen. In view of this complication, the experiments were carried out in nitrogen. With *tert.*-amyl and tetrahydronaphthyl hydroperoxides the amount of iodine liberated was less than the stoicheiometric amount when the reaction was carried out in the absence of oxygen, as shown in Table 1.

Table 1. *Liberation of iodine by* tert.*-amyl and tetrahydronaphthyl hydroperoxides.*

tert.-Amyl peroxide : initial concn., $3{\cdot}16 \times 10^{-3}$M.			Tetrahydronaphthyl peroxide : initial concn., $2{\cdot}0 \times 10^{-3}$M.		
[Catalyst]/[RO_2H], initial	[I^-]/[RO_2H], initial	Iodine liberated, % of theory	[Catalyst]/[RO_2H], initial	[I^-]/[RO_2H], initial	Iodine liberated, % of theory
0·075	60	64	0·12	50	19
0·038	60	85	0·24	50	17
0·075	150	79	0·60	50	15
0·038	150	91	1·20	50	13
0·075	300	87	0·60	250	21
0·038	300	92	0	300	83

These results show that the catalysed reaction with iodide is not suitable for estimating peroxides in general, although for αα-dimethylbenzyl and *tert.*-butyl hydroperoxides it affords an extremely convenient method of estimation for aqueous solutions (see preceding paper). The product of the peroxide decomposition was found to be 2-phenylpropan-2-ol from αα-dimethylbenzyl hydroperoxide, and *tert.*-butyl alcohol from *tert.*-butyl hydroperoxide (see p. 2171).

Factors affecting Catalysis.—The effect of adding fluoride is to stop the catalysis, no more iodine being liberated. The rate of reaction is decreased slightly by increasing the amount of sulphuric acid present, but is very nearly independent of acid concentration in a perchloric acid medium free from sulphate ions. Other things being equal, the rate of reaction is about 20% greater in the perchloric acid medium. There is a very slight increase in the rate when the perchloric acid concentration is increased, probably owing to the well-known equilibrium :

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$$

The addition of concentrated sodium sulphate solution decreased the rate to about 10% of its normal value; this, taken in conjunction with the above results, suggests that the complexes formed between ferric ions and sulphate ions react more slowly with iodide than do ferric ions. If insufficient acid is present the alkali formed during the reaction eventually causes precipitation of ferric ions, stopping the reaction. The above evidence leaves no doubt that the reduction of ferric ions to ferrous ions is concerned in the catalysis.

The Reaction with Excess of Ferrous Ions in the Presence of Fluoride.—Although the addition of fluoride stops the catalysis, it is possible to investigate the reaction in the presence of fluoride when an excess of ferrous ions over peroxide is added. Preliminary experiments showed that a large excess of fluoride (~100-fold) was then required to eliminate the catalysis. If the peroxide was added to a mixture of ferrous ions and fluoride, no iodine was liberated. If, on the other hand, the ferrous solution was added to a mixture of peroxide and fluoride, some iodine was produced. Experiments were therefore carried out in which the ferrous solution was added slowly and continuously to the reaction mixture containing excess of fluoride. The total amount of iodine liberated was obtained by titration with thiosulphate. The residual ferrous ion was estimated by the 2 : 2′-dipyridyl method. Typical results for αα-dimethylbenzyl hydroperoxide are shown in Table 2. It will be observed that the sum of the iodine liberated and the ferrous ion oxidised per mole of peroxide is constant at about 1·5. Similar results were obtained for tetrahydronaphthyl hydroperoxide.

TABLE 2. *Iodine liberation and ferrous-ion consumption in presence of fluoride.*

Rate of addition of ferrous ion : 10^{-5} mole/l./min.	4·7	18·8	47
Moles of I_2 liberated per mole of RO_2H	0·39	0·25	0·14
Moles of Fe^{2+} oxidised per mole of RO_2H	1·07	1·23	1·33
Sum of previous two lines	1·46	1·48	1·47

Mechanism of the Reaction.—The above results indicate that the mechanism of the catalysis is the alternate oxidation of ferrous ions :

$$Fe^{2+} + RO_2H \longrightarrow Fe^{3+} + RO\cdot + OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and the reduction of ferric ions by iodide :

$$Fe^{3+} + I^- = Fe^{2+} + \tfrac{1}{2}I_2$$

The mechanism of the latter reaction is rather complicated (Fudge and Sykes, *J.*, 1952, 119); hence it is not easy to suggest a complete kinetic scheme for the catalysis.

The fluoride experiments (Table 2) suggest that, as the ferrous-ion concentration decreases, the amount of iodine liberated tends to one-half of that equivalent to the peroxide present. This would be expected if, in the absence of fluoride, one-half of the iodine liberated came from the ferric ions produced by reaction (1) (this step being now blocked by the fluoride) and the other half from the RO· radicals by a mechanism not involving ferric ions :

$$RO\cdot + I^- \longrightarrow RO^- + I\cdot \qquad\qquad 2I\cdot \longrightarrow I_2$$

In the presence of fluoride at higher ferrous-ion concentrations, the amount of iodine liberated tends to zero. This is explained if either the RO· radicals or species produced by them oxidise ferrous ions to ferric ions which cannot liberate iodine because of the fluoride present. The obvious reaction :

$$Fe^{2+} + RO\cdot \longrightarrow Fe^{3+} + RO^- \qquad\qquad RO^- + H^+ \longrightarrow ROH$$

has been shown in the preceding paper to be unlikely to occur in these conditions. This leaves as a possibility: $Fe^{2+} + I\cdot \longrightarrow FeI^{2+}$ (using Fudge and Sykes's reaction). The complex FeI^{2+} ultimately reacts in the presence of fluoride: $FeI^{2+} \longrightarrow Fe^{3+} + I^-$.

The rate constant of reaction (1) can be obtained from the catalytic experiments by making certain assumptions. The first is that at high iodide concentrations the rate of reaction becomes limited by the rate of reaction (1), *i.e.*, the reaction of iodide is fast enough to keep the iron salts mostly in the ferrous state; and the second is that the amount of iodine liberated is equivalent to the peroxide consumed, *i.e.*, that the concentration of transient species, such as I_2^-, is small compared with the concentrations of reactants. We then have that the rate of peroxide disappearance is given by $-dp/dt = k_1px_0 + k'[I^-]p$ where x_0 is the total concentration of iron salts present and k' is the rate of the uncatalysed reaction between iodide and peroxide.

From the graph of log p against t (Fig. 1) values of $(k_1x_0 + k'[I^-])$ were obtained. It will be seen that good linear plots were obtained even at low iodide concentrations, although the slope varies with the iodide concentration. Fig. 2 shows the apparent value of k_1 as a function of the iodide concentration. The value of k' was found in separate experiments to be given under the present conditions by $k' = 1{\cdot}1 \times 10^{12}\exp\{-15{,}200/\boldsymbol{R}T\}$ l. mole^{-1} min.$^{-1}$.

FIG. 1.

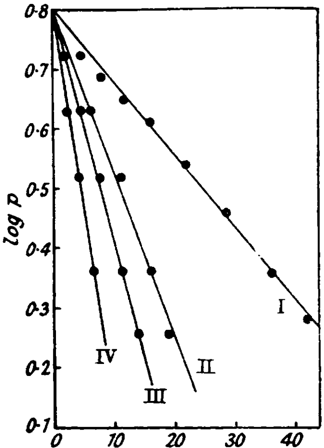

FIG. 2.

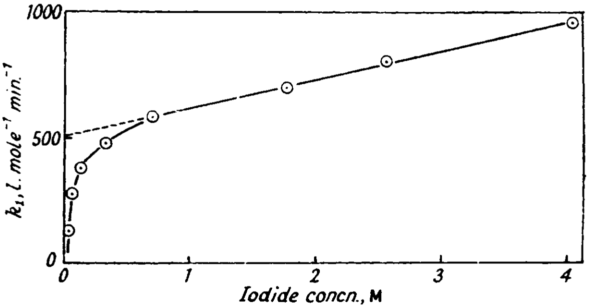

FIG. 1. *Graph of log* p *against time for various iodide concentrations. Curves* I—IV, 0·0325, 0·065, 0·131, *and* 0·330M, *respectively. Iron salt concentration was* $2{\cdot}3 \times 10^{-4}$M.

FIG. 2. *Graph of the apparent value of* k_1 *against iodide concentration.*

As expected, the value of k_1 changes as the iodide concentration increases, at first increasing rapidly and then more slowly. The increase at high iodide concentrations is apparently due to salt effects. The extrapolation shown to zero salt concentration, however, gives a value for k_1 of 510 l. mole^{-1} min.$^{-1}$, which compares satisfactorily with the value of 485 calculated from Fordham and Williams's results (*J. Amer. Chem. Soc.*, 1951, **73**, 1634).

The results with *tert.*-amyl and tetrahydronaphthyl hydroperoxides are more complicated owing to the participation of other reactions. The fact that the total amount of iodine liberated is less than the stoicheiometric amount is explained for *tert.*-amyl hydroperoxide by the greater instability of the RO· radical: $CMe_2Et{\cdot}O\cdot \longrightarrow COMe_2 + Et\cdot$. The ethyl radical may disappear without liberating iodine, *e.g.*, by reaction with hydroperoxide, $Et\cdot + RO{\cdot}OH \longrightarrow RO\cdot + EtOH$, or it may, as suggested by Merz and Waters (*J.*, 1949, S 15), react with the iodine already liberated.

With tetralin hydroperoxide there is a catalytic decomposition by ferrous ions in the absence of iodide. If this catalytic decomposition is significant in the presence of iodide, the amount of iodine liberated would be less than that equivalent to the peroxide, as was found experimentally. There are two possible explanations of this catalytic decomposition : (i) that the RO• radical causes a catalytic decomposition of the peroxide to α-tetralone, being itself regenerated; (ii) that ferrous ions are regenerated from ferric ions by reaction with RO• radicals : $>\!CH{-}O{-} + Fe^{3+} \longrightarrow\ >\!C{=}O + Fe^{2+} + H^{-}$. In favour of this type of reaction is the fact that a mixture of ferrous ions and tetrahydronaphthyl hydroperoxide will reduce mercuric ions.

A kinetic examination of these two possibilities has shown that scheme (ii) is the more probable. With scheme (i) the ratio of iodine liberated to peroxide consumed should increase with iodide concentration, but should be independent of the ferrous-ion concentration, and in the absence of ferrous ions the same ratio should be found. For scheme (ii), again, it is found that the amount of iodine liberated increases as the iodide concentration is increased, but it decreases as the catalyst concentration is increased. This fits qualitatively the results shown in Table 1.

EXPERIMENTAL

Catalysed Iodide Reaction.—50 Ml. of aqueous peroxide solution (1 g./l. in most cases), 2 ml. of 10N-sulphuric acid, and 2—25 ml. of 50% sodium iodide, made up to a volume of 150 ml. with doubly distilled water, were placed in a flask contained in a thermostat. Nitrogen was bubbled through the mixture. The reaction was started by adding 1 ml. of ferrous sulphate solution (10 g./l. of $FeSO_4,7H_2O$), and the liberated iodine was titrated continuously with 0·1N-sodium thiosulphate from a burette. In the experiments shown in Fig. 2, the solution was made 0·1N in perchloric acid, and the catalyst solution was ferrous perchlorate. In the fluoride experiments, the solutions were as above except that 25 ml. of water were replaced by sodium fluoride solution (20 g./l.). The ferrous solution was added from a burette in increments every 15 sec.

Products of Reaction.—(a) *αα-Dimethylbenzyl hydroperoxide.* In one experiment, 0·5 g. of peroxide in 500 ml. of 0·1N-sulphuric acid reacted with 20 ml. of ferrous sulphate solution (10 g. of $FeSO_4,7H_2O$ per l.) and 5 ml. of saturated potassium iodide solution. The reaction was complete within a few minutes. The iodine was removed with thiosulphate, and the mixture extracted with 30-ml. portions of carbon tetrachloride. This solution was concentrated by distillation, and the dried solution analysed by infra-red spectroscopy; 80% of the peroxide was recovered, of which 96% was in the form of 2-phenylpropan-2-ol and 4% acetophenone. In another experiment, 5. g. of hydroperoxide reacted with 10 ml. of the ferrous sulphate solution in 200 ml. of 0·1N-sulphuric acid. Saturated potassium iodide was added in 0·5-ml. increments at intervals of 15 min. The reaction required 2 hr. for completion. In this case 70% of the peroxide was recovered, all as the alcohol. No acetophenone could be detected.

(b) tert.-*Butyl hydroperoxide.* (Experiment with DR. J. B. WILLIAMSON.) 4·5 G. of *tert.*-butyl hydroperoxide reacted with 50 ml. of 50% (w/w) potassium iodide in 500 ml. of 0·1N-sulphuric acid, 25 ml. of the ferrous sulphate solution being used as catalyst. After the addition of thiosulphate, the solution was distilled. 11 G. of distillate were extracted with ether. The extract was concentrated to one-quarter of its original volume by fractionation in a 5-plate column; material equivalent to 85% of the original hydroperoxide was recovered, all of which was found by infra-red analysis to be *tert.*-butyl alcohol (acetone not detected, *i.e.*, <0·5% of the hydroperoxide).

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