

**253.** *Hydroperoxides as Initiators for the Polymerisation of Styrene.*

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A number of hydroperoxides have been examined as initiators for the polymerisation of styrene. Apart from more rapid initiation due to aryl groups, changes of structure have only slight effect. The proportion of catalyst taking part in the polymerisation which effects initiation is suggested as a measure of catalyst efficiency; the hydroperoxides are of moderate efficiency.

THE author has shown (*J.*, 1951, 3106; 1952, 2408) that polymerisation data can be used to give information on the decomposition reactions of diacyl peroxides. It seemed desirable to extend this work to hydroperoxides, and to look for regularities between their activity as catalysts in bulk polymerisation and their known activity in emulsion polymerisation.

Eleven hydroperoxides were examined as initiators for the polymerisation of styrene and the data are summarised in Table 1. Except where stated the temperature was 70°, and the catalyst concentration 0.014 mole/l. The symbols and units are those used in the earlier papers:  $k_i$ ,  $k_p$ , and  $k_t$  are the rates of initiation, propagation, and termination, respectively;  $R_c$  is the rate of catalysed and  $R_T$  the rate of thermal polymerisation,  $C_m$  is the monomer transfer coefficient,  $\bar{P}_n$  the number-average degree of polymerisation;  $C$  and  $M$  are the concentrations of catalyst and monomer respectively.

TABLE 1.

| Hydroperoxide   | $10^4 R_p$ | $10^6 k_t$ | $(\eta)$ | $10^{-3} \bar{P}_n$ | Efficiency<br>(see eqn., p. 1270) |
|---|------------|------------|----------|---------------------|-----------------------------------|
| Bu <sup>t</sup> OOH .....   | 0.285      | 0.36       | 1.42     | 2.60                | 0.70                              |
| CMe <sub>2</sub> Et·OOH .....   | 0.44       | 0.87       | 1.12     | 1.88                | 0.70                              |
| CPhMe <sub>2</sub> ·OOH .....   | 0.49       | 1.08       | 0.98     | 1.57                | 0.64                              |
| Pr <sup>i</sup> -C <sub>6</sub> H <sub>4</sub> ·CMe <sub>2</sub> ·OOH <sup>a</sup> .....        | 0.48       | 1.02       | 0.91     | 1.42                | 0.57                              |
| <i>p</i> -Bu <sup>t</sup> -C <sub>6</sub> H <sub>4</sub> ·CMe <sub>2</sub> ·OOH .....           | 0.39       | 0.67       | 1.20     | 2.06                | 0.69                              |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> (CMe <sub>2</sub> ·OOH) <sub>2</sub> <sup>b</sup> ..... | 0.42       | 0.74       | 1.16     | 1.98                | 0.70                              |
| C <sub>6</sub> H <sub>10</sub> (OH)·OOC <sub>6</sub> H <sub>10</sub> (OOH) <sup>b</sup> .....   | 1.25       | 6.9        | 0.45     | 0.55                | 0.50                              |
| <i>p</i> -Menthane <sup>c</sup> .....   | 0.48       | 1.02       | 1.16     | 1.98                | 0.79                              |
| <i>p</i> -Cymene <sup>c</sup> .....   | 0.52       | 1.19       | 1.00     | 1.61                | 0.68                              |
| Pinane <sup>d</sup> .....   | 0.365      | 0.65       | 1.12     | 1.88                | 0.60                              |
| 1 : 2 : 3 : 4-Tetrahydronaphthalene...  | 0.455      | 0.91       | 1.10     | 1.83                | 0.57                              |

<sup>a</sup> Mainly the *p*-isomer but some of the *m*-isomer may be present. <sup>b</sup> These compounds were examined at 0.007 mole/l. to give the same active oxygen concentration as the other peroxides. <sup>c</sup> These compounds could be peroxidised at the C<sub>(7)</sub> or the C<sub>(8)</sub> atoms. The latter is more probable, but according to Helberger, Rebay, and Fettback (*Ber.*, 1939, 72, 1643), the primary C<sub>(7)</sub> carbon atom of *p*-cymene is attacked, since on decomposition the hydroperoxide forms cuminaldehyde. <sup>d</sup> This compound is probably the C<sub>(1)</sub> hydroperoxide. It was examined at 0.0125 mole/l.

*Discussion.*—The most interesting feature of this group is the relatively small and apparently unconnected variation of polymerisation rates by the different hydroperoxides. *tert.*-Butyl hydroperoxide and 1-hydroxycyclohexyl 1-hydroperoxycyclohexyl peroxide [which dissociates in solution to give 1 : 1-bishydroperoxycyclohexane (Cooper and Davison, *J.*, 1952, 1180)] being excluded, there is a variation of only 25% from the mean. This would imply either that there is little dependence of decomposition rate on structure or that the method is insensitive to such changes. The major change is the increase in rate brought about by substitution of a methyl group in *tert.*-butyl hydroperoxide by an ethyl or an aryl group. It is noteworthy that the two peroxide linkages in *p*-di-(1-hydroperoxy-1-methylethyl)benzene appear to break down independently of one another, and that there is no noticeable increase in the degree of polymerisation resulting from biradical initiation (transfer reactions with the monomer to form mono-radicals may mask any such effect).

The introduction of alkyl substituents into the phenyl group of  $\alpha$ -cumyl hydroperoxide is accompanied by a considerable increase in the rate of polymer formation in emulsion polymerisation at low temperatures in the presence of reducing agents. In this system initiation is effected mainly by one-electron addition by a variable-valency ion to the peroxide link (Fordham and Williams, *J. Amer. Chem. Soc.*, 1950, 72, 4465; 1951, 73, 1634), and other controlling factors may be the diffusion of hydroperoxide from the monomer to the soap micelles and reaction with the thiol modifier which is usually present.

For these reasons the lack of correspondence between their properties in bulk and in emulsion polymerisation is not unexpected.

The liquid hydroperoxides are difficult to obtain pure. Kharasch, Fono, and Nudenberg (*J. Org. Chem.*, 1951, 16, 113) have pointed out the great effect of traces of impurities, particularly acids or alkalis, on the rate of decomposition of  $\alpha$ -cumyl hydroperoxide. In the present work it was found particularly important to remove all trace of the peroxidation catalyst from the crude hydroperoxide: the effect of small amounts of copper (as the naphthenate) on its ability to initiate the polymerisation of styrene illustrates this (temp. 70°, catalyst concn. 0.014 mole/l.):

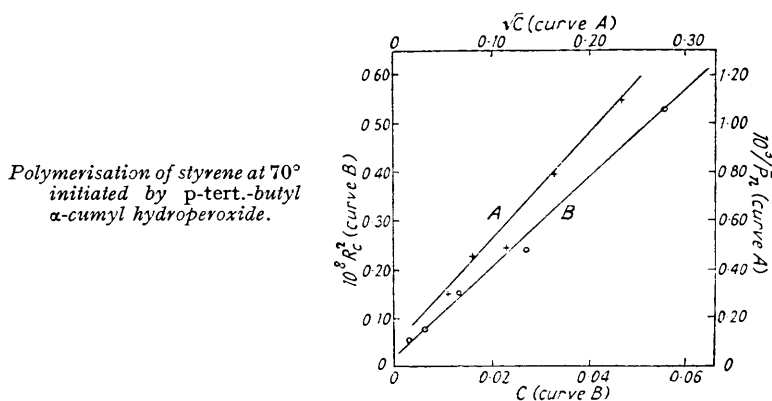
| Cu <sup>++</sup> (mole/l.) | $10^4 R_p$ | $(\eta)$ | Cu <sup>++</sup> (mole/l.) | $10^4 R_p$ | $(\eta)$ |
|----------------------------|------------|----------|----------------------------|------------|----------|
| 0                          | 0.49       | 0.98     | 0.000125                   | 3.07       | 0.28     |
| 0.000031                   | 2.08       | 0.32     | 0.001                      | 4.00       | 0.15     |

It is seen that even at the lowest copper concentration over 90% of the hydroperoxide decomposing does so by reactions involving copper ions. The lack of simple proportionality between the copper concentration and the rate of polymerisation indicates that the reactions are very complex.

It was decided to study one of the more readily purified hydroperoxides in greater detail. In the Figure are shown the effects of catalyst concentration on the rate of poly-

merisation and the chain length of the polymer for *p*-tert.-butyl  $\alpha$ -cumyl hydroperoxide. The results are plotted as  $R_c^2$  against  $C$  and as  $1/\bar{P}_n$  against  $\sqrt{C}$ . They are related to the catalyst concentration by  $R_c^2 = R_T^2 + 2k_p^2 M^2 k_i C/k_t$  and  $1/\bar{P}_n = f \sqrt{2k_i k_t C/k_p M} + C_m$  (any reaction of the peroxide with growing polymer chains being ignored at this stage). It follows that the product of the slope of the  $R_c^2$  against  $C$  and the square of the slope of  $1/\bar{P}_n$  against  $\sqrt{C}$  lines will be equal to  $4k_i^2 f^2$ , where  $f$  has the value of 1 or  $\frac{1}{2}$  depending on whether deactivation occurs by disproportionation or by combination. The actual values give  $4k_i^2 f^2 = 1.77 \times 10^{-12} \text{ sec.}^{-2}$ , whence it follows that  $k_i = 0.66 \times 10^{-6} \text{ sec.}^{-1}$  if the chains disproportionate, and  $1.32 \times 10^{-6} \text{ sec.}^{-1}$  if combination occurs.\*

The former is in excellent agreement with the result calculated from the single experiments, but such internal consistency of the results cannot be taken as evidence for the mode of deactivation. The constants used in the calculation of  $k_i$  were based on results which assumed disproportionation to occur. In fact, although the problem has not been finally settled, the overall balance of evidence supports the view that combination is the more likely reaction. [Combination termination with transfer would lead to changes in



the polymer distribution from system to system. However, any effect that this may have on the  $\bar{P}_n$ - $(\eta)$  relation is probably small since Mayo *et al.* found no significant change in this for polymers prepared thermally (with or without solvents) or with peroxide catalysts; presumably any change in the polymer distribution has an effect which is within their experimental error in establishing the relation from osmotic pressure determinations.]

The effect of temperature on the initiation rates and molecular weights by *p*-tert.-butyl- $\alpha$ -cumyl hydroperoxide (0.014 mole/l.) is shown by the results in Table 2. The rate

TABLE 2.

| Temp. | $10^5 R$ | $10^7 k_i$ | $(\eta)$ | $10^{-3} \bar{P}_n$ | Temp. | $10^5 R$ | $10^7 k_i$ | $(\eta)$ | $10^{-3} \bar{P}_n$ |
|-------|----------|------------|----------|---------------------|-------|----------|------------|----------|---------------------|
| 70°   | 3.9      | 6.7        | 1.20     | 2.06                | 49.8° | 0.81     | 0.65       | 1.70     | 3.32                |
| 60    | 1.8      | 2.0        | 1.36     | 2.46                | 30    | 0.16     | 0.065      | 2.30     | 5.05                |

constants for the three higher temperatures give a good Arrhenius plot from which  $E_i = 28$  kcal./mole. The 30° rate is somewhat high, and is evidently subject to some error, of which there would be a greater probability at such low reaction rates. The corresponding viscosity data have a somewhat small negative temperature coefficient ( $E_v = -4.6$  kcal./mole), which shows that transfer reactions of the growing polymer with monomer and with hydroperoxide are of some importance.

*Efficiency of Polymerisation Initiators.*—Frequently the data on the reactions of a peroxide in a monomer are not sufficiently detailed or accurate to give full details of its be-

\* From the extrapolation of the curve for  $R_c^2$  against  $C$  to zero catalyst concentration,  $R_T^2 \approx 0.015 \times 10^{-6} \text{ sec.}^{-2}$ . This gives a value for  $R_T$  about double that determined directly from the thermal polymerisation. A similar feature was observed and discussed in some detail by Mayo, Gregg, and Matheson (*J. Amer. Chem. Soc.*, 1951, **73**, 1691). Haward and Simpson (*Trans. Faraday Soc.*, 1951, **47**, 212), however, obtained satisfactory agreement between the extrapolated and the measured thermal values.

haviour. It is convenient, however, to estimate the activity of a catalyst quickly from a few results. If it is assumed that there are no secondary reactions, the product of the number-average degree of polymerisation and the rate of polymerisation is given by  $1/(K + C_m/R_c)$ , where  $K = f k_t/k_p^2 M^2$ . The values of  $K$  and  $C_m$  for styrene at 70° have been found to be 6.5 and  $0.85 \times 10^{-4}$  (Cooper, *loc. cit.*). The efficiency of a catalyst then may be taken as the ratio of the observed product  $\bar{P}_n R_c$  from the polymerisation data to the theoretical value given above, *i.e.*,

$$\begin{aligned} \text{Efficiency} &= R_c \bar{P}_n (K + C_m/R_c) \\ &= 6.5 R_c \bar{P}_n (1 + 1.3 \times 10^{-5}/R_c). \end{aligned}$$

With catalysts which produce radicals of high activity this equation gives the ratio of the rates of chain termination and transfer for the ideal to the actual polymerisation reaction. It obviously refers only to the catalyst taking part in the polymerisation and is not necessarily related to the true efficiency as defined by  $k_i/k_d^*$ .

By using this equation the efficiencies of the hydroperoxides can be calculated from the data in Table 1 and are inserted in the last column of that table. It is seen that the hydroperoxides, apart from the much less stable substituted *cyclohexyl* peroxide, have comparable efficiencies. For comparison, values for dibenzoyl peroxide [which is the reference compound for all the peroxides, its efficiency being calculated from the decomposition data of Bartlett and Nozaki (*J. Amer. Chem. Soc.*, 1946, **69**, 1686)], di-*m*-nitrobenzoyl peroxide, azodi(*isobutyronitrile*), and *p-tert.*-butylthioazobenzoic acid from this equation are 0.87, 0.31, 0.88, and 0.81, respectively. It is seen that by comparison the hydroperoxides are of relatively low efficiency. This is probably due to their tendency to undergo secondary decomposition.

#### EXPERIMENTAL

*Preparation of Hydroperoxides.*—*tert.*-Butyl and *tert.*-amyl hydroperoxides were prepared and purified as described by Milas and Surgenor (*J. Amer. Chem. Soc.*, 1946, **68**, 205, 643). A proportion of the dialkyl peroxide remained in the hydroperoxides used, but it was found that at 70° the dialkyl peroxides have negligible catalytic activity. A fraction of *tert.*-butyl hydroperoxide was used, of b. p. 35°/15 mm.,  $d_{20}^{20}$  0.900,  $n_D^{20}$  1.3995 (Found: active O, 16.1. Calc. for  $C_4H_{10}O_2$ : active O, 17.8%). (The active oxygen concentrations were determined iodometrically by use of a solution of the hydroperoxide in acetic acid and saturated aqueous potassium iodide at room temperature for 15 min. Under these conditions di-*tert.*-butyl and diamyl peroxides do not liberate iodine.)

*tert.*-Amyl hydroperoxide, purified through the sodium salt and by distillation, had b. p. 68°/43 mm.,  $d_{20}^{20}$  0.910,  $n_D^{20}$  1.4145 (Found: active O, 15.0. Calc. for  $C_5H_{12}O_2$ : active O, 15.4%).  $\alpha$ -Cumyl hydroperoxide was prepared by oxidation of cumene by gaseous oxygen in the presence of copper naphthenate. The conditions for efficient peroxidation by this method are rather critical, but the following method was found to be satisfactory. Dry oxygen was circulated by a pump through cumene (1 l.) kept at 45° and containing copper naphthenate (1 g.). The normal induction period was reduced to a very short time by addition of 1% of previously peroxidised cumene containing copper naphthenate. Peroxidation then occurred smoothly at 0.5% per hour for 48 hours. At this stage the partly peroxidised hydrocarbon was washed thoroughly with dilute hydrochloric acid and then potassium hydrogen carbonate solution. In order to obtain a stable product it was important to carry out this process very carefully. To the solution was then added, with cooling, 40% aqueous sodium hydroxide (300 g.). The homogeneous solution gradually set to a mass of crystals. After being collected, washed with light petroleum (b. p. 40—60°), and air-dried, they were decomposed with cold 5*N*-hydrochloric acid. (Analysis then showed 65% of  $CPhMe_2 \cdot O \cdot ONa$ , so the crystals are evidently hydrated.) The organic layer, after being washed with potassium hydrogen carbonate solution and water, was dried ( $MgSO_4$ ); the yield was 85% (350—370 g.) of 90—95% pure hydroperoxide, the purity depending on the efficiency of washing of the sodium salt.

\* The only hydroperoxides for which decomposition rates have been determined are tetrahydro-naphthyl hydroperoxide (Waters, *J.*, 1948, 1579),  $\alpha$ -cumyl hydroperoxide (Fordham and Williams, *Canadian J. Res.*, 1949, **27**, B, 943; Karasch *et al.*, *loc. cit.*), and *p-tert.*-butyl  $\alpha$ -cumyl hydroperoxide (technical data sheet, Phillips Petroleum Co., U.S.A.): values of  $k_d$  calculated from these results are of the same order as the estimates of  $k_t$  made here, but they are insufficient for any true comparison to be made.

The amounts of catalyst and the temperature were found to be very important. Copper, cobalt, and manganese naphthenates were studied, the efficiency of the reaction varying from 5 to 56% on total oxygen absorption, but the best results (with a reasonable reaction rate) were obtained with the conditions given above.

Fractionation of the residual liquid gave recovered cumene (580 ml.),  $\alpha\alpha$ -dimethylbenzyl alcohol (100 g.), and a small amount of 2 : 3-dimethyl-2 : 3-diphenylbutane, m. p. 115° (formed by combination of some of the  $\alpha$ -cumyl radicals formed during the peroxidation).

$\alpha$ -Cumyl isopropyl hydroperoxide (purity 96%) was prepared and isolated in a similar way to  $\alpha$ -cumyl hydroperoxide. *p*-*tert*-Butyl  $\alpha$ -cumyl hydroperoxide was also obtained by using the above method. The crude hydroperoxide recrystallised from light petroleum (b. p. 40—60°) as colourless needles, m. p. 73° (Found : active O, 7.6. Calc. for  $C_{13}H_{20}O_2$  : active O, 7.7%). 1 : 2 : 3 : 4-Tetrahydro-1-naphthyl hydroperoxide was prepared by oxidation with air at room temperature of carefully purified tetralin (100 ml.) containing 0.1% of cobalt naphthenate. The crude hydroperoxide obtained *via* the sodium salt was extracted with warm light petroleum (b. p. 40—60°). The extracts at 0° gave needles, which were recrystallised several times from alcohol-carbon tetrachloride (yield 13 g. ; m. p. 54°) (Found : active O, 9.7. Calc. for  $C_{10}H_{12}O_2$  : active O, 9.75%).

1-Hydroxycyclohexyl 1-hydroperoxycyclohexyl peroxide, m. p. 78°, was made as described by Cooper and Davison (*loc. cit.*). *p*-Cymene and *p*-menthane hydroperoxides were obtained as *ca.* 25% solutions of the crude oxidation products. As the gelatinous sodium salts were too soluble to be isolated directly, the solutions were first concentrated at 12 mm. to about 60% hydroperoxide content. After being washed repeatedly with light petroleum (b. p. 30—40°), the sodium salts gave on decomposition hydroperoxides of 99% and 98.5% purity, respectively.

*p*-Di-(1-hydroperoxy-1-methylethyl)benzene, recrystallised from benzene-light petroleum (b. p. 40—60°), had m. p. 141° (Found : active O, 13.7. Calc. for  $C_{12}H_{18}O_4$  : active O, 14.1%). Pinane hydroperoxide, from the Hercules Powder Co., U.S.A., was of 78% purity.

The methods used for obtaining the polymerisation data have been described in the earlier papers (*loc. cit.*).

The author thanks Dr. H. L. Williams of Polymer Corporation, Sarnia, Canada, for several of the hydroperoxides, and the Dunlop Rubber Co. Ltd. for permission to publish this paper.

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[Received, November 12th, 1952.]