130. *The Autoxidation of* iso*Propylbenzene.**

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A new technique has been used for the autoxidation of *iso*propylbenzene to give αα-dimethylbenzyl hydroperoxide. An alkaline (pH 8·5—10·5) oil-in-water emulsion of the hydrocarbon absorbs oxygen at 85° to give a good yield of the hydroperoxide identical with that previously reported by Hock and Lang (*Ber.*, 1944, **77**, 257). The characteristics of the autoxidation are consistent with a radical-chain mechanism.

The autoxidation of *iso*propylbenzene to the hydroperoxide has been described by Hock and Lang (*Ber.*, 1944, **77**, 257), who oxidised the dry purified hydrocarbon at 85° while irradiating it with ultra-violet light.

$$C_6H_5{\cdot}CHMe_2 + O_2 \longrightarrow C_6H_5{\cdot}CMe_2{\cdot}O{\cdot}OH$$

The sodium salt of the hydroperoxide was precipitated from the product by treatment with 25% aqueous sodium hydroxide; the free hydroperoxide was liberated from the salt by careful treatment with the calculated amount of mineral acid, and further purified by distillation *in vacuo*. The overall yield of hydroperoxide was 90% based on the oxygen consumed, but the rate of oxidation was slow, only 0·2 g.-mol. of oxygen being absorbed by 3 g.-mols. of *iso*propylbenzene in 24 hours.

In 1945 when the present work was commenced, the only other reported work on the uncatalysed liquid-phase autoxidation of *iso*propylbenzene was that of Stephens (*J. Amer. Chem. Soc.*, 1926, **48**, 2920), who treated *iso*propylbenzene with oxygen in dim diffused light for 3—5 weeks at 80—104°, and obtained acetophenone and formic acid in low yields, as well as a little unidentified oil. He did not report the occurrence of peroxides in his products but observed that the presence of water favoured the oxidation slightly, whereas with toluene and ethylbenzene water inhibited oxidation.

After the work described below had been completed, the Hercules Powder Co. (U.S.P. 2,438,125) described the autoxidation of *iso*propylbenzene with air or oxygen at low temperatures in the presence of dilute alkali and activated carbon. The products contained peroxides which were not isolated but were subsequently destroyed by hot sodium hydroxide solution.

Several reports describe the metal-catalysed autoxidation of *iso*propylbenzene, the earliest being D.R.P. 522,255 (I.G. Farbenind. A.-G.; *Zentr.*, 1931, I, 3721). Acetophenone and phenyldimethylcarbinol were identified among the products. Similar results were obtained by the Monsanto Chemical Co. (U.S.P. 2,447,400) who used oxygen in the presence of calcium hydroxide.

We found the rate of absorption of oxygen by an alkaline oil-in-water emulsion of *iso*propylbenzene at 85° to be much more rapid than that reported by Hock and Lang (*loc. cit.*), and obtained considerably higher concentrations of hydroperoxide in the products. The hydroperoxide was isolated from the oxidised hydrocarbon layer by fractional distillation *in vacuo*, or by precipitation of the hydrated sodium salt with 25% w/w sodium hydroxide solution and

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subsequent regeneration of the free hydroperoxide with carbon dioxide. Contrary to the implied observation of Hock and Lang precipitation of the sodium salt with a slight excess of sodium hydroxide was only about 50% complete, several treatments with fresh batches of alkali being necessary to complete the precipitation. Similarly several extractions with an excess of dilute (8%) sodium hydroxide were necessary for complete extraction of the hydroperoxide into aqueous solution. This behaviour is typical of a very weak acid.

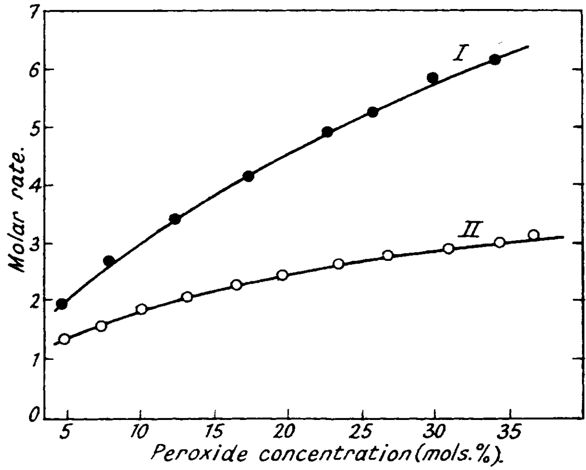
The structure of the hydroperoxide was confirmed by decomposition of the pure hydroperoxide with aqueous (10% w/v) sulphuric acid under reflux to give phenol (70—80%) and

$$C_6H_5\cdot CMe_2\cdot O\cdot OH \longrightarrow C_6H_5\cdot OH + Me_2CO$$

acetone (70%) (cf. Hock and Lang, *loc. cit.*). Small amounts of acetophenone and α-methylstyrene were obtained as by-products. It is of interest that this decomposition can be carried out equally well with the hydroperoxide in the untreated oxidation product.

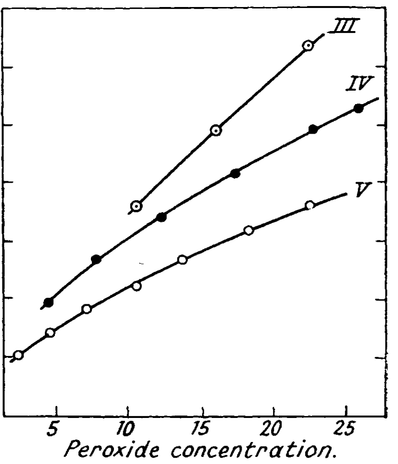
Reduction of the hydroperoxide with aqueous sodium hydrogen sulphite gave phenyldimethylcarbinol, some α-methylstyrene being formed by dehydration of the carbinol; and traces of acetophenone were again obtained.

FIG. 1.



I. 0·3% *Sodium stearate.* II. 0·4% *Teepol.*

FIG. 2.



III. *Phase ratio* 5 : 1. IV. *Phase ratio* 2 : 1. V. *Phase ratio* 1 : 1.

Preliminary work on the oxidation indicated that acids were produced in small quantities which lowered the pH of the emulsion sufficiently to slow down the oxidation. The initial presence of sodium carbonate (1·3% of the aqueous phase) provided a sufficient reserve of alkalinity without producing too high a pH in the initial stages. The presence, in the *iso*propylbenzene, of styrene and α-methylstyrene also retarded the oxidation and increased the rate of acid formation. Satisfactory starting material was obtained by hydrogenation of the crude hydrocarbon and careful fractionation of the product.

Under neutral (pH 7·4) or acid (pH 4·7) conditions, or at alkaline pH in the absence of emulsifying agent, the rate of oxidation was slow, being of the same order as the rate in the homogeneous phase at the same temperature. At high alkalinity (5—10% NaOH), the reaction efficiency (based on oxygen absorbed and hydroperoxide produced) was low, being of the order of 50%. The optimum conditions of alkalinity for a high efficiency at a reasonable rate were pH 8·5—10·5, conveniently achieved by the addition of sodium carbonate.

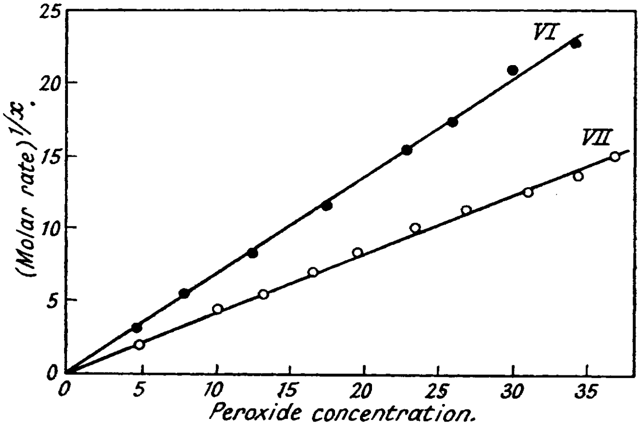
Two emulsifying agents were tried, sodium stearate and " Teepol " (an aqueous solution of mixed sodium higher-alkyl sulphates). Variation of the sodium stearate concentration between 0·09 and 0·35% w/v or of that of " Teepol " between 0·2 and 2·5% v/v in the aqueous phase did not significantly change the respective oxidation rates. However, the rate at any given hydroperoxide concentration was higher in the case of sodium stearate (Fig. 1).

The molar rate of oxidation, expressed as mols. of oxygen absorbed per hour per 100 mols. of *iso*propylbenzene present, increased with increasing water : oil phase ratio (Fig. 2), although the oxygen absorption rate per unit volume of total liquid decreased.

In the early stages of the reaction the yield of hydroperoxide based on oxygen absorbed was almost quantitative, but at 20% hydroperoxide concentration it had fallen to about 90%. The reaction was very sensitive to traces of metallic impurities, the addition of copper or lead, even as the metals, producing an immediate effect; a sharp initial rise in the rate of oxidation was followed by a rapid decline to a low value. The oxidation efficiency also fell rapidly, and the products contained up to 1 part of acetophenone for every 2 parts of hydroperoxide.

The oxidations followed a course analogous to other free-radical-chain autoxidations, for example, those of tetralin (Robertson and Waters, *Trans. Faraday Soc.*, 1946, **42**, 201) and ethyl linoleate (Bolland, *Proc. Roy. Soc.*, *B*, 1946, **186**, 218). In the absence of added catalysts an induction period of about 1·5 hours, during which the oxygen absorption was almost imperceptible, was followed by an autocatalytic reaction. Subsequently the oxidation rate passed through a maximum value. The induction period could be eliminated by the addition of organic peroxides (benzoyl, lauryl) or of the hydroperoxide itself. Phenol inhibited the oxidation, and styrene and α-methylstyrene exerted a retarding influence (see above).

FIG. 3.



	k.	x.
VI. 0·3% *Sodium stearate*	0·80	0·58
VII. 0·4% *Teepol*	0·69	0·42

The molar rate of oxygen absorption in the autocatalytic reaction depended on the hydroperoxide concentration according to the relation

$$\text{Molar rate} = \frac{-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t}{[\mathrm{RH}]} = k[\mathrm{RO{\cdot}OH}]^x$$

For a unimolecular rate of hydroperoxide decomposition the value of x expected on theoretical grounds would be 0·5 (Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 241). The values found approximated to this figure (Fig. 3), but with some variation. In particular the use of " Teepol " as emulsifying agent led to values of x below 0·5. A full investigation of the kinetics of the autoxidation of *iso*propylbenzene in both emulsion and single phase has been made (Twigg *et al.*, unpublished work).

The relation given above was valid up to a certain hydroperoxide concentration, which varied from one experiment to another, the highest found being 34 molar-%. Soon after this the rate passed through its maximum value. The hydroperoxide concentration continued to increase after the maximum rate had been passed, and in some cases also passed through a maximum. Where the maximum rate was observed at 34 molar-% of hydroperoxide, the concentration of the latter increased to 47 molar-% without having reached a maximum value. In other cases maximum values of both rate and hydroperoxide concentration were reached at lower extents of oxidation.

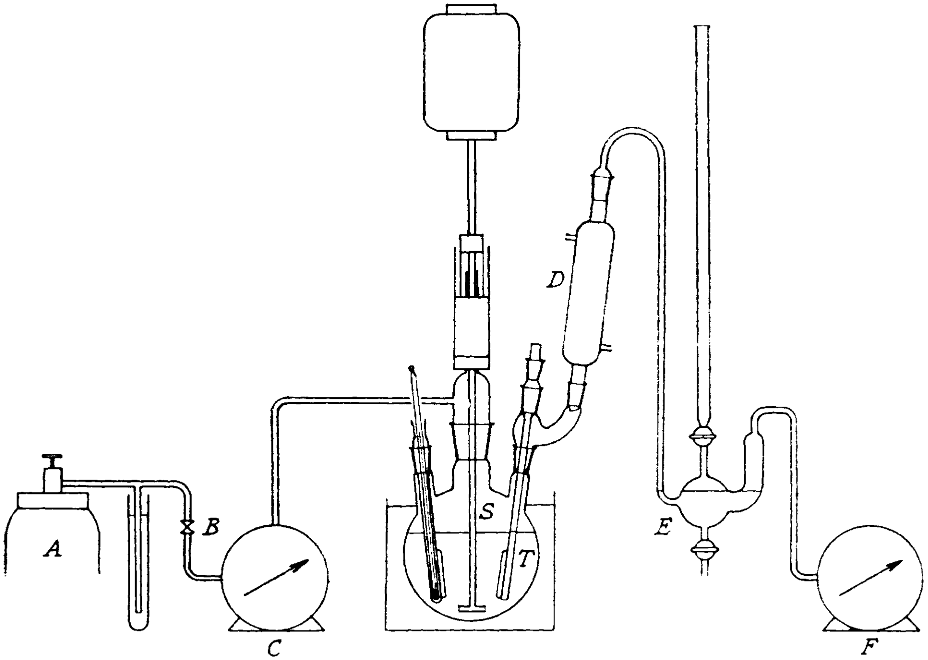
EXPERIMENTAL.

M. p.s and b. p.s are uncorrected.

Oxidation Apparatus (Fig. 4).—The oxygen feed from the supply cylinder *A* was controlled by a valve *B* operating at constant up-stream pressure, and passed *via* a ½-l. wet gasmeter *C* to the vapour space above the liquid in the reaction vessel (a 1-l. Pyrex flask). The gas in the reaction vessel was circulated continuously through the liquid by a recycle stirrer *S*, before passing *via* the reflux condenser *D* and a bubbler *E* to a second gasmeter *F*. The bubbler contained aqueous phenolphthalein and was fitted with a burette for the addition of 0·2N-sodium hydroxide, as a rough indication of the carbon dioxide evolved. The reaction vessel was immersed in a thermostatically controlled bath, and was fitted with a thermometer pocket and a liquid-sampling tube *T*, to which were sealed glass strips to act as baffles and prevent swirling of the liquid. The seal on the stirrer shaft was filled with mercury or liquid paraffin.

Materials.—Oxygen was obtained in about 98% purity from standard commercial cylinders. *iso*Propylbenzene was received as a commercial grade containing 1—5% of styrene + α-methylstyrene. The crude material was hydrogenated for 2 hours at 60—80° and atmospheric pressure with 5% of Raney nickel as catalyst, and the hydrogenated product fractionated to give, as main fraction, *iso*propylbenzene, b. p. 153·5—154°/753 mm., n_D^{20} 1·4911, containing less than 0·005% of styrene (by ultra-violet absorption). The other materials used were of " AnalaR " grade, or in the case of sodium stearate the purest obtainable (British Drug Houses, Ltd.; made from purified stearin). " Teepol " was the commercial product supplied by Shell Chemicals Ltd.

FIG. 4.



Analytical.—*iso*Propylbenzene was examined for styrenes by ultra-violet absorption by Mr. A. R. Philpotts of this Department, whom we thank. The oxidation products were analysed for hydroperoxide as follows: Samples (1 ml.) of emulsion were pipetted into 250-ml. conical flasks each containing 25 ml. of freshly redistilled glacial acetic acid. The air in each flask was displaced by nitrogen (from cylinders; " oxygen-free " grade), and 1 ml. of saturated aqueous potassium iodide added. The flasks were stoppered and set aside for 15 minutes at room temperature, after which the liberated iodine was titrated with 0·05N-thiosulphate. Blank determinations on the acetic acid required about 0·1 ml. of 0·05N-thiosulphate.

Oxidation Procedure.—The thermostat was brought to the required temperature (normally 85°), and the air in the reaction vessel replaced by oxygen. The alkaline aqueous phase containing the emulsifying agent was introduced and allowed to reach the bath temperature. *iso*Propylbenzene was then added and the stirrer and gas circulation were started. Samples were withdrawn periodically for hydroperoxide analysis, and regular readings taken of the gasmeters.

Recovery of the Hydroperoxide.—The oxidation product was cooled to room temperature, saturated with carbon dioxide, the oil layer separated, and its hydroperoxide content determined. Subsequent treatment of the oil layer was by one of the following methods:

(*a*) The oil was cooled below room temperature, stirred, and treated dropwise with a slight excess (calculated on the oxygen absorption) of cold 25% w/w aqueous sodium hydroxide. The white crystals which separated were collected, washed with light petroleum (b. p. 40—60°), and dried in a vacuum. The *iso*propylbenzene mother-liquors still contained hydroperoxide, most of which was recovered as sodium salt by successive treatments with strong alkali as outlined above.

The sodium salt was converted into free hydroperoxide, if desired, as follows. A suspension of the salt in water was covered with light petroleum and saturated with carbon dioxide. The upper layer was separated, washed with a little water, dried (Na_2SO_4), and evaporated *in vacuo*. Distillation of the residual free hydroperoxide at low pressure gave a colourless oil, b. p. 53°/0·0005 mm. (pump pressure), n_D^{20} 1·5242, d_4^{20} 1·062 (Found: C, 71·4; H, 8·05; active O, 10·5. Calc. for $C_9H_{12}O_2$: C, 71·05; H, 7·95; active O, 10·5%) (Hock and Lang, *loc. cit.*, give b. p. 53°/0·1 mm., 60°/0·2 mm., n_D^{20} 1·52424, d_4^{20} 1·06189). M_D^{20} was 43·86 (Calc. for *iso*propylbenzene: 40·16); the increment for the –O–O– group was thus 3·70.

(*b*) The oil was distilled *in vacuo*. The unchanged *iso*propylbenzene was recovered first, at 41—46°/13 mm. It contained traces of α-methylstyrene (identified by its ultra-violet absorption) and acetophenone (identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen 242—244°). When all the low-boiling material had been removed, a residue of hydroperoxide remained which was distilled *in vacuo*.

Acid Decomposition of the Hydroperoxide (cf. Hock and Lang, *loc. cit.*).—(*a*) A mixture of the sodium salt (2 g.) of the hydroperoxide and 10% w/w sulphuric acid (25 c.c.) was refluxed for 1½ hours, the top of the reflux condenser being connected to a tube dipping into ice-cold water. A very slow current of water at 50—60° was passed through the condenser. When the heating was stopped the liquid in the trap connected to the top of the condenser was treated with a solution of 2 : 4-dinitrophenylhydrazine in 5N-hydrochloric acid. The yellow flocculent precipitate which separated was recrystallised from 95% ethanol; it formed yellow needles, m. p. 126—127°, undepressed on admixture with authentic acetone 2 : 4-dinitrophenylhydrazone.

The acid hydrolysate obtained was treated with sodium hydroxide pellets (3·5 g.) and filtered, and the filtrate benzoylated at 0° with benzoyl chloride. The solid which separated was recrystallised from 95% ethanol, whereafter it had m. p. 67°, undepressed on admixture with authentic phenyl benzoate.

In a subsequent similar experiment the hydrolysate was steam-distilled, the distillate acidified and treated with excess of bromine water, then with excess of potassium iodide solution, and finally with sodium thiosulphate solution to remove free iodine. 2 : 4 : 6-Tribromophenol, m. p. 93—94°, was obtained (lit., 92° to 96°).

(*b*) A mixture of the sodium salt (50 g.) of *iso*propylbenzene hydroperoxide (equivalent to 25·5 g. of free hydroperoxide) and dilute sulphuric acid (560 c.c. of water and 35 c.c. of concentrated sulphuric acid) was steam-distilled until free from phenol (bromine water test on the distillate). The main bulk of distillate, which contained some water-insoluble oil, was treated with excess of sodium hydroxide solution, and the aqueous layer was separated. The remaining oil was washed with dilute sodium hydroxide solution and then with water, dried (Na_2SO_4), and filtered. A colourless oil (4·5 c.c.) was obtained. A portion gave acetophenone 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p.). The main bulk of the oil was distilled at atmospheric pressure, the following fractions being obtained: (i) b. p. 160—165° (0·9 c.c.), n_D^{20} 1·5370, (ii) b. p. 165—210° (2·8 c.c.), n_D^{20} 1·5325, and (iii) b. p. 240—250° (0·5 c.c.), n_D^{20} 1·5467.

Fraction (i) was α-methylstyrene (lit., b. p. 162—164°, n_D^{20} 1·5384), its identity being confirmed by its ultra-violet absorption. Fraction (ii) was refractionated, more α-methylstyrene being obtained (2·1 c.c.; b. p. 160—173°). The high-boiling material was not identified.

(*c*) A mixture of sulphuric acid (17 c.c. of concentrated sulphuric acid and 270 c.c. of water) and a solution (175 c.c.) of *iso*propylbenzene hydroperoxide (65·6 g.) in *iso*propylbenzene was stirred vigorously and refluxed for 90 minutes. Steam-distillation of the mixture yielded a distillate consisting of two layers. The acetone content of the aqueous layer was determined by oximation, and the phenol content by the bromide–bromate method.

The acetone content of the oil layer was determined by repeated washing of an aliquot with water and determination of acetone in the washings. The phenol content of the layer was determined by extracting an aliquot with a large excess of N-sodium hydroxide and determining the phenol content of the alkaline extract. The total yields of phenol and acetone were 82% and 74%, respectively, based on the initial weight of *iso*propylbenzene hydroperoxide.

Reduction of the Hydroperoxide with Sodium Hydrogen Sulphite.—The hydrated sodium salt (830 g.) of the hydroperoxide (equiv. to *ca.* 410 g. of free hydroperoxide) was added gradually to a vigorously stirred aqueous solution (2·4 l.) of sodium hydrogen sulphite (480 g.) which was kept at <20°, the resultant mixture stirred for a further 45 minutes at room temperature, and the oil extracted with ether. The ethereal solution was washed with dilute sodium hydroxide solution and then with water, and dried (Na_2SO_4), and the ether distilled off, to yield an oil (295 g.) which was fractionated *in vacuo* through a 30 × 1·5-cm. helices-packed, jacketed, glass column. α-Methylstyrene (38 g.) was collected, mainly at 51·5—52·5°/12 mm., and, after a small intermediate fraction, phenyldimethylcarbinol (246 g.) distilled at 90—92°/11 mm. This material (n_D^{20} 1·5210) contained traces of acetophenone from which it cannot readily be separated by distillation (cf. Klages, *Ber.*, 1902, **35**, 2637). When kept, it yielded large, transparent, colourless crystals, m. p. 25—27°, which on recrystallisation from light petroleum (b. p. 40—60°), cooled in ethanol–solid carbon dioxide, yielded small white crystals, m. p. 34—35° (Matsubara and Perkin, *J.*, 1905, 671, give m. p. *ca.* 35—37°). The carbinol on dehydration with boiling acetic anhydride (Staudinger and Breusch, *Ber.*, 1929, **62**, 449) gave α-methylstyrene, b. p. 50—50·5°/11 mm., n_D^{20} 1·5384, in good yield.

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