318. *Studies of the Autoxidation of Tetralin. Part II. The Decomposition of Tetralin Hydroperoxide.*

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The decomposition of pure tetralin hydroperoxide has been examined quantitatively. In both tetralin and chlorobenzene solutions it is substantially a first-order reaction, but at high concentrations there are divergencies from the simple homolysis $C_{10}H_{11}\cdot O\cdot OH \longrightarrow C_{10}H_{11}O\cdot +$ OH which indicate that chain reactions of ·OH, etc., are to some extent involved.

Methods have been developed for the analysis of the various decomposition products, and these show that the production of ·OH and $C_{10}H_{11}O\cdot$ radicals is followed both by intramolecular changes (giving α-tetralone and water) and by true free-radical reactions (giving α-tetralol, oxygen, and other products). The Franck–Rabinowitch " cage effect " of solvent molecules is invoked to explain the formation of a constant percentage of α-tetralone. The decomposition has also been studied in the presence of cobalt naphthenate. Though then much accelerated, it still has substantially the same kinetic characteristics, and yields the same range of products.

Our earlier studies of the autoxidation of tetralin (*Trans. Faraday Soc.*, 1946, **42**, 201) indicated that decomposition of tetralin hydroperoxide provides free radicals which act as chain-starters for the oxygen-uptake process. It therefore seemed probable that the uncatalysed thermal decomposition of tetralin hydroperoxide in solution might involve (*a*) the slow unimolecular homolysis (1) followed by (*b*) more rapid reactions of free hydroxyl and of free alkoxyl radicals.

$$C_{10}H_{11}\cdot O\cdot OH \longrightarrow C_{10}H_{11}\cdot O\cdot + \cdot OH \quad . \quad . \quad . \quad . \quad . \quad (1)$$

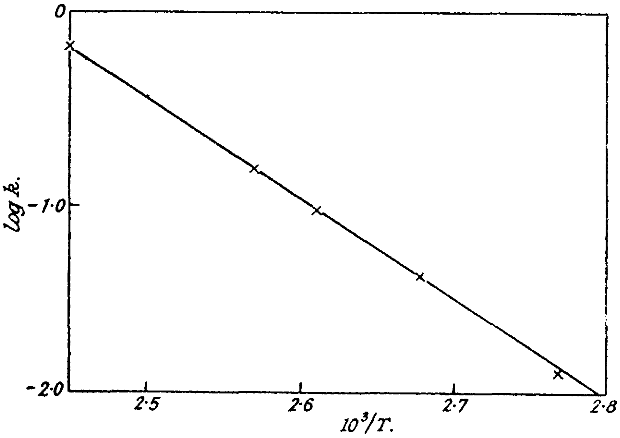
Moreover, it seemed plausible to hope that a study of the kinetics of the decomposition of tetralin hydroperoxide might provide a quantitative measure of the rate of the chain-starting reaction of the oxygen-uptake cycle. The present work, however, has revealed that the thermal decomposition of tetralin hydroperoxide is far more complex than was at first thought.

Kinetic studies of the rate of decomposition of tetralin hydroperoxide were first carried out in tetralin solution under a nitrogen atmosphere which prevented concurrent autoxidation of the solvent. The results, at first, indicated that the decomposition was a first-order reaction, for at a series of temperatures ranging from 88° to 135° excellent linear plots of log (peroxide destroyed) against reaction time were obtained. These gave the first-order reaction-velocity constants which have been plotted·Fig. 1, and correspond to the Arrhenius equation

$$k = 2{\cdot}27 \times 10^{9}e^{-24,400/RT} \text{ g.-mol./l./sec.}$$

Heats of activation, ranging from 20 to 30 k.-cals. for the fission of the O–O link in analogous peroxides have been recorded by many other workers. Bolland (*Proc. Roy. Soc.*, 1946, *A*, **186**, 218) gives 26 k.-cals. as the activation energy for the second-order decomposition of the hydroperoxide of ethyl linoleate, though, with Gee (*Trans. Faraday Soc.*, 1946, **42**, 244), he estimates the O–O covalent bond strength as 66 k.-cals.

FIG. 1.



However, the thermal decomposition of tetralin hydroperoxide in solution is not a simple unimolecular homolysis corresponding to equation (1). Ivanov, Savinova, and Mikhailova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 34) had reported that the velocity of decomposition of tetralin hydroperoxide depends upon the nature of the solvent used. This fact became more significant when a series of solvents of different chemical type were investigated, as shown by our results in Table I. This marked solvent influence indicates that the free radicals produced by the decomposition process (1) react with the solvent, and initiate chain reactions which by some means bring about a radical-catalysed decomposition of the tetralin hydroperoxide which proceeds concurrently with its uncatalysed decomposition (compare Nozaki and Bartlett's kinetic studies of the decomposition of dibenzoyl peroxide, *J. Amer. Chem. Soc.*, 1946, **68**, 1686).

TABLE I.

Solvent effects on the rate of decomposition of tetralin hydroperoxide.

Solvent.	% Hydroperoxide decomposed after 1 hour at 116°.	Solvent.	% Hydroperoxide decomposed after 1 hour at 116°.
Tetralin	10	*cyclo*Hexanone	41
Chlorobenzene	10	*cyclo*Hexanol	78
o-Dichlorobenzene	30	*a*-Chloronaphthalene	100

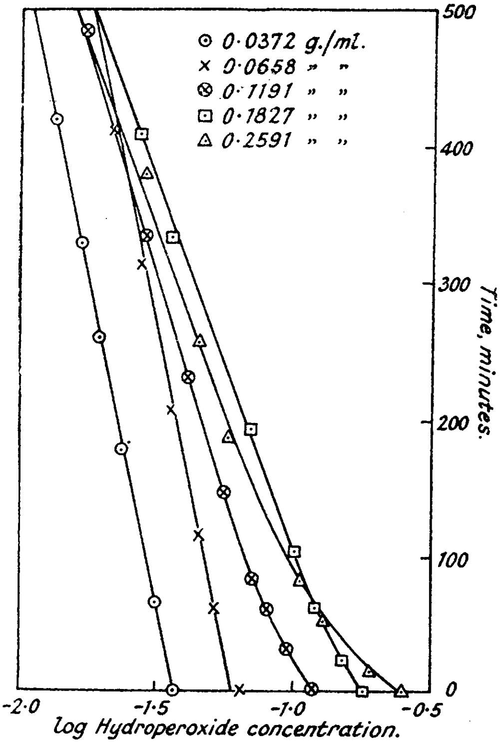
Radical-catalysed decompositions of this type should become more pronounced the greater the concentration of the dissolved hydroperoxide, since only when the solute is present in very low concentration can it safely be presumed that all the active free radicals generated by process (1) will react with, and be rendered inert by, solvent molecules. At higher concentrations chain reactions, such as (2) may occur :

$$\left.\begin{array}{l} \cdot OH + R''CH{\cdot}O{\cdot}OH \longrightarrow H_2O + R''\overset{|}{C}{\cdot}O{\cdot}OH \\ R''\overset{|}{C}{\cdot}O{\cdot}OH \longrightarrow R''C{=}O + \cdot OH \end{array}\right\} \textit{chain} \quad . \quad . \quad . \quad (2)$$

Fig. 2 shows that this concentration effect does complicate the first-order decomposition of tetralin hydroperoxide. The decomposition appears to be strictly of first order at concentrations below 0·12 g./ml. but becomes noticeably more rapid at higher concentrations.

These physicochemical studies, however, give us no more than a superficial knowledge of the reaction process. Its real complexity has been revealed by quantitative study of the decomposition products formed. The compounds described in Part I (previous paper) were all isolated from the mixture obtained by decomposing tetralin hydroperoxide in tetralin under nitrogen. α-Tetralone and α-tetralol are both major products of the decomposition, and quantitative methods for their estimation were worked out (see Experimental). Some previous workers have either failed to detect α-tetralol (*e.g.*, Medvedev and Podyapolskaya, *J. Phys. Chem. Russia*, 1939, **12**, 719) or have confidently assumed that it was not formed (*e.g.*, George and Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 309) and have, in consequence, been seriously misled in their interpretations of the kinetics of autoxidation. The presence of α-tetralol in this reaction has, however, been noted by Sully (*Trans. Faraday Soc.*, 1946, **42**, 261) and by the author of French Patent 37,351 of 1929. We have confirmed Sully's statement that the α-tetralone which is obtained from tetralin by the standard autoxidation procedure (*Org. Synth.*, **20**, 94) contains about 20% of tetralol, which cannot be separated by distillation. In order to obtain pure α-tetralone it was necessary to prepare its crystalline semicarbazone (Kipping and Hill, *J.*, 1899, **75**, 144) and regenerate the ketone from this.

FIG. 2.



Water is always formed in appreciable amounts. It was estimated on the small scale by the cinnamoyl chloride method (van Niewenberg, *Microchim. Acta*, 1937, **1**, 71) since the reaction mixtures were too deeply coloured for the use of the Karl Fischer reagent. Larger-scale confirmations were carried out by the Dean and Stark method. Rather unexpectedly, it was found that *oxygen* is evolved during the thermal decomposition of tetralin hydroperoxide in inert solvents such as chlorobenzene. This observation is of special significance in relation to the kinetics of autoxidation (Part III) since it indicates that the critical chain-breaking reaction may be (3). However, in the decomposition of tetralin hydroperoxide, under nitrogen, the

$$R''CH{\cdot}O{\cdot}O{\cdot} + {\cdot}OH \rightleftharpoons R''CH{\cdot}OH + O_2 \quad . \; . \; . \; . \; . \quad (3)$$

oxygen evolution is far too small to account for the whole of the production of α-tetralol along the lines of equation (3). Most of the tetralol must be derived from $C_{10}H_{11}O{\cdot}$ radicals which have oxidised (*i.e.*, dehydrogenated) other organic material.

Our analytical results, which were quite reproducible, are given in Table II. Figures obtained for the decomposition of tetralin hydroperoxide in tetralin solution (under nitrogen) were identical with those for its decomposition in chlorobenzene.

TABLE II.

The decomposition products of tetralin hydroperoxide, moles %.

Ketones (calc. as α-tetralone)	48·0
Alcohols (calc. as α-tetralol)	30·0
Acids (calc. as monobasic)	7·5
Saponifiable material	5·0
Water (Dean and Stark method)	55·5
,, (cinnamoyl chloride method)	54·5
Oxygen	1·5

It has often been suggested that epoxides are possible autoxidation products of hydrocarbons. However, prolonged hydrolysis of the decomposition mixture with dilute acid did not alter appreciably the ketone/alcohol ratio, so that epoxides cannot be present in significant bulk in the finally decomposed mixture. Attempts to isolate diols as their phenyl- or naphthyl-urethanes failed completely. It may be suggested that under the conditions of the reaction any tetralin epoxide which might have been formed would tend to isomerise to β-tetralone, which would then be oxidised rapidly. It should be noted, however, that our figures for alcohols include the phenolic acids (5) and (6) of Part I, though to balance this slight error " saponifiable material " will include some tetralyl esters. The net figure of 30 moles % of α-tetralol cannot therefore be much in error.

We have been unable to substantiate Medvedev's suggestion (*Acta Physicochim. U.R.S.S.*, 1938, **9**, 395) that tetralin hydroperoxide and α-tetralone combine to form a stable hydroxy-peroxide. In fact, the decomposition of tetralin hydroperoxide is rapid in ketonic solvents, and a concentrated solution (20%) of tetralin hydroperoxide gave a slightly higher yield (49·5%) of α-tetralone than did one half of this strength (see Table II).

Evidence for the Presence of Free Radicals during the Decomposition of Tetralin Hydroperoxide.—(1) Table III shows that tetralin hydroperoxide and dibenzoyl peroxide are comparable as catalysts for initiating the chain polymerisation of olefins. This is a reaction which involves the presence of active free radicals.

TABLE III.

Tetralin hydroperoxide as a catalyst for polymerisation processes.

Polymerisation.	Peroxide, %.		Induction period, mins.	Appearance.
Styrene: heated at 115° in sealed tubes; air present	Tetralin hydroperoxide	1	150	Solidified on cooling
		5	120	
	Benzoyl peroxide	1	95	,,
		5	55	
	None		180	Still mobile
Methyl methacrylate: heated at 50°; air atmosphere	Tetralin hydroperoxide	1	145	Viscous liquid
		5	65	
	Benzoyl peroxide	1	30	,, ,,
		5	25	
	None		180	Mobile
Vinyl cyanide: heated at 55°; air present	Tetralin hydroperoxide	1	1	Polymer deposited
		5	5	
	Benzoyl peroxide	1	105	,, ,,
		5	19	
	None		120	Still clear

(2) It has been suggested by one of us (Waters, *Trans. Faraday Soc.*, 1946, **42**, 184; *Nature*, 1946, **158**, 380) that the splitting of α-glycols to aldehydes and ketones by lead tetra-acetate, or by Fenton's reagent, is due to their dehydrogenation by free $\cdot O\cdot CO\cdot CH_3$ or $\cdot OH$ radicals. The thermal decomposition of tetralin hydroperoxide at 135° in various glycols was therefore examined. Both ethylene glycol and glycerol yielded formaldehyde, 2 : 3-butylene glycol yielded acetaldehyde, and pinacol yielded acetone. Under the same conditions, *cyclo*hexanol, previously freed from ketone by distilling it from 2 : 4-dinitrophenylhydrazine, gave some *cyclo*hexanone. Presumably some of the tetralone originates in this way from tetralol.

(3) Attempts to establish the presence of the free hydroxyl radical by its substitution in benzene, chlorobenzene, chloronaphthalene, nitrobenzene, *p*-nitrotoluene, and *m*-dinitrobenzene were also made, but the corresponding phenolic compounds could not be isolated, though Milas (*J. Amer. Chem. Soc.*, 1937, **59**, 2342) has reported that aromatic compounds can be hydroxylated with *tert.*-butyl hydroperoxide. It may be concluded, therefore, that the phenolic by-products of the decomposition of tetralin hydroperoxide are not formed by free-radical hydroxylation, but rather by the molecular rearrangement process suggested in Part I.

The Decomposition of Tetralin Hydroperoxide in the Presence of Cobalt Naphthenate.—Cobalt naphthenate, which is one of the most active of the metal-salt catalysts of autoxidation, is also a potent catalyst for the decomposition of tetralin hydroperoxide (compare Ivanov, Savinova, and Mikhailova, *loc. cit.*; Cook, *J.*, 1938, 1774). Fig. 3 shows that, in tetralin solution at 20°, the catalysed decomposition is still of first order with respect to tetralin hydroperoxide until about 90% of the material has been destroyed, but thereafter the reaction rate shows signs of decreasing. This may be due to a slow decomposition of the catalyst, for solid is eventually deposited from these solutions. Fig. 4 shows that, provided only small amounts of catalyst be added, the rate of decomposition of tetralin hydroperoxide is also of first order with respect to cobalt naphthenate (compare George, Rideal, and Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 288).

FIG. 3.

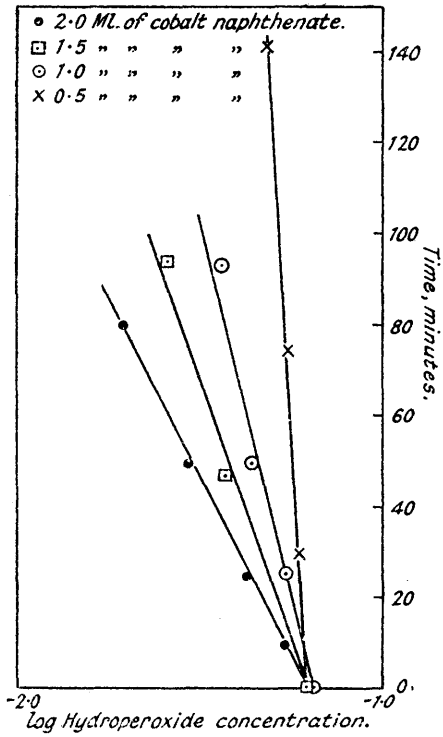
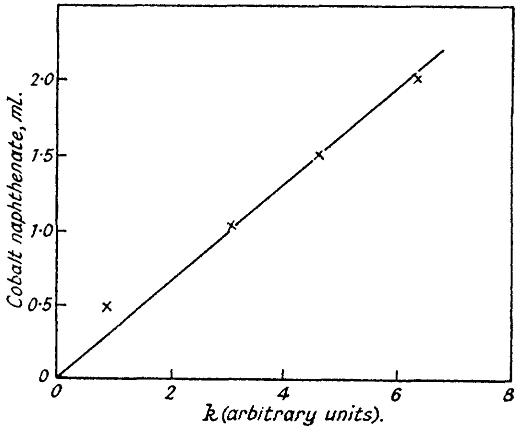


FIG. 4.



Immediately tetralin hydroperoxide is added to a reddish-brown solution of cobalt naphthenate in any organic solvent the colour changes to a pale yellow, and decomposition sets in. This colour change is probably an indication of the oxidation of the cobaltous ion to a higher valency state (*e.g.*, Co^{+++}).

TABLE IV.

The decomposition of tetralin hydroperoxide in the presence of cobalt naphthenate at 76°.

Product.	Yield, moles %.
Ketones (as α-tetralone)	48·0
Alcohols (as α-tetralol)	33·0
Acids (as monobasic)	2·0
Saponifiable material	1·0
Oxygen evolved	16·1

Table IV, which gives the results of a quantitative analysis of the products of the catalysed decomposition in the presence of 4% of cobalt naphthenate, shows that the catalysed decomposition, like the uncatalysed decomposition (Table II), is still a complex process. An increase in the quantity of catalyst had no significant effect upon the ketone/alcohol ratio.

A comparison of Tables II and IV shows that the relative yields of the two main decomposition products, *viz.*, α-tetralone and α-tetralol, are very little altered by the presence of the catalyst. Much more oxygen is evolved in the catalysed decomposition, however, and correspondingly the quantity of complex oxidation products (acid and saponifiable material) becomes less. In fact, the quantity of oxygen evolved in the catalysed decomposition becomes nearly equivalent to the amount of α-tetralol formed, suggesting that the reaction $2C_{10}H_{11}\cdot O\cdot OH = 2C_{10}H_{11}\cdot OH + O_2$ has now become important.

Since cobalt naphthenate strongly catalyses the autoxidation of tetralin, it may be inferred that peroxide radicals, $C_{10}H_{11}\cdot O\cdot O\cdot$, are abundant in these decomposing mixtures. Consequently, the following reaction sequence, which accords with the chain-ending process to be discussed in Part III (following paper), may be suggested in order to account for this large oxygen evolution.

$$C_{10}H_{11}\cdot O\cdot OH \longrightarrow C_{10}H_{11}\cdot O\cdot + \cdot OH \quad . \ . \ . \ . \ . \ . \quad (4)$$

$$C_{10}H_{11}\cdot O\cdot OH + \cdot OH \text{ (or } \cdot OR) \longrightarrow C_{10}H_{11}\cdot O\cdot O\cdot + H_2O \text{ (or HOR)}$$

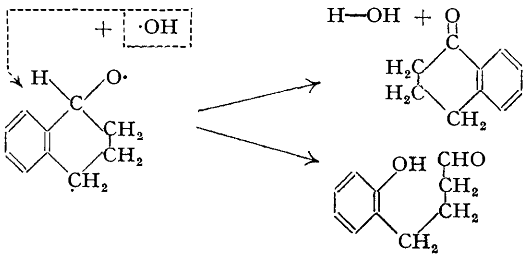
$$C_{10}H_{11}\cdot O\cdot O\cdot + \cdot OH \longrightarrow C_{10}H_{11}\cdot OH + O_2 \text{ (chain-ending)}$$

In these circumstances, the hydroperoxide decomposes so rapidly that the radicals $C_{10}H_{11}O\cdot$ and $\cdot OH$ are present in high concentration. The reaction chains in which they are concerned then become very short, on account of the high probability of mutual encounter of two radicals, and in the main lead to the conversion of tetralin hydroperoxide into α-tetralol and oxygen. In the absence of a catalyst the hydroperoxide decomposes so slowly that the radicals, formed only in very low concentration, have a greater chance of dispersing, and of reacting with other solute molecules, *e.g.*, of oxidising tetralone to acid substances.

The foregoing suggestion depends upon the proposition that free radicals are produced during the metal-salt-catalysed decomposition of tetralin hydroperoxide. This has been supported by showing that glycol fission (of ethylene glycol, glycerol, 2 : 3-butylene glycol, and pinacol) could be effected, even at moderate temperatures, in the presence of the cobalt naphthenate catalyst.

Discussion.—Our kinetic work has indicated that both in absence and in presence of a metal-salt catalyst the thermal decomposition of tetralin hydroperoxide is substantially a first-order reaction, giving a complicated mixture of products such as one would expect from a homolytic reaction in which free neutral radicals had been produced. The natures of the subsidiary oxidation products and the evidence of glycol fission both suggest that these free radicals are hydroxyl and alkoxyl ($C_{10}H_{11}\cdot O\cdot$). Nevertheless, in all circumstances about half the tetralin hydroperoxide seems to decompose according to the simple equation $C_{10}H_{11}\cdot O\cdot OH = C_{10}H_{10}O + H_2O$, whilst a slight amount seems to undergo a molecular rearrangement to an isomer, γ-*o*-hydroxyphenylbutaldehyde [(4) of Part I]. Although these products may in part be produced by free-radical reactions (*e.g.*, by the oxidation of α-tetralol), it is much more likely that they both result from intramolecular decompositions.

In order to explain why the quantum efficiencies of photolyses in solution were usually very low indeed, Franck and Rabinowitch (*Trans. Faraday Soc.*, 1934, **30**, 120) pointed out that whenever a molecule decomposed into two radicals, within a liquid, then the dissociated fragments would tend to be driven together again by the collisions of the surrounding solvent molecules, and only in the exceptional circumstances of their possessing high translational energy would they be able to drift far apart before recombining. Now this " cage effect " of solvent molecules will explain very well the high, and constant, yield of α-tetralone in the thermal decomposition of tetralin hydroperoxide, for, following the simple homolysis (1) (p. 1578), there may occur (*a*) direct recombination of radicals, as postulated by Franck and Rabinowitch, or (*b*) the reactions illustrated below, in which the radicals have had sufficient independent existence to change their relative alignments by translational motion, but not the opportunity to become really " free ".



The formation of γ-*o*-hydroxyphenylbutaldehyde has its direct analogy in the decomposition of diphenylmethane hydroperoxide to benzaldehyde and phenol, noted by Hock and Lang (*Ber.*, 1944, **77**, 257), and in the decomposition of triphenylmethane hydroperoxide to benzophenone and phenol (Wieland and Maier, *Ber.*, 1931, **64**, 1205).

The direct recombination (*a*) would merely have the effect of reducing the observed velocity of decomposition of tetralin hydroperoxide below that which one might calculate on the supposition that bond fission occurs whenever the molecule gets enough activation energy. This, of course, will be common to all decompositions in solution. It accords with the observed low value ($2{\cdot}27 \times 10^9$) of the reaction constant (p. 1579).

The cage effect (*b*), though structural in the sense that different molecules would undergo intramolecular processes of different types, again depends in magnitude upon the probability of separation of a pair of freshly-formed radicals, but should be independent of the molar concentration of the decomposing substance, though possibly dependent upon the temperature and upon the nature of the solvent.

Consequently, the rate of production of a free radical of any one species can be written as

$$+\ \mathrm{d[OH]}/\mathrm{d}t = \rho k[\text{Hydroperoxide}]$$

where ρ represents the fraction of freshly-formed radicals which become " free " enough to act as chemical reagents, or as chain-starting catalysts, and k is the measured unimolecular decomposition-velocity constant. Part III seems to indicate that only one of the free radicals produced by the thermal decomposition of tetralin hydroperoxide is catalytically active. In this following paper the factor k_c is used to represent the product ρk.

The reaction mechanism for the catalysed decomposition has already been considered by us (*Trans. Faraday Soc.*, *loc. cit.*), and our previous conclusion, *viz.*, that it is a chain reaction in which the metal cation undergoes reversible one-electron oxidation–reduction (*e.g.*, $Co^{++} \rightleftharpoons Co^{+++} + e$) does not need substantial modification, though it now becomes necessary to stress the fact that the reaction chains involving the radicals $\cdot OH$ and $C_{10}H_{11}O\cdot$ must all be short. It is noteworthy, however, that this consideration of the catalysed reaction led to the conclusion that the catalytically active radical was free hydroxyl, $\cdot OH$, and not $C_{10}H_{11}O\cdot$; though this view was based upon the report that tetralone rather than tetralol was formed in quantity. Though the true nature of the active catalyst radical in autoxidation is still in doubt between these two alternatives we may point out that, as a chain-breaking reaction, the process $C_{10}H_{11}{\cdot}O{\cdot}O\cdot + \cdot O{\cdot}C_{10}H_{11} \longrightarrow O_2 + C_{10}H_{11}{\cdot}O{\cdot}C_{10}H_{11}$ does not seem to occur to any appreciable extent, because we have been unable to isolate ditetralyl ether from any of our reactions.

EXPERIMENTAL.

Preparation of Pure Tetralin Hydroperoxide.—Tetralin containing 0·01% of cobalt naphthenate as catalyst was charged into a flask equipped with a reflux condenser, with ground glass joints, and a glass frit gas-distributor spoon. (Rubber connections must be avoided, as rubber is very quickly destroyed by tetralin.) The tetralin was then air-blown for 25—30 hours. The resulting solution (*ca.* 25% peroxide) was then distilled in an all-glass apparatus under nitrogen at 1 mm., a water-bath being used which was not heated to above 60°, and about 80% of the tetralin was removed at about 52°. The concentrate was stored overnight at – 10°, and the resulting crystalline product was collected on a sintered-glass filter, pressed dry, and crystallised at least three times from light petroleum (b. p. 40—60°). The pure product melted at 56°; yield 17—20%.

Estimation of Tetralin Hydroperoxide (in kinetic studies, etc.).—In a conical flask, fitted by a ground glass joint to a glass bubble-trap containing potassium iodide solution, were placed 20 ml. of glacial acetic acid, 1·5 g. of sodium hydrogen carbonate, and just sufficient water to cause carbon dioxide evolution (a few drops only). The sample for analysis was added from a syringe pipette, which was rinsed out with glacial acetic acid, the rinsings being added to the flask also. A slight excess of 50% potassium iodide solution was then added, the bubble-trap placed in position, and the flask heated at 80° for 15 mins. After this had been kept in the dark for 1 hour, the combined contents of both the flask and the trap were diluted with water, and titrated with thiosulphate, starch being used as indicator. Very viscous samples were syringed into a tared, dry flask, which had been purged with nitrogen to prevent oxidation, stoppered, and weighed. The estimation was then completed by adding acetic acid and potassium iodide and proceeding as above.

Under these conditions our purest tetralin hydroperoxide regularly gave 97% of the calculated quantity of iodine. Only 85% reaction occurred if mixtures were merely left in stoppered flasks for 24 hours. The prompt fitting of the bubble-trap was essential to secure reproducibility and accuracy.

Kinetic Measurements.—Kinetic measurements of the decomposition of tetralin hydroperoxide in solution were carried out in 50-ml. tubes, fitted with a glass stopper, and provided with gas inlet and exit tubes. These reaction tubes were heated to constant temperatures by immersion in the vapours of suitable refluxing liquids (trichloroethylene, water, toluene, *n*-butanol, and ethylbenzene). In each experiment about 1 g. of pure tetralin hydroperoxide was weighed accurately into a reaction tube and dissolved in 15 ml. of tetralin or other solvent, air was displaced by nitrogen, the stopper inserted, and the tube then placed in its vapour-bath. A very slow stream of nitrogen was maintained throughout. Periodically, samples were withdrawn by means of a syringe pipette. Six or more samples were taken in each experiment at times which covered the range 10—90% decomposition. Good logarithmic plots, resembling those in Fig. 2, could always be constructed. Duplicate runs were concordant.

Quantitative Methods for the Analysis of Reaction Products.—(1) *α-Tetralone.* (*a*) Gravimetric method. The weighed sample of oil was dissolved in 30 ml. of 50% ethanol and treated with an excess of a filtered solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, with vigorous shaking. After 1 hour the solution was filtered through a sintered-glass crucible, and washed well with the acid and finally with distilled water. It was weighed after being dried at 100° : 1 g. of dinitrophenylhydrazone corresponds to 0·4478 g. of α-tetralone. This method was practicable only for samples of high purity. In presence of tetralin the dinitrophenylhydrazone formed a red oil which could not be filtered. Tetralin hydroperoxide oxidised the reagent.

(*b*) Volumetric method. This was much more widely applicable, but again peroxide had to be absent. (Omission of this precaution vitiates nearly all the analytical results of Larsen, Thorpe, and Armfield, *Ind. Eng. Chem.*, 1942, **34**, 282.) 20 Ml. of a 20% solution of pure hydroxylamine hydrochloride in 80% methanol, and 20 ml. of methanol were added to each of two conical flasks. The solutions were adjusted to neutrality to dimethyl-yellow indicator (used as a 0·1% methanolic solution), N/10-methanolic sodium hydroxide being used. The sample to be analysed was added to one flask, and both flasks were then heated, under reflux condensers, for 2 hours on a water-bath. After cooling, both samples were titrated to neutrality with N/10-methanolic sodium hydroxide, the same indicator being used. 1 Ml. of this alkali is equivalent to 0·0146 g. of α-tetralone.

With pure α-tetralone (*ex* its semicarbazone) this method gave 98·5% of the theoretical value. Bromophenol-blue (pH range 3·0—3·6) could be used in place of dimethyl-yellow (pH range 2·8—4·6). When deeply-coloured oxidation products were being examined this colorimetric end-point could not be used, and the following trustworthy modification was adopted. After being refluxed, the blank solution was transferred to a beaker, a glass electrode inserted, the system connected to a calomel half-cell, and the pH determined by means of a Cambridge pH meter. This process was then repeated with the sample solution, which was titrated with the methanolic alkali until the pH was identical with that of the blank (approx. 3·5).

(2) α-*Tetralol.* The sample, from a specimen freed from water by azeotropic distillation, was refluxed on a water-bath with a suitable quantity of acetic anhydride in anhydrous pyridine, and a blank mixture was submitted to a similar treatment. After 2 hours' refluxing, both samples were well diluted with distilled water and titrated with N/5-alcoholic sodium hydroxide with phenolphthalein as indicator. Allowance was made for the free acid in the sample: 1 ml. of N/5-sodium hydroxide corresponds to 0·0296 g. of α-tetralol. By this method pure α-tetralol gave 97% of the theoretical titre, and so did equimolar mixtures of tetralol and tetralone.

(3) *Water.* The Dean and Stark method was used for the decomposition of 16—20-g. samples of tetralin hydroperoxide dissolved in 75 ml. of dried chlorobenzene, a receiving vessel calibrated to 0·05 ml. being used.

For the cinnamoyl chloride method, 1 g. of tetralin hydroperoxide was dissolved in 2·5 ml. of sodium-dried tetralin, and heated, in a slow stream of phosphoric oxide-dried nitrogen, in a small flask immersed in oil at 140°. The gases were passed through a bubbler containing cinnamoyl chloride maintained at 40°, and thence into distilled water, where the hydrochloric acid, equivalent to the water produced in the decomposition, was collected and finally titrated with N/10-sodium hydroxide.

(4) *Oxygen.* Decompositions were carried out in boiling chlorobenzene solution. a slow stream of purified nitrogen being used. The gases were collected and measured, and their oxygen content was determined by absorption in pyrogallol.

Catalysed Decompositions.—The cobalt naphthenate catalyst was a typical technical product, taken from a stock of material normally used as an autoxidation catalyst. A stock 1% solution in tetralin was made, by prolonged shaking in a closed bottle, and portions were filtered before use. The solution gradually deteriorated over a period of months, and reproducible results could not be obtained from samples which had been exposed to the air.

Glycol Fision Experiments.—The decomposition of solutions of tetralin hydroperoxide in a number of glycols was carried out both by thermal treatment at 135° and by the addition of cobalt naphthenate catalyst. Vapours from the solution of the decomposing hydroperoxide were blown by a nitrogen stream through an air condenser and thence to bubblers containing a suitable test reagent (dimedone or 2 : 4-dinitrophenylhydrazine). Derivatives of any aldehydes or ketones present in the decomposition products were filtered off, recrystallised, and compared with samples of authentic specimens.

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