

345. *The Decomposition of Decalin Hydroperoxide: A Kinetic Study.**

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The decomposition of decalin hydroperoxide in solution has been investigated under a wide variety of conditions. The overall decomposition was of first order at low concentrations (<0.01 — $0.03M$), and k did not depend on initial concentration. In neutral solvents of low dielectric constant (*e.g.*, decalin, *o*-dichlorobenzene, ethylene glycol), homolytic fission of the hydroperoxide molecules (activation energy ~ 32 — 33 kcal.) occurred, followed by a free-radical chain decomposition; and in neutral solvents of high dielectric constant (*e.g.*, nitrobenzene) some ionic decomposition was superimposed on this chain reaction. Addition of water increased the rate of decomposition in acetic acid to a maximum with 60 moles % added. The overall activation energy also increased from 16.7 to 22.1(4) kcal. Probably, addition of water suppressed an induced ionic chain decomposition occurring in the dry acetic acid. The decomposition, though not affected even by strong bases, was subject to acid catalysis in chlorobenzene solution.

HYDROPEROXIDES are now recognised as the most important intermediate in the catalysed and non-catalysed oxidation by molecular oxygen of hydrocarbons in solution. They are formed by a chain mechanism in the first stage of the oxidation, and then decompose or react to give the final products (Bolland, *Quart. Reviews*, 1949, **3**, 1). There is now strong evidence that hydroperoxide decomposition can occur in several ways: (*a*) by molecular rearrangement, (*b*) by an initial split into free radicals, followed usually by a chain reaction, or (*c*) by heterolytic fission, especially in the presence of acids (*e.g.*, see Robertson and Waters, *J.*, 1948, 1578; Kharash, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 748; 1951, **16**, 113, 128; Witkop and Patrick, *J. Amer. Chem. Soc.*, 1951, **73**, 2196). However, little systematic work has been reported on the kinetics of the decomposition of any particular hydroperoxide under widely different conditions. This paper, therefore, presents the results of a kinetic study of the decomposition of decalin hydroperoxide.

Decalin hydroperoxide is an example of a tertiary hydroperoxide with no double bonds or unsaturated rings in the molecule. Its decomposition has apparently not been studied previously, though Criegee (*Annalen*, 1948, **560**, 127) has found that decalin perbenzoate rearranges in solution by an ionic mechanism to give 1-benzoyloxy-1:6-epoxycyclodecane. In the present investigation, low concentrations of hydroperoxide and a colorimetric method of estimation were generally used, since the yield in the preparation was so small.

At least at low concentrations (<0.01 — $0.03M$) the overall decomposition in an inert atmosphere was of first order and k did not vary with the initial concentration. (Fig. 1 shows a selection of the results.) In nearly all cases the rate constants were consistent to within a few units %. However, as the following Table shows, the rate of decomposition was greatly different in different solvents: c is the initial molar concentration, and t_1 the time of half-change (in min.).

* A brief summary of a small portion of this work has been published in *Discuss. Faraday Soc.*, 1951, **10**, 331.

Decomposition of decalin hydroperoxide in various solvents at 130° (nitrogen was passed through the solution).

Solvent	10 ³ c	t _{1/2}	Solvent	10 ³ c	t _{1/2}
Chlorobenzene	2.7	§	Nitrobenzene	5.4	244
Butyl alcohol	2.7	†	Ethylene glycol	2.7	70
Decalin	25.3	819 ‡	Pyridine	2.7	~40–50 ‡
<i>o</i> -Dichlorobenzene	2.7	258 ‡	Acetic acid	2.7	21 ‡

§ <10% Decomposition in 3 hours.

† No appreciable decomposition at 100°.

‡ Obtained by extrapolation of the Arrhenius plot.

Obviously the solvent played an important part in the reaction, and attention was first directed to the neutral solvents of low dielectric constant, which are unfavourable for ionic decomposition.

The overall activation energies for the decomposition in decalin, *o*-dichlorobenzene, and ethylene glycol, calculated from the Arrhenius plots (Fig. 2, *a*, *b*, and *c*), are 32.1, 30.2(5),

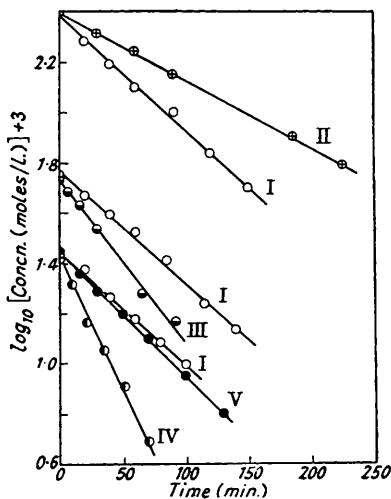
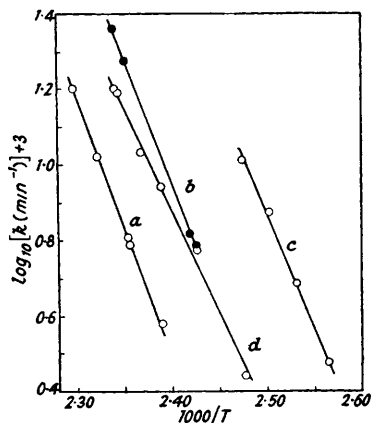


FIG. 2. Arrhenius plots of the decomposition of decalin hydroperoxide. Nitrogen passed through solution.

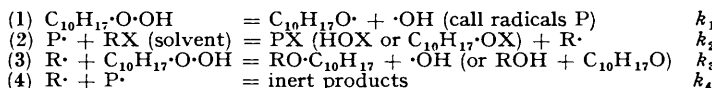
- (a) Solvent—decalin. Initial concn. = 0.025M.
 (b) " — *o*-dichlorobenzene. " = 0.0027M.
 (c) " — ethylene glycol. " = 0.0027M.
 (d) " — nitrobenzene " = 0.0054M.

FIG. 1. Decomposition of decalin hydroperoxide in various solvents. Nitrogen passed through solution. Initial concns. = 0.025, 0.0054, and 0.0027M.

- I. ○ Solvent—ethylene glycol. Temp. = 131.0°.
 II. ⊕ " — decalin. " = 151.2°.
 III. ⊖ " — nitrobenzene. " = 153.5°.
 IV. ⊙ " — *o*-dichlorobenzene. " = 154.4°.
 V. ● " — acetic acid. " = 109.6°.



and 28.0 kcal., respectively (temperature-independent factors: 8.5×10^{13} , 2.2×10^{13} , and 4.0×10^{12} sec.⁻¹). Thus the order of increasing activation energy is that of decreasing rate of reaction. This suggests that, as k did not depend on the initial concentration of hydroperoxide, the decomposition in these solvents involved a chain mechanism of the same type as that suggested for the decomposition of *p*-anisoyl *p*-nitrobenzoyl peroxide (Leffler, *J. Amer. Chem. Soc.*, 1950, 72, 67). There was probably a unimolecular split into free radicals, which reacted with solvent molecules giving solvent radicals. These could have reacted with further hydroperoxide molecules, thus:



If we assume that the rate of production of P and R radicals equalled their rate of removal, the overall rate of decomposition is found to be of first order with respect to hydroperoxide

concentration. The overall rate constant is a complicated function of k_1 , k_2 , k_3 , k_4 , and the solvent concentration, but the general effect is that the chain reaction decreased the overall activation energy.

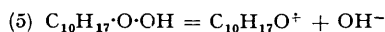
The reaction scheme proposed, though probably over-simplified, is supported by the fact that, when hydroperoxides decompose in neutral solvents containing active hydrogen atoms, considerable amounts of the corresponding alcohol together with water are found in the products (see, *e.g.*, Robertson and Waters, *loc. cit.*; Kharasch, Fono, and Nudenberg, *loc. cit.*, p. 116; Bartlett and Cotman, *J. Amer. Chem. Soc.*, 1950, 72, 3095). Also, it was found that the addition of 0.304 mole/l. of acrylonitrile or 1:3:5-trinitrobenzene, known to be retarders of free-radical chain reactions, to a 0.0027M-solution of decalin hydroperoxide in ethylene glycol reduced the rate of decomposition considerably at 153.4°. The time of half-decomposition was raised from 10.5 to 27.5 or 60–90 min., respectively. The addition of acenaphthene or ethyl chlorofumarate increased the rate of decomposition somewhat, presumably owing to the radicals produced from these compounds having been more reactive than those from ethylene glycol at the relatively high temperature. Oxygen had no effect at 131°.

The reaction in ethylene glycol catalysed the polymerisation of acrylonitrile, confirming the presence of free radicals. The complete decomposition of 25 ml. of a 0.025M-solution of hydroperoxide in ethylene glycol + 8 vol. % of acrylonitrile gave 0.388 g. of polymer at 131.6°.

Unfortunately, trinitrobenzene, the best retarder, tended to interfere with the analysis of the hydroperoxide, and only qualitative rate measurements, and no determination of the activation energy of the retarded reaction, were possible. However, since the decomposition in decalin was slow even at 153.4° ($t_{\frac{1}{2}} = 91.4$ min.), and this rate is comparable with the rate in ethylene glycol in the presence of trinitrobenzene, it is likely that only a small amount of induced decomposition occurred in decalin solution. Thus the value for the activation energy of the homolytic fission of decalin hydroperoxide in solution, *i.e.*, of reaction (1), is probably about 32–33 kcal.

Two points concerning the suggested reaction scheme should be considered. First, the results do not preclude the possibility that some decomposition occurred by a molecular mechanism, but the evidence, *e.g.*, of retardation, etc., points to the chain reaction as the more important, if not the only, method of decomposition in these solvents. Secondly, it is always likely, when molecular fission occurs in solution, that the "cage" effect will lead to primary recombination of the fragments. In effect this would reduce the observed rate of decomposition below that calculated on the assumption that bond fission occurred whenever a molecule obtained an energy greater than the activation energy. However, since the temperature-independent factor for the decomposition in decalin was $\sim 10^{14}$, *i.e.*, about the value for "normal" unimolecular decompositions, it seems probable that primary recombination was not marked in this case.

At 117.0° addition of water to the ethylene glycol (thus presumably greatly increasing the dielectric constant of the solvent) caused the rate of decomposition to increase to some extent, though the results were rather erratic. Possibly some ionic decomposition, *e.g.*,



was occurring together with the free-radical chain reactions.

Removal of traces of impurity from pyridine for use as solvent was very difficult, and thus the results were not consistent and can only be regarded as approximate. The high rate of decomposition of decalin hydroperoxide in pyridine was at first thought to be due to a base-catalysed reaction, especially as addition of water appeared to increase the rate somewhat. However, addition of 0.304 mole/l. of acrylonitrile reduced the rate of reaction at 110° very considerably, and large amounts of polymer (0.536 and 0.804 g., respectively) were formed during the complete decomposition of 25 ml. of a solution of 0.025M-hydroperoxide in pyridine and pyridine-water (40 vol. %) with 8% by vol. of acrylonitrile added. It seems that the high rate and low overall activation energy (<20 kcal.) were due to a very rapid, induced radical decomposition. The decomposition of benzoyl

peroxide is also very rapid in pyridine, and addition of water increases the rate (Tipper, *J.*, 1952, 2966). The addition of 0.4 mole/l. of sodium hydroxide to a 0.0027M-solution of hydroperoxide in ethylene glycol-water (24 : 1 by vol.) had no appreciable effect on the rate of reaction. Hence, decalin hydroperoxide does not undergo base-catalysed decomposition in most circumstances.

With nitrobenzene as solvent, the rate of decomposition at 130° was approximately the same as in *o*-dichlorobenzene, although the overall activation energy was only 24.5 kcal. (Fig. 2, line *d*, shows the Arrhenius plot). Addition of 0.305 mole/l. of acrylonitrile reduced the rate constant at 139.6° from 0.00603 to 0.00357 min.⁻¹, this retardation being considerably less than that with ethylene glycol as the solvent at a higher temperature. Thus ionic as well as free-radical decomposition of the hydroperoxide probably occurred owing to the high dielectric constant of nitrobenzene. The anomalous value of the activation energy would then be explained by assuming that the activation energy for heterolytic fission was less than 24.5 kcal. No precipitate was formed when the decomposition took

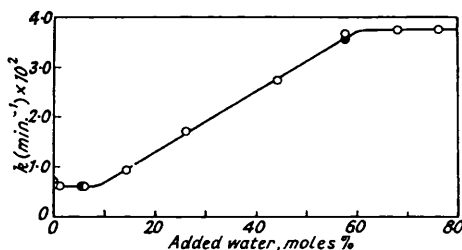


FIG. 3. Effect of water on the rate of decomposition of decalin hydroperoxide in acetic acid.

Temp. = 99.75°.

Initial concn. = 0.0027M.

- , Nitrogen passed through solution.
- , Oxygen passed through solution.

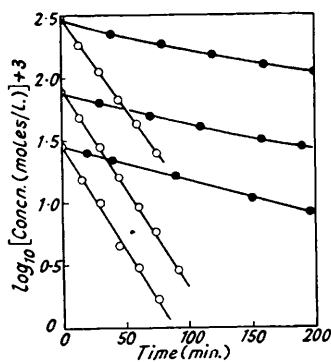


FIG. 4. Decomposition of decalin hydroperoxide in acetic acid-water mixtures.

Temp. = 99.3°.

Nitrogen passed through solution.

Initial concns. = 0.0027, 0.0077, and 0.030M

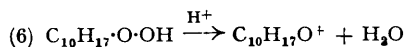
- , 6.1 Moles % H₂O.
- , 67.9 Moles % H₂O.

place in nitrobenzene + 8% by vol. of acrylonitrile, but this may have been due to the molecular weight of the polymer produced having been too low.

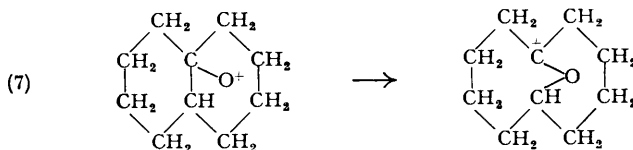
The rate of decomposition of decalin hydroperoxide in dry acetic acid at 100° was variable, but the addition of a small amount of water enabled consistent results to be obtained, the value of k being a little lower than with the dry acid. Addition of up to 7–8 moles % of water had no further effect on the rate. Further addition, up to 60 moles %, caused a large increase (~6-fold), but still further addition had little effect (Fig. 3).

The decomposition in acetic acid containing 6.1, 26.1, and 67.9 moles % of water was further investigated. With 6.1 moles % the decomposition tended to a higher order than unity at the higher concentrations, though the initial rate was approximately the same, whilst with 67.9 moles % the decomposition was always of the first order but at the highest initial concentration used k was slightly smaller (Fig. 4). The overall activation energies were 16.7, 19.5, and 22.1(4) kcal. and the "temperature-independent factors" were 6.1×10^5 , 7.7×10^7 , and 5.7×10^9 sec.⁻¹ in acetic acid with 6.1, 26.1, and 67.9 moles % of added water respectively (Fig. 5). Additions of acrylonitrile caused little or no retardation of the decomposition (Fig. 5), and only small amounts of polymer were formed (0.170 or 0.029 g., severally) during the complete reaction of 25 ml. of a 0.025M-hydroperoxide solution in acetic acid containing 6.1 or 67.9 moles % of added water and 8 vol. % of added acrylonitrile. The presence of oxygen also had little effect (Fig. 3).

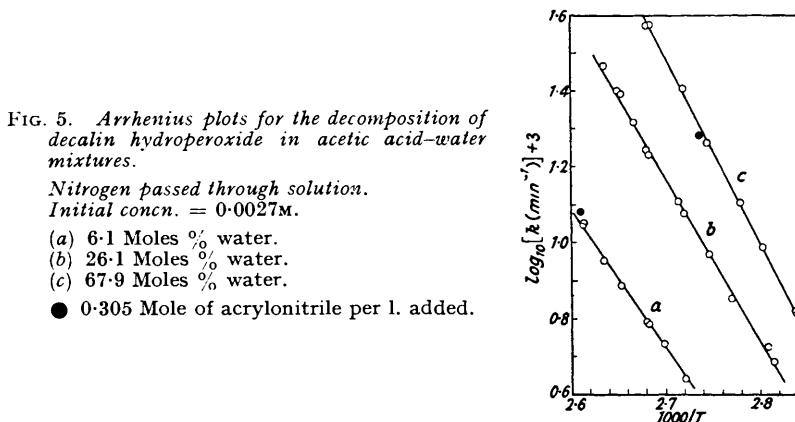
Obviously, little free-radical decomposition was occurring, and probably the first step in the decomposition in aqueous acetic acid was



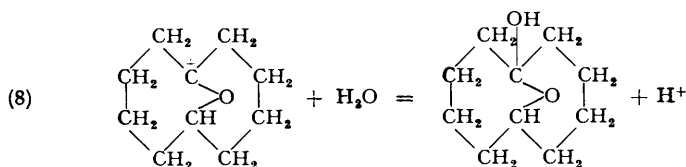
followed by the rearrangement of the $\text{C}_{10}\text{H}_{17}\text{O}^+$ ion postulated by Criegee (*loc. cit.*):



The rate of reaction (6) would have increased with increasing water content. The fact that the overall activation energy increased as water was added suggests that this addition was suppressing an induced chain decomposition of the hydroperoxide. It seems likely that



the carbonium ion either attacked an acetic acid or decalin hydroperoxide molecule causing an ionic chain reaction, combined with an acetate ion to give 6-acetoxycyclodecanone, or reacted with a water molecule:



It has been found (personal communication from Dr. J. Thomas, Cardiff) that, in general, carbonium ions are not very stable in aqueous media. Reaction (8) must then have predominated in mixtures with a high water content. An ionic chain mechanism has actually been proposed for the decomposition of $\alpha\alpha$ -dimethylbenzyl hydroperoxide in acetic acid (Kharasch, Fono, and Nudenberg, *loc. cit.*, p. 124).

Although decalin hydroperoxide was stable in chlorobenzene for several hours at 117°, yet addition of small amounts of acetic acid caused a decomposition of the first order to occur, the rate being approximately dependent on the square-root of the acid concentration. Addition of chloroacetic acids of greater strength caused increased catalysis, and, except for the very strong trichloroacetic acid, there was a linear relationship between $\log K_a$ and $\log k$, as shown by the following table.

The dissociation constants in the table refer to water as solvent at 25°, but their ratios should be the same under the conditions used in this work (Bell, "Acid-Base Catalysis," Oxford, 1941, p. 108). The results are in general agreement with Brønsted's criteria for acid catalysis.

Acid catalysis of the decomposition of decalin hydroperoxide.

Solvent, chlorobenzene. Nitrogen passed through solution. Temp. = 117.2°. Initial concn. of hydroperoxide = 0.0027M.

Acid added	Concn., mole % (m)	K_a for acid	k , min. ⁻¹	\sqrt{m}/k	$[(\log_{10} k) + 1.90]/\log_{10} K$
CH ₃ -CO ₂ H	0.394	1.74×10^{-5}	0.00213	295	0.162
"	1.97	"	0.00601	233	—
"	4.01	"	0.00856	234	—
"	8.19	"	{ 0.0104 0.0101	279	—
CH ₂ Cl-CO ₂ H	0.394	1.38×10^{-3}	0.00433	—	0.162
CHCl ₂ -CO ₂ H	0.394	5.0×10^{-2}	0.00774	—	0.163
CCl ₃ -CO ₂ H	0.394	2.0×10^{-1}	0.0691	—	-1.04

In conclusion, it may be said that homolytic and heterolytic fission of decalin hydroperoxide have been distinguished, and much information on the mechanism of the decomposition obtained, by kinetic measurements, though detailed study of the products formed under various conditions would be required to determine complete reaction schemes.

EXPERIMENTAL

The apparatus and procedure for the kinetic experiments were as described by Tipper (*loc. cit.*). With low initial concentrations, the hydroperoxide content of the samples was determined by the ferrous thiocyanate colorimetric method (Young, Vogt, and Nieuland, *Ind. Eng. Chem. Anal.*, 1936, **8**, 198). This method was used entirely empirically. The ferric compound formed was determined photometrically, the Spekker photometer being calibrated by means of solutions of pure decalin hydroperoxide of known concentration in each particular solvent under investigation. The repeat calibration curves agreed to within 3%. Usually the full colour developed after a minute or two, but when the hydroperoxide was dissolved in nitrobenzene, 15–20 min. were required. When pyridine was used as solvent, it gave a precipitate with the methyl alcohol in which the ferrous thiocyanate was dissolved. This precipitate was filtered off under gravity by means of a coarse, sintered-glass funnel before the depth of colour was measured. With higher initial concentrations the hydroperoxide content was determined by the modified iodometric method of Wagner, Smith, and Peters (*ibid.*, 1947, **19**, 976). Polymerisations were carried out as previously described (Tipper, *loc. cit.*). No polymer was formed under any conditions if no hydroperoxide was present.

Decalin hydroperoxide was prepared from the purified hydrocarbon by Criegee's method (*Ber.*, 1944, **77**, 22). It was found that, if the decalin was oxidised for more than 24 hours at 100°, breakdown products of the hydroperoxide interfered with its separation. It was also found helpful, after shaking the oxidised decalin with sodium hydroxide solution, to shake it with several portions of ethylene glycol as recommended by Cope and Holzmann (*J. Amer. Chem. Soc.*, 1950, **72**, 3062). The crude hydroperoxide was crystallised several times from light petroleum (b. p. 40–60°). The purified product melted at 94–95° and released 98.5–99.5% of the theoretical amount of iodine from acidified sodium iodide. The yield was very small (~0.1–0.2%).

"AnalaR" acetic acid was fractionally distilled with 1% of "AnalaR" anhydride in the presence of nitrogen. Both "AnalaR" and ordinary pyridine were used: they were fractionally distilled twice and then kept at -80° *in vacuo* until required, or were purified by means of the zinc chloride compound (Heap, Jones, and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936). Other solvents were dried if necessary and fractionally distilled twice in the presence of nitrogen. Decalin was passed down a column of activated silica, and *o*-dichlorobenzene was shaken with concentrated sulphuric acid and then water, before this treatment. The purified solvents were protected from atmospheric damp, and to prevent any oxidation the decalin was kept *in vacuo* at -80° and distilled *in vacuo* before each experiment. 1:3:5-Trinitrobenzene and acenaphthene were recrystallised from alcohol, and ethyl chloroformate and dichloroacetic acid were distilled before use. "AnalaR" mono- and tri-chloroacetic acid and "AnalaR" sodium hydroxide were used directly. Nitrogen, oxygen, and acrylonitrile were purified as already described (Tipper, *loc. cit.*).

The author thanks Dr. T. R. Bolam for helpful comments.