# *Kinetics of the Decomposition of Tetralin Hydroperoxide in Acidic and Basic Solvents.*

By (MISS) J. E. HAY, (MISS) N. M. JOHNSTONE, C. F. H. TIPPER, and R. K. WILLIAMS.

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The kinetics of the decomposition of tetralin hydroperoxide have been investigated under conditions which should favour heterolytic fission of the hydroperoxide molecules. The overall decomposition was of the first order at concentrations below 0·2M, and *k* did not depend on the initial concentration. Addition of water increased the rate of reaction in acetic acid and also the overall activation energy. Probably the water tended to suppress a chain reaction occurring in the dry acid. The decomposition was subject to acid catalysis in chlorobenzene solution. Addition of small amounts of sodium hydroxide greatly increased the rate of decomposition in ethylene glycol–water mixture (24 : 1; by vol.), and reduced the overall activation energy from 24·8 to 19·4 kcal. Reaction schemes involving ions are suggested.

With nitrobenzene and pyridine as solvents, however, the decomposition probably does not involve ions.

THE decomposition of tetralin hydroperoxide has been investigated by a number of workers (see Robertson and Waters, *J.*, 1948, 1578, for references). The solvents used were nearly all neutral organic compounds of low dielectric constant. Robertson and Waters (*loc. cit.*), who studied both the kinetics and the products, concluded that in such solvents the decomposition occurred by two simultaneous mechanisms: a molecular re-arrangement, and a split into free radicals followed by an induced chain reaction probably involving solvent radicals. It was suggested, however, that ionic decomposition could occur, especially in the presence of acids. Recently Kharasch and Burt (*J. Org. Chem.*, 1951, **16**, 150) and Kharasch, Fono, Nudenberg, and Bischoff (*ibid.*, 1952, **17**, 207) have investigated the products formed when tetralin hydroperoxide was decomposed in acid or alkaline solution, and have proposed reaction mechanisms involving ionic intermediates. As a complement to this work the kinetics of the decomposition (in an inert atmosphere) under acidic and basic conditions have been studied, iodometric titration or a colorimetric method being used to determine the hydroperoxide.

The plots of log [hydroperoxide] against time were straight lines, up to 75—95% decomposition (as far as the reaction was followed), under nearly all conditions. Fig. 1 shows a selection of the results. The velocity constants were reproducible to within 5%, different samples of hydroperoxide or solvent being used. The initial concentration of hydroperoxide varied but was always less than 0·3M.

As a preliminary, the decomposition in nitrobenzene, a neutral solvent of high dielectric constant, was studied. The rate of reaction became appreciable above 130°, *k* being 1·40, 2·57, and 9·43 × $10^{-3}$ min.$^{-1}$ at 131·2°, 139·6°, and 153·0°, respectively, and an initial concentration of 0·12M. The overall activation energies, calculated for the lower and the higher temperature range, were 24·1 and 33·6 kcal., respectively, as compared with 24·4 kcal. for the decomposition in tetralin (Robertson and Waters, *loc cit.*). The difference is well outside the experimental error and the explanation is not apparent. The % of decomposition in one hour at 116°, calculated by using the lower value of the activation energy, was

3·0%, less than that found by Robertson and Waters (*loc. cit.*) with chlorobenzene as solvent at the same temperature. Thus it seems unlikely that any appreciable ionic decomposition was occurring in nitrobenzene, and no further experiments were performed.

The effect of addition of water on the decomposition in acetic acid is shown in Fig. 2. The use of distilled or undistilled "AnalaR" glacial acetic acid gave identical results, within the experimental error. Addition of up to 5 mole % of water had little effect, but further addition up to about 45—50 mole % greatly increased the rate of decomposition. Still further increase in the water content had no further effect. Change in the initial hydroperoxide concentration from 0·06 to 0·3M caused less than 5% change in the first-order rate constant in aqueous acid containing 3·2 or 67·9 mole % of water, and thus at these relatively low concentrations the decomposition is of the first order. The overall activation energies of decomposition in these two aqueous acids were 18·4 and 20·7 kcal./mole, and the temperature-independent factors were $1·3 \times 10^7$ and $3·1 \times 10^9$ sec.$^{-1}$, respectively (Fig. 3). The addition of 0·76 mole/l. of acrylonitrile to these two solvents caused no appreciable change in the rate of decomposition (Fig. 3), and only small amounts of polymer were formed (0·194 or 0·002 g., severally) during the complete reaction of 20 ml. of 0·06M-hydroperoxide solution in acetic acid containing 3·2 or 67·9 moles % of added water and 10 vol. % of added acrylonitrile.

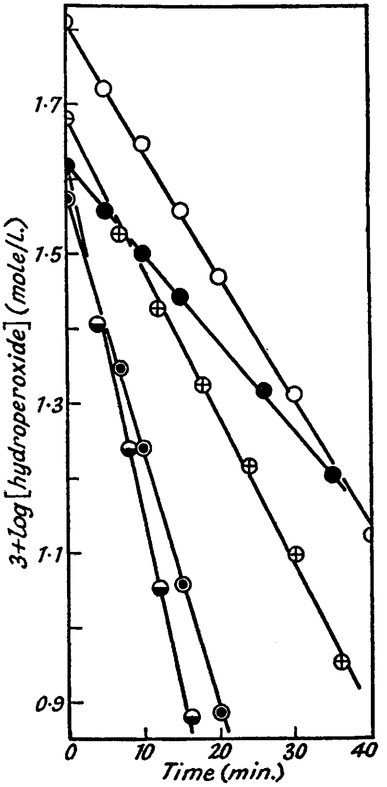


FIG. 1. *Decomposition of tetralin hydroperoxide in various solvents. Nitrogen was passed through the solution.*

○ Solvent, acetic acid + 3·2 mole % of water. Temp. = 114·4°. Initial concn. = 0·065M.

⊕ Solvent, ethylene glycol–water (24 : 1) + 0·02 mole/l. of NaOH. Temp. = 77·7°. Initial concn. = 0·048M.

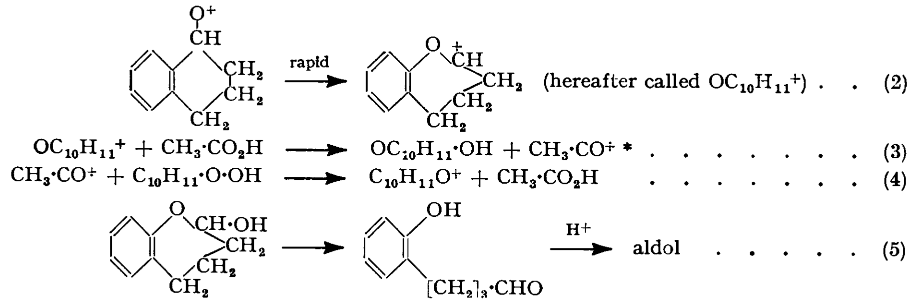
● Solvent, ethylene glycol–water (24 : 1). Temp. = 114·9°. Initial concn. = 0·042M.

⊖ Ordinate + 0·2. Solvent, acetic acid + 67·9 mole % of water. Temp. = 98·9°. Initial concn. = 0·069M.

◉ Ordinate − 1·1. Solvent, chlorobenzene + 0·35M-monochloroacetic acid. Temp. = 115·9°. Initial concn. = 0·003M.

The results show that little free-radical decomposition occurred, and they are similar to those obtained from a study of the decomposition of decalin hydroperoxide in aqueous acetic acid (Tipper, *J.*, 1953, 1675). Probably the explanation of the increase in overall activation energy as well as of *k* as the water content was increased is again that addition of water suppressed an induced ionic chain decomposition. Kharasch and Burt (*loc. cit.*) found that the main product of the decomposition of tetralin hydroperoxide in glacial acetic acid containing 0·1 mole % of perchloric acid was the aldol of γ-(*o*-hydroxyphenyl)butyraldehyde, and Kharasch, Fono, Nudenberg, and Bischoff (*loc. cit.*) state that in dilute solution the reaction was of the first order at 25°. The following simple scheme, which is an adaptation of that proposed by Kharasch and Burt (*loc. cit.*), explains the results quite reasonably.

$$C_{10}H_{11}{\cdot}O{\cdot}OH + H^+ \longrightarrow C_{10}H_{11}O^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$



(hereafter called $OC_{10}H_{11}^+$) . . (2)

$$OC_{10}H_{11}^+ + CH_3{\cdot}CO_2H \longrightarrow OC_{10}H_{11}{\cdot}OH + CH_3{\cdot}CO^+ \,* \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CH_3{\cdot}CO^+ + C_{10}H_{11}{\cdot}O{\cdot}OH \longrightarrow C_{10}H_{11}O^+ + CH_3{\cdot}CO_2H \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

. . . . . (5)

$$\left.\begin{array}{ll} & OC_{10}H_{11}^+ + CH_3{\cdot}CO^+ \longrightarrow \\ \text{or} & OC_{10}H_{11}^+ + C_{10}H_{11}{\cdot}O{\cdot}OH \longrightarrow \\ \text{or} & CH_3{\cdot}CO^+ + C_{10}H_{11}{\cdot}O{\cdot}OH \longrightarrow \end{array}\right\} \text{inert products} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \left\{\begin{array}{l}(6a)\\(6b)\\(6c)\end{array}\right.$$

* The $CH_3{\cdot}CO^+$ ion, once formed, might exist in acetic acid through successive regeneration reactions:

$$CH_3{\cdot}CO^+ + CH_3{\cdot}CO_2H = CH_3{\cdot}CO_2H + CH_3{\cdot}CO^+$$

It being assumed that the concentrations of the $OC_{10}H_{11}^+$ and $CH_3{\cdot}CO^+$ ions were stationary and that the hydrogen-ion concentration was constant, it can be shown that the scheme with equation (6*a*), (6*b*), or (6*c*) as the termination reaction yields a first-order rate expression for the decomposition. The justification for any of the three termination reactions can only be that the correct rate expression is obtained since any products postulated will merely be speculative. Reactions (6*b*) and (6*c*) are perhaps more likely than (6*a*) since the last involves the reaction of similarly charged ions. With higher initial concentrations of the hydroperoxide, reaction of some $OC_{10}H_{11}^+$ ions with undecomposed molecules (7) would be expected to occur as postulated by Kharasch and Burt (*loc. cit.*). This would cause

$$OC_{10}H_{11}^+ + C_{10}H_{11}{\cdot}O{\cdot}OH = OC_{10}H_{11}{\cdot}OH + C_{10}H_{11}O^+ \quad . \; . \; . \; . \; . \quad (7)$$

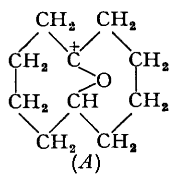
deviation from first order and Kharasch, Fono, Nudenberg, and Bischoff (*loç. cit.*) in fact state that the decomposition of concentrated solutions in acetic acid at 25°, catalysed by perchloric acid, is of the second order. As water was added to the acetic acid reaction (3) was probably progressively replaced by

$$CH_3{\cdot}CO^+ + H_2O = CH_3{\cdot}CO_2H + H^+ \quad . \; . \; . \; . \; . \; . \; . \quad (8a)$$

$$OC_{10}H_{11}^+ + H_2O = OC_{10}H_{11}{\cdot}OH + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8b)$$

leading to the elimination of the chain reaction [cf. Tipper, *loc cit.*, reaction (8)].

A detailed mechanism for the ionic chain decomposition of decalin hydroperoxide in dry acetic acid was not proposed previously (Tipper, *loc. cit.*), but it is quite likely that one exactly similar to the above [excluding reaction (5)] occurred, *A* being the active carbonium ion. If this were so, then the reaction analogous to (7) must have occurred even at fairly low concentrations since the overall order of the decomposition was greater than unity except with very dilute solutions.



(*A*)

The first-order decomposition of tetralin hydroperoxide in chlorobenzene [an average of 13% decomposition in 1 hour at 116° as compared with 10% decomposition reported by Robertson and Waters (*loc. cit.*)] was catalysed by small amounts of acetic acid. The degree of catalysis at 117·3° did not depend on the concentration of acid (up to 0·7M) within the experimental error, in contrast with the results with decalin hydroperoxide, but increased with increasing initial hydroperoxide concentration ($k_{\text{cat.}} = 0{\cdot}0536$ min.$^{-1}$ with 0·05M-hydroperoxide and 0·00567 min.$^{-1}$ with 0·0031M). The overall activation energy of the catalysed part of the decomposition was very roughly 19 kcal./mole ($k_{\text{cat.}} = 0{\cdot}00355$ min.$^{-1}$ at 110·1° and 0·0031M-hydroperoxide). Mono-, di-, and tri-chloroacetic acid were increasingly powerful catalysts, but, since in these cases the rate appeared to depend on the acid concentration, nothing quantitative can be deduced. However the results are in general accord with theoretical expectation.

The decomposition in pyridine at 80—100° was very rapid for the first few minutes and then became slower, and the plot of log of concentration against time became straight. However doubling the initial concentration increased $k$ considerably ($k$ = 0·00357 min.$^{-1}$ with 0·05M and 0·00500 min.$^{-1}$ with 0·10M at 98·9°). The initial rapid decomposition was probably due to traces of impurities, produced by a very small amount of oxidation of the redistilled solvent, since, on leaving this overnight in the presence of air, the initial decomposition was greatly prolonged. The overall activation energy of the uncatalysed decomposition was about 23·5 kcal./mole ($k$ = 0·000560 min.$^{-1}$ at 79·2° and 0·05M initial concentration), and probably the high rate (55% decomposition in 1 hour at 116°) and variation of

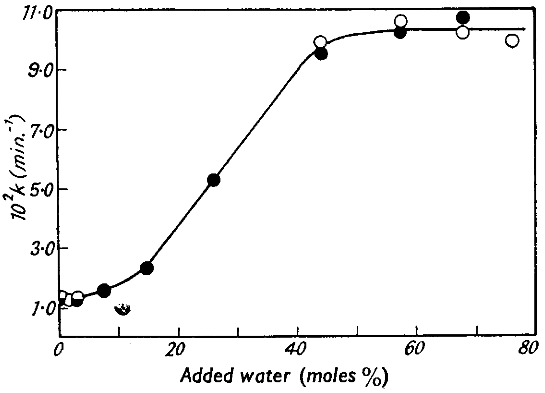
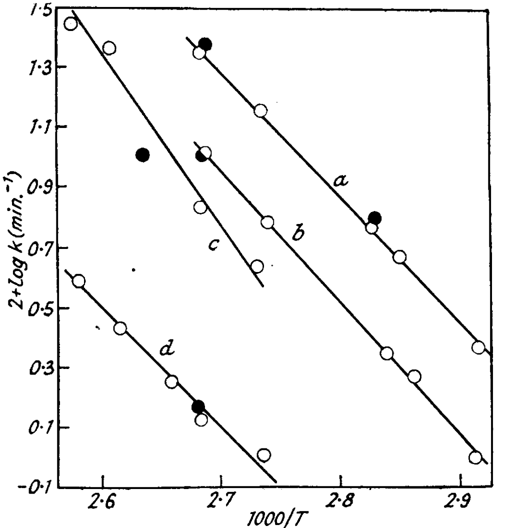


FIG. 2. *Effect of water on the rate of decomposition of tetralin hydroperoxide in acetic acid. Temp.* = 99·5°. *Initial concn.* = 0·122M. *Nitrogen passed through solution.*

● Undistilled "AnalaR" acetic acid.

○ Distilled acid.

FIG. 3. *Effect of temperature on the decomposition of tetralin hydroperoxide. Nitrogen passed through solution.*



● 0·76 mole/l. acrylonitrile added.

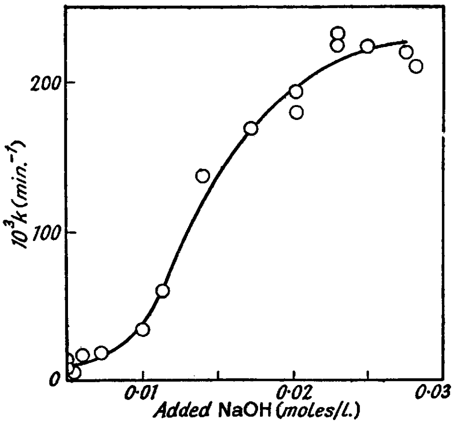
*a*, Solvent, 24/1 ethylene glycol–water mixture + 0·02 mole/l. NaOH. Initial concn. = 0·049M.

*b*, Solvent, acetic acid + 67·9 mole % of water. Initial concn. = 0·061M.

*c*, Solvent, 24 : 1 ethylene glycol–water mixture. Initial concn. = 0·049M.

*d*, Solvent, acetic acid + 3·2 mole % of water. Initial concn. = 0·061M.

FIG. 4. *Effect of sodium hydroxide on the decomposition of tetralin hydroxide in ethylene glycol–water* (24 : 1 *by vol.*). *Temp.* = 99·0°. *Initial concn.* = 0·049M. *Nitrogen passed through solution.*



*k* with initial concentration were due to a rapid free-radical chain reaction as with decalin hydroperoxide.

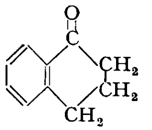
In contrast to the results with decalin hydroperoxide, addition of small amounts of sodium hydroxide to a solution of tetralin hydroperoxide in ethylene glycol–water (4 vol. % of $H_2O$) at 100° caused a very considerable increase in the rate of decomposition (Fig. 4). The velocity constant remained unchanged, within the experimental error, over the range of initial hydroperoxide concentration 0·0375—0·113M, for the decomposition with or without added sodium hydroxide, and thus the reaction is of the first order at least under these conditions. The overall activation energies of decomposition without alkali and with 0·02 mole/l. of sodium hydroxide were 24·8 and 19·4 kcal./mole, respectively (Fig. 3). Addition of 0·76 mole/l. of acrylonitrile retarded the reaction in the neutral alcohol–water mixture (Fig. 3) and 1·29 g. of polymer were formed during the complete reaction of 25 ml. of 0·05M-hydroperoxide solution containing 8 vol. % of the monomer. Probably a free-radical chain reaction was occurring. However, in the presence of 0·02 mole/l. of sodium hydroxide, acrylonitrile caused no retardation (Fig. 3), and no polymer was precipitated. Obviously no free radicals were present during the decomposition in an alkaline medium.

It has been known for some time that aqueous sodium hydroxide decomposes tetralin hydroperoxide, and Kharasch, Fono, Nudenberg, and Bischoff (*loc. cit.*) found that in concentrated alkali the rate was rapid at 25°. Water, tetralone, and higher oxidation products were formed by using *tert.*-butyl alcohol as the solvent. Probably the $C_{10}H_{11}O{\cdot}O^-$ ion was formed in the initial step:

$$C_{10}H_{11}{\cdot}O{\cdot}OH + OH^- \longrightarrow C_{10}H_{11}O{\cdot}O^- + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

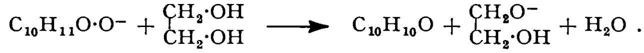
followed by

$$C_{10}H_{11}O{\cdot}O^- \longrightarrow$$

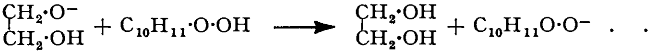


$$+ \ OH^-\ * \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or if an induced chain decomposition was occurring then the following reactions might possibly have been in competition with (10).



$$C_{10}H_{11}O{\cdot}O^- + \begin{matrix}CH_2{\cdot}OH\\ CH_2{\cdot}OH\end{matrix} \longrightarrow C_{10}H_{10}O + \begin{matrix}CH_2O^-\\ CH_2{\cdot}OH\end{matrix} + H_2O \quad . \quad . \quad . \quad . \quad (11)$$



$$\begin{matrix}CH_2{\cdot}O^-\\ CH_2{\cdot}OH\end{matrix} + C_{10}H_{11}{\cdot}O{\cdot}OH \longrightarrow \begin{matrix}CH_2{\cdot}OH\\ CH_2{\cdot}OH\end{matrix} + C_{10}H_{11}O{\cdot}O^- \quad . \quad . \quad . \quad . \quad . \quad (12)$$

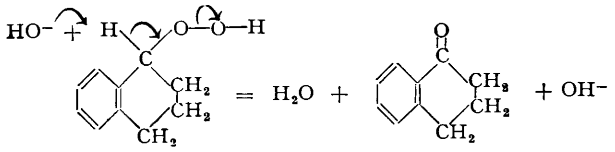
Thus it is probably not permissible to associate the activation energy of 19·4 kcal. with reaction (9).

## EXPERIMENTAL

The kinetics of the decomposition were studied as described previously (Tipper, *J.*, 1952, **2966**). The hydroperoxide was determined by the iodometric method of Wagner, Smith, and Peters (*Ind. Eng. Chem. Anal.*, 1947, **19**, 976) or by the ferrous thiocyanate method (Tipper, *loc. cit.*).

Tetralin hydroperoxide was prepared by the oxidation of tetralin for 12—18 hr. at 100°. Unchanged hydrocarbon was distilled off, the syrup remaining was left in the refrigerator for several days, and the solid was then filtered off. The crude hydroperoxide was recrystallised at least three times from light petroleum (b. p. 40—60°). The final product melted at 55°, and released 97—99% of the theoretical quantity of iodine from acidified potassium iodide.

* A referee has suggested that the formation of tetralone directly (*i.e.* not by a chain mechanism) is better expressed by



Then any $C_{10}H_{11}O{\cdot}O^-$ ions formed would have reacted by (11).

"AnalaR" sodium hydroxide and "AnalaR" mono- and tri-chloroacetic acid were used directly. "AnalaR" acetic acid and dichloroacetic acid were fractionally distilled once, and nitrobenzene, chlorobenzene, ethylene glycol, and "AnalaR" pyridine twice, in a stream of nitrogen.

The amount of polymerisation of acrylonitrile was determined as before (Tipper, *J.*, 1952, 2966).

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CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH.
[Present address (C. F. H. T.): DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY, LIVERPOOL.]

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