895. *The Thermal Decomposition of* cyclo*Hexenyl Hydroperoxide in Hydrocarbon Solvents.*

By L. Bateman and (Mrs.) Hilda Hughes.

Kinetic and product data on the thermal decomposition of *cyclo*hexenyl hydroperoxide in benzene and in various olefins in the concentration range 0·03—1·4M are reported. In the olefins, decomposition proceeds by a chain mechanism involving the solvent, and characterized by an initiation step which is of the second order with respect to the peroxide. In benzene, the chain process is almost completely suppressed and the decomposition approximates to a one-stage second-order reaction. Earlier conclusions concerning the initiation step in olefinic autoxidations under similar concentration conditions are thus verified. Reference is made to work revealing that at concentrations lower than specified above alkenyl hydroperoxides decompose largely by a first-order process, and it is argued that this rather unique change in reaction order with concentration expresses the different decomposition tendencies of associated and unassociated O_2H groups.

Detailed information on liquid-phase hydroperoxide decompositions remains meagre, despite its especial significance to hydrocarbon autoxidations. Methyl (Medvedev and Podyapolskaya, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 487), *tert.*-butyl (Bell, Raley, Rust, Seubold, and Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 242), *cyclo*hexyl (Farkas and Passaglia, *J. Amer. Chem. Soc.*, 1950, **72**, 3333), and tetralyl (Yamada, *J. Soc. Chem. Ind. Japan*, 1936, **39**, 450; Ivanov, Saminova, and Mikhailova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 34; Robertson and Waters, *J.*, 1948, 1578) hydroperoxides exhibit complex kinetic behaviour, which has been interpreted generally in terms of a composite process similar to that recognized for diperoxides, *viz.*, a primary *unimolecular* scission accompanied by decomposition induced by radical attack on the peroxide. This interpretation is supported by the claim that the order of the reaction, normally between 1 and 2, tends nearer to 1 as the initial peroxide concentration is reduced and the conditions for induced decomposition become less favourable. In the systems *tert.*-butyl hydroperoxide–benzyl alcohol (Stannett and Mesrobian, *J. Amer. Chem. Soc.*, 1950, **72**, 4125) and cumyl hydroperoxide–1-phenylethanol (Kharasch, Fono, and Nudenburg, *J. Org. Chem.*, 1951, **16**, 113), the solvent is thought to participate in the primary reaction.

The kinetics of oxidizing olefins, on the other hand, imply that allylic hydroperoxides at concentrations greater than about 0·02M yield radicals *via* a *bimolecular* process (Bolland, *Quart. Reviews*, 1949, **3**, 1). This implication is not necessarily inconsistent with the other conclusions because of differences in hydroperoxide type and in environment, and because of the relative crudity of much of the direct kinetic data. Its validity requires to be tested by a thorough study of the decomposition of an allylic hydroperoxide under comparable conditions to those employed in the autoxidation experiments. The decomposition of *cyclo*hex-2-enyl hydroperoxide in *cyclo*hexene at 60—80° has thus been examined. To check the main conclusions, similar reactions in oct-1-ene, acyclic 1 : 4-dienes, and in benzene, have also been investigated. The choice of hydroperoxide was dictated (i) by the fact that the symmetry of the parent olefin leads unequivocally to the formation of a homogeneous hydroperoxide on oxidation (at least two isomers can be formed from symmetrical acyclic mono-olefins as a consequence of allyl-radical mesomerism, while 1-methyl*cyclo*hexene, for example, possibly yields five—see Bolland, *Trans. Faraday Soc.*, 1950, **46**, 358); (ii) by the absence of inhibitory or catalytic substances among its decomposition products (contrast, *e.g.*, tetralyl hydroperoxide); and (iii) by reports (since discovered to be erroneous) of isolation of the hydroperoxide in pure form.

Experimental

Materials.—Immediately before use, all solvents, either neat or in light petroleum (b. p. <40°), were run through an alumina column to remove any traces of peroxide.

cyclo*Hexene.* A laboratory sample, shaken with aqueous ferrous sulphate, dried ($CaCl_2$, then Na), and fractionated through a Fenske column, had b. p. 81·5°/763 mm., n_D^{16} 1·4490.

Benzene. The " AnalaR " grade was refluxed over Raney nickel for 1·5 hours, then filtered, dried, and fractionated from sodium; it had b. p. 79·3—79·4°/755 mm., n_D^{22} 1·4990.

Oct-1-*ene.* See Bateman and Cunneen (*J.*, 1950, 941).

2 : 6-*Dimethylhepta*-2 : 5-*diene.* This olefin, b. p. 150—151°/758 mm., n_D^{20} 1·4490, was kindly supplied by Dr. J. I. Cunneen (Bateman, Cunneen, and Waight, *J.*, 1952, 1714). Its intense oxidizability necessitates especial care in storage.

Ethyl linoleate. Crude linoleic acid from cotton-seed oil was purified *via* its crystalline tetrabromide, m. p. 115·5° (Found : Br, 52·9, 53·6. Calc. for $C_{18}H_{32}O_2Br_4$: Br, 53·3%). The acid regenerated after debromination with *powdered* zinc in ethanol was esterified (hydrogen chloride), and the yellow product in light petroleum solution was run through an alumina column to remove any free acid and oxidized material. The recovered, colourless ester had n_D^{20} 1·4600 (lit., n_D^{25} 1·4582, n_D^{30} 1·4562) (Found : C, 77·9; H, 11·9. Calc. for $C_{20}H_{36}O_2$: C, 77·9; H, 11·8%). Spectroscopic examination revealed the presence of traces of hydroxyl and conjugated triene and tetraene groups, but no conjugated diene. Further selective chromatography reduced these impurities to negligible proportions.

cyclo*Hex*-2-*enyl hydroperoxide.* (*a*) From the photo-oxidation of *cyclo*hexene. *cyclo*Hexene (200 g.) in a silica flask connected to an oxygen reservoir was irradiated with an S.500 Hanovia mercury-arc lamp and shaken for 6 hours at the ambient temperature; *ca.* 7% of oxygen was absorbed. The product, on short-path distillation at 20° and 10^{-3}—10^{-4} mm. to a condenser at 0°, gave fractions : (i) n_D^{20} 1·4902, peroxidic O * (determined iodometrically, see below) 27·9, (by direct combustion) 27·2, 27·4% (Calc. for $C_6H_{10}O_2$: O, 28·0%); (ii) n_D^{20} 1·4903, peroxidic O, 28·0%. Analyses for carbon and hydrogen showed these fractions not to have the purity indicated by the peroxidic oxygen determinations [Found for (ii) : C, 64·0, 64·4; H, 8·95, 8·85. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%]. This finding conflicts with earlier reports (Farmer and Sundralingham, *J.*, 1942, 121) but has been confirmed by Barnard and Hargrave (*Analyt. Chim. Acta*, 1951, **5**, 476), who have shown that such peroxide samples are 85% pure.

(*b*) From the thermal oxidation of *cyclo*hexene. The olefin was stirred in the dark at 55° under efficient condensing conditions, and dry oxygen passed over the liquid surface for 24 hours. The hydroperoxide (n_D^{20} 1·4901) was isolated as under (*a*) [Found : C, 63·3; H, 8·9; peroxidic O (iodometric), 32·0%]. Barnard and Hargrave (*loc. cit.*) estimate the purity of similar samples as 96% by their stannous chloride method. This figure is not raised appreciably by fractionation, partial steam-distillation, and chromatography. The nature of the impurity is obscure; it cannot be simply *cyclo*hex-2-enol, di*cyclo*hex-2-enyl ether, or di*cyclo*hex-2-enyl peroxide. It is evidently inert under the present decomposition conditions, since hydroperoxide samples containing different proportions decomposed at equivalent rates.

Peroxide Estimations.—*Iodometric method.* To the sample in 10 ml. of a 3 : 2 mixture of acetic acid and carbon tetrachloride was added 1 ml. of a 5% solution of potassium iodide in methanol, and the mixture kept stoppered in the dark for 20 minutes; water (20 ml.) was added, and the liberated iodine titrated with 0·002N-sodium thiosulphate (starch).

The analyses recorded above for the *cyclo*hexenyl hydroperoxide preparations point to high estimates' being obtained by this method. Its stoicheiometry was therefore investigated by comparing such estimates with oxygen absorptions accurately measured during the oxidation of *cyclo*hexene :

Oxygen uptake, % w/w (*A*)	Peroxidic oxygen, % w/w (*B*)	*B*/*A*, %
0·58	$0·66_5$, $0·65_4$, $0·66_3$	114
0·29	$0·33_6$, $0·33_5$	116

The value of *B*/*A* agree closely with the ratio of estimated/theoretical peroxide content given for the peroxide in (*b*) above. The cause of this discrepancy—which has been confirmed by the development of a truly stoicheiometric analytical method (Barnard and Hargrave, *loc. cit.*)—is unknown, but depends on the presence of oxygen (low values being obtained in its absence). However, in view of the experimental convenience, sensitivity, and reproducibility of the iodometric determinations, and the fact that numerous blank experiments showed the stoicheiometric correcting factor to be constant over a wide range of concentration, the routine peroxide analyses in the present work were carried out by the iodometric method, and a correcting factor of 100/115 applied.

Rate Measurements.—Approximately 0·1-ml. portions of the peroxide solution of known concentration (in the range 0·03—1·40M) were introduced into the bottom of weighed Pyrex

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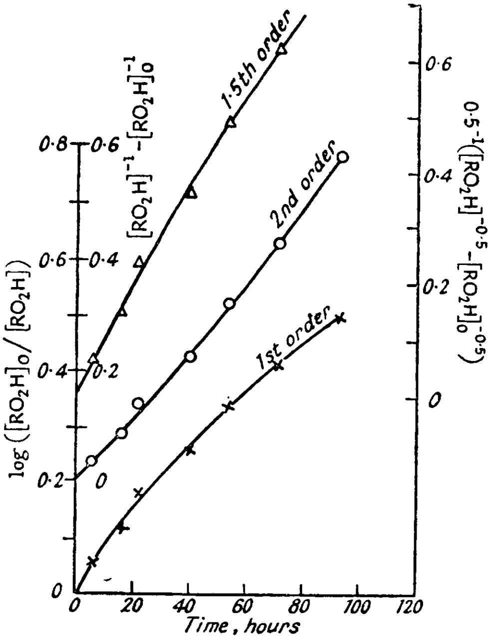
* Throughout this paper, peroxidic oxygen designates both oxygen atoms in RO_2H or RO_2R.

tubes, in such a way as to avoid contamination at a constriction. After being reweighed and de-gassed, the tubes were sealed under a vacuum. Two were retained for " initial " peroxide estimations, and the remainder heated for different times in a thermostat regulated to ±0·02°. Scrupulous attention to the filling, sealing, and cleanliness of the reaction tubes was essential; they were scrubbed and rinsed several times with distilled water (not with acid cleaning mixtures), then with dry acetone, and vacuum-dried. The extents of decomposition were determined by dissolving the contents in carbon tetrachloride, and carrying out iodometric estimations on aliquot portions as described above.

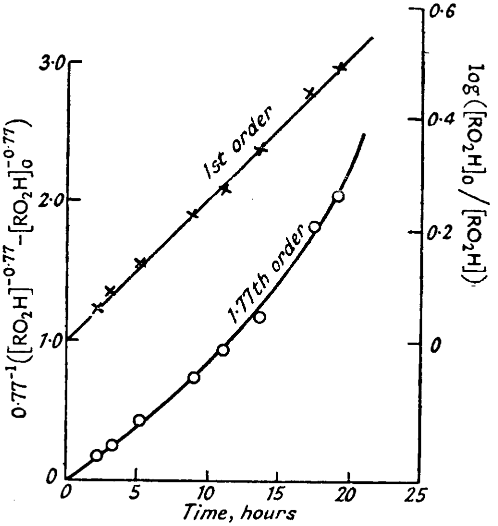
Determination of Reaction Order.—A plot of the extent of decomposition against time for *cyclo*hexenyl hydroperoxide in *cyclo*hexene yields a smooth conventional-type curve up to about 70% decomposition, whereat an anomalous increase in rate occurs. This change undoubtedly reveals a departure from a homogeneous reaction since the solution concurrently develops an opaqueness due to separation of water. Plots of such data in accordance with first-, three-halves-, and second-order relationships are shown in Fig. 1. Such representation, as used by previous workers (p. 4594), evidently lacks sensitivity for precise definition and the following procedure was therefore adopted :

FIG. 1.



[RO$_2$H] *units:* % *peroxide oxygen* (w/w).

FIG. 2.



[RO$_2$H] *units:* % *peroxide oxygen* (w/w).

Four or more extents of decomposition less than 30% were measured and expressed according to the first- and second-order rate equations, $k_1t = \ln [RO_2H]_0/[RO_2H]$ and $k_2t = [RO_2H]^{-1} - [RO_2H]_0^{-1}$, respectively, where $[RO_2H]_0$ and $[RO_2H]$ represent the peroxide concentrations initially and at time t, respectively, and the corresponding initial rates $k_1[RO_2H]_0$ and $k_2[RO_2H]_0^2$ were calculated. The slope of the linear plot of log (initial rate) against log $[RO_2H]_0$ then gives the true order of the reaction. Some typical data given in Table 1 illustrate that the initial rates thus determined are largely insensitive to the assumed order of reaction (1 or 2). Similar insensitivity extends to the derived true order, plots based on assumed orders of 1 and 2 yielding values of the true order of 1·78 and 1·76, respectively. These plots appear linear over the concentration range covered. Since, from the above, $-d[RO_2H]/dt = k[RO_2H]^{1\cdot77}$, a plot of $0{\cdot}77^{-1}([RO_2H]^{-0\cdot77} - [RO_2H]_0^{-0\cdot77})$ against t should be linear, and the data given in Fig. 1 fulfil this condition accurately up to 70% decomposition.

The order of the decomposition in benzene was determined similarly. For oct-1-ene and

2 : 6-dimethylhepta-2 : 5-diene, less precise but sufficiently definite values were deduced from careful measurements of the overall decomposition.

TABLE 1.

$[RO_2H]_0$, % (w/w)	Velocity constant 10$^3k_1$ (hr.$^{-1}$)	 10$^3k_2$ (% peroxidic oxygen^{-1}/hr.)	10^3 × Initial rate Calc. from k_1 (% peroxidic oxygen/hr.)	 Calc. from k_2
5·39	6·2	1·3	33	37
3·57	3·5	1·0	12	13
3·55	4·2	1·4	14	16
2·27	3·8	1·8	8·7	9·8
1·71	2·3	1·5	4·0	4·4
0·898	1·7	2·0	1·6	1·6
0·433	0·82	2·1	0·36	0·41
0·147	0·33	2·6	0·049	0·056

Kinetic Results.—Data not given elsewhere in the paper are summarized below.

(i) *Temperature coefficient of the decomposition rate in* cyclo*hexene.* At 60° k = 5·2 × 10^{-3}; at 80° k = 2·1 × 10^{-2} mole$^{-0\cdot7}$ l.$^{0\cdot7}$ hr.$^{-1}$. The derived Arrhenius activation energy is 16·5 kcal., which, however, is without quantitative significance owing to the narrow temperature range and the non-linear relationship between log k and $1/T$ implied in general (see scheme on p. 4599).

(ii) *General rate expression for the decomposition in benzene.* At 80°, k = 5·0 × 10^{-3}; at 100°, k = 3·7 × 10^{-2} mole^{-1} l. hr.$^{-1}$. Hence, $k = 6\cdot5 \times 10^{13} \exp(-26{,}000/\boldsymbol{R}T)$ mole^{-1} l. hr.$^{-1}$. Here, the E term possesses its ordinary significance.

(iii) *Effect of air on the decomposition in benzene.* For decompositions carried out in air at 100°, k = 4·8 × 10^{-2} mole^{-1} l. hr.$^{-1}$.

(iv) *Effect of powdered glass on the decomposition in benzene.* Powdered glass of surface area 3800 cm.^{2}/g. was washed several times with hot distilled water, then with purified acetone, and dried in a vacuum, 50-mg. portions added to the reaction mixture thus increasing the surface area about 100-fold. At 100°, k = 3·8 × 10^{-2} mole^{-1} l. hr.$^{-1}$, *i.e.*, practically identical with that found in (ii) above.

Products of the Decomposition of cyclo*Hexenyl Hydroperoxide in* cyclo*Hexene.*—Farmer and Sundralingam (*loc. cit.*) isolated *cyclo*hex-2-enol as the principal volatile product from the decomposition of the hydroperoxide in *cyclo*hexene at 100°. Their yield was only 59% and much dimeric or similar material was formed, possibly because of the highly concentrated solution employed (50%) and possibly because of secondary reactions occurring during the isolation process. The first difficulty being avoided, the second may be eliminated by using an analytical procedure based on the different infra-red absorptions by the unassociated OH groups in *cyclo*hexenol and *cyclo*hexenyl hydroperoxide. In carbon tetrachloride solution (*ca.* 1%), the characteristic absorptions at 3600 and 3540 cm.$^{-1}$, respectively, are distinctively resolved by a lithium fluoride prism.

The peroxide (1·1M) in *cyclo*hexene was heated at 80° for 51 hours, its concentration then having been reduced to 0·46M. An aliquot portion of the solution was diluted about 10-fold by carbon tetrachloride, and the absorption intensity at 3600 cm.$^{-1}$ measured quantitatively. By comparison with appropriate calibration curves, the *cyclo*hexenol content was estimated as 0·83M (±0·05), *i.e.*, 130% yield on the peroxide decomposed. This estimate is a minimum, however, since absorption at 3300 cm.$^{-1}$ (sodium chloride prism) is indicative of some associated OH groups also being present (not from water). The reaction mechanism advanced later (p. 4599) requires a yield of about 180% for the chain length probably applicable.

Products of the Decomposition of cyclo*Hexenyl Hydroperoxide in Benzene.*—(1) *Identification of* cyclo*hex-2-enone and* cyclo*hex-2-enol.* A 15·6% solution of the hydroperoxide in benzene (28·5 g.) was sealed under vacuum and heated at 100° for 42 hours, 63% decomposition then having occurred. The solution was pale yellow and water had separated. After drying (Na_2SO_4), the benzene was evaporated at 0·1 mm. and condensed in a trap at −78°. Infra-red analysis showed the condensate to be benzene containing traces of a carbonyl compound. The remaining product gave the following fractions : (i) b. p. <29°/0·06 mm., 0·50 g., $\lambda_{\max.}$ 2240 Å, $E^{1\%}_{1\,\mathrm{cm}}$ 870, $\lambda_{\max.}$ 3210 Å, $E^{1\%}_{1\,\mathrm{cm.}}$ 2·55 (Found : C, 73·2 ; H, 9·0% ; *M*, 112, 105. Calc. for C_6H_8O : C, 75·0 ; H, 8·3% ; *M*, 96. Calc. for $C_6H_{10}O$: C, 73·5 ; H, 10·2% ; *M*, 98. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·9%; *M*, 114); (ii) b. p. 29—33°/0·06 mm., 0·32 g., $\lambda_{\max.}$ 2260 Å, $E^{1\%}_{1\,\mathrm{cm.}}$ 567, $\lambda_{\max.}$ 3200 Å, $E^{1\%}_{1\,\mathrm{cm.}}$ 1·82 (Found : C, 72·9; H, 9·2%); (iii) b. p. 33—49°/0·06 mm., 0·19 g.; (iv) b. p. 49—54°/0·06 mm., 0·67 g. (Found : C, 64·5; H, 8·9%); (v) b. p.

54—60°/0·06 mm., 0·59 g. (Found: C, 63·9; H, 9·3%); (vi) residue, 1·3 g. (Found: C, 61·2; H, 8·2%; *M*, 204). Short-path distillation of (vi) gave a product having C, 59·2; H, 8·8%. In terms of *cyclo*hexenyl hydroperoxide, the peroxide contents were (i) 1·3%; (iii) 25·8%; (iv) 84·0%; (v) 81·0%; (vi) 15·0%. Fractions (i) and (ii) reduced ammoniacal silver nitrate in the cold and Fehling's solution on warming; they did not react with dimedone; they gave an orange 2 : 4-dinitrophenylhydrazone, m. p.s and mixed m. p. 159—160°, which on repeated crystallization from aqueous ethanol was raised to 161° (Found: C, 52·2; H, 4·4; N, 20·6. Calc. for $C_{12}H_{12}O_4N_4$: C, 52·2; H, 4·4; N, 20·3%); they yielded an oxime, m. p. 87—89°. The carbonyl-containing material is thus identified as *cyclo*hex-2-enone. Paper chromatography of the crude 2 : 4-dinitrophenylhydrazone indicated it to be homogeneous. The analytical data suggest that it is probably contaminated with *cyclo*hexenol, and spectroscopic examination confirmed this. The pure ketone has $\lambda_{max.}$ 2245 Å, $E^{1\%}_{1\,cm.}$ 1134, $\lambda_{max.}$ 3200 Å, $E^{1\%}_{1\,cm.}$ 3·6; hence its concentration in fractions (i) and (ii) is estimated to be 77 and 50%, respectively. The infra-red spectra of the fractions revealed that hydroxyl groups were present, and the spectrum of (i) was found to be almost identical with that of a synthetic mixture of the ketone (70%) and alcohol (30%). Finally, fraction (i) yielded the α-naphthylurethane of *cyclo*hex-2-enol, m. p. and mixed m. p. 155—156°. The nature of (vi) was not determined: its infra-red spectrum had an absorption band at 1710 cm.$^{-1}$, possibly indicative of an unconjugated carbonyl compound, but no 2 : 4-dinitrophenylhydrazone could be prepared.

(2) *Estimation of the water produced.* 7·501 G. of a 13·8% solution of the hydroperoxide in benzene was decomposed to the extent of 23·3% as described under (1). The solution was then transferred quantitatively to an all-glass distillation unit in which the only detachable joints were from an 8-cm. column above the flask (125 ml.) to a condenser and from the condenser outlet to the titration vessel of a Mullard–B.T.L. potentiometric titration apparatus. Dry nitrogen was passed through a bubbler sealed into the flask and the receiver was protected from moisture. After the addition of dry benzene (100 ml.), the mixture was boiled until 25 ml. of distillate had been collected—the decomposition of the peroxide during this process being negligible. Any water remaining in the condenser was washed into the titration vessel with 8 ml. of dry methanol, a small excess of Karl Fischer reagent added, and the solution back titrated with a standard solution of water in dry methanol (Wernimont and Hopkinson, *Analyt. Chem.*, 1943, **15**, 272). Total amount of water estimated: 23·6 mg. Blank experiments with solutions containing the amount of hydroperoxide undecomposed in the above experiment gave values of 5·1 and 8·7 mg. Hence, amount of water formed = 17 mg./2·12 × 10^{-3} mole = 0·44 mole/mole of peroxide decomposed. A repeat of the experiment exactly duplicated this result.

(3) *Estimation of the oxygen evolved.* 1·03 G. of a 14·0% solution of the peroxide in benzene were introduced into a tube apparatus containing an internal breakable seal. After evacuation, the tube was sealed and heated at 100° for 19 hours. It was then connected to a vacuum line and, after appropriate evacuation, the breakable seal was broken by a steel ball. The solution was de-gassed in the usual way, the pressure measured on a McLeod gauge, and the peroxide content of the solution subsequently determined. Oxygen evolved = 4·53 × 10^{-5} mole/4·03 × 10^{-4} mole = 0·11 mole/mole of peroxide decomposed.

(4) *Product balance.* The above experiments lead to the following approximate product balance:

	*cyclo*Hex-2-enone	*cyclo*Hex-2-enol	Oxygen	Water	Residue
%, w/w	25	11	3	7	47
%, mole/mole	30	13	11	44	27 *

* *M* being taken as 200.

(5) *Examination for phenol.* A solution of the peroxide (0·200 g.) in benzene (1·411 g.) was decomposed to the extent of 26·8% as described under (1). 0·5 Ml. of the solution was extracted with two 1-ml. portions of 10% aqueous sodium hydroxide, the extract acidified (hydrochloric acid), and bromine water added: no precipitate was formed. In a blank experiment, 0·25 ml. of a 13·5% solution of the peroxide in benzene containing 0·09% w/w of phenol when treated as above gave a precipitate of tribromophenol, but 0·1 ml. did not. Hence, phenol present in the decomposition mixture is <0·05% w/w, *i.e.*, is <0·0005 mole/100 g. The peroxide decomposed = 0·029 mole/100 g.; therefore, phenol formation is <0·02 mole/mole of peroxide decomposed.

(6) *Examination for diphenyl.* Measurement of the absorption intensity at 2510 Å, rather than at the peak wave-length, 2490 Å, allows diphenyl to be estimated in the presence of benzene

(the respective $E^{1\%}_{1\,\text{cm.}}$ are 1126 and 9·1). A 14% solution of the peroxide in benzene, 88 mg. in 100 ml. of ethanol having $E^{1\%}_{1\,\text{cm}} = 0{\cdot}715$, was decomposed to the extent of 32·5% as described under (1), and 101 mg. in 100 ml. of ethanol then had $E^{1\%}_{1\,\text{cm.}} = 0{\cdot}869$. On the assumption that the increased absorption is due entirely to diphenyl, 0·04% is present in the heated solution, *i.e.*, <0·01 mole/mole of peroxide decomposed.

Development of Conjugation during the Decomposition of cyclo*Hexenyl Hydroperoxide in* 1 : 4-*Dienes*.—(a) *In* 2 : 6-*dimethylhepta*-2 : 5-*diene*. 0·1 G. of a 0·91M-solution was heated at 80° under vacuum for 3 hours, the extent of decomposition then being 37·6% ($4{\cdot}3 \times 10^{-5}$ mole). The heated solution showed maximal ultra-violet absorption at 2370 Å. The difference in $E^{1\%}_{1\,\text{cm.}}$ at this wave-length between the heated and unheated solutions was 37·8. ε for $CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}$ groups being taken as 25,000, and thus $E^{1\%}_{1\,\text{cm}}$ as 2030, the number of these groups produced = $(37{\cdot}8/2030) \times (0{\cdot}1/123) \times (100/87) = 1{\cdot}74 \times 10^{-5}$ mole-units, *i.e.*, 40% of the O_2H groups decomposed.

(b) *In ethyl linoleate*. 3·2 G. of a 1·0M-solution were heated at 60° under vacuum for 162 hours, $8{\cdot}0 \times 10^{-4}$ mole of the peroxide then having decomposed. The peak absorption intensity developed at 2330 Å corresponded to an increase in $E^{1\%}_{1\,\text{cm.}}$ of 23, giving the number of $\cdot CH{:}CH{\cdot}CH{:}CH{\cdot}CH\cdot$ groups produced as $3{\cdot}2 \times 10^{-4}$ mole-units, *i.e.*, 40% of the O_2H groups decomposed. A portion of the heated solution was transferred to a small still fitted with a " cold finger " containing liquid oxygen. On gentle agitation of the solution magnetically and evacuation to 10^{-5} mm., the volatile decomposition products and most of the residual hydroperoxide, but not the linoleate compounds, condensed on the cold finger (as determined by trial experiment). After 48 hours, when further distillation was undetectable, the hydroxylated residue was dissolved in petrol (b. p. 40—60°; 50 ml.) and run through a 12-cm. alumina column, which was subsequently washed with more solvent (100 ml.). The two recovered solutions were mixed, and the solvent was removed under vacuum to yield a residue free from conjugated diene units and with a barely detectable hydroxyl content.

DISCUSSION

The decomposition in *cyclo*hexene is characterized by (i) the reaction order of 1·77, (ii) the inappreciable variation in this order over the concentration range studied, and (iii) the formation of *cyclo*hex-2-enol as the major product. The following reaction scheme is in accord with these features :

$$\begin{array}{rl} 2RO_2H \longrightarrow & RO\cdot + RO_2\cdot + H_2O \\ RO\cdot + R'H \longrightarrow & ROH + R'\cdot \\ R'\cdot + RO_2H \longrightarrow & R'OH + RO\cdot \end{array} \qquad \left.\begin{array}{r} 2R' \longrightarrow \\ R'\cdot + RO\cdot \longrightarrow \\ 2RO\cdot \longrightarrow \end{array}\right\}\begin{array}{l}\text{Inactive}\\ \text{products}\end{array}$$

where $R = C_6H_9$ and R'H denotes the solvent (for *cyclo*hexene, R' = R). The $RO_2\cdot$ radical is considered to react analogously to RO· with R'H, this being without effect on the overall reaction order.

This scheme is also in accord with the variation in decomposition rates and reaction orders on replacing *cyclo*hexene by other olefins and by benzene (Table 2). In benzene, the chain process is practically suppressed; in the olefins, the lack of equivalence between the lability of H in R'H, as expressed by k_3, the velocity coefficient of the reaction $RO_2\cdot + R'H \longrightarrow RO_2H + R'\cdot$, and the corresponding decomposition rates, together with the order changes, indicate that the two propagation reactions proceed with comparable facility, with the first one tending to be rate-determining with olefins having low k_3 values,

TABLE 2. *Decomposition of* cyclo*hexenyl hydroperoxide in hydrocarbons at* 80°.

Solvent	$[RO_2H]$ (mole/l.)	Order	Decompn. rate at 1M (10^3 mole l.$^{-1}$ hr.$^{-1}$)	k_3 (80°) (mole^{-1} l. sec.$^{-1}$)
Benzene	0·90	$1{\cdot}9_5$	5	—
Oct-1-ene	0·94	1·5	12	1·2
*cyclo*Hexene	0·89	$1{\cdot}7_7$	21	7·9
2 : 6-Dimethylhepta-2 : 5-diene	0·83	2·0	200	320

the second with those having high values. Consideration of both kinetic and product data is essential in arriving at these conclusions.

The Primary Decomposition Reaction.—The most important conclusion from our work is that the primary generation of radicals occurs in a reaction of the second-order with respect to the hydroperoxide within the concentration range investigated. Direct confirmation is thus obtained that the observed rate equation for the autoxidation of an olefin containing hydroperoxide at an approximately similar concentration, $r = \text{const.} \times [RO_2H]$, maintains consistency with the theoretical equation, $r = \text{const.} \times \sqrt{r_i}$, by being of the form $r = \text{const.} \times \sqrt{\text{const.} \times [RO_2H]^2}$, where r is the rate of oxidation and r_i is the rate of chain initiation (cf. p. 4594). Since analogous oxidations catalysed by light (Bateman and Gee, *Proc. Roy. Soc.*, 1948, *A*, **195**, 376) and by the unimolecularly dissociating substances benzoyl peroxide (Bolland, *Trans. Faraday Soc.*, 1948, **44**, 669) and azobis(*iso*butyronitrile) (Bateman, Gee, Morris, and Watson, *loc. cit.*) also conform to the theoretical equation, its completely general validity cannot be in doubt. Accordingly, the recent finding that in olefins containing hydroperoxides at lower concentrations than considered above the applicable rate equation is $r = \text{const.} \times [RO_2H]^{\frac{1}{2}}$ is indicative of initiating radicals' being evolved from the peroxide in a *first-order* reaction (Bateman, Hughes, and Morris, *Discuss. Faraday Soc.*, in the press). In considering the nature of the primary decomposition process, therefore, it is necessary to reckon with this unique change in reaction order with concentration. The clue to the basis of this behaviour is thought to be contained in Fig. 3, which shows the changes in the infra-red spectrum of *cyclo*hexenyl hydroperoxide on successive dilution in benzene. In the neat peroxide the OH groups appear entirely in hydrogen-bonded complexes (broad absorption about 3350 cm.$^{-1}$), which dissociate progressively on dilution until at concentrations less than *ca.* 0·05M only unbonded groups are detectable (absorption at 3500 cm.$^{-1}$). Thus it is deduced that the kinetic form of the primary decomposition act at *low concentration* relates to the *unimolecular* scission of the hydroperoxide *monomer*, but *at high concentration* to the *unimolecular* scission of the hydroperoxide *dimer* :

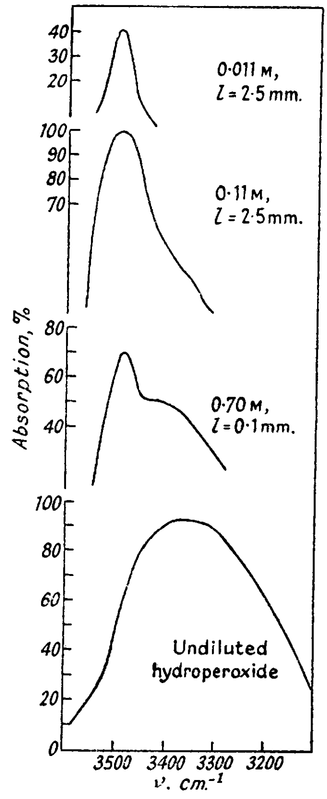


FIG. 3.

$$2(RO\cdot + \cdot OH) \longleftarrow 2(RO\cdot OH) \rightleftharpoons (RO_2\cdot H \ldots\ldots \underset{H}{O}\cdot OR) \longrightarrow RO_2\cdot + H_2O + \cdot OR$$

Monomer decomposition Dimer decomposition

The generality of this phenomenon for solutions of alkenyl hydroperoxides in the parent olefins is evident from the oxidation kinetics, which also reveal that the two decomposition modes, in their appropriate concentration regions, proceed singly at not greatly dissimilar rates at the same temperature (Bateman, Hughes, and Morris, *loc. cit.*). Factors influencing the equilibrium between the monomeric and dimeric hydroperoxide structures will therefore be important in determining the decomposition path followed. The almost overwhelming predominance of the second-order process under the conditions of liquid-phase olefinic oxidations at temperatures below 100° (cf. Bolland, *loc. cit.*, 1949) should diminish with structural or environmental changes which displace the monomer–dimer equilibrium to the left. Such displacement would result from raising the temperature, by passing from the liquid- to the gas-phase, and by R being a group with steric or electronic properties unfavourable to the associated state. The recognition of these effects would seem to permit unification of many of the diverse observations on hydroperoxide decomposition.

The bond breakages postulated for the decomposition of the dimer express the culmination of the donor–acceptor hydrogen-bonding interaction of the O_2H groups. Substances having either stronger donor (HX) or acceptor (Y) properties, by complicating the monomer–dimer equilibrium thus

$$\begin{tikzcd}
(X\cdot H \ldots\ldots O\cdot OR) \arrow[r, leftrightharpoons, "HX"] & RO_2H \arrow[r, leftrightharpoons, "Y"] \arrow[d, leftrightharpoons, "RO_2H"] & (RO_2\cdot H \ldots\ldots Y) \\
 & (RO_2\cdot H \ldots\ldots \underset{H}{O}\cdot OR) &
\end{tikzcd}$$

should therefore introduce significant modifications. Since the relative stability of the heterogeneous complexes and the dimer is not generally predictable, it is impossible to decide whether facilitation of the decomposition is a necessary consequence, but the site of primary bond fission and the kinetic characteristics should be affected. With *cyclo*hexenyl hydroperoxide under conditions conducive to homolytic processes, typical examples of HX and Y, stearic acid and diphenyl sulphoxide, respectively, both cause accelerated decompositions. The reaction order has not yet been determined for the sulphoxide system, but the decomposition of the peroxide in *cyclo*hexene changes from 1·8- to first-order in the presence of the acid (Fig. 2).

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British Rubber Producers' Research Association,
48 Tewin Road, Welwyn Garden City, Herts.

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