

at higher temperatures is substantiated by results from n.m.r. work by Burger, *et al.*¹³

From the model a heat capacity curve can be calculated and compared with the experimental values. Figure 5 presents the experimental heat capacity for four hydrogen atoms and a palladium atom from the data of Nace and Aston² between 10°K. and 180°K. It also presents the calculated curve from the model along with the individual components that make up the calculated values.

Curve A of Fig. 5 gives a graph of the contribution due to three torsional Debye modes with $\theta = 200^\circ\text{K}$. Curve B represents the heat capacity contribution of three hindered rotational degrees of freedom calculated from eq. 7

$$V = V_0(1 - \cos 3\varphi)/2 \quad (7)$$

where V_0 is arbitrarily picked at 390 cal. mole⁻¹ to fit the maximum in the heat capacity curve. Curve C represents the Debye lattice contribution of the motions of the centers of gravity with $\theta = 275^\circ\text{K}$. which is the experimental value for pure palladium. Curve D represents the heat capacity of a Debye lattice containing four hydrogen atoms with $\theta = 950^\circ\text{K}$. The reason for this choice is that these hydrogen atoms form a superlattice of highly hindered translators. Since the lower levels of such a system evidently approximate those of a harmonic oscillator, the whole assembly becomes a Debye sublattice of three degrees of freedom.

The solid curve is made up of curves A and C up to 50°K. From 50 to 65°K. it is curve B and C.

(13) J. P. Burger, N. J. Paulis and W. P. Hass, *Physica, del.*, **27**, 514 (1961).

Curves C and D then made up the calculated curve from 65°K on. The resulting curve, E, reproduces the shape and values of the experimental points of Nace and Aston² quite well and produces additional evidence that the model presents a correct picture.

Figure 6 presents a comparison of the measured and calculated heat capacity contribution of two hydrogen atoms in the range of 100° to 300°K. (curve D). A Debye superlattice of 6 degrees of freedom per H₂ with $\theta = 950^\circ\text{K}$. was of course assumed. Curve F is a curve similar to curve D calculated for deuterium with $\theta = 950^\circ/\sqrt{2} = 750^\circ$ for the torsional modes. The experimental points for deuterium are those of Nace and Aston.²

It has previously been found that the zero point entropy of two Pd₂H units in palladium black is 1.18 ± 0.36 cal. deg.⁻¹ mole⁻¹.² At the composition 0.50 H/Pd, if certain hydrogens on the corner palladium atoms move to adjacent sites, the sheets suffer a sharp bend by $\pi/2$. Since two Pd₂H units contain one corner palladium atom and three face-centered ones, the unit involved in the sheets is PdH₂. Thus, if the bending of the planes by $\pi/2$ is performed at random the situation is numerologically equivalent to that of ice for which the theoretical zero point entropy is 0.82 cal. deg.⁻¹ mole⁻¹. This is within experimental error of the zero point entropy found.

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The Origin of Epoxides in the Liquid Phase Oxidation of Olefins with Molecular Oxygen¹

BY WILLIAM F. BRILL

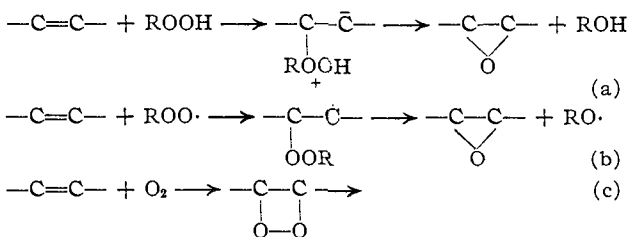
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In the liquid phase oxidation of cyclohexene and 2,4,4-trimethyl-1-pentene with molecular oxygen, epoxides are formed in addition to hydroperoxides as a primary product of the radical chain reaction. It was demonstrated unequivocally that the non-catalytic reaction of hydroperoxides with olefins is able to produce epoxides. However, oxidation by hydroperoxide is not rapid enough to account for epoxide formed during olefin autoxidation. Attack of alkyl peroxy radical on the double bond is the most likely source of epoxide.

The origin of epoxides in olefin autoxidation products has important implications on olefin oxidation theory and on the potential use of autoxidation as a synthetic method. While the major products reported for the oxidation of olefins are hydroperoxides, aldehydes, ketones and acids, the formation of minor amounts of epoxides was noted by early investigators working with rubber and drying oils. Recently it has been reported that many olefins may be autoxidized by a variety of techniques in the liquid phase to practical synthetic yields of epoxides. Yields of 50% or better may be obtained from the oxidation of 2,4,4-trimethyl-1-pentene,² 2-methyl-1-butene³ and cyclooctene.⁴ Even the simplest low molecular weight olefins give epoxides in fair yields—propylene, 26%⁵; butene-2, 38%⁶; butene-1, 30%; and isobutene, 18%.³ These yields

suggested that the importance of epoxide formation had not been fully recognized and a close examination of its role in autoxidation was justified.

Various mechanisms have been proposed to explain epoxide formation, but no specific studies have been reported. It has been proposed that double bonds react with (a) hydroperoxide or (b) peroxy radical or (c) molecular oxygen to yield epoxides as:



Farmer proposed the reaction of hydroperoxide with oxygen (a), but failed to demonstrate its importance experimentally.⁷ He also proposed the reaction of peralkoxy radical with olefin (b), but did not give it further consideration. Closure of the intermediate

(1) Presented at the Second Princeton Scientific Community Conference, Princeton, N. J., November 16, 1961.

(2) E. J. Gasson, *et al.*, *J. Chem. Soc.*, 2161 (1954).

(3) W. F. Brill and B. J. Barone, unpublished work.

(4) W. Reppe, O. Schlichting and K. Mueiler-Glieman, U. S. Patent 2,769,017 (1956).

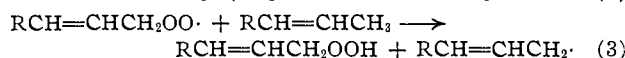
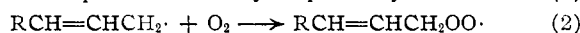
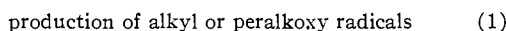
(5) J. Gardner and N. Robertson, U. S. Patent 2,780,635 (1957).

(6) A. F. Millidge and W. Webster, U. S. Patent 2,741,623 (1956).

radical has been used to explain the presence of isobutylene oxide in the decomposition products of *tert*-butyl peroxide.⁸ Mechanism b has been considered to explain the formation of epoxide in the oxidation of 2,4,4-trimethyl-1-pentene.^{2,9}

The reaction of molecular oxygen with a double bond (c) forms part of one of the earliest theories of autoxidation.¹⁰ The cyclic peroxide postulated^{11,12} is, of course, better suited to explaining hydroxylation and fission products than epoxides, and appears to be definitely involved only in the radiolytic oxidation of propylene to acetol.¹³ Oxygen may also react directly with dienes by a copolymerization. The polymeric radical formed may react as in b, and in the special case of styrene the formation of epoxide has been explained by these reactions.¹⁴

It is implicit in the widely accepted mechanism of olefin oxidations developed mainly by workers at the British Rubber Producers Research Laboratories¹⁵ that the early stages of autoxidation produce only hydroperoxides by the steps



Epoxides must arise by a secondary reaction such as a. Yet there are no convincing demonstrations of this reaction for simple olefins. Farmer obtained only a small yield of diol, presumed to have arisen from cyclohexene oxide on heating cyclohexene hydroperoxide with cyclohexene.¹⁶ The oxidation of olefinic linkages by hydroperoxide has been reported for fatty esters.^{17,18} However, many hydroperoxides have been thermally decomposed in unsubstituted olefins without the formation of epoxides being observed.^{16,19-20}

In the present work the reaction of hydroperoxides and of peralkoxy radicals with olefins was investigated and related to the autoxidation of cyclohexene and 2,4-trimethyl-1-pentene. It was discovered that under neutral and non-catalytic conditions hydroperoxides do oxidize simple olefins to epoxides. Of more immediate interest, however, oxidation with hydroperoxide was found to be too slow to explain the formation of epoxide during the autoxidation of the olefins studied. Evidence that peralkoxy radicals do react with olefins to yield epoxides was obtained.

Experimental

Materials.—Olefins were Phillips pure grade and fractionated before use. *tert*-Butyl hydroperoxide was distilled to about 94% purity. Cyclohexene hydroperoxide which appeared to be better than 60% pure by titration was prepared by the non-catalytic oxidation of cyclohexene at 60° followed by distillation.

(7) E. H. Farmer, G. F. Bloomfield, A. Sundralingam and D. A. Sutton, *Trans. Faraday Soc.*, **38**, 348 (1942).

(8) E. R. Bell, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 337 (1950).

(9) (a) G. H. Twigg, *Chem. Eng. Sci.*, **3**, Special Supplement 14 (1954), "The Proceedings on the Conference on Oxidation Processes". (b) G. H. Twigg, *Chemistry & Industry*, 4 (1962).

(10) See ref. 16 and ref. 21 for detailed discussion and references.

(11) C. Paquot, *Bull. soc. chim. France*, **12**, 120 (1945).

(12) H. Von Risseghem, *Bull. soc. chim. Belg.*, **87**, 5 (1948).

(13) B. M. Mikhailov and V. G. Kiselev, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 527 (1961).

(14) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958).

(15) L. Bateman, *Quart. Revs.*, **8**, 1947 (1954).

(16) E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 121 (1942).

(17) C. E. Swift and F. G. Doller, *J. Am. Oil Chem. Soc.*, **25**, 52 (1948).

(18) G. King, *J. Chem. Soc.*, 4324 (1961).

(19) L. Bateman and H. Hughes, *ibid.*, 4594 (1952).

(20) M. S. Kharasch, P. Pawson and W. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951).

(21) E. G. E. Hawkins and D. C. Quin, *J. Appl. Chem.*, **6**, 1 (1956).

(22) V. Stannett and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 4125 (1950).

Analytical.—Hydroperoxides were determined by heating at incipient boiling 1 ml. to 10 ml. of the sample in 50 ml. of isopropyl alcohol containing 1 ml. of saturated potassium iodide and 5 ml. of acetic acid and titrating the liberated iodine with 0.1 *N* or 0.05 *N* potassium thiosulfate. Epoxide and other products were determined by gas chromatography, generally using a 2-meter column of diisodecyl phthalate on Celite with 25 p.s.i. of helium carrier gas at 130°. It should be noted that while no rearrangement of 1,2-epoxy-2,4,4-trimethylpentane to aldehyde occurred on this column, more acidic supports such as acid-washed Chromosorb must be avoided. Epoxide concentrations were occasionally checked by direct titration with hydrogen bromide in acetic acid, although low values are obtained for 1,2-epoxy-2,4,4-trimethylpentane.²³

To follow epoxide concentrations during autoxidation at very low conversions, a large sample of oxidate, 50 microliters, was gas chromatographed. While overloading of the column produced a distorted olefin peak, epoxide and other products produced peaks whose heights remained linear with concentration as shown by the behavior of dilute standard solutions. In this way epoxide concentrations to below 0.0004 *M* could be determined.

Oxidation of Olefins with Hydroperoxide.—When feasible, glassware was new and reserved for either non-catalytic or catalytic studies. Cleaning with hydrochloric acid and rinsing with dilute ammonia, distilled water and acetone when required appeared to give a clean surface for this reaction. Reactions were conducted by heating in either sealed tubes or reaction flasks under a nitrogen atmosphere in a constant temperature bath. Products were isolated by fractionation through a concentric tube or Teflon coated spinning band column and further purified when necessary by gas chromatography. Infrared spectra and physical properties were used for identification. Yields were computed from the gas chromatographic analysis and iodometric titration for peroxide of the crude reaction product.

Rates were studied by using a single solution of the hydroperoxide in olefin made up to the highest concentration studied. With *tert*-butyl hydroperoxide, 5-ml. samples were sealed under nitrogen in ampules which were either unpacked, packed with clean glass helices or wrapped in foil to exclude light. Periodically after the start of the reaction tubes were removed, titrated for peroxide and analyzed by gas chromatography. In 2,4,4-trimethyl-1-pentene the first-order decomposition rate ($k_1 = 2.1 \times 10^{-6} \text{ sec.}^{-1}$ at 90°) was determined from a single plot in which unpacked, packed and dark data appeared to fit equally well. Decomposition of 500 ml. of a 0.92 *M tert*-butyl hydroperoxide solution in a 1-l. round-bottom flask proceeded at the same rate and produced sufficient product to allow isolation directly by fractionation.

In initial attempts to inhibit hydroperoxide decomposition, hydroquinone was added to hydroperoxide solutions. Peroxide values were immediately lowered and an insoluble yellow oil formed. In contrast, *o,o'*-di-*tert*-butyl-*p*-methylphenol produced a water-white solution with no detectable change in peroxide concentrations at concentrations of inhibitor of up to 5 mole %.

The Formation of Epoxide and Hydroperoxide by Autoxidation.—Olefins were oxidized with U.S.P. oxygen at atmospheric pressure in a carefully cleaned glass reaction flask from which samples could be withdrawn periodically for analysis without disturbing the reaction. A Teflon coated magnet stirred the reaction at approximately 1600 r.p.m. Peroxide was determined iodometrically and epoxide chromatographically on the same samples.

Catalytic Oxidation of Olefins with Hydroperoxides.—*cis*-Butene-2 was treated with *tert*-butyl hydroperoxide under conditions similar to those required for the autoxidation of butene-2.³ In a 1.4-l. stirred autoclave, 273 g. (4.9 moles) of *cis*-butene-2, 150 g. (1.7 moles) of *tert*-butyl hydroperoxide, 1 g. of cobalt acetylacetonate and 30 g. of light calcium oxide in 351 g. of benzene were heated at 120° under nitrogen at 300 p.s.i. for 3 hours. Under these conditions isomerization of the olefin and the epoxide does not occur.

While the *cis*- and *trans*-oxides have sufficiently different retention times on either diisodecyl phthalate or Carbowax adsorbants, the *cis* isomer did not separate by chromatography from *tert*-butyl alcohol in the first case or acetone in the second. The *cis:trans* ratio was determined by correcting the *cis*-oxide concentration for alcohol or acetone, and also from the total epoxide concentration determined by titration of the crude product with hydrogen bromide²³; the *trans*-oxide concentration determined by chromatography.

The cobalt-catalyzed decomposition of hydroperoxides in other olefins was carried out and products and rates determined in the same manner as for the uncatalyzed decompositions. The reactions of *tert*-butyl hydroperoxide with cyclohexene gave yields of epoxide which decreased with the extent of reaction to

(23) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

around 1% for $3 \times 10^{-3} M$ catalyst ($k_1 = 1.5 \times 10^{-5} \text{ sec.}^{-1}$) and 0.1% for $3 \times 10^{-4} M$ catalyst ($k_1 = 3.5 \times 10^{-6} \text{ sec.}^{-1}$) at 50% reacted. Extrapolation of the yields at various times indicates epoxide yields at zero time to be around 18 and 8%, respectively. As observed for the uncatalyzed reactions also, the *tert*-butyl alcohol formed initially appears to account for all the hydroperoxide decomposed but at more than 50% reacted it accounts for only about half.

Catalyzed decomposition of 0.75 *M* cyclohexene hydroperoxide in 2,4,4-trimethyl-1-pentene at 60° with $6 \times 10^{-4} M$ cobalt gave an epoxide yield decreasing from 10 to 6% compared to a 39% yield for the uncatalyzed reaction, while a 0.55 *M* solution gave maximum epoxide yields of 9 and 39%, respectively. The second-order rates were $k_2 = 7.7 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$ for the catalyzed decomposition and $k_2 = 1.4 \times 10^{-6} M^{-1} \text{ sec.}^{-1}$ ($k_{1.7} = 1.3 \times 10^{-6} M^{-0.7} \text{ sec.}^{-0.7}$) for the thermal reaction.

Ceric Sulfate Oxidation of *tert*-Butyl Hydroperoxide in Olefins.—In a closed system under nitrogen, 6.6 g. (0.02 mole) of finely pulverized anhydrous ceric sulfate was added to 25 ml. of a vigorously stirred solution of 0.79 *M tert*-butyl hydroperoxide (1.3 g., 0.02 mole) in 2,4,4-trimethyl-1-pentene. A rapid evolution of gas immediately occurred. After 20 minutes negligible gas was evolved and the solid phase formed a single mass. Analysis of the supernatant liquid after 95 minutes showed that 97% of the hydroperoxide had reacted to give the following yields on hydroperoxide: oxygen, 12%; *tert*-butyl alcohol, 55%; 4,4-dimethyl-2-pentanone, 10%; and 2,4,4-trimethylpentanal, 4%. Using a stream of nitrogen (75 ml./min.) to sweep out the oxygen generated resulted in little change in the product distribution. When the quantity of ceric sulfate was reduced to one-tenth, only a slight decomposition of peroxide occurred indicating that no significant catalysis is involved. In the absence of ceric sulfate, no peroxide reaction is observed at room temperature over several months time.

When 3.3 g. of ceric sulfate was stirred with 1.3 g. of 1,2-epoxy-2,4,4-trimethylpentane in 10 ml. of trimethylpentane for 2 hours the epoxide reacted completely, approximately 50% of it isomerizing to 2,4,4-trimethylpentanal. After 4 hours the same aldehyde concentration was found. No additional product was detected in adequate amounts by gas chromatography at 200° using a silicon absorbent. A trace of 4,4-dimethyl-2-pentanone, which had been a possible expected product, present as an impurity in the epoxide neither increased or decreased in concentration.

tert-Butyl hydroperoxide was treated with a slight molar excess of pulverized ceric sulfate in a 20-fold excess of vigorously stirred cyclohexene at room temperature for several hours. No epoxide was detected by gas chromatography in the filtered product or the residue after removal of the cyclohexene. In the presence of oxygen, vigorous oxidation occurred to the usual products except that no epoxide was found. When cyclohexene oxide in cyclohexene or toluene was treated with ceric sulfate no epoxide remained after several hours. Gas chromatography under conditions suitable for material with retention times as long as that of cyclohexene glycol failed to reveal the products.

Results and Discussion

Epoxidation with Hydroperoxides.—When hydroperoxide is heated with olefin under nitrogen using clean conditions to avoid catalyzed decomposition, the alcohol corresponding to the hydroperoxide used and yields of the olefin oxide generally above 30% are obtained. Only results relating epoxidation with hydroperoxide to olefin oxidation with molecular oxygen will be reported here. Epoxide yields based on peroxide, some of which are shown in Table I, give no clue as to the possible role of this reaction in autoxidation, but it is curious that cyclohexene oxide may be produced by reaction with hydroperoxide in yields higher than the 12% obtained by autoxidation,¹¹ while the inverse is true for 2,4,4-trimethyl-1-pentene which gives an oxide in 50% yield. These olefins were selected for rate studies since they show the widest divergency in epoxide yields on autoxidation.

In cyclohexene, epoxide yields based on hydroperoxide decomposed did not decrease greatly with conversions over the portion of the reaction susceptible to kinetic treatment,¹⁹ and in 2,4,4-trimethyl-1-pentene yields remained constant to nearly complete hydroperoxide decomposition. This allowed the kinetics for hydroperoxide decomposition to be equated directly to the kinetics for epoxide formation. The insensitivity

TABLE I

EPOXIDATION WITH HYDROPEROXIDES			
Cyclohexene		2,4,4-Trimethyl-1-pentene	
% reacted	Yield, %	% reacted	Yield, %
<i>tert</i> -Butyl hydroperoxide			
9	32	12	45
22	23	14	40
43	14	22	47
54	10	32	45
72	9	71	51
Cyclohexene hydroperoxide			
9	40	13	36
40	34	28	32
45	35	48	37
59	32	62	38
77	21	74	37

of epoxide yield to the complicated kinetic results found probably indicates a common rate-controlling step in which an intermediate is formed. This intermediate may then break down to epoxide and alcohol or to olefin, alcohol and other products.

It has not been possible to relate the reported failure of the rate behavior at higher conversions¹⁹ to the decreasing cyclohexene oxide yields reported here and, in fact, the reason for the instability of the epoxide could not be discovered. It was noted that when cyclohexene oxide is present during the hydroperoxide oxidation of 2,4,4-trimethyl-1-pentene it slowly disappears. In contrast, 1,2-epoxy-2,4,4-trimethylpentane is stable to whatever intermediates are present during the epoxidation.

Although the production of epoxide had not been previously reported in other rate studies of hydroperoxide decompositions, the kinetic results in the present work and previously reported work proved very similar.^{19,24,25} Reaction orders appear to vary with the hydroperoxide and the concentration range, and the rates are sensitive to the cleanliness of the equipment. However, reported rates for cyclohexene hydroperoxide could be reproduced.

If the mechanism of hydroperoxide epoxidation involves decomposition of hydroperoxide to peroxy radicals ($2\text{ROOH} \rightarrow \text{ROO}\cdot + \text{RO}\cdot + \text{H}_2\text{O}$) it would be unimportant during autoxidations since the primary source of such radicals would be the reaction of alkyl radicals with oxygen. However, present evidence indicates that hydroperoxide epoxidation is molecular and that free radicals or radical chains are not involved. Thus inhibitors have no effect on the rate or products, the rate in the dark or in daylight is the same, and no induction period is observed. In addition, the metal ion-catalyzed decomposition of hydroperoxide, which will be described later, occurs more rapidly probably by a free radical mechanism and produces only about a fifth as much epoxide.

It was, therefore, necessary to consider whether molecular epoxidation is rapid enough at the hydroperoxide concentrations encountered during autoxidations to be a possible source of the epoxide produced or if another mechanism not involving hydroperoxide must be operating.

Autoxidative Epoxidation.—The relationship between hydroperoxide and epoxide concentration was examined for the oxidation of cyclohexene and 2,4,4-trimethyl-1-pentene with molecular oxygen with a special effort to obtain the rate of formation of products at low olefin conversions.

(24) B. K. Morse, *J. Am. Chem. Soc.*, **79**, 3375 (1957).(25) J. R. Thomas, *ibid.*, **77**, 246 (1955).

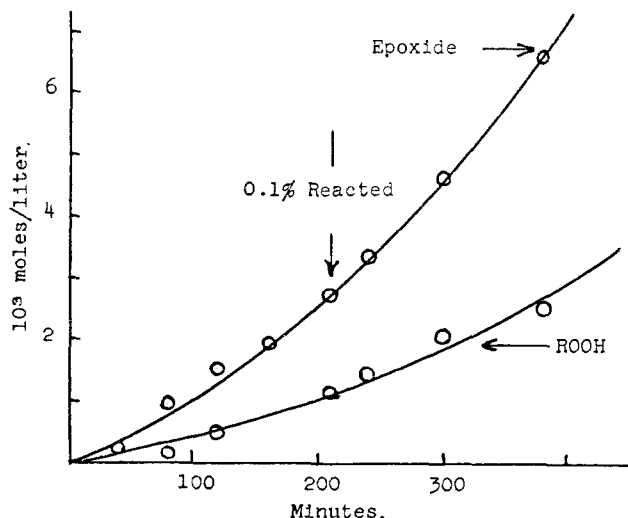


Fig. 1.—Oxidation of 2,4,4-trimethyl-1-pentene at 90°.

The increase in cyclohexene hydroperoxide concentration determined by iodometric titration, and the increase in cyclohexene oxide concentration determined by gas chromatography at various times for the oxidation of cyclohexene at 60° under clean conditions are shown in Table II.

TABLE II
AUTOXIDATION OF CYCLOHEXENE, 60°

Min.	ROOH, $M \times 10^2$	Epoxide, $M \times 10^4$	$\frac{d(\text{Epoxide})}{dt}$, $M, \text{sec.}^{-1}$		Found/ calcd.	Yield, ^b %
			Found $\times 10^3$	Calcd. $\times 10^{10a}$		
130	0.86	0.95	2.3	1.0	230	
205	1.57	2.37	3.3	2.9	110	
278	2.75	4.74	6.0	8.1	74	
340	...	7.58	10.3	2.4
404	5.15	12.32	12.0	24.0	50	2.0
420	5.60	13.74	13.0	28.0	43	3.0
687	13.71	31.75	23	138	17	
1367	76.12	293.8	128	2870	5	4.0
1649	133.8	606.6	175	7800	2	7.2

^a Calcd. using $d(\text{epoxide})/dt = 1.4 \times 10^{-9}(\text{ROOH})^{1.77}$ (ref. 19).

^b Wt. epoxide/total products $\times 100$.

All the data obtained before 1649 minutes represent conversions of less than 2%, defined as the mole % of olefin reacted. As expected, the hydroperoxide is unusually stable and can be formed in high concentrations by long oxidation. Epoxide constitutes but a small portion of the product, but if its concentration is plotted against time a smooth curve going back to zero time results. From the curve, which is similar in shape to the oxygen absorbed-time curve, the rates of epoxidation at various times, shown in column 4, are obtained.

Assuming that molecular epoxidation may occur during free radical oxidations, its maximum possible rate may be calculated from the known hydroperoxide thermal decomposition rate constant and the observed hydroperoxide concentrations. From the ratio of the observed rate of epoxide formation and the calculated rate of hydroperoxide decomposition it may be seen that olefin is being oxidized to epoxide at the time of the first analysis around 200 times faster than epoxide could be produced by the direct reaction of hydroperoxide. On extended oxidation the possible contribution of molecular epoxidation increases and may be added to that of the radical oxidation to explain the increase in epoxide yield shown in the last column. It may be anticipated that other olefins may show an increase

in hydroperoxide epoxidation with time depending on the concentrations of hydroperoxide produced.

For cyclohexene, it may also be shown that the relationship between the observed hydroperoxide concentrations and epoxidation rates is not appropriate for the molecular epoxidation. The data from Table II reveal a linear relationship when the epoxidation rates are plotted against the hydroperoxide concentration to the first power instead of the higher order expected for molecular epoxidation.

The oxidation of 2,4,4-trimethyl-1-pentene represents a very different product distribution, the observed epoxide concentration being always higher than the hydroperoxide concentration. In Fig. 1 it appears that epoxide arises simultaneously with hydroperoxide and in higher yield at zero time. The apparent relationship between the rate of epoxide formation and hydroperoxide concentration is second order $d(\text{epoxide})/dt = 5 \times 10^{-2}(\text{ROOH})^2$ and the necessary rate of hydroperoxide decomposition to account for molecular epoxidation must be many orders of magnitude faster than that observed for cyclohexene hydroperoxide, the only allylic hydroperoxide whose decomposition rate is available. It could be assumed that since it is produced only in low concentrations by autoxidation and its isolation has never been reported, the hydroperoxide of 2,4,4-trimethyl-1-pentene does in fact decompose very rapidly. As discussed later, the present study suggests that it is more likely that not very much hydroperoxide is being produced, epoxide being the preferred product from peroxy radical in the propagation steps of the oxidation.

The reactivity of the hydroperoxide of 2,4,4-trimethyl-1-pentene was approximated by heating crude oxidate which was 0.07 M in hydroperoxide under nitrogen. The decrease in hydroperoxide concentration indicates the presence of a very reactive and an almost unreactive hydroperoxide present in approximately equal concentrations in the solution produced by this particular degree of oxidation. If a second-order plot is made using the titrimetric values, a good fit is obtained with a sharp break in the slope presumably after the more reactive hydroperoxide is exhausted. A rate constant of $8 \times 10^{-4} M^{-1} \text{sec.}^{-1}$ is obtained for the reactive hydroperoxide which indicates that hydroperoxide decomposition is still around 100 times too slow. This treatment involves the assumption that for second-order hydroperoxide decompositions, association between mixed hydroperoxides assumes the same importance as association between identical hydroperoxide molecules. It could not be demonstrated that 2,4,4-trimethyl-1-pentene hydroperoxide can epoxidize 2,4,4-trimethyl-1-pentene since a relatively high concentration of epoxide was always present in the oxidate and a slight decrease in epoxide concentration was detected over the course of the hydroperoxide decomposition experiment. The reactive hydroperoxide is undoubtedly the primary isomer while the unreactive hydroperoxide must be the secondary or hindered isomer. The unreactive isomer must also form slowly on oxidation since it accounts for only half of the total peroxide even though it is essentially stable during the reaction times involved. This assumption seems reasonable since the end products of an extended oxidation contain only minor yields of compounds, such as *tert*-butyl alcohol and methacrolein, expected from this hydroperoxide. It is concluded that while the degree of participation, if any, for hydroperoxide epoxidation in the case of 2,4,4-trimethyl-1-pentene could be demonstrated only if the isolated hydroperoxides were available, a free radical epoxidation must be initially the primary mechanism operating.

That this is also true at higher conversion may be indicated by the failure of metal ion catalysis to lower epoxide yields during autoxidations.

Alkylperoxy Radicals with Double Bonds.—The first indication that peroxy radical attack on the double bond is involved in epoxide formation during olefin oxidations is the production of mixed *cis*- and *trans*-butylene oxides by the oxidation of pure *cis*- and pure *trans*-butene-2 in benzene. The ratio of *trans*- to *cis*- epoxide from *cis*-butene-2 was approximately 1.5 while *trans*-butene-2 gave a ratio of 3.3. No isomerization of the olefin occurred during the oxidation and the epoxide was found to be stable when heated under equivalent conditions. These results were best explained by addition of the peroxy radical as shown in eq. b to give an intermediate in which rotation can occur before closure to epoxide with formation of alkoxy radical. When peroxy radical is generated by the cobalt-catalyzed decomposition of *tert*-butyl hydroperoxide, it reacts with *cis*-butene in the same manner to give approximately four times as much *trans*- as *cis*-oxide.

In order to examine the reaction of alkyl peroxy radicals with olefins it was necessary to find a suitable method of generating radicals under conditions similar to those encountered in autoxidations. Besides the autoxidation of hydrocarbons and olefins the only reported radical source is the oxidation of hydroperoxides with metal ions. Metal ion oxidations have been classified²⁶ as (1) oxidation with irreversible reduction of the metal ion as represented by Ce^{+4} and (2) oxidations in which the metal ion is subsequently reoxidized by the hydroperoxide as for Co^{+3} .

The formation of epoxide from either cyclohexene or 2,4,4-trimethyl-1-pentene and *tert*-perbutoxy radicals generated from the action of ceric sulfate on *tert*-butyl hydroperoxide was examined with limited success. Cyclohexene oxide was found to be rapidly destroyed by reaction with ceric sulfate and no evidence for its formation was obtained. 1,2-Epoxy-2,4,4-trimethylpentane also reacted rapidly with ceric sulfate, but in accord with its reported susceptibility to rearrangement²⁷ approximately half of the epoxide forms 2,4,4-trimethylpentanal. Since this aldehyde is not likely to form by direct oxidation of olefin, its detection in the products from the reaction of 2,4,4-trimethyl-1-pentene, *tert*-butyl hydroperoxide and ceric sulfate indicates prior formation of epoxide. The yield of aldehyde based on hydroperoxide reacted was only 4%, along with 52% *tert*-butyl alcohol, 10% 4,4-dimethyl-2-pentanone and 11% oxygen. The possibility exists that the molecular oxygen liberated was responsible for epoxide and other olefin oxidation products. However, when the reaction mixture was swept with a vigorous stream of nitrogen during the oxidation, the product distribution remained the same.

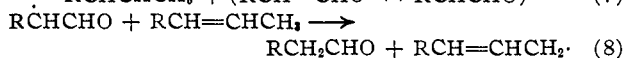
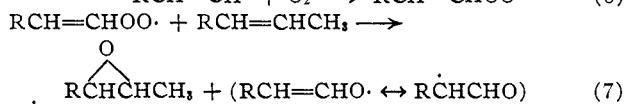
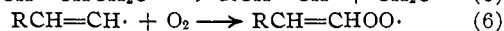
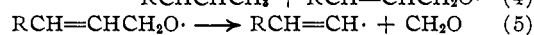
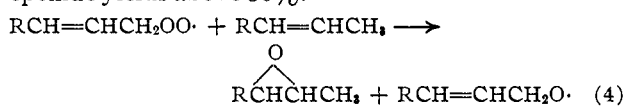
The second peralkoxy radical producing reaction investigated, the cobalt acetylacetonate-catalyzed decomposition of hydroperoxides, produces equal quantities of alkoxy radical. In addition the various possible radical-radical and radical-hydroperoxide interactions favored by the relatively high radical concentrations produced reduces the probability of peralkoxy interaction with the olefin by either addition or hydrogen abstraction. That the yield of epoxide from the catalyzed decomposition of cyclohexene hydroperoxide is only about a fifth of that from the molecular reaction was therefore expected. Since the rate was up to 100 times faster than that for the uncatalyzed

reaction, most of the epoxide must have arisen from radical attack and not molecular epoxidation.

The radical epoxidation could best be related to autoxidations by demonstrating that for a series of olefins the ratio of double bond attack to hydrogen abstraction is independent of how peroxy radical is generated. This has not yet been done.

Another area examined only briefly thus far is the production of peroxy radicals by the oxidation of hydrocarbons in the presence of olefins. If the saturated alkyl peroxy radical produced shows a different preference from that of the allylic peroxy radical from the olefin, the epoxide-olefin hydroperoxide ratio will be modified. Mixtures of cumene with 2,4,4-trimethyl-1-pentene and cyclohexene were oxidized and the product yields determined at low conversions. No change in the distribution of major products from the olefins was noted by gas chromatography, indicating that the structure of the peroxy radical is not important in determining the preference for double bond addition or hydrogen abstraction.

The early formation of epoxide by a mechanism not involving hydroperoxide requires that the presently accepted mechanism for the propagation and termination steps in olefin oxidations be modified. The following additional reactions take into account the nature of products other than epoxide and hydroperoxide, the absence of alcohol in the products, and allow for epoxide yields above 50%.



< Radical-radical interactions (termination)

The decomposition of allylic alkoxy radical (5) allows each molecule of olefin undergoing hydrogen abstraction to form two peroxy radicals and thus, in the absence of hydrogen abstraction, form two epoxide and one carbonyl or enol molecule (sum of reactions 4, 5, 6 and 7). For the oxidation of 2,4,4-trimethyl-1-pentene, the carbonyl product would be 4,4-dimethyl-2-pentanone which is actually produced in yields above 25% or in amounts which are approximately half as much as the epoxide products. The proposed decomposition of allylic alkoxy radical receives support from the recent report that the sole reaction of a similar benzyl alkoxy radical in cyclohexene is decomposition.²⁸ Although some of the remaining products may arise similarly by reaction at the secondary allylic position, this mechanism implies a strong preference by peroxy radical for addition instead of hydrogen abstraction. The lower relative reactivity of alkoxy radical²⁹ in the abstraction step 8 should then be reflected in a slower over-all oxidation rate for olefins which produce epoxide most readily.

Although the large number of termination steps make a steady state treatment of this mechanism very complicated, it can be shown that for only one type of termination, such as the usually assumed $2ROO\cdot \rightarrow$ non-propagating, the same rate equation can be derived by a steady state treatment as for the previously proposed mechanisms.¹⁵

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