167–169°, demonstrated to be adduct **23a** by mixture melting point (167–169°) and identical infrared spectra.

Thermal Stability of the Adducts **23**. The adduct from 1-carbomethoxyazepine and tetracyanoethylene (**23d**, 200 mg., m.p. 165–167°) was refluxed in chlorobenzene (20 ml., b.p. 132°) for 3 hr. The adduct **23d**, m.p. 163–166°, was quantitatively recovered by complete distillation of the solvent. Its identity was confirmed by matched infrared spectra.

Liquid-Phase Oxidations of Cyclic Alkenes[1]

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This work was undertaken to relate the initial products of liquid-phase oxidations of unsaturated hydrocarbons under mild conditions (and thus their mechanisms of oxidation) to the structures of the hydrocarbons. Results with cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclododecene, methylenecyclohexane, and vinylcyclohexane at 50–70° are discussed in terms of the addition and hydrogen-abstraction mechanisms. Indicated rates of addition of alkylperoxy radicals to the corresponding cyclic alkenes are very similar. Indicated rates of abstraction (per hydrogen atom) differ by a factor of 22 and depend partly on the degree of reorganization required to give a planar allyl radical. In over-all rate of oxidation, cyclopentene is most reactive and cyclooctene is least reactive. While the other alkenes give mostly allylic hydroperoxides, 70% of the cyclooctene reacts by the addition mechanism, producing epoxide, suberic aldehyde, and polymer. These results are compared with the work of others. The "dimeric" peroxides from cyclopentene and cyclohexene are shown to be 2-(3-cycloalkenylperoxy)cycloalkanyl hydroperoxides.

Introduction

The objective of this work was to relate the initial products of oxidation of unsaturated hydrocarbons under mild conditions (and thus their mechanisms of oxidation) to the structures of the hydrocarbons. Previous workers have established the hydroperoxide or abstraction mechanism for the autoxidation of many olefins.[2,3] In 1956 and 1958, characteristics of the addition mechanism were reported. Two summarizing papers[4] showed that many olefins react partly or entirely through addition of peroxy radicals to double bonds rather than by hydrogen abstraction (or "transfer"). In 1961, quantitative studies were begun on the competition between the abstraction and addition mechanisms of oxidation of alkenes as a function of their structure. This report summarizes our studies on cyclic olefins. Similar research on acyclic olefins is still in progress.

Experimental Section

1. Materials. Cyclopentene was either Phillips research grade or carefully fractionated samples from Columbia Chemical Co.; cyclohexene (reagent grade) was from Matheson Coleman and Bell; cycloheptene was from Columbia (reagent grade) and from the Aldrich Chemical Co. (technical grade). The latter material was fractionated on a Hastelloy helices column of about 90 theoretical plates; the resulting distillate, b.p. 114° (760 mm.), showed two small peaks in the g.l.p.c. (Carbowax 20 M, 18-ft. column) just preceding the main hydrocarbon peak. The combined area of the impurities was 1.6% of the total. G.l.p.c. analysis of the Columbia material indicated a like amount of (presumably) the same impurities. The cyclooctene was obtained from Aldrich and was acid and base washed prior to distillation. The g.l.p.c. trace showed a peak trailing the main hydrocarbon and the impurity is estimated at 1%. The cyclododecene was a complimentary sample from Columbian Carbon Co. The *cis* and *trans* isomers could not be effectively separated by distillation and the experiments were performed on material that was approximately 90% *trans*, 10% *cis*. Methylenecyclohexane and vinylcyclohexane were obtained from Columbia Chemical Co.

All hydrocarbons were routinely distilled and then passed over activated alumina immediately prior to use. Except as noted, the materials appeared homogeneous in g.l.p.c. In a test case, no isomerization of methylenecyclohexane to methylcyclohexene could be detected as a result of the alumina treatment. ABN, azobis(2-methylpropionitrile), was Eastman White Label and was recrystallized from acetone. Triphenylphosphine (Matheson Coleman and Bell) was recrystallized from 95% ethanol and then sublimed.

Hydroperoxide samples, where used as initiators, were prepared by high-vacuum (0.05 mm.) distillation of the products from the oxidation of the corresponding olefin. The purity of the samples, as well as the determination of hydroperoxides for other analyses, was established by the Wibaut[5] titration procedure.

(2) L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954).
(3) D. Barnard, L. Bateman, J. I. Cunneen, and J. T. Smith, "The Chemistry and Physics of Rubber-Like Substances," L. Bateman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 17.
(4) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2497 (1958); F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958).
(5) J. P. Wibaut, A. B. van Leeuwen, and B. van der Wal, *Rec. Trav. Chim.*, **23**, 1033 (1954).

2. Oxidation Procedure Rates. Our method of following oxidation rates by pressure drop in a constant-volume apparatus is described elsewhere.[6] In the case of cyclohexene, the rate determined by pressure drop starting from 80 p.s.i.g. (or less) was identical within experimental error (2%) with that measured at constant pressure near 1 atm. total pressure. A gas buret and manometer were attached to the previously described apparatus and the initial rate of oxidation of neat cyclohexene, 0.010 M in ABN at 20°, was measured at 760 mm. of oxygen. The rate found was 57.3 mmoles/l. hr., while with an identical solution at 77 to 70 p.s.i.g. the oxidation rate was 58.2.

3. Product Studies. Oxidations for product studies were carried out similarly on neat hydrocarbons with ABN or added olefin hydroperoxide as initiator. Conversions were about 5%. We had initially hoped that our oxidation mixtures could be hydrogenated selectively so that all O–O bonds would be converted to hydroxyl groups and so that g.l.p.c. analysis would indicate the composition of the original mixture. This scheme gave apparently satisfactory results with methylenecyclohexane and vinylcyclohexane. However, when applied to cyclopentene and cyclohexene, relatively large amounts of unsaturated ketone and less allylic alcohol than original hydroperoxide were obtained. Consequently, for these olefins, the volatile and nonvolatile products were separated before chemical reduction. Selective hydrogenation was employed with cyclooctene, but some conversion of hydroperoxide to ketone may have occurred.

For gas chromatography a Carbowax on firebrick column (5-ft.) in a Wilkins A90P instrument was used. A few analyses on hydrocarbon fractions were done with G.E. SF-96 silicone oil partitioning agent.

The total weights of oxidates injected into the columns were known and the areas of the various peaks on the resulting traces were taken as proportional to the weight fractions of the components. Correcting factors were obtained for products from cyclopentene, cyclohexene, and methylenecyclohexane but not with the other four systems reported because enough standards were not available. In the latter systems, the indicated corrections would be less than 20% of the reported proportions of minor components. The oxygen accounted for in the vinylcyclohexane oxidation is too high. This high result may have one or more origins (other than our assumption about peak area and weight fractions): (1) our balances in Table VII assume that one molecule of water was formed for each allylic ketone molecule, and each molecule of unidentified material; (2) our balances assume that each molecule of dimer accounts for two molecules of oxygen, too much if the dimer contained some ether or hydroxyl groups; (3) some hydrogen was evolved but not allowed for.

A. Cyclopentene, Cyclohexene, and Cycloheptene. An initial titration of the oxidized hydrocarbon was made to serve as a partial check on the calculated oxygen consumption during an experiment. A portion of the oxidized hydrocarbon was then weighed into a Claisen head distillation apparatus with bubble capillary and the unreacted hydrocarbon was removed at a pressure reduced so that about 90% of the hydro-

carbon would distil away at room temperature (~25°). This hydrocarbon distillate (A) after drying with magnesium sulfate and after addition of sufficient triphenylphosphine to react with all hydroperoxide present (starch–KI test) was examined for reaction products by g.l.p.c. The residue remaining in the still was weighed and a known portion was transferred to a small distillation rig where all that was volatile at 0.05–0.10 mm. at pot temperatures up to 90° could be taken off as distillate B. The residue (C) remaining from these distillations was weighed and then made up to a larger volume (total known weight) with absolute alcohol. Both the ethanol solution of residue C and the peroxide distillate B were titrated by the usual iodometric procedure, then further analyzed as indicated below.

a. Reduction of Peroxide Distillate. The hydroperoxides from endocyclic olefins are reduced cleanly by triphenylphosphine.[7] In our experience, catalytic hydrogenation of these hydroperoxides leads to considerable side dehydration to α,β unsaturated ketone. A weighed amount of distillate B was diluted 5-fold with absolute ethanol, cooled to 0°, and a 1% excess (calculated from the hydroperoxide titer) of solid triphenylphosphine was added. The solution could then be analyzed directly by g.l.p.c. where the triphenylphosphine oxide did not interfere. In the case of cyclohexene, cyclohexenone was not readily resolved from cyclohexenol and the ketone was determined by infrared (carbonyl stretching band at 5.9 μ) directly on unreduced distillate.

b. Hydrogenation of Residue Solution. The ethanol solution C was hydrogenated directly with the Lindlar catalyst (poisoned palladium on calcium carbonate)[8] without additional catalyst poisons (quinoline). After completion of hydrogen uptake, the catalyst was removed by filtration and the ethanol solution was mixed with benzene and distilled under a small spinning-band column. Additions of benzene and distillations were continued until all ethanol and water had been removed and a relatively concentrated solution of the products in benzene was obtained. This procedure was assumed safe since the boiling points of the alcohols and glycols expected as products are at least 50° higher than benzene (cyclopentenone b.p. 135°). The resulting solution was then analyzed by g.l.p.c.
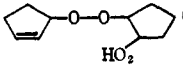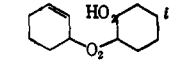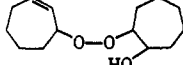
B. Other Hydrocarbons. Work-up of cyclooctene oxidation was complicated by the involatility of the products and the phase separation that occurs even at conversions as low as 0.4%. We separated the hydrocarbon phase by decantation from the film of heavy syrup in the flask. This syrup was washed twice with small portions of light petroleum ether; the combined washings were evaporated, and the small amount of residue was combined with the hydrocarbon layer. The remaining syrup was weighed and then made up to known total weight with ethanol.

The supernatant phase was analyzed as described in the previous section. The unreacted cyclooctene was removed by vacuum distillation (distillate saved for

(6) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4832 (1965).

(7) L. Horner and W. Jurgleit, *Ann. Chem.*, **591**, 138 (1955).

(8) H. Lindlar, *Helv. Chim. Acta*, **35**, 450 (1952). A recent improvement on this method is reported by M. Rebeller and G. Clément, *Bull. soc. chim. France*, 1302 (1964).

Table I. Products from the Oxidations of Cyclopentene, Cyclohexene, and Cycloheptene[a]

Charge and conversion[b] data	Product and identification[d–i]	Products, mmoles — Dist. A	Dist. B	Residue	Total	Alkene converted, %
Cyclopentene, 50°, 38.004 g. (557.9 mmoles); 0.00095 M in ABN, absorbed 23.8 mmoles of O_2 in 18.06 hr.; conversion, 4.26%	cyclopentenyl–O_2H [e]	0.61	17.92	0.17	18.70	77.6
	cyclopentenyl–OH [e,f]		0.0–0.30[c]		0.15	0.6
	cyclopentenone =O [e,f]		0.15		0.15	0.6
	cyclopentene oxide –O [g]	0.19	0.10		0.29	1.2
	peroxide –O–O– with HO_2 [i]			2.41	2.41	20.0
Cyclohexene, 60°, 39.925 g. (486.0 mmoles); 0.00095 M in ABN, absorbed 30.0 mmoles of O_2 in 13.52 hr.; conversion, 6.15%	cyclohexenyl–O_2H [j]	0.34	25.13	0.98	26.45	80.4
	cyclohexenyl–OH [d]		2.30		2.30	7.0
	cyclohexenone =O [k,i]		1.55		1.55	4.7
	cyclohexene oxide –O [g]	0.03	0.25		0.28	0.9
	peroxide HO_2 –O_2 [i]			1.16	1.16	7.0
Cycloheptene, 60° (80°), 36.034 g. (375.0 mmoles), with no initiator, absorbed 34.6 mmoles of O_2 in 45.5 hr. at 60°; conversion, 9.22% (387 mmoles with no initiator absorbed 21.2 mmoles of O_2 in 5.17 hr. at 80°; conversion, 5.47%)	cycloheptenyl–O_2H [h]	0.36 (0.31)	16.96 (10.29)	(0.20)	16.98 (10.80)	53.9 (51.2)
	cycloheptenyl–OH [d]		1.55 (1.83)			4.9 (8.7)
	cycloheptenone =O [g]		3.48 (2.07)		3.48 (2.07)	11.1 (9.8)
	cycloheptene oxide –O [d]	0.70 (0.31)	1.34 (1.22)		2.04 (1.53)	6.5 (7.3)
	peroxide –O–O– with HO_2 [i]			3.71 (2.42)	3.71 (2.42)	23.6 (23.0)

[a] O_2 pressures ranged from 80 to 20 p.s.i.g. [b] Conversions = moles of O_2 absorbed/initial moles hydrocarbon. [c] Alcohol produced expected to lie within these limits. [d] Infrared spectrum of sample trapped from g.l.p.c. effluent identical with authentic sample. [e] N.m.r. of trapped or distilled sample in accord with assigned structure. [f] Mass spectrum of trapped or distilled sample in accord with assigned structure. [g] G.l.p.c. retention time identical with authentic sample. [h] Structure assumed from alcohol formed on reduction. [i] See parts 2 and 5 of Discussion. [j] Products from this oxidation previously reported by E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 121 (1942).
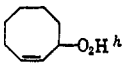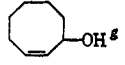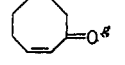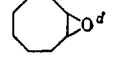
analysis) and the residue then was distilled under high vacuum. The high-vacuum distillate showed no significant hydroperoxide titer and was directly analyzed by g.l.p.c. The residue was hydrogenated with the 5% Rh-on-alumina catalyst and then titrated for free acid. After removal of the acidic fraction (by continuous ether extraction of an aqueous alkaline suspension of the products) the remaining hydrogenation products were acetylated with acetic anhydride prior to analysis by g.l.p.c.

A sample of the ethanol solution of the syrup fraction was titrated for both free acid and hydroperoxide. The remainder was then selectively hydrogenated with Lindlar catalyst and the acidic portion was extracted from the hydrogenation products. The neutral oil remaining was then analyzed by g.l.p.c. The acid fraction was assumed to consist of suberic acid and the corresponding hemiacid–aldehyde and was not investigated further after isolation and weighing.

For methylenecyclohexane and vinylcyclohexane, excess hydrocarbon was removed from the oxidized materials in the usual manner. Instead of separating the products into peroxide distillate and residue, direct selective hydrogenation was employed, followed by g.l.p.c. analysis. A high-vacuum distillation of the reduced products gave only a small nonvolatile residue.

Table II. Oxidation of Cyclooctene at 70 °[a,b]

Product	Hydrocarbon phase — Hydrocarbon dist.	"Peroxide" dist.	Residue	Syrup Phase	Totals	Alkenes converted, %
(cyclooctenyl)—O_2H[h]				2.6	2.6	6.1
(cyclooctenyl)—OH[g]		1.5		0.4	1.9	4.4
(cyclooctenyl)=O[g]		2.3		0.9	3.2	7.5
(epoxide) O[d]	3.0	12.7	0.7	0.6	17.0	39.9
[(cyclooctenyl)—O_2H]$_n$[i]			10.3/n[c]		10.3/n	24.2
$HOOC(CH_2)_6COOH$[j]			0.9	0.8[c]	1.7	4.0
$HOOC(CH_2)_6CHO$[k]			1.7	1.6[c]	3.3	7.7
$OHC(CH_2)_6CHO$[g]				1.3	1.3	3.1
Unidentified				1.3	1.3	3.1
CO[f]					0.2	
CO_2[f]					1.2	
H_2[f]					2.8	

[a] 706.9 mmoles of C_8H_{14} + 0.00955 M ABN in 1437 min. absorbed 41.7 mmoles of O_2; initial R_{O_2} = 0.023 mole/l. hr.; products in millimoles.   [b] Superscripts $d-i$ have the same significance as in Table I.   [c] In acid fraction of syrup.   [j] Melting point and mixture melting point identical with authentic sample.   [k] Assumed structure of acidic material other than suberic acid.

The original composition of the products was calculated from the g.l.p.c. data, the peroxide titer, and the residue weight.
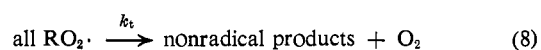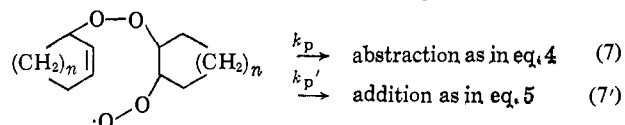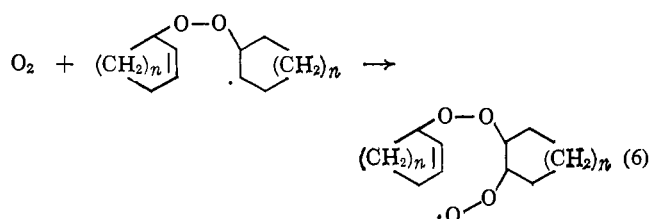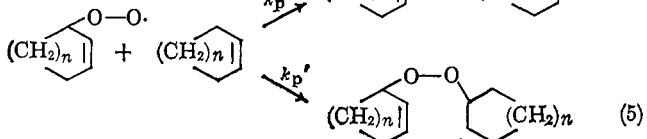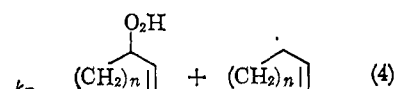
With cyclododecene, only the hydroperoxide yield from oxidation was determined by direct titration, 61 % of theory.

Results

The products found from the oxidation of the neat hydrocarbons are listed in Tables I to III. Rate data for ABN-initiated oxidations of these hydrocarbons in the neat liquid phase are collected in Table IV. Table V lists the products found after reduction of residues from cyclopentene and cyclohexene oxidations.

Definitions and Conventions

Our results will be discussed in terms of the following simplified mechanism.

initiator (ABN or RO_2H) $\longrightarrow$ 2X·

$$\text{rate of initiation} = R_i \quad (1)$$

X·(or $XO_2·$ if X· alkyl) + (CH₂)ₙ cyclic $\longrightarrow$

$$XH + \text{(cyclic radical)} \quad (2)$$

$$\text{(cyclic radical)} + O_2 \longrightarrow \text{(cyclic—O—O·)} \quad (3)$$

$$\xrightarrow{k_p} \text{(cyclic—}O_2H\text{)} + \text{(cyclic radical)} \quad (4)$$

$$\text{(cyclic—O—O·)} + \text{(cyclic radical)} \xrightarrow{k_p'} \text{(cyclic peroxide)} \quad (5)$$

$$O_2 + \text{(cyclic—O—O—cyclic)} \longrightarrow$$

$$\text{(cyclic bis-peroxide)} \quad (6)$$

$$\text{(cyclic peroxy radical)} \xrightarrow{k_p} \text{abstraction as in eq. 4} \quad (7)$$

$$\xrightarrow{k_p'} \text{addition as in eq. 5} \quad (7')$$

$$\text{all } RO_2· \xrightarrow{k_t} \text{nonradical products} + O_2 \quad (8)$$
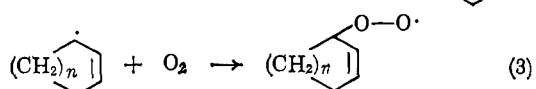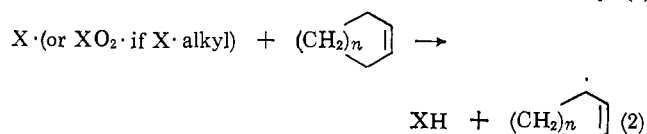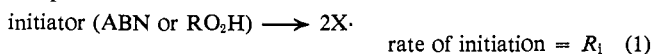
Since rates of oxidation are independent of the oxygen pressures employed, terminations involve only peroxy radicals (or alkoxy radicals from their interaction), and reactions 4 and 5 are the rate-determining propagation steps. The expected rate law is then eq. 9. We

$$\frac{-d[O_2]}{dt} = R_{O_2} = (R_i/2k_t)^{1/2}(k_p + k_p')[\text{alkene}] \quad (9)$$
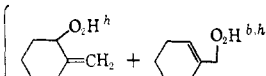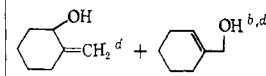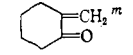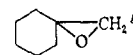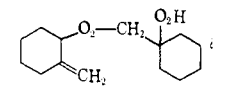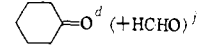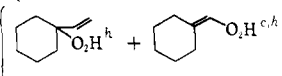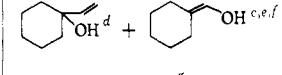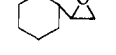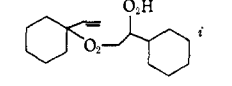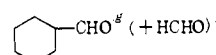
assume further that all types of peroxy radicals (reactions 2, 3, and 6) have identical termination constants, k_t. All concentrations and rates are in moles per liter and hours.

Rates of initiation for ABN-initiated oxidations are calculated from eq. 10. The value of e is taken as 0.60

$$R_i = 2ek_d[\text{ABN}] \quad (10)$$

in all cases (see appendix to ref. 6). The values of k_d used are 0.00842/hr. (50°), 0.0358/hr. (60°), and 0.144/hr. (70°).

Table III. Products from the Oxidations of Methylenecyclohexane and Vinylcyclohexane[a]

Charge and conversion data	Products in mmoles		Alkene converted, %
Methylenecyclohexane, 70°; 408 mmoles 0.00946 M in ABN, absorbed 19.0 mmoles of O_2 in 12.8 hr.; conversion, 4.65%.	(structure) O_2H^h $=CH_2$ + (structure) $O_2H^{b,h}$	6.19	31.9
	(structure) OH $=CH_2$ [d] + (structure) $OH^{b,d}$	2.76	14.2
	(structure) $=CH_2$ [m] O	0.52	2.7
	(structure) CH_2^g O	0.80	4.1
	(structure) O_2—CH_2 O_2H $=CH_2$ [i]	0.62	6.4
	(structure) $=O^d$ (+HCHO)[j]	5.18	26.7
	HCOOH[j]	1.88	...
	Involatile residue[k]	2.46	12.7
	CO_2,[j] CO[j]	0.21, 0.13	...
	Unidentified	0.25	1.3
Vinylcyclohexane, 70°; 108.7 mmoles 0.00947 M in ABN, absorbed 5.46 mmoles of O_2 in 13.75 hr.; conversion 3.97%.	(structure) O_2H^h + (structure) $O_2H^{c,h}$	4.18	61.4
	(structure) OH^d + (structure) $OH^{c,e,f}$	1.18	17.3
	(structure) O [g]	0.08	1.2
	(structure) O_2H O_2 [i]	0.19	5.6
	(structure) —CHO[g] (+HCHO)[j]	0.23	3.4
	Involatile residue[l]	0.16	2.3
	Unidentified (two)	0.43, 0.17	6.3, 2.5

[a] Superscripts d–i have the same significance as in Table I. [b] Actual ratio of secondary to primary alcohol in hydrogenated products was 1.31. [c] Actual ratio of secondary to primary alcohol in hydrogenated product was 1.88. [j] Concomitant formation of HCHO is assumed, the HCOOH arising from further oxidation. [k] Closest empirical formula, $C_7H_{10}O_2$. [l] Closest empirical formula, $C_8H_{12}O_2$. [m] Structure assumed to correspond to alcohols.

Cyclooctene gives large proportions of epoxide, presumably via[9] addition of peroxy radicals (eq. 11)

$$RO_2\cdot + \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{CH=\!\!=\!\!=CH} \rightarrow \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{RO_2CH\!\!-\!\!\overset{\cdot}{C}H} \rightarrow$$

$$RO\cdot + \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{\overset{O}{CH\!\!-\!\!CH}} \quad (11)$$

and large proportions of alkoxy radicals must be

(9) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958); F. R. Mayo and A. A. Miller, *ibid.*, **80**, 2480, 6701 (1958); F. R. Mayo, *ibid.*, **80**, 2497 (1958). The latter paper contains references to several previous workers who reported epoxides as oxidation products.

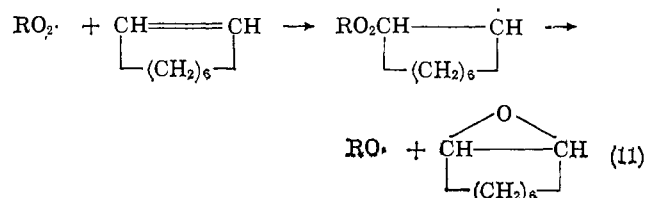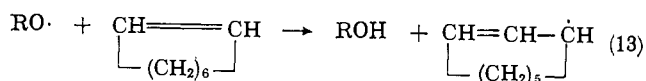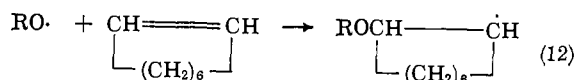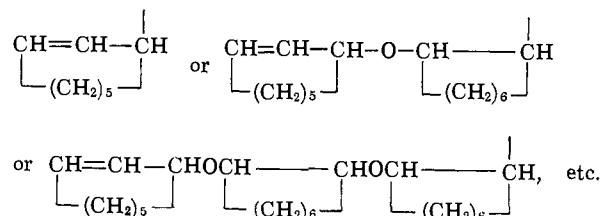$$RO\cdot + \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{CH=\!\!=\!\!=CH} \rightarrow \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{ROCH\!\!-\!\!\overset{\cdot}{C}H} \quad (12)$$

$$RO\cdot + \underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{CH=\!\!=\!\!=CH} \rightarrow ROH + \underset{\underset{(CH_2)_5}{\rule{1cm}{0.4pt}}}{CH\!\!=\!\!CH\!\!-\!\!\overset{\cdot}{C}H} \quad (13)$$

accounted for (eq. 12 and 13). Then $(CH_2)n$ (structure) in eq. 3 becomes R (eq. (3a)) where R =

$$\underset{\underset{(CH_2)_5}{\rule{1cm}{0.4pt}}}{CH=CH\!\!-\!\!CH} \quad \text{or} \quad \underset{\underset{(CH_2)_5}{\rule{1cm}{0.4pt}}}{CH=CH\!\!-\!\!CH\!\!-\!\!O\!\!-\!\!CH}\underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{\rule{1cm}{0.4pt}\!\!CH}$$

$$\text{or} \quad \underset{\underset{(CH_2)_5}{\rule{1cm}{0.4pt}}}{CH=CH\!\!-\!\!CHOCH}\underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{\rule{1cm}{0.4pt}CHOCH}\underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{\rule{1cm}{0.4pt}CH}, \quad \text{etc.}$$

Appropriate substitutions of RO_2 into eq. 4–8 give eq. 4a–8a.

An additional reaction of alkoxy radicals[4] must be introduced to account for formation of suberaldehyde.

$$\underset{\underset{(CH_2)_6}{\rule{1cm}{0.4pt}}}{ROCH\!\!-\!\!\!-\!\!CHO\cdot} \rightarrow R\cdot + OHC(CH_2)_6CHO \quad (14)$$
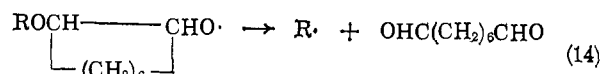
Discussion

1. Primary and Secondary Oxidation Products. The following considerations show that the products in Tables I to III are predominantly primary oxidation products. From previous work[9] and the mechanism just above, hydroperoxides, polymeric peroxides of established structure, and aldehydes and ketones formed by cleavage at the double bond are all primary oxidation products. Nearly all the epoxide is primary oxidation product although a little may arise from the action of hydroperoxide on alkene (next section and ref. 10). This reaction is relatively slow and inefficient at best, and in the presence of oxygen only the stereospecific, nonchain portion[10] counts as secondary reaction. α,β-Unsaturated alcohols and ketones (proportions usually small) are primary oxidation products when they arise from decomposition of hydroperoxides or oxidation of alcohol. Acids, CO, and CO_2 are secondary products. Poorly defined residues (sections 2 and 5) and unidentified compounds cannot be assigned. The assignment of these products as arising by the hydrogen abstraction or the addition mechanisms is detailed in Table VII.

2. Structures of "Dimers" or Residues. Characteristic of every oxidation is a quantity of nonvolatile (at 90° and 0.1 mm.) residue. From our mechanism, these residues are presumably mostly "dimers" (and some "trimers") formed by reactions 3, 5, 6, and 7. Our data on the catalytic hydrogenation of residues from cyclopentene (Table V), cyclohexene (Table V), and cycloheptene[11] are in general accord with our assumed structures.

(structure) $(H_2C)n$ O—O $(CH_2)n$ HOO
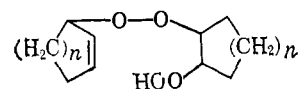
(10) (a) W. J. Brill, *ibid.*, **85**, 141 (1963); (b) E. M. Amir, Preprints of Papers, Division of Petroleum Chemistry, 144th National Meeting of

Table IV. Initial Rates of Oxidation of Cyclic Olefins $[R_{O_2}]_0$

Hydrocarbon	Reacn. temp., °C	$[ABN]_0$, M	$[R_{O_2}]_0$, mole/l. hr.	$(k_p + k_p')/(2k_t)^{1/2}$ (l./mole hr.)$^{1/2}$	Densities 20°	Densities Reacn. temp.	Auto-catalysis[a]
Cyclopentene	50	0.00962	0.029	0.27	0.772	0.743	++
Cyclohexene	60	0.00953	0.058	0.31	0.810	0.772	++
Cycloheptene	60	0.00963	0.036	0.022	0.823	0.790	++
Cyclooctene	70	0.00948	0.023	0.078	0.850	0.806	0 or +
Cyclododecene	70	0.00957	0.032	0.157	0.875	0.837	+
Methylenecyclohexene	70	0.00946	0.024	0.076	0.801	0.755	+
Vinylcyclohexane	70	0.00922	0.025	0.090	0.809	0.766	+

[a] ++, +, and 0 signify strong, weak, and no autocatalysis, respectively.

Table V. Products from the Reduction of Oxidation Residues from Cyclopentene and Cyclohexene

Cyclopentene Product	Peak area, %	Cyclohexene Product	Peak area, %
⬡—OH[g]	16.9	⬡=O[g]	
⬡=O[g]	8.9	⬡—OH[g]	42.4
⬡—OH[e,f]	15.2		
⬡=O[e,f]	0.9	⬡=O[g]	
⬡—OH[d]—OH	31.2	⬡—OH[d]—OH	42.8[b]
OCH—(CH₂)₃CHO[g]	22.3	CHO(CH₂)₄CHO[a]	8.0
...	2.0	...	4.5
...	1.5	...	2.4

[a] Identity assumed by analogy with cyclopentene. [b] Combined area of two peaks. [d-g] Have the same significance as in Table I.

The reduction to equal proportions of unsaturated alcohol and saturated glycol was not as clean as we had expected; the results suggest that some peroxide links were cleaved to free radicals which disproportionated or cleaved further. However, for all three residues, nearly equal amounts of monosubstituted and disubstituted products are formed. An n.m.r. spectrum of the dimer of cyclopentene (summarized in Table VI) further supports the proposed structure, but the presence of about 20% of monomeric hydroperoxide (as indicated by titration) gives nonintegral ratios of peak areas.

The residue does not arise from epoxide or its reaction with peroxide; 0.32 M cyclopentene oxide and 0.92 M cyclopentenyl hydroperoxide were heated for 24 hr. in cyclopentene in the absence of oxygen. Under these conditions (with more oxidation products than are usually formed), the concentration of epoxide increased by 12%, but no high-boiling residue was found.

The hydrogenation of the residue from the oxidation of cyclooctene (Table II) was less satisfactory than with any of the other "dimers"; only 1.07 of the expected 3.4 moles of hydrogen were absorbed per C_8H_{13}-

the American Chemical Society, Los Angeles, Calif., April 1963, Vol. 8, No. 1, p. 33.

(11) With out Lindlar catalyst, cycloheptene residue gave nearly equal proportions of cycloheptenol and cycloheptanediol as major products.

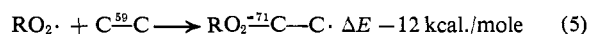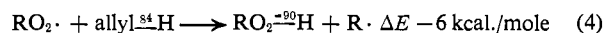Table VI. N.m.r. Spectrum of Cyclopentene Peroxide Dimer

Peak, τ	Multiplicity	Area	Assignment
~1	Singlet broad	5	i
3.9	Complex	4.5	b
4.1	Complex	4.5	a
4.9	Complex	5.5	c
5.5	Complex	7.5	g,h
7.7	Complex	40	e
7.7–8.6	Complex	40	d,e,f,j,k

$(O_2C_8H_{14})_{1.4}O_2H$ unit of the residue with fully active 5% rhodium on alumina. The implications of this result will be considered in section 5.

In the analyses of products from methylenecyclohexane and vinylcyclohexane (Table III), where no separation of volatile and nonvolatile products was made, the constitution of the original product mixtures is surmised by assuming that each molecule of glycol and an equivalent amount of alcohol in the reduced product correspond to one molecule of dimer. In view of the tendency of the catalyst to produce carbonyl derivatives from peroxides, the stated amounts of unsaturated ketone may be high at the expense of the corresponding alcohol.

3. Effect of Temperature on Products. The oxidation of cycloheptene was carried out at both 60 and 80° to determine the effect on the competition of reactions 4 and 5. This hydrocarbon was chosen because the competition is close enough that a change might be detected experimentally. Table I shows that 18.3% of the cycloheptene reacted by addition at 60°; 18.8% at 80°. The difference is within experimental error.

For the indicated bond dissociation energies,[12] reaction 5 is more exothermic than reaction 4. In

$$RO_2\cdot + \text{allyl}\underline{^{84}}H \longrightarrow RO_2\underline{^{-90}}H + R\cdot \quad \Delta E -6 \text{ kcal./mole} \quad (4)$$

$$RO_2\cdot + C\underline{^{59}}C \longrightarrow RO_2\underline{^{-71}}C—C\cdot \quad \Delta E -12 \text{ kcal./mole} \quad (5)$$

the oxidation of cyclopentene[6] (86% abstraction), E_4 was found to be 6.9 kcal./mole. If the more exothermic addition reaction implies a lower energy of activation, then increased temperature should favor more abstraction, but the 20° temperature change was insufficient to bring out the small difference.

(12) S. W. Benson, *J. Am. Chem. Soc.*, 87, 972 (1965).

Table VII. Addition and Abstraction Mechanisms in Autoxidation of Cyclic Alkenes

Hydrocarbon	Reacn. Temp., °C	Mechanism Abstn., %[a]	Addn., %[b]	O_2 acctd. for, %[c]	Ratios of rate constants at 70°,[d] (l./mole hr.)$^{1/2}$ $(k_p + k_p')/(2k_t)^{1/2}$	$k_p'/(2k_t)^{1/2}$ (addition)	$k_p/(2k_t)^{1/2}$ (abstraction)
Cyclopentene	50	86	11.2	101	0.61	0.079	0.132
Cyclohexene	60	88	4.4	105	0.47	0.047	0.105
Cycloheptene	60	63	18.3	86	0.33	0.073	0.064
Cyclooctene	70	30	71.0[e]	89	0.078	0.055	0.006
Cyclododecene	70	63			0.157	0.058	0.025
Methylenecyclohexane	70	58	39.5[f]	99	0.076	0.031	0.011
Vinylcyclohexane	70	74	8.3[g]	113	0.090	0.013	0.077

[a] Per cent of O_2 absorbed titrated as hydroperoxide in the oxidation mixture before product separation. [b] Per cent of all cycloalkene reacting and accounted for in Tables I to III as products of addition mechanism: epoxide, carbonyl compounds from cleavage at double bond, and half the dimer (or two-thirds of the trimer). Hydroperoxides, allylic alcohols, α,β-unsaturated ketones, and half the dimer (or one-third of the trimer) are products of the abstraction mechanism (even if the alcohol and ketone arise from radical interactions). [c] For basis of calculation and possible errors, see text. [d] Apportionment of rates to addition and abstraction is best compromise between methods in footnotes a and b. [e] Counting residue as $(C_8H_{14}O_2)_{2.4}$; 68.9% if residue is dimer, 73.0% if residue is trimer. [f] Neglects substantial unidentified residue. [g] Neglects unidentified materials; if they are all counted as addition products, the per cent addition would be 18.5%.

4. Effect of Structure on Products and Rates.

Table VII summarizes our rate and product data. Two independent estimates of the contributions of the addition and abstraction mechanisms are usually given, as specified, and weighted in notes to Table VII. The estimates are fairly consistent in adding up to 100%. The per cent abstraction values will be low if much hydroperoxide decomposed during oxidation, high if any dialkyl peroxide (in dimer) or H_2O_2 was titrated. The per cent addition values are based on product analyses. With vinylcyclohexane these analyses account for 113% of the O_2 absorbed by weight (cf. section 3 of the Experimental Section); the unidentified products are neglected in calculating the per cent addition but not the O_2 balance or the alkene converted. On either product basis, the proportion of addition at 50–70° varies from about 10% for cyclohexene to 70% for cyclooctene.

An effect of ring size on products has previously been indicated in the literature. Hargrave and Morris[13] oxidized cyclohexene at 55° without added initiator and found 96% of the absorbed oxygen to appear as hydroperoxide by their stannous chloride method (we found 92% by an iodometric method in an ABN-initiated reaction at 60°). Reppe and co-workers[14] obtained 66% yield of epoxide from the autoxidation of cyclooctene with a cobalt catalyst at 60°.

Since most of the olefins described in this report give measurable quantities of both epoxide (reaction 11) and polymer (reaction 6 of the same radical), either the competitions between these reactions depend on oxygen pressure[9] or else there is some other unsuspected route to epoxide formation. Appropriate studies are in progress.

Table VII also lists our estimates of the individual rates of abstraction and addition. The experimental values of $(k_p + k_p')/(2k_t)^{1/2}$ are corrected to 70° when necessary by assuming a 1.5-fold increase per 10° rise in temperature. Values of $k_p/(2k_t)^{1/2}$ are stated on a per hydrogen basis. The table shows that, for the hydrocarbons with ring unsaturation, the composite rate constants for addition are nearly equal. The

greatest discrepancy, with cyclohexene, is associated with the greatest proportional uncertainty in addition. The composite constants for addition of peroxy radicals to methylenecyclohexane and vinylcyclohexane are lower than for the olefins with ring unsaturation. However, if we divide all the values of $k_p'/(2k_t)^{1/2}$ for the latter olefins by 2, to allow for their ability to add radicals at two identical positions, then all the composite constants for addition fall surprisingly close together. This similarity may mean either that both k_p' and k_t remain nearly constant for these olefins or that changes in one are compensated by changes in the other.

The composite rate constants for abstraction vary by a factor of 22, with a regular decrease from cyclopentene to cyclooctene over this range. Nearly half of the factor of 22 is accounted for by the decrease in the number of effectively available hydrogen atoms from 4 in cyclopentene to ca. 2 in cyclooctene. Another factor appears to be the ability of each system to form an allyl radical of maximum orbital overlap. This factor is recognized in rates of base-catalyzed isomerization of exomethylene cyclic hydrocarbons[15] and in solvolysis of benzocycloalkene tosylates.[16] Since the cyclopentene ring is the most nearly planar of the unsaturated rings,[17] the removal of an allylic hydrogen gives a system which already has the correct geometry for maximum π-overlap; the least realignment of nuclei is necessary. Cyclohexene, however, has a skew ring with four carbon atoms in a plane and one below and one above this plane. To gain maximum overlap for the allyl radical (which presumably resembles the transition state for abstraction), one of these latter two carbon atoms must be brought into the plane of the others. With cycloheptene and cyclooctene the skewing is more acute and interference between ring hydrogen atoms in models makes the ring increasingly rigid. These relations could account for an increase in free energy of activation, either from an entropy standpoint, from an increase in strain,[18] or from loss of allyl resonance.

(13) K. R. Hargrave and A. L. Morris, Trans. Faraday Soc., 52, 89 (1956).

(14) W. Reppe, O. Schlichting, and K. Mueller-Gliemann, U. S. Patent 2,769,017 (1956); details on the corresponding German Patent 923,185: Chem. Abstr., 52, 4685 (1958).

(15) A. Schriesheim, R. J. Muller, and C. A. Rowe, J. Am. Chem. Soc., 84, 3164 (1962).

(16) A. Streitwieser, Jr., Chem. Rev., 56, 670 (1956).

(17) G. W. Rathjens, Jr., J. Chem. Phys., 36, 2401 (1962).

(18) The strain energy increases smoothly from 1.5 to 4.0 kcal./mole in going from cyclohexane to cyclohexadiene: K. S. Pitzer, Science, 101,

Table VIII. Steady-State Attack of 100 Molecules of Cyclooctene by 58 $RO_2 \cdot$ and 42 $RO \cdot$ [a]

Attacking radical	Addition	Abstraction
$RO_2 \cdot$	$42[40]RO_2 \cdot \rightarrow RO \cdot + $ epoxide (eq. 11)	$8[8]RO_2 \cdot \rightarrow$ monomeric RO_2H (eq. 4)
		$8[8]^bRO_2 \cdot \rightarrow$ polymeric RO_2H (eq. 4a)
$RO \cdot$	$15[15]RO \cdot \rightarrow$ cleavage (eq. 12, 3a, 11, 14)[c]	$11[10.4]^dRO \cdot \rightarrow$ monomeric ROH (eq. 13)
	$14[14]^bRO \cdot \rightarrow$ addition (eq. 12, 3a, 11)[c]	$2[2]^bRO \cdot \rightarrow$ polymeric ROH (eq. 13)

[a] Brackets indicate experimental values from Table II. [b] Assuming that the residue averages 2.4 cyclooctene units per molecule; the ROH end groups are then determined by difference. The 2.4 is only a convenient and reasonable number between 2 and 3 for calculations. [c] Reaction 12 consumes the cyclooctene and is followed by reactions 3a and 11 of $RO_2 \cdot$. Whether the C_8H_{14} consumed in reaction 12 is cleaved or incorporated in polymer is determined later by competition between reactions 12, 13, and 14. [d] Includes cyclooctenone; calculated from combined stated yields of cyclooctenyl hydroperoxide, cyclooctenol, and cyclooctenone, minus volatile titratable peroxide.

The above discussion of the effect of structure on rates of hydrogen abstraction implies that the effect is largely in k_p and this is probably true for the larger differences. However, recent studies by D. G. Hendry on the cooxidation of these cyclic alkenes with butadiene (unpublished work in this laboratory) show that $k_t^{1/2}$ may sometimes contribute nearly as much as k_p to relative values of the composite rate constants. Small differences in composite rate constants are therefore difficult to interpret.

In the oxidation of cyclohexene, the amounts of alcohol and ketone formed far exceed those accounted for by chain termination. Thus most of these products arise from either hydroperoxide decomposition or non-terminating interactions of peroxy radicals. Our ratio of epoxide to total hydroperoxide (0.0097) is close to the value of 0.0110 at 60° reported by Brill.[10a]

5. The Oxidation of Cyclooctene. The previous section showed that cyclooctene differs from its homologs. Here we shall examine our results in more detail and then compare them with those of others. The high yields of epoxide reported require an accounting for the alkoxy radicals produced in reaction 11.

Table VIII represents a scheme for a steady-state, long-chain, oxidation of cyclooctene in which 100 molecules of cyclooctene are attacked by 58 peroxy ($RO_2 \cdot$) and 42 alkoxy ($RO \cdot$) radicals. This scheme is based on our experimental data in Table II (in brackets in Table VIII, accounting for only 97% of the cyclooctene), our mechanism, the assumption that the nature of R does not affect the reactions of $RO \cdot$ or $RO_2 \cdot$, and the other assumptions in Table VIII. These relations interlock so well that we think the scheme is a useful approximation to the actual oxidation.

From this scheme these conclusions (approximations) follow. (1) In order to maintain a steady ratio of $RO_2 \cdot$ and $RO \cdot$ radicals, all additions of $RO_2 \cdot$ must lead to formation of epoxide (reaction 11) and all the resulting $RO \cdot$ groups must be converted back to $RO_2 \cdot$ by reactions 12, 13, or 14, and 3a. All the reactions of $RO_2 \cdot$ except 11 produce more $RO_2 \cdot$ and so a steady ratio of $RO_2 \cdot$ is maintained. (2) Since all possible radicals undergo reaction 11, the competition between reactions 6 and 11 is not sensitive to oxygen pressure at the 40–80 p.s.i.g. which we used. (3) To achieve the $RO \cdot : RO_2 \cdot$ balance, the internal oxygen links in the polymer must be ether rather than peroxide links. (The minor proportions of diol found on hydrogenation might have come from

cleavage of allylic ether links by the exceptionally active catalyst.) (4) Polymer end groups (80%) are RO_2H rather than ROH but only $8/(11 + 8)$ or 42% of the monomeric units are RO_2H instead of ROH. (This discrepancy may arise in the peroxide determination in the polymer or in the counting of ketone as alcohol, or in chain termination; see below.) (5) Cyclooctene (58%) is attacked by $RO_2 \cdot$ radicals, 42% by $RO \cdot$. (6) $RO_2 \cdot$ radicals (42/58 or 72%) react with cyclooctene by addition; 29/42 or 69% of the $RO \cdot$ react in that manner. Thus any differences in addition/abstraction ratios of $RO \cdot$ and $RO_2 \cdot$ are well within our experimental error. (7) The addition/abstraction *ratios* for cyclooctene in Table VII need no corrections for $RO \cdot$ radicals but the apparent composite rate constants for this alkene should be multiplied by 0.58 if they are to apply only to $RO_2 \cdot$ radicals. (Because of complications from different chain termination, we are not sure that this correction is helpful.)

We now consider how this scheme for long chains is affected by chain initiation and termination. In the experiment in Table II, the initial rate of radical production from ABN was 0.00165 mole/l. hr. ([ABN] $\times 2 \times k_1 \times$ efficiency $= 0.00955 \times 2 \times 0.144 \times 0.60$). This rate was maintained fairly well by auto-catalysis in spite of rapid disappearance of ABN. From Table II, the initial rate of reaction of cyclooctene is 42.6/34.7 times the rate of reaction of oxygen, or 0.0282 mole/l. hr. On the average, 17 cyclooctenes react per radical produced. Thus we would expect that 6 of the 58 peroxy radicals used in a cycle in Table VIII are 2-cyano-2-propylperoxy radicals and that 6% of the products correspond to chain-termination reactions. Not counting hydroxyl and ketone groups in the residue, Table II shows twice as much cyclooctenol and cyclooctenone as needed to account for our estimated chain termination. We conclude that these considerations do not greatly affect our main scheme or conclusions except for reaction 4. Most of the initiator residues were probably lost as volatile peroxides or as acetone and HCN; they may contribute a small proportion of the residues.

Recently, de Roch and Balaceanu[19] have reported a detailed study of the oxidation of *cis*-cyclooctene. The rate of their ABN-initiated oxidation at 70° agrees very well with our own and their product studies at higher temperatures supplement ours at 70°. Our combined results show how further oxidation of suberic aldehyde at higher temperatures and conversions makes possible high yields of cyclooctene oxide.

672 (1945). Three sp^2 carbon atoms in the molecule should fit into the same sequence.

(19) J. S. de Roch and J. C. Balaceanu, *Bull. soc. chim. France*, 1392 (1964).

Table II shows that, at 5.6% conversion of cyclooctene at 70° and an average of 60 p.s.i.g. of oxygen, 40% of the alkene reacting is converted to epoxide, 18% to cyclic hydroperoxide, alcohol, and ketone, 24% to residue, and 15% to suberic aldehydes and acids. At 21% conversion at 95° and about 1 atm. of oxygen, 65% of the alkene appears as epoxide,[19] 10% as cyclic hydroperoxide, alcohol, and ketone, 24% as high-boiling materials containing acid, alcohol, and ester groups, and about 1% as CO and CO_2. Thus, the higher temperature and conversion together have sharply increased the yield of epoxide at the expense of the suberic derivatives, but the poor definition of the residue at higher temperatures precludes more detailed discussion.

The 60–70% yields of cyclooctene oxide reported by others[14,19] deserve further discussion. Each molecule of epoxide formed by addition of $RO_2\cdot$ to cyclooctene (reaction 11) produces an $RO\cdot$ radical which must be converted to another $RO_2\cdot$ radical before the chain can produce more epoxide. (Test calculations indicate that no more than 50% of the oxygen consumed can appear in epoxide.) Each molecule of suberaldehyde[20]

(20) Our data give no support to the suggestion of de Roch and Balaceanu[19] that the open-chain compounds arise by cleavage of cyclooctenyl-3-oxy radicals to give unsaturated aldehydes, but do not exclude his possibility at higher temperatures.

may indeed provide many conversions of $RO\cdot$ to $RO_2\cdot$ as it is oxidized to carbon oxides, but we are left with a serious selectivity problem. Our data indicate that about 70% of the cyclooctene reacting with peroxy radicals reacts by *addition* to give epoxide, the rest by hydrogen abstraction. This restriction alone puts a 70% ceiling on the yield of epoxide at 70°. Further, there is one $RO\cdot$ radical to be disposed of for each $RO_2\cdot$ radical which produces epoxide. The reaction medium is principally cyclooctene, but if many of the $RO\cdot$ react with cyclooctene in any manner, we cannot obtain the stated 65–70% yield of cyclooctene oxide.[21] Unless much of the epoxide comes from peracids from suberic and lower aldehydes (in which case larger proportions of acids should have been found[19]), or unless the effect of temperature is unexpectedly large, or unless there is some other major flaw in our argument above, the data indicate that alkoxy radicals have little tendency to react with cyclooctene at 95° (contrary to our evidence at 70°).

Acknowledgment. Dr. Theodore Mill interpreted the n.m.r. spectrum of the cyclopentene dimer.

(21) From Figure 3 in ref. 19, 78% of the cyclooctene reacting at 106° was converted to epoxide at reaction of 0.067 mole of O_2/mole of initial alkene. Considering the small proportion of by-products available to convert $RO\cdot$ to $RO_2\cdot$, these results seem unrealistic to us at this time.

The Liquid-Phase Oxidation of Cyclopentene[1]

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This work was undertaken to elucidate autocatalysis in the autoxidation of alkenes. Cyclopentene was chosen for study because it gives a high yield of hydroperoxide (75%) at 50°. In benzene solution, the rate of oxidation is first order in cyclopentene. In neat cyclopentene, the rate is half order in azo initiator and first order in added 3-cyclopentenyl hydroperoxide. The rate of initiation by hydroperoxide corresponds closely to its second-order rate of decomposition; it is an efficient initiator of oxidation. The hydroperoxide is more stable in benzene solution and no autocatalysis of the oxidation of cyclopentene is observed in benzene at 50°. Relations between hydroperoxide concentrations and rates of oxidation show that a retarder is formed during the autoxidation of cyclopentene. An intermediate steady rate of oxidation therefore may only represent a transition from initial autocatalysis to later autoretardation.

Introduction

The objective of this work was to obtain some reliable, fundamental information on autocatalysis in

oxidation of alkenes. Our efforts have been directed to cyclopentene at 50° because it oxidizes readily under mild conditions and gives a high yield (75%) of 3-cyclopentenyl hydroperoxide.

In spite of well-recognized autocatalysis in the oxidation of olefins, very little quantitative information is available. Tobolsky, Metz, and Mesrobian[2] proposed a theory of steady or maximum rates based on equal rates of formation and destruction of initiating hydroperoxide. Although several other workers have cited this paper when they have observed a steady or maximum rate in an autoxidation, this paper is seldom really relevant in regions of kinetic interest. As clearly stated by Tobolsky, *et al.*, their rate becomes steady when the rate of formation of peroxide equals the rate of decomposition of peroxide and the chain length becomes unity; here the conversions may be so high that the assumed constant concentration of hydrocarbon is invalid.

Jackson and Verhoek[3] investigated the autoxidation of cyclohexene and concluded that a steady rate of oxidation does not necessarily indicate a steady con-

(2) A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, 72, 1942 (1950).
(3) W. E. Jackson and R. H. Verhoek, Report to Air Force Office of Scientific Research by C. E. Boord, TR 58-82, AD 158 384, Armed Services Technical Information Agency, Arlington, Va., p. 1.