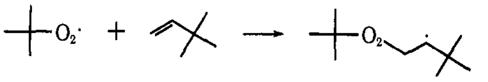
reacted by the addition mechanism. This result is consistent with at least 24% addition in the oxidation of 1-butene where the allylic hydrogen atom is more reactive than in propylene.

6. Oxidations of *t*-Butyl- and Neopentylethylenes. The oxidations of these alkenes are exceptional in giving products which are not predicted in eq 1–10.

In spite of the absence of allylic hydrogen atoms, *t*-butylethylene was rather reactive in oxidation and more reactive toward addition of peroxy radicals than other more substituted ethylenes. The reaction was nearly self-sustaining; the final oxidation rate was nearly equal to the initial rate (~95%) in spite of 95% decomposition of the ABC. The aldehyde formed may be responsible.

To account for epoxide and *t*-butyl alcohol as main volatile products, the following chain sequence is proposed.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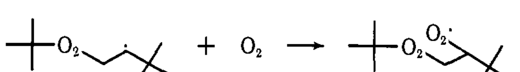
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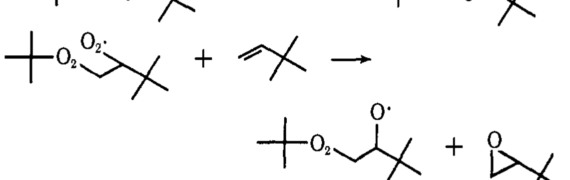
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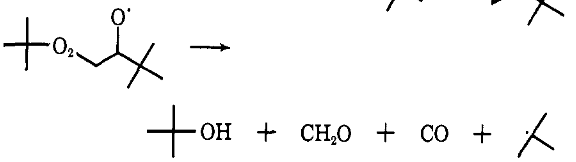
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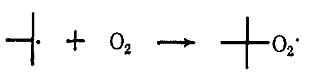
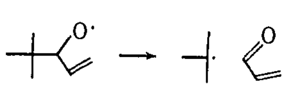

(19)

Step 18 proposes, in effect, that the β-peroxyalkoxy radical gives a *t*-butyl radical, formaldehyde, *t*-BuOH, and CO simultaneously. If the substantial concentration of a facile hydrogen donor (pivaldehyde) is never attained, the absence of acetone in the products seems to require the absence of free *t*-butoxy radicals. The yield of CO is below that of *t*-BuOH and the presence of hydrogen suggests additional complicating reactions.

Neopentylethylene provided the most complicated of all our oxidations. By no means could all the products be identified and the low oxygen balance suggests that some may have been missed; the presence of *t*-butyl alcohol, acetone, and acrolein suggests that the process (eq 20) plays an important part in the oxidation


(20)

mechanism. Both acrolein and *t*-butyl vinyl ketone might have contributed to the substantial residue found.

7. Oxidations of 1- and 3-Hexynes. 3-Hexyne oxidizes rapidly (~three times as fast as cyclohexene) and gave 67% yield of the propargyllic hydroperoxide (structure based on alcohol found upon reduction). 1-Hexyne oxidizes ~five times as fast as 1-hexene. It gave only 17% yield of volatile hydroperoxide on the O_2 consumed but gave several unidentified volatile products. The reduction of the hydroperoxide with triphenylphosphine was inefficient (intense yellow color formed) and the amount of oxygen accounted for from the glpc of the reduced product was well below the amount absorbed by oxidation.

Effects of Experimental Variables in Oxidations of Alkenes[1]

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Abstract: The yield of epoxide (Y) in olefin oxidations increases to a limiting value with decreasing oxygen pressure according to the relation, $Y = 1/(A + B[O_2])$. Such increases were observed in oxidations of cycloheptene, trimethylethylene, and cyclooctene. Rates of rearrangement of nine β-(alkylperoxy)alkyl radicals to epoxides are compared. The abstraction/addition ratio is nearly independent of temperature in oxidations of isobutylene and cycloheptene and of solvent changes in oxidations of cyclopentene, tetramethylethylene, and cyclooctene. Epoxide yields in cycloheptene oxidations are moderately higher at higher temperatures. Composite rate constants, $(k_p + k_p')/(2k_t)^{1/2}$, are increased 1.5-fold for each 10° temperature rise and up to fivefold by use of acetonitrile instead of benzene as solvent. For oxidations where little cleavage occurs, product yields do not depend much on conversion. Where aldehydes are produced, cooxidation of aldehyde and olefin may increase epoxide yields. Recent work on oxidation of alkenes is reviewed.

A previous[2a] and an accompanying paper[2b] discuss the products of oxidation of several alkenes in terms of the addition and hydrogen-abstraction mechanisms of oxidation. The present paper evaluates the importance of oxygen pressure, temperature, solvent, and conversion on the products of oxidation of some of these alkenes. Control of temperature and

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[1] Research sponsored by AFOSR (SRC)-OAR, U. S. A. F. Contract No. AF49 (638)-1102.

[2] (a) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965); (b) D. E. Van Sickle, F. R. Mayo, R. M. Arluck, and M. G. Syz, *ibid.*, **89**, 967 (1967).

Table I. Effect of Temperature and Oxygen Pressure on Epoxide Yield in Oxidation of Cycloheptene

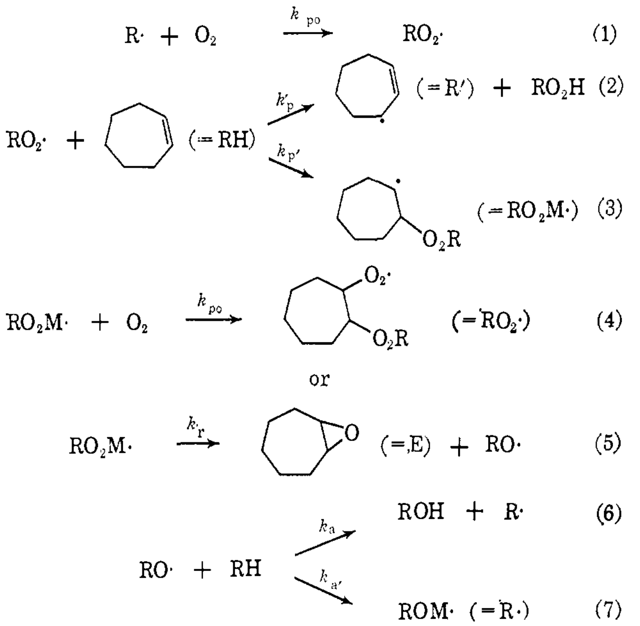
Temp, °C	$\bar{P}_{O_2}$,[a] psia	$[C_7H_{12}]$ in C_6H_6	Initiator[b]	M	Y_p[c]	Y_6[c]	From eq 12 A	From eq 12 B
60	50	8.22[d]	None	...	0.065	0.10[e]	9.4	176
60	850	8.22[d]	ABN	0.0097	0.009			
70	6.8	1.96	ABN	0.0094	0.13	0.13		
90	6.1	1.89	ABC	0.0092	0.17	0.17	5.5	108
90	62	1.89	ABC	0.0093	0.10			
110	23	1.81	t-Bu_2O_2	0.0098	0.12			

[a] $\bar{P}_{O_2}$ = average pressure of O_2; 1 psia = 1/14.7 atm. [b] See ref 2a. [c] Y_p = yield at indicated pressure; Y_6 = Y_p at 6 psia. [d] No solvent. [e] Extrapolated from 50 and 850 psia experiments.

oxygen pressure is important in maximizing yields of epoxides in oxidations of alkenes, but the effect of solvent change is small. The effects of degree of conversion on products depends mostly on secondary oxidations of primary products and is largest when aldehydes are prominent primary products; cooxidations of aldehydes and alkenes give epoxides. These conclusions are supported by comparison of our own experiments with those in the recent literature.

Effect of Oxygen Pressure on Epoxide Yield

1. **Theory.** With an oxidation as simple as that of cycloheptene,[2a] the following model is a good approximation.



For long chains, where consumption of reactants in termination steps can be neglected, the steady-state equation for $RO_2M\cdot$ radicals is

$$k_p'[RO_2\cdot][RH] = k_r[RO_2M\cdot] + k_{po}[RO_2M\cdot][O_2] \quad (8)$$

and for the $RO\cdot$ radicals is

$$k_r[RO_2M\cdot] = (k_a + k_a')[RO\cdot][RH] \quad (9)$$

The rate of epoxide formation, $d[E]/dt$, by reaction 5 is

$$d[E]/dt = k_r[RO_2M\cdot] \quad (10)$$

and the total rate of reaction of alkene is

$$-d[RH]/dt = (k_p + k_p')[RO_2\cdot][RH] + (k_a + k_a')[RO\cdot][RH] \quad (11)$$

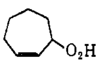
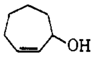
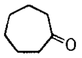
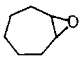
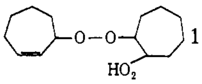
The yield of epoxide, Y, as a function of oxygen concentration is defined as $d[E]/-d[RH]$ and from eq 8 to 11 is

$$Y = \frac{d[E]}{-d[RH]} = \frac{k_r f_a}{k_r(1 + f_a) + k_{po}[O_2]} = \frac{1}{A + B[O_2]} \quad (12)$$

where[2,3] $f_a = k_p'/(k_p + k_p')$ = the fraction of peroxy radicals which add to the olefinic double bond, $A = (1 + 1/f_a)$, and $B = k_{po}/k_r f_a$.

2. **Results.** Table I shows epoxide yields from oxidation of cycloheptene at 60–110° with and without benzene as solvent. Table II gives complete product

Table II. Effects of Oxygen Pressure and Conversion on Products of Oxidation of Undiluted Cycloheptene at 60°

Product	mmoles of product 30 psia, 19%[a]	50 psia, 9%[b]	850 psia, 5%[c]	Yield on alkene, % 30 psia, 19%[a]	50 psia, 9%[b]	850 psia, 5%[c]
	31.48	16.98	5.44	53.2	53.9	55.6
	0[e]	1.55	~0[d]	0.0	4.9	0.0
	9.36	3.48	0.97	15.8	11.1	9.9
	5.96	2.04	0.09	10.0	6.5	0.9
	11.29	3.71	1.57	19.1	23.6	32.1
Unidentified volatiles	1.13[f]		0.14[g]	1.9		1.5

[a] 40.554 g, 422 mmoles, C_7H_{12}, 0.0096 M in ABN, absorbed 80.2 mmoles of O_2 in 32.1 hr at $\bar{P}_{O_2}$ = 30 psia; 19% of the alkene was converted. The sample taken for analysis corresponds to 75.9 mmoles of O_2. [b] From ref 2a; 36.034 g, 375 mmoles, C_7H_{12}, without added initiator, absorbed 34.6 mmoles of O_2 in 45.5 hr at $\bar{P}_{O_2}$ = 50 psia; 9.22% of the alkene was converted. [c] 20.51 g, 213 mmoles, C_7H_{12}, 0.0097 M in ABN, was shaken in a rocking, glass-lined bomb with O_2 at an average pressure of 850 psia; an estimated 5.25% of the alkene was converted; 18.14 g of the solution was taken for analysis. [d,e] 0.20[d] or 0.8[e] mmole less $C_7H_{11}OH$ found by glpc than $C_7H_{11}O_2H$ titrated before reduction. [f] Six products. [g] Five products.

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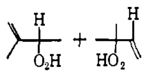
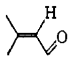
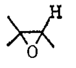
(3) An equation of similar form for the oxidation of α-methylstyrene was obtained by F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2487, 6701 (1958). Strictly, eq 12 applies to oxidations at constant oxygen pressure. In our calculations which follow, we have assumed that the experimentally measured epoxide yield $\bar{Y}$ corresponds to the average oxygen pressure $\bar{P}_{O_2}$ according to eq 12. Test calculations with A = 5.5 and B = 108, for a change in oxygen concentration from 0.01 to 0.1 M, indicate that an 18% error in Y may arise from this assumption.

analyses for the three oxidations of undiluted cycloheptene at 60°. Tables III and IV show the product analyses for oxidations of neat trimethylethylene and cyclooctene, each at two different pressures. In all cases, in agreement with eq 12, yields of epoxide are lower at higher oxygen pressure.

Table III. Effect of Oxygen Pressure on the Oxidation of Undiluted Trimethylethylene at 60°

Product	mmoles of product		Yield on alkene, %	
	4.2 psia[a]	34 psia[b]	4.2 psia[a]	34 psia[b]
Primary RO_2H + 	4.17	3.74	23.8	19.4
Alcohols[c]	0.22	0.63	1.3	3.3
	0.23	0.23	1.3	1.2
	6.41	1.94	36.5	10.1
CH_3CHO	1.32	1.28	*d*	*d*
Acetone[d]	1.75	2.08	8.0[d]	9.1[d]
Unidentified (4)	0.77	1.54	4.4	8.0
Residue	4.35[e]	9.45[e]	24.8	49.0
	14.7 O_2	18.9 O_2		

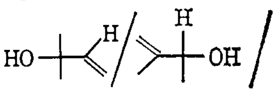
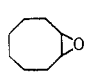
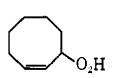
[a] 32.57 g, 464.4 mmoles, 0.0093 *M* in ABN, absorbed 17.5 mmoles of O_2 in 13.0 hr at $\bar{P}_{O_2} = 4.2$ psia; 3.8% of the alkene was converted; the sample taken for analysis corresponds to 17.0 mmoles of O_2. [b] 32.61 g, 465 mmoles, C_5H_{10}, 0.0094 *M* in ABN, absorbed 21.3 mmoles of O_2 in 13.1 hr at $\bar{P}_{O_2} = 34$ psia; 4.6% of the alkene was converted; the sample taken for analysis corresponds to 18.3 mmoles of O_2. [c] Total alcohols after reduction minus hydroperoxides; ratio of  all primary alcohols was 1.42/1.39/1.47 for the 4.2 psia experiment and 1.70/1.44/1.23 for the 34 psia experiment. [d] For calculations, 0.35 mmole of AcMe is assumed to come from ABN in the 4.2 psia experiment, 0.32 mmole in the 34 psia experiment; AcH equivalent to AcMe from C_5H_{10} is assumed to have been formed. [e] For the 4.2 psia run, 456.7 mg of residue averaged $C_5H_{9.52}O_{2.21}$ and contained 1.85 mmoles of titratable hydroperoxide. For the 34 psia run, 990 mg of residue averaged $C_5H_{9.76}O_{2.18}$ and contained 3.79 mmoles of titratable hydroperoxides.

Table IV. Effect of Oxygen Pressure on Oxidation of Cyclooctene in Benzene at 70°

Product	mmoles of product		Yield on alkene, %	
	51 psia[a]	780 psia[b]	51 psia[a]	780 psia[b]
Suberic acid	1.46	0.91	8.3	9.5
	7.05	2.38	39.9	24.8
	0.37	0.32	2.1	3.3
Other volatile[c]	1.35	1.17	7.6	12.2
Residue[d]	7.43	4.83	42.1	50.3

[a] 361.2 mmoles in 517 mmoles of C_6H_6, 0.0093 *M* in ABN, absorbed 19.8 mmoles of O_2 in 23.6 hr at $\bar{P}_{O_2} = 51$ psia; 5.6% of the alkene was converted. [b] 148.7 mmoles in 212 mmoles of C_6H_6, 0.0094 *M* in ABN, was oxidized for 21.9 hr at $\bar{P}_{O_2} = 780$ psia. [c] Suberaldehyde, cyclooctenone, etc., also 0.91 mmole of CO_2 in 51-psia experiment. [d] Millimoles of $C_8H_{14}O_2$ units by weight; 2.98 mmoles of titratable RO_2H in 51-psia run, 1.26 in 780-psia run.

3. Discussion. In Table I, yields of epoxides at various oxygen pressures (Y_p) are used to evaluate the constants A and B in eq 12. Since A and B values are used to estimate the temperature coefficient of k_{po}/k_r in the Epoxide Yields section, our choices are discussed here. The 90° value for A, 5.5, corresponds to f_a = 22%, the fraction of cycloheptene reacting by addition, agreeing within 2% with the results based only on known products of oxidation from our previous paper.[2a] We therefore take $A = 5.5$, independent of temperature. We attach less importance to the 60° value of A because the 60° Y_p values are smaller, closer together, and less accurate, and because this A value corresponds to only 12% reaction by addition. The B value[4] (in l./mole) at 60° is therefore also uncertain. The corresponding k_{po}/k_r values are given in Table V.

Table V. Evaluation of k_{po}/k_r for Substituted β-Alkylperoxyethyl Radicals

Alkene	Reaction temp, °C	k_{po}/k_r, *M*	Ref
Cyclooctene (in benzene)	70	2.2	
Tetramethylethylene	50	32	2b
Cycloheptene (no solvent)	60	34	
(in benzene)	90	25	
2-Methyl-1-pentene	70	110	2b
2-Butene	70	110	2b
Trimethylethylene	60	150	
Cyclopentene	50	220	2a
α-Methylstyrene (high O_2 press.)	50	5,900	3
(low O_2 press.)	50	11,000	
Styrene (high O_2 press.)	50	53,000	5
(low O_2 press.)	50	154,000	

Application of eq 12 to the data on trimethylethylene in Table III gives a negative value for B. Reactions 5, 6, and 7 require that the products of reaction of alkoxy radicals (alcohols and ether groups in the residue) be equivalent to the epoxide formed. There is a clear deficiency of such groups in the 4.2-psia experiment in Table III. Such deficiencies are discussed in the Effects of Solvent Polarity section. If we take f_a to be 50% ($A = 3$, consistent with both trimethylethylene experiments), then the 10% yield of epoxide in the 34-psia experiment gives $B = 300$ and k_{po}/k_r = 150, the value chosen for the summarizing Table V. To obtain the same value from the 4.2-psia experiment in Table III, the yield of epoxide should be 25% instead of 36.5%. The yield of alcohols plus possible ether groups in the residue is far short of accounting for radicals to correspond to the epoxide found.

In the oxidation of cyclooctene at 51 psia (Table IV) there are also insufficient alkoxy radical residues to account for the epoxide formed. Nevertheless the two experiments give, without any corrections to eq 12, $A = 2.4$ and $B = 3.08$. The value of A corresponds to 71.4% of alkylperoxy radicals reacting by addition (close to 77.2 and 77.6% addition estimated from the data in Table IV by the method described in Table VII of ref 2a) and to k_{po}/k_r = 2.2, the value given in Table V. The latter is the smallest and least certain such ratio in Table V; up to one-third of the epoxide

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(4) 1 psia = 1/14.7 atm; solubility of oxygen in hydrocarbons taken to be 0.01 *M*/atm.

may have been formed *via* acylperoxy radicals (see the Epoxide Yields from Cycloheptene section).

4. Evaluation of k_{po}/k_r for Other Alkenes. For comparison with the results cited above, we have calculated values of k_{po}/k_r for several other alkenes listed in our previous papers[2] where the values of the fraction of alkene reacting with peroxy radicals by addition and the yields of epoxide are well enough known to give results to ±30%. The alkenes in Table V are arranged in order of decreasing ability of their β-alkylperoxyalkyl radicals to rearrange to epoxide at 50° instead of reacting with any common concentration of oxygen. On the latter standard, the cyclooctene radical rearranges about 25,000 times as fast as the styrene radical. The substituted benzyl radicals in oxidizing styrene and α-methylstyrene are least reactive in attacking the β-peroxide group, and the rearrangement is least exothermic because of the resonance energy lost. The dependence of rearrangement constant on oxygen pressure with the styrenes seems to be real and was attributed[3,5] to differences in the oxygen content of the residues beyond the peroxide links. The slowest rearrangement of the aliphatic alkenes listed is the formation of cyclopentene oxide, probably the most strained oxide listed. The other alkenes in Table V with greater tendencies to rearrange include both secondary and tertiary β-alkylperoxy radicals. Models suggest that there can be steric effects on both reactions 4 and 5; we found no obvious separation of these effects.

When considerable cleavage occurs at the double bond in oxidation, eq 12 may not be strictly applicable. This equation allows for cleavage by simple depolymerization of polyperoxide radicals,[3,5] but, if additionel cleavage occurs by another route recognized for styrene[5] and α-methylstyrene,[3] and possibly applying to tetramethylethylene

$$RO_2M\cdot + O_2 \xrightarrow{k_{ch}} RO_2\cdot + R'{=}O + R''{=}O \qquad (13)$$

then application of eq 12 gives $(k_{po} + k_{ch})/k_r$ instead of k_{po}/k_r.

Effect of Temperature on Rates and Products

1. Rate and Peroxide Yield in Isobutylene Oxidation. In the oxidation of cycloheptene,[2a] the ratio of addition to abstraction was insensitive to temperature over a 20° range. This conclusion is now supported by an oxidation of isobutylene in benzene solution at 90° with ABC initiator. Iodometric titration of the whole reaction mixture (after first removing unreacted isobutylene) showed that 13% of the oxygen was present as hydroperoxide, the same as at 80°. The rate of oxidation at 90° gave a calculated value of the composite rate constant, $(k_p + k_p')/(2k_t)^{1/2}$, of 0.142 $(M\ \text{hr}^{-1})^{1/2}$, as compared with 0.095 at 80°. Thus the 1.5-fold increase in $(k_p + k_p')/(2k_t)^{1/2}$ per 10° rise in temperature applies to acyclic as well as to cyclic alkenes.[2a]

Although the two oxidations cited above show little or no effect of temperature on the competition between the addition and abstraction mechanisms, other studies suggest that the abstraction/addition ratio increases with temperature (at least with alkenes which favor addition at low temperatures). These ratios indicate that the activation energy for abstraction is greater than for addition by 2370 cal/mole for methyl radicals with allyl acetate,[6] and 970, 2670, and 2360 cal/mole for reactions of trichloromethyl radicals[7] with cyclopentene, cyclohexene, and cycloheptene, respectively. Any reversibility of the addition reaction[8] at higher temperatures would also favor the abstraction mechanism.

2. Epoxide Yields. Eq 12 shows that temperature changes may affect yields of epoxides through either the fractions of peroxy radicals reacting by addition, f_a, or through k_{po}/k_r. Since we have so far found no significant effect of temperature in f_a (previous section 1), we shall assume that temperature affects only k_{po}/k_r, that is, B in eq 12. In Table I, the increase in Y_6 with temperature (yield of epoxide at 6 psia of oxygen) establishes that k_{po}/k_r and B decrease with increasing temperature. Since the 60° values of A and B in Table I are dubious (Results section), we have calculated values of B at 60° using the experimental Y values and $A = 5.5$. We obtain $B = 291$ and 183 from the 50 and 850 psia experiments. These values together with $B = 108$ at 90° give $E_r - E_{po}$ equal to 8.0 and 4.2 kcal/mole, respectively. Since E_{po} probably differs from zero only by the activation energy of diffusion, ~2 kcal/mole, we conclude that E_r is 8 ± 2 kcal/mole.

Since the Evaluation of k_{po}/k_r for Other Alkenes section showed that cycloheptene is one of the most active alkenes in the rearrangement reaction 5, we anticipate that other activation energies for rearrangement are higher than for cycloheptene and conclude that epoxide formation is always favored by higher temperatures, at least up to the temperatures where the reverse of reaction 3 begins to compete with epoxide formation (but then reaction 4 may also become reversible).

Effects of Solvents on Rates and Products of Oxidation

1. Effects of Dilution. Dilution[9] of cyclopentene by benzene causes a slight increase in the calculated value of $(k_p + k_p')/(2k_t)^{1/2}$, and cyclohexane as solvent causes a decrease in this ratio.[9] To investigate the possibility that dilution of an alkene with inert solvent might alter the abstraction/addition ratio, the oxidation of cyclopentene was investigated in benzene solution. Table VI shows that there is no significant change in yields of either total hydroperoxide or dimeric hydroperoxide when the concentration of cyclopentene is changed (at 50–70°) from 10.92 to 2.69 M.

2. Effects of Solvent Polarity. Although free-radical reactions, as a class, are much less sensitive to solvent effects than are heterolytic reactions, significant changes in the rates of homolytic reactions have occasionally resulted from changes in solvent. The autoxidation of cyclohexene in acetonitrile at 60° is over twice as rapid as in *t*-butylbenzene,[10] whereas the corresponding change in solvent accelerates the autoxi-

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[5] F. R. Mayo, *J. Am. Chem. Soc.*, 80, 2465 (1958).

[6] R. P. Buckley, F. Leavitt, and M. Szwarc, *ibid.*, 78, 5557 (1956).

[7] E. S. Huyser, *J. Org. Chem.*, 26, 3261 (1961).

[8] S. W. Benson, *J. Am. Chem. Soc.*, 87, 972 (1965).

[9] D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *ibid.*, 87, 4832 (1965).

[10] D. G. Hendry and G. A. Russell, *ibid.*, 86, 2368 (1964).

Table VI. Effect of Solvents and Dilution on Oxidations of Alkenes at 50–70°[a]

Alkene mmoles	Alkene M	Solvent	[ABN], mM	Time, hr	ΔO_2, mmoles	Yields, % RO_2H[b]	Yields, % Residue[c]	Addn, %[a,d]	R_{O_2}[e]	$\frac{(k_p + k_p')}{(2k_t)^{1/2}}$
				Cyclopentene						
557.9	10.92	None	0.95	18.06	23.8	86	20.2	(50°)	0.010	0.28[f]
243.7	4.73	C_6H_6	9.6	4.16	11.3	90	20.2	(60°)	0.046	0.48
120.8	2.35	C_6H_6	9.6	4.15	5.55	91			0.027	0.56
63.3	1.236	C_6H_6	9.6	4.17	2.87	90			0.014	0.56
142	2.69	C_6H_6	3.8	4.32	10.95	91	20.8	5.8	0.048	0.702
142	2.69	MeCN	3.8	1.82	14.40	89	16.1	5.8	0.119	1.74
				Tetramethylethylene						
21.2	2.03	C_6H_6	5.6	5.00	2.20			62	0.044	0.703
21.2	2.03	MeCN	4.9	1.17	2.75			53	0.163	2.74
				Cyclooctene						
96.5	3.67	C_6H_6	9.4	23.6	19.8	17	37.5	73	0.056	0.102
361.2	1.83	MeCN	4.2	21.8	9.53			67	0.024	0.49

[a] First experiment at 50°, next three at 60°, all others at 70° Details of 70° experiments in Table VII. [b] Total $RO_2H/\Delta O_2$. [c] Residues assumed to be $C_5H_7O_2C_5H_8O_2H$ or $(C_8H_{14}O_2)_n$. [d] Epoxide, cleavage products, and (residue + unidentified products)/2 as per cent of alkene accounted for. [e] Initial rate of oxidation in M hr^{-1}. [f] From ref 2a.

dation of cumene tenfold.[11] Since the magnitude of such solvent effects differs for different reactions, the ratio of products from competing reactions in a given system may also vary more than tenfold with solvent.[12,13]

In the present investigation of solvent effects, our main interest was the possible variation in the proportions of reaction products. Two solvents, benzene and acetonitrile, having greatly different dielectric constants (2.3 *vs.* 38)[10] were used. Rate data (Table VI), confirming previous work, show that oxidations are faster in acetonitrile than in benzene (2.5 times as fast for cyclopentene, 3.9 times for tetramethylethylene, and 4.9 times for cyclooctene). Product data (Tables VI and VII) show no clearly significant effect of solvent on the addition/abstraction ratio, but they suggest that the unimolecular rearrangement reaction 5 is favored over the competing bimolecular reaction 4 in the nitrile solvent of higher dielectric constant. Details are discussed below.

For cyclopentene, the ratio of epoxide to dimer seems significantly higher in acetonitrile than in benzene. The idea that this shift is due to a relatively higher rate of the unimolecular rearrangement reaction has an excellent precedent in the work of Walling and Wagner with *t*-butoxy radicals[13] and some analogy in the effects of solvents on the unimolecular deposition of dibenzoyl peroxide.[14] In the oxidation of tetramethylethylene, the trends in yields of epoxide, acetone, and residue give qualitative support to the idea of easier rearrangement in the more polar solvent, but the quantitative relations are inconclusive. In the oxidation of cyclooctene, nearly all of the β-peroxyalkyl radicals rearrange in benzene, and so this rearrangement cannot be obviously enhanced in acetonitrile. Unidentified products obscure any other trends in the effect of solvent change with this alkene.

The epoxide yields from cyclopentene and tetramethylethylene at 70° in Table VII are significantly higher than those reported without solvent[2] at 50°. At least part of this increase is due to the higher temperature (Epoxide Yields section).

In many cases the epoxide yield exceeds the yield of α,β-unsaturated alcohol. While this discrepancy is marginal in cyclopentene and cycloheptene, it is well beyond experimental error with tetramethylethylene, trimethylethylene (low pressure, Table III), and cyclooctene. The fate of the alkoxy radicals from epoxidation of cyclooctene has been discussed previously[2a] and is mentioned further in the Cooxidation of Aldehydes and Alkenes section. Similar considerations apply also to trimethylethylene and tetramethylethylene. However, with these alkenes, any certain explanation is excluded by the high proportions of residue (which may contain the missing alkoxy groups or their oxidation and polymerization products) and by the method of determining unsaturated alcohol (total volatile hydroperoxide before reduction minus total allylic alcohols after reduction).

Secondary Oxidation Reactions

1. Effect of Conversion on Products of Oxidation of Cycloheptene. Cycloheptene was chosen for a study of the effect of conversion on products because it gives a clean oxidation by both addition (>18%) and abstraction (>63%) mechanisms[2a] and produces no aldehydes. The moderate differences between 9 and 19% conversion experiments in Table II are probably due mostly to irregularities in triphenylphosphine reduction and to the difference (50 and 30 psia) in oxygen pressure. There is no significant difference in the proportions of cycloheptene reacting by addition and abstraction. Further, the 5.5% conversion run at 80° and 50 psia[2a] is nearly identical with the 9% conversion run at 50° and the same pressure. These comparisons show that the products are essentially primary products.

The above considerations apply when oxidation produces little aldehyde.

2. Cooxidation of Aldehydes and Alkenes. For olefins which undergo substantial cleavage by autoxidation, aldehydes (primary products) often accumulate and the oxidation soon becomes a cooxidation of aldehyde and alkene. To investigate this process in an extreme case, cyclooctene was cooxidized at low pres-

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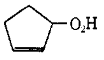
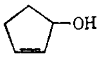
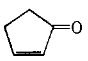
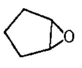
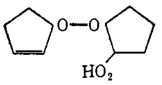
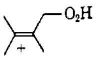
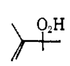
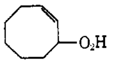
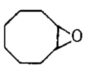
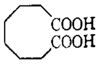
(11) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 1250 (1964).

(12) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(13) C. Walling and P. Wagner, *ibid.*, **86**, 3368 (1964).

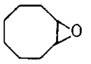
(14) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946), report that the spontaneous (noninduced) decomposition of benozyl peroxide is over four times as rapid in ethyl acetate as in CCl_4 at 80°.

Table VII. Oxidations of Cyclopentene, Tetramethylethylene, and Cyclooctene in Benzene and Acetonitrile Solutions at 70°[a]

Product	mmoles of product C_6H_6	mmoles of product CH_3CN	Yield on alkene, % C_6H_6	Yield on alkene, % CH_3CN
Cyclopentene in 33.0 g of C_6H_6 or 29.4 g of MeCN; $\bar{P}_{O_2}$ = 70 psia				
	7.52	11.64	68	72
	0.38	0.08	3.5	0.5
	0.16	0.72	1.5	4.4
	0.69	1.46	6.3	9.0
	1.14	1.16	20.7	14.3
$Me_2C{=}CMe_2$ in 6.60 g of C_6H_6 or 5.87 g of MeCN; $\bar{P}_{O_2}$ = 70 psia				
	0.78	1.10	31	36
				
Alcohols	0.00[c]	0.12	0	4
	0.75	1.02	29	34
AcMe	1.35	0.89	27	15
Residue[b]	0.17	0.16	13	11
Cyclooctene in 40.4 g of C_6H_6 or 29.4 g of MeCN; $\bar{P}_{O_2}$ = 50 psia				
	0.37	0.95	2.1	12
	7.05	2.97	39.9	37
Other volatiles	1.35	*c*	7.6	~0
	1.46	0.67[d]	8.3	8.3[d]
Residue[e]	7.43	3.52	42.1	43.4

[a] Some experimental details in Table VI. [b] Assumed to be dimeric peroxide; formula wt, 232. [c] Very little in excess of peroxide titrated. [d] Acid fraction not separated.[2a] Nonvolatile residue assumed to be 16% (by weight) suberic acid. [e] Units of $C_8H_{14}O_2$.

Table VIII. Cooxidation of Valeraldehyde with Cyclooctene at 70°[a]

Product	mmoles	mmoles of O_2
Involatile residue	2.62[b]	2.62
Low boilers[c]	3.4	1.70
	18.1	9.10
PrCHO (+ H_2O)	5.54	5.54
BuOH	9.91	4.95
CO_2	11.6	11.6
		35.6

[a] 46.72 mmoles of BuCHO and 344.2 mmoles of C_8H_{14}, [ABN] = 0.0094, absorbed 34.5 mmoles of O_2 in 393 min at an initial rate of 0.21 M hr^{-1} and a final rate of 0.086; $\bar{P}_{O_2}$ = 6.7 psia. By glpc, 15 mmoles of BuCHO reacted. [b] 372 mg of material taken as monomeric with the average composition $C_8H_{14}O_2$. [c] Three unidentified peaks; the formula CH_2O was used for calculations (101 mg total in glpc trace).

sure (6 psia) at 70° with 12 mole % valeraldehyde (Table VIII). The initial reaction rate was nine times as fast as for cyclooctene alone under similar conditions (0.208 *vs.* 0.023 M hr^{-1}).

The product analysis in Table VIII shows that the net reaction was approximately (quantities in millimoles)

$$\begin{array}{c} 20.7\ \text{cyclooctene} + 16.5\ \text{BuCHO} + 34.5\ O_2 \longrightarrow \\ 18.1\ \text{cyclooctene oxide} + 5.54\ \text{PrCHO} + 11.6\ CO_2 + \\ \underset{\text{(assumed)}}{2.6\ C_8H_{14}O_2\ \text{residue}} + \underset{\text{(av low boiler)}}{\underset{1.70\ C_2H_4O_2}{9.91\ \text{BuOH}}} \underset{\text{(to balance)}}{- 11\ C - 65\ H + 20\ O} \end{array}$$

Too much C and H were found in the products, but only 83% of the oxygen (including that in the reacted valeraldehyde) is accounted for.

This balance shows that 87% of the cyclooctene accounted for was found as epoxide and that still more of this alkene probably reacted by the addition mechanism. It indicates also that just about 1.0 aldehyde was degraded (counting butyraldehyde going to low boilers) for each epoxide formed. The aldehydes apparently react mostly through the sequence

$$\begin{array}{l} RCH_2CHO \xrightarrow{RO\cdot} RCH_2\dot{C}O \xrightarrow{O_2} RCH_2CO_3\cdot \xrightarrow{C{=}C} \\ (\text{epoxide} +)\ RCH_2CO_2\cdot \longrightarrow CO_2 + RCH_2\cdot \xrightarrow{O_2} RCH_2O_2\cdot \xrightarrow{C{=}C} \\ \qquad (\text{epoxide} +)\ RCH_2O\cdot \xrightarrow{RCH_2CHO} RCH_2OH + RCH_2\dot{C}O, \text{etc.} \end{array}$$

and much of the epoxide is formed by reaction of alkene with acylperoxy radicals (which could but do not produce two molecules of epoxide per aldehyde degraded). On this basis, the shorter chain aldehydes arise mostly from oxidation of alcohols or dehydration of alkylhydroperoxides (chains are long enough to exclude much product by termination), and some alkylperoxy radicals contribute to the oxidation. As in our previous discussion of the oxidation of cyclooctene,[2a] we are still left with a serious selectivity problem: nearly all the peroxy radicals seem to react with alkene instead of aldehyde, and nearly all the alkoxy radicals react with aldehyde or disappear by other routes (because of the absence of cyclooctene by-products).

The possibility that much epoxide arises by reaction of peracid with alkene is excluded here because we have been unable to find the equivalent acid or ester.

From the average of the initial and final quantities of valeraldehyde and butyraldehydes (41.13 mmoles) and cyclooctene (333.9 mmoles) and the amounts of aldehydes (16.5 valeraldehyde and about 1.70 butyraldehyde) and alkene (20.7) reacting, cyclooctene is 0.14 as reactive as the aliphatic aldehydes toward the average radicals in solution. A similar ratio for cyclooctene and suberaldehyde is indicated for our oxidation of neat cyclooctene.[2a]

Discussion of Previous Work

Since very few previous oxidations of alkenes have been reported for the low temperatures, low conversions, and known rates of initiation used in this and the previous report,[2b] the present and previous work are discussed and compared here in terms of the effects of experimental conditions.

Table IX. Oxidation of 4 *M* Propylene[16] in Benzene at 150°

Product	Moles	Reaction assumed for calculations	Reactants accounted for		
			O_2, mole	C_3H_6, mole	C_3H_6, %
Propylene oxide	0.0315	$C_3H_6 + 0.5O_2$	0.0158	0.0315	26
Propylene glycol	0.0227	$C_3H_6O + H_2O^a$	0.0114	0.0227	18.6
AcH + H_2CO	0.0052	$C_3H_6 + O_2$	0.0052	0.0026	2
AcOH + HCO_2H	0.0425	$C_3H_6 + 2O_2{}^{a,b}$	0.0425	0.0212	18
Esters	0.0105	$C_3H_6O + RCO_2H^{a,c}$	0.0158	0.0158	13
Residue	0.0259	$C_3H_6 + O_2{}^{a,d}$	0.0259	0.0259	21
CO_2	0.0045	$C_3H_6 + 4.5O_2{}^a$	0.0068	0.0015	1
CO	0.0016	$C_3H_6 + 3O_2{}^a$	0.0016	0.0005	0.4
Total			0.1250	0.1217	100.0

[a] Our assumption or estimate. [b] $C_3H_6 + 2O_2 + Na_2CO_3 \rightarrow AcONa + HCO_2Na + H_2O + CO_2$. [c] Ester taken as $RCO_2C_3H_6OH$. [d] Residue taken as $(C_3H_6O_2)_m$, either polyperoxide, or polyacrolein + H_2O, or both.

Perhaps the most numerous recent experiments are those of Brill and co-workers.[15] Both they and we have reported on seven alkenes: propylene, three butenes, trimethylethylene,[15a] 3-methyl-1-butene,[15b] and 2-methyl-1-pentene.[15b] They studied the liquid-phase oxidations of alkenes at 120° to conversions averaging 30–40%.[15a,b] Comparison of their work with our own shows the effects of higher temperatures and conversions on the primary reactions emphasized in our work. The discussion below shows how their analytical method further complicates the comparison.

In the detailed paper,[15a] the reaction products were analyzed directly by gas chromatography. Hydroperoxides and residue were not reported as such; they decomposed in the vaporizer and their volatile decomposition products are included among the other oxidation products. In these experiments, more than 80% of the reacted alkene was usually accounted for. A major difference from our results is the absence of hydroperoxides and residues in their products determined by glpc. We ascribe this difference to the higher reaction temperature and conversion as well as to their analytical method. For 3-methyl-1-butene[15b] at 120°, 44% hydroperoxide and 9% epoxide were found at 30% conversion, as compared with 73 and 1% found by us[2b] at 3.3% conversion and 70°. The difference illustrates the decomposition of peroxide in their experiments and formation of some epoxide in secondary reactions.

The most perplexing difference between the two sets of results is the high proportion of products which we attribute to the addition mechanism in their oxidations of 1-butene and trimethylethylene. Their principal products are epoxides, glycols, glycol esters, and aldehydes, ketones, and acids corresponding to cleavage at the double bond. Notable are their very small yields of allylic derivatives corresponding to the abstraction mechanism. We conclude that either (1) pyrolyses and losses (see next paragraph) during analyses have obscured the differences between the two mechanisms; (2) the epoxide, glycols, and their derivatives are partly secondary products; or (3) any effect of temperature on the competition between the addition and abstraction mechanisms is larger and different in direction than indicated in the Rate and Peroxide Yield in Isobutylene Oxidation section.

The oxidations of propylene[16] and the *n*-butenes[17] at 65–140° have been investigated extensively at the Institut Français du Pétrole. Their oxidation of propylene[16] supplements and extends to 150° (said to be optimum for epoxide preparation) our own data[2b] at 60–110°. As also found by numerous previous workers, they report that the presence of sodium carbonate (or some other acid absorber) increases the yield of epoxide and decreases the yield of glycol and esters. From their graphs, tables, and personal letter, the material balance in Table IX has been deduced for absorption of 0.12 mole of oxygen (12 mole % on the initial propylene) in 250 ml of 4 *M* propylene in benzene at 150° in the presence of 6 g of sodium carbonate. Table IX shows that 53% of the propylene reacting appeared as epoxide or its solvolysis products. However, the high yields of acids (18%) and the low yields of aldehydes (2%) and carbon oxides (2%) indicate that most of the formaldehyde and acetaldehyde formed by cleavage (0.0530 out of 0.0643 mole counting CO and CO_2) was oxidized to acids without loss of CO_2. These results show that little of the epoxide arose by reaction of acylperoxy radicals with propylene (with accompanying decarboxylation), but that most of the aldehydes could have been oxidized to peracids which then epoxidized the propylene in a nonradical reaction. The free and esterified acids (0.053 mole) then account for most of the epoxide generated (0.0647 mole). Thus the higher temperature and higher conversion employed by Lanos, Clément, and Pouligen apparently resulted in extensive secondary oxidation of aldehydes to peracids, and the latter are responsible for much of the good yield of epoxide.

As in Brill's[15] work at 120°, nearly all their identified reaction products correspond to the addition mechanism of oxidation (they found very little acrolein and only at the beginning of the reaction).

In the oxidations of both *n*-butenes, hydroperoxides are considered to be the sole primary product within experimental error in the early papers[17a–c] but not in the latest one.[17d] Carbonyl compounds, acids, and (from 2-butene) epoxide appear subsequently. In oxidations of 2-butene at 65 and 80°, the fraction of reacting oxygen appearing as epoxide increases rapidly

(15) (a) W. F. Brill and B. J. Barone, *J. Org. Chem.*, **29**, 140 (1964); (b) W. F. Brill, "Selectivity in the Liquid-Phase Autooxidation of Olefins," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 70; (c) *J. Am. Chem. Soc.*, **85**, 141 (1963).

(16) F. Lanos, G.-M. Clément, and F. Pouliguen, *Chim. Ind.* (Paris), **91** (1), 47 (1964), and private communication.

(17) (a) A. Chauvel, G. Clément, and J.-C. Balaceanu, *Bull. Soc. Chim. France*, 1774 (1962); (b) *ibid.*, 2025 (1963); (c) P. Menguy, A. Chauvel, G. Clément, and J.-C. Balaceanu, *ibid.*, 2643 (1963); (d) I. Serée de Roch, *ibid.*, 1979 (1965).

with conversion;[17b] at 120°, the concentrations of hydroperoxides and of epoxide go through successive maxima.[17d]

These conclusions are in general agreement with our own, which show more clearly the contributions of the addition and abstraction mechanisms to the initial oxidations of the *n*-butenes.[2b] These contributions, however, must include minor ones from acylperoxy radicals as well as major ones from allylperoxy radicals. These and other results[2b] bring out the different effects of methyl and ethyl groups on reactivity. The combined results on propylene and the butenes show that methyl groups at the double bonds increase susceptibility to oxidation mostly through the addition mechanism, while an ethyl group favors oxidation by the abstraction mechanism.

Moss and Steiner oxidized a 25 wt % solution of 1-hexene in propionic acid at 80–85° to 8% conversion with 0.2% of cobalt propionate as catalyst.[18] Their results differ notably from our own;[2b] their unsaturated alcohol (as esters), aldehyde, and acid were all derivatives of 2-hexene, while we found about equal proportions of isomeric allylic alcohols and carbonyl compounds. Possibly their vinyl ketone appeared as unidentified products or residue. They also report considerably more conjugated aldehyde (+ acid), epoxide (+ glycol), and CO_2, and much less hydroperoxide and residue. We are unable to unravel these combined effects of temperature, solvent, and metal catalyst.

Menguy, *et al.*,[17c] showed that 1- and 2-butenes do not give the same mixture of allylic oxidation products; the shift of the double bond is less than complete. At 65° 1-butene gave 90% of 3 substitution while 2-butene gave only 45% of 1 substitution. Similar differences have been observed in chlorinations of alkenes with *t*-butyl hypochlorite,[19] and high-pressure oxygen can intervene in the isomerization of *cis*- to *trans*-decalyl radicals.[20] However, Brill[21] recently reported that the two isomeric hydroperoxides from 4-methyl-2-pentene, $Me_2C(O_2H)CH{=}CHMe$ and $Me_2C{=}CHCH(O_2H)Me$, are readily interconvertible in the presence of free radicals at 40°. Both of these apparently conflicting results are consistent with our own.[2b] In our oxidations of the *n*-butenes, 1-butene gave 46% of (isomerized) primary alcohol and 2-butene gave 34% of (isomerized) secondary alcohol in the alcohol mixtures, indicating incomplete equilibration. In our oxidations of 3-methyl-1-butene and trimethylethylene, the same mixture of relevant primary and tertiary alcohols was produced, within experimental error.

Serée de Roch[17d] and Brill[15c] have shown that the interactions of hydroperoxides with alkenes are too slow to account for much of the epoxide formation observed in most oxidations. On the other hand, epoxide formation from these reagents is specifically catalyzed by chromium, vanadium, and molybdenum salts.[22] Serée de Roch has also shown that the presence of acetaldehyde contributes strongly to the formation of epoxide from 2-butene. Since this contribution is largely nonstereospecific, it must involve acetylperoxy radicals rather than peracetic acid. However, in some cooxidations of an alkene with an aldehyde,[23] most of the aldehyde is converted to carboxylic acid, and peracid must therefore have contributed substantially to the good yields of epoxide. Similar problems with other alkenes were mentioned in the Effects of Solvent Polarity section and the Cooxidation of Aldehydes and Alkenes section and ref 2b, and we propose to carry out further experiments to resolve the contributions of various mechanisms to epoxide formation under representative conditions.

Experimental Section

1. **Rates and Product Analyses.** Procedures for oxidizing at moderate pressures in glass bulbs were described previously along with techniques for analysis of the products.[2b] The rate and product data at 50–100 psia of Tables II–VII were obtained by these procedures.

In the case of cyclooctene (Table IV), working up a second layer[2a] was avoided by combining all material in a separatory funnel with sodium bicarbonate solution. After thorough mixing, the nonacidic material formed one organic phase. The bicarbonate solution was acidified; the free organic acids were isolated by continuous extraction with ether. The ether solution was dried and freed of ether at reduced pressure and the acidic material was weighed.

For conducting oxidations at 800 psi, an American Instrument Co. autoclave was used with a glass liner. Temperature control was accomplished by a Brown pyrometer which held the temperature within ±2° of the setting. The pressure was read on a meter connected to the oxygen supply line. Pressure drops during the oxidation were erratic, and reliable oxidation rates could not be obtained.

2. **Epoxide Yields from Cycloheptene.** For those experiments with cycloheptene where only the epoxide yield is reported (Table I) a different procedure was used. Benzene solutions of the alkene were made up and the glpc calibrated with the known mixture. Precision of 0.5 to 1% could be obtained. ABN (or di-*t*-butyl peroxide) was added and the solution oxidized at the stated temperature or pressures to conversions of 10–15%. A sample of the oxidate was then distilled (0.1 mm) to separate all volatile material from the residue, and the distillate was reduced with triphenylphosphine followed by glpc analysis. The consumption of cycloheptene and the formation of epoxide were calculated from their peak areas and that of benzene. Precision of the reported yields is expected to be about 10%.

3. **Calculation of Oxygen Pressure.** Oxygen pressures were determined for runs at pressures over 10 psia by subtracting from the total pressure the vapor pressure of the hydrocarbon plus the partial pressure of the nitrogen (that initially present plus the amount formed from ABN). In runs at lower oxygen pressures, the oxidation cycles were allowed to proceed without repressuring until all oxygen had been consumed above the liquid, thus giving a measured sum of hydrocarbon and inert gas pressures. A curve prepared from several such points in one experiment permitted corrections at all points of the oxidation. The average oxygen pressure for oxidations over several pressure cycles was calculated from $\bar{P}_{O_2} = \Sigma \bar{P}_{O_2}\Delta P_{O_2}/\Sigma \Delta P_{O_2}$.

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