1-Acetyl-1-methylcyclohexane: bp 68–70° (7 mm) [lit.[25] bp 80–85° (16 mm)]; 13.8 g (66% based upon 150 mmol of olefin) isolated; ir 1700 cm^{-1}; nmr τ 8.0 and 9.0 [sharp s, $H_3CCOCCH_3$]; vpc (130° and 150°)[18] showed a single compound. The 2,4-DNP had a melting point of 131–132° (lit.[26] mp 132°) and the semicarbazone melted at 183–185° (lit.[26] mp 186–187°).

3,3-Dimethyl[3.2.1]bicyclooctanone-2 (**7**): bp 30–40° (0.3 mm); ir 1710, 3050, and 1610 cm^{-1} (the latter indicated olefinic contamination); vpc (200°)[18] indicated three compounds present. The distillate, dissolved in petroleum ether (bp 30–60°), was placed upon a column containing 30 g of neutral alumina. Elution with petroleum ether yielded an unidentified olefin, ir 3050 and 1610 cm^{-1}, no carbonyl or hydroxyl absorptions present. Elution with 50% (v/v) benzene–petroleum ether yielded 2 g of **7** (13% based upon 100 mmol of 2-isopropylidenenorbornane used): ir 1705 cm^{-1}; vpc (200°)[18] indicated 85% purity;[12] nmr τ 8.9 and 9.0 [d, sharp $-COC(CH_3)_2$]; the 2,4-DNP had a melting point of 103–105°(EtOH).

Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.02; N, 16.86. Found: C, 57.91; H, 6.16; N, 17.01.

A small amount of **7** was treated with trifluoroacetic acid-*d* (10% solution) at 80° for 24 hr; the nmr of the product showed no deuterium exchange.

Registry No.—**1** (*n* = 4), 42393-47-5; **1** (*n* = 5), 42393-48-6; **1** (*n* = 6), 42393-49-7; **2**, 42393-50-0; **5**, 42393-51-1; **5** 2,4-DNP, 42393-52-2; **7**, 42393-53-3; **7** 2,4-DNP, 42393-54-4; **8**, 42393-55-5; **11**, 15446-32-9; *m*-chloroperbenzoic acid, 937-14-4; isopropylidenecyclohexane, 5749-72-4; isopropylidenecyclopentane epoxide, 42393-57-7; isopropylidenecyclopentane, 765-83-3; isopropylidenecycloheptane epoxide, 42393-59-9; isopropylidenecycloheptane, 7087-36-7.

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[25] O. Sakur, *C. R. Acad. Sci.*, **208**, 1092 (1939).

[26] H. Pines and J. Marechal, *J. Amer. Chem. Soc.*, **77**, 2819 (1955).

Intramolecular Propagation in the Oxidation of *n*-Alkanes. Autoxidation of *n*-Pentane and n-Octane

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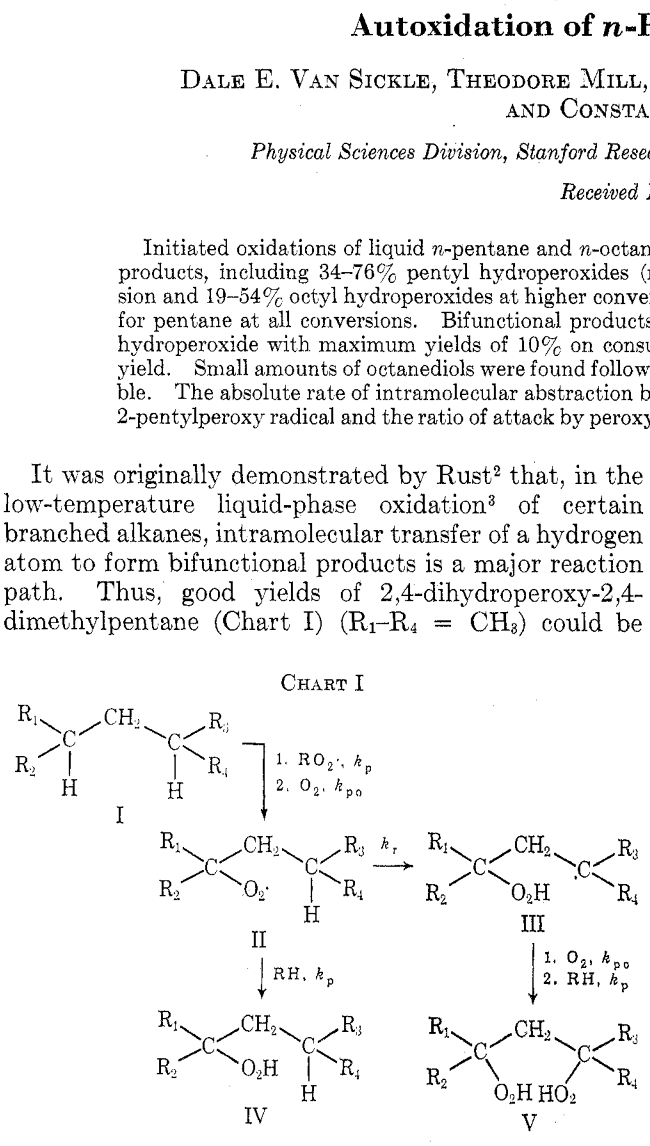
Initiated oxidations of liquid *n*-pentane and *n*-octane at 100 and 125°, respectively, give complex mixtures of products, including 34–76% pentyl hydroperoxides (mostly secondary monohydroperoxides) at <1% conversion and 19–54% octyl hydroperoxides at higher conversions. More cleavage products are found for octane than for pentane at all conversions. Bifunctional products from pentane include dihydroperoxide or diol and keto-hydroperoxide with maximum yields of 10% on consumed oxygen. Added *tert*-BuO_2H markedly reduced this yield. Small amounts of octanediols were found following reduction but no reliable estimates of yields were possible. The absolute rate of intramolecular abstraction by *sec*-pentyl peroxy radicals is $^{1}/_{80}$ of that of 2,4-dimethyl-2-pentylperoxy radical and the ratio of attack by peroxy radicals at secondary and primary CH bonds is 38.5:1.

It was originally demonstrated by Rust[2] that, in the low-temperature liquid-phase oxidation[3] of certain branched alkanes, intramolecular transfer of a hydrogen atom to form bifunctional products is a major reaction path. Thus, good yields of 2,4-dihydroperoxy-2,4-dimethylpentane (Chart I) (R_1–R_4 = CH_3) could be obtained from the oxidation of 2,4-dimethylpentane (2,4-DMP); oxidation of 2,5-dimethylhexane gave a lower yield of the difunctional product. Recent work by Mill and Montorsi[4] showed that, at 100°, over 90% of the oxygen consumed by 2,4-DMP could be accounted for by hydroperoxide and that the ratio of mono- to difunctional hydroperoxide products was 1:7. The apparent generality of intramolecular propagation in the oxidation of alkanes with alternating *tertiary* hydrogens was confirmed by Van Sickle in the oxidation of 2,4,6-trimethylheptane[5] (2,4,6-TMH) [Chart I, R_1–R_3 = CH_3; R_4 = $CH_2CH(CH_3)_2$] where the major oxidation product is 2,4,6-trihydroperoxy-2,4,6-trimethylheptane and the calculated value for the ratio of rate constants of inter- to intramolecular propagation, k_p/k_r, is practically identical with that of 2,4-DMP[4] (0.015 M^{-1} *vs.* 0.013 M^{-1}).

CHART I



The question now arises as to what proportions of bifunctional reaction products are formed in low-temperature (100–125°) liquid-phase oxidations of *n*-alkanes. *A priori*, one might expect the reaction scheme in Chart I to be valid for the general case where R_1, R_3 = H and R_2, R_4 = any alkyl group. In gas-phase oxidations[6] above 200°, cyclic ethers, expected to arise from III of Chart I, are major products.

Although the liquid-phase oxidation of *n*-alkanes has been reported for various homologs, the results have not been analyzed from the standpoint of intra–intermolecular propagation. We now report the results of an investigation of the oxidation of *n*-pentane at 100° and *n*-octane at 125° where we have searched specifically for bifunctional products expected to be derived from intermediate III of Chart I.

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[1] To whom correspondence should be addressed.

[2] F. F. Rust, *J. Amer. Chem. Soc.*, **79**, 4000 (1957).

[3] F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968).

[4] T. Mill and G. Montorsi, *Int. J. Chem. Kinet.*, **5**, 119 (1973).

[5] D. E. Van Sickle, *J. Org. Chem.*, **37**, 755 (1972).

[6] A. Fish, *Advan. Chem. Ser.*, **76**, 69 (1968).

TABLE I

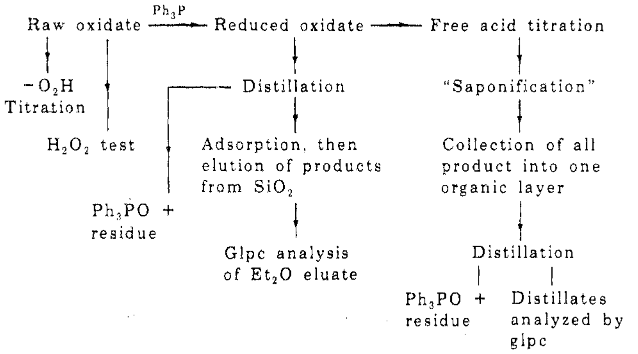
RATES OF OXIDATION OF OCTANE AT 125°

	Run no.									
	92	78	96	108	140	143	126	146	67[a]	74[b]
Time, min	620	470	410	270	320	465	1930	565	600	350
Vol of soln, ml	52.5	56.1	51.3	52.5	52.2	50.5	48.7	50.8	49.0	56.8
$[C_8H_{18}]_0$, m*M*	5410	5410	5410	5410	4330[c]	3540[c]	2720[c]	2090[c]	5450	5360
$[t\text{-}Bu_2O_2]_0$, m*M*	4.8	9.2	19.6	47.8	11.4	12.6	13.6	12.0	26.3	18.4
$\Delta[O_2]$, mmol	7.9	6.90	7.2	6.7	2.92	3.15	9.04	2.5	7.4	10.7
R_i,[d] $(M/\text{min}) \times 10^6$	8.2	15.7	33.3	81	19.3	21.5	23.2	20.3	24.6	55.0
R_0,[d] $(M/\text{min}) \times 10^4$	2.4	2.6	3.4	4.7	1.95	1.38	1.33	0.93	1.73	6.25
$R_0/R_i^{1/2}$, $(M/\text{min})^{1/2}$	0.084	0.066	0.059	0.052	0.044	0.029	0.028	0.021	0.035	0.084
$\Delta[O_2]/[C_8H_{18}]_0$, %	2.2	2.3	2.6	2.4	1.3	1.8	6.8	2.4	2.8	3.5
Yield RO_2H, % on O_2		54			54	47	19	36	50	41

[a] 120°. [b] 130°. [c] Benzene solutions. [d] R_i = rate of initiation = $2k_d[t\text{-}Bu_2O_2]$; $k_d = 4.7 \times 10^{-4}$/min at 120°, 8.5×10^{-4}/min at 125°, 1.5×10^{-3}/min at 130°; R_0 = initial rate of oxygen consumption.

CHART II

ANALYSIS OF OCTANE OXIDATION



Experimental Section

Materials.—The *n*-pentane and *n*-octane used were either Phillips Petroleum Co. "Pure Grade" (99%) or "Research Grade" (99.7%) materials. They were distilled and passed over neutral alumina just before use. The $t\text{-}Bu_2O_2$ was distilled (70°, 197 Torr) and stored at −20°; titrations on other samples treated this way have indicated 99+% purity. For solution oxidations, Matheson Coleman and Bell "Chromatoquality" benzene was used directly. Triphenylphosphine (same supplier) was purified by short-path sublimation using a standard sublimation apparatus. All other materials were reagent grade and used directly.

Apparatus and Oxidation Procedure.—Octane oxidations were performed in an apparatus consisting of a heavy glass bulb connected to an oxygen reservoir. The use of this apparatus has been described elsewhere.[7] Solutions of the octane with $t\text{-}Bu_2O_2$, and in some cases benzene, were made up in volumetric flasks before transfer to the reaction bulbs. The bulbs were pressured with oxygen and shaken at the required temperature in a thermostated oil bath, and the drop in pressure was followed. After the desired extent of oxidation had been attained (and in one case after the gas in the void space of the reaction bulb had been sampled for mass spectral analysis), the solutions were cooled and saved for product analysis.

n-Pentane oxidations were done at 100° by a sealed-tube technique similar to that used for isobutane.[8] The reactants were sealed in glass bulbs with a known amount of oxygen and then shaken in the thermostated bath for the indicated time.

Analytical Procedure.—The most elaborate analytical procedure used for octane oxidation analysis is summarized in Chart II; it was used for the 6.6-psia run in Table II. Analyses on some other oxidates were abbreviations of this procedure. The titration procedure[9] was Hercules Method I. The triphenylphosphine-reduced[10] oxidate was divided for different work-ups in order to determine the possible residue-forming effect on the saponification procedure (heating to 100° the mixture of water, added during titration, and oxidate with 2- to 3-mmol excess sodium hydroxide). The distillations of Chart II collected all the materials up to temperatures of 100° at pressures of 0.1 Torr. The amounts of residues remaining, small in comparison with triphenylphosphine oxide, were determined by subtracting the expected quantities of this material. Where desirable, the volatile oxidation products could be isolated from the large quantities of unreacted octane by absorption on silica, followed by elution with ether.

In some experiments, as in procedure A of the 85-psia experiment (Table II), the volatile products were further reduced with sodium borohydride in isopropyl alcohol before glpc analysis on a 15 ft × 0.25 in. column of 15% Carbowax 20M on Chromosorb R; also, in procedure B of the 85-psia experiment, the aqueous layer present from the saponification procedure was separated and continuously extracted with ether after acidification to isolate the product acids for identification. After treatment of the ether extract with diazomethane, only acetic and propionic acids with a trace of butyric acid could be found (as methyl esters) by glpc.

Analysis of the pentane oxidation products was more direct. After the gases in the bulb void space were analyzed on the vacuum line to determine oxygen absorbed and an aliquot was titrated for hydroperoxide yield, an additional aliquot was reduced[11] with triphenylphosphine and analyzed by glpc. Low-boiling products were determined on a 20-ft 20% Carbowax 20M column, first at 100° for 36 min, then programmed at 2°/min to 160°, with toluene as internal standard. High boilers were determined on a 6-ft XE60 on Chromosorb G column (runs 3 and 4) or a 10-ft 2% Carbowax 20M on Chromosorb G column (runs 5 and 6) isothermally at 105° for 12 min, then programmed at 4°/min to 170°. In runs 3 and 4, peaks were estimated relative to toluene; in 5 and 6 the product 1-pentanol was employed as a secondary standard to estimate the relative peak sizes.

Results and Discussion

The rates and products of oxidation of octane are listed in Tables I and II and the same information for pentane is summarized in Table III. The footnotes make the tables mostly self-explanatory.

The equations listed below (Charts III and IV) are believed to be likely and reasonable routes to the products found. They have been grouped according to whether the products are primary or secondary (derived from subsequent attack on the primary products). R represents either a secondary pentyl or octyl radical while R′ and R″ are any primary alkyl radical from methyl to hexyl. Nonfree-radical reactions, which may lead to some of the products found, are not listed but are mentioned in the discussion. Formation of

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[7] D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, **87**, 4832 (1965).

[8] D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Advan. Chem. Ser.*, **76**, 40 (1968).

[9] R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

[10] D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Amer. Chem. Soc.*, **82**, 1393 (1960).

[11] R. Hiatt in "Organic Peroxides," Vol. II, C. D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, p 94.

TABLE II

OXIDATION OF *n*-OCTANE (5.41 *M*) AT 125°[q]

Products	$\bar{P}_{O_2}$ = 85 psia				
	Work-up A	Work-up B	$\bar{P}_{O_2} \sim 10$ psia	$P_{O_2} = 6.6$ psia	$\bar{P}_{O_2}{}^a = 40$ psia
$[t\text{-}Bu_2O_2]_0$	12.0	12.0	10.0	11.0	12.6
Time, min	375	375	489	353	465
$\Delta[O_2]$	114	114	187	115	62.4
Titratable $-O_2H$	61.5	61.5	75.3	56.7	30.0
(% on $\Delta[O_2]$)	(54)	(54)	(40)	(49)	(48)
Octanones	*b*	2.5	*b*	7.5,[c] 7.9[d]	0.8
Octanols[e]	34	36	51.8[f]	30,[c] 33.6[d]	16.7
Octanediols[g]	0.7	0	1.6	0	0
CO_2	1.9[h]	1.9[h]	3.2	1.9[h]	1.2[h]
H_2	1.1[h]	1.1[h]	1.8	1.1[h]	0.8[h]
Free acids	12.9	12.9	26.4	12.3[d]	13.5
Esters	3.2	7.1	15.3	10.2[d]	4.0
Unidentified products					
Volatile	6.4[g,i]	16.2[j]	7.0[i]	9.5[c,k]	
Residue				5.2,[c,l] 16.2[d,m]	
C_8H_{18} accounted for[n]	49.2	71.7	93.1	73.6,[c] 88.6[d]	30.2
$[O_2]$ accounted for,[o] %	78 (68)	87 (76)	122 (65)	96,[c] 92[d] (83)(80)	48 (77)
Chain length[p]	13	13	14	14	10

[a] $[C_8H_{18}]_0 = 3540$, benzene diluent. [b] Not determined; converted to octanols by $NaBH_4$ reduction. [c] In the unsaponified aliquot. [d] In the saponified aliquot. [e] After Ph_3P reduction. [f] Product was 2.2, 20.6, 15.5, and 13.5 m*M* in 1-, 2-, 3-, and 4-octanols, respectively. [g] After $NaBH_4$ reduction. [h] Estimated by analogy from 10-psia experiment. [i] Probably butanol, pentanol, or hexanol. [j] 128 mg of material in octane layer plus 112 mg of material extracted from basic aqueous layer. This material is assumed for calculation to be $C_8H_{18}O$. [k] 107 mg of material (four peaks that elute between Et_2O solvent and 4-octanone); assumed mol wt 100. [l] 76 mg; assumed mol wt 130, corresponding to 1 mol of O_2. [m] 238 mg; assumed mol wt 130, corresponding to 1 mol of O_2. [n] Octanols + ketones + esters + unidentified + (lower alcohols + acids + esters)/2. [o] Including accompanying water; $\Delta[O_2]$ = hydroperoxide + octanones + 1.5 CO_2 − 0.5 H_2 + 0.75 acid + 1.5 ester + residue. Volatile unidentified products were not counted in oxygen balance and in the saponified aliquot of the 6.6-psia experiment; ester was not counted in lieu of the higher residue figures. [p] Initial R_0/R_i (see Table I). [q] Concentrations in m*M*.

CHART III

PRIMARY REACTIONS

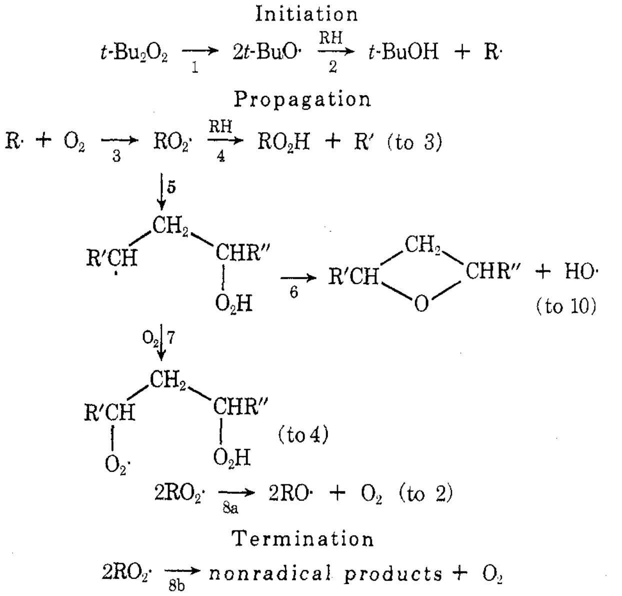
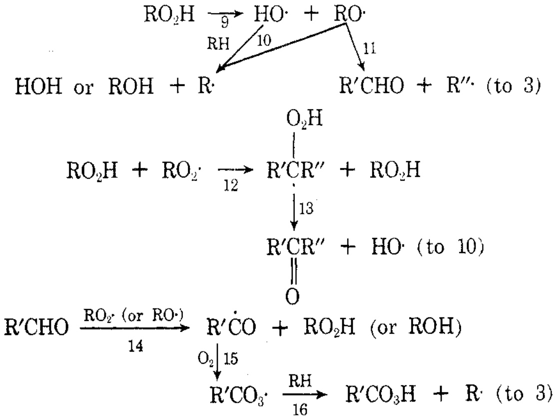


CHART IV

SECONDARY REACTIONS



alkoxy radicals is depicted as arising both from simple unimolecular decomposition of primary product hydroperoxide, RO_2H (eq 9), although, in actuality, "decomposition" is certainly more complex than this, and from nonterminating interaction of *sec*-peroxy radicals (eq 8); 50–70% of the interactions of *sec*-butyl peroxy radicals have been estimated[12] to be nonterminating at 100–125°.

Rates of Oxidation.—The data of Table I show that, in spite of the product complexity of the reaction, the oxidation of *n*-octane fits the relatively simple rate law

$$\text{initial oxidation rate} = R_0 = (R_i/2k_t)^{1/2}\,k_p[C_8H_{18}]$$

That the *n*-oxtane oxidation is nearly one-half order in rate of initiation was established by plotting log R_0 *vs.* log $[t\text{-}Bu_2O_2]$ for runs 92, 78, 96, and 108 (Figure 1). Two lines, drawn as limits to the best fit, have slopes of 0.48 and 0.57. If the datum of run 3, Table III, is omitted from a similar log–log plot, the average oxidation rate of *n*-pentane appears to be ~0.68 order in initiation. These results support the idea that termination involves principally the interaction of *sec*-alkyl peroxy radicals.[13]

A plot of the rate of *n*-octane oxidation, corrected to unit initiation, $R_0/R_i{}^{1/2}$, against hydrocarbon concentra-

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(12) T. Mill, D. Allara, F. R. Mayo, H. Richardson, and K. C. Irwin, *J. Amer. Chem. Soc.*, **94**, 6802 (1972).

(13) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, **75**, 6 (1967).

Table III

Oxidation of Neat n-Pentane (7.44 M) at 100°[g]

	Run					
	1	2	3	4	5	6[a]
Initial Conditions						
Time, min	2390	3836	4137	200	1444	200
RH, mmol	36.6	35.7	57.8	83.8	43.7	34.0
t-Bu_2O_2	97	50	54	43	9.8	9.8
O_2, mmol	968	369	1062	887	879	1066
Products						
O_2 absorbed ($\Delta[O_2]$)	82	73	47	4.7	10.7	−9.7[b]
RO_2H	28	39	32	1.95	8.2	−60[b]
$RO_2H/\Delta[O_2]$, %	34	54	68	41	76	
2- and 3-AmOH	37	34	23	1.6	5.9	88.3
2- and 3-$C_5H_{10}O$	15	7.8	4.2	0.26	0.51	5.6
n-AmOH		1.2			0.26	2.3
AcH	Trace	0.6	2.5			
EtOH	Trace	0.2	0.9			
$(MeCHOH)_2CH_2$			2.4	0.21	0.13	0.18
Ac_2CH_2					0.07	
Residue	3-6 mg		9[c]		0.18[c]	
Rates × 10_6, M/min						
R_i[d]	7.5	4.1	4.4	3.5	0.82	
$R_0 = \Delta[O_2]/\Delta t$	34	19	11	24	7.4	
R_0/R_i	4.6	4.5	2.6	6.9	9.1	
$\Delta[O_2]/[AmH]_0$, %	0.9	0.7	0.55	0.065	0.12	
O_2 accounted for, %[e]	52	64	77	47	87	
$k_p/(2k_t)^{1/2} \times 10^3$[f]	1.32	0.99	0.42	1.45	0.97	

[a] 1.81 M t-BuO_2H added initially; RO_2H in products corrected accordingly. [b] Net evolution of O_2 and loss of RO_2H. [c] Estimated mM of unknown product. [d] $R_i = 2k_d[t\text{-}Bu_2O_2]$; $k_d = 4.08 \times 10^{-5}$/min (ref 8). [e] Arbitrarily calculated from RO_2H + mono- and diketones. [f] Calculated from $R_0 = R_i/2a + (R_i/2k_t)^{1/2}k_p[RH]$ with $a = 0.5$ (ref 12). [g] Other concentrations in mM.

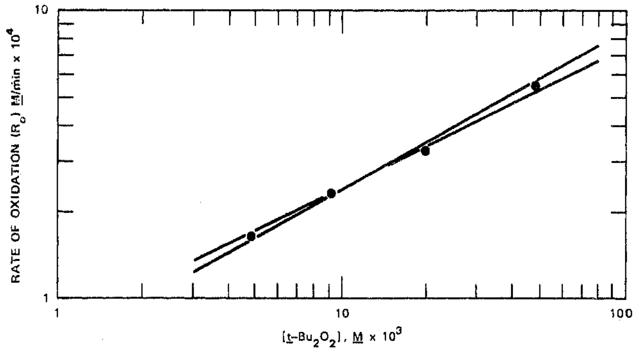

Figure 1.—Plot of log R_0 vs. log [t-Bu_2O_2] for oxidation of n-octane at 125°.

tion for all 125° runs gives a fairly good straight line, excepting the datum of run 143 (Figure 2). The value of the composite rate constant, $k_p/(2k_t)^{1/2}$, from the slope of the plot is $0.011/(M\ \text{min})^{1/2}$; for n-butane,[12] the composite rate constant is $0.0028/(M\ \text{min})^{1/2}$, which value is 20% lower on a per secondary hydrogen basis and identical within the experimental error.

The limited rate data for oxidation of n-pentane at 100° fit the theoretical equation less well than those of octane. (Experiments were done over too small a range of R_i and with chain lengths too short to expect close agreement.) If we assume that the oxidation obeys the extended rate law for oxidation of n-butane (eq 9 of ref 12) then an average value for $k_p/(2k_t)^{1/2}$ at 100° is $1.2 \times 10^{-3}/(M\ \text{min})^{1/2}$ (excluding runs 3 and 6), in good agreement with the value for n-butane of 0.76×10^{-3}, taking into account the difference in numbers of secondary hydrogens.

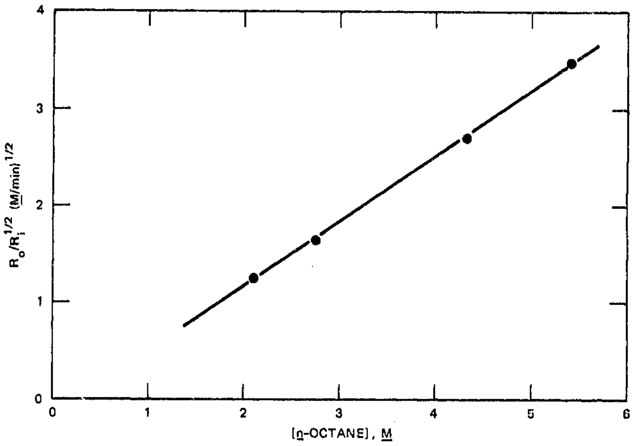

Figure 2.—Plot of $R_0/R_i^{1/2}$ vs. [n-octane] for oxidation of n-octane at 125°.

An attempt to determine the overall energy of activation for octane oxidation from an Arrhenius plot of $R_0/R_i^{1/2}$ vs. $1/T$ for runs 67, 92, and 74 gives an unreasonably high value for $E_p - E_t/2$ of 26 kcal/mol. A value of 14–16 kcal/mol is expected.[12] This result suggests that a significant contribution to the rate of initiation is made by decomposition of product octyl hydroperoxides at the higher temperatures (reaction 9) and/or additional complications.

Products.—Unfortunately, in the oxidation of n-alkanes larger than n-pentane the multiplicity of products is so great and, therefore, the analyses so complex that only qualitative conclusions can be drawn about the relative importance of the postulated steps of the reaction mechanism. One indication of the complications present is the strong inverse dependency of total hydroperoxide yield on conversion. For the *n*-octane oxidations which were carried out at relatively high conversions, hydroperoxide yields range from 54 to 19%. For the pentane oxidations, where all conversions are less than 1%, hydroperoxide yields range from 76 to 34%. Because of analytical difficulties, the lowest conversion *n*-pentane run (4) does not fit the trend. Nonetheless, it seems reasonable to conclude that hydroperoxides are the principal primary products of these oxidations under most conditions.

By the somewhat arbitrary procedure of accounting for oxygen in the products, as detailed in the table footnotes, up to 83% of the consumed oxygen can be accounted for in the 6.6-psi oxidation of *n*-octane. Oxygen balances for other runs are lower. Similarly, for *n*-pentane, where the basis for accounted oxygen has been simplified, products of one run account for 87% of consumed oxygen but other runs are less satisfactory. Part of the problem with oxygen balances lies in the discrepancy between titrated hydroperoxide and octanols or pentanols detected after triphenylphosphine reduction of the oxidates. With the higher conversion octane oxidations, the octanol yields are only about 50% of the hydroperoxide titre while with the pentane oxidations, excepting run 1, the pentanols account for 70–80% of the titrated hydroperoxide. The source of the remaining titrated hydroperoxide is uncertain, although peracids (reaction 16) seem a likely possibility. For most of the octane analyses, the acid found by titration taken with the octanols is still insufficient to account for all of the titrated hydroperoxide.

Turning to the original objective of this work, we find that the yield of readily identifiable bifunctional products from both octane and pentane oxidations is small, in marked contrast to the results for oxidation of 2,4-dimethylpentane[4] and 2,4,6-trimethylheptane,[5] where bi- or polyfunctional products predominate. Further, the yields of the bifunctional products seem to be an erratic function of the conversion, and the oxidation state of the bifunctional products is variable. For runs 3 and 4 of the pentane oxidation, pentanediol is about 10% of pentanols and pentanones, although conversions are substantially different. However, at an intermediate conversion, run 5, the combined yield of pentanediol and pentanedione is only 3.1% of the monofunctional products. The marked reduction of pentanediol yield to 0.2% of the pentanols in run 6 (Table III) made with added t-BuO$_2$H confirms that intramolecular propagation is the source of the small yields of these products in these experiments. The hydroperoxide would be expected to chain transfer[13] efficiently with intermediate II with near elimination of intramolecular propagation. Criegee and Ludwig[14] have shown that in autoxidations of some cyclic hydrocarbons such as 1,4-dimethylcyclohexane, bishydroperoxides can arise from secondary oxidation of monohydroperoxide intermediates but at substantially higher conversions than used here.

Despite the semiquantitative character of these results, we can calculate the approximate ratio of rate constants for intra- and intermolecular hydrogen transfer (k_r/k_p) from the amounts of difunctional (D) and monofunctional (M) pentane products, including diols, keto alcohols and residue and secondary alcohols and ketones, from the equation

$$mk_r/nk_p = \frac{[D][RH]}{[M]}$$

where m and n refer to the number of possible CH bonds available for reaction. For run 5, $[D] \sim 0.38$ mM, $[M] \sim 6.41$ mM, and RH = 7.44 M. On a per hydrogen basis, with the assumptions that only the 2-pentyl peroxy radical gives significant intramolecular abstraction at the 4 position and that only *sec*-CH bonds are attacked in intermolecular abstraction, $2k_r/6k_p \sim 0.45$ M and $k_r/k_p \sim 1.4$ M. This may be compared with a value of 83 M for 2,4-dimethylpentane[4]. The absolute value of 48/min for k_r is estimated using a value of 37/M min for k_p[15] for pentane.

For octane oxidations product identification and analyses are even less certain than with pentane, but rough calculations of k_r/k_p give values in the same range ($\sim$1 M) as found for pentane; the proportion of intramolecular propagation does not significantly change with chain length.

The detection of 1-pentanol and 1-octanol allows an estimation of relative reactivities of primary and secondary hydrogens by the radicals present. In *n*-pentane, a reliable value of k_p(secondary)/k_p(primary) at 100° obtained from expt 6 (Table III) where the principal chain carrier is *tert*-butylperoxy radical is 88/2.3 = 38.5. Based on the 10-psia octane experiment at 125° (Table II), the ratio seems as low as 11, $= (6/12) \times [(20.6 + 15.5 + 13.5)/2.2]$. Analysis of *n*-butane oxidation[12] gave relative reactivities of secondary and primary hydrogens of *n*-butane toward *sec*-peroxy radicals of 45:1 at 100° while the same ratio for alkoxy radicals was stated to be 8:1 at 100°. The octane result appears to give a low value, even taking into account the higher temperatures, indicating a change to less selective radical chain carriers (such as RO· and HO· radicals) as conversions are increased.

Other investigators[16–18] have reported results similar to our octane experiments in the oxidation of other *n*-alkanes: about 50% of the alkane is converted to hydroperoxide, 10–12% to acids, and 5–15% to ketone. At higher temperature and lower oxygen pressures,[17] small amounts of cyclic ethers can be detected, but, in all cases, the amount of intramolecular propagation, as measured by diols or cyclic ethers, is minor.

In conclusion, the question must be asked as to why the *n*-alkanes give so little intramolecular propagation while 2-4-dimethylpentane and 2,4,6-trimethylheptane give so much under similar conditions. Explanations based on a high degree of reversibility for reaction 5 in the *n*-alkane case do not seem satisfactory.[4] Nor do the pentane data support the idea that, at moderate conversions, the reactive oxidation products, including α hydrogens of *sec*-ROOH, intercept *sec*-RO$_2$ radicals before they can undergo intramolecular abstraction.

Our previous studies[4,5] together with this one indicate

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(14) R. Criegee and P. Ludwig, *Erdoel Kohle*, **15**, 523 (1962).

(15) Estimated from the cooxidation of *n*-BuH and *i*-BuH (ref 12), with the assumption that *sec*-RO$_2$· is ten times as reactive as t-RO$_2$· toward the same CH bond (private communication from K. U. Ingold).

(16) A. W. Dawkins, *Eur. Chem. News, Normal Paraffin Suppl.*, 50 (Dec 2, 1966).

(17) R. D. Boss and R. N. Hazlett, *Can. J. Chem.*, **47**, 4175 (1969); numerous pertinent references to Russian investigators of *n*-alkane oxidations are cited in this article.

(18) G. H. Twigg, *Chem. Eng. Sci., Suppl.*, **3**, 5 (1954).

that only a very limited number of hydrocarbon substrates oxidize with major participation of intramolecular abstraction. Normal and cyclic[14] alkanes may, therefore, be the general case and explanations are required, instead, for the exceptional cases of alternately branched alkanes. We can only speculate at this time that unusual steric factors operate in the alternately branched alkanes which promote reaction 5 by a favored orientation–restricted chain rotation mechanism. Partial screening of the reactive tertiary hydrogens of the substrate from external attack (reaction 4) by the clusters of methyl groups present must also be a factor.[4]

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Registry No.—*n*-Pentane, 109-66-0; *n*-octane, 111-65-9.

A Kinetic Investigation of the Configurational Isomerization of Geometrically Isomeric Nitrones[1a]

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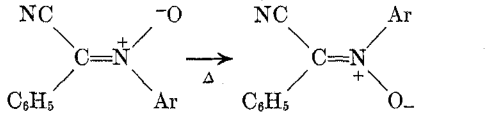
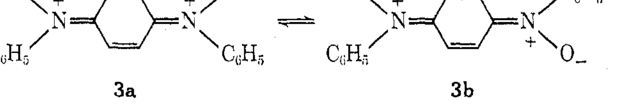
The *Z* and *E* isomers of *N*-methyl-α-(*p*-tolyl)-α-phenyl nitrone (**7a** and **8a**) and the *Z* and *E* isomers of *N*-benzyl-α-(*p*-tolyl)-α-phenyl nitrone (**9a** and **10**) were prepared. Alkylations of isomeric oxime anions and the reaction of *N*-benzylhydroxylamine (**13**) with 1,1-dichloro-4′-methyldiphenylmethane (**14**) were employed in the syntheses. The first-order rates for thermal approach to geometric equilibrium of **7a**, **8a**, **9a**, and **10** were determined in degassed *tert*-butyl alcohol solutions. Activation parameters for the isomerization of **9a** were determined in the same solvent and are $\Delta E^{\ddagger} = 33.6 \pm 1.4$ kcal/mol; $\Delta S^{\ddagger} = -4 \pm 4$ eu. The energy barrier to isomerization is substantially larger than would be anticipated from the limited data available from previous studies of geometric isomerizations of nitrones. These results are briefly discussed.

The existence of separate geometric isomers of unsymmetrical nitrones has been reported on several occasions. A modest configurational stability of α,α-diaryl-*N*-methyl nitrones has been inferred from the apparent absence of geometric isomerization during recrystallizations and upon melting.[2,3] By contrast, Barrow and Thorneycroft[4] observed that the cis isomers (**1**) of some *N*-aryl-α-phenyl nitrones slowly isomerized to the trans isomers (**2**) during melting point determinations. Koyano and Tanaka[5] investigated this isomerization in *n*-butyl alcohol. The activation energy for the cis to trans isomerization of *N*,α-diphenyl-α-cyano nitrone ($\mathbf{1} \rightarrow \mathbf{2}$; Ar = C_6H_5) was found to be 24.6 kcal/mol. Layer and Carman[6] have reported a study of the geometric isomerization of *N*,*N*′-diphenyl-*p*-benzoquinonediimine *N*,*N*′-dioxide (**3a** and **3b**). The pmr study in deuteriochloroform provided an estimate of the energy barrier ($\Delta F^{\ddagger}$ below room temperature) of about 12 kcal/mol from data obtained at the coalescence temperature. More recently Boyle, Peagram, and Whitham estimated the rate constant for the "configurational exchange" of the vinyl protons for *N*-(1-ethylcyclohexyl) nitrone (**4**) by pmr methods.[7] From the first-order rate constant at 180°, a free energy of activation of 23.2 kcal/mol was calculated.

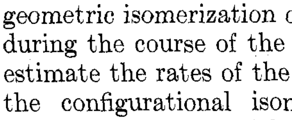


1 **2**



3a **3b**

Our interest in obtaining rates and activation energies for the geometric isomerization of certain nitrones derives from our investigation of the stereochemical course of the N to O rearrangements of (*Z*)- (**5**) and (*E*)- (**6**) *N*-benzhydryl-α-(*p*-tolyl)-α-phenyl nitrone.[8]



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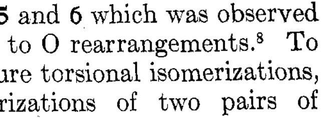

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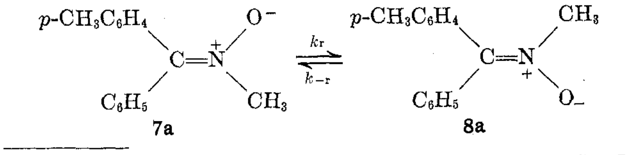
Evidence was obtained[8] that these rearrangements proceed *via* intermediate benzhydryl and rapidly interconverting iminoxy radicals. Since it was also discovered that these radicals recombine at nitrogen as well as oxygen, this provided a potential route to the geometric isomerization of **5** and **6** which was observed during the course of the N to O rearrangements.[8] To estimate the rates of the pure torsional isomerizations, the configurational isomerizations of two pairs of isomeric nitrones which do not appear to dissociate to alkyl and iminoxy radicals were investigated. The nitrones chosen for this study were the *Z* and *E* isomers of *N*-methyl-α-(*p*-tolyl)-α-phenyl nitrone (**7a** and



7a **8a**

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[1] (a) Taken in part from the Ph.D. Thesis of Thomas S. Dobashi, California State University, San Diego, and the University of California, San Diego, 1973. (b) NDEA Fellow, 1967–1971. (c) NSF College Teacher Reseasch Participant, summer, 1971.

[2] O. L. Brady and R. P. Mehta, *J. Chem. Soc.*, 2297 (1924).

[3] L. Semper and L. Lichtenstadt, *Chem. Ber.*, **51**, 928 (1918).

[4] F. Barrow and F. J. Thorneycroft, *J. Chem. Soc.*, 722 (1934); 769 (1939).

[5] K. Koyano and I. Tanaka, *J. Phys. Chem.*, **69**, 2545 (1965).

[6] R. W. Layer and C. J. Carman, *Tetrahedron Lett.*, 1285 (1968).

[7] L. W. Boyle, M. J. Peagram, and G. H. Whitham, *J. Chem. Soc. B*, 1728 (1971).

[8] T. S. Dobashi and E. J. Grubbs, *J. Amer. Chem. Soc.*, **95**, 5070 (1973).