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Chemistry of Alkoxy Radicals: Cleavage Reactions

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Intramolecular and intermolecular rates of *t*-alkoxy radical fragmentation into alkyl radicals and ketones have been investigated. The most important factor which determines these rates is the bond dissociation energies of the fissionable alkoxy radical. With simple alkyl substituents it is in the order: ethyl > *n*-propyl > *n*-butyl ≫ CH_3. Benzyl groups are very rapidly cleaved. Quantitative results are given at several temperatures. Alkoxy radicals derived from purely thermolytic processes behave in the same manner as those obtained from metal ion reductions of alkyl hydroperoxides.

Introduction

The two competitive unimolecular and bimolecular routes by which *t*-butoxy radicals react in typical free radical reactions are (a) hydrogen abstraction to form *t*-butyl alcohol and (b) fragmentation to acetone and methyl radicals.[1,2]

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (2)$$

Since the fragmentation reaction has been shown to be unimolecular,[3-5] reactions 1 and 2 together have been used to measure chain transfer activity of various hydrogen donor substrates, RH.[4,5] These reactions are generally considered to be applicable to other *t*-alkoxy radicals.[2]

In this study we were concerned with the structural features of *t*-alkoxy radicals which determine the progress of the fragmentation reaction. In a highly substituted *t*-alkoxy radical, $R_1R_2R_3CO\cdot$, it is theoretically possible for three fragmentation patterns to be obtained.

$$R_1R_2R_3CO\cdot \begin{cases} \xrightarrow{a} R_1\cdot + R_2COR_3 \\ \xrightarrow{b} R_2\cdot + R_1COR_3 \\ \xrightarrow{c} R_3\cdot + R_2COR_1 \end{cases} \qquad (3)$$

It has been generally accepted[2,6] that the predominant cleavage is that which forms the largest alkyl radical, R_i. The dissociation energies of a series of alkanes obtained from electron impact experiments in the gas phase, however, are not consistent with this sentiment.[7a]

In order to obtain a quantitative measure of the relative ease of cleavage reactions (3) in solution, a series of substituted alkoxy radicals were examined. They were obtained from (1) the redox reaction between alkyl hydroperoxides and reducing metal ions and (2) the thermolysis of dialkyl peroxides.

$$t\text{-}RO_2H + M^{+n} \longrightarrow t\text{-}RO\cdot + MOH^{+n} \qquad (4)$$

$$RO{-}OR' \xrightarrow{\Delta} RO\cdot + R'O\cdot \qquad (5)$$

Results

Reaction of Alkyl Hydroperoxides with Reducing Metal Ions.—The stoichiometric reduction of cumene hydroperoxide by ferrous ion is given by the equation

$$C_6H_5C(CH_3)_2O_2H + Fe^{+2} \longrightarrow C_6H_5C(CH_3)_2O\cdot + FeOH^{+2} \qquad (6)$$

However, the reduction of alkoxy radicals as in eq. 7 and the induced decomposition of hydroperoxide as in eq. 8 conspire to disrupt this ideal stoichiometry.

$$C_6H_5C(CH_3)_2O\cdot + Fe^{+2} \longrightarrow C_6H_5C(CH_3)_2OFe^{+2} \qquad (7)$$

$$C_6H_5C(CH_3)_2O\cdot + C_6H_5C(CH_3)_2OOH \longrightarrow \text{Products} \qquad (8)$$

In the presence of excess reducing metal ion the induced decomposition 8 is largely obviated.[8] Under these conditions the two predominant routes for disappearance of alkoxy radical formed in the initial step 6 is (a) unimolecular fragmentation to ketone and alkyl radical and (b) bimolecular reduction to alcohol. The degree to which reduction competes with fragmentation is dependent on the metal ion. The yields of alcohol and ketone obtained from *t*-butyl hydroperoxide and various reducing agents are given in Table I.

TABLE I

PRODUCTS FROM *t*-BUTYL HYDROPEROXIDE AND REDUCING AGENTS AT 25°

Reducing agent	*t*-Butyl alcohol, %	Acetone, %
$TiCl_3$	37	63
$FeSO_4$	52–45	48–55
$CrCl_2$	81	19
$Cr(ClO_4)_2$	84	16
VSO_4	~50	50
$V_2(SO_4)_3$	42	58
$VO(SO_4)$	70	30
$K_4Fe(CN)_6$	90–95	10–5
$Na_2S_4O_6$	95	5

The variations in yields of *t*-butyl alcohol and acetone are attributed to the reduction reaction since the rates of *t*-butyl alcohol formation by hydrogen abstraction (eq. 1) and acetone by fragmentation (eq. 2) are more or less constant in these reaction systems. In general, it appears that the most effective reducing agents like chromous ion, vanadous and ferrocyanide are also most effective in converting hydroperoxides to alcohol. A similar

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[1] F. F. Rust, *et al.*, *J. Am. Chem. Soc.*, **70**, 88, 95, 1336 (1948); **72**, 337, 338 (1950); *Disc. Faraday Soc.*, **10**, 1 (1951).

[2] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959); *Trans. Faraday Soc.*, **55**, 760 (1959).

[3] A. L. Williams, E. A. Oberright and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

[4] J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957); R. Brinton and D. Volman, *J. Chem. Phys.*, **20**, 25 (1952).

[5] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

[6] J. C. Bevington, "Radical Polymerization," Academic Press, Inc., New York, N. Y., 1961, p. 11.

[7] (a) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953); (b) E. Butler and M. Polanyi, *ibid.*, **39**, 19 (1943); **41**, 298 (1945); (c) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[8] (a) A. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 95 ff.; (b) R. J. Orr and H. L. Williams, *J. Am. Chem. Soc.*, **78**, 3273 (1956), and earlier papers.

reactivity sequence is obtained in the metal ion reduction of methyl radicals.[9]

The importance of cleavage reactions is dependent on the alkoxy radical structure. Various alkyl hydroperoxides were treated with ferrous sulfate under standard conditions. If it is assumed that the rates of alkoxy radical reductions (7) are approximately the same, the amount of fragmentation (ketonic products) is related to the unimolecular rate of decomposition of the alkoxy radical. In Table II is illustrated the wide variation in the fragmentation behavior of substituted *t*-alkoxy radicals under similar conditions.

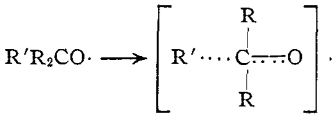
TABLE II

THE REACTION OF ALKYL HYDROPEROXIDES WITH FERROUS SULFATE. THE DEGREE OF REDUCTION AND FRAGMENTATION OF ALKOXY RADICAL

Hydroperoxide	Reduction, %	Fragmentation, %
t-Butyl	52–45	48–55
t-Amyl	19–13	81–87
α,α-Dimethylphenethyl	<5	95–100
2-Phenyl-2-butyl	8	92
Cyclohexyl	22	78
n-Butyl	77–72	23–28
α-Butoxyethyl	10	90

These results show that one of the most important factors involved in the cleavage of alkoxy radicals is the nature of the alkyl radical generated. Although polar and steric effects may be important in cleavage reactions of other alkoxy radicals, they do not constitute important factors with *these simple alkoxy radicals*. Benzyl radical is cleaved so rapidly[10] from α,α-dimethylphenethoxy radical that less than 5% parent alcohol could be detected, even under conditions in which excess ferrous ion was present.

Since the transition state for the cleavage of an alkoxy radical involves the stretching of the alkyl-carbon bond, the free energy of activation of the cleavage would be expected to be lowered as the stability of the leaving alkyl radical is increased.



$$R'R_2CO\cdot \longrightarrow \left[R'\cdots\overset{R}{\underset{R}{C}}\cdots O \right]\cdot \longrightarrow R'\cdot + R_2CO$$

In this respect the ease of cleavage is in the order:

$$C_6H_5CH_2\cdot >> C_2H_5\cdot > n\text{-}C_3H_7\cdot >> CH_3$$

In addition to the considerations regarding the stability of the departing radical as a factor in the cleavage reactions, it is not inappropriate to consider also the stability of the ketone that is formed. Thus, enhanced stability of the ketone should also be reflected in the ease of cleavage. The relative cleavages of *t*-amyloxy and 2-phenyl-2-butoxy radicals are 87 and 92%, respectively. Both alkoxy radicals give predominantly ethyl radical cleavage and the slight difference in the amounts of cleavage products indicates that the structure of the fragmented ketone is a consideration since acetophenone is more stable than acetone. The predominant driving force for the cleavage, however, is the stability of the newly formed alkyl radical.

TABLE III

INTRAMOLECULAR CLEAVAGE RATES OF ALKOXY RADICALS FROM ALKYL HYDROPEROXIDES AND REDUCING METAL IONS AT 25°

Alkoxy radical ($R_1R_2R_3CO\cdot$)			Reducing agent	Alkyl radical formed, %					Relative rates	
R_1	R_2	R_3		$CH_3\cdot$	$C_2H_5\cdot$	n-$C_3H_7\cdot$	n-$C_4H_9\cdot$	φ-$CH_2\cdot$	$C_2H_5\cdot/n$-$C_3H_7\cdot$	n-$C_3H_7\cdot/n$-$C_4H_9\cdot$
CH_3	CH_3	C_2H_5	$FeSO_4$	0.3	99.7	..	..	..	..	..
			$TiCl_3$	.3	99.7	..	..	..	..	..
CH_3	C_2H_5	C_6H_5	$FeSO_4$	.1	99.9	..	..	..	..	..
			$TiCl_3$	.1	99.9	..	..	..	..	..
CH_3	CH_3	$C_6H_5CH_2$	$FeSO_4$	0	..	..	..	100	..	..
			$CrSO_4$	0	..	..	..	100	..	..
CH_3	C_2H_5	n-C_3H_7	$FeSO_4$	0	62	38	..	..	1.63	..
			$TiCl_3$	0	60	40	..	..	1.50	..
C_2H_5	C_2H_5	n-C_3H_7	$FeSO_4$	..	75	25	..	..	3.00	..
			$TiCl_3$	..	74	26	..	..	2.84	..
			$TiSO_4$	..	74	26	..	..	2.84	..
			$V_2(SO_4)_3$	..	74	26	..	..	2.84	..
CH_3	n-C_3H_7	n-C_4H_9	$TiSO_4$	0	..	61	39	..	..	1.56
C_2H_5	n-C_3H_7	n-C_4H_9	$FeSO_4$	..	48	31	21	..	1.55	1.48
			$TiCl_3$	..	52	28	20	..	1.86	1.40
			$TiSO_4$	..	51	29	20	..	1.76	1.45

Intramolecular comparisons of the cleavage reactions were also investigated. Alkoxy radicals were produced by the oxidation–reduction reactions in 50% v. aqueous isopropyl alcohol. Under these conditions the alkyl radical fragments from the cleavage reactions (3) yielded the corresponding alkanes. The gaseous alkane mixture was analyzed quantitatively by mass spectral techniques. Table III lists these competitive fragmentation reactions from various *t*-alkoxy radicals and reducing agents.

Within experimental limits, the intramolecular rates of *t*-alkoxy radical cleavage are independent of the metal ion reducing agent and the ketonic fragment formed. The ratio of the rates of ethyl to *n*-propyl cleavage is the same in 3-ethyl-3-hexoxy

[9] H. E. De La Mare, J. K. Kochi and F. F. Rust to be published.

[10] It is possible that α,α-dimethylphenethyl hydroperoxide reacts with reducing metal ion in a termolecular decomposition step, so that α,α-dimethylphenethoxy radicals are not actual intermediates. Multibond peroxide cleavage

$$C_6H_5CH_2C(CH_3)_2O_2H + M^{+n} \longrightarrow C_6H_5CH_2\cdot + CH_3COCH_3 + MOH^{+n}$$

reactions in some cases have been advocated by Bartlett and coworkers: P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

radical (1.4–1.5) as it is in 3-methyl-3-hexoxy radical (1.5–1.6) if the statistical factor is included. It is also the same in the more highly strained 4-ethyl-4-octoxy radical. Similar results were obtained in the ratio of the rates of *n*-propyl to *n*-butyl cleavage from 4-methyl-4-octoxy radical (1.5–1.6) and 4-ethyl-4-octoxy radical (1.4–1.5).

The relative rates of cleavage at 25° of simple normal radicals calculated on this basis are listed in Table IV.

TABLE IV

RELATIVE INTRAMOLECULAR CLEAVAGE RATES OF SIMPLE ALKYL GROUPS FROM *t*-ALKOXY RADICALS AT 25°

Radical	Relative rate
CH_3	~0.003
CH_3CH_2	1.0
n-C_3H_7	0.65
n-C_4H_9	0.43

There is a linear correlation between the C–H bond dissociation energies obtained by Stevenson and the logarithms of relative cleavage rates given above for ethyl, *n*-propyl and *n*-butyl radicals. Methyl radical, however, does not fit this correlation. Although good relative rate values were not obtained due to the small amount of methyl cleavage, the degree of deviation is much beyond the experimental scatter. Methyl radical is cleaved approximately 100 times slower than would be predicted from the dissociation energy of methane.

These rates of radical cleavage are not correlatable with the bond dissociation energies of alkyl iodides obtained in the early studies by Butler and Polanyi.[6b,c] Their results showed a *monotonic decrease* in bond dissociation energies from methyl iodide to *n*-butyl iodide, whereas Stevenson's and our result indicate a definite minimum at ethyl. However, more recent investigations[11] of the pyrolyses of alkylbenzenes have cast doubt on Butler and Polanyi's values.

The differences in the activation energies for the intramolecular cleavage reactions were determined for ethyl, *n*-propyl and *n*-butyl radicals from 4-ethyl-4-octoxy radical. The compositions of the gaseous products obtained from the reduction of 4-ethyl-4-octyl hydroperoxide with titanous chloride at various temperatures are given in Table V.

TABLE V

ALKYL FRAGMENTS FROM THE REDUCTION OF 4-ETHYL-4-OCTYL HYDROPEROXIDE WITH TITANOUS CHLORIDE AT SEVERAL TEMPERATURES

	Fragments, %		
Temp., °C.	C_2H_5	C_3H_7	C_4H_9
90	42	32	25
24	51	28	21
0	55	27	18

The difference in activation energy for ethyl and *n*-propyl cleavages ($\Delta H^{\ddagger}_{C_3H_7} - \Delta H^{\ddagger}_{C_2H_5}$) is 1.0 kcal./mole and that between *n*-propyl and *n*-butyl ($\Delta H^{\ddagger}_{C_4H_9} - \Delta H^{\ddagger}_{C_3H_7}$) is 0.5 kcal./mole.

Thermolysis of Dialkyl Peroxides.—The dialkyl peroxides were thermolyzed in 50% v. aqueous isopropyl alcohol solution at 130° (sealed tubes). Under these conditions alkyl radicals react by hydrogen abstraction from isopropyl alcohol to produce the corresponding alkane. The formations of radical coupling and disproportionation products are minimal. Thus, di-*t*-butyl peroxide under these conditions yields 99.5% methane and < 0.5% ethane. Di-*t*-amyl peroxide yields 2.5% methane, 96.0% ethane, < 0.5% ethylene and 1.1% *n*-butane.

The intramolecular cleavage rates of several *t*-alkoxy radicals were calculated from the composition of the gaseous mixtures. Values listed in Table VI were normalized after subtracting methane and small amounts of isopropyl alcohol, acetone and carbon dioxide.

The consistency of the cleavage rates is shown in the last two columns of Table VI in which the relative rates of cleavage between ethyl and propyl and propyl and butyl radicals are calculated. Since large changes in alkoxy radical structures were not made, it is not too surprising to find that these relative rates of intramolecular cleavage are independent of the ketonic product. If the rates of ethyl to propyl cleavage obtained from 3-ethyl-3-hexoxy radical are corrected for the statistical factor they fall in line with that obtained from 3-methyl-3-hexoxy and 4-ethyl-4-octoxy radicals.

The ratio of ethyl to *n*-propyl cleavage is calculated to be 1.21 at 130°, if a difference in activation energies of 1.0 kcal./mole found in the metal ion reduction of alkyl hydroperoxides is assumed. In a similar manner, the ratio of *n*-propyl to *n*-butyl cleavage rates found in the thermolysis experiments (1.0) is nearly that extrapolated (1.06) from the metal salt–hydroperoxide fragmentation patterns.

These results coupled with other observations of the similar behavior of alkoxy radicals obtained from hydroperoxides and various metal ions lead us to believe that metal ions do not influence the mode of *t*-alkoxy radical cleavage.[12]

If values of the differences in activation energies of 1.0 and 0.5 kcal./mole are accepted for *n*-propyl/ethyl and *n*-butyl/*n*-propyl cleavages, the temperature at which inversion in the cleavage rates (isokinetic temperature[13a]) occurs is approximately 190°. It is apparent that the relative rates of intramolecular alkoxy radical cleavages are very much a function of temperature.[13b] The results further reinforce the exercise of caution which is necessary when correlations between activation processes and thermodynamic properties are made.[2]

The intermolecular comparisons of the rates of decomposition of *t*-alkoxy radicals can be obtained from the fragmentation products of *t*-butyl *t*-alkyl peroxides, if several assumptions are made. (1) *t*-Butyl *t*-alkyl peroxides decompose by O–O bond fission to produce two alkoxy radicals,[3] *t*-butoxy and *t*-alkoxy, in equivalent environments. (2) The rates of chain transfer with isopropyl alcohol are reasonably independent of structure for the similarly constituted *t*-alkoxy radicals. (3) The formation of methane is solely from the *t*-butoxy moiety.[14]

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(11) C. Leigh and M. Szwarc, *J. Chem. Phys.*, **20**, 403, 407 (1952).

(12) J. Kochi and F. Rust. *J. Am. Chem. Soc.*, **83**, 2017 (1961).

(13) (a) J. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) *cf.* ref. 2 on relative rates of cleavage reactions.

(14) The intramolecular rate difference between methyl and higher alkyl radicals is large.

TABLE VI

INTRAMOLECULAR CLEAVAGE RATES OF *t*-ALKOXY RADICALS FROM THERMOLYSIS OF *t*-BUTYL *t*-ALKYL PEROXIDES AT 130°

t-Alkoxy radical ($R_1R_2R_3CO\cdot$)			Alkyl cleavage, %				Relative rates	
R_1	R_2	R_3	C_2H_5	n-C_3H_7	n-C_4H_9	i-C_4H_9	C_2H_5/n-C_3H_7	n-C_3H_7/n-C_4H_9
CH_3	C_2H_5	n-C_3H_7[a]	56.9	43.1	..	..	1.32	..
CH_3	C_2H_5	n-C_3H_7	57.1	42.8	..	..	1.33	..
C_2H_5	C_2H_5	n-C_3H_7	71.6	28.4	..	..	2.52	..
CH_3	n-C_3H_7	n-C_4H_9	..	50.2	49.8	..	..	1.0
C_2H_5	n-C_3H_7	n-C_4H_9	37.7	30.1	32.2	..	1.25	0.94
CH_3	C_2H_5	i-C_4H_9	62.4	..	..	37.6	..	..

[a] From bis-(3-methyl-3-hexyl) peroxide.

TABLE VII

THE RELATIVE RATES OF *t*-ALKOXY RADICAL FRAGMENTATION FROM THE THERMOLYSIS OF *t*-BUTYL *t*-ALKYL PEROXIDES

t-Alkoxy radical ($R_1R_2R_3CO\cdot$)			
R_1	R_2	R_3	Relative fragmentation rate
CH_3	CH_3	CH_3	1.00
CH_3	C_2H_5	n-C_3H_7	6.3
C_2H_5	C_2H_6	n-C_3H_7	7.3
CH_3	n-C_3H_7	n-C_4H_9	6.2
C_2H_5	n-C_3H_7	n-C_4H_9	5.5
CH_3	C_2H_5	i-C_4H_9	4.3
CH_3	n-C_3H_7	i-C_4H_9	3.8

If these assumptions are valid the yield of methane relative to the sum of the higher alkanes is directly related to the cleavage rates of *t*-butoxy and the *t*-alkoxy radical concomitantly formed from the thermolysis of *t*-butyl *t*-alkyl peroxides.

The relative rates of fragmentation of several *t*-alkoxy radicals calculated on this basis are listed in Table VII.[15]

Acknowledgment.—I wish to thank Mr. F. F. Rust and Dr. D. P. Stevenson for several helpful discussions, and Mr. Edward Butts for numerous mass spectroscopic analyses.

Experimental

Preparation of Alcohols.—The tertiary alcohols were prepared by the Grignard procedure from alkyl halide and the corresponding ketones. Distillation often yielded the alcohol contaminated with ketonic impurities. These were readily removed by the treatment with Girard P reagent in methanol with acetic acid catalyst.

Preparation of Alkyl Hydroperoxides.—The alkyl hydroperoxides were prepared from the corresponding alcohol and aqueous hydrogen peroxide by Milas' procedure.[16] With these highly substituted hydroperoxides, the acid concentration, temperature and length of stirring were critical factors in obtaining reasonable yields of products. If care is not exercised in adjusting these parameters, the final products are those which result from the acid-catalyzed dehydration of alcohol and rearrangement of peroxides, *viz.*, olefins and ketones and lower molecular weight alcohols.

Hydroperoxides could be prepared only from the unbranched alcohols. With others extensive rearrangement or dehydration (at high acid concentrations or temperatures) resulted. The procedures are given below for the alkyl hydroperoxides which were successfully prepared.

3-Methyl-3-hexyl Hydroperoxide.—A 69% sulfuric acid solution (100 g. of H_2SO_4 and 45 g. of H_2O) was chilled to 0° and 116 g. of 3-methyl-3-hexyl alcohol was added with rapid stirring and cooling. It was followed by 135 g. of 50% hydrogen peroxide. The reaction was stirred at 0° for 1 hour and at 10° overnight. The 3-methyl-3-hexyl hydroperoxide was obtained (99 g., 75%) as liquid boiling at 43–46° (1 mm.) (n^{20}D 1.4306). The hydroperoxide assay was 94%. It was purified *via* the sodium salt and redistilled (b.p. 43–44° (1 mm.), n^{20}D 1.4302). *Anal.* Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20; hydroperoxide equiv. wt., 132.20. Found: C, 63.8; H, 12.5; hydroperoxide equiv. wt., 134, 134.5.

3-Ethyl-3-hexyl Hydroperoxide.—A solution of 100 g. of concd. sulfuric acid and 45 g. of water was cooled to 0°. 3-Ethylhexanol-3 (130 g.) was added dropwise with rapid stirring at such a rate to maintain the temperature at 0°. This was followed by the addition of 135 g. of 30% hydrogen peroxide under the same conditions. The heterogeneous reaction was then stirred rapidly for 24 hours at 10–15°. Excess ice-water and 100 ml. of ether were added and the organic layer separated. It was washed with sodium bicarbonate twice, dried with anhydrous sodium carbonate and distilled *in vacuo*. The forerun which was refractionated was a mixture (69 g.) of octenes (b.p. 118–112° (760 mm.), n^{20}D 1.4197–1.4212) which correspond to 3-ethylhexene-2 (b.p. 120–121°, n^{20}D 1.4246) and 3-ethyl-hexene-3 (b.p. 119°, n^{20}D 1.404). The crude hydroperoxide boils at 39–42° (1 mm.) (44 g., 30%). The hydroperoxide equivalent weight was 180. It was purified through the sodium salt (b.p. 47–48° (1 mm.), n^{20}D 1.4371). *Anal.* Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41; hydroperoxide equiv. wt., 146.22. Found: C, 65.9; H, 12.1; hydroperoxide equiv. wt., 150, 152.

3-Methyl-4-octyl Hydroperoxide.—3-Methyl-4-octanol (26 g.) was added to 90 g. of a 65% sulfuric acid solution at 5°. A solution of 50% hydrogen peroxide was added at 8–10° and the heterogeneous mixture rapidly stirred at 8–10° for 9 hours. The hydroperoxide (14 g.) was isolated *via* the sodium salt and distilled, boiling range 55–60° (1 mm.), n^{25}D 1.4334. *Anal.* Calcd. for $C_9H_{20}O_2$: C, 67.45; H, 12.58; hydroperoxide equiv. wt., 160. Found: C, 67.6 H, 12.4; hydroperoxide equiv. wt., 164, 166.

4-Ethyl-4-octyl Hydroperoxide.—To 90 g. of a solution of 65% sulfuric acid at 0° was added dropwise 22 g. of 4-ethyl-4-octanol. A prechilled solution (84 g.) of 50% hydrogen peroxide was added at 0–5° with vigorous stirring. The mixture was stirred further at 5–8° for 6 hours. The crude hydroperoxide (19 g., 85%) was purified through the sodium salt and distilled; boiling range: 62–63° (1 mm.), yield 12.5 g., n^{25}D 1.4409. *Anal.* Calcd. for $C_{10}H_{22}O_2$: C, 68.91; H, 12.72; hydroperoxide equiv., 174. Found: C, 68.5; H, 12.7; hydroperoxide equiv., 169, 177.

2-Phenyl-2-butyl Hydroperoxide.—Pure *sec*-butylbenzene (340 g., 2.5 moles) was autoxidized at 126–127° at 35–36 p.s.i. oxygen pressure and 1 g. of di-*t*-butyl peroxide for 7.5 hours. The total oxygen consumption was 8.70 moles; or 27% of the hydrocarbon was converted. The titrated yield of hydroperoxide was 61%. It was concentrated by vacuum distillation at 50°. The concentrate was extracted with 42% solution of sodium hydroxide. The crystalline sodium salt was filtered and washed with Skelly B. It was neutralized by dissolution in water and addition of Dry Ice. The separated hydroperoxide was extracted with ether and the ethereal solution dried with sodium sulfate and distilled. 2-Phenyl-2-butyl hydroperoxide was obtained as a liquid boiling at 68–71° (0.1 mm.), n^{20}D 1.5222, yield 50 g. (46%

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(15) There is some question regarding the validity of these intermolecular comparisons of decomposition rates. For example, the relative rate between 3-methyl-3-hexoxy and *t*-butoxy radical given in Table VII is several orders of magnitude less than that obtained from the sum of the partial rates calculated from the intramolecular rates listed in Tables IV and VI. I wish to thank the referee for pointing this out.

Since the calculated rates are a very sensitive function of the yields of products, this discrepancy may be attributed to the invalidity of the assumptions made in deriving the intermolecular rate comparisons. This is particularly true if induced decompositions are occurring.

(16) N. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205, 643 (1946); N. Milas and L. H. Perry, *ibid.*, **68**, 1938 (1946).

based on oxygen consumed). *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; hydroperoxide equiv., 166. Found: C, 72.5; H, 8.3; hydroperoxide equiv., 167.8, 168.3.

Symmetrical Dialkyl Peroxides.—Symmetrical *t*-butyl, *t*-amyl and *t*-hexyl peroxides can be made relatively easily.[16] The higher homologs are more difficult to prepare since the acid concentrations and temperatures required to effect condensation lead to dehydration of the alcohol and rearrangement of the hydroperoxide components. Symmetrical 3-methyl-3-hexyl peroxide was made in low yield. The higher homolog, bis-3-ethyl-3-hexyl peroxide, could not be prepared under various conditions of acid strength and temperature.

Bis-(**3-methyl-3-hexyl**) **Peroxide.**—A 65% sulfuric acid solution (65 g. of sulfuric acid and 35 g. of water) was chilled to 0°. To the reaction were added 42 g. of 3-methyl-3-hexanol and 40 g. of 3-methyl-3-hexyl hydroperoxide and the reaction stirred overnight at 0° with rapid stirring. The hydroperoxide titer decreased to 58%. In addition to the recovered alcohol (40%) and hydroperoxide (45%) there was obtained 50% of dehydration products consisting of a mixture of heptenes (b.p. 86–95° (760 mm.), n^{20}_{D} 1.4051–1.4103; lit. 3-methyl-hexene-2, b.p. 93°, n^{20}_{D} 1.4075; 3-methyl-hexene-3, b.p. 94°, n^{20}_{D} 1.4050) and 3 g. of bis-(3-methyl-3-hexyl) peroxide. The repetition of this procedure several times yielded sufficient peroxide to distil (b.p. 42–43° (1 mm.), n^{20}_{D} 1.4302). *Anal.* Calcd. for $C_{14}H_{30}O_2$: C, 72.98; H, 13.13. Found: C, 73.0, 72.7; H, 13.0, 13.0. Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.7; H, 14.4.

t-Butyl *t*-**Alkyl Peroxides.**—Although symmetrical dialkyl peroxides of the higher homologs could not be prepared by the sulfuric acid method, the unsymmetrical *t*-butyl peroxides could be made. The unbranched *t*-alkyl *t*-butyl peroxides were synthesized from the alcohol and *t*-butyl hydroperoxide. However, branching in one of the carbinol substituents often caused substantial amounts of rearranged products to be formed. Thus, methylethylisopropylcarbinol and *t*-butyl hydroperoxide yielded a mixture of *t*-butyl 2,3-dimethyl-3-pentyl peroxide and *t*-butyl 2,3-dimethyl-2-pentyl peroxide. Similarly, methylisopropylbutylcarbinol and methylpropyl-*sec*-butylcarbinol all gave *t*-butyl *t*-alkyl peroxide mixtures. The criterion for rearrangement in this series of *t*-butyl alkyl peroxides was the examination of the thermolysis products. Thus, "*t*-butyl 2,3-dimethyl-3-pentyl peroxide" on thermolysis yielded butene (30%) in addition to the expected ethane (50%) and propane (40%). The other branched alcohols also yielded peroxides which produced anomalous alkane fragments on thermolysis.

3-Methyl-3-hexyl *t*-Butyl **Peroxide.**—A sulfuric acid solution (65%, 65 g. of sulfuric acid and 35 g. of water) was chilled to 0° and 40 g. of 3-methylhexanol-3 and 30 g. of *t*-butyl hydroperoxide were added. The reaction was stirred for 4 hours at 0° and 18 hours at 13°. Ether was added and the ethereal solution washed with water, dried with sodium carbonate and distilled. The peroxide 3-methyl-3-hexyl *t*-butyl peroxide is obtained in 93% (60 g.) yield (b.p. 39–40° (1 mm.), n^{20}_{D} 1.4124). *Anal.* Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.4, 70.3; H, 12.9, 12.8.

3-Ethyl-3-hexyl *t*-Butyl **Peroxide.**—A 65% sulfuric acid solution (65 g. of sulfuric acid and 35 g. of water) was chilled to 0°. With rapid stirring and chilling 40 g. of 3-ethyl-3-hexanol was added and followed by 30 g. of *t*-butyl hydroperoxide. The reaction was stirred at 0° for 15 hours. Ether (100 ml.) was added and the organic layer separated. It was washed with water, dried with sodium carbonate and distilled. The 3-ethyl-3-hexyl *t*-butyl peroxide was obtained as a liquid boiling at 52–53° (1 mm.) in 88% (53 g.) yield (n^{20}_{D} 1.4195). *Anal.* Calcd. for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.8, 71.7; H, 13.0, 13.0.

4-Methyl-4-octyl *t*-butyl **peroxide** was obtained from 24 g. of 4-methyl-4-octanol, 32 g. of *t*-butyl hydroperoxide (TBHP) and 100 g. of 65% H_2SO_4 at 0° which was stirred at 5–6° for 20 hours; yield 26 g., boiling range 53–54° (1 mm.), n^{25}_{D} 1.4179. *Anal.* Calcd. for $C_{13}H_{26}O_2$: C, 72.16; H, 13.05; mol. wt., 216. Found: C, 71.7, 71.8, H, 13.0, 13.1; mol. wt., 220.

4-Ethyl-4-octyl *t*-butyl **peroxide** was prepared from 4-ethyl-4-octanol (21 g.), TBHP (32 g.) and 100 g. of 65% sulfuric acid at 0°. The mixture was stirred 16 hours at 0° and 7 hours at 4–8° to yield 21 g., boiling range 53–54°(1 mm.), n^{25}_{D} 1.4232. *Anal.* Calcd. for $C_{14}H_{30}O_2$: C, 72.98; H, 13.13; mol. wt., 230 Found: C, 73.0, 72.9; H, 13.0, 13.1; mol. wt., 225.

Analysis of Gases.—The gas samples were collected from the reaction mixtures by distillation into a liquid nitrogen trap. The molecular distillation was repeated and the gas sample analyzed mass spectroscopically. Mixtures were also examined by gas liquid chromatograph on a 50-ft. dimethyl sulfolane–firebrick column at 0°: air, 5.1′; ethane, 6.2′; propane, 9.2′; and butane, 19.2′. Methane was separated from air on an 8 ft. silica gel column at 0°: air, 1.0′; methane, 2.0′; ethane, 12.5′.

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Some Factors Affecting the Site of Alkylation of Oxime Salts

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The product ratio for alkylation of oxime salts on oxygen to that on nitrogen has been studied by chromatographic separation. In the methylation and benzylation of *p,p*′-disubstituted benzophenone oxime sodium salts in ethanol, electron-withdrawing groups markedly promote alkylation on oxygen. In the alkylation of benzophenone oxime sodium salt with *p*-substituted benzyl halides, electron-withdrawing substituents also favor alkylation on oxygen, but only weakly. No systematic difference in product ratio was detected among oxime salts of lithium, sodium, potassium and tetramethylammonium. O-Alkylation is increased mildly in 1:1 acetone–ethanol solution, but is not affected by small amounts of water in ethanol. Heterogeneous experiments in acetone show overwhelming O-alkylation, but in toluene O-alkylation is slightly depressed. Variation of leaving groups among benzyl chloride, bromide and tosylate showed a questionably small effect on the O/N ratio. Treatment of benzophenone oxime with neat benzyl bromide heavily favored N-alkylation, but resulted in a much slower reaction.

Interest in the alkylation of ambident anions from both the standpoints of mechanism and synthesis has increased considerably in recent years. Several unanticipated effects of structural changes and of experimental conditions have been reported, and different theories have been advanced in their explanation.[2-4] Most of the systematic work has been done with only a small variety of systems, principally nitrite and phenol salts; only the latter are susceptible to the study of substituent effects on the anion, but this has not yet been reported.

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