

TABLE II

Polymer series	Concn. ^a and type of catalyst	Bath temp., °C.	Time, min.	Yield ^b of crude polymer, %	M_n^c of crude polymer	Melting-range of crude polymer, °C.	Approx. M_n range of major portion of center fractions ^d
IIIb	1% ZnCl ₂	120	60	91	1210	80-95	1000-2100
	2% ZnCl ₂	120	30	86 ^e	1100 ^e	75-100 ^e	1200-2500 ^e
	2% ZnCl ₂	140	60	93	1370	85-105	1200-3500
	10% ZnCl ₂	140	10	90	1990	100-130	1300-3900
	0.7% AlCl ₃	120	60	87	1120	80-110	900-2200
IIIc	1% HCl	110	40	87 ^f	790	50-90	800-1400
	1.5% ZnCl ₂	120	60	93 ^g	2180	120-150	1900-4000
	1.5% ZnCl ₂	125	180	94	2500	120-155	2200-5000
	3.2% ZnCl ₂	125	180	89	3000	135-170	2500-5000
	5% ZnCl ₂	120	20	92	2120	110-145	1500-3000
	1% AlCl ₃	100	40	86	2730	135-165	2500-5000
	1.5% HCl	125	180	85 ^g	1910	100-135	1600-2800

^a See ref. 6. ^b See ref. 27. ^c See ref. 7. ^d All center fractions totaling approximately one-half the over-all polymer weight after fractionation. ^e Essentially the same results with corresponding diether in lieu of carbinol. ^f Last 2 fractions exhibit ether bands. ^g Last fraction exhibits weak ether bands.

Condensation of α -Hydroxybenzylferrocene (IIc); Formation of IIIc.—The experimental details are given in Table II. Five characteristic polymer fractions are recorded in Table I. In

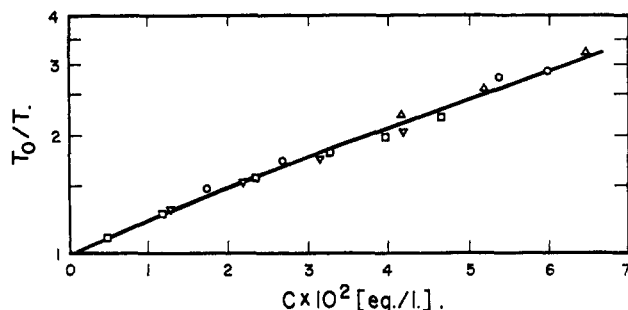


Fig. 4.—Intensity ratio T_0/T of the 9- μ band vs. equivalent concentration of unsubstituted π -cyclopentadienyl rings: O, ferrocene; □, triphenylmethylferrocene; ∇, 1,2-diferrocenylethane; Δ, diferrocenyl.

contrast to IIIa and IIIb, even fractions with M_n as high as 6000 proved to be soluble in dimethylformamide. Also, a diminished tendency of the low members toward sintering was noticed, facilitating their isolation in powdery form.

Determination of Percentage Homoannularity.—In Fig. 4, for several known homoannular ferrocene compounds, the intensity ratio for the 9- μ band, $(T_0/T)_{9\mu}$, is plotted on a semilogarithmic paper against the respective concentration, C , in equivalents of unsubstituted π -cyclopentadienyl rings per liter of solution. T_0 and T , the apparent intensities of the incident and transmitted radiation, respectively, were determined at $25 \pm 1^\circ$ in CS₂ solution, employing the base-line method of Heigl, *et al.*³¹ The path length was 0.10 cm. To obtain the percentage homoannular content (% homoannularity) of a polymer of unknown substitution pattern, the T_0/T ratio was determined by the same procedure as above, applying a polymer concentration such as to confine the numerical value of T_0/T within the range from ca. 1.3 to 2.5. For this ratio, the pertinent equivalent concentration, C , was read off the curve in Fig. 4. This found value of C , divided by one-hundredth the actually applied polymer concentration expressed as equivalents of ferrocene units per liter, provided the per cent content of homoannularly-linked ferrocene nuclei (% homoannularity) in the given polymer fraction.

The method was checked on a number of monomeric ferrocene derivatives containing unsubstituted rings and was found to hold with an average deviation of $\pm 6\%$ for all compounds investigated except those bearing carbonyl, ether or other polar groups, for which a greater deviation occurred.

(30) Terminology chosen in accordance with D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952); cf. also R. N. Jones, *et al.*, *ibid.*, **74**, 80 (1952), and R. R. Hampton and J. E. Newell, *Anal. Chem.*, **21**, 914 (1949).

(31) J. J. Heigl, *et al.*, *ibid.*, **19**, 293 (1947). While its weaknesses are well recognized, this method was chosen for simplicity, its accuracy and reproducibility being sufficient for the present purpose.

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The Decomposition of Peroxides Catalyzed by Copper Compounds and the Oxidation of Alkyl Radicals by Cupric Salts¹

BY JAY K. KOCHI

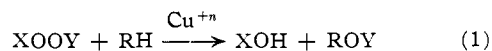
RECEIVED JANUARY 9, 1963

Diacyl and dialkyl peroxides, peresters and alkyl hydroperoxides as classes of peroxides are catalytically decomposed by copper salts in non-aqueous solutions. It is demonstrated that the decomposition is initiated by the one-electron reduction of the peroxidic bond by cuprous salt to form cupric species and oxy free radicals, which yield alkyl radicals on fragmentation. Cuprous catalyst is regenerated by the subsequent cupric oxidation of the alkyl free radicals. The catalysis is inhibited by halogens which readily oxidize cuprous salts. The oxidation of the isomeric butyl radicals exclusively to butenes occurs with no skeletal rearrangement. The approach to statistical distribution of butene-1 and *trans*- and *cis*-butene-2 from the oxidation of *sec*-butyl radicals is discussed. Neopentyl radicals are not as efficiently oxidized as those radicals which possess a β -hydrogen and products of rearrangement are obtained. The mechanism of the oxidation of alkyl radicals by simple and complex copper salts is discussed.

Introduction

Substitution reactions effected by peroxides in the presence of metal salts such as copper, cobalt and manganese have been described by Kharasch and co-

workers.² These reactions are given by eq. 1 in which a hydrogen donor (RH) undergoes a metathetical re-



(1) (a) Part VI. Reactions of Peroxides Catalyzed by Metal Salts. Part V: *J. Am. Chem. Soc.*, **84**, 3271 (1962). (b) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13, 1962.

(2) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958); **24**, 606 (1959); M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959); G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960).

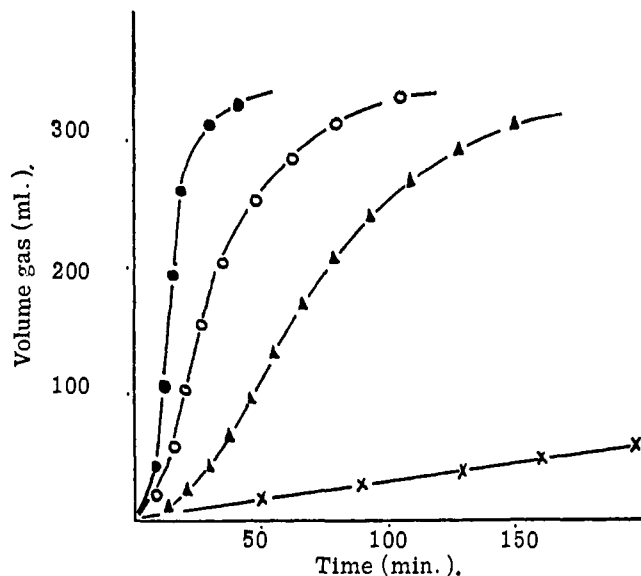
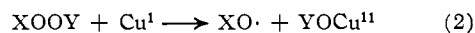


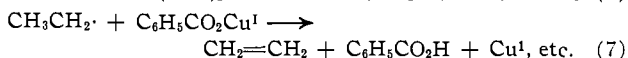
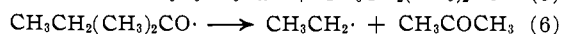
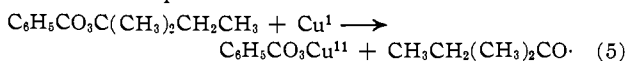
Fig. 1.—Catalyzed decomposition of valeryl peroxide (0.50 *M*) in glacial acetic acid at 55°; cupric octanoate: ●, 2.11×10^{-1} *M*; ○, 2.07×10^{-2} *M*; ▲, 5.01×10^{-3} *M*; ×, none.

action with a peroxide (XOOY ; X, Y = H, alkyl, acyl). We have interpreted³ these reactions as proceeding *via* several discrete steps which involve free radical intermediates.



The success of these reactions to yield substitution products, ROY, depends to a large extent on the chain transfer step 3. Since oxy radicals ($\text{XO}\cdot$) are relatively selective,⁴ the types of radicals ($\text{R}\cdot$) produced are limited to those derived from rather good chain transfer agents.^{5b} Of the systems examined so far, the majority involve either *t*-butoxy or benzoyloxy as the chain transfer agent. This has been of fortuitous value since these particular oxy radicals, in addition to being derived from commercially available peroxides, are (of their class) the least prone to undergo fission.^{5,6}

Recently we have demonstrated^{5b} that peroxides derived from sources other than the *t*-butylperoxy moiety, *viz.*, the *t*-amylperoxy group, are catalytically decomposed by copper salts in the *absence* of hydrogen donor substrates. For example *t*-amyl perbenzoate is decomposed by copper salts to benzoic acid, ethylene and acetone. The following scheme analogous to reactions 2–4 was postulated



This differs from the decomposition of *t*-butyl peroxy compounds only in that the intermolecular chain transfer step to produce carbon radicals (3) is replaced by the decomposition of the oxy radical intermediate (6).

In this report we wish to present evidence which substantiates a scheme such as that outlined in eq. 5–7 as the process which generally applies to the copper-catalyzed decomposition of a number of types of peroxides and includes the class of substitution reactions

(3) (a) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962); (b) *Tetrahedron*, **18**, 483 (1962).

(4) C. Walling, *et al.*, *J. Am. Chem. Soc.*, **84**, 3326 (1962); **83**, 3877 (1961); **82**, 6108, 6113 (1960); G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(5) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(6) G. S. Hammond and L. Soffer, *ibid.*, **72**, 4711 (1950).

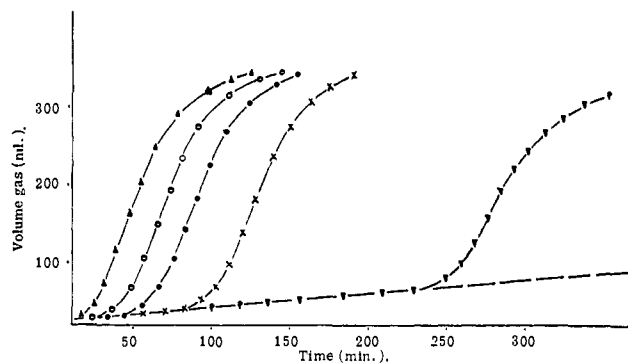


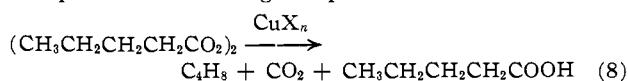
Fig. 2.—Inhibition of copper salt-catalyzed decomposition of valeryl peroxide by bromine in acetonitrile at 55° (peroxide, 0.50 *M*; $\text{Cu}(\text{OAc})_2$, 0.020 *M*); bromine: ▲, none; ○, 2.10×10^{-4} *M*; ●, 4.20×10^{-4} *M*; ×, 8.40×10^{-4} *M*; ▼, 2.10×10^{-3} *M*.

(eq. 1) discovered by Kharasch.² Furthermore, the catalyzed decomposition of suitably constituted peroxides by metal salts allows for a facile examination of the oxidation of a variety of free alkyl radicals by cupric salts (*e.g.*, eq. 4 and 7) in non-aqueous solutions. The isomeric butyl and neopentyl radicals have been subjected to this study and they compare with studies done earlier⁷ with simple alkyl radicals in aqueous solution. Recently Goldschmidt, *et al.*,⁸ have also reported on the decomposition of some diacyl peroxides by copper salts.

Results

The Reduction of Peroxides by Cuprous Salts.—

The decomposition of divaleryl peroxide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2$)₂ proceeds at 55° with a half-life of approximately 12 hours in solvents such as heptane, benzene, acetonitrile and acetic acid. The products of decomposition are *n*-butane, valeric acid, *n*-butyl valerate and CO_2 , which are typical products of thermal decomposition of diacyl peroxides.⁹ In the presence of copper salts (cupric acetate, acetylacetonate, stearate or octanoate) the decomposition is markedly accelerated and proceeds according to eq. 8



The yields of gas (butene and CO_2) were determined by gas chromatography coupled with titrimetric (bromine for butene) and absorption (Ascarite for CO_2) techniques. The carboxylic acids were determined by titration with alkali. Figure 1 shows the catalytic effect of copper salts. When *cupric* salts are used, the reaction initially shows an induction period which is more marked at low cupric concentrations than at high concentrations. Although the variation in rate with catalyst is more sensitive at low cupric concentrations, the limiting rate of the reaction is not simply related to the copper salt concentration.

The induction period can be systematically controlled by the addition of reagents which destroy or inactivate the cuprous species. These include such oxidants as molecular chlorine or bromine and such complexing agents as phenanthroline or bipyridyl which stabilize the cuprous valence state (*vide infra*). With bromine as oxidant the inhibition is uniformly proportional to the amount of bromine added as shown in Fig. 2. With the

(7) H. E. DeLaMare, J. K. Kochi and F. F. Rust, *ibid.*, **83**, 2013 (1961); **85**, 1437 (1963).

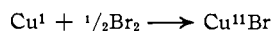
(8) S. Goldschmidt, H. Späth and L. Beer, *Ann.*, **649**, 1 (1962).

(9) (a) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., 1961, New York, N. Y., p. 302ff; (b) D. F. DeTar, *et al.*, *J. Am. Chem. Soc.*, **81**, 122 (1959); **79**, 3041, 3845 (1957); **78**, 4296 (1956); (c) J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956).

TABLE I
 OXIDATION OF *n*-BUTYL RADICALS^a BY CUPRIC SALTS

Temp., °C.	Copper ^b salt, <i>M</i>	Peroxide, <i>M</i>	Solvent	CO ₂ ^c yield, %	C ₄ -Hydro-carbon ^c yield, %	Composition of C ₄ -mixture <i>n</i> -Butane	Butene-1	RCO ₂ H ^d yield, %	Rate, ^e ml./min.
70	0	0.44	C ₆ H ₆	154	74	91	9	18	0.76
70	0	.43	HOAc	119	79	100	0		1.5
55	0	.47	HOAc	123	86	100	0		0.22
85	0.054A ^f	.66	C ₆ H ₆	94	86	0	100	95	...
70	.053A ^f	.61	C ₆ H ₆	91	89	1	99	91	3.8
55	.023E	.45	C ₆ H ₆	89	93	0	100	102	0.42
70	.070A	.60	HOAc	95	88	2	98	...	>70 ^g
55	.211E	.50	HOAc	97	98	0	100	...	29
55	.021E	.53	HOAc	95	93	3	97	...	8.1
55	.0050E	.51	HOAc	92	88	12	88	...	3.5
55	.019B ^f	.48	HOAc	92	85	16	84
55	.022A	.49	CH ₃ CN	92	90	1	99	98	8.2
55	.013B	.45	CH ₃ CN	94	89	2	98	97	3.6
55	.11B	.48	CH ₃ CN	90	89	0	100	94	Immed.
55	.021E	.49	CHCl ₃	84	93	51	49	98	0.95
55	.022E	.55	IPA ^h	94	95	1.5	98.5	96	2.7
55	.024R(1:1) ⁱ	.54	HOAc	91	93	2	98	...	8.6
55	.024R(1:2) ⁱ	.48	HOAc	70	74	36	64	...	1.51
55	.024R(1:2.5) ⁱ	.56	HOAc	65	69	57	43	...	0.67

^a From valeryl peroxide. ^b Copper salt charged: E = cupric 2-ethyl hexanoate; A = cupric acetate; B = cuprous bromide; R = cupric-bipyridyl complex (Cu/bip). ^c All yields based on stoichiometry of 1 mole of product per mole of peroxide. ^d Valeric acid. ^e "Apparent rate" measured by rate of gas evolution only. ^f Maximum concentration, copper salt not all initially in solution. ^g After short induction period, reaction is exothermic. ^h Isopropyl alcohol. ⁱ Ratio cupric/bipyridyl.

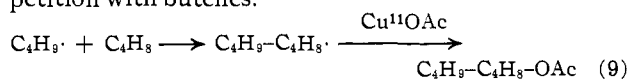


exception of small amounts of butyl bromide (formed by the reaction of butyl radicals with cupric bromide¹⁰) the products, stoichiometry and apparent rate are unchanged by the addition of the bromine inhibitor. Chlorine shows similar behavior, but reproducible results are more difficult to obtain because of its relatively high vapor pressure.

That cuprous salts are responsible for the destruction of the peroxide is further demonstrated by the rapid and exothermic decomposition of peroxides by cuprous salts in homogeneous solution. Since cuprous chloride or bromide (the reasonably stable and available simple cuprous salts) is not very soluble in the usual organic solvents, previous studies^{2,3,11} employing these salts showed very little apparent qualitative or quantitative difference from cupric salts. However, degassed solutions of acetonitrile form stable cuprous halide solutions and these are quite efficacious in destroying diacyl peroxides and peresters. With as little as 20 mole % cuprous salt the reaction is quite exothermic and approximately 60% of the peroxide is immediately destroyed accompanied by oxidation of colorless cuprous species to green cupric salts. The reaction is then completed at a rate similar to that obtained from reactions charged with equivalent amounts of cupric salt. The reactions initiated by cuprous salts show no induction period. At low cuprous concentrations (3 mole %) the reaction resembles (except for an immediate color change from colorless to green) the cupric-catalyzed reactions at equivalent concentrations, but the induction period is largely but not completely removed. These results indicate that cuprous species in homogeneous solution in acetonitrile are being partially consumed during the decomposition. The amount consumed is roughly related to the total copper concentration, the higher the cupric concentration the smaller the amount consumed. For example, the addition of small amounts of cuprous chloride to cupric acetate generates a catalytic system which rapidly decomposes

peroxide with no induction period. In these studies the yields of products were independent of the catalytic copper species charged.

The formation of butyl radicals from the decomposition of valeryl peroxide by copper salts is indicated by the competitive formation of butanes at low cupric concentrations, or in the presence of active hydrogen donor solvents as shown in Table I. Among the solvents we investigated, chloroform and to a lesser degree cumene were the only substrates that competed with cupric salts for the butyl radicals. As would be expected, these results are similar to those obtained by DeTar and Wells¹² from their study of the chain transfer activity of solvents toward the *n*-hexyl radical. The butyl radicals have also been trapped with conjugated olefins such as butadiene and styrene.¹³ With the former in acetic acid as solvent, octenyl acetates are formed in competition with butenes.



Oxidation of Alkyl Radicals by Cupric Salts.—Alkyl radicals were generated from several peroxide sources and the oxidation of each radical by cupric salts was found to proceed in the same manner regardless of its origin. The oxidation of the alkyl radicals by cupric salts was also found to be largely independent of the solvent which included benzene (11 *M*), heptane (6.8 *M*), isopropyl alcohol (13 *M*), acetonitrile (19 *M*) and acetic acid (17 *M*).

n-Butyl radicals were oxidized by cupric salts to butene-1. Within the limits of our analytical techniques (g.l.c.) we could not detect the presence of either *cis*- or *trans*-butene-2. However, small amounts (<0.3%) of methylcyclopropane¹⁴ often accompanied the butene-1, but it was also present in small amounts in the uncatalyzed thermolyses. The conversion of *n*-butyl radicals to methylcyclopropane¹⁵ appears to be independent of the presence of copper salts.

(12) D. F. DeTar and D. V. Wells, *J. Am. Chem. Soc.*, **82**, 5839 (1960).

(13) Unpublished observations, J. Kochi.

(14) The author is indebted to Dr. L. Friedman for this identification.

(15) Cf. P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962, 3963 (1962); **82**, 2971 (1960); M. S. Silver, *ibid.*, **82**, 2971 (1960); **83**, 3482 (1961).

(10) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); J. Kumamoto, H. E. DeLaMare and F. F. Rust, *ibid.*, **82**, 1935 (1960).

(11) S. Lawesson, *et al.*, *Arkiv. Kemi*, **17**, 465, 475 (1961), and earlier papers.

TABLE II
 OXIDATION OF ISOBUTYL RADICALS BY CUPRIC SALTS

Temp., °C.	Copper ^a salt, M	Peroxide, ^b M	Solvent	CO ₂ ^c yield, %	C ₄ -Hydro- carbon yield, ^e %	Composition of C ₄ -mixture		RCO ₂ H ^d yield, %	Rate, ^f ml./min.
						Isobutane	Isobutylene		
70	0	0.52V	C ₆ H ₆	165	78	92	8	14	1.1
70	0	.57V	HOAc	115	81	98.5	1.5	...	1.7
55	0	.53V	HOAc	124	76	100	0	...	0.24
60	0	.54V	CHCl ₃	100	0
65	0.087AA	.59V	C ₆ H ₆	95	97	0	100	100	4.4
55	.23E	.54V	C ₆ H ₆	92	95	0	100	101	0.57
65	.070AA	.60V	HOAc	90	87	0	100 ^f
55	.17A	.67V	HOAc	95	98	0	100	...	29
55	.021A	.64V	HOAc	94	96	5	95	...	8.9
55	.0052A	.61V	HOAc	89	92	19	81	...	3.4
60	.11P(1:1)	.50V	HOAc/cum.	91	89	5	95	...	8.9
55	.023R(1:1.8)	.57V	HOAc	89	87	27	73	...	2.2
55	.023R(1:2.6)	.57V	HOAc	92	83	95	5	...	0.50
50	.070AA	.62V	CHCl ₃	88	89	38	62	99	59
50	.090A ^g	.58V	CHCl ₃	83	85	60	30 ^h	94	...
						35	65 ⁱ		
121	0	.54P	HOAc/cum.	...	79	100	050
110	0.099A	.62P	HOAc/cum.	...	67	1	99	...	1.6
110	.076P(1:1)	.42P	HOAc/cum.	...	59	21	79	...	0.48
124	.080A	.42H	HOAc/cum.	...	61	2	98

^a Copper salt charged: AA = cupric acetylacetonate; E = cupric 2-ethylhexanoate; A = cupric acetate; P = cupric-1,10-phenanthroline complex (Cu/phen); R = cupric-bipyridyl complex (Cu/bip). ^b V = isovaleryl peroxide; P = *t*-butyl 2,3-dimethyl-2-pentyl peroxide; H = *t*-butyl 2,4-dimethyl-4-heptyl peroxide. ^c All yields based on stoichiometry of 1 mole of product per mole of peroxide. ^d Isovaleric acid. ^e Apparent rate as measured by rate of gas evolution at 30% decomposition. ^f After short induction period reaction is exothermic. ^g Maximum concentration, copper salt initially not all in solution, homogeneous at end. ^h Composition of first 10%. ⁱ Composition of last 10% gas evolved.

The formation of solvolysis products⁷ from the oxidation of butyl radicals was carefully examined. In acetic acid solvent the copper salt-catalyzed decomposition of either valeryl peroxide or *t*-butyl 2-methyl-2-hexyl peroxide yielded no butyl acetate. However, the much slower simple thermolysis of valeryl peroxide in acetic acid yields both *n*-butyl acetate (7–10%) and *sec*-butyl acetate (3–6%) in small amounts depending on the temperature of decomposition. These esters undoubtedly arise in the uncatalyzed reaction from valeryl peroxide by heterolytic reactions (*vide infra*). No butyl acetates are formed from the uncatalyzed decomposition of dialkyl peroxides. The formation of solvolytic products from the decomposition of valeryl peroxide in the presence of the complex cupric-bipyridyl complexes in acetic acid is related to the composition of the complex. A cupric-monobipyridyl complex yields *n*-butyl acetate in 9% yield; a 1:2.3 complex (mixture of bis and tris) yields *n*-butyl acetate in 30–36% yield and no (or very little) *sec*-butyl acetate is formed.

The yield of valeric acid obtained from the thermolysis of valeryl peroxide represents a small part (about 0.18 mole per mole of peroxide) of the reactant peroxide. However, in the copper salt-catalyzed reactions a mole of valeric acid is formed for each mole of peroxide decomposed.

Isobutyl radicals were generated from the decomposition of isovaleryl peroxide and *t*-butyl 2,4-dimethyl-2-pentyl peroxide. The yields of isobutylene in various solvents and copper salt concentrations are given in Table II. The results are similar to those obtained with *n*-butyl radicals. If one assumes that the reactivity of *n*-butyl and isobutyl radicals toward chain transfer are the same,¹⁶ then the relatively higher yields of isobutane compared to *n*-butane (formed from their respective peroxides at equivalent cupric salt concentrations, compare Tables I and II) indicates that *n*-butyl radicals are oxidized slightly faster than isobutyl radicals by cupric salts. This effect is magnified with cupric-bipyridyl as oxidant.

(16) Cf. A. F. Trotman-Dickenson, "Free Radicals," Methuen and Co., London, 1959, p. 61 ff.

The simple thermolysis of isovaleryl peroxide in acetic acid yields, besides isobutane, appreciable amounts of isobutyl (8–11%) and *sec*-butyl acetates (4–6%). None of these esters is formed in the presence of simple copper salts or catalysts. However small amounts are formed when cupric-bis-bipyridyl is employed (4–7% isobutyl and 1–2% *sec*-butyl acetates).

sec-Butyl radicals were produced from 2-methyl butyryl peroxide, *t*-butyl 2,3-dimethyl-2-pentyl peroxide, *t*-butyl 3,4-dimethyl-3-heptyl peroxide and *t*-butyl 3,4-dimethyl-3-hexyl peroxide. The thermal decomposition of 2-methylbutyryl peroxide is more facile than diacyl peroxides which yield primary alkyl radicals. In the presence of most solvents the easily disproportionated¹⁷ *sec*-butyl radicals yield a mixture of *n*-butane, butene-1 and *cis*- and *trans*-butene-2. Only in the presence of such good hydrogen donor solvents as chloroform and butyl mercaptan are the butenes minor products. In the presence of copper salts, *sec*-butyl radicals are effectively oxidized to butenes even in good donor solvents as shown in Table III.

In addition to the formation of 2-methylbutyric acid, CO₂ and the C₄-gases, the decomposition of 2-methylbutyryl peroxide leads to ester products much more readily than those peroxides with no α -branch. The yield of 2-methylbutyric acid from the thermal decomposition in benzene constitutes 11% and the butyl 2-methylbutyrate esters approximately 35% of the peroxide. In acetic acid, *sec*-butyl acetate (15%) and *sec*-butyl alcohol (35%) are formed. These products do not arise from the presence of adventitious water since neither the addition of water (10%) nor the use of scrupulously dry acetic acid¹⁸ significantly affects their yields. The yields of 2-methylbutyric acid from the copper-catalyzed decompositions are not quantitative (75–90%) due to the competitive formation of esters (4–10%) and *sec*-butyl alcohol (1–4%). Whereas butyl acetates are absent in catalyzed decompositions in

(17) A. F. Trotman-Dickenson, in "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, 1962, p. 107 ff.

(18) L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., Chicago, Ill., 1957, p. 281.

TABLE III
 OXIDATION OF *sec*-BUTYL RADICALS BY CUPRIC SALTS

Temp., °C.	Copper ^a salt	Peroxide ^b	Solvent ^c	CO ₂ ^d yield, %	C ₄ -Hydro- carbon yield, ^d %	Composition of C ₄ -mixture				RCO ₂ H ^e yield, %	Rate, ^f ml./min.
						<i>trans</i> - <i>n</i> -Butane	Butene-1	butene-2	<i>cis</i> - butene-2		
65	0	.68B	C ₆ H ₆	156	72	41	40	13	6	9	100
31	0	.59B	C ₆ H ₆	141	68	41	37	15	7	11	0.50
55	0	.55B	Cum.	129	58	56	31	9	4	14	16
31	0	.44B	Cum.	112	43	61	27	8	4	8	0.43
55	0	.60B	IPA	139	65	28	39	24	8	19	35
31	0	.44B	HOAc	94	37	21	42	29	8	..	0.68
55	0	.50B	Cum./BuSH	122	54	100
50	0	.57B	CHCl ₃	138	62	95	9	19
40	0	.55B	CHCl ₃	129	59	94	12	2.4
31	0	.44B	CHCl ₃	93	35	94	17	0.58
65	0.053A	.64B	C ₆ H ₆	92	88	4	52	22	22	90	.. ^g
31	.022A	.58B	C ₆ H ₆	87	85	5	51	22	22	78	3.8
55	.064A	.48B	IPA	81	83	0	55	28	17	85	80
40	.018S	.61B	CHCl ₃	79	67	20	45	20	15	73	40
31	.031S	.46B	CHCl ₃	85	75	16	46	21	18	75	8.4
31	.09N	.53B	CHCl ₃	85	76	6	56	21	17	79	8.0
31	.098AA	.53B	CHCl ₃	87	78	6	53	23	18	82	7.7
31	.097AA	.54B	CHCl ₃ /HOAc	79	70	5	54	23	18	..	8.9
31	.028S	.66B	CHCl ₃ /cum.	88	84	13	53	18	16	79	7.9
31	.11S	.64B	CHCl ₃ /cum.	90	86	4	55	21	20	82	36
31	.021E	.53B	HOAc	83	77	3	46	27	24	..	14
31	.14E	.55B	HOAc	87	83	2	49	26	23	..	32
31	.090(1:1)	.49B	CHCl ₃ /HOAc	78	69	12	50	17	21	..	2.8
31	.023P(1:1)	.59B	HOAc	79	69	2	50	24	24	..	9.7
31	.023R(1:1)	.54B	HOAc	81	69	2	50	24	24	..	14
31	.024P(1:2)	.53B	HOAc	70	74	8	50	27	15	..	3.9
31	.089P(1:2)	.55B	CHCl ₃ /HOAc	64	69	55	26	13	6	..	1.6
31	.023R(1:2.5)	.62B	HOAc	68	64	14	46	27	13	..	2.6
31	.023B(1:2.5)	.58B	HOAc	63	62	14	46	27	13	..	1.9
31	.12B(1:2.5)	.57B	HOAc	66	64	10	46	30	14	..	3.9
31	.088P(1:3)	.54B	CHCl ₃ /HOAc	60	59	58	23	15	4	..	0.73
129	0	.34S	BuPh	85	7.2	5.3	2.5
127	0.076B	.73S	BuPh	46	27	27
127	.060B	.60T ^h	BuPh	45	27	28
120	.080A	.46S	HOAc	47	28	25
120	.080A	.33S	PhCN	45	28	27
126	.080A	.29S	DMSO	50	27	23
126	.061B	.52S	ROH	49	28	23

^a A = cupric acetate; S = cupric stearate; N = cupric naphthanate; AA = cupric acetylacetonate; E = cupric 2-ethylhexanoate; B = cuprous bromide; P = cupric-1,10-phenanthroline (Cu/phen); R = cupric-bipyridyl (Cu/bip). ^b B = bis-2-methylbutyryl peroxide; S = *t*-butyl 3,4-dimethyl-3-hexyl peroxide; T = *t*-butyl 4,5-dimethyl-4-heptyl peroxide. ^c Cum. = cumene; IPA = isopropyl alcohol; CHCl₃/HOAc is 80% v. CHCl₃; CHCl₃/cum. is 50% v.; BuPh = *t*-butylbenzene; ROH = cyclohexanol. ^d All yields based on stoichiometry of 1 mole of product per mole of peroxide. ^e 2-Methylbutyric acid. ^f Apparent rate. ^g Reaction is exothermic after short induction period, too fast to measure. ^h In addition to pentene mixture; composition: pentene-1 (45%), *trans*-pentene-4 (36%) and *cis*-pentene-2 (20%).

acetic acid from valeryl or isovaleryl peroxides, they are formed in significant, albeit low yields (4–6%) from the 2-methyl butyryl peroxide. The fact that these esters do not arise from the oxidation of *sec*-butyl radicals by copper salt is indicated by their absence when these radicals are generated from *t*-butyl *t*-alkyl peroxides mentioned earlier. The effects of complex cupric-bis-bipyridyl salts on 2-methylbutyryl peroxide in acetic acid are similar to those with valeryl and isovaleryl peroxides. The relatively large amounts of *sec*-butyl acetate (12–17%) and *sec*-butyl alcohol (25–32%) are due to the incursion of the ionic reactions in the presence of the slow catalytic reaction.

Neopentyl radicals were produced from bis-*t*-butyl-acetyl peroxide. The thermolysis of this peroxide in benzene or acetic acid yielded neopentane and carbon dioxide as gaseous products together with neopentyl *t*-butylacetate and *t*-butylacetic acid. In addition, small amounts of neopentyl acetate (8%) and *t*-amyl acetate (6%) were formed in acetic acid. *t*-Amyl acetate, together with the rearranged elimination

products 2-methylbutene-1 and 2-methylbutene-2, is formed in larger yields in the presence of copper catalysts as indicated in Table IV. The formation of neopentane could not be completely eliminated even at relatively high copper concentrations (under conditions where all the isomeric butyl radicals are oxidized completely to butenes). Furthermore, in benzene or acetonitrile solutions only trace amounts of methyl butenes and large amounts of neopentane are formed. These results contrast strongly with those obtained from the butyl systems.¹⁹

2-Methyl-2-hexyloxy radicals were generated from three peroxidic sources: 2-methyl-2-hexyl hydroperoxide, 2-methyl-2-hexyl *t*-butyl peroxide and 2-methyl-2-hexyl peracetate. This radical undergoes two competitive reactions: cleavage to acetone and *n*-butyl radical⁵ and intramolecular 1,5-hydrogen abstraction to




(19) The possibility of the *t*-amyl acetate being formed in acetic acid by an ionic rearrangement of the peroxide cannot at present be rigorously eliminated. On the basis of aforementioned results it appears unlikely, but see J. Smid, A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3315 (1956).

TABLE IV
 OXIDATION OF NEOPENTYL RADICALS BY CUPRIC SALTS

Temp., °C.	Copper ^a salt, M	Peroxide, ^b M	Solvent	CO ₂ ^c yield, %	2-Methyl- butene-1, %	2-Methyl butene-2, %	Neo- pentane, %	<i>t</i> -Amyl acetate, %	Neopentyl acetate, %	<i>t</i> -Butyl- acetic acid, %
78	0	0.41	HOAc	122	0	0	81	5	6	..
80	0	.46	HOAc	116	0	0	87	5	7	..
65	0.034E	.30	HOAc	81	5	7	31	38	8	..
68	.096E	.36	HOAc	70	7	8	16	36	7	..
65	.12E	.46	HOAc	78	6	7	13	39	8	..
65	.21E	.29	HOAc	75	7	8	14	41	8	..
65	.28E	.30	HOAc	72	6	7	14	47	8	..
65	.024E	.52	C ₆ H ₆	94	1	0.5	56	56
65	.10E	.35	C ₆ H ₆	96	0.5	.5	45	98
65	.037R(1:2.3)	.50	CH ₃ CN	97	.5	.2	78	61
65	.075A	.35	CH ₃ CN	98	.4	.2	87	93

^a E = cupric 2-ethylhexanoate; R = cupric-bipyridyl (Cu/bip); A = cupric acetate. ^b Bis-*t*-butylacetyl peroxide. ^c All yields based on stoichiometry of 1 mole of product per mole of reactant.

 TABLE V
 FORMATION AND PRODUCTS OF 2-METHYL-2-HEXYLOXY RADICALS FROM SEVERAL PEROXIDE SOURCES AND COPPER SALTS

Temp., °C.	Copper ^a salt, M	Peroxide, ^b M	Solvent	C ₄ -Hydro- carbon yield, ^c %	Composition of C ₄ -mixture		<i>n</i> -Butyl acetate	 + OH	 + OH	 + OH
					<i>n</i> -Butane	Butene-1				
122	0	0.59A	HOAc	85	100	0	0.7	12	0	0
122	0	.45A	HOAc	89	100	0	.5	7	0	0
121	0.022E	.76A	HOAc	61	1	99	.4	16	1.6	8.5
121	.023E	.78A	HOAc	64	3	97	0	22	1.3	8.9
121	.023R(1:2.7)	.60A	HOAc	67	50	50	7.8	16	2.0	4.8
121	.025R(1:2.5)	.60A	HOAc	60	51	49	5.6	13	2.1	4.0
95	0	.61P	HOAc	44	100	0	48.5	7.0	0	0
86	0	.59P	C ₆ H ₆	57	62	38
86	0.023E	.61P	HOAc	69	2	98	4.9	1.3	3.5	18.5
86	.026A	.60P	CH ₃ CN ^d	53	0	100	..	2.7	4.7	21.8
86	.023E	.61P	C ₆ H ₆ ^e	59	0	100	..	.8	5.2	17.4
115	0	.76H	HOAc	53	95	5	37	9.7	0	0
115	0.024E	.81H	HOAc	68	7	93	2.4	8.6	3.5	14.8
115	0.024E	.79H	Cum.	63	10	90	..	9.6	4.1	15.5

^a See Table I for abbreviations. ^b A = *t*-butyl 2-methyl-2-hexyl peroxide; P = 2-methyl-2-hexyl peracetate; H = 2-methyl-2-hexyl hydroperoxide; cum. = cumene. ^c Yields based on stoichiometry of 1 mole of product per mole of peroxide. ^d 102% acetic acid formed. ^e 99% acetic acid formed.

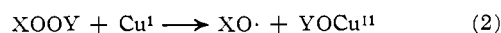
yield 5-hydroxy-5-methyl-2-hexyl radical²⁰ (CH₃CH-CH₂CH₂C(CH₃)₂OH). In the presence of copper salts the oxy radical itself is unaffected, but each carbon radical derived therefrom is oxidized to the olefin: butene-1 from *n*-butyl radical and a mixture of 2-methyl-5-hexenol-2 and 2-methyl-4-hexenol-2 from 5-hydroxy-5-methyl-2-hexyl radical. These products from the catalyzed decomposition of the three peroxides are given in Table V.

Discussion

The study of the decomposition of peroxides by copper salts involves at least two main considerations: (1) the nature of the initial decomposition of the peroxide by the metal salt and (2) the oxidation of the carbon radicals which result from the oxy radical intermediates. These two points are, of course, intimately related since they must function together in order that the metal salts act as catalysts. However, for purposes of discussion it is convenient to discuss separately these two aspects of the catalyzed decomposition of peroxides by metal salts.

Decomposition of Peroxides.—In homogeneous solutions our experiments have demonstrated that the peroxide is destroyed by a reducing agent, *viz.*, a cuprous species.^{21a} The rapid exothermic reaction

by cuprous salts in homogeneous solution, the induction period and the autocatalytic nature of the decomposition in the presence of cupric species,^{21b} and the inhibition of the decomposition by reagents which effectively oxidize cuprous salts all point to *cuprous species as responsible for the initial decomposition of the peroxide*. The formation of an equivalent amount of free acid²² and the production of products corresponding to oxy radical intermediates (*vide infra*) indicate that the stoichiometry of the reduction by cuprous salts is eq. 2 (X, Y = H, alkyl, acyl).



With diacyl peroxides (X, Y = acyl) the reduction leads to carboxylate ion and acyloxy radicals. The fate of the latter, depending on its structure, is either chain transfer with a hydrogen donor, addition to an unsaturated compound or fragmentation. The relatively long-lived²³ benzoyloxy radicals from benzoyl peroxide have been shown to react mainly by the first two modes in suitable media.²⁴ The aliphatic

charged with cupric species is due to the build-up of cuprous species from reaction with carbon radicals formed from the thermal decomposition^{2b} (*e.g.*, reactions 3, 4, 6 and 7). Thus, the rate of decomposition during the inhibition period (see base line, Fig. 2) corresponds to the rate of the thermal decomposition of the peroxide.

(2) *Cf.* ref. 8.

(23) C. G. Swain, L. J. Schaad and A. J. Kresge, *J. Am. Chem. Soc.*, **80**, 5313 (1958).

(24) J. K. Kochi, *ibid.*, **84**, 1572 (1962).

(20) F. D. Greene, *et al.*, *J. Am. Chem. Soc.*, **83**, 2196 (1961); C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961); M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961); P. Kabasakalian, *et al.*, *ibid.*, **84**, 2711, 2718 (1962).

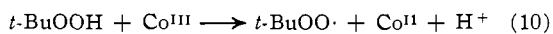
(21) (a) The reduction of peroxides by metal salts has been described previously.² (b) The induction period when the solutions of peroxides are

analogs, however, generally fragment too rapidly^{9b,c,25} to trap as carboxylate moieties and the resultant reactions observed are those of the products of fragmentation, carbon dioxide and alkyl free radicals. For this reason the stoichiometry given in eq. 8 is generally observed⁸ with aliphatic diacyl peroxides.

Peresters (X = alkyl, Y = acyl) present two possible modes of reduction by cuprous salt. It has been shown^{3,26} that *t*-butyl peracetate and perbenzoate are specifically reduced by cuprous salts to generate alkoxy radicals (X = *t*-butyl) and carboxylate anion (Y = acetyl, benzoyl). Studies here with *t*-heptyl peracetate also obey this scheme.²⁷

The decomposition of **dialkyl peroxides**, especially di-*t*-butyl peroxide under various conditions, is perhaps one of the most extensively studied free radical phenomena. Di-*t*-butyl peroxide with copper salts yields in addition to the *t*-butylate ion, the relatively stable *t*-butoxy radical which reacts readily by hydrogen abstraction³ or addition²⁶ in suitable media. It is less prone to fragment to acetone and methyl radical than the homologous *t*-amyl radical which easily yields acetone and ethyl radical.⁵ Unsymmetrical di-*t*-alkyl peroxides²⁸ again present two paths of reduction by cuprous salts. Our studies with *t*-butyl *t*-hexyl peroxides and related homologs indicate that cleavage to form *t*-heptyloxy (or highly substituted *t*-alkoxy) radicals (X = *t*-heptyloxy) is slightly preferred to that forming *t*-butoxy radical.²⁹

Alkyl hydroperoxides decompose thermally by a complex process involving paths of varying kinetic order.³¹ The decomposition of *t*-butyl hydroperoxide by several metal salts (cobalt,³² copper-phenanthroline³³) has been reported to yield mainly oxygen and *t*-butyl alcohol. The formation of these products has been postulated to arise *via* *t*-butylperoxy intermediates formed from the *oxidation* of *t*-butyl hydroperoxide by metal species. The disproportionation of *t*-butylperoxy



radicals yields oxygen and *t*-butoxy radicals (or di-*t*-butyl peroxide).

On the other hand, our studies show that in the presence of copper salts, 2-methyl-2-hexyl hydroperoxide behaves in the same manner as other classes of peroxides previously mentioned, in that *reduction* of the hydroperoxide by cuprous species is the primary step. We scrutinized the gases for the presence of oxygen and could find less than 1%. The sole gases were butene-1 (94%) and *n*-butane (6%) with traces of CO₂ and ethylene. The normal expected catalytic behavior in the presence of copper salts, the low yields of 2-methyl-2-hexanol together with the absence of oxygen,³⁴ leads us

(25) H. J. Shine, J. A. Waters, and D. M. Hoffman, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, Abstracts p. 67Q.

(26) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2785 (1962).

(27) Studies are in progress to determine structural features that are necessary for the alternative cleavage to be obtained (X = acyl, Y = alkyl).

(28) Secondary and primary dialkyl peroxides are decomposed by copper salts mainly to ketones or aldehydes and alcohols.

(29) (a) This statement is based on yields of *t*-heptyl alcohol obtained from the catalyzed decomposition. Unfortunately we were unable to obtain complete material balance with the *t*-butyl moiety. (b) Multibond cleavage²⁹ may be responsible for the preference for *t*-heptyloxy cleavage.

(30) 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); P. D. Bartlett, in "Peroxide Reaction Mechanisms," J. Edwards, Editor, Interscience Publishers, Inc., New York, N. Y., 1962, p. 1 ff.

(31) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

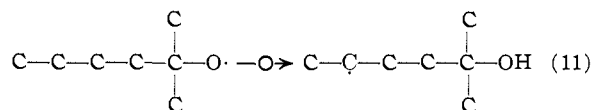
(32) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958).

(33) H. Berger and A. F. Bickel, *ibid.*, **57**, 1325 (1961).

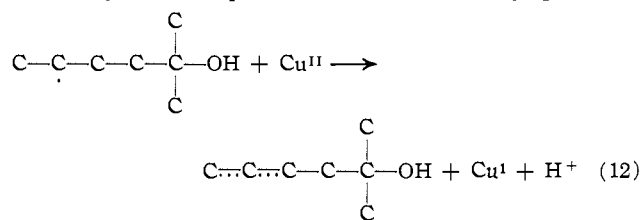
(34) The absence of oxygen among the products is not unequivocal since it is possible that the oxygen formed reacts with the butyl radicals coincidentally present. Since alkoxy radicals do not react with oxygen and *t*-butoxy radical cleaves more slowly than its higher homologs, the formation

to postulate that the important peroxide-destroying reaction is eq. 2 (X = alkyl, Y = H). The postulation of other reactions such as eq. 2 (X = H, Y = alkyl) or the oxidation of the hydroperoxide by cupric salts to form an alkylperoxy radical intermediate appears to be unnecessary; but they, particularly the latter, cannot be dismissed entirely on the basis of evidence presently at hand.³⁵

Alkoxy radicals formed from the catalyzed decomposition of dialkyl peroxides, alkyl peresters and alkyl hydroperoxides all behave in the same manner. For example, the 2-methyl-2-hexyloxy radical produced from these three sources undergoes at least four reactions: chain transfer by hydrogen abstraction or reduction by cuprous species^{6,24} to form 2-methyl-2-hexanol, cleavage to acetone and *n*-butyl radicals and intramolecular chain transfer²⁰ to form 5-methyl-5-hydroxy-2-hexyl radical. Evidence for the latter in our system is obtained by isolation of products of oxidation by



cupric species, 2-methylhexen-5-ol-2 and 2-methylhexen-4-ol-2. That these heptenols are still formed at relatively high temperatures (120° for dialkyl peroxides



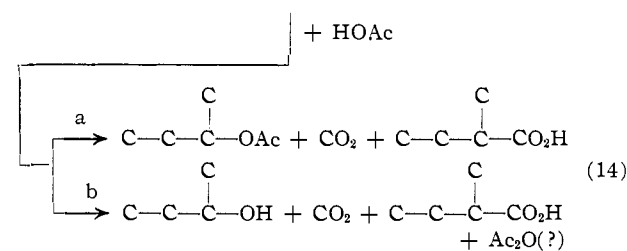
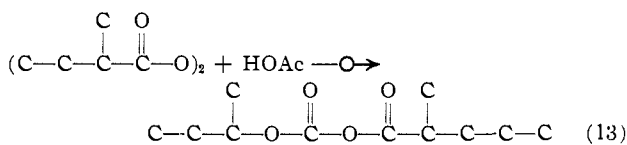
and 115° for alkyl hydroperoxides) indicates that the activation energy for the intramolecular hydrogen transfer reaction is not widely different from the fragmentation reaction.

Thus, the decompositions of various types of peroxides by cuprous salts can be uniformly considered in the same light to produce an oxy radical (acyloxy, alkoxy, etc.) and a cupric oxy salt (carboxylate, alkoxide, hydroxide, etc.) by the reduction reaction 2. In addition to the classical homolytic thermal reactions and the copper-catalyzed decomposition described here, peroxides are known to decompose by ionic routes.³⁶ In general, the ionic decompositions are catalyzed by acids and we have found that they compete with the thermal and the copper-catalyzed reactions under suitable conditions. The degree of competition is highly dependent on the structure of the peroxide and the solvent. For example, valeryl and isovaleryl peroxides in acetic acid undergo less than 10% ionic decomposition. The isomer 2-methylbutyryl peroxide, on the other hand, leads to greater than 50% ionic decomposition (yielding *sec*-butyl acetate and alcohol).³⁷ However, the ionic of oxygen from *t*-butyl hydroperoxide² and its absence in the higher homologs are not necessarily inconsistent.

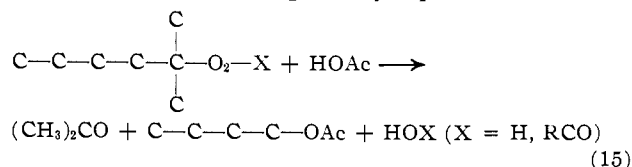
(35) If reactions such as these played an important role, in addition to the formation of oxygen, it should be possible to trap such an alkylperoxy intermediate. In one case such was not possible.²⁶ However, since such a reaction is *cuprous-producing*, a significant part of the reaction proceeding in this manner would result in the consumption of cupric species and relatively high steady state concentrations of cuprous species and alkoxy free radicals (by reaction 2). That such may be the case is indicated by the slightly higher yields of butanes (7%) formed from hydroperoxide than from either dialkyl peroxide (1-2%) or perester (2%) under the same gross copper concentrations (see Table V).

(36) (a) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p. 143 ff. (b) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950); (c) J. E. Leffler, *ibid.*, **72**, 67 (1950); (d) D. B. Denney, *et al.*, *ibid.*, **84**, 2455 (1962); **79**, 4806 (1957); **78**, 590 (1956); (e) G. A. Razuvaev, *et al.*, *Tetrahedron Letters*, **No. 15**, 527 (1961); (f) H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

decomposition in most cases is slow compared to the copper-catalyzed reaction even at low catalyst concentrations in acetic acid and does not in practice interfere with the latter. Each of these peroxides in non-acidic solvents such as benzene, heptane and acetonitrile decompose thermally by the usual homolytic process. The ionic decomposition presumably occurs by the carboxyl inversion reaction described by Leffler^{36b} with diaroyl peroxides, and is only important with aliphatic diacyl peroxides with branching at the α -carbon (reactions 13 and 14).



Di-*t*-alkyl peroxides are unaffected by moderately strong acids, and there is no evidence that they undergo acid-catalyzed decomposition, probably due to the sterically hindered nature of the peroxidic site. However, tertiary alkyl peresters and hydroperoxides are more susceptible to ionic decomposition³⁸ than di-*t*-alkyl peroxides. For example, during the decomposition in acetic acid in the absence of metal salts, *t*-butyl 2-methyl-2-hexyl peroxide gives a maximum of 5% ionic decomposition at 120°, whereas 2-methyl-2-hexyl peracetate yields approximately 55% at 95° and 2-methyl-2-hexyl hydroperoxide about 45% at 115° ionic decomposition. In each case these ionic decompositions proceed at significantly slower rates than the reactions catalyzed by copper salts. The acid-catalyzed decompositions of these peroxides derived from the 2-methyl-2-hexyl moiety are similar to that described for diacyl peroxides. A 1,2-migration of a butyl group to oxygen from the oxonium intermediate, followed by reaction with acetate, would yield butyl acetate. The stoichiometry of the reaction is given by eq. 15. In such non-



polar and non-acidic solvents as benzene, heptane, chloroform and acetonitrile, however, the simple peroxidic homolysis constitutes the main course of the reaction.

We postulate that the butyl acetates formed from the decomposition of these peroxides in acetic acid arise from competitive ionic reactions which are acid catalyzed. In the presence of simple copper salts, both the homolytic thermal and ionic acid-catalyzed reactions

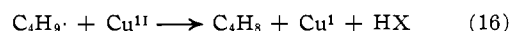
(37) In addition to the formation of *sec*-butyl acetate and *sec*-butyl alcohol by an ionic route in acetic acid, some of the butenes may also arise by an intramolecular elimination of the type discussed by J. Smid, A. Reinbaum and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3315 (1956). (See, however, D. Lefort, D. Tempier and J. Sorba, *Bull. soc. chim. France*, 442 (1960).)

(38) In these systems the criterion for the amount of ionic decomposition is the formation of butyl acetates. The possibility of all the butyl acetate being formed from the peracetate in such sizable yields by a cage recombination of *n*-butyl and acetoxy radicals produced from the homolysis is considered unlikely.

are relatively slow and unimportant except in those cases, like α -methyl-butyl peroxide, which are labile to acid-catalyzed rearrangements.

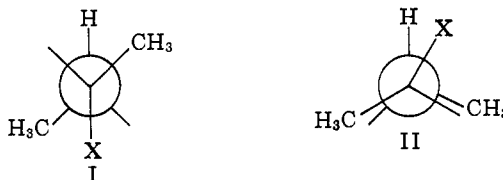
Oxidation of Alkyl Radicals by Cupric Salts.—The evidence for the formation of alkyl radicals during the decomposition of peroxides catalyzed by copper salts is based on several lines of evidence: (a) trapping them with butadiene; (b) competitive formation of butanes in effective hydrogen donor solvents as chloroform and to a lesser degree cumene; (c) comparison of their behavior with the 5-methyl-5-hydroxy-2-hexyl radical formed from the intramolecular hydrogen abstraction of 2-methyl-2-hexyloxy radical; (d) the formation of *t*-alkoxy radicals from copper salts and dialkyl peroxides,^{3b} perester^{3a} and hydroperoxides,²⁶ and the known fragmentation patterns of *t*-alkoxy radicals to ketones and alkyl radicals.⁵

The formation of butenes from butyl radicals by oxidation with cupric salts according to eq. 16 follows from our earlier studies⁷ in aqueous solution. It is striking



that oxidation of butyl radicals by cupric salts competes favorably with such facile reactions as hydrogen transfer from chloroform¹² as solvent. The oxidation is further unique in that it leads cleanly to β -elimination of a hydrogen atom with no rearrangement of the carbon skeleton, in solvents which vary as widely in polarity, dielectric constant, and ability to form hydrogen bonds as water and alcohols on one hand and heptane, chloroform and benzene on the other.

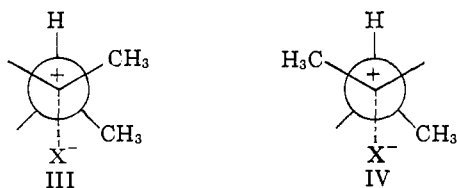
The study of the oxidation of *sec*-butyl radicals by copper salts is particularly illuminating since it is possible to obtain some information about the molecular requirements of the transition state. Elimination reactions from the *sec*-butyl systems have been extensively studied for the distribution of the three isomeric butenes formed therefrom.³⁹ The ratio of isomers is taken as a measure of the relative rates of elimination. The relative rates in turn are related to the population of the various conformations available in the transition states by considering non-bonded interactions^{39a} and the geometrical requirements of the elimination process. In systems involving concerted elimination the ratio of *trans*-butene-2 to *cis*-butene-2 varies from 1.9 (acetate pyrolysis),^{39d} 1.8 (amine oxide),^{39e} 2.2 (xanthate),^{39f} 2.0 (photolysis of esters),^{39g} 2.8 (base-catalyzed E₂),^{39c} 2.5 (nitrosoacetanilide)^{39h} to 3.0 (deamination).^{39a,b} The predominance of *trans*-butene-2 has been attributed to the higher population of more stable conformer I in *transoid* elimination^{39a} and conformer II in *cisoid* elimination^{39d,f} in which the methyl groups are maximally separated.



Reactions in which elimination is not concerted (or which involve a high degree of C-X bond breaking) yield about equal amounts of *cis*- and *trans*-butene-2.

(39) (a) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (b) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); (c) W. B. Smith and W. H. Watson, *ibid.*, **84**, 3174 (1962); (d) C. H. DePuy, *et al.*, *ibid.*, **83**, 2152 (1961); **81**, 643 (1959); (e) A. C. Cope, N. A. LeBel, N. H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957); (f) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 433 (1960); (g) R. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1053 (1961); (h) E. H. White, *ibid.*, **77**, 6014 (1955); (j) C. H. DePuy, R. W. King and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959).

The solvolysis of *sec*-butyl tosylate⁴⁰ (*trans/cis* = 1.1) and the elimination of *sec*-butyl halides by silver salt^{39c} (*trans/cis* = 1.2–1.3) are such examples. It has been argued that in these cases the transition states III and IV leading to *cis*- or *trans*-butene-2 are of approximately equal energy, and therefore equally populated, due to the trigonal character of the incipient carbonium ion.



Information regarding the disproportionation of *sec*-butyl radicals is meager. Calvert and Kraus⁴¹ indicate the *trans/cis*-butene-2 ratio to average around 2.5 in the vapor phase at 100° from photolysis studies of 3,5-dimethylheptanone-4 and 2-methylbutanone-1. From the decomposition of peroxides in solution we obtain a *trans/cis* of 2.1 at 120° and 2.3–3.0 at 55°. The transition state for the disproportionation of free alkyl radicals is in all probability a reasonably ordered one.^{17,42}

Just as the ratio of *trans*- to *cis*-butene-2 is indicative of the approach to a trigonal carbon center in the transition state, the ratio of butene-1 to butene-2 can be employed as a measure of the driving force for the reaction (the degree of breaking the β -hydrogen-carbon bond). In pyrolytic eliminations the ratio approaches the statistical value of 1.5 based on the number of available β -hydrogens. For example, the butene-1/butene-2 ratio is 1.3 (acetate pyrolysis at 450°),^{39d} but 0.20 at 200°,^{39g} 0.70 (xanthate at 350°),^{39f} 2.0 (amine oxide at 150°)^{39e} and 1.1 (nitrosoacetanilide at 25°).^{39h} The solvolytic processes lead to relatively low yields of the thermodynamically least stable butene-1; the butene-1/butene-2 ratio is 0.11 (tosylate solvolysis),⁴⁰ 0.33 (deamination)^{39a} and 0.25 (base-catalyzed E₂).^{39c}

Stated in terms of Hammond's postulate⁴³ for *sec*-butyl derivatives, *sec*-BuX, the approach to an equimolar yield of *cis*- and *trans*-butene-2 is indicative of a high degree of carbon-X bond-breaking in the transition state. In a similar manner a high yield of butene-1 relative to butene-2 can be used as a measure of a relatively low degree of stretching in the β -carbon-hydrogen bond.

Such a rationalization would lead to the prediction^{39a,c} that a simple *sec*-butyl carbonium ion would eliminate a β -proton to yield butene-1 and *cis*- and *trans*-butene-2 in random fashion; that is, in yields of 60%, 20% and 20%, respectively. To our knowledge no such statistical elimination has been observed from any *sec*-butyl system. These ratios differ significantly from those based on the thermodynamic stabilities of the butenes at 30°: butene-1 (2%), *cis*-butene-2 (23%) and *trans*-butene-2 (75%). The elimination from the *sec*-butyl radical by cupric salt oxidation closely approximates a statistical distribution of butene isomers; the ratio is butene-1, *trans*-butene-2 and *cis*-butene-2: 46–50%, 27–28% and 23–28% at 120° and 53–55%, 22–27% and 18–24% at 30–40°. Moreover, the distribution of products is largely independent of the milieu.

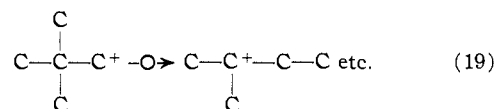
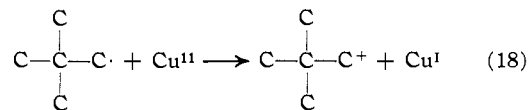
At this juncture it is tempting to postulate the oxidation of alkyl radicals by cupric salts as proceeding *via* an

electron transfer reaction^{3,7,44} to form an alkyl carbonium ion as an intermediate. That such is an over-



simplification is indicated by the relatively slow rate of oxidation of neopentyl radicals. Under conditions of cupric salt concentration where *n*-butyl, isobutyl and *sec*-butyl radicals (all possessing β -hydrogens) are efficiently oxidized to butenes, neopentyl radical is largely unaffected (*cf.* Tables I, II, III and IV). If an electron transfer mechanism, as in eq. 17, were operative, it is expected that neopentyl radicals would be as easily oxidized as either *n*-butyl or isobutyl radicals, since the ionization potentials⁴⁵ of all three radicals are very nearly the same.⁴⁶

However, in acetic acid the neopentyl moiety is converted¹⁹ to 2-methylbutene-1 and 2-methylbutene-2 and *t*-amyl acetate. If the properties of *t*-butyl acetyl peroxide are analogous to either valeryl or isovaleryl peroxide (which it resembles in thermal stability) then it is extremely unlikely that these rearrangement products arise *via* an ionic route, especially in such high yields. More reasonably these arise by the oxidation of neopentyl radicals⁴⁷ by cupric salts albeit relatively inefficiently (compared to radicals with β -hydrogens) to a neopentyl carbonium ion which undergoes the well known Wagner-Meerwein rearrangement.⁴⁸ The relatively higher yields of solvolytic products (*t*-amyl ace-



tate) from the tertiary carbonium ion relative to elimination products (*t*-amylenes) is consistent with our earlier observations in aqueous solutions. The approximately equal yield of 2-methylbutene-1 and 2-methylbutene-2 contrasts with the preponderant formation of the more stable 2-methylbutene-2 from the solvolysis of *t*-amyl systems.⁴⁹ This is analogous to the random

(44) J. K. Kochi, *ibid.*, **84**, 3271 (1962).

(45) R. Taubert and F. P. Lossing, *ibid.*, **84**, 1523 (1962); J. B. deSousa and F. P. Lossing, *ibid.*, **81**, 281 (1959).

(46) This refers to gas phase values. In solvents such as benzene, solvation of cations, differing as little in structure as do these moieties, would not be considered to vary significantly. Solvation in the transition state of an incipient neopentyl carbonium ion, however, may be significantly different from that of a relatively unhindered butyl carbonium ion.

(47) We are unable to state at present the explicit reason neopentyl radicals are apparently oxidized in acetic acid and little affected in benzene or acetonitrile. Part of this is due to the formation of neopentylbenzene in the former solvent. Since the butyl radicals show little difference in behavior in acetic acid compared to benzene, it is unlikely that this difference can be attributed to the different copper species extant in these solvents. The importance of solvation⁴⁵ as a factor for this difference is being examined.

At this stage we cannot be too dogmatic concerning the origins of the *t*-amylenes and *t*-amyl acetate in acetic acid. For example, Szwarc, *et al.*,¹⁹ have indicated that propionyl peroxide undergoes some ionic (intramolecular) decomposition to form ethylene, carbon dioxide and propionic acid, especially in polar solvents such as acetic acid. An analogous route is not available to *t*-butyl acetyl peroxide. However, an ionic transition state (perhaps of the conjugate acid of the peroxide) can be formulated which leads to "neopentyl carbonium ion character" similar to those discussed by Lefler.^{36b} There is no apparent driving force for such a rearrangement with *t*-butyl acetyl peroxide beyond either valeryl or isovaleryl peroxide.

(48) There is no good evidence that neopentyl-type free radicals rearrange; R. Freidlina, V. Kost, M. Khorlina, *Russian Chem. Rev.*, **32**, 1 (1962) (English trans.).

(49) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **77**, 3623 (1955); E. D. Hughes, *J. Chem. Soc.*, 2065 (1948). For example, the solvolysis of dimethyl *t*-amylsulfonium salts in 95% ethanol yields 85% 2-methylbutene-2 isomer; *t*-amyl bromide yields 80% 2-methylbutene-2 isomer in 80% ethanol.

(40) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3614 (1955); S. Winstein, *et al.*, *ibid.*, **74**, 1113 (1952).

(41) J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

(42) J. R. McNesby, C. M. Drew and A. S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955); M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951); J. N. Bradley, *J. Chem. Phys.*, **34**, 749 (1961).

(43) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

distribution of butene isomers from the cupric oxidation of *sec*-butyl radical (*vide supra*).

Complex copper salts with 1,10-phenanthroline or α, α' -bipyridyl as ligands show variable behavior as catalysts. The monobipyridyl and monophenanthroline copper complexes are approximately as effective as the uncomplexed copper species as measured by the rate of peroxide decomposition and by the oxidation of butyl radicals to butenes. However, the rate of peroxide decomposition in the presence of the bis-phenanthroline or bis-bipyridyl copper complex is not as rapid as with the uncomplexed catalyst, and the butyl radicals are not as efficiently oxidized to butenes. This contrasts with the comparable effectiveness of bis-bipyridyl copper complex and the simple copper salts in the reactions of *t*-butyl peresters with butenes.^{3,44} Although the composition of the ester products differed with the catalytic copper species, the *over-all yields* of butenyl esters were largely unaffected.⁴⁴ Since the step involving the reduction of peroxides by cuprous salt is similar in both types of reactions, the difference in efficiency of the catalytic copper species must be attributed to the step involving the oxidation of the carbon radicals (alkyl or allylic). It would be expected that allylic radicals are more easily oxidized than primary or secondary alkyl radicals,⁵⁰ and the difference in catalytic efficiency of bis-phenanthroline or bipyridyl copper complexes⁵¹ is probably due to the less facile oxidation of alkyl radicals by the more heavily coordinated cupric species; with the more easily oxidized allylic radicals, complexed as well as simple species are effective oxidants.⁵³

The ease of oxidation of carbon radicals by cupric salts thus shows subtle behavior with structure of the radical and the nature of the copper complex. On one hand, neopentyl radicals, which possess no β -hydrogens, are only slowly oxidized by simple cupric salts, but in the oxidation of allylic radicals which do not involve β -hydrogens, complex cupric species are as efficacious as simple salts. Butyl radicals which are oxidized by loss of a β -hydrogen show discrimination between simple and complex cupric ion oxidants.

The presence of solvolytic products (butyl acetates) from the oxidation of butyl radicals by cupric salts in acetic acid was examined. No butyl acetates were found as products from the oxidation of *n*-butyl or isobutyl radicals with cupric acetate. Small amounts (2–6% *sec*-butyl acetate and 5–8% *sec*-butyl alcohol) were found from the oxidation of *sec*-butyl radicals from 2-methylbutyryl peroxide. The ester and alcohol arise predominantly from the ionic decomposition of the diacyl peroxide since *t*-butyl 3,4-dimethyl-3-hexyl peroxide yielded *sec*-butyl acetate in low yields (1–2%). The slower decomposition of valeryl and isovaleryl peroxides in the presence of bis-bipyridyl copper complex yields significant amounts of butyl acetates in addition to a mixture of butenes and butanes (Tables I and II). Although some of the butyl acetates in acetic

(50) *E.g.*, compare ionization potentials, F. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

(51) From the standpoint of oxidation–reduction potentials alone, the bis-bipyridyl cupric complex should be at least as effective as either the monobipyridyl or simple copper salt. The difference may be due to the necessity of simultaneously removing a β -proton (or hydrogen atom) from an alkyl radical (*vide infra*) during the oxidation process. Since allylic radicals suffer oxidation by *substitution* only the problem of removing the β -hydrogen is non-existent. The formation of hydrogen–copper bonds has been discussed by Halpern,⁵² and would be expected to be least likely with multi-coordinated copper species.

(52) J. Halpern, *Advances in Catalysis*, **9**, 302 (1957).

(53) However the tris-bipyridyl or phenanthroline copper complexes are not as effective as the bis-complex, although it does yield the same distribution of butenyl esters.⁴⁴ The efficiency of various copper species as oxidants and catalysts is being investigated quantitatively in systems involving the simultaneous formation of alkyl and allylic radicals.

acid may arise *via* an acid-catalyzed ionic decomposition, the amounts so formed in the presence of bis-bipyridyl copper salt far exceed that formed in the absence of metal salt. Moreover, *t*-butyl 2-methyl-2-hexyl peroxide which is not subject to acid-catalyzed decomposition yields 6% *n*-butyl acetate in the presence of the bis-bipyridyl complex.

We postulate, tentatively, that simple cupric acetate and the complex bis-bipyridyl cupric acetate oxidize butyl radicals by different processes much like the oxidation of allylic radicals previously examined.⁴⁴ The oxidation of *butyl radicals* by the *bis-bipyridyl cupric complex*, unlike the simple cupric salt, yields solvolytic as well as elimination products much like the partitioning of butyl carbonium ion formed by conventional procedures.⁵⁴ A reaction with a large component of electron transfer is indicated. Whether a discrete carbonium ion as such is formed as an intermediate in the process is difficult at present to state. The formation of exclusively elimination products from the oxidation of *alkyl radicals* by *simple cupric salts* is interpreted as involving the simultaneous removal of a β -hydrogen and electron transfer to the copper moiety. That part of the driving force for this oxidation is derived from the removal of the β -hydrogen is consistent with the unreactivity of neopentyl radicals. However, the geometrical requirements for concomitant removal of the β -hydrogen cannot constrain the transition state too greatly (*i.e.*, the β -carbon–hydrogen bond is not highly stretched) since selectivity studies on the *sec*-butyl system have indicated it to have relatively "free" carbonium ion character.⁵⁵

In summary, the oxidation of alkyl radicals by cupric species differs from the oxidation of allylic radicals. In the latter case, oxidation by cupric salts yielded only substitution products, no elimination products being evident with butenyl radicals. The oxidation of allylic radicals by electron transfer and ligand transfer by simple and complex cupric salts has been delineated.⁴⁴ If the alkyl radical possesses a removable β -hydrogen, oxidation by simple cupric salts is facile. In the absence of hydrogens so disposed, the oxidation by simple cupric salts proceeds at a significantly slower rate, and carbonium ions formed by an electron transfer reaction appear to be intermediates. Complex copper salts are not as effective as simple cupric salts in the oxidation of alkyl radicals (as contrasted from allylic radicals) and they function mainly in an electron transfer capacity. The criterion which we have applied to describe electron transfer processes is the formation of solvolytic products from carbonium ion or incipient carbonium ion intermediates. Further studies to ascertain the carbonium ion nature of the intermediates are in progress.

Experimental

Materials. Metal Salts.—Cupric acetate hydrate, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Mallinckrodt analytical reagent; cupric acetylacetonate, $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$; cupric stearate, $\text{Cu}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$, cupric naphthenate, 80% solution in mineral oil, Harshaw Chemical Co.; cupric 2-ethylhexanoate (octanoate) $\text{Cu}(\text{C}_8\text{H}_{15}\text{O}_2)_2$, Shepherd Chemical Co., Cincinnati, O.

Acids and Acid Chlorides.—Valeric, 2-methylbutyric and isovaleric acids, Eastman Kodak Co. White Label, were converted to the acid chlorides by Brown's procedure,⁵⁶ which employs benzoyl chloride. Each acid chloride was carefully checked for adulteration from its isomers by conversion to the methyl ester. These were analyzed by g.l.c. (15-ft. diethylene glycol on firebrick at 100°): methyl 2-methylbutyrate, 14.0 min.; methyl isovalerate, 15.4 min.; methyl valerate, 21.5 min.

(54) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(55) It is attractive to postulate an intramolecular removal of the β -hydrogen especially in view of the freedom from solvent effects. Studies are now underway to determine β -hydrogen isotope effects.

(56) H. C. Brown, *J. Am. Chem. Soc.*, **60**, 1325 (1938).

Alcohols.—The saturated tertiary alcohols 2-methylhexanol-2, 2,3-dimethylpentanol-2 and 2,4-dimethylpentanol-2 were synthesized from acetone and the corresponding butyl halide by the Grignard reaction.

2-Methylhexen-5-ol-2 was synthesized in a similar manner from allylacetone and methylmagnesium bromide; yield 93%, boiling range 143–144°, n_D^{20} 1.4305. On hydrogenation with Pt-C it yielded 2-methylhexanol-2. *Anal.* Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.7; H, 14.2.

2-Methylhexen-4-ol-2 was synthesized from isobutylene oxide and 1-propenyl-lithium.¹³

Peroxides. Diacyl Peroxides.⁵⁷—In a typical procedure, 44 ml. of 50% hydrogen peroxide (du Pont Co., Albone 50) was added slowly with rapid stirring to a chilled solution of 110 ml. of pyridine and 35 ml. of ether contained in a Morton flask. It was followed by the dropwise addition of 85 g. of redistilled valeryl chloride so that the temperature did not exceed 4°. The reaction was vigorously stirred for 2 hours at 5° and 100 ml. of ether was added. It was followed by a chilled solution of 50 ml. of concd. H_2SO_4 in 200 ml. of water. The phases were separated and the aqueous solution quickly re-extracted with 100 ml. of ether. The chilled combined ether extract was washed with chilled dilute sulfuric acid, water and $NaHCO_3$ twice. All operations were carried out at 0° and the ethereal solution dried over Na_2SO_4 . The ether was removed *in vacuo* with a rotary evaporator; the colorless peroxide was obtained in 60–80% yields, and assayed by the iodometric technique⁵⁸ to 97% or better.

***t*-Butyl acetyl peroxide** obtained in this manner was a stable crystalline solid melting at 43.6–44.3°. It was recrystallized from isopentane at 0°. *Anal.* Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63; peroxide equiv., 230. Found: C, 62.8; H, 9.4; peroxide equiv., 225. With the exception of bis-2-methylbutyryl peroxide, all the diacyl peroxides studied were relatively stable compounds. If 2-methylbutyryl peroxide is allowed to warm to room temperatures, extreme care must be exercised in handling the material. On several occasions small amounts contained in vials exploded violently when inadvertently left at room temperatures for less than 15 minutes.

***t*-Butyl *t*-heptyl peroxides.**—Mixed *t*-butyl *t*-heptyl peroxides were synthesized from *t*-butyl hydroperoxide and the isomeric *t*-heptanols in aqueous sulfuric acid solutions.⁵ In a typical procedure 100 ml. of 65% sulfuric acid was chilled to 0° and 40 g. of 2-methylhexanol-2 was added dropwise at a rate to maintain the temperature. This was followed by 30 g. of 95% *t*-butyl hydroperoxide. The reaction was stirred overnight at 8–15° and excess water added. Ether was added and the peroxidic solution separated, washed with saturated $NaHCO_3$ solution and dried over $CaCl_2$. Distillation gave a 75–90% yield of *t*-butyl *t*-heptyl peroxide.

***t*-Butyl 2-methyl-2-hexyl peroxide:** b.p. 38–39° at 1 mm., n_D^{20} 1.4069. *Anal.* Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85; mol. wt., 188.3. Found: C, 70.4; H, 12.7; mol. wt. (cryoscopic), 185.

***t*-Butyl 2,4-dimethyl-2-pentyl peroxide:** b.p. 37–38° at 1 mm., n_D^{20} 1.4061. *Anal.* Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85; mol. wt., 188.3. Found: C, 70.5; H, 12.6; mol. wt. (cryoscopic), 183.

***t*-Butyl 2,3-dimethyl-2-pentyl peroxide** could not be prepared pure in this manner. It was contaminated with *t*-butyl 2,3-dimethyl-3-pentyl peroxide which resulted from the Wagner-Meerwein rearrangement of the oxonium ion intermediate from 2,3-dimethylpentanol-2. The thermal decomposition of the mixture of isomeric peroxides yielded both *sec*-butyl and isopropyl radicals. Similarly, *t*-butyl 3,4-dimethyl-4-heptyl peroxide, prepared from *t*-butyl hydroperoxide and 3,4-dimethylheptanol-4 was contaminated with *t*-butyl 3,4-dimethyl-3-heptyl peroxide. The mixture on decomposition yielded both *sec*-butyl and *sec*-pentyl radicals. *t*-Butyl 3,4-dimethyl-3-hexyl peroxide was prepared from 3,4-dimethylhexanol-3 and yielded *sec*-butyl and ethyl radicals on thermolysis. Each of the peroxide precursors for *sec*-butyl radicals given above were prepared in poor yields (15–30%) due to competitive dehydration. In general, tertiary alcohols which have a β -tertiary center under acidic conditions invariably led to a mixture of peroxides (independent largely of acid strength) in poor yields. However, results of studies on the decomposition of peroxides indicated that the *sec*-butyl radicals formed from each of these sources all behave in the same manner regardless of their origin.

***t*-Butyl 2,3-dimethyl-2(3)-pentyl peroxide:** boiling range 37–38° (1 mm.), n_D^{20} 1.4118. *Anal.* Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85; mol. wt., 188.3. Found: C, 70.1; H, 12.7; mol. wt. (cryoscopic), 181.

(57) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954).

(58) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

***t*-Butyl 3,4-dimethyl-4(3)-heptyl peroxide:** boiling range 41–42° (1 mm.), n_D^{20} 1.4235. *Anal.* Calcd. for $C_{13}H_{26}O_2$: C, 76.16; H, 13.05; mol. wt., 216. Found: C, 71.9; H, 12.8; mol. wt. (cryoscopic), 210.

***t*-Butyl 3,4-dimethyl-3-hexyl peroxide:** boiling range 42–43° (2 mm.), n_D^{20} 1.4199. *Anal.* Calcd. for $C_{12}H_{24}O_2$: C, 71.23; H, 12.95; mol. wt., 202. Found: C, 71.3; H, 12.9; mol. wt. (cryoscopic), 200.

2-Methyl-2-hexyl Hydroperoxide.—To a chilled solution of 69% sulfuric acid (145 g.) was added dropwise with vigorous stirring 132 g. of 2-methyl-2-hexanol and the reaction maintained at 0°. A chilled solution of 50% hydrogen peroxide (135 g.) was added dropwise during 1 hour and the mixture vigorously stirred at 0° for an hour, 3 hours at 10° and then at 20–25° for 3 hours. Approximately 100 ml. of ether was added and the aqueous solution separated. The ethereal solution was washed with saturated $NaHCO_3$ solution and then vigorously shaken with a chilled solution of 150 g. of $NaOH$ in 20 ml. of water. The slurry was vacuum filtered and the colorless crystalline hydroperoxide salt repeatedly washed with ether and acetone until it appeared dry. It was then dissolved in water, the solution neutralized with carbon dioxide and extracted with ether. The dried ethereal solution yielded 95 g. of 2-methyl-2-hexyl hydroperoxide boiling at 57–59° at 2 mm., n_D^{20} 1.4237. *Anal.* Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20; hydroperoxide equiv., 132.2. Found: C, 63.4; H, 12.4; hydroperoxide equiv., 129.

2-Methyl-2-hexyl Peracetate.—Sodium 2-methyl-2-hexyl peroxide (120 g.) was suspended in 150 ml. of ether at 0° and a solution of 79 g. of acetyl peroxide in 50 ml. of ether added dropwise. The reaction was stirred for 2 hours at room temperature and then solid $NaHCO_3$ added until evolution of CO_2 ceased. Water and ether were added and the ethereal solution washed with $NaHCO_3$ solution twice and dried over Na_2SO_4 . Distillation *in vacuo* yielded 80 g. of 2-methyl-2-hexyl peracetate boiling at 81–83° at 2 mm., n_D^{20} 1.4208. *Anal.* Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.3; H, 10.5.

Procedure for Decomposition of Peroxides.—The peroxides were decomposed in a magnetically stirred solution contained in a 50-ml. round-bottom flask maintained at constant temperature ($\pm 0.1^\circ$) by an oil-bath. Solutions containing 20 ml. of solvent were swept either with helium or nitrogen and the liberated gases collected over mercury and analyzed by g.l.c.: 50-ft. dimethyl sulfolane on firebrick at room temperature: air, 5.1 min.; methane, 5.4 min.; carbon dioxide, 12.0 min.; isobutane, 14.5 min.; *n*-butane, 18.5 min.; butene-1, 20.8 min.; isobutene, 21.8 min.; *trans*-butene-2, 26.3 min.; *cis*-butene-2, 30.2 min.; or 15-ft. Dowtherm on firebrick: air, 4.4 min.; carbon dioxide, 5.7 min.; isobutane, 10.9 min.; *n*-butane, 16.4 min.; butene-1 and isobutene, 23.7 min.; *trans*-butene-2, 30.0 min.; *cis*-butene-2, 34.9 min.; at higher gas pressures: CO_2 , 2.1 min.; neopentane, 6.9 min.; 2-methylbutene-1, 22.2 min.; 2-methylbutene-2, 29.1 min. The total CO_2 and olefin yields were determined by sweeping the solutions finally with helium and absorbing the CO_2 on Ascarite. The butene was condensed in a cold trap with liquid nitrogen and determined by bromine titration.⁵⁹

In those reactions employing copper salts as catalysts the salts were first dissolved in the solvent, the solution swept with nitrogen and peroxide quickly added under reverse nitrogen flow. The solution was swept for 5 additional minutes. When halogen was used as inhibitor a standard solution was made up and an aliquot of it was added to the reaction mixture. The rate measured by gas evolution was reproducible and in the region of 20–60% decomposition the rate of gas evolution was linear with time. The rate at 30% reaction was arbitrarily chosen as a quantitative measure of the rates (see Tables I, II, III and IV). The reaction mixture was diluted to 50 ml. in a volumetric flask and aliquots titrated for free acid by first treating with a measured excess of standard alkali and back titrating with acid. Ester yields were determined by g.l.c. using the marker method. Results within a few per cent were the same regardless of whether the crude reaction mixture or the solution obtained by first extracting the copper salts and free acid were used. The identities of the ester and alcohol products were finally determined by trapping the g.l.c. peaks and comparing the infrared spectra of the trapped material with authentic specimens.

Acknowledgments.—The author is grateful to the National Science Foundation and the Case Institute Research Fund for generous grants which supported this investigation.

(59) S. Siggia, "Quantitative Organic Analysis by Functional Groups," J. Wiley and Sons, Inc., New York, N. Y., 1954, p. 68; J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 275.