firmed by the infrared (gas phase) and/or n.m.r. (CDCl₃ solution) spectrum of the product mixture. The infrared spectrum of the product was completely accounted for by the components tabulated, with the exception of bands attributable to carbon dioxide and nitrous oxide.

Reaction of 9-Bromofluorene with Molten Nitrate. A mixture of 0.245 g. (1.00 mmole) of 9-bromofluorene (Matheson Coleman and Bell, recrystallized from hexane) and 0.361 g. (1.00 mmole) of tetra-*n*-pentylammonium nitrate was heated at 105° for 0.25 hr., cooled, and chromatographed in benzene on 11 g. of silicic acid. With 200 ml. of benzene, 0.177 g. of yellow solid (A) was eluted; 250 ml. of benzene then eluted 0.024 g. (0.13 mmole, 13%) of fluorenol, m.p. 155.5–157°, m.m.p. with an authentic sample (m.p. 156.6–158°) 155.5–157° after recrystallization from isooctane. Fraction A was rechromatographed in benzene-pentane (1:2) on 11 g. of silicic acid. After elution of 0.059 g. of unidentified solids with 600 ml. of solvent, an additional 350 ml. eluted 0.095 g. (0.53 mmole, 53%) of fluorenone, m.p. 71–72.5° or 84–85°,[30] infrared spectrum and mixture melting point identical with those of authentic material, m.p. 83.5–85°.

Reaction of p-Nitrobenzyl Bromide with Molten

(30) The various fractions crystallized either in modification I or II (L. Kofler and A. Kofler, "Thermo-Mikro-Methoden," Verlag Chemie, Weinheim, 1954, p. 419).

Nitrate. The orange oil obtained by heating 0.432 g. (2.00 mmoles) of *p*-nitrobenzyl bromide with 0.722 g. (2.00 mmoles) of tetra-*n*-pentylammonium nitrate for 1 hr. at 105° was dissolved in carbon tetrachloride. On cooling, *p*-nitrobenzyl *p*-nitrobenzoate, 0.077 g. (0.26 mmole, 26%), separated as white needles which were recrystallized from acetic acid in 94% recovery; m.p. 168°, resolidification, m.p. 171.5–172.5°, infrared spectrum and mixture melting point identical with those of an authentic specimen prepared according to Lyons and Reid[31] (m.p. 168, 172.5–173.5°). The original carbon tetrachloride solution was evaporated and the residue was chromatographed on 12 g. of silicic acid. With 150 ml. of benzene 0.047 g. (0.31 mmole, 15%) of crude *p*-nitrobenzaldehyde, m.p. 70–97°, infrared spectrum identical with that of an authentic specimen, was eluted. After 0.011 g. of intermediate, 150 ml. of benzene and 350 ml. of benzene-chloroform (3:1) eluted 0.150 g. of a mixture from which 0.022 g. (0.13 mmole, 6%) of *p*-nitrobenzoic acid, identified by melting point (237–239°) and infrared spectrum, and 0.037 g. (0.24 mmole, 12%) of *p*-nitrobenzyl alcohol, m.p. and m.m.p. 91–93°, were obtained by crystallization from toluene and toluene–hexane.

(31) E. Lyons and E. E. Reid, *J. Am. Chem. Soc.*, 39, 1727 (1917). Only the lower-melting modification was reported, m.p. 168.5°.

Studies of Ligand Transfer between Metal Halides and Free Radicals from Peroxides[1]

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The role of ligand transfer in the catalytic decomposition of peroxides by metal species has been examined in the presence of halide salts. The catalytic reaction is generally clean; for example, valeryl peroxide and halide afford valerate, alkyl halide, and carbon dioxide in excellent yields. However, acyl peroxides are susceptible to nucleophilic attack by halide ions; and hypohalites formed as intermediates retard the chain decomposition of peroxides by copper salts by effectively scavenging the cuprous salts essential for the catalysis. The deleterious effect of these halogen-producing reactions to the catalytic process can be removed by the addition of reagents capable of quenching acyl hypochlorites and chlorine. The effectiveness of a reagent in this capacity, 1,3-dimethoxybenzene > styrene > octene-1 ≃ mesitylene ≃ anisole >> toluene, is related to its reactivity in electrophilic chlorination. Nucleophilic attack by bromide on peroxides is very rapid. Its contribution to the over-all decomposition of diacyl peroxides, however, is largely masked by a much more facile radical-chain com-ponent in the presence of cupric bromide. The catalytic process with bromide, unlike chloride, is not substantially inhibited by molecular bromine due to the formation of cuprous bromide in equilibrium with bromine by disproportionation of cupric bromide in nonaqueous media. The formation of alkyl halides by ligand transfer in the free-radical chain decomposition of peroxides is retarded by oxygen. These reactions are compared to the copper-catalyzed decomposition of peroxides in the absence of halide.

Introduction

The decomposition of organic peroxides is markedly accelerated by small amounts of metal salts.[2–4] Diacyl peroxides, peresters, and hydroperoxides are catalytically decomposed at temperatures lower than that required for the thermolysis. With aliphatic analogs, complications which often lead to a variety
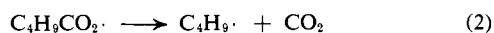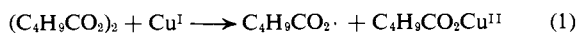
(1) Part II. Reaction of Peroxides with Halides. Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) J. K. Kochi, *J. Am. Chem. Soc.*, 85, 1958 (1963).
(3) S. Goldschmidt, H. Späth, and L. Beer, *Ann.*, 649, 1 (1962).
(4) L. S. Silbert and D. Swern, *Anal. Chem.*, 30, 385 (1958); *J. Am. Chem. Soc.*, 81, 2365 (1959).

of products[5] in the thermolysis can be obviated in the reactions catalyzed by metal salt. For example, the decomposition of valeryl peroxide catalyzed by copper salts in aprotic solvents such as benzene, hexane, and acetonitrile as well as acetic acid affords excellent yields of butene-1, valeric acid, and carbon dioxide.[2] It has been shown that the reaction is catalyzed by copper(I) species. A chain mechanism which involves the capacity of copper species to undergo oxidation and reduction with free-radical intermediates as given in reactions 1 to 3 has been proposed.[2] Each step of this mechanism has been discussed and elaborated.[6]

$$(C_4H_9CO_2)_2 + Cu^I \longrightarrow C_4H_9CO_2 \cdot + C_4H_9CO_2Cu^{II} \quad (1)$$

$$C_4H_9CO_2 \cdot \longrightarrow C_4H_9 \cdot + CO_2 \quad (2)$$

$$C_4H_9 \cdot + Cu^{II}O_2CC_4H_9 \longrightarrow C_4H_8 + C_4H_9CO_2H + Cu^I \text{ etc.} \quad (3)$$

The last step (reaction 3) in the sequence is of particular interest since it involves the oxidation of an alkyl radical by a carboxylatocopper(II) species. Such an oxidation of alkyl radicals (eq. 4) appears to

$$R \cdot + M^{+n} \longrightarrow R^+ + M^{+n-1} \text{ etc.} \quad (4)$$
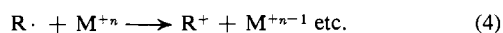
be general for copper(II) salts bonded with ligands through an oxygen atom, and it has been designated as oxidation of a free radical by *electron transfer*.[6,7] An alternative mode of oxidation of free radicals by *ligand transfer*,[8] involving the direct transfer of a ligand from the initial complex to the free radical (eq. 5),

$$R \cdot + M^{+n}X_n \longrightarrow R-X + M^{+n-1}X_{n-1} \quad (5)$$
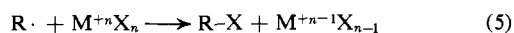
is particularly favored by halides[8,9] (especially chloride and bromide), pseudo halides[8,9] (thiocyanate, cyanide, and azide), and olefins. The concept of atom or group transfer is mainly due to Taube and co-workers,[10] and the nature of the bridged activated complex in inorganic systems has been elegantly delineated.

Since peroxides represent a reliable,[11] convenient, and versatile[12] source of free radicals we have pursued the examination of their reaction with metal salts in detail. In this paper we wish to describe studies directed toward obtaining the catalytic decomposition of peroxides, in which the oxidation step of the chain mechanism involves ligand transfer. Chloride and bromide as halides were chosen for investigation as electron mediators with cupric species as oxidant.

(5) D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, 78, 4296 (1956); 79 3041, 3045 (1957); D. F. DeTar and R. A. J. Long, *ibid.*, 80, 4742 (1958); D. DeTar and R. C. Lamb, *ibid.*, 81, 122 (1959); Ya. K. Syrkin and I. I. Moiseev, *Usp. Khim.*, 29, 193 (1960).

(6) E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel, and S. Tazuke, *Discussions Faraday Soc.*, 29, 188 (1960); J. K. Kochi, *Tetrahedron*, 18, 483 (1962); H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, 83, 2013 (1961); 85, 1437 (1963).

(7) J. K. Kochi and R. D. Gilliom, *ibid.*, 86, 5251 (1964); J. K. Kochi and D. M. Mog, *ibid.*, 87, 522 (1965).

(8) (a) C. H. Bamford, A. Jenkins, and R. Johnson, *Proc. Roy. Soc. (London)*, A239, 214 (1957); (b) J. K. Kochi, *J. Am. Chem. Soc.*, 78, 4815 (1956); 79, 2942 (1957); 84, 2121 (1962); (c) J. Kumamoto, H. E. De La Mare, and F. F. Rust, *ibid.*, 82, 1935 (1960); (d) it has also been called redox transfer (*cf.* H. Asscher and D. Vofsi, *J. Chem. Soc.*, 3921 (1963)).

(9) (a) F. Minisci, *Gazz. chim. ital.*, 89, 1910, 1943, 1302, 2428, 2440 (1959); *Tetrahedron Letters*, 357 (1963); 533 (1962); (b) A. H. Hyson, U. S. Patent 2,710,302 (1955).

(10) H. Taube, Advances in Inorganic and Nuclear Chemistry, Vol. I, Academic Press Inc., New York, N. Y., 1959, p. 1; E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, 86, 1318 (1964), and earlier papers; J. Halpern, *Quart. Rev.* (London), 15, 207 (1961).

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

(12) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961.

Results and Discussion

Ligand Transfer with Chloride. The thermal decomposition of valeryl peroxide, $(CH_3CH_2CH_2CH_2CO_2)_2$, in acetic acid at 55° occurs slowly with an approximate half-life of 12 hr. (Figure 1). The disappearance of peroxide consists of two simultaneous reactions: a homolytic dissociation to form a pair of valeroxy radicals[13] and an acid-catalyzed reaction.[14] A variety of products are formed under these conditions, among which are butane, carbon dioxide, and valeric acid from the former process and butyl valerate and acetate, carbon dioxide and valeric acid from the ionic reaction.[15] In the presence of lithium chloride (1.1 M), the disappearance of peroxide at 50° is approximately twice as fast as the purely thermal reaction as shown in Figure 1, under otherwise the same experimental conditions. The yield of valeric acid (110–120%)[16] is markedly altered, and n-butyl chloride (45–60%) is a major product in addition to carbon dioxide and small amounts of n-butane ($\sim$5%) (Table I). In the presence of 50%

Table I. The Reaction of Valeryl Peroxide with Chloride Salts[a]

| | Reactants | | Products | |
Solvent, vol. %	Valeryl peroxide, M	Chloride, M	Valeric acid, %	Butyl chloride, %
HOAc, 100	0.19	LiCl, 0.89	115	50
HOAc, 50 PhCH₃, 50	0.23	LiCl, 0.49	99	10[b]
HOAc, 100	0.26	LiCl, 0.54 CuCl₂, 0.057	130	77
HOAc, 100	0.096	LiCl, 0.58 CuCl₂, 0.058	120	87[c]
CH₃CN, 100	0.14	CuCl₂, 0.18 LiCl, 0.13	96	95
HOAc, 50 PhOCH₃, 50	0.21	LiCl, 0.46	116	48[d]
HOAc, 70 PhOCH₃, 30	0.15	LiCl, 0.38 CuCl₂, 0.041	123	84[e]

[a] At 50°. [b] 50% benzyl chloride. [c] Successive additions of cuprous chloride made to enable the cuprous-catalyzed reaction to predominate. [d] 2% chloroanisole, 5% butyl acetate. [e] 10% chloroanisole.

v./v. toluene–acetic acid, the rate is slightly diminished.[17] An equivalent of valeric acid in addition to benzyl chloride ($\sim$50%), n-butyl chloride ($\sim$10%), n-butane, and carbon dioxide is formed in the reaction.

The decomposition of valeryl peroxide (0.26 M) in acetic acid solutions containing lithium chloride (0.54 M) and cupric chloride (0.057 M) is not significantly faster than those runs without cupric chloride. The effect is unchanged in toluene–acetic acid solutions. Significantly, the yields of valeric acid (120–130%)

(13) See, however, M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964); M. Szwarc, "Peroxide Mechanisms," J. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 153 ff.

(14) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, 72, 67, 3030 (1950).

(15) *Cf.* F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *ibid.*, 86, 2080 (1964).

(16) Yields reported herein are based on a one-to-one stoichiometry, each peroxide equivalent to one valeric acid, carbon dioxide, and butyl moiety. A maximum of 200% of valerate is possible (*vide infra*).

(17) The slightly increased rate of decomposition and the formation of small amounts of butane, together with the alteration in the yields of major products, indicate that the reaction of valeryl peroxide with chloride is only slightly faster than the thermal reaction in acetic acid.
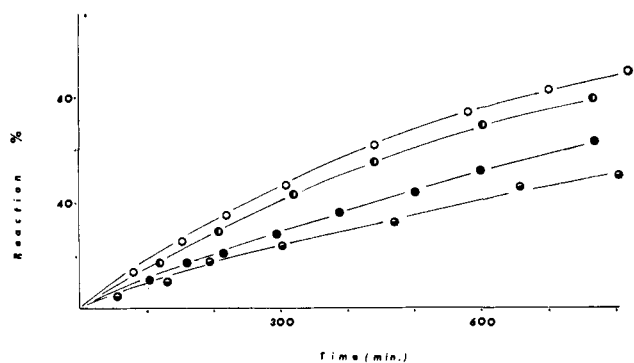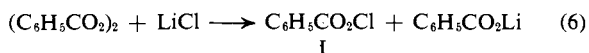
Figure 1. Decomposition of valeryl peroxide by chloride in acetic acid at 50°. ◒, no chloride at 55°; ●, chloride in 29% v./v. toluene–acetic acid; ◐, chloride; and ○, cupric chloride.

and n-butyl chloride (75–85%) are enhanced in the presence of cupric chloride compared to equivalent experiments with only lithium chloride in acetic acid. Moreover, in toluene–acetic acid solutions, the decomposition of valeryl peroxide with a lithium (0.42 M) and cupric chloride (0.038 M) mixture yielded valeric acid ($\sim$100%) and butyl chloride (74%) in high yields, but only insignificant amounts of benzyl chloride (<2%) and no butane. The decomposition of valeryl peroxide in acetonitrile solutions can be studied at higher cupric chloride (0.18 M) concentrations due to increased solubility. At a total chloride concentration of 0.47 M (by added lithium chloride) the rate is approximately three times faster than the reaction at lower copper concentration in acetic acid. Furthermore, the increased rate is associated with a high yield of n-butyl chloride (92–100%) and 1 equiv. of valeric acid.[18]

The formation of electrophilic chlorinating agents from valeryl peroxide (0.21 M) and lithium chloride (0.46 M) is indicated by the chlorination of anisole. Chloroanisoles (76% para isomer) are formed in 2% yield in addition to n-butyl chloride (48%) and valeric acid (116%). The material balance among butyl chloride (84%), chloroanisoles (10%), and valeric acid (123%) is considerably improved by the addition of cupric chloride (0.041 M).

From these results it can be deduced that at least two concurrent processes are competing in the decomposition of valeryl peroxide induced by chloride and cupric salts. The previous study[19] with benzoyl peroxide revealed that benzoyl peroxide was susceptible to nucleophilic attack by halide ion (reaction 6) in acetic acid and formed aroyl hypohalites I as intermediates.

$$(C_6H_5CO_2)_2 + LiCl \longrightarrow C_6H_5CO_2Cl + C_6H_5CO_2Li \quad (6)$$
$$I$$

In the absence of reagents reactive to electrophilic or homolytic halogenation, benzoyl hypochlorite yielded a variety of products in low yields (chlorobenzene, carbon dioxide, methyl chloride, biphenyl, and chlorine). However, in the presence of reagents such as toluene, which are readily attacked by free radicals and
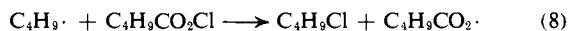
electrophiles, good yields of chlorinated products were obtained.

A similar reaction is possible between lithium chloride and valeryl peroxide, the slow step (reaction 7) being the nucleophilic attack on peroxide to yield valeryl hypochlorite II. Such an aliphatic acyl hypo-

$$(C_4H_9CO_2)_2 + LiCl \longrightarrow C_4H_9CO_2Cl + C_4H_9CO_2Li \quad (7)$$
$$II$$

chlorite as an intermediate is expected to be more easily decarboxylated to butyl chloride than an aroyl hypochlorite. The higher yields of butyl chloride compared with chlorobenzene from benzoyl peroxide under equivalent conditions are in accord with this. The route by which acyl hypochlorites decompose to alkyl halides is not completely clear. The formation of benzyl chloride and decreased yields of butyl chloride from the reaction of valeryl peroxide with lithium chloride in the presence of toluene indicates that free radicals are generated in the reaction. The radical-chain nature of the chlorination of toluene is demonstrated by its virtual elimination in the presence of cupric chloride.[19]

Acyl hypohalites have been postulated[20] as intermediates in the decarboxylation of silver salts by halogens. We have observed[21] that a mixture of chlorine and silver acetate or benzoate reacts rapidly even at 0° with cyclohexane and toluene to afford cyclohexyl chloride and benzyl chloride in good yields. Undoubtedly valeryl hypochlorite induces homolytic reactions much like t-butyl hypochlorite[22] and similar compounds.[23] However, the mechanism of the formation of butyl chloride by a homolytic chain process such as reactions 8 and 9, or a concerted one-step

$$C_4H_9\cdot + C_4H_9CO_2Cl \longrightarrow C_4H_9Cl + C_4H_9CO_2\cdot \quad (8)$$
$$C_4H_9CO_2\cdot \longrightarrow C_4H_9\cdot + CO_2 \text{ etc.} \quad (9)$$

mechanism similar to that obtained with chlorosulfites[24] and chlorocarbonates,[25] cannot be ascertained on the basis of the evidence at hand.[26]

Valeryl hypochlorite is also prone to react (reaction 10) with chloride ion to form valerate and chlorine,

$$C_4H_9CO_2Cl + Cl^- \longrightarrow C_4H_9CO_2^- + Cl_2 \quad (10)$$

and for this reason the stoichiometry of the reaction requires that more than 1 equiv. of valerate be formed from each mole of peroxide. However, valeryl hypochlorite undergoes rapid decarboxylation, and the competing transchlorination reaction (10) is minor. The yield of butyl chloride is only slightly affected by the addition of the easily chlorinated anisole.

The increase in yield of butyl chloride which accom-

(18) The increased rate and clean stoichiometry obtained in acetonitrile reactions are partly due to higher concentrations of cupric salt attainable in this medium. In addition, it is possible that cupric chloride in acetonitrile disproportionates (vide infra) to chlorine and cuprous salt, the latter being stable in nitrile solutions (R. C. Larson and R. T. Iwamoto, J. Am. Chem. Soc., 82, 3239, 3526 (1960)).

(19) J. K. Kochi, B. Graybill, and M. Kurz, ibid., 86, 5257 (1964). Also compare H. Bredereck, et al., Angew. Chem., 71, 340 (1959).

(20) R. G. Johnson and K. K. Ingham, Chem. Rev., 56, 219 (1956); C. V. Wilson, Org. Reactions, 9, 332 (1957).

(21) J. Mark, unpublished studies.

(22) C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108, 6113 (1960).

(23) (a) M. Anbar and D. Ginsburg, Chem. Rev., 54, 925 (1954); (b) F. D. Greene, J. Am. Chem. Soc., 83, 2196 (1961); (c) C. Walling and A. Padwa ibid., 85, 1597 (1963).
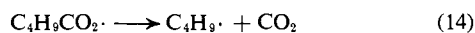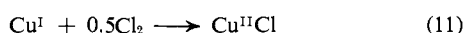
(24) C. E. Boozer and E. S. Lewis, ibid., 74, 308 (1952); 75, 3182 (1953); G. M. Coppinger and E. S. Lewis, ibid., 76, 796 (1954).

(25) K. B. Wiberg, and T. M. Shryne, ibid., 77, 2774 (1955); E. S. Lewis and W. C. Herndon, ibid., 83, 1955, 1961 (1961); E. S. Lewis. W. C. Herndon, and D. C. Duffey, ibid., 83, 1959 (1961).

(26) The absence of chlorobenzene as an important product from benzoyl hypochlorite in the benzoyl peroxide–chloride reaction does not militate against a radical-chain mechanism due to the relatively slow fragmentation of benzoyloxy radical: G. S. Hammond and L. Soffer, ibid., 72, 4711 (1950).

panies the addition of cupric chloride to the reaction between valeryl peroxide and lithium chloride indicates that it is being formed by a supplementary mode. The contribution from the cupric chloride under these conditions is small as indicated by the very slight increase in rates and enhancement in butyl chloride yield over that solely with lithium chloride. The weak catalysis by cupric chloride under these conditions is in strong contrast to the catalysis by copper salts in the absence of chloride,[2] the latter being at least an order of magnitude greater than the former. The reaction catalyzed by cupric acetate is also strongly inhibited by oxygen, whereas the cupric chloride reaction is only slightly affected.

We attribute the minor importance of a catalytic reaction by copper salts in the presence of chloride in acetic acid or toluene–acetic acid solutions to the presence of valeryl hypochlorite and molecular chlorine. These halogenating agents, particularly the latter, are responsible for the effective removal[2] of any copper-(I) species so vital to the catalytic process as represented in sequence 12 to 15. This mechanism is analogous

$$Cu^I + 0.5Cl_2 \longrightarrow Cu^{II}Cl \qquad (11)$$

$$(C_4H_9CO_2)_2 + Cu^I \longrightarrow C_4H_9CO_2\cdot + Cu^{II}O_2CC_4H_9 \qquad (12)$$

$$Cu^{II}O_2CC_4H_9 + Cl^- \rightleftharpoons Cu^{II}Cl + C_4H_9CO_2^- \qquad (13)$$

$$C_4H_9CO_2\cdot \longrightarrow C_4H_9\cdot + CO_2 \qquad (14)$$

$$C_4H_9\cdot + Cu^{II}Cl \longrightarrow C_4H_9Cl + Cu^I, \text{ etc.} \qquad (15)$$

to the reaction catalyzed by cupric acetate (carboxylate), but is differentiated by the inclusion of a ligand transfer[8] (reactions 15 and 5) rather than an electron transfer[6,7] (reactions 3 and 4) step in the cuprous regenerating reaction.

The role which valeryl hypochlorite and chlorine play in the retardation of the copper chloride catalyzed reaction is dramatically demonstrated by the great enhancement in rate by additives capable of facile reaction with these chlorinating agents (Figure 3). Anisole, mesitylene, octene-1, styrene, and 1,3-dimethoxybenzene are all reagents[27] readily chlorinated by chlorine or valeryl hypochlorite in acetic acid solutions. Anisole, the least reactive member of this series, is at least 10^5 times more reactive to electrophilic chlorination than toluene.[28] With the exception of their susceptibility to electrophilic attack, e.g., by chlorine and acyl hypochlorites, these reagents are structurally quite unique. These reagents themselves do not affect the ionic decomposition of valeryl peroxide induced by chloride ion; in actual fact the rate of decomposition of valeryl peroxide in dimethoxybenzene–acetic acid solutions is slightly slower than in glacial acetic acid alone (Figure 2). Though quantitative data is not available with regard to their rates of chlorination, the order of effectiveness of these reagents in removing the retardation as shown in Figure 2 is in qualitative agreement with that expected on the basis of limited study.[28] We attribute the increased rate of decomposition of valeryl peroxide by cupric chloride in the presence of dimethoxybenzene, styrene, and octene-1 solely to the incursion of the catalytic reaction given in reaction schemes 12 to 15.

(27) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp. 620f, 148.
(28) P. B. D. De La Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959, p. 131 ff.
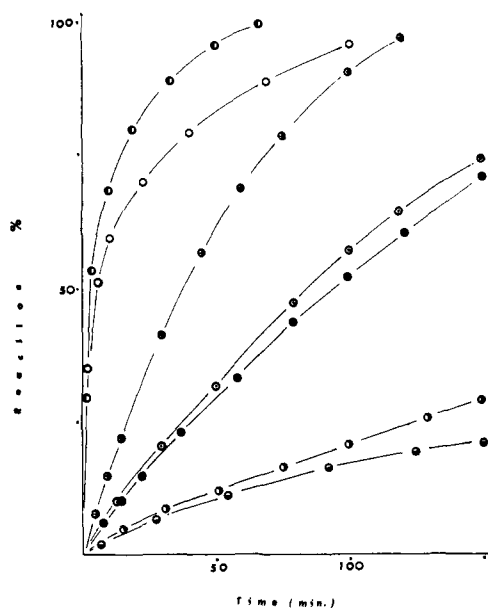
Figure 2. Copper salt catalysis in the decomposition of valeryl peroxide by chloride in acetic acid solutions containing: ◐, 1,3-dimethoxybenzene (standard, no copper salt); ◑, toluene; ●, anisole; ○, mesitylene; ◐, octene-1; ○, styrene; and ◐, 1,3-dimethoxybenzene at 50°.

In the presence of reagents capable of scavenging electrophilic chlorine species, not only is the copper chloride catalysis markedly improved, but the yields of products closely follow the expected stoichiometry given in eq. 16. In the presence of dimethoxybenzene,

$$(C_4H_9CO_2)_2 + Cl^- \longrightarrow C_4H_9CO_2^- + C_4H_9Cl + CO_2 \qquad (16)$$

mesitylene, anisole, styrene, and octene-1, the yields of butyl chloride range from 85 to 98%. However, the yields of products alone cannot be employed to support a mechanism since the ionic reaction 6 and the catalytic reaction render the same stoichiometry, although butyl chloride arises from two entirely independent routes.

It is apparent from Figure 2 that the contribution of the ionic reaction in the presence of cupric chloride in toluene–acetic acid solutions is considerable due largely to the inability of toluene to scavenge chlorine effectively by either electrophilic or homolytic chlorination.[18] However, the yield of butyl chloride (84%) under these circumstances is high. The magnitude of the retardation of the reaction by oxygen, leads us to believe that the catalytic and ionic reactions are roughly competitive in toluene and acetic acid solutions. The rapid rate in the presence of dimethoxybenzene is mainly due to the predominance of the catalytic reaction, which at 50° is largely unaffected by oxygen. At lower temperatures (39°), the catalytic reaction is slower and oxygen retardation can be observed (Figure 3). Retardation rather than inhibition in the latter cases is due to the low concentrations of oxygen dissolved and the relatively slow reaction with cuprous species under these conditions. We expect that oxidants which are capable of selective and efficient oxidation of cuprous species will truly inhibit the reaction in dimethoxybenzene.

Ligand Transfer with Bromide. Valeryl peroxide reacts with lithium bromide instantaneously at 40°, and very rapidly at 0° in acetonitrile solutions. Two
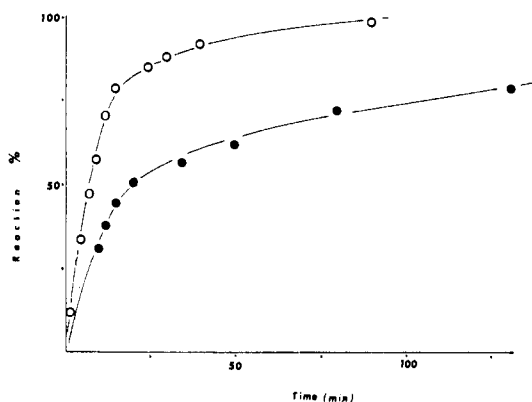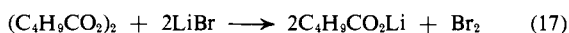
Figure 3. Retardation by oxygen of the copper chloride catalyzed decomposition of valeryl peroxide (9.9 × 10^{-2} M) in 70% v./v. acetic acid-m-dimethoxybenzene at 39°: O, no oxygen and ●, 7.7 mole % oxygen.
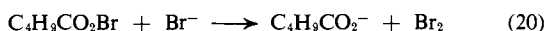
moles of lithium valerate and 1 mole of bromine are formed in a clean reaction (17) in which only trace

$$(C_4H_9CO_2)_2 + 2LiBr \longrightarrow 2C_4H_9CO_2Li + Br_2 \quad (17)$$

amounts of butyl bromide and carbon dioxide could be detected. In the presence of anisole a quantitative yield of bromoanisole (96% para) is formed. The stoichiometry of this reaction can be easily determined in acetonitrile by quenching the reaction and titrating the aqueous and anisole layers separately for lithium valerate and valeric acid with standard acid (eq. 18).

$$(C_4H_9CO_2)_2 + C_6H_5OCH_3 + LiBr \longrightarrow C_4H_9CO_2H +$$
$$C_4H_9CO_2Li + BrC_6H_4OCH_3 \quad (18)$$
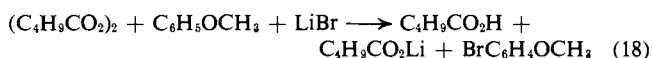
The reaction between valeryl peroxide and bromide is the same as that reported earlier with benzoyl peroxide.[19] It proceeds by a nucleophilic attack (eq. 19) on valeryl peroxide by bromide followed by a rapid transbromination (eq. 20) of the valeryl hypobromite.

$$(C_4H_9CO_2)_2 + Br^- \longrightarrow C_4H_9CO_2Br + C_4H_9CO_2^- \quad (19)$$

$$C_4H_9CO_2Br + Br^- \longrightarrow C_4H_9CO_2^- + Br_2 \quad (20)$$

The latter reaction (20) is more rapid than the trans-chlorination of valeryl hypochlorite (vide supra) which is consistent with the relative reactivity of chlorine and bromine toward nucleophiles.[29]
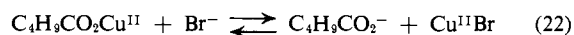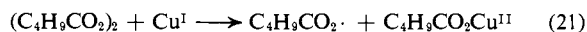
The immediate development of the orange color of bromine indicated that anisole was brominated in a step subsequent to the formation of bromine. We have been unable to obtain any other evidence for valeryl hypobromite, whose existence in excess bromide is apparently fleeting. Though acyl hypobromites postulated as intermediates in the Hunsdiecker reaction afford alkyl bromides and carbon dioxide in high yield,[20] the exchange reaction (20) in the presence of bromide apparently supersedes decarboxylation of this transient intermediate as a significant reaction.

The over-all rate of reaction between valeryl peroxide and cupric bromide at ∼50° is very fast. The reaction proceeds instantaneously, similar to the reaction of the peroxide with lithium bromide at equivalent concentrations. But in the former case, carbon dioxide (∼75%) and significant though minor amounts of butane (<3%) and butene-1 (<0.5%) are revealed,

(29) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y. 1962, p. 446; M. Eigen and K. Kustin, J. Am. Chem. Soc., 84, 1355 (1962).

and butyl bromide (70%) and valeric acid (after hydrolysis, 120%) are major products. Bromine could not be extracted from the reaction mixture.

Since the ionic reaction of valeryl peroxide with bromide yields no n-butyl bromide, we attribute its formation to a free-radical component during the course of decomposition. A chain sequence (reactions 14, and 21–23) involving copper species equivalent to that presented for the copper chloride catalyzed reactions can be considered. The lack of inhibition or retardation of this chain reaction by bromine, formed

$$(C_4H_9CO_2)_2 + Cu^I \longrightarrow C_4H_9CO_2\cdot + C_4H_9CO_2Cu^{II} \quad (21)$$

$$C_4H_9CO_2Cu^{II} + Br^- \rightleftharpoons C_4H_9CO_2^- + Cu^{II}Br \quad (22)$$

$$C_4H_9\cdot + Cu^{II}Br \longrightarrow C_4H_9Br + Cu^I \text{ etc.} \quad (23)$$

easily by the ionic reaction, and high yields of butyl bromide bespeak for the efficiency[30] of the radical-chain reaction. Furthermore, such an efficient chain mechanism can occur only if cuprous species are able to coexist with bromine in solution.

Although cuprous chloride is oxidized quantitatively by chlorine in acetic acid, the analogous reaction of cuprous bromide and bromine is reversible. In an elegant study employing measurements of absorption spectra and magnetic susceptibility of acetonitrile solutions containing cupric bromide, Schneider and Zelevsky[31,32] have shown that cuprous ion and bromine are formed quantitatively by eq. 24. In very slightly

$$2Cu^{II}Br_2 \rightleftharpoons Cu^I + Cu^{II}Br_4^- + 0.5Br_2 \quad (24)$$
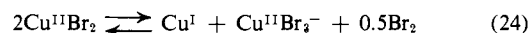
aqueous solutions, the equilibrium constant of the cuprous–cupric exchange with bromine given in eq. 25 was estimated to be 3 × 10^3. They have also shown

$$2Cu^{II} + 2Br^- \rightleftharpoons 2Cu^I + Br_2 \quad (25)$$
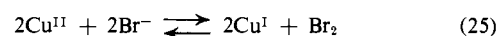
that the addition of excess bromine to an anhydrous acetonitrile solution of cuprous ion has a second-order effect in diminishing the cuprous concentration due to equilibria such as eq. 26.

$$2Cu^IBr + 0.5Br_2 \rightleftharpoons Cu^I + Cu^{II}Br_4^- \quad (26)$$
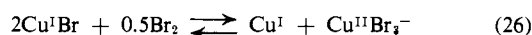
Thus, solutions of cupric bromide under these conditions are largely comprised of cuprous bromide and bromine. The presence of bromine is indicated by the facile bromination of anisole by "cupric bromide" solutions. Bromination with cupric bromide has been reported in a number of cases.[33] Water and dimethylformamide are known to stabilize the cupric state,[34] and Schneider and Zelevsky indeed have found the deleterious effect of these reagents on the cuprous–cupric bromide equilibrium. Chemically, the disproportionation of cupric bromide is even evident in acetic acid–water, acetonitrile–water, and acetonitrile–dimethylformamide solutions of composition chosen from Schneider and Zelevsky's result to promote no disproportionation of cupric bromide. Table I shows that significant amounts of butyl bromide are formed

(30) This could be due to the high concentration of cuprous ions in the system (vide infra).
(31) W. Schneider and A. von Zelevsky, Helv. Chim. Acta, 46, 1848 (1963).
(32) Cf. also J. Barnes and D. N. Hume, Inorg. Chem., 2, 444 (1963).
(33) (a) A. W. Fort, J. Org. Chem., 26, 765 (1961); (b) K. B. Doifode and M. G. Marathay, ibid., 29, 2025 (1964); (c) P. Kovacic and K. Davis, J. Am. Chem. Soc., 86, 427 (1964).
(34) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, J. Inorg. Nucl. Chem., 22, 279 (1961); Inorg. Chem., 1, 151 (1962).

Table II. The Reaction of Valeryl Peroxide with Bromide Salts at 50°

Solvent, %	Reactants Valeryl peroxide, M	Bromide, M	Products Valeric[a] acid, %	Butyl bromide, %	Bromine, %
CH$_3$CN, 100	0.27	LiBr, 0.75	180	O	76[b]
PhOCH$_3$–CH$_3$CN,[c] 50	0.14	LiBr, 0.46	195	d	0
PhOCH$_3$–HOAc, 33	0.14	LiBr, 0.80	200	e	0
CH$_3$CN, 100	0.17	CuBr$_2$, 0.13	121	75	..
HOAc–H$_2$O, 67	0.18	CuBr$_2$, 0.23	140	58	11[f]
CH$_3$CN–DMF, 83	0.092	CuBr$_2$, 0.13	122	82	8[f]
CH$_3$CN–H$_2$O, 83	0.074	CuBr$_2$, 0.13	146	73	7[f]
CH$_3$CN, 100	0.10	CuBr$_2$, 0.064	132	48	0
		CuCl$_2$, 0.060		35[g]	
CH$_3$CN,[h,i] 100	0.19	CuBr$_2$, 0.067	131	40	
		CuCl$_2$, 0.068		45[g]	i
CH$_3$CN,[h,k] 100	0.17	CuBr$_2$, 0.062	130	70	
		CuCl$_2$, 0.061		35[g]	i
CH$_3$CN,[h,l] 100	0.15	CuBr$_2$, 0.051	135	87	
		CuCl$_2$, 0.052		16[g]	i
CH$_3$CN,[h,m] 100	0.085	CuBr$_2$, 0.051	132	88	
		CuCl$_2$, 0.052		5[g]	i

[a] After hydrolysis. [b] By titration, does not include amount lost by vaporization. [c] 65°. [d] 95% bromoanisole. [e] 93% bromoanisole. [f] By extraction. [g] Butyl chloride. [h] Contains added bromine. [i] 2×10^{-3} M. [j] In these reactions the material balance exceeds 100% (~120%). Some of the butyl bromide undoubtedly arises from reaction with bromine. [k] 1.2×10^{-2} M. [l] 3.0×10^{-2} M. [m] 4.7×10^{-2} M.

in these mixed solvent systems. Butyl bromide formation is diagnostic of the copper bromide catalyzed reaction, and we take this as evidence that even under conditions in which *equilibrium* concentrations of cuprous ion and bromine from the disproportionation of cupric bromide are not observable by the techniques of Schneider and Zelevsky, there is always sufficient cuprous species present to catalyze the radical-chain decomposition of valeryl peroxide.

In the presence of a mixture of cupric bromide (0.06 M) and cupric chloride (0.06 M) under conditions in which the ionic chloride reaction is minor, both butyl bromide and chloride are formed (Table II). Since the identity and population of the various halocupric species under these condition is not known the relative ratio of ligand transfer from cupric bromide and chloride cannot be ascertained from the yields of butyl bromide and chloride, respectively. The effect of bromine on these reactions is shown in Figure 4. The retarding effect of bromine is only apparent at relatively high bromine concentrations and is consistent with the earlier discussion of the equilibria involved. In the absence of added halide, bromine was found to be an excellent inhibitor of the copper salt catalyzed reactions of peroxides. In those earlier studies,[2] the minor amounts of halogen introduced was insufficient to effect the equilibrium formation of cuprous species by equations 24 or 25.

Conclusions

The catalytic decomposition of diacyl peroxides by copper halides proceeds by a chain mechanism; cuprous halides reduce peroxides to oxy radicals and cupric halides. Alkyl radicals formed by fragmentation are oxidized by cupric halide to alkyl halides by ligand transfer, and cuprous species are regenerated. Aroyl peroxides are only slowly decomposed by cupric salts due to the relatively inefficient dissociation of aroyloxy radicals.

Diacyl peroxides as sources of alkyl radicals, for the study of ligand transfer oxidation with halides as elec-

tron mediators, are somewhat limited due to competing reactions involving nucleophilic attack by halide ion. In the presence of chloride, the products of the nucleo-
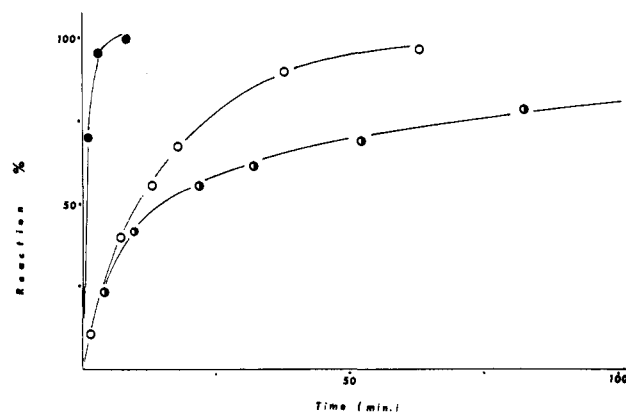

Figure 4. Decomposition of valeryl peroxide (1.7 × 10^{-1} M) by cupric bromide (6.2 × 10^{-2} M) and cupric chloride (6.2 × 10^{-2} M) in acetonitrile at 25°. Retardation by bromine: ●, none (<2 × 10^{-3} M); O, 1.2 × 10^{-2} M; and ◑, 3 × 10^{-2} M.

philic reaction (acyl hypochlorite and chlorine) oxidize the cuprous initiator and retard the chain decomposition of the peroxide by metal salt. This retardation can be removed by reagents, such as olefins and arenes, which effectively scavenge all electrophilic chlorinating species. Retardation due to the ionic reaction could not be entirely removed with bromide since the nucleophilic reaction itself is so facile. However, retardation of the catalytic reaction by bromide is not large in nonaqueous solutions since a high equilibrium concentration of cuprous salt is maintained in the presence of molecular bromine by disproportionation of cupric bromide.

Experimental

Materials. Cupric bromide (CuBr$_2$) was Baker Analyzed. Cupric chloride (CuCl$_2$·2H$_2$O), lithium

bromide (LiBr), and lithium chloride (LiCl) were Mallinckrodt A.R. grade. Cupric chloride anhydrous was prepared from the dihydrate by heating (100°) in a rotary evaporator. Ferric bromide anhydrous (FeBr$_3$) was Fisher purified grade. Toluene was Mallinckrodt A.R. grade. Anisole was Fisher certified reagent. Acetonitrile was Fisher certified distilled over phosphorus pentoxide. Acetic acid was DuPont glacial. N,N-Dimethylformamide was Eastman White Label. n-Valeryl chloride was Eastman White Label redistilled before use and checked for absence of isomers by conversion of a sample to methyl ester and gas chromatography (diethylene glycol succinate (DEGS) at 80°; shown to be greater than 99.5% pure).

n-Valeryl Peroxide. To a cooled (−10°) mixture of 158 ml. (2 moles) of pyridine and 50 ml. of ether, 62.5 ml. (0.55 mole) of 30% hydrogen peroxide was added dropwise without allowing the temperature to exceed 10°. One mole of the acid chloride was then added dropwise keeping the heterogeneous reaction mixture well agitated at −5° to −10°. The stirring was continued at 0° for 2 additional hr. After neutralizing with chilled, dilute (∼10%) sulfuric acid, the reaction mixture was extracted twice with ether and pentane and washed with dilute sulfuric acid, aqueous sodium carbonate, and distilled water (below 0°). The extract was then dried over anhydrous sodium sulfate and the solvent was evaporated by a rotary evaporator at ice-bath temperatures. The colorless peroxide (∼90% yield) was determined by titration to be greater than 99% pure. The peroxidic doublet at 5.52 and 5.62 μ was observed in the infrared spectrum, uncontaminated by other carboxylic adulterants (∼5.85 μ).

Decompositions. General Procedure. A solution (20–30 ml.) of the desired metal salts was added to a 50-ml. reaction flask equipped with an 8-mm. side arm, flushed with nitrogen, and the side arm was then stoppered with self-sealing rubber caps. The peroxide solution was added through the side arm, and the reaction was run in a thermostated bath. The evolved gases were collected over mercury in gas burets. In those runs containing only cupric bromide in acetonitrile or cupric chloride in acetic acid, a reverse procedure was followed and the solution of cupric halide was added to a weighed amount of peroxide dissolved in the appropriate solvent contained in the reaction flask. The latter was done for procedural reasons only, and the order of addition of peroxide and metal salt had no effect on the results.

Analysis. Butane, butene-1, and CO$_2$ were identified by gas chromatography (g.c.) on a 15-ft. column of 30% Dowtherm on firebrick and also on a 20-ft. column of 30% silver nitrate-benzyl cyanide on Chromosorb P.

The reaction solutions were made to known volumes and aliquots were used for analysis by g.c. An internal standard method was employed on an Aerograph Hy-Fi with a hydrogen flame detector. For determination of valeric acid, butyric acid marker was added to an aliquot of the crude reaction mixture, which was then analyzed on a 6-ft. column of terephthalic acid-20% Carbowax 4000 on Chromosorb W (butyric acid 7 min., valeric acid 10.5 min. at 155°, 10 p.s.i.). Neutral reaction solutions in acetonitrile were acidified to liberate acids from the salts before analysis. n-Butyl bromide and n-amyl bromide were used as markers for n-butyl chloride and butyl bromide, respectively. The reaction mixture with the marker was extracted into hexane and washed free of acids before being used for analysis on a 12-ft. column of bentone 34 and didecyl phthalate on Chromosorb W (n-butyl chloride 5.5 min., n-butyl bromide 9.5 min., and n-amyl bromide 19 min. at 100°, 10 p.s.i.). Hexane extraction did not introduce errors in the analysis and yielded the same results as those in which the crude reaction mixture was used. The former was preferred since the carboxylic acids were long retained on the column. p-Chloroanisole was used as marker for bromoanisole analysis on 1-m. diethylene glycol succinate (p-chloroanisole 7 min. and p-bromoanisole 12.5 min. at 120°, 12 p.s.i.). In the absence of copper salts, particularly in the decomposition of valeryl peroxide with lithium bromide in acetonitrile-anisole solutions, the reaction mixture could be separated into an organic and an aqueous phase by adding excess water. The aqueous layer was titrated with standard hydrochloric acid for lithium valerate (pH meter). The organic layer contained free valeric acid and bromoanisole which could be determined by gas chromatography.