Indolylpotassium.—A solution of 5.0 g of indole in 20 ml of THF was slowly added to 2 g of molten potassium in 40 ml of refluxing THF. The solution was refluxed for an additional 12 hr. With HMPT the reaction was complete in 30–60 min at room temperature.

Exchange Studies.—The indolyl metal derivative was prepared as above except that an excess of indole was utilized. The relative amounts of indole and its salt present in solution were determined by integrating the 3- and N-hydrogen resonances in the nmr.

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I. Ligand Transfer of Halides (Cl, Br, I) and Pseudohalides (SCN, N_3, CN) from Copper(II) to Alkyl Radicals

C. L. Jenkins and J. K. Kochi*

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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The ligand transfer oxidation of alkyl radicals by a variety of copper(II) halides (X = Cl, Br, I) and copper(II) pseudohalides (X = SCN, N_3, CN) is described: $n\text{-}C_4H_9\cdot + Cu^{II}X \longrightarrow n\text{-}C_4H_9X + Cu^I$. Alkyl radicals are generated during the copper-catalyzed reaction of diacyl peroxides in the presence of $Cu^{II}X$. Initiation of the chain process by copper(I) depends on whether the copper(II) halide or pseudohalide undergoes disproportionation in solution. In the absence of disproportionation, the deliberate addition of catalytic amounts of copper(I) allows the catalytic process to be carried out at 0°, and deleterious side reactions involving nucleophilic attack on the peroxide by halide or pseudohalide are minimized. *n*-Butyl radicals formed under these conditions from valeryl peroxide are efficiently trapped by $Cu^{II}X$ to form *n*-butyl chloride, bromide, iodide, thiocyanate, azide, and cyanide in good yields. Other competing reactions of *n*-butyl radicals are not important under most conditions.

Oxidation–reduction reactions of free radicals constitute important steps in a number of organic reactions catalyzed by metal complexes.[1] The oxidation of alkyl radicals by metal complexes has been classified into two categories which have been described as electron transfer[1,2] and ligand transfer.[1,3] In the latter, the ligand X associated with the metal complex MX_n is transferred to the alkyl radical R· during the oxidation process (eq 1). The transfer of chlorine and bromine from

$$R\cdot + M^{+n}X_n \longrightarrow RX + M^{+n-1}X_{n-1} \qquad (1)$$

copper(II) complexes to *n*-butyl radicals was reported earlier.[3] The study of these elementary processes depends on a general, reliable, and unequivocal method of generating alkyl radicals.

The decomposition of diacyl peroxides are induced by a variety of copper(II) complexes and the stoichiometry can be deliberately altered. For example, the copper-catalyzed decomposition of valeryl peroxide in the presence of cupric chloride is given by eq 2. The

$$(n\text{-}BuCO_2)_2 + Cl^- \xrightarrow{Cu^{II}} n\text{-}BuCl + CO_2 + n\text{-}BuCO_2^- \qquad (2)^4$$

mechanism of reaction 2 includes a step involving the efficient ligand transfer (eq 5, X = Cl) of chlorine from copper(II) chloride to *n*-butyl radicals as shown by the radical chain process (eq 3–5). In the earlier study[3] the

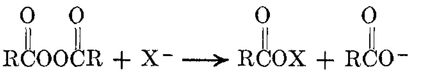
$$(n\text{-}BuCO_2)_2 + Cu^I \longrightarrow n\text{-}BuCO_2Cu^{II} + n\text{-}Bu\cdot + CO_2 \qquad (3)^5$$

$$n\text{-}BuCO_2Cu^{II} + X^- \rightleftharpoons n\text{-}BuCO_2^- + Cu^{II}X \qquad (4)$$

$$n\text{-}Bu\cdot + Cu^{II}X \longrightarrow n\text{-}BuX + Cu^I\text{, etc.} \qquad (5)$$

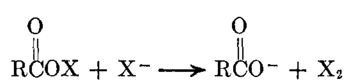
reaction between valeryl peroxide and cupric chloride was carried out at 55° by using catalytic amounts of copper(II) chloride. The induction period was attributed to the formation of butyl radicals by the limiting homolysis (eq 6) of the peroxide, followed by the production of the copper(I) initiator (eq 5). There are two limitations to this procedure as a general method: (a) the competing heterolytic rearrangement of the peroxide[6] and (b) the nucleophilic attack on the peroxide by ionic chloride (eq 7, X = Cl).[7] The latter is

$$(n\text{-}BuCO_2)_2 \xrightarrow{\Delta} 2n\text{-}Bu\cdot + 2CO_2 \qquad (6)$$



$$R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R + X^- \longrightarrow R\overset{O}{\overset{\|}{C}}OX + R\overset{O}{\overset{\|}{C}}O^- \qquad (7)$$

particularly deleterious because the acyl hypochlorite



$$R\overset{O}{\overset{\|}{C}}OX + X^- \longrightarrow R\overset{O}{\overset{\|}{C}}O^- + X_2 \qquad (8)$$

and molecular chlorine formed as intermediates oxidize copper(I) and inhibit the chain process (eq 8).[3] Both side reactions increase in importance at higher temperatures.

In this report we wish to describe an improved method of generating alkyl radicals in high yields from diacyl peroxides at low temperatures. The efficient generation of alkyl radicals provides the opportunity to examine the ligand transfer of a variety of halogens (chlo-

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[1] J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966); J. K. Kochi, *Science*, **155**, 3761 (1967); J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970); J. K. Kochi and J. M. Anderson, *ibid.*, **92**, 2450 (1970); J. K. Kochi, R. A. Sheldon, and S. S. Lande, *Tetrahedron*, **25**, 1197 (1969); J. Kumamoto, H. E. De LaMare, and F. F. Rust, *J. Amer. Chem. Soc.*, **82**, 1935 (1960); M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964); F. Minisci, *et al.*, *Tetrahedron Lett.*, 2531, 3163 (1965), and related papers.

[2] J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.*, **87**, 4855 (1965); J. K. Kochi and A. Bemis, *ibid.*, **90**, 4038 (1968); J. K. Kochi, A. Bemis, and C. L. Jenkins, *ibid.*, **90**, 4616 (1968).

[3] J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).

[4] In this and subsequent equations no attempt will be made to include all the coordination around copper or the charge on the ion unless pertinent to the discussion.

[5] The valeryloxy radical may be an intermediate in this step.

[6] F. D. Greene, H. S. Stein, C. C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2081 (1964); S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind. (London)*, 1964 (1965); J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

[7] J. K. Kochi, B. M. Graybill, and M. Kruz, *ibid.*, **86**, 5257 (1964); N. J. Bunce and D. D. Tanner, *ibid.*, **91**, 6096 (1969).

TABLE I

DETERMINATION OF THE KINETIC CHAIN LENGTH IN THE COPPER(I)-CATALYZED REACTION OF VALERYL PEROXIDE AND CUPRIC CHLORIDE AT 0°[a]

Reactants, mmol				Products			Minimum[b] chain length
$CuCl_2$	LiCl	Valeryl peroxide	Added CuCl	CO_2, %	Recovered CuCl	% CuCl lost	
0	0	0	0.607		0.607	0	
0.162	1.00	1.00	0.607	100	0.540	11	14
0.145	1.00	1.00	0.607	100	0.544	10	15
0.210	1.00	1.00	0.607	100	0.611	0	>50[c]

[a] Carried out in HOAc–CH_3CN 60:40 by volume. [b] Minimum chain length = peroxide decomposed/CuCl lost. [c] Assuming copper(I) analysis valid to ±2%.

TABLE II

REACTION OF VALERYL PEROXIDE WITH CUPRIC CHLORIDE CATALYZED BY COPPER(I) AT 0°[a]

			Reactants, *M*			Products, mol %		
Run	Solvent	Temp, °C	Valeryl peroxide	$CuCl_2$	LiCl	CO_2	BuCl	$BuCO_2H$
1	CH_3CN	Room temp	0.040	0.020	0	99	90	N.D.[f]
2	CH_3CN	Room temp	0.040	0.040	0	98	91	
3	CH_3CN	Room temp	0.040	0.040	0	100	91	N.D.[f]
4	CH_3CN	Room temp	0.040	0.080	0	102	97	N.D.[f]
5	CH_3CN	Room temp	0.040	0.120	0	102	98	N.D.[f]
6	HOAc–CH_3CN	0	0.020	0.0100	0.020	100	95	104
7	(60:40 v/v)	0	0.020	0.0028	0.041	100	89	112
8	(60:40 v/v)	0	0.020	0.0013	0.026	100	89	117
9	(60:40 v/v)	0	0.020	0.0030	0.094	100	87	112
10	(60:40 v/v)	0	0.020	0.0034	0.020	103	89	111
11	(60:40 v/v)	0	0.020	0.0160	0.020	108	89	110
12	(60:40 v/v)	0	0.020	0	0.020	100	93	114
13	(60:40 v/v)	0	0.020	0.020[b]	0	100	82[c]	99
14	(60:40 v/v)	0	0.020	0.020[b]	0	100	81[d]	99
15	Pyridine[g]	0	0.020	0.033	0.033	100	70[e]	99
16	Pyridine[g]	0	0.020	0.025	0.017	100	65[e]	99

[a] All reactions catalyzed by 0.008 *M* Cu^ICl. [b] 2 equiv of pyridine added. [c] 4.4% butene-1. [d] 2% butene-1. [e] Trace (<1%) of butene-1. [f] N.D. = not determined. [g] Pyridine–HOAc–CH_3CN in 50:30:20 v/v.

rine, bromine, and iodine) as well as pseudohalogens (cyanide, thiocyanate, and azide) to alkyl radicals. We also wish to show that a common chain mechanism (eq 3–5) applies generally to the reactions, diacyl peroxides with a variety of halides and pseudohalides in the presence of copper complexes.

Results and Discussion

Ligand Transfer of Chlorine.—Solutions of copper(I) chloride in acetonitrile could be conveniently prepared[8] simply by reacting either copper(II) or commercial copper(I) chloride with an excess of powdered copper metal according to eq 9. These solutions were

$$Cu^{II}Cl_2 + Cu^0 \rightleftharpoons 2Cu^ICl \qquad (9)$$

colorless and could be kept indefinitely in the absence of oxygen. The concentration of copper(I) was determined by oxidation with ferric chloride followed by titration with standard dichromate or ceric solutions.

The catalytic reaction between valeryl peroxide and cupric chloride was readily initiated by copper(I) chloride. The reaction under these conditions proceeded with little or no induction period and was essentially complete in 15–30 min at 0°. In a typical procedure a solution of 0.020 *M* valeryl peroxide, 0.010 *M* cupric chloride, and 0.020 *M* lithium chloride in 60–40% acetic acid–acetonitrile was flushed with helium to remove oxygen. A catalytic amount of cuprous chloride was added and the course of the reaction monitored by the evolution of carbon dioxide.

The amount of copper(I) remaining at the end of the reaction was compared with the copper(I) charged initially (Table I). The high recovery (90–100%) indicated that the side reactions generating acyl hypochlorite (eq 7, X = Cl) and chlorine (eq 8) by nucleophilic displacement were unimportant under these conditions. Further, a minimum kinetic chain length for the reaction could be computed by determining the amount of peroxide decomposed relative to the copper(I) lost.

The stoichiometry of the reaction between valeryl peroxide and cupric chloride catalyzed by copper salts was given by eq 2′ and examined under various conditions listed in Table II.

$$(n\text{-}C_4H_9CO_2)_2 + Cl^- \xrightarrow{Cu^{I,II}} n\text{-}C_4H_9Cl + CO_2 + n\text{-}C_4H_9CO_2^- \qquad (2')$$

The results show that the efficiency of chlorine transfer to *n*-butyl radicals (eq 5) was not seriously impeded over a range of copper(II) concentrations (runs 1–5). Moreover, less than 0.1% *n*-butane was formed in all of these reactions, indicating no significant attack on solvent. The reaction in acetonitrile was also highly efficient in the utilization of chloride (runs 1, 10, 12). In the presence of acetic acid or pyridine, however, more chloride was required relative to copper for high conversion to *n*-butyl chloride (*cf.* runs 6–12). Otherwise, butene-1 was also produced (*cf.* runs 13–16), albeit in low yields. The latter no doubt was attributable to equilibria such as eq 10 which produced copper(II)

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(8) *Cf.* J. K. Kochi and A. Bemis, *Tetrahedron*, **24**, 5099 (1968).

TABLE III
CATALYZED REACTION OF VALERYL PEROXIDE WITH CUPRIC BROMIDE

Run	Solvent	Temp, °C	Reactants, *M*: Valeryl Peroxide	Reactants, *M*: $CuBr_2$	Reactants, *M*: LiBr	Products, mol %: CO_2	Products, mol %: BuBr	Products, mol %: $BuCO_2H$
18	$HOAc-CH_3CN$	0	0.020[a]	0.0068	0.020	100	86	
19	(60:40 v/v)	0	0.020[a]	0.0064	0.020	100	90	97
20	(60:40 v/v)	0	0.020[a]	0.034	0.020	100	91	
21	(60:40 v/v)	0	0.020[a]	0.018	0.020	100	84	100
22	CH_3CN	Room temp	0.040[b]	0.040	0	93	85	N.D.[c]
23	CH_3CN	Room temp	0.040[b]	0.040	0	93	88	N.D.[c]
24	CH_3CN	Room temp	0.040[b]	0.040	0.040	90	88	N.D.[c]
25	CH_3CN	Room temp	0.040[b]	0.040	0.040	94	82	N.D.[c]

[a] Reaction catalyzed by addition of 0.0040 *M* cuprous bromide. [b] Peroxide added to cupric bromide solution. [c] N.D. = not determined.

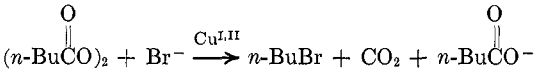
$$Cu^{II}Cl + HOAc \rightleftharpoons Cu^{II}OAc + HCl \qquad (10)$$

acetate or pyridinate species capable of electron transfer oxidation of *n*-butyl radicals to butene-1 (eq 11).[2]

$$Cu^{II}OAc + CH_3CH_2CH_2CH_2\cdot \longrightarrow CH_3CH_2CH{=}CH_2 + HOAc + Cu^{I}, \text{ etc.} \qquad (11)$$

The formation of valerate in yields higher than that required by eq 2 was particularly noticeable at low concentrations of copper (runs 7–12). Under these conditions the competition from nucleophilic displacement (eq 7) leading to valerate (eq 8) increased in importance, a complication which was supported by the observation of a diminished kinetic chain length for the reaction (Table I).

Ligand Transfer of Bromine.—Copper(I) bromide could be prepared from copper(II) bromide and copper metal by a procedure analogous to the production of copper(I) chloride. However, it was not possible to determine a kinetic chain length for the catalytic reaction between valeryl peroxide and bromide ion (eq 12) due to complications from the facile equilibria



$$(n\text{-Bu}\overset{O}{\overset{\|}{C}}O)_2 + Br^- \xrightarrow{Cu^{I,II}} n\text{-BuBr} + CO_2 + n\text{-Bu}\overset{O}{\overset{\|}{C}}O^- \qquad (12)$$

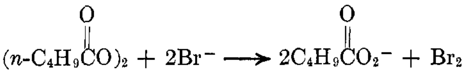
extant between copper(I) and copper(II) species. The net equilibrium given in eq 13 favors a small but discrete concentration of copper(I) and bromine in acetonitrile solutions.[9] Such an equilibrium complicated the analysis of copper(I), the titer of which varied with the rate of titration.

$$2Cu^{II}Br_2 \rightleftharpoons 2Cu^{I}Br + Br_2 \qquad (13)$$

The copper-catalyzed reaction 12 between valeryl peroxide and cupric bromide was facilitated by the addition of small amounts of copper(I) at 0° as shown by runs 18–21 in Table III. The reaction also proceeded at room temperature in the absence of *added* copper(I) bromide (runs 22–25) due to the presence of equilibrium 13. The latter also contributed to the observed *retardation* of reaction 12 by added molecular bromine. Thus, the behavior of bromide was in marked contrast to chloride, since reaction 2 was *inhibited* completely by molecular chlorine. Under these conditions the analogous equilibrium 14 involving copper(I) and molecular chlorine lay entirely toward copper(II) chloride.

$$2Cu^{I}Cl + Cl_2 \longrightarrow 2Cu^{II}Cl_2 \qquad (14)$$

In the presence of copper, reaction 12 occurred despite the facile nucleophilic displacement by ionic bromide (eq 15) observed in the absence of copper.[10] The high



$$(n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}O)_2 + 2Br^- \longrightarrow 2C_4H_9\overset{O}{\overset{\|}{C}}O_2^- + Br_2 \qquad (15)$$

yields of carbon dioxide shown in Table III indicated that the nucleophilic reaction 15 was readily overwhelmed by the catalytic reaction 12, especially in the presence of added copper(I) bromide (see runs 18–21). We favor a chain mechanism similar to that postulated for the analogous chloride reactions (eq 3–5), in which ligand transfer of bromine forms an important link in the catalytic cycle (eq 16). The alternative possibility

$$n\text{-Bu}\cdot + Cu^{II}Br \longrightarrow n\text{-BuBr} + Cu^{I}, \text{ etc.} \qquad (16)$$

that bromine was the transfer agent (eq 17) was disfavored by the observation that alkyl bromides are generally formed from alkyl radicals under these conditions by a process kinetically first order in copper(II) bromide.[11]

$$n\text{-Bu}\cdot + Br_2 \longrightarrow n\text{-BuBr} + Br\cdot, \text{ etc.} \qquad (17)$$

Ligand Transfer of Iodine.—Copper(II) iodide is thermodynamically unstable and cannot be prepared as such.[12] The addition of iodide to a solution of copper(II) salts led to an immediate reduction of cupric ion according to eq 18.

$$2Cu^{II} + 5I^- \longrightarrow 2Cu^{I}I + I_3^- \qquad (18)$$

Copper(I) iodide was soluble in acetonitrile and afforded a pale yellow solution. Upon addition of valeryl peroxide to a deaerated solution of copper(I) iodide, an immediate deep green solution was formed with the spontaneous liberation of carbon dioxide. However, the yields of carbon dioxide (Table IV) seldom exceeded 60%, despite the rapid and complete decomposition of valeryl peroxide. The formation of *n*-butyl iodide and carbon dioxide always in equimolar amounts was in agreement with reaction 19 and in accord with

$$(n\text{-BuCO}_2)_2 + I^- \xrightarrow{Cu^{I,II}} n\text{-BuI} + CO_2 + n\text{-BuCO}_2^- \qquad (19)$$

expectations based on analogous reactions of chloride (eq 2) and bromide (eq 12). Products such as *n*-butane and butene-1 were absent.

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[9] W. Schneider and A. von Zelevsky, *Helv. Chim. Acta*, **46**, 1848 (1963); D. I. Hilden and N. W. Gregory, *J. Phys. Chem.*, **75**, 592 (1971).

[10] Unpublished results. Compare ref 3.

[11] C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3103 (1971).

[12] D. F. Morris, *J. Phys. Chem. Solids*, **7**, 214 (1958).

TABLE IV

REACTION OF VALERYL PEROXIDE WITH CUPROUS IODIDE[a]

Run	Reactants, M CuI	KI	$(BuCO_2)_2$	Products, mol % BuI	$BuCO_2H$	Temp, °C
26	0.040	0	0.040	63	143	Room temp
27	0.040	0	0.040	62	135	Room temp
28	0.080	0	0.040	62	129	Room temp
29	0.080	0	0.040	63	127	Room temp
30	0.040	0.040	0.040	52	127	Room temp
31	0.040	0.040	0.040	52	130	Room temp
32	0.040	0	0.040	57	122	0
33	0.040	0	0.040	63	121	0
34	0.040	0	0.040	57	128	0
35	0.080	0	0.040	57	128	0
36	0	0.080	0.040	26	161	0
37	0	0.080	0.040	23	168	0

[a] All reactions carried out in 100% CH_3CN.

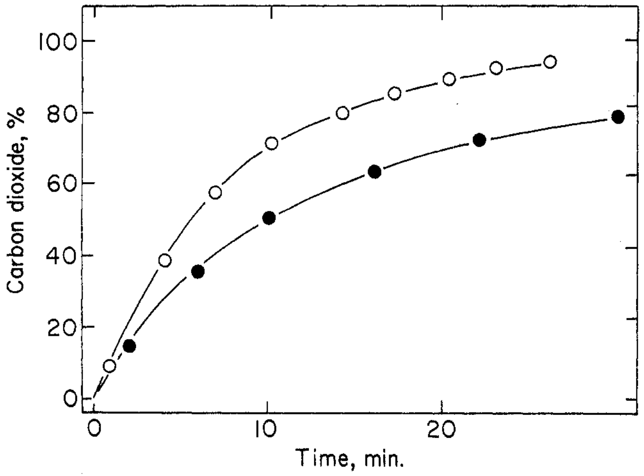

Figure 1.—Reaction of 0.040 M valeryl peroxide with, ○, 0.040 copper(II) thiocyanate and 0.080 M potassium thiocyanate; ●, 0.020 copper(II) thiocyanate and 0.020 M potassium thiocyanate.

The reaction between valeryl peroxide and ionic iodide (eq 20) was itself, however, very rapid in the *absence of copper* complexes, no doubt due to facile nucleophilic attack by iodide.[13] Furthermore, the quantitative liberation of iodine (no carbon dioxide) constitutes the basis for the widely accepted procedure for the analytical determination of peroxides (eq 21).[14] A large excess of ionic iodide is generally used in this analysis. When *stoichiometric* amounts of valeryl peroxide and iodide were employed as shown in runs 36–37 of Table IV, small but significant amounts of n-butyl iodide and carbon dioxide (and less than 2 mol of valerate) were also produced. The acyl hypoiodite intermediate is longer lived under these conditions and homolysis would have led to n-butyl iodide much as in the Hunsdiecker reaction (eq 22, 23).[15]

$$(n\text{-BuCO}_2)_2 + 2\text{I}^- \longrightarrow 2n\text{-BuCO}_2^- + \text{I}_2 \qquad (20)$$

$$(n\text{-BuCO}_2)_2 + \text{I}^- \longrightarrow n\text{-BuCO}_2\text{I} + n\text{-BuCO}_2^- \qquad (21)$$

$$n\text{-BuCO}_2\text{I} \longrightarrow n\text{-Bu}\cdot + \text{CO}_2 + \text{I}\cdot \qquad (22)$$

$$n\text{-Bu}\cdot + \text{I}_2 \text{ (or } n\text{-BuCO}_2\text{I)} \longrightarrow n\text{-BuI} + \text{I}\cdot \text{ (or } n\text{-BuCO}_2\cdot) \qquad (23)$$

Competition from reaction 20 accounted for the less than quantitative yields of n-butyl iodide and carbon dioxide generated in the copper-catalyzed reaction of valeryl peroxide and iodide. The yields of valerate (Table IV) in excess of that given by eq 19 are also in accord with this conclusion. Nonetheless, the relatively high yields of n-butyl iodide and carbon dioxide, despite the facility of reaction 20, attests to the rapidity of the copper-catalyzed reaction 19. We infer that a process similar to that postulated earlier (*e.g.*, eq 3–4) for chloride and bromide is also applicable to iodide. The relevant oxidation step (24) in this reaction involves ligand transfer of iodine from a copper(II) complex. The metastable copper(II) iodide apparently is sufficiently long-lived under these conditions (particularly in the absence of excess iodide) to minimize complications from disproportionation (eq 18).

$$(n\text{-BuCO}_2)_2 + \text{Cu}^{\text{I}}\text{I} \longrightarrow n\text{-Bu}\cdot + \text{CO}_2 + \text{Cu}^{\text{II}}(\text{O}_2\text{CBu})\text{I}$$
$$n\text{-Bu}\cdot + \text{Cu}^{\text{II}}(\text{O}_2\text{CBu})\text{I} \longrightarrow n\text{-BuI} + \text{Cu}^{\text{I}}(\text{O}_2\text{CBu}) \qquad (24)$$

Ligand Transfer of Thiocyanate.—Copper(II) thiocyanate or isothiocyanate was not very soluble in aqueous or organic media presumably due to its polymeric structure in the solid. However, when it was mixed with 2 equiv of potassium thiocyanate in acetonitrile, a deep red solution resulted. The visible absorption spectrum of this solution revealed a strong band at 450 nm with an extinction coefficient of 1.3 × 10^4 M^{-1} cm^{-1} which we tentatively assign to the tetrathiocyanatocopper(II) species.[16]

$$\text{Cu}^{\text{II}}(\text{NCS})_2 + 2\text{KSCN} \rightleftharpoons \text{Cu}^{\text{II}}(\text{NCS})_4^{-2}\, 2\text{K}^+ \qquad (25)$$

Carbon dioxide evolved *immediately* when a solution of valeryl peroxide was added at 0° to a deaerated solution of copper(II) thiocyanate and potassium thiocyanate in acetonitrile as shown in Figure 1. The stoichiometry of the reaction was represented by eq 26

$$(n\text{-BuCO}_2)_2 + \text{SCN}^- \xrightarrow{\text{Cu}^{\text{I,II}}} n\text{-BuSCN} + \text{CO}_2 + n\text{-BuCO}_2^- \qquad (26)$$

as shown in Table V.

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[13] J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience New York, N. Y., 1962, p 67 ff.

[14] L. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

[15] R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956); F. R. Jensen, L. H. Gale, and S. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968).

[16] (a) W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969). (b) See also J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968); R. Barbucci, *et al.*, *J. Chem. Soc. A*, 1775 (1969); B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 254 (1964); J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

Table V

Reaction of Valeryl Peroxide with Cupric Thiocyanate[a]

	Reactants, M			Products, mol %[c]				
Run	Valeryl peroxide	$Cu(NCS)_2$	Ligand[b] added	CO_2			BuSCN	$BuCO_2H$
38	0.040	0.040[d]	0	107	3	*e*	103	109
39	0.040	0.040	0.080 A	103	2	*e*	100	110
40	0.040	0.020	0.040 A	104	5.5	*e*	94	110
41	0.040	0.010	0.020 A	100	18.4	*e*	75	98
42	0.080	0.010	0.020 A	176[g]	73	*e*	99	*f*
43	0.040	0.040[d]	0.248 B	110	7	*e*	88	*f*
44	0.040	0.040[d]	0.040 C	108	5	*e*	65	*f*
45	0.040	0.040[d]	0.048 C	113	22	2.5	69	*f*
46	0.040	0.040[d]	0.084 C	99	*e*	14.6	65	*f*
47	0.040	0.040	0.080 D	99	11	*e*	83	*f*
48	0.040	0	0.080 A	3	*e*	*e*		194

[a] Reactions carried out in acetonitrile at 0°. [b] A = KSCN, B = pyridine, C = $P(Ph)_3$, D = ethylenediamine. [c] Based on 1 mmol of peroxide (0.040 M). [d] Heterogeneous. [e] Too small to measure. [f] Not determined. [g] Products determined after 7 hr.

The reaction between valeryl peroxide and ionic thiocyanate in the absence of copper complexes produced only thiocyanogen according to eq 27.[17] Valerate (2

$$(n\text{-}BuCO_2)_2 + 2SCN^- \longrightarrow 2n\text{-}BuCO_2^- + (SCN)_2 \quad (27)$$

equiv) but no carbon dioxide or other products derived from the butyl moiety were found. The formation of thiocyanogen according to reaction 27 is analogous to the formation of bromine and chlorine from ionic bromide (eq 15) and chloride (eq 7 and 8, X = Cl), respectively, under the same conditions.[3,7] The second-order rate constant at 0° was $1.36 \times 10^{-4}\ M^{-1}\ sec^{-1}$ for the reaction given in eq 27 which was first order in peroxide and thiocyanate.[17] Simple calculations showed that the nucleophilic displacement (eq 27) could have accounted at most for 1–2% of the decomposition of the peroxide in the time (30 min) that the reaction induced by copper (eq 26) was complete. This conclusion was also supported by the stoichiometric relationship among products given in Table V.

We postulate that the reaction (26) between valeryl peroxide and copper(II) thiocyanate is a further example of the chain decomposition cited earlier for the halogens (eq 3–5). However, the spontaneous reaction between valeryl peroxide and thiocyanate without the deliberate addition of copper(I) species led us to infer that thiocyanate induced the rapid equilibration of copper(II) and copper(I) species in acetonitrile, similar to that shown by bromide (eq 13) in a reaction such as eq 28.

$$2Cu^{II}(NCS)_4^{-2} \rightleftharpoons 2Cu^{I}(NCS)_3^{-2} + (SCN)_2 \quad (28)$$

Direct evidence for a dynamic equilibrium such as 28 is difficult to obtain as it is with bromide.[9] The presence of such an equilibrium is shown indirectly in Figure 2 by the effect of thiocyanogen on the rate of reaction 26. The larger retardation induced by successive increases in added thiocyanogen is consistent with the lowering of the concentration of the copper(I) initiator as demanded by the principle of mass action. A similar retardation could be achieved by the addition of molecular chlorine, an effect which is equivalent to the oxidation of thiocyanate (eq 29). On the other hand,

$$Cl_2 + 2SCN^- \longrightarrow 2Cl^- + (SCN)_2 \quad (29)$$

molecular oxygen is incapable of oxidizing either copper(I) thiocyanate or ionic thiocyanate at a measureable rate under these conditions. The slight retardation shown (Figure 2) in the presence of oxygen is attributable to competition between copper(II) thiocyanate and oxygen for n-butyl radicals. Reaction with oxygen represents a chain termination process whereas the reaction with copper(II) thiocyanate is a key step in

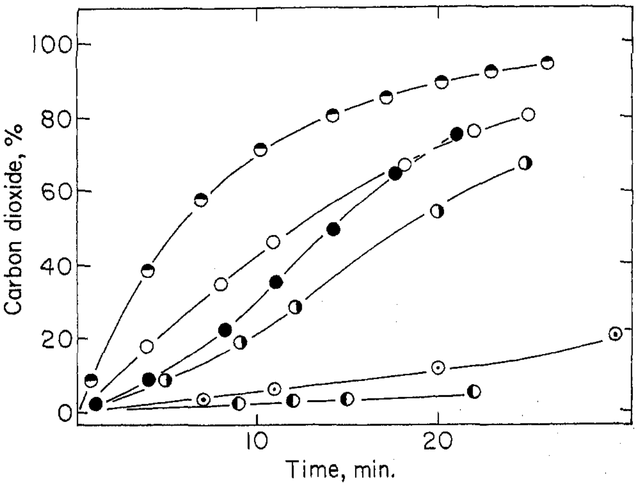

Figure 2.—Retardation of the reaction of 0.04 M valeryl peroxide with 0.080 M potassium thiocyanate and 0.040 M copper(II) thiocyanate: ◒, none; ○, 5 mmol of oxygen; ●, 0.2 mequiv of chlorine; ◑, 0.12 mequiv of thiocyanogen; ⊙, 0.25 mequiv of thiocyanogen; ◐, 1.0 mequiv of chlorine.

$$n\text{-}Bu\cdot + O_2 \longrightarrow n\text{-}BuOO\cdot,\ \text{etc.} \quad (30)$$

$$n\text{-}Bu\cdot + Cu^{II}NCS \longrightarrow n\text{-}BuSCN + Cu^{I},\ \text{etc.} \quad (31)$$

the catalytic cycle represented by eq 3–5 (X = SCN). The low yields of n-butyl thiocyanate (40–50%) obtained relative to the carbon dioxide liberated under these conditions follow from the competitive scavenging of n-butyl radicals by oxygen (eq 30, 31).

The ligand transfer of thiocyanate from copper(II) to n-butyl radicals was especially interesting, since there existed the possibility of obtaining two isomeric products. Studies carried out on the structure of copper(II) thiocyanate and a variety of other copper(II) complexes containing thiocyanate indicate that the preferred bonding of the thiocyanato ligand to copper(II) is through nitrogen.[16,18] Thus, ligand transfer

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[17] C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3053 (1971).

[18] R. H. Toeniskoetter and S. Solomon, *Inorg. Chem.*, **7**, 617 (1968); R. N. Raymond and F. Basolo, *ibid.*, **5**, 1632 (1966); R. C. Slade, *et al.*, *J. Chem. Soc. A*, 61 (1968); J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

TABLE VI
REACTION OF VALERYL PEROXIDE WITH CUPRIC AZIDE[a]

Reactants, *M*			Products, mol %				
$Cu(N_3)_2$	NaN_3	Valeryl peroxide	CO_2			BuN_3	$BuCO_2H$
0.0031	0.019	0.019	100	21	19	52	98
0.0070	0.018	0.018	101	*b*	*b*	51	77
0.0132	0.015	0.015	101	21	28	49	104
0.0074	0.015	0.015	110	21	30	50	91
0.0064	0.016	0.016	106	19	30	47	93

[a] Reactions carried out in 60% HOAc–40% CH_3CN at 0°; catalyzed by addition of 1 equiv of cuprous acetate relative to peroxide over a 5-hr period. [b] Not determined.

oxidation of *n*-butyl radicals by an inner-sphere mechanism (bridge activated complex) may well involve attack at the remote sulfur site of the ligand (eq 32).

$$n\text{-Bu}\cdot + \text{Cu}^{II}\text{NCS} \longrightarrow [\text{Bu}\cdots\text{SCN}\cdots\text{Cu}^{II,I}]^{\ddagger} \longrightarrow \text{BuSCN} + \text{Cu}^{I} \quad (32)$$

On the other hand, *n*-butyl isothiocyanate may have been expected from a ligand transfer oxidation proceeding *via* an outer-sphere mechanism to generate a butyl cationoid intermediate (eq 33).[19] *n*-Butyl thiocyanate was the only product observed under a variety of conditions listed in Table V. In order to determine the stability of *n*-butyl isothiocyanate, 1.08 mmol was added to a mixture of 2.0 mmol of potassium thiocyanate, 1.0 mmol of copper(II) thiocyanate, and 1.0 mmol of valeryl peroxide in 25 ml of acetonitrile. After reaction, 1.05 mmol of *n*-butyl isothiocyanate was detected together with 0.93 mmol of *n*-butyl thiocyanate.

$$n\text{-Bu}\cdot + \text{Cu}^{II}\text{NCS} \longrightarrow [\text{Cu}^{I}\text{NCS} + \text{Bu}^{+}] \longrightarrow [\text{BuNCS} + \text{BuSCN}] + \text{Cu}^{I} \quad (33)$$

n-Butyl thiocyanate was clearly the isomer resulting from ligand transfer of thiocyanate from copper(II) to *n*-butyl radicals under kinetically controlled conditions. The interpretation given above in eq 32 and 33, however, is not without ambiguity. Thus, copper(II) complexes are highly labile and isomerization of the complex

$$\text{Cu}^{II}\text{NCS} \rightleftharpoons \text{Cu}^{II}\text{SCN} \quad (34)$$

(eq 34) seriously complicates the nature and concentration of the copper(II) species extant in solution.

The copper(II) species also change during the course of the reaction between valeryl peroxide and thiocyanate. In particular, the concentration of valerate builds up according to eq (26) and would be further involved in equilibria such as eq 35.

$$\text{Cu}^{II}\text{NCS} + \text{BuCO}_2^{-} \rightleftharpoons \text{Cu}^{II}(\text{NCS})(\text{O}_2\text{CBu}) \rightleftharpoons \text{Cu}^{II}\text{O}_2\text{CBu} + \text{SCN}^{-} \quad (35)$$

The importance of carboxylatocopper(II) species in the formation of butene-1 from *n*-butyl radicals was demonstrated earlier in the catalytic cycle for peroxide decomposition by electron transfer processes.[3] The utilization of thiocyanate to produce *n*-butyl thiocyanate was not complete, since run 41 (Table V) shows that 20% of the *n*-butyl radicals was diverted by reaction 36.

$n\text{-Bu}\cdot + \text{Cu}^{II}\text{O}_2\text{CBu} \longrightarrow$  $+ \text{BuCO}_2\text{H} + \text{Cu}^{I}$, etc. (36)

The importance of reaction 36 increased at lower concentrations of thiocyanate (run 42) and decreased with higher concentrations but did not disappear even in the presence of a twofold excess of thiocyanate (run 39). It

$$(n\text{-BuCO}_2)_2 + \text{Cu}^{I}\text{SCN} \longrightarrow n\text{-Bu}\cdot + \text{CO}_2 + \text{Cu}^{II}(\text{NCS})(\text{O}_2\text{C-}n\text{-Bu})$$

is also possible, of course, that a mixed ligand species, such as $Cu^{II}(NCS)(O_2CBu)$ formed in the initial step, would afford both *n*-butyl thiocyanate and butene-1. However, thiocyanate transfer seems to be favored, judging by the high yields of *n*-butyl thiocyanate obtained in the absence of added ionic thiocyanate (run 38). Other ligands such as pyridine, triphenylphosphine, and ethylenediamine also appeared to promote electron transfer oxidation (runs 43–47), although the interpretation is ambiguous due to the heterogeneity of the reaction.

Ligand Transfer of Azide.—Copper(II) azide is quite unstable in the pure and dry state,[20] and it was therefore handled as a solution in a mixture of acetic acid and acetonitrile (60:40 v/v). A solution of valeryl peroxide was stable in the presence of sodium azide. Copper(I) acetate could be used to initiate the reaction between valeryl peroxide and azide at 0°. However, the kinetic chain length for the reaction was apparently short since additional copper(I) had to be added periodically in order to effect complete decomposition of the peroxide. Excellent yields of carbon dioxide and valerate were obtained under these conditions (Table VI), but only 50% of the *n*-butyl radicals were converted to *n*-butyl azide. The stoichiometry of the partial reaction can be written as shown in eq 37. The remainder

$$(n\text{-BuCO}_2)_2 + \text{N}_3^{-} \xrightarrow{\text{Cu}^{I,II}} n\text{-BuN}_3 + \text{CO}_2 + \text{BuCO}_2^{-} \quad (37)$$

of the *n*-butyl radicals was converted to *n*-butane and butene-1. The latter no doubt arose from electron transfer oxidation of *n*-butyl radicals (eq 36),[3] in favorable competition with the azide transfer step (eq 38) involved in the catalytic cycle (eq 3–5, X = N_3) represented for reaction 37.[20b] The relatively large amounts of copper(I) required for these reactions also indicated that the propagation step 38 was not so facile as that studied with other ligands. Butane may have arisen from *n*-butyl radicals by either attack on solvent or reduction by copper(I) followed by protonation.

$$n\text{-Bu}\cdot + \text{Cu}^{II}\text{N}_3 \longrightarrow n\text{-BuN}_3 + \text{Cu}^{I}, \text{etc.} \quad (38)$$

Ligand Transfer of Cyanide.—The simple salt of copper(II) cyanide is thermodynamically unstable and has not been characterized. Upon addition of cyanide to a solution of copper(II) complex, an oxidation–reduc-

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[19] *Cf.* A. Ceccon, I. Papa, and A. Fava, *J. Amer. Chem. Soc.*, **88**, 4643 (1966); *ibid.*, **91**, 5547 (1969).

[20] (a) M. Straumanis and A. Circulis, *Z. Anorg. Alleg. Chem.*, **251**, 315 (1943); (b) see also V. Gutmann and O. Leitman, *Monatsh. Chem.*, **97**, 926 (1966), for copper(II) azides.

Table VII
Reaction of Valeryl Peroxide with Cyanide Salts[a]

Reactants, *M*			Products, mol %			
Copper salt[b]	KCN	Valeryl peroxide			BuCN	$BuCO_2H$
0.020 A	0	0.020	3.1	44.5	8.0	103
0.015 A	0	0.020	3.9	41.5	8.5	98
0.021 A	0	0.020	4.5	37.0	14.4	98
0.025 A	0	0.020	3.3	41.0	10.4	97
0.020 B	0	0.020	*c*	0	60.5	121
0.030 B	0	0.020	*c*	0	63.4	120
0.021 B	0	0.020	*c*	0	66.0	118
0.040 C	0	0.040	0	0	54.0	129
0.040 C	0	0.040	0	0	57.0	126
0.040 C	0.040	0.040	0	0	46.0	130
0.040 C	0.040	0.040	0	0	55.0	130
0	0.080	0.040	0	0	0	1.85
0	0.080	0.040	0	0	0	1.80

[a] All reactions carried out at room temperature. [b] A = $Cu_3(NH_3)_4(CN)_4$ in 60% HOAc–CH_3CN (heterogeneous) (registry no. 12403-36-0); B = $Cu_3(en)_2(CN)_4$ in 60% CH_3CN–H_2O (registry no. 12524-89-9); C = $[Ph_3PCH_2Ph]Cu(CN)_2$ in 100% CH_3CN (registry no. 31361-66-7). [c] Trace.

tion reaction[21] analogous to those described for copper(II) iodide, bromide, and thiocyanate ensues (eq 39).

$$2Cu^{II} + 4CN^- \rightleftharpoons 2Cu^ICN + (CN)_2 \qquad (39)$$

At equilibrium copper(I) is heavily favored as it is with the iodide analog.

Several mixed valence complexes containing copper(II), -(I), and cyanide have been prepared and characterized. Although most of them are insoluble in organic solvents, we found that $Cu_3(en)_2(CN)_4$[22] could be employed in a mixture of acetonitrile and water (60:40 v/v). This complex can be formulated as $Cu^{II}(en)_2[Cu^I(CN)_2]_2$.

Carbon dioxide was liberated spontaneously when valeryl peroxide was added to a solution of $Cu_3(en)_2(CN)_4$ in aqueous acetonitrile at room temperature. The reaction between ionic cyanide and valeryl peroxide under these conditions was negligible. The highest yield of butyl cyanide that we were able to obtain was 65% using several copper(II) cyanide complexes given in Table VII.

In analogy with the previous studies involving iodide, a mixture consisting of copper(I) cyanide, alkali metal cyanide, and valeryl peroxide could have provided a route to alkyl cyanides. Such mixtures, however, were generally insoluble. By complexing the anionic copper(I) cyanide $[Cu^I(CN)_2^-]$ with the large triphenylbenzylphosphonium cation, a salt $[Ph_3PCH_2Ph][Cu(CN)_2]$ was obtained which was soluble in anhydrous acetonitrile. This salt reacted rapidly with valeryl peroxide by liberating carbon dioxide but produced *n*-butyl cyanide in an approximate yield of only 50%.

The stoichiometry of the reaction to produce *n*-butyl cyanide from valeryl peroxide can be written as shown in eq 40. Since cyanide transfer to *n*-butyl radicals

$$(n\text{-BuCO}_2)_2 + CN^- \xrightarrow{Cu^{I,II}} n\text{-BuCN} + CO_2 + n\text{-BuCO}_2^- \qquad (40)$$

only occurred in the presence of copper salts, we infer from earlier studies that a chain process (eq 3–5, X = CN) also pertained in which the ligand transfer step can be written as shown in eq 41. Only one of the two

$$n\text{-Bu}\cdot + Cu^{II}CN \longrightarrow n\text{-BuCN} + Cu^I \qquad (41)$$

possible isomeric products, alkyl cyanide, was obtained from the reaction of *n*-butyl radicals with these copper(II) cyanides. *n*-Butyl isocyanide could be readily detected in trace quantities due to its pungent odor or by gas chromatographic analysis. Control experiments showed that *n*-butyl isocyanide was stable under conditions of the reaction and was not a product.

Summary.—The copper-catalyzed reaction of valeryl peroxide with various halides and pseudohalides proceeds according to eq 42. The same general mech-

$$(n\text{-BuCO}_2)_2 + X^- \xrightarrow{Cu^{I,II}} n\text{-BuX} + CO_2 + n\text{-BuCO}_2^- \qquad (42)$$

anism applies to chloride, bromide, iodide, thiocyanate, azide, and cyanide. The relevant steps in the chain processes involve the production of butyl radicals by one-equivalent reduction of the peroxide (eq 3). The butyl derivative BuX is formed in a subsequent oxidation of the *n*-butyl radicals by transfer of halogen or pseudohalogen from the copper(II) halide or pseudohalide, respectively (eq 5). Qualitatively, the rates of ligand transfer from copper(II) to *n*-butyl radicals can be determined by the importance of side products and generally decrease in the order iodide > bromide > chloride > thiocyanate > azide > cyanide. The presence initially of copper(I), by deliberate addition or by disproportionation of the copper(II) complex *in situ*, allows for the catalytic reaction to be carried out at 0° and side reactions of the peroxidic precursor are minimized.

Experimental Section

Materials.—Common materials and reagents were obtained from commercial sources.

Cupric Thiocyanate.—Cupric sulfate pentahydrate (0.5 mol) was dissolved in 750 ml of water and potassium thiocyanate (1.0 mol) was added slowly with rapid stirring under an argon blanket. The black precipitate was filtered and washed twice with ethanol and three times with ethyl ether. The material was then dried overnight in a vacuum oven at 20 mm and 50° giving a 63% yield of $Cu(NCS)_2$. The copper content was determined by electrolysis. *Anal.* Calcd for $Cu(NCS)_2$: Cu, 35.4. Found: Cu, 37.4.

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[21] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 896; S. K. Tobia and M. F. El-Shahat, *J. Chem. Soc. A*, 2444 (1968).

[22] (a) D. Cooper and R. A. Plane, *Inorg. Chem.*, **5**, 1677 (1966); (b) compare also A. Longo and T. Buch, *ibid.*, **6**, 556 (1967).

Cupric Azide.—Cupric sulfate was dissolved in water and allowed to react with 2 equiv of potassium azide to yield a dark precipitate. The solid was filtered, washed several times with water, and then, while the material was still moist, dissolved in a mixture consisting of 60% acetic acid and 40% acetonitrile. The thoroughly dried material detonated upon scratching with a metal spatula.

Triphenylbenzylphosphonium Dicyanatocopper(I).—Cuprous cyanide was dissolved in water containing 1 equiv of potassium cyanide, and 1 equiv of triphenylphosphonium chloride was added. The white precipitate was filtered and recrystallized from 70% ethanol-water at 0°. The white crystalline $Ph_3PCH_2PhCu(CN)_2$ was finally collected and dried in a vacuum desiccator. *Anal.* Calcd for $C_{27}H_{22}CuN_2P$: C, 69.15; H, 4.69; N, 5.97. Found: C, 70.04; H, 5.10; N, 5.53.

Preparation of $Cu_3(NH_3)_4(CN)_4$ and $Cu_3(en)_2(CN)_4$.—The method of Cooper and Plane[22a] was used to prepare $Cu_3(en)_2(CN)_4$ and $Cu_3(NH_3)_4(CN)_4$.

Preparation of Thiocyanogen.—A solution of thiocyanogen in 75 ml of acetonitrile was prepared by reacting 0.0187 mol of bromine in 50 ml of acetonitrile with 0.0218 mol of lead thiocyanate in 25 ml of acetonitrile. The unreacted $Pb(NCS)_2$ and $PbBr_2$ were removed by filtration. The concentration of thiocyanogen in solution was determined by iodometric titration[11] to be 0.246 *f*.

n-**Butylisonitrile** was prepared by the dehydration of *n*-butylformamide with phosphorus oxychloride in pyridine. *n*-Butyl azide was previously prepared by P. Mocadlo.

Solutions of copper(I) chloride, bromide, and acetate in acetonitrile were prepared by simply reacting the copper(II) salt and copper metal in a closed deaerated vessel fitted with a rubber septum. The resulting copper(I) solution was standardized by reaction with an excess of acidic ferric chloride solution and then titrating the ferrous produced with cerium(IV) to a ferrous phenanthroline endpoint.

Copper(I) iodide was prepared by the addition of potassium iodide (5 equiv) in water to an aqueous solution of copper(II) sulfate (2 equiv). The resulting precipitate of cuprous iodide was filtered and washed several times with water and finally with chloroform. The material was then dried in a vacuum oven at 50°.

Valeryl peroxide was prepared by reacting 88.5 g of valeryl chloride (0.74 mol) in 118 ml of pyridine (1.48 mol) with 56 ml of 30% H_2O_2 (0.495 mol) and 25 ml of diethyl ether. The reaction was worked up at 0° as follows. 10% sulfuric acid was added slowly with cooling until the mixture was neutral and was separated, and the aqueous layer was extracted with pentane. The organic layer and extract were combined and washed three times with 10% sulfuric acid, three times with saturated sodium bicarbonate, and then three times with distilled water. The material was dried over sodium sulfate and the solvent was removed at 0° on a rotary evaporator using first with a water aspirator and finally a vacuum pump. The peroxide was 97+% pure as checked by iodine titration.[14]

General Procedure A.—A standard solution (1.0 mmol in 25 ml) of valeryl peroxide was prepared in 60% acetic acid–40% acetonitrile and added by means of a pipet to the solution containing the copper(II) salt and corresponding alkali salt in 25 ml of 60% acetic acid–40% acetonitrile, in a 125-ml flask. The flask was then capped with a rubber septum and flushed with nitrogen for 15 min. The reactions were stirred magnetically and maintained at room temperature, or 0°, by means of an ice bath. The reactions were then initiated by the corresponding curpous species or cuprous acetate in a solution of acetonitrile. The reactions were monitored continuously by following the evolution of carbon dioxide by gas chromatography using ethane as an internal standard and were run until quantitative carbon dioxide was obtained.

General Procedure B.—In those cases which required no initiation, the following procedure was used. The appropriate amount of copper species and alkali salt was taken from a stock solution or weighed into a 125-ml flask and the volume was then adjusted to 20 ml. The vessel was capped with a rubber septum and flushed for 15 min with a stream of helium. The reactions were then stirred magnetically and maintained at room temperature, or at 0°, by means of an ice bath. From a stock solution of 5 *M* valeryl peroxide in acetonitrile (5 *M*) 5 ml of solution was added by means of a syringe. Reactions were then run until carbon dioxide evolution ceased.

Analytical Procedures. Gases.—Carbon dioxide, butane, and butene-1 were analyzed by gas chromatography using the internal standard method described elsewhere.[3]

Liquids.—All liquid products were also analyzed by the internal standard method involving gas chromatography. In most cases an aliquot of the reaction mixture was extracted and mixed with a known amount of marker solution. The solution was then flooded with water and extracted with pentane or ethyl ether and washed several times with water and dilute 10% sodium bicarbonate solution. This procedure removed the inorganic salts and acetic acid when present. Valeric acid was analyzed also by gas chromatography by the internal standard method; this analysis gave results to within ±10%.

Registry No.—Valeryl peroxide, 925-19-9; cupric chloride, 7447-39-4; cupric bromide, 7789-45-9; cuprous iodide, 7681-65-4; copper(II) thiocyanate, 15192-76-4; cupric azide, 14215-30-6.

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