Solvolytic Routes *via* Alkylcopper Intermediates in the Electron-Transfer Oxidation of Alkyl Radicals

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Abstract: A metastable alkylcopper species, previously shown to be an intermediate in electron-transfer oxidations of alkyl radicals by copper(II) acetate, is capable of producing highly unencumbered carbonium ions. Simply replacing the acetate ligand on the copper nucleus with the weakly coordinating perchlorate or trifluoromethanesulfonate ligands results in a dramatic enhancement of oxidative solvolysis. Even primary alkyl radicals such as *n*-butyl and isobutyl as well as methyl radicals are readily converted to carbonium ions which resemble in reactivity those generated only by solvolysis in highly ionizing and poorly nucleophilic solvents or in the demercuration of alkylmercurinium ions. The analogy to solvolysis is carried further by the susceptibility of the alkylcopper species to a type of "special salt effect" induced by lithium perchlorate and a unique solvent sensitivity when cyclobutyl radicals are oxidized by copper(II) acetate. Oxidative displacement involving an intramolecular decomposition of the alkylcopper intermediate is also presented to describe the oxidation of methyl radicals.

The oxidation of alkyl radicals by metal complexes has been classified into two categories which have been described as electron-transfer and ligand-transfer processes.[1] The mechanistic interpretation of the *ligand-transfer* oxidation of alkyl radicals by copper(II) halides and pseudohalides is described in the following article.[2] Alkyl radicals are also efficiently oxidized by other copper(II) complexes, particularly those containing oxygen or nitrogen ligands such as acetate, bipyridine, or phenanthroline, by a process which has been described as *electron transfer*, largely on the basis that alkenes R(-H) and alkyl derivatives (R-OAc) formed as products could have arisen from carbonium ion precursors. However, subsequent experiments showed[3] that a metastable alkylcopper species is the actual intermediate which is partitioned to alkene and alkyl derivatives by two competing routes described as oxidative elimination and oxidative solvolysis, respectively.[4] There are three questions of especial relevance in connection with the mechanism of electron-transfer oxidation of alkyl radicals which merit further study. These problems are related to the nature of (a) the metastable alkylcopper intermediate, (b) the competition between oxidative elimination and oxidative solvolysis, and (c) the reactivity of carbonium ions formed as intermediates in oxidative solvolysis. In this paper we focus our attention on the variation of the copper(II) oxidant, by examining the role of the oxyanion (*i.e.*, the counterion), the solvent, and neutral or special salt effects. The 5-hexenyl radical as well as the homoallylic (cyclobutyl, cyclopropylmethyl, and allylcarbinyl) radicals serve as probes for these studies. Finally, the test for carbonium ions as intermediates in electron-transfer oxidation is carried out with simple alkyl moieties such as methyl, *n*-propyl, *n*-, *sec*-, and isobutyl radicals.

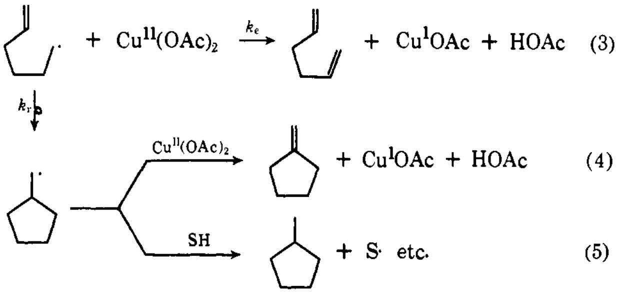
The examination of these elementary reactions has been greatly facilitated by the development of a catalytic method for the decomposition of peroxides.[5] For example, the copper-catalyzed reaction of diacyl peroxides is described by the following mechanism, in which the propagation step (2) is relevant to the oxidation of alkyl radicals described in this study.

$$RCO_2O_2CR + Cu^I \longrightarrow RCO_2Cu^{II} + R\cdot + CO_2 \qquad (1)$$

$$R\cdot + Cu^{II} \longrightarrow R_{ox} + Cu^I, \text{ etc.} \qquad (2)$$

Results

The Rate of Oxidation of 5-Hexenyl Radical by Copper(II) Acetate. The first-order cyclization of the 5-hexenyl radical proceeds with a rate constant estimated to be 1 × 10^5 sec^{-1} at 25°.[6] Cyclopentylmethyl and 5-hexenyl radicals were independently generated from cyclopentyl acetyl and 6-heptenoyl peroxide, respectively, by the catalytic procedure utilizing copper acetate as described previously.[5] The oxidation of 5-hexenyl radicals by copper(II) acetate under these conditions may be represented by the following kinetic scheme. Since the isomerization is irreversible,[6b] the ratio of 1,5-hexadiene to methylenecyclopentane and methylcyclopentane may be expressed as



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[1] J. K. Kochi, *Rec. Chem. Progr.*, 27, 207 (1966); *Science*, 155, 3761 (1967).

[2] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 94, 856 (1972).

[3] (a) J. K. Kochi, A. Bemis, and C. L. Jenkins, *ibid.*, 90, 4616 (1968); (b) *ibid.*, 90, 4038 (1968).

[4] The term "electron transfer" is, thus, no longer truly descriptive and even somewhat misleading for the mechanism of oxidation of alkyl radicals by copper(II) acetate, but it is retained here for convenience. An alternative formulation is given in the following paper.[2]

[5] (a) J. K. Kochi, *J. Amer. Chem. Soc.*, 85, 1958 (1963); (b) J. K. Kochi and A. Bemis, *Tetrahedron*, 24, 5099 (1968).

[6] (a) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 90, 7047 (1968); (b) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, 85, 3483 (1963); C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, 88, 5363 (1966); G. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1968); J. Eastham, *Chem. Commun.*, 139 (1969); J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, 92, 137 (1970); J. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 140 (1971).

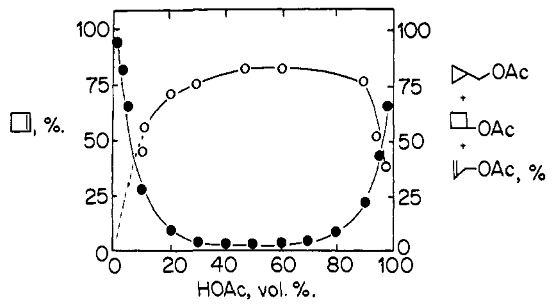
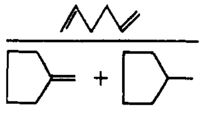
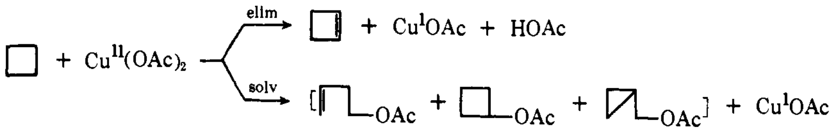


Figure 1. The effect of solvent composition (acetic acid-acetonitrile) on the yields of cyclobutene (●) and homoallylic acetates (○) from the oxidation of cyclobutyl radicals by copper(II) acetate.



$$= \frac{k_e}{k_r}[\mathrm{Cu^{II}(OAc)_2}] \qquad (6)$$

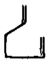
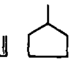
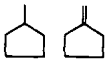
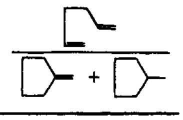
The formation of methylcyclopentane was insignificant except at very low concentrations of copper(II) acetate. Other products such as 5-hexenyl, cyclopenylmethyl, and cyclohexyl acetates as well as cyclohexene and cyclohexane were absent (<0.5%). The data in Table I were plotted according to eq 6 after correction for the monomer-dimer equilibrium ($K = 5.1 \times 10^{-2}\ M$) of copper acetate.[7] The value for k_e of $1.2 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ obtained in this manner compared reasonably well with the value of $k_e = 3.1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ for the oxidation of *n*-butyl radicals under slightly different conditions using isobutyraldehyde as a hydrogen donor.[7b]



(7)

(8)

Table I. Reaction of 5-Hexenyl and Cyclopentylmethyl Radicals with Copper(II) Acetate[a]

Reactants, M			Products, mol %			
Cu(OAc)$_2$	Peroxide[b]	CO$_2$				
0.008	0.022 H	94	4.5	6.8	68	0.058
0.020	0.022 H	98	9.5	4.2	84	0.11
0.040	0.022 H	102	12	2.4	75	0.15
0.080	0.022 H	100	17	0.9	64	0.26
0.120	0.022 H	100	29	*c*	69	0.43
0.138	0.022 H	96	25	*c*	54	0.46
0.147	0.022 H	95	23	*c*	49	0.49
0.040	0.020 C	94	0	4.7	77	0
0.080	0.020 C	93	0	3.7	79	0

[a] All reactions were run in HOAc-CH_3CN (60:40) and catalyzed by 0.010 M cuprous acetate at room temperature. [b] H = 6-heptenoyl peroxide, C = cyclopentyl acetyl peroxide. [c] Too small to measure.

Solvent Effects on the Oxidation of Cyclobutyl Radicals by Copper(II) Acetate. Cyclobutyl radicals were chosen for further study since oxidative elimination and oxidative solvolysis are highly competitive in this system.[4,8] Thus, the electron-transfer oxidation of cyclobutyl radicals by copper(II) acetate affords cyclobutene by oxidative elimination (eq 7) and a mixture of isomeric C_4H_7 acetates by oxidative solvolysis (eq 8). A previous study[3] showed that the mixture of allylcarbinyl, cyclobutyl, and cyclopropylmethyl acetates (88%) was the major product of oxidation from the catalyzed decomposition of cyclobutanecarbonyl peroxide in a solvent consisting of 60 vol % acetic acid-acetonitrile. On the other hand, the copper(II) oxidation of cyclobutyl radicals derived from the lead tetraacetate decarboxylation of cyclobutanecarboxylic acid afforded mainly cyclobutene (78%) in a solution consisting mostly of benzene.[8] Replacement of benzene by acetonitrile, moreover, reversed the distribution to that more akin to that shown in eq 8. Thus, the results obtained by variation of the solvent were independent of the source of cyclobutyl radicals. Other solvents exerted similar effects in varying degrees.[8b]

The dichotomy between oxidative elimination and oxidative solvolysis was examined further in the range of solvents consisting of nearly *pure* acetic acid to nearly *pure* acetonitrile. The cyclobutyl radical was generated during the copper-catalyzed decomposition of cyclobutanecarbonyl peroxide initiated at 0° by copper(I) acetate. The results summarized in Figure 1 showed that cyclobutene was indeed the major product and formed in yields up to 85% when either acetic acid or acetonitrile was the principal constituent of the solvent, and mixtures of C_4H_7 acetates were the major products in a broad intermediate mixture of solvents. The combined yields of cyclobutene and the mixture of C_4H_7 acetates remained relatively unchanged if sufficient acetic acid was present in the solvent. The composition of the mixture of isomeric acetates, consisting of 3% allylcarbinyl, 53% cyclobutyl, and 44% cyclopropylmethyl acetates, was also invariant under all conditions. Furthermore, it could be shown that each isomeric acetate as well as cyclobutene were stable under reaction conditions. The material balance made up of cyclobutene and the mixture of C_4H_7 acetates was not as complete in the region consisting mostly of acetonitrile. Under these circumstances the cationoid intermediate was, no doubt, trapped by other nucleophiles due to the limited availability of acetic acid. One such possibility is acetonitrile which has been shown to trap carbonium ions under similar conditions,[3] in a process reminiscent of the Ritter reaction.[9]

$$R^+ + CH_3CN \longrightarrow RNCCH_3^+,\ \text{etc.} \qquad (9)$$

Salt Effects on the Oxidation of Cyclobutyl Radicals by Copper(II) Acetate. The partitioning of the cyclobutyl moiety between oxidative elimination and oxidative solvolysis was also examined in the presence of

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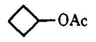
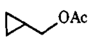
[7] (a) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, 4, 1527 (1965); (b) *J. Amer. Chem. Soc.*, 87, 4855 (1965); (c) see also A. T. A. Cheng and R. A. Howald, *Inorg. Chem.*, 7, 2100 (1968).

[8] (a) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 33, 83 (1968); (b) *ibid.*, 33, 2746 (1968); (c) *Tetrahedron*, 24, 2215 (1968).

[9] J. Ritter and P. Minieri, *J. Amer. Chem. Soc.*, 70, 4045, 4048 (1948); L. Miller and A. Hoffman, *ibid.*, 89, 593 (1967); Y. Pocker and D. Kevill, *ibid.*, 87, 4711 (1965).

Table II. Effect of Lithium Perchlorate on Oxidation of Cyclobutyl Radicals by Cupric Acetate[a]

		Products, mol %				% distr		
Solvent	LiClO$_4$, *M*	CO$_2$			C$_4$H$_7$OAc			
CH$_3$CN[b]	0	103	2.8	83[c]	2.9[d]	4	55	41
	0.004	101	2.5	84	8.0	3	53	44
	0.008	101	2.2	53	25	3	53	44
	0.020	102	2.0	19	38	3	53	44
	0.040	101	1.9	11	42	3	54	43
	0.080	87.5	1.8	5.0	30	4	55	41
	0.120	87.5	1.7	3.5	29	4	54	42
	0.180	100	1.7	4.2	37	4	55	41
	0.220	96.5	1.6	2.9	33	3	56	41
HOAc[g]	0	107	2.9	53[e]	15[f]	10	46	44
	0.004	100	3.0	50	22	8	47	45
	0.008	98.5	3.0	39	25	9	49	43
	0.014	98.5	3.1	32	36	8	47	45
	0.020	98.5	3.3	22	47	10	46	44
	0.040	104	3.2	9.6	56	7	48	45
	0.080	105	3.2	4.0	65	8	47	45
	0.120	104	3.2	2.7	69	8	47	45
	0.160	103	3.1	1.9	70	8	47	45
EtOH[h]	0	93	1.9	97				
	0.200	93	1.1	34	22	2	58	40
					20[i]	4	54	42

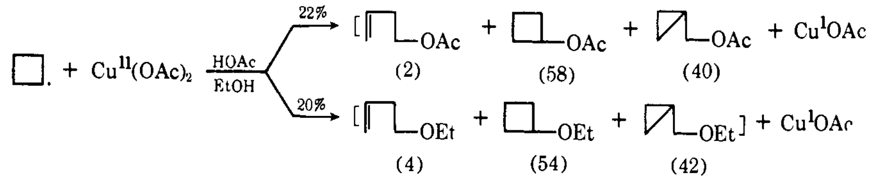
[a] Reactions carried out at room temperature; $Cu^{II}(OAc)_2 = 0.020$ *M;* $Cu^{I}(OAc) = 0.010$ *M;* cyclobutanecarbonyl peroxide = 0.040 *M.* [b] With 2% acetic acid. [c] In addition to 3.5% 1,3-butadiene. [d] In addition to 6.7% 1-cyclobutyl-3-acetoxybutene-1 and 2.1% 1-cyclobutyl-4-acetoxybutene-2. [e] 1% 1,3-butadiene. [f] 3% cyclobutylbutenyl acetates. [g] With 2% acetonitrile. [h] With 58% acetonitrile and 2% acetic acid. [i] Ethyl ethers.

added salts. The availability of salts for study was somewhat limited because salts such as alkali halides and pseudohalides react with copper(II) and a complete change in mechanism of oxidation would have occurred.[2,10]

Lithium perchlorate appeared to be well suited for these studies due to the weakly nucleophilic properties of the perchlorate ion. Furthermore, complexation with copper(II) acetate was relatively minor since lithium perchlorate had little or no effect on the visible absorption spectrum in the range of concentrations studied. Lithium perchlorate was also quite soluble in acetic acid and in acetonitrile over the concentrations employed.

The dramatic effect of small amounts of lithium perchlorate on the yield of cyclobutene is illustrated in Figure 2. The effect was especially pronounced in 98% acetic acid or 98% acetonitrile (Table II). The decrease in the yield of cyclobutene was reflected by a corresponding increase in the yield of the mixture of C$_4$H$_7$ acetates. Lithium perchlorate did not affect the stability of cyclobutene in this medium.

When the acetonitrile was diluted to 58 vol % by ethanol, the yield of cyclobutene was almost quantitative. The addition of lithium perchlorate to this medium also caused a decrease in the cyclobutene yield to 34%, although the magnitude was not as great as that observed in either 98% acetonitrile or acetic acid. Interestingly, the isomeric compositions of the mixture of C$_4$H$_7$ acetates and ethyl ethers were essentially the same (eq 10 and 11). The effects of tetramethylammonium tetrafluoroborate in acetonitrile and lithium acetate in acetic acid were also investigated (Table III). The addition of tetramethylammonium tetrafluoroborate induced no discernible change over the concentration range in which lithium perchlorate had its largest effect. Similarly, the addition of lithium acetate had little effect up to 0.18 *M*, and may have even caused a slight increase in the yield of cyclobutene. Although lithium perchlorate had a pronounced influence on the oxidation of cyclobutyl radicals by copper(II) acetate, it had no apparent effect on the oxidation of *n*-butyl radicals. The formation of butene-1 was unaffected by the addition of lithium perchlorate to the medium. Furthermore, no butyl acetate was found under any conditions.



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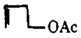
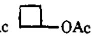
The Oxidation of Alkyl Radicals by Copper(II) Triflate and Perchlorate. The effects exerted by the solvent and added salt on the course of oxidation of the cyclobutyl radicals indicated that subtle changes around the copper(II) acetate strongly influenced the relative importance of oxidative elimination and oxidative solvolysis. Replacement of the acetato ligand itself, by this reasoning, should induce even larger and further changes in these pathways. In order to test this possibility, the oxidation of simple alkyl radicals was reinvestigated with copper(II) salts containing various anionic ligands. Acetato and trifluoromethanesulfonato (triflate) ligands, we shall show, represented the extremities of this change.

(10) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, 37, 3095 (1972).

Table III. Effect of Lithium Acetate, Tetramethylammonium Tetrafluoroborate, and Bipyridine on the Oxidation of Cyclobutyl Radicals with $Cu(OAc)_2$[a]

		Products, mol%								
HOAc,[b] vol %	Salt,[c] *M*	CO_2				C_4H_7-OAc	 distribution, %			C_8H_{13}-OAc[d]
98	0.020 A	100	4.6	75	3.3	13	10	43	47	9.0
98	0.100 A	95	5.1	72	2.4	13	12	42	46	7.4
98	0.140 A	101	5.4	75	2.2	13	12	43	45	7.2
2	0.012 B	97	*g*	83	2.3	*g*				*g*
98	0.18 A–0.045 P	94	11	38	0.9	35	27	32	41	2.5[f]
98	0 A–0.060 P	96	8.0	27	1.8	39	20	36	44	*g*
98	0 A–0.12 P	102	6.7	2.3	5.3	27	6	39	55	*g*

[a] Reaction carried out at room temperature; $Cu^{II}(OAc)_2$ = 0.020 *M*; $Cu^{I}(OAc)$ = 0.010 *M*; cyclobutanecarbonyl peroxide = 0.040 *M*. [b] Remainder acetonitrile. [c] A = LiOAc, B = $(CH_3)_4NBF_4$, P = bipyridine. [d] c-$C_4H_7C_4H_6OAc$. 3-OAc, 77%; 1-OAc, 23%. [f] 3-OAc, 41%. [g] Not determined.

The oxidation of *n*-butyl radicals derived from the catalytic decomposition of valeryl peroxide is presented in Table IV. Copper(II) acetate and trifluoroacetate oxidized *n*-butyl radicals to butene-1 only. Copper(II) nitrate showed no catalytic activity since the copper(I) initiator preferentially reacted with nitrate. The copper(II) salts of tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-), and triflate ($CF_3SO_3^-$), under the same conditions, oxidized the *n*-butyl radicals to a mixture of products given in Table IV. Not only were the rearranged *cis*- and *trans*-butene-2 formed under these conditions, but a sizable fraction of the butyl radicals was converted to *n*- and *sec*-butyl acetates.

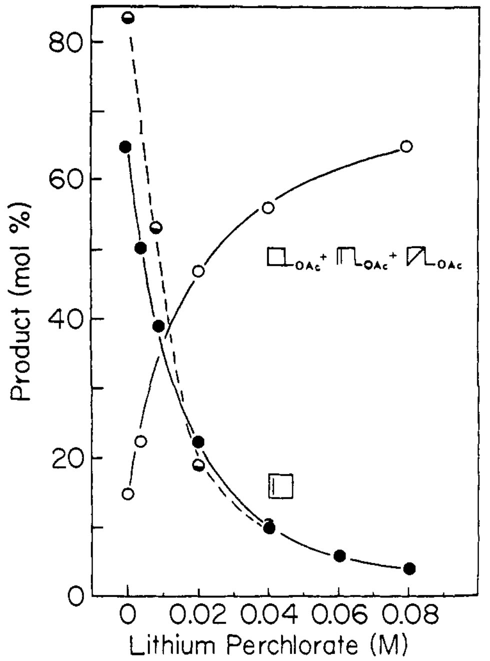
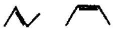
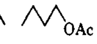
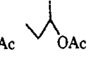


Figure 2. The "special salt" effect by lithium perchlorate on the relative rates of oxidative elimination and solvolysis of cyclobutyl radicals by cupric acetate: formation of cyclobutene in acetonitrile (◒) and acetic acid (●); homoallylic acetates (○) in acetic acid solutions.

Table IV. Reaction of *n*-Butyl Radicals with Various Copper(II) Salts in HOAc[a]

		Products, mol%					
$Cu^{II}Y_2$	CO_2						
$Cu(OAc)_2$[b]	104	2	94	0	0	0	0
$Cu(OAc)_2$[c]	89	1	76	0	0	6.8[e]	3.0[e]
$Cu(O_2CCF_3)_2$[c]	95	0.5	87	0	0	4.4[e]	0.8[e]
$Cu(NO_3)_2$[c]	2						
$Cu(BF_4)_2$[c]	89	*d*	21	6.4	2.8	22	23
$Cu(ClO_4)_2$[c]	93	*d*	22	7.7	4.4	25	23
$Cu(O_3SCF_3)_2$[c]	93	*d*	24	6.5	3.6	36	19

[a] In solutions containing 0.042 *M* valeryl peroxide and 0.040 *M* copper(II) salts at 25°. [b] Initiated by 0.0050 *M* CuOAc. [c] Initiated by 0.0035 *M* CuO_3SCF_3. [d] Absent. [e] From Cu(I) triflate used as initiator.

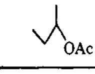
The extensive rearrangement of the *n*-butyl moiety during oxidation by copper(II) triflate was practically the same in acetic acid solutions as it was in acetonitrile. The yield of butene-1 was lower in acetonitrile as shown in Table V and the butyl acetates were replaced by products derived from solvent (compare eq 9). No significant amount of trifluoromethanesulfonic acid was present under these conditions. Since it is a potent acid catalyst, the butenes as well as the esters were subjected to solutions of trifluoromethanesulfonic acid dissolved in acetic acid but no evidence for isomerization or reaction was found.

The oxidation of *n*-butyl radicals by various copper(II) salts was examined under *aqueous conditions*. The results in Table VI show that copper(II) acetate, sulfate, perchlorate, and triflate are almost indistinguishable as oxidants in a medium consisting of 60% water. The leveling effect exerted by water on these copper(II) salts is, no doubt, due to the extensive hydrolysis of solutes in this medium to aquocopper(II) cations. No rearranged butenes were observed, but varying amounts of 1- and 2-butanol were formed.

The *oxidations of sec-butyl radicals* derived from 2-methylbutyryl peroxide by copper(II) acetate and triflate are compared in Table VII. Butenes were the major products (92%) when the oxidant was copper(II) acetate, whereas a significant amount of *sec*-butyl acetate (45%) accompanied the butenes when copper(II) triflate was employed.

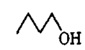
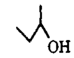
The difference in the *oxidation of isobutyl radicals* carried out with copper(II) acetate and triflate was also quite dramatic. Isobutylene was the exclusive product (>95%) of oxidation of isobutyl radicals by copper(II) acetate as shown in Table VIII. On the other hand,

Table V. Reaction of *n*-Butyl Radicals with Copper(II) Triflate[a]

HOAc,[b] vol %	CuT_2, *M*	CuT, *M*	Products, mol % CO_2						
98	0.008[c,d]	0.010[g]	101	0.9	28	3.7	2.2	38	13
98	0.008[c,e]	0.010[g]	102	0.3	20	4.2	2.6	48	19
100	0.008[c,f]	0	0.01						
2	0.008[c,e]	0.010[g]	92	6	13	6.0	3.1	5.2	12.2
0	0.020[h]	0.002[i]	98	*k*	16	5.2	2.7	*j*	*j*
0	0.040[h]	0.002[i]	92	*k*	15	4.9	2.8	*j*	*j*
0	0.080[h]	0.002[i]	91	*k*	15	4.8	2.9	*j*	*j*
92	0.040[h]	0.004[i]	98	*k*	24	6.5	3.6	36	19

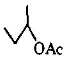
[a] From solutions containing 0.040 *M* valeryl peroxide at 25°. [b] Remainder is acetonitrile. [c] Prepared *in situ* from copper(II) acetate and CF_3SO_3H in the following amounts. [d] 0.016 *M*. [e] 0.047 *M*. [f] 0.062 *M*. [g] Copper(I) acetate. [h] Copper(II) triflate. [i] Copper(I) triflate. [j] Not determined. [k] Less than 0.1%.

Table VI. Reaction of *n*-Butyl Radicals with Various Copper(II) Salts in Aqueous Solution[a]

Cu(II) *M*	X_2	Products, mol % CO_2				Mass balance[b]
0.016	SO_4	101	61.5	18.2	20.0	98
0.016	$(OAc)_2$	92	57.0	12.2	17.5	94
0.016	$(O_3SCF_3)_2$	102	54.0	32.8	11.0	96
0.016	$(ClO_4)_2$	91	42.5	27.0	14.0	92

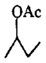
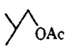
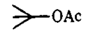
[a] Consisting of water–CH_3CN (60:40, vol %) and 0.040 *M* valeryl peroxide. Initiated by 0.0018 *M* copper(I) triflate at 25°. [b] *n*-Butane too small to measure in all runs.

Table VII. Oxidation of *sec*-Butyl Radicals by Copper(II) Acetate and Triflate[a]

Reactants, *M* Cu(II)	X_2	CuX	Products, mol % CO_2					
0.022	$(OAc)_2$	0.005	99	1.5	38	27	27	3.0
0.021	$(OAc)_2$	0.005	96	1.3	35	24	25	4.2
0.020	$(O_3SCF_3)_2$	0.0035	92	0.7	11	21	17	46
0.020	$(O_3SCF_3)_2$	0.0035	93	0.7	11	22	19	43

[a] In HOAc–CH_3CN (92:8, vol %) containing 0.040 *M* 2-methyl butyryl peroxide, at 25°C.

Table VIII. Reaction of Isobutyl Radicals with Copper(II) Acetate and Triflate[a]

Cu(II), *M*	X_2[b]	Products, mol % CO_2								
0.020	$(OAc)_2$	99	3.4	96	0	0	0	0	2.0	0
0.021	$(O_3SCF_3)_2$	105	0.2	4.3	0.6	3.1	1.8	12	4.0	52
0.020	(O_3SCF_3)	106	0.2	4.3	1.0	3.1	1.8	12	3.7	56

[a] In solutions containing 0.040 *M* isovaleryl peroxide at 25°. [b] Acetate in HOAc–CH_3CN (99:1, vol %) initiated by 0.005 *M* copper(I) acetate. Triflate in HOAc–CH_3CN (92:8, vol %) initiated by 0.0035 *M* copper(I) acetate.

a rather complex mixture of butenes (10%) and butyl acetates (70%) resulting from methyl and hydrogen migration was produced during the oxidation of isobutyl radicals by copper(II) triflate.

The *oxidation of n-propyl radicals* produced from *n*-butyryl peroxide is compared in Table IX. Propylene was the exclusive product of oxidation by copper(II) acetate. On the other hand, the oxidation of *n*-propyl radicals by copper(II) triflate produced a mixture of *n*- and isopropyl acetates (55%) as well as propylene (35%) and cyclopropane (1%). Similar results were obtained with copper(II) methanesulfonate as oxidant, with the outstanding exception that significant amounts (35%) of *n*-propyl methanesulfonate were also found. The *n*- and isopropyl methanesulfonates are solvolytically stable under these reaction conditions. Small amounts of *N*-propylacetamides were also detected.

Oxidation of Methyl Radicals by Copper(II) Acetate and Triflate. The oxidation of methyl radicals represented a particular challenge since the vertical ionization potential of this radical is more than 28 kcal/mol higher (in the gas phase) than that of other primary alkyl radicals.[11] The catalyzed decomposition of acetyl peroxide with copper(II) acetate and triflate is represented in Table X. In the presence of copper(II)

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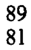
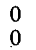
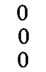
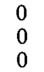
(11) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

Table IX. Oxidation of *n*-Propyl Radicals by Copper(II) Acetate, Methanesulfonate, and Triflate[a]

HOAc,[b] vol %	$Cu^{II}X_2$,[c] *M*	Products, mol %					
		CO_2					
98	0.010 A	102	3.1	97	0	0	0
94	0.019 A	100	3.5	98	0	0	0
60	0.00	105	5.8	89	0	0	0
50	0.019 A	95	4.1	81	0	0	0
100	0.027 T	90	0	48	0	50	0.2
76	0.027 T	104	0	31	1.3	30	20[h]
60	0.0094 T	102	0	27	1.3	26	17[i]
95	0.012 M	100	0	99	*d*	*d*	0
85	0.014 M	101	0	26	*d*	26[e]	11
76	0.020 M	101	0	28	*d*	19[f]	8[j]
60	0.020 M	95	0	29	*d*	17[g]	8[k]

[a] Catalyzed decomposition of *n*-butyryl peroxide at 25°. [b] Remainder was acetonitrile. [c] A = acetate, T = triflate, M = methanesulfonate; acetate runs initiated by 0.0050 *M* copper(I) acetate; triflate runs initiated by 0.0011 *M* copper(I) triflate, methanesulfonate runs initiated by 0.0076 *M* copper(I) methanesulfonate. [d] Traces, <0.5%. [e] 39% *n*-propyl methanesulfonate also found. [f] 37% *n*-propyl and 2% isopropyl methanesulfonate also formed. [g] 32% *n*-Pr- and 2% *i*-PrO_3SCH_3. [h] 7% *n*-propyl- and 15% isopropylacetamide also formed. [i] 9% *n*-Pr- and 22% *i*-PrNHAc. [j] 3% *n*-Pr- and 9% *i*-PrNHAc. [k] 5% *n*-Pr- and 11% *i*-PrNHAc also formed.

Table X. Oxidation of Methyl Radicals by Copper(II) Acetate and Triflate[a]

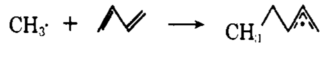
Solvent	$Cu^{II}X$,[b] *M*	$Cu^{I}X$,[b] *M*	Products, mol %			
			CO_2	CH_4	C_2H_6	CH_3OAc
HOAc[c]	0.040 A	0.022A	105	7.0	14	58
HOAc[d]	0.0040A	0.034A	100	11	19	50
CH_3CN[e]	0.040A	0	116	12	0	65
CH_3CN[f]	0.004A	0.034A	96	11	5	51
HOAc[g]	0.040T	0.004T	100	0	0	83
HOAc	0.020T	0.0009T	101	*h*	0	73
CH_3CN[i]	0.040T	0.0017T	95	*h*	0	*j*

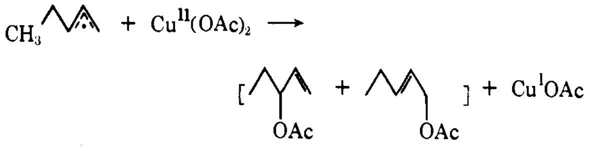
[a] Catalyzed decomposition of 0.042 *M* acetyl peroxide at 25°. [b] X = A (acetate); T (triflate). [c] Containing 8 vol % acetonitrile. [d] Containing 16 vol % acetonitrile. [e] No acetic acid; decomposed at 60°. [f] Containing 8 vol % acetic acid. [g] Containing 20 vol % acetonitrile. [h] Traces. [i] No acetic acid. [j] No methyl acetate; other products unidentified.

acetate the reaction proceeded with a relatively short kinetic chain length, that is, rather large amounts of copper(I) acetate were required for complete reaction. Appreciable amounts of methane and ethane were formed in addition to methyl acetate. Interestingly, high yields of methyl acetate were also obtained even in acetonitrile solutions containing no added acetic acid. The acetate moiety in this case was derived entirely from the copper(II) oxidant.

No methane or ethane was detected when the catalytic decomposition of acetyl peroxide was carried out with copper(II) triflate in acetic acid. Methyl acetate was formed in high yields. Furthermore, the kinetic chain length of the catalytic reaction was significantly longer (>50) than that observed with copper(II) acetate (~2). An excellent yield of carbon dioxide was obtained in acetonitrile with copper(II) triflate and facile oxidation of the methyl radicals by copper(II) triflate was indicated by the absence of methane and ethane. We were unable, however, to identify the products of oxidation of the methyl radical under these conditions, but we inferred that the methyl moiety underwent cationic attack on the acetonitrile in the absence of other nucleophiles to form *N*-methylacetamide (compare eq 9).

In order to show that methyl radicals were precursors to methyl acetate, the catalyzed decomposition of acetyl peroxide was carried out in the presence of 1,3-butadiene. Other studies have demonstrated that alkyl radicals were readily trapped under these conditions, and the resulting allylic radicals were further oxidized to a mixture of allylic acetates.[12] Similarly, from acetyl peroxide the results given below in Table XI showed

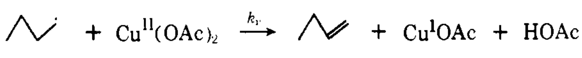

(12)


(13)

that a 74% yield of pentenyl acetates was formed under these conditions in addition to 13% methyl acetate. As expected, only a small amount of methane was obtained.

The favorable stoichiometry obtained under these conditions allowed us to examine the rate of oxidation of methyl radicals by copper(II) acetate. The technique involved the competitive oxidation of methyl radicals and *n*-butyl radicals derived simultaneously from the catalytic decomposition of a mixture of acetyl peroxide and valeryl peroxide in the presence of excess butadiene. The ratio of the second-order rate constants for the oxidation of methyl radicals and *n*-butyl radicals was

$$CH_3\cdot + Cu^{II}(OAc)_2 \xrightarrow{k_s} CH_3OAc + Cu^{I}OAc \qquad (14)$$


(15)

represented as k_s/k_e. This ratio was evaluated as 0.5

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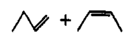
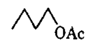
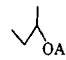
[12] J. K. Kochi and H. E. Mains, *J. Org. Chem.*, 30, 1862 (1965).

Table XI. Reaction of Methyl and Butyl Radicals with $Cu(OAc)_2$ in the Presence of Excess Butadiene[a]

Reactants, mmol					Products,[c] mmol				
HOAc,[b] vol %	$Cu(OAc)_2$	$Cu(OAc)$	$(CH_3CO_2)_2$	$(C_4H_9CO_2)_2$	C_4H_8	CH_3OAc	C_5H_9OAc	$C_8H_{15}OAc$	k_s/k_e[d]
60	0.25	0.84	1.05	0	0	0.133	0.75	0	
60	0.25	0.84	1.05	1.00	0.26	0.144	0.72	0.52	0.50
86	0.20	0.56	1.05	1.00	0.17	0.098	0.76	0.76	0.50
92	0.20	0.56	0.42	2.00	0.42	0.058	0.26	1.23	0.64
76	0.20	0.56	2.10	0.50	0.14	0.280	1.48	0.30	0.44

[a] Butadiene = 3-4 M excess. [b] Remainder of solvent is acetonitrile. [c] The yield of carbon dioxide was quantitative in each case. [d] k_s/k_e = $MeOAc/C_5H_9OAc$ divided by $C_4H_8/C_8H_{15}OAc$; see text; unaccounted for mass calculated as butadiene adduct.

Table XII. Rate Constants for the Oxidation of n-Butyl Radical with Copper(I1) Acetate and Triflate[a]

$Cu^{II}X_2$, M	Product	Rate Constant k_i	$M^{-1}\,sec^{-1}$
$Cu(OAc)_2$		k_e	3.1×10^6 [b]
$Cu(OAc)_2$		k_e	2.7×10^6
$Cu(O_3SCF_3)_2$		k_e	1.0×10^7
$Cu(O_3SCF_3)_2$		k_e'	0.2×10^7
$Cu(O_3SCF_3)_2$		k_s	0.8×10^7
$Cu(O_3SCF_3)_2$		k_s'	0.4×10^7
$Cu(O_3SCF_3)_2$	$(C_4H_9)_{ox}$	k_{ox}	2.3×10^7
$Cu(O_3SCF_3)_2$	n-Butyl → *sec*-butyl reagent	k_{rgt}	0.6×10^7

[a] Determined relative to hydrogen abstraction (k_H), $1 \times 10^4\ M^{-1}\ sec^{-1}$ (ref 3). [b] Reference 7.

(see Experimental Section) and found to be invariant with experimental conditions. Since k_e was previously determined as equal to $3.1 \times 10^6\ M^{-1}\ sec^{-1}$, the second-order rate constant for the oxidation of methyl radicals was $1.5 \times 10^6\ M^{-1}\ sec^{-1}$.

The facile oxidation of methyl radicals by copper(II) acetate represented by eq 14 suggested that a cationic methyl moiety may not be involved. For example, methyl acetate could have resulted from oxidative α elimination (eq 16), followed by acetolysis of the carbenoid intermediate (eq 17). The latter was ruled out since the catalytic decomposition of acetyl peroxide in acetic acid-d_1 produced no deuteriated methyl acetate. Methyl acetate collected by preparative gas chromatography and analysis of the pmr spectra showed two of the methyl resonances in a 1:1 intensity ratio within experimental error.

$$CH_3\cdot + Cu^{II}OAc \longrightarrow CH_2{:} + Cu^I + HOAc \qquad (16)$$

$$CH_2{:} + HOAc \longrightarrow CH_3OAc \qquad (17)$$

Comparison of the Rates of Oxidation of Butyl Radicals by Copper(II) Acetate and Triflate. The rate of oxidation of n-butyl radicals by copper(II) triflate was measured relative to hydrogen abstraction from isobutyraldehyde by a technique described previously.[4,7] The relevant competition is given by eq 18-20 in which

$$C_4H_9\cdot + Cu^{II} \xrightarrow{k_{ox}} (C_4H_9)_{ox} + Cu^I \qquad (18)$$

$$C_4H_9\cdot + C_4H_7CHO \xrightarrow{k_H} C_4H_{10} + C_4H_7CO\cdot \qquad (19)$$

$$C_4H_9\cdot + CH_3CO_2H \xrightarrow{k_H'} C_4H_{10} + \cdot CH_2CO_2H \qquad (20)$$

$(C_4H_9)_{ox}$ represents the combination of butenes and butyl acetates. The ratio of n-butane to the total yield of products of oxidation $(n\text{-}C_4H_9)_{ox}$ may be expressed as

$$\frac{C_4H_{10}}{[(C_4H_9)_{ox}]} = \frac{k_H[C_3H_7CHO]}{k_{ox}[Cu^{II}]} + \frac{k_H'[HOAc]}{k_{ox}[Cu^{II}]} \qquad (21)$$

The overall second-order rate constant for oxidation, k_{ox}, represented a combination of specific rate constants k_i for the formation of individual products, *i.e.*

$$k_{ox} = \Sigma k_i \qquad (22)$$

The linear dependence of the formation of each product of oxidation on the aldehyde and copper(II) triflate concentrations is shown in Figure 3. The specific rate constants k_i listed in Table XII were obtained from each of the slopes, using a value of $k_H = 1 \times 10^4\ M^{-1}\ sec^{-1}$ for the hydrogen transfer from isobutyraldehyde (eq 19).[3] The value of $k_{ox} = 2.3 \times 10^7\ M^{-1}\ sec^{-1}$ for the oxidation of n-butyl radical by copper(II) triflate was approximately an order of magnitude larger than the value of $k_e = 2.7 \times 10^6\ M^{-1}\ sec^{-1}$ obtained from the oxidative elimination of n-butyl radicals by copper(II) acetate under the same conditions.

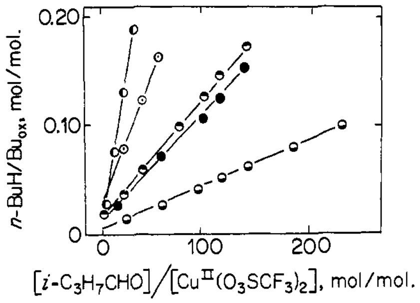


Figure 3. Relative rates of hydrogen transfer (n-BuH) to oxidation (Bu_{ox}) of n-butyl radicals in the presence of isobutyraldehyde and copper(II) triflate, respectively: Bu_{ox} = *cis*- and *trans*-butene-2 (◐); sec-butyl acetate (⊙); n-butyl acetate (◓); butene-1 (●); total oxidation (butenes and butyl acetates) (⊖).

Copper(II) Complexes in Solution. The visible absorption spectra of various copper(II) salts were examined in glacial acetic acid solutions. Copper(II) acetate exists in this medium primarily as a binuclear species, although kinetic studies show that only the monomeric form reacts with alkyl radicals.[7] Conductivity studies indicate that copper(II) acetate even as a monomeric species is tightly associated as $Cu(OAc)_2$.[13] The visible absorption bands listed in Table XIII are

(13) O. W. Kolling and J. C. Lambert, *Inorg. Chem.*, 3, 202 (1964).

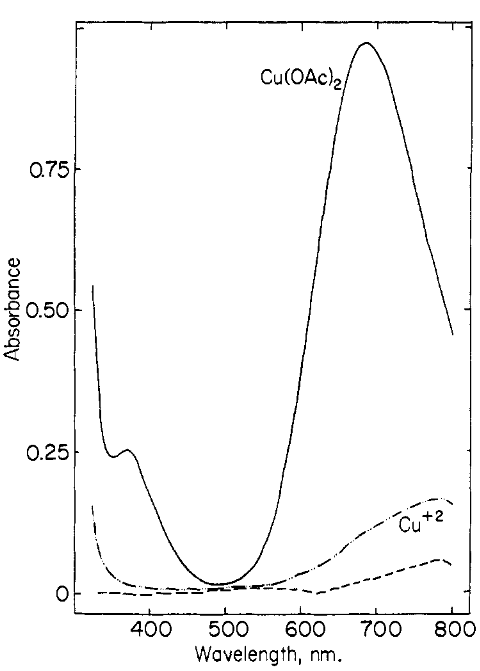


Figure 4. Absorption spectra of 4.90×10^{-3} M copper(II) acetate (——) and 4.25×10^{-3} M copper(II) triflate in glacial acetic acid (—··—). Comparison with 4.80×10^{-3} M copper(II) sulfate in water (- - -).

in accord with this formulation.[14b] A similar description applies to copper(II) trifluoroacetate.

Table XIII. Visible Spectra of Copper(II) Complexes in Glacial Acetic Acid

Copper(II)X$_2$	Concn, M	λ_{max}, nm	Absorbance	ϵ,[a] M^{-1} cm^{-1}
Cu(OAc)$_2$	0.005	680	0.880	176
		365	0.212	42.4
Cu(O$_2$CCF$_3$)$_2$	0.005	680	1.02	204
		365	0.252	50.4
Cu(BF$_4$)$_2$	0.010	685	0.875	87.5
		360	0.245	24.5
Cu(ClO$_4$)$_2$	0.050	730	1.155	23.0
Cu(O$_3$SCF$_3$)$_2$	0.050	737	1.070	21.4
Cu(OAc)$_2$ + 2HO$_3$SCF$_3$	0.050	737	1.130	22.4

[a] Apparent extinction coefficient.

On the other hand, acetic acid solutions of the copper(II) salts of tetrafluoroborate, perchlorate, and triflate are distinctively different from those of copper(II) acetate or trifluoroacetate as illustrated in Figure 4. Furthermore, the position of the absorption bands (737 nm) and their intensity (ϵ 21–23 M^{-1} cm^{-1}) are essentially the same as the hexaaquocopper(II) species obtained by dissolving copper(II) perchlorate, acetate, or sulfate in water.[14] Conductivity and other recent studies have also shown[15] that copper(II) salts of very strong acids are highly dissociated even in nonaqueous solvents such as acetic acid or acetonitrile.

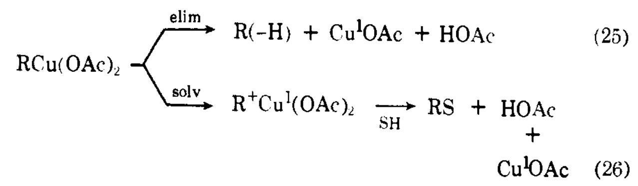
Solutions of copper(II) perchlorate and triflate are almost colorless in glacial acetic acid in contrast to the dark green color of copper(II) acetate. The difference is so striking that solutions of copper(II) acetate can actually be titrated with anhydrous trifluoromethanesulfonic acid to a visual end point.

$$\mathrm{Cu^{II}(OAc)_2 + 2CF_3SO_3H \longrightarrow Cu^{II}(O_3SCF_3)_2 + 2HOAc} \qquad (23)$$

Discussion

The mechanism presented in eq 24–26 forms the general framework for discussion of the oxidation of alkyl radicals by copper(II) acetate.[16] This mech-

$$\mathrm{R\cdot + Cu^{II}(OAc)_2 \rightleftharpoons RCu(OAc)_2} \qquad (24)$$



$$\mathrm{RCu(OAc)_2 \xrightarrow{elim} R(-H) + Cu^{I}OAc + HOAc} \qquad (25)$$

$$\mathrm{RCu(OAc)_2 \xrightarrow{solv} R^+Cu^{I}(OAc)_2 \xrightarrow[SH]{} RS + HOAc + Cu^{I}OAc} \qquad (26)$$

anism was deduced largely on the basis of previous results which we summarize as follows. The electron-transfer oxidation of various alkyl radicals by different copper(II) complexes occurs readily with second-order rate constants[3,7] in excess of 10^6 M^{-1} sec^{-1}. The rates of oxidation of alkyl radicals with copper(II) acetate are rather insensitive to structure, and are not strongly coupled to the ionization potential, since they vary by only an order of magnitude from methyl to *tert*-butyl or allyl radicals.[7] The rates of oxidation with copper(II) triflate may only be a factor of 10 faster. Oxidative elimination is the predominant path by which simple alkyl radicals react with copper(II) acetate and provides an excellent procedure for the production of alkenes from alkyl radicals.[5,8c] Oxidative elimination takes place with low selectivity[5] and the small β-d kinetic isotope effects are also consistent with an exothermic process in which the transition state occurs early along the reaction coordinate.[3] The importance of oxidative substitution as a competing route in the oxidation of alkyl radicals by copper(II) acetate is related largely to the carbonium ion stability of the alkyl moiety. In general, the oxidation of allylic and benzylic radicals as well as of those radicals such as cyclobutyl, β-anisylethyl, and α-alkoxyalkyl which generate relatively stable carbonium ions affords primarily products of oxidative substitution.[3,12,17] The earlier study of the oxidation of substituted β-phenethyl radicals by copper(II) acetate also demonstrated that oxidative elimination and oxidative solvolysis occurs in a step which is independent of and subsequent to the rate-limiting step.[3] A common intermediate is indicated. Furthermore, isotopic labeling with deuterium proved that oxidative elimination occurred by specific loss of a β-hydrogen, whereas oxidative substitution proceeded independently *via* a carbonium ion intermediate.[3] An alkylcopper species was postulated as the common intermediate and not a carbonium ion since the relative amounts of oxidative elimination and oxidative solvol-

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(14) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," second ed, Interscience, New York, N. Y., 1966, p 906; (b) R. P. Eswein, E. S. Howald, R. A. Howald, and D. P. Keeton, *J. Inorg. Nucl. Chem.*, 29, 437 (1967).

(15) J. B. Milne, *Can. J. Chem.*, 48, 75 (1970); M. J. Baillie, D. H. Brown, R. C. Moss, and D. W. A. Sharp, *Chem. Commun.*, 91 (1965).

(16) (a) In these equations no attempt will be made to include all the coordination (including solvent) around copper or the charge on the ion unless pertinent to the discussion. (b) The *formal* oxidation state of copper is III in these metastable alkyl derivatives. For the properties of aquocopper(III) see D. Meyerstein, *Inorg. Chem.*, 10, 638 (1971).

(17) H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 85, 1437 (1963); J. K. Kochi, *Tetrahedron*, 18, 483 (1962); J. K. Kochi and R. D. Gilliom, *J. Amer. Chem. Soc.*, 86, 5251 (1964).

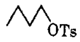
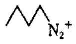
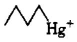
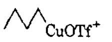
ysis also depend on the structure of the copper(II) oxidant. In this mechanism the association of the alkyl radical with the copper(II) complex in eq 24 constitutes the rate-limiting step, although there is some evidence of reversibility.[3]

Solvolytic Routes in the Oxidation of Alkyl Radicals by Copper(II) Triflate. Particularly germane to the mechanism is the formation of an alkylcopper intermediate and its subsequent partitioning between oxidative elimination (eq 25) and oxidative solvolysis (eq 26). The results of this study show that the driving force for oxidative solvolysis can be enhanced in a remarkable way by simply replacing the acetate in the copper(II) complex by a ligand less strongly coordinating, such as a perchlorate or a triflate. Thus, the oxidation of simple alkyl radicals (*e.g.*, *n*-butyl radicals) by copper(II) triflate proceeds with a high degree of carbonium ion character, which is indicated by the extensive rearrangement of the *n*-butyl to the *sec*-butyl moiety, resulting in the formation of *cis*- and *trans*-butene-2 as well as *sec*-butyl acetate and substantial amounts of butyl acetate. All four of these products were absent in the oxidation of *n*-butyl radical by copper(II) acetate under the same conditions. The extent of the cationoid rearrangement of the *n*-butyl moiety has been cited by Jensen[18] to be a measure of the degree to which the carbonium ion is unencumbered in the solvolysis.[19] Some representative examples are given in Table XIV.

The high degree of cationic driving force is also shown in the oxidation of isobutyl radicals by copper(II) triflate, since the formation of butene-1, *cis*-butene-2, *trans*-butene-2, and *sec*-butyl acetate as a result of methyl migration, and *tert*-butyl acetate by hydrogen migration occurs readily only in systems undergoing cationoid rearrangements. Under the same conditions isobutyl radicals are oxidized by copper(II) acetate specifically to only isobutylene.

The solvolysis of primary alkyl tosylates has been recently investigated in trifluoroacetic, fluorosulfuric, and sulfuric acids.[22,23] The rather large α-*d* and β-*d* kinetic isotope effects observed in these media support the mechanism involving near limiting solvolysis of isobutyl tosylate.[24] Comparable kinetic studies cannot be carried out with our system since the alkylcopper species are formed only as reactive intermediates. However, the internal competition between hydrogen and methyl migration in the anchimerically assisted solvolysis of isobutyl tosylate is minimal only in highly ionizing and poorly nucleophilic solvents (see Table XV, third column) and can be used as a measure of the reactivity of the isobutyl cation. A high degree of a cationoid transition state is indicated in the deamination of isobutylamine[25] on this basis, as it is in the oxidation of isobutyl radicals by copper(II) triflate despite the relatively weakly ionizing and highly nucleophilic character of acetic acid.

Table XIV. Rearrangement Accompanying Solvolysis of *n*-Butyl Derivatives

System	Reaction	Rearrangement, %	Ref
	Solvolysis	0	*a*
	Deamination	25	*b*
	Demercuration	16	*c*
	Oxidation	35–50	This work

[a] A. Streitwieser and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 6233 (1957). [b] J. H. Bayless, F. D. Mendicino, and L. F. Friedman, *ibid.*, **87**, 5790 (1965); A. Streitwieser and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957). [c] Reference 18.

The comparison of the visible absorption spectra of copper(II) acetate and copper(II) triflate in acetic acid solutions shows clearly that the principal difference between these two oxidants is associated with the ionization of the ligand. Copper(II) acetate is present in

$$\mathrm{Cu(OAc)_2} \rightleftharpoons \mathrm{CuOAc^{+}OAc^{-}} \qquad (27)$$

$$\mathrm{Cu(OTf)_2} \rightleftharpoons \mathrm{CuOTf^{+}OTf^{-}} \rightleftharpoons \mathrm{Cu^{2+}} + \mathrm{2OTf^{-}} \qquad (28)$$

acetic acid largely as an undissociated inner sphere complex.[14b,26] On the other hand, copper(II) triflate, like the perchlorate, is highly dissociated and exists largely as an outer sphere complex.[15,27]

In an analogous manner, the alkylcopper species formed as an intermediate in the oxidation of alkyl radicals by copper(II) acetate and triflate must also reflect these differences in the abilities of acetato and triflato

$$\mathrm{RCu(OTf)_2} \rightleftharpoons \mathrm{RCuOTf^{+}OTf^{-}} \rightleftharpoons \mathrm{RCu^{2+}2OTf^{-}} \qquad (29)$$

$$\mathrm{RCu(OAc)_2} \rightleftharpoons \mathrm{RCuOAc^{+}OAc^{-}} \qquad (30)$$

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(18) F. R. Jensen, R. Ouellette, G. K. Knutson, D. Babbe, and R. Hartgerink, *Trans. N. Y. Acad. Sci., Ser. II*, 30, 751 (1968).

(19) Two possible routes for the rearrangement of the *n*-butyl moiety are represented schematically: *n*-$\mathrm{BuCuOTf^{+}} \xrightarrow{\curvearrowright}$ *sec*-$\mathrm{BuCuOTf^{+}}$, etc., or *n*-$\mathrm{BuCuOTf^{+}} \rightarrow \mathrm{Cu^{I}OTf}$ + *n*-$\mathrm{Bu^{+}} \xrightarrow{\curvearrowright}$ *sec*-$\mathrm{Bu^{+}}$, etc. If the rearrangement of the butylcopper species were involved, it might be expected that the same results would be observed from the oxidation of *sec*-butyl radicals. The scrutiny of the results in Tables VI and VII indicates that the formation of *cis*- and *trans*-butene-2 as well as *sec*-butyl acetate (the only products in common) differs depending on whether *n*-butyl or *sec*-butyl radical is oxidized. The high rate of rearrangement reported in Table XII for the conversion of *n*-butyl to *sec*-butyl ($k = 10^{7}\ \mathrm{sec^{-1}}$) is consistent with facile cationic rearrangements.[20] There is also evidence for some reversible isomerization of the alkylcopper intermediate. For example, see the cationic rearrangement of cyclobutylcopper to allylcarbinylcopper species in ref 21.

(20) *Cf.* M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, 90, 6881, 6883 (1968); M. Saunders and P. Vogel, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Mar 30, 1971, Abstracts, No. 077 ORGN.

(21) Small but significant amounts of 1,3-butadiene were also formed in the catalytic decomposition of cyclobutanecarbonyl peroxide especially in the presence of added salts as shown in Table III. Additionally, adducts of cyclobutyl radicals to butadiene were also found and identified.[12] The yield of butadiene was increased substantially when copper(II) bipyridine was employed. The material balance was mediocre under these conditions and there was also a significant change in the composition of the mixture of isomeric $\mathrm{C_4H_7}$ acetates. There is no evidence for the isomerization of cyclobutyl radicals to allylcarbinyl radicals under these conditions. Since the appearance of butadiene is related to the copper(II) species, we associate its formation with the oxidation process itself. The partial rearrangement of the cyclobutylcopper intermediate to the allylcarbinyl isomer (probably by ion-pair return) would allow for the formation of butadiene by the oxidative elimination pathway which was established previously for the oxidation of allylcarbinyl radicals.[3b]

(22) A. Diaz, I. L. Reich and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635, 5637 (1969); C. C. Lee and W. K.-Y. Wang, *Can. J. Chem.*, **48**, 1025 (1970).

(23) P. C. Myhre and K. S. Brown, *J. Amer. Chem. Soc.*, **91**, 5639, 5641 (1970).

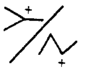
(24) G. A. Dafforn and A. Streitwieser, *Tetahedron Lett.*, 3159 (1970).

(25) G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 621 (1970); C. J. Collins, *Accounts Chem. Res.*, **4**, 315 (1971).

(26) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(27) (a) *Cf.* also triflate, A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971); (b) perchlorate, M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Amer. Chem. Soc.*, **83**, 2038 (1961); (c) V. Gutmann, "Chemistry of Nonaqueous Solvents," J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1970, p 431 ff; (d) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 433 (1962).

Table XV. Competitive Hydrogen and Methyl Migration in the Solvolysis of Isobutyl Derivatives

Leaving group	Solvent		k_t, 10^6 sec^{-1}	k_Δ, %	Ref
OTs	EtOH		78	1.3	*a*
OTs	HOAc	40	2.8	79	*a*
OTs	HCO_2H	20	2.2	97	*a*
OTs	CF_3CO_2H	4	3.0×10^2	100	*a*
OTs	H_2SO_4		7.5×10^2	100	*b*
OTs	FSO_3H	1.5	5.4×10^6	100	*a, b*
N_2	H_2O	4			*c*
Cu^I	HOAc	3			This work

[a] Reference 22. [b] Reference 23. [c] Reference 25.

to coordinate with the copper nucleus. Copper(II) complexes are substitution labile.[28] For example, the rate of water exchange from the hexaaquacopper(II) ion is in excess of 10^9 sec^{-1}. The rates of anation of copper(II) complexes are also, no doubt, extremely fast and would not be expected to impose large kinetic limitations on the behavior of the metastable alkylcopper intermediates.

We propose that coordinately unsaturated species such as $RCuOTf^+$ and RCu^{2+} as well as $RCuOAc^+$ are responsible for the generation of carbonium ion intermediates, *e.g.*[3,29]

$$RCuOTf^+ \longrightarrow R^+ + Cu^IOTf \qquad (31)$$

$$RCuOAc^+ \longrightarrow R^+ + Cu^IOAc \qquad (32)$$

Oxidative solvolysis is associated directly with heterolysis of these metastable species.[30] Since oxidative solvolysis and oxidative elimination both proceed from the common alkylcopper intermediate, their relative importance is also kinetically related to the dissociation constant of the alkylcopper intermediates (eq 29 and 30). Thus, copper(II) triflate promotes oxidative solvolysis more than copper(II) acetate for a given alkyl radical. Conversely, oxidative elimination is assisted by copper(II) acetate more than triflate. Furthermore, other factors being equal, heterolysis represented in eq 31 or 32 is more favored by alkyl moieties most able to attain carbonium ion stability. For this reason, oxidations of most alkyl radicals with copper(II) *acetate* usually circumvent the route involving oxidative solvolysis and usually proceed *via* oxidative elimination if facile loss of a β hydrogen is possible.[4,5]

Oxidative solvolysis induced by ionization has a formal analogy to the solvolytic demercuration of organomercurials reported by Jensen and Ouellette.[33] Thus, alkylmercury(II) acetates in acetic acid only undergo protonolysis. However, in the presence of perchloric

$$RHgOAc + HOAc \longrightarrow RH + Hg(OAc)_2 \qquad (33)$$

acid, demercuration readily occurs with the liberation of free mercury. A large driving force is provided by a cationoid transition state, and the following mechanism was proposed (eq 34 and 35). The facile re-

$$RHgOAc + HClO_4 \rightleftharpoons RHg^+ClO_4^- + HOAc \qquad (34)$$

$$RHg^+ \longrightarrow R^+ + Hg^0, \text{etc.} \qquad (35)$$

duction of mercury as a result of the heterolysis of the alkylmercurinium ion in eq 35 is analogous to the oxidative solvolysis of alkylcopper cations presented in eq 31 and 32.

Oxidation of Cyclobutyl Radicals by Copper(II) Acetate. Cyclobutyl radical represents an example where oxidative elimination and oxidative solvolysis are delicately balanced during oxidation by copper(II) acetate.[8] It is, thus, a convenient radical in which to readily detect small changes in this competition.

The visible absorption spectrum of copper(II) acetate in acetic acid is unaffected by lithium perchlorate, yet the addition of lithium perchlorate effects a remarkable increase in oxidative substitution during the oxidation of cyclobutyl radicals by copper(II) acetate shown in Figure 2. These observations are accommodated by ligand exchange of perchlorate for acetate in the cyclobutylcopper intermediate. The resulting cyclobutyl-

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(28) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 151 ff.

(29) Loss of a neutral solvate from these cationic species is implied.

(30) (a) It is also conceivable that oxidative solvolysis of primary alkyl radicals by copper(II) triflate proceeds *via* an alkyl triflate intermediate, followed by rapid subsequent solvolysis, *e.g.*

$$R\cdot + Cu^{II}(OTf)_2 \longrightarrow Cu^IOTf + R\text{-}OTf \xrightarrow[HOAc]{} ROAc + HOTf$$

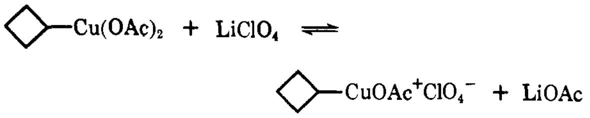
However, *no rearrangement* was observed (by pmr analysis) during acetolysis of *n*-propyl triflate,[24] whereas the oxidation of *n*-propyl radicals by copper(II) triflate in acetic acid affords substantial amounts of isopropyl acetate in addition to cyclopropane (Table VII). The latter is also produced during deamination of *n*-propylamine and is diagnostic of the formation of a *n*-propyl cationoid intermediate.[31] Furthermore, tetrafluoroborate derivatives of copper(II) cannot generate alkyl tetrafluoroborates as intermediates during oxidation of alkyl radicals, but the oxidation of *n*-butyl radicals with copper(II) tetrafluoroborate affords essentially the *same mixture of rearranged butyl derivatives* as those derived from copper(II) triflate or perchlorate (Table IV). An alkylcopper intermediate is the only species these three oxidants have in common. (b) A path involving prior formation of alkyl triflate may contribute *partially* to oxidative solvolysis, since the oxidation of *n*-propyl radical by copper(II) methanesulfonate (which is structurally related to trifluoromethanesulfonate) does afford some of the solvolytically stable *n*-propyl methanesulfonate (Table IX). The mechanism of the formation of alkyl sulfonate esters probably involves oxidative displacement similar to the formation of methyl acetate from methyl radical and copper(II) acetate (see also ref 32). It should be noted that the relative amounts of *n*-propyl and isopropyl isomers differ according to whether they are acetate, methanesulfonate, or acetamide derivatives. The preponderant amount of unrearranged *n*-propyl methanesulfonate (35%) compared to isopropyl methanesulfonate (2%) can be interpreted as direct attack (or insertion) by methanesulfonate into the propylcopper bond. In situations such as this, it is difficult at present to clearly distinguish between oxidative solvolysis and oxidative displacement.

(31) G. J. Karabatsos, C. E. Orzech, J. L. Fry, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 606 (1970); C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967); C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970).

(32) (a) Compare also ref 30. (b) Strictly speaking, the data at present do not allow us to distinguish "internal return" from "neighboring group participation" or direct "insertion." Cationoid transition states appear to be involved in oxidative displacement, although the formation predominantly of *n*-propyl methanesulfonate compared to isopropyl methanesulfonate indicates that direct attack by nucleophile on the propylcopper bond may also be possible (see Table IX).

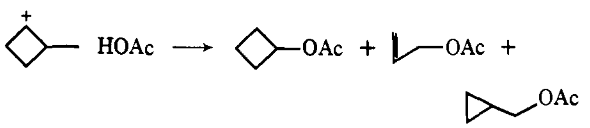
(33) F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363 (1963). See, also: G. A. Olah and P. R. Clifford, *ibid.*, **93**, 1261 (1971) and C. C. Lee and J. Law, *Can. J. Chem.*, **49**, 2746 (1971).

copper cation subsequently undergoes ready solvolysis (eq 37 and 38).[21]



(36)

(37)



(38)

On the other hand, the oxidation of *n*-butyl radicals by copper(II) acetate is insensitive to the presence of lithium perchlorate. The difference between *n*-butyl and cyclobutyl radicals in this regard may be attributed to the relatively difficult ionization of the *n*-butylcopper intermediate to a *primary* butyl cation, in contrast to the ready formation of a homoallylic cation (eq 37). Under such circumstances the competition from the facile oxidative elimination to butene-1 far overshadows the cationic route.

The effect induced by lithium perchlorate is analogous to that shown in the limiting solvolysis of a variety of alkyl derivatives, and has been described as the "special salt effect."[34] The analogy, however, is somewhat limited, since lithium perchlorate in solvolysis retards ion-pair return and operates directly at the carbonium ion stage. Lithium perchlorate exerts a secondary effect in the example presented here.[35]

The Oxidation of Methyl Radicals by Copper(II) Acetate. The ready oxidation of methyl radicals by copper(II) acetate to methyl acetate merits separate attention, since the methyl radical has a high ionization potential relative to other alkyl radicals.[11] Furthermore, unlike other primary alkyl radicals, a pathway involving oxidative elimination is unavailable to the methyl radical, and α elimination does not occur. Neopentyl radical, which also has no β hydrogens, undergoes complete rearrangement *via* the carbonium ion to the *tert*-amyl cation under these conditions.[3]

The oxidation of methyl radical by copper(II) acetate to methyl acetate proceeds at approximately one-half the rate at which *n*-butyl radical is oxidized to butene-1. The singular absence of *n*-butyl acetate among the products of oxidation of *n*-butyl radicals by copper(II) acetate indicates that its rate of formation must be at least one hundred times slower than the formation of methyl acetate. Such large rate differences between methyl and *n*-butyl radicals do not support a bimolecular mechanism involving direct transfer of an acetate ligand from copper(II) to the methyl radical, and we conclude that methyl acetate also arises from a methylcopper intermediate. Moreover, the postulation of an alkylcopper species which can be partitioned between alkene and alkyl acetate is also consistent with the absence of alkyl acetates from the oxidation of most other alkyl radicals by copper(II) acetate, and is in accord with the earlier conclusions based on the polar effects.[3]

The high yields of methyl acetate derived from the oxidation of methyl radicals by copper(II) acetate even in pure acetonitrile and in the absence of other sources of acetate suggest that the acetate moiety is transferred internally, *e.g.*

$$CH_3CuOAc^+ \rightleftharpoons CH_3{}^+Cu^IOAc \longrightarrow CH_3OAc + Cu^I \quad (39)$$

Such a pathway, which we describe as *oxidative* displacement, is usually not important with most alkyl radicals, since it can be readily circumvented by oxidative elimination of the alkylcopper intermediate. Oxidative displacement as described in eq 39 is a type of "ion-pair return" which has been so well delineated in solvolytic mechanisms.[32,34]

The oxidation of methyl radicals by copper(II) triflate affords even higher yields of methyl acetate in acetic acid solution. Oxidation also proceeds rapidly in the absence of acetic acid, and solvation by acetonitrile and other nucleophiles is inferred (eq 40). Cationic methylation of arenes under these conditions will be reported later.

$$[CH_3{}^+\ Cu^IOTf] + CH_3CN \longrightarrow [CH_3CNCH_3{}^+\ CuOTf],\ \text{etc.} \quad (40)$$

Summary

The electron-transfer oxidation of alkyl radicals by copper(II) complexes proceeds *via* a metastable alkylcopper intermediate, which is partitioned primarily between oxidative elimination and oxidative solvolysis. The anionic counterion exerts a dominant effect in the selection of pathways. Acetato ligand promotes oxidative elimination with most alkyl radicals. The importance of oxidative solvolysis increases as the alkyl moiety becomes capable of carbonium ion stabilization. Oxidative solvolysis is also induced in cyclobutyl radicals by lithium perchlorate and an acetic acid–acetonitrile solvent. Triflato ligand promotes oxidative solvolysis as the major route even with simple primary alkyl radicals. Finally, oxidative displacement involving an intramolecular delivery of a ligand from copper to the alkyl group is a path available for the decomposition of the alkylcopper intermediate when elimination or solvolysis is hindered or unavailable, as in the oxidation of methyl radical. The following generalized scheme is proposed for electron-transfer oxidation.

In this mechanistic scheme, the *dissociation of the ligand* from the alkylcopper intermediate provides the driving force required for oxidative solvolysis to take place in competition with oxidative elimination during electron-transfer oxidation of alkyl radicals by copper(II) complexes. The coupling of such an ionization to a solvolytic process is a natural consequence of the generalized concepts formulated for organic systems by Winstein[34] and elaborated to inorganic reactions by

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(34) (a) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965); see also K. T. Leffek, *Can. J. Chem.*, **48**, 1 (1970), and C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K.-U. Yang, *J. Org. Chem.*, **36**, 887 (1971); (b) for "ion-pair return" see H. L. Goering, *et al.*, *J. Amer. Chem. Soc.*, **93**, 1224 (1971), and earlier papers, and S. G. Smith and J. P. Petrovich, *J. Org. Chem.*, 30, 2882 (1965).

(35) (a) There is no evidence for the "special salt effect" operating on the solvolysis of cyclobutyl derivatives, and we tentatively reject an alternative explanation represented as, $RCu(OAc)_2 + LiClO_4 \rightleftharpoons R^+ClO_4^- + LiCu^I(OAc)_2$, etc. The structures of the ion pairs in these two systems are, of course, different and the parallel drawn may not be applicable. (b) Oxidative solvolysis of cyclobutyl radicals can also be induced by changing the solvent from pure acetonitrile or acetic acid to mixtures as shown in Figure 1. Solvent-induced ionization of the type presented here is consistent with this mechanism, and the use of mixtures of acetic acid and acetonitrile to inhibit ion-pair return in solvolysis is being investigated. See also A. Ehret and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2048 (1966).

Scheme I. Mechanism of the Electron-Transfer Process

Formation of an alkylcopper complex

$$\mathrm{R\cdot + CuX_2 \rightleftharpoons [RCuX_2]}$$

Oxidative elimination

$$\mathrm{[RCuX_2] \longrightarrow R(\text{-}H) + HX + Cu^{I}X}$$

Oxidative solvolysis

$$\begin{tikzcd}
\mathrm{[RCuX_2]} \arrow[r, shift left] & \mathrm{RCuX^+X^-} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{LiClO_4}"] \arrow[dr, shift left] & \mathrm{RCuX^+ClO_4^- + LiX} \arrow[l, shift left] \arrow[d, shift left] & \\
& & \mathrm{R^+CuX} \arrow[ul, shift left] \arrow[u, shift left] \arrow[r, "\mathrm{SH}"] & \mathrm{R\text{-}S + Cu^{I}X}
\end{tikzcd}$$

Oxidative displacement

$$\mathrm{[RCuX_2] \rightleftharpoons R^+CuX_2^- \longrightarrow R\text{-}X + Cu^{I}X}$$

Langford and Gray.[36] It further allows homolytic and heterolytic pathways to be interrelated naturally in organic reaction mechanisms.

Experimental Section

Materials. Hexene-1, diallyl, methylcyclopentane, and methylenecyclopentane were obtained from Aldrich Chemical Co. Cyclobutene, cyclobutyl acetate, allylcarbinyl acetate, and cyclopropylmethyl acetate as well as the alcohols were described previously.[8] Other common reagents and solvents were obtained from commercial sources. Trifluoromethanesulfonic acid was kindly donated by the 3M Corporation. Acetonitrile was distilled from phosphorous pentoxide before use.

Preparation of Cupric Triflate. Cupric carbonate, 5 g (0.0405 mol), was slurried with 200 ml of acetonitrile and 12 g of trifluoromethanesulfonic acid (0.080 mol) was added slowly, as vigorous evolution of carbon dioxide took place. The solution was stirred for 30 min and filtered; the resulting blue filtrate was concentrated to dryness. The crude salt was rinsed several times with light petroleum ether and then redissolved in acetonitrile. Diethyl ether was added until the solution was cloudy and the solution was allowed to cool to −20° in a freezer. A light blue precipitate was obtained which was dried in a vacuum oven at 130° and approximately 20 mm for 8 hr. The yield of pale blue salt obtained was 8 g. The visible spectrum was identical with that obtained from trifluoromethanesulfonic acid (2 equiv) and copper(II) acetate (1 equiv).

Preparation of Cuprous Triflate. Cupric triflate, 1.0 g, and 3.0 g of copper metal (powdered) were stirred in a deoxygenated solution of 200 ml of acetonitrile and 0.25 ml of trifluoromethanesulfonic acid until the solution was colorless. The reaction vessel was equipped with a rubber septum through which aliquots could be removed with a hypodermic syringe. Standardization of this solution was accomplished by removing an aliquot to a solution of ferric chloride (excess) in 2 *N* sulfuric acid. The resulting ferrous chloride was titrated with a standard solution of dichromate using diphenylamine as the indicator. The molarity of the solution obtained by this method was 4.4×10^{-2} *M* cuprous triflate.

The General Procedure for the Catalytic Decomposition of Diacyl Peroxides. The copper(II) complex and other additives were dissolved in the appropriate solvent contained in a 125-ml Erlenmeyer flask. The diacyl peroxide was added as a standard solution with a glass pipet. The flask was capped with a rubber septum and flushed with helium for approximately 15 min to remove any oxygen from the system. The appropriate copper(I) species in solution was then added by means of a hypodermic syringe through the rubber septum to initiate decomposition. The reactions were run until carbon dioxide was quantitatively evolved.

Analysis. Carbon dioxide, methane, ethane, and ethylene were determined by gas chromatography on a 2-ft Porapax Q (150–200 mesh) column at room temperature using detection by thermal conductivity. Gaseous hydrocarbons were determined on a 15-ft column containing 15% Dowtherm A on firebrick or on a 20-ft column containing 20% silver nitrate and 15% benzonitrile on Chromosorb W.

The analyses for liquid products were performed by removing an aliquot of the reaction mixture and an aliquot of the internal standard solution to a separatory funnel. Water was added to the organic products extracted with an appropriate solvent, usually ethyl ether or pentane. The extract was then washed several times with water and 10% sodium bicarbonate to remove the solvents (usually acetonitrile and acetic acid). In those cases where the products were water soluble the reaction mixture was analyzed directly by gas chromatography after addition of an aliquot of the internal standard to an aliquot of the reaction mixture. Standard mixtures of products were used in the calibration.

The Catalytic Decomposition of Acetyl Peroxide. The catalytic reaction of acetyl peroxide with copper(II) acetate was readily induced at 25° by copper(I) acetate. The decomposition, however, unlike that of other diacyl peroxides, proceeded with a short kinetic chain length. At moderate concentrations of copper(II) acetate the minimum chain length was two. At low concentrations of copper(II), nearly stoichiometric amounts of copper(I) were required to decompose acetyl peroxide completely. The yields of methane and ethane (based on the carbon dioxide liberated) were substantial as shown in Table XVI, and varied according to the nature of copper(II) species present. Methyl acetate was formed in approximately 50% yields which appeared to be invariant with the composition of the solvent. The formation of ethane was inhibited by bipyridine and the yields of methane as well as methyl acetate increased correspondingly. The addition of either lithium perchlorate or lithium acetate, on the other hand, caused a significant increase in the yield of ethane. When both lithium acetate and bipyridine were added, the only products observed were methane and methyl acetate.

The formation of ethane was apparently associated with the presence of copper(I), since its yield increased with added copper(I) acetate. The thermal decomposition of acetyl peroxide in acetonitrile in the absence of copper salts afforded only methane and small amounts of methyl acetate, but no ethane. The role played by copper(I) and other copper(II) species in the formation of ethane is not clear at this juncture. Furthermore, the reactions of other alkyl radicals in the presence of relatively high concentrations of copper(I) also have not been adequately studied. The coupling of alkyl radicals induced by a variety of other transition metal complexes may be related to this phenomenon.[37]

Table XVI. Reaction of Methyl Radicals with Copper(II) Acetate[a]

HOAc,[b] vol %	Cu-(OAc)$_2$, *M*	CuOAc, *M*	Products, mol % CO$_2$	CH$_4$	C$_2$H$_6$[c]	CH$_3$OAc
4	0.004	0.022	87	12	3.8	*d*
6	0.004	0.034	96	11	5.4	51
8	0.004	0.045	100	12	7.6	51
10	0.004	0.056	100	11	7.4	*d*
8	0.008	0.045	93	9.0	5.2	*d*
8	0.016	0.011	96	7.8	4.8	*d*
84	0.004	0.034	100	11	18.8	50
60	0.004	0.034	96	14	8.0	52
92	0.040	0.022	105	7.0	14	58
88	0.004[e]	0.034	101	25	0	63
60	0.040[e]	0.034	100	18	0	66
6	0.004[e]	0.034	94	17	13	48
88	0.004[f]	0.034	105	8.6	32	33
88	0.004[g]	0.034	103	8.4	28	35
88	0.004[h]	0.034	102	9.1	22	44
88	0.004[i]	0.034	100	8.4	18	47
88	0.004[j]	0.034	108	7.6	47	35
88	0.004[k]	0.034	98	4.0	30	33
88	0.004	0.034	100	4.2	31	55
88	0.004[e,h]	0.034	105	26	0	59
88	0.004[e,i]	0.034	103	25	0	62
0	0	0	175[m]	140	0	11
0	0.040	0	116[m]	12	0	65

[a] Reactions carried out at 25° with 0.042 *M* acetyl peroxide. [b] Remainder of solvent is acetonitrile. [c] Ethane yield includes a factor of 2. [d] Not determined. [e] In addition 0.040 *M* bipyridine. LiClO$_4$ was included in the following amounts. [f] 0.020 *M*. [g] 0.060 *M*. [h] 0.10 *M*. [i] 0.20 *M*. LiOAc was included in the following amounts. [j] 0.10 *M*. [k] 0.20 *M*. [l] 0.30 *M*. [m] Decomposed thermally at 60°.

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[36] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

Control experiments were performed to establish that methyl acetate was formed primarily as a result of the oxidation of methyl radicals by copper(II) acetate. Thus, acetyl peroxide was quantitatively reduced by potassium iodide in the presence of catalytic amounts of ferric chloride. Analysis of the reaction mixture showed no methyl acetate (<0.5%). Solutions of acetyl peroxide in acetonitrile were decomposed photochemically and thermally as shown in Table XVII, under conditions in which methyl acetate was stable. The small amounts of methyl acetate found were consistent with the cage combination of methyl and acetoxy radicals.[38]

Table XVII. Decomposition of Acetyl Peroxide in Acetonitrile

$(CH_3CO_2)_2$, M	Method	mol %			
		CO_2	CH_4	C_2H_6	CH_3OAc
0.042	$h\nu$, 2537 Å, 3 hr	190	81	39	3.2
0.042	$h\nu$, 2537 Å, 3 hr	188	74	39	3.3
0.042	Δ, 60°, 12 hr	176	140	<0.5	10.7

The stability of alkenes in the presence of small amounts of trifluoromethanesulfonic acid is shown in Table XVIII.

Table XVIII. Stability of Olefins to HO_3SCF_3 in Glacial Acetic Acid[a]

HO_3-SCF_3, M	Time, hr				%  reacted
0.058	0	0.710	0.490	0.400	0
0.058	24	0.680	0.460	0.370	4.0
0.160	0	1.10			0
0.160	4	1.04			5.5
0.160	16	0.95			14.0

[a] Isobutane was used as an internal standard for these reactions.

The Rate of Oxidation of Methyl Radicals by Copper(II) Acetate. The catalytic decomposition of a mixture of acetyl peroxide and valeryl peroxide by copper acetate was carried out in the presence of excess butadiene in acetic acid. Two simultaneous sets of reactions involving methyl radicals and *n*-butyl radicals were formulated in the following manner. The oxidation of methyl and *n*-butyl radicals by copper(II) acetate affords methyl acetate (eq 14) and butene-1 (eq 15), respectively. Both radicals add irreversibly to 1,3-butadiene in competing reactions to form pentyl (eq 12) and octenyl radicals which are subsequently oxidized by copper(II) acetate to mixtures of 1-acetoxypentene-2 and 3-acetoxypentene-1 (eq 13) and 1-acetoxyoctene-2 and 3-acetoxyoctene-1, respectively.[8,12]

The following assumptions were made in order to evaluate the rate of oxidation of methyl radicals by copper(II) acetate: (1) the rates of irreversible addition of methyl radicals and *n*-butyl radicals to butadiene were the same,[39] (2) an excess of butadiene was maintained throughout the reaction, and (3) kinetic dependence on this component was pseudo zero order. Under these conditions the ratio of methyl acetate to the methyl adducts CH_3-C_4H_6OAc was related to butene-1 and the butyl adducts n-C_4H_9-C_4H_6OAc according to eq 41. The products were readily analyzed by gas chromatography and the ratios of second-order rate constants k_8/k_e were relatively constant under various conditions as shown in the last column of Table XI.[12]

$$\frac{[CH_3OAc]/[CH_3C_4H_6OAc]}{[C_4H_8]/[C_4H_9C_4H_6OAc]} = \frac{k_s}{k_e} \tag{41}$$

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(37) J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.*, **83**, 2017 (1961).

(38) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970).

(39) The extent to which the rate of addition of methyl radical to butadiene is faster than that of *n*-butyl radical will also be reflected in higher rates of oxidation of methyl compared to butyl. Based on the rates of addition to ethylene in the gas phase: J. A. Kerr and A. D Trotman-Dickenson, *Progr. Reaction Kinet.*, **1**, 119 (1961).