

so that

$$\log k_r/k_0 \cong \frac{-R + 7.5}{\text{\AA}} \quad (7)$$

That the decrease in R , on monosubstitution in the 3-position, is not reflected in a change of ΔpK_a may be attributed to the only other variable in eq. 5, *i.e.*, D_E . The term D_E is a dielectric constant in name only, being a function of the shape of the molecule (for a spherical model the square of the ratio of the distance of the protons from the center of the sphere and the radius of the sphere), the dielectric constant of the molecule, and the dielectric constant of the solvent. The lack of sensitivity of ΔpK_a to changes in R on monosubstitution may be ascribed to an opposite and almost equal change in D_E . In unsubstituted glutaric

acid the electrostatic influence of carboxyl groups occur primarily through the low dielectric of the molecular backbone since, due to solvation of the polar carboxyl groups, the molecule exists in an extended conformation. Monosubstitution in the 3-position brings about a decrease in R accompanied by a greater fraction of the electrostatic effect occurring through the high dielectric of the solvent, and the decrease in R is matched by an increase in D_E so that the product of $D_E R$ in eq. 5 is not significantly altered. The conformational changes brought about by 3-*gem* substitution are greater than those brought about by the monosubstituents examined, and most of the electrostatic interaction occurs through the solvent so that D_E is essentially constant and the product of $R D_E$ becomes smaller with increasing steric requirements of the *gem* substituents.

By the reasoning presented above the similar influence of 3-*gem* substitution on $\log K_1/K_0$ and $\log k_r/k_0$ and the grossly greater sensitivity of $\log k_r/k_0$ to 3-monosubstitution is explained.

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Kinetics of Electron-Transfer Oxidation of Alkyl Radicals by Copper(II) Complexes

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Alkyl radicals are generated by the catalyzed decomposition of peroxides with Cu(II) complexes. They suffer oxidation to alkene by Cu(II) and reduction to alkane by a variety of hydrogen-donor substrates. The competitive formation of alkane and alkene has been utilized to evaluate the ratio of second-order rate constants for reduction and oxidation, k_h/k_e . Oxidation of alkyl radicals is half order in total Cu(II) species in glacial acetic acid and first order in aqueous acetic acid. Cupric acetate in glacial acetic acid is highly dimerized, but the dissociation constant can be determined kinetically. Water, pyridine, and acetate ions effect dissociation of the dimer. Only the monomeric Cu(II) entities are effective oxidants, the dimer of cupric acetate being inactive. The effect of altering the Cu(II) species on oxidation is discussed. By extrapolating values of hydrogen-transfer rates obtained in the gas phase to solution, it is possible to estimate the absolute rates of oxidation of alkyl radicals by Cu(II) complexes. These rates approach the diffusion-controlled limit. They are compared qualitatively with other facile "outer sphere" reactions of inorganic ions in the light of Marcus' theory of electron transfer.

Introduction

A sizeable body of qualitative information has accumulated concerning the oxidation and reduction of organic free radicals by metal salts. Among metal oxidants, Cu(II), Pb(IV), Fe(III), and Co(III) have been those best studied. At least two mechanisms have been described for the oxidation of carbon-centered free radicals by Cu(II) compounds; these are ligand transfer¹ and electron transfer.² The qualitative difference between these two modes of oxidation has been delineated.³

The importance of these reactions lies in their rapid rates, such that they can be utilized in synthetic schemes involving reactive free radicals.⁴ However, quanti-

(1) (a) C. H. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957); (b) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); **84**, 2124 (1962); (c) J. Kumamoto, H. De La Mare, and F. F. Rust, *ibid.*, **82**, 1935 (1960).

(2) (a) E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel, and S. Tazuke, *Discussions Faraday Soc.*, **29**, 188 (1960); (b) H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).

(3) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

(4) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774, 1572, 2121, 2785 (1962); G. Sosnovsky and S. O. Lawesson, *Angew. Chem. Intern. Ed. Engl.*, **3**, 269 (1964).

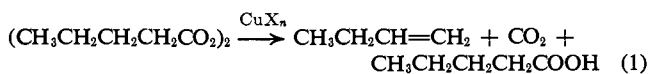
tative data pertaining to the rates of these reactions are meager. In the following discussion, we will be primarily concerned with oxidation by electron transfer.

Dainton and co-workers⁵ have examined the oxidation of α -carbamido radicals ($\sim\text{CHCONH}_2$) derived from acrylamide in aqueous solutions. Employing the polymerization of this monomer as a monitoring reaction, they obtained absolute rate constants for the oxidation and reduction of the α -carbamido radicals by a number of metal oxidation-reduction couples. Their technique is limited to radicals ($\sim\text{CHX}$) obtainable from a polymerizable monomer ($>\text{C}=\text{CHX}$) since only under these conditions are the absolute rate constants readily determined.⁶ Such polymerizable monomers generally contain unsaturated or electronegative groups (X) such as carbamido, cyano, phenyl, vinyl, halo, etc. The types of free radicals available for study by this method, particularly simple alkyl radicals, are restricted.

It had been qualitatively observed that the electronic nature of X profoundly affects the ease of oxidation of carbon-centered radicals by Cu(II) oxidants.⁷ Thus, an α -cyano radical is inert to oxidation by electron transfer, although it is readily oxidized by ligand transfer.⁸ A similar dichotomy was shown to apply to α -formyl and α -carbalkoxyl radicals,⁷ and it is presumably extendible to free radicals containing the polar α -carbamido group.

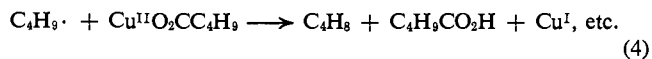
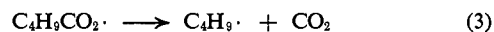
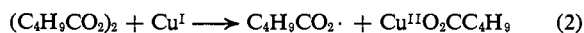
More quantitative information concerning the rates of oxidation of simple alkyl radicals is desirable. Such radicals are readily oxidized by Cu(II) salts. Unlike the free radicals discussed above, the oxidation of simple alkyl radicals by an electron-transfer and a ligand-transfer mechanism are both facile processes. For example, the oxidation of *n*-butyl radical with cupric acetate by the former oxidation path produces butene-1.^{2b} The same radical is oxidized by cupric chloride to *n*-butyl chloride *via* the ligand-transfer oxidation path in equally good yields.⁹

In this study, the kinetics of the oxidation of free alkyl radicals by electron transfer involving copper(II) acetate as oxidant will be examined. The system chosen for examination is the catalytic decomposition of peroxides by Cu(II) salts.^{10,11} In the presence of sufficient copper(II) acetate ($\sim 0.05 M$), valeryl peroxide (0.6 *M*), in a variety of solvents, is decomposed to butene-1, carbon dioxide, and valeric acid (eq. 1).



The stoichiometry of the reaction is remarkably straightforward (considering the homolysis of a peroxide)¹² and no other products are formed in signifi-

cant amounts. The mechanism of the reaction is given by eq. 2-4.¹⁰ Such a mechanism is applicable



to a variety of structural types of peroxides, and it can be utilized in slightly modified form for other catalytic reactions.¹³

Step 4 of the chain sequence is a typical example of an electron-transfer oxidation of an alkyl radical to alkene with carboxylatocopper(II) species. In the presence of hydrogen donor substrates (RH) the alkyl radical can be diverted to alkane by hydrogen-abstraction (reduction) reaction 5. Thus, from the catalytic decomposition of valeryl peroxide, the competition for *n*-butyl radicals by either Cu(II) species (eq. 4) or hydrogen donor (eq. 5) can be measured readily.



The method involves the examination of the products of oxidation and reduction, *i.e.*, butene-1 and butane, respectively, at various concentrations of Cu(II) and hydrogen donor.

Results

Studies in Aqueous Acetic Acid. In 33% v/v. (64 mole %, 34 wt. %) aqueous acetic acid solutions, valeryl peroxide (0.13 *M*) is decomposed at a low concentration of cupric acetate ($1.94 \times 10^{-3} M$) to a mixture of butene-1 (97%) and butane (3%). If *n*-butyraldehyde (1.61 *M*) is added, there is an increase in the relative yield of butane (17%) which is proportional to the aldehyde added. Butane is derived from butyl radical by reaction with both acetic acid and butyraldehyde. The relative yield of butane and butene observed, $[\text{C}_4\text{H}_{10}/\text{C}_4\text{H}_8]_{\text{obsd}}$, is given by eq. 6 and 7, where

$$\left[\frac{\text{C}_4\text{H}_{10}}{\text{C}_4\text{H}_8} \right]_{\text{obsd}} = \left[\frac{\text{C}_4\text{H}_{10}}{\text{C}_4\text{H}_8} \right]_{\text{RH}} + \left[\frac{\text{C}_4\text{H}_{10}}{\text{C}_4\text{H}_8} \right]_{\text{SH}} \quad (6)$$

$$= \frac{k_b[\text{RH}]}{k_d[\text{Cu(II)}]} + \frac{k_s[\text{SH}]}{k_d[\text{Cu(II)}]} \quad (7)$$

k_s is the hydrogen-transfer constant for the solvent (SH = acetic acid).

The solvent blank, $[\text{C}_4\text{H}_{10}/\text{C}_4\text{H}_8]_{\text{SH}}$, is obtained from an independent series of experiments at various cupric acetate concentrations without added hydrogen donor. The correction for butane from acetic acid is small at the concentrations of hydrogen donor and cupric acetate usually employed. The relative rates of reduction and oxidation of an alkyl radical is obtained by plotting the relative amounts of butane and butene-1 (after correction for the blank) against the molar ratios of hydrogen donor RH and copper(II) acetate.

As shown in Figure 1, the slope, which measures k_b/k_s , is linear over a range of ratios of hydrogen donor/cupric acetate. Furthermore, the correlation is independent of the concentration of cupric acetate or hydrogen donor. For a particular hydrogen donor, the same slope is obtained regardless of whether the Cu(II) salt is kept constant and RH is varied, or, conversely, the concentration of RH is maintained and cupric

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

(5) E. Collinson, F. S. Dainton, B. Mile, S. Tazuke, and D. R. Smith, *Nature*, 198, 26 (1963).

(6) F. S. Dainton and M. Tordoff, *Trans. Faraday Soc.*, 53, 499, 667 (1957); J. Betts, F. S. Dainton, and K. J. Irvin, *ibid.*, 58, 1203 (1962); C. H. Bamford, A. D. Jenkins, and R. Johnston, *ibid.*, 58, 1213 (1962); E. R. Entwistle, *ibid.*, 56, 284 (1960); M. Mullier, *J. chim. phys.*, 52, 565 (1955); H. Monteiro, *ibid.*, 59, 2 (1962).

(7) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, 84, 3946 (1962).

(8) J. K. Kochi and D. M. Mog, *ibid.*, 87, 522 (1965).

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

(10) J. K. Kochi, *ibid.*, 85, 1958 (1963).

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

(12) Cf. D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, 81, 122 (1959); D. F. DeTar and C. Weis, *ibid.*, 79, 3041, 3045 (1957); J. Smid and M. Szwarc, *ibid.*, 78, 3322 (1956), and earlier papers.

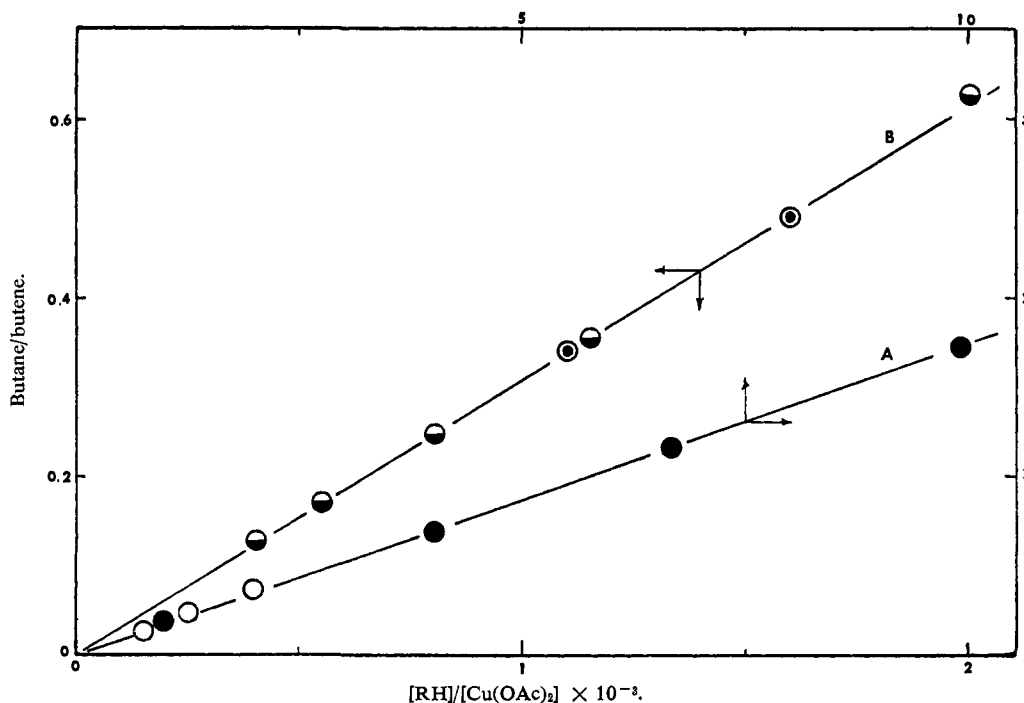


Figure 1. First-order kinetics at constant hydrogen donor and at constant cupric acetate concentrations. (A) *n*-Butyraldehyde: ○, 2.58 *M*, varying [Cu(II)]; ●, [Cu(II)] = 1.30×10^{-3} *M*, varying butyraldehyde. (B) Dichloroacetic acid: ◐, 1.04 *M*, varying [Cu(II)]; ◑, [Cu(II)] = 1.91×10^{-3} *M*, varying dichloroacetic acid.

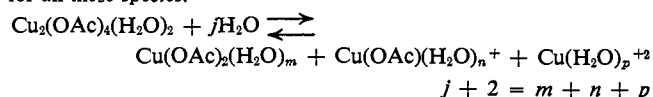
acetate is varied. In practice, the latter method is preferred, since the concentration of cupric acetate ($\sim 10^{-4}$ *M*) is much smaller than RH ($\sim 10^{-1}$ *M*). It is, thus, amenable to a wider change of concentrations without affecting the properties of the medium.

The linear variation of the butane/butene ratio with RH/cupric acetate indicates that both reduction (eq. 5) and oxidation (eq. 4) are first order in hydrogen donor and cupric acetate, respectively. Furthermore, since k_b/k_e is independent of the concentration of cupric acetate or hydrogen donor, both reactions must be of the same kinetic order with respect to butyl radicals. Transfer reactions in the gas phase are first order in free radical, and there is no reason to doubt that the same kinetics also pertain to reactions in solution. Therefore, the oxidation reaction is likewise considered to be kinetically first order in butyl radicals. The ratio of second-order rate constants for reduction and oxidation, k_b/k_e , of butyl radicals from valeryl peroxide and a variety of hydrogen donors are listed in Table I.

Since k_e represents here the oxidation of butyl radical by cupric acetate, in a given solvent it is the same irrespective of hydrogen donor.¹⁴ On this basis, it is possible to calculate the hydrogen-transfer constant k_b' of butyl radicals with these donors relative to acetic acid. These are also tabulated in Table I.

Hydrogen-donor activity of aldehydes is derived mainly from the formyl hydrogen.¹⁵ Aliphatic alde-

(14) In highly aqueous solutions of cupric acetate, several monomeric Cu(II) species are present, and k_e actually represents a composite value for all these species.



(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 273 ff.

hydes have values of k_b/k_e which range between 10^{-3} and 10^{-4} . The values depend slightly on structure. Phenylacetaldehyde is the most reactive of the aldehydes examined, followed by those aldehydes which carry α -tertiary hydrogens in the hydrocarbon chain,

Table I. Reactivity of Substrates to Hydrogen Abstraction by Butyl Radicals in Competition with Oxidation by Cupric Acetate in 67% (v/v.) Acetic Acid-Water at 57°^a

Hydrogen donor	k_b/k_e	$k_b',^d$
Phenylacetaldehyde	6.7×10^{-4}	2.9×10^2
Chloroform ^b	7×10^{-4}	3×10^2
Isobutyraldehyde	4.6×10^{-4}	2.0×10^2
Dichloroacetic acid	3.1×10^{-4}	1.4×10^2
2-Ethylbutyraldehyde ^c	3.1×10^{-4}	1.4×10^2
Dibenzyl ether ^c	3×10^{-4}	1.3×10^2
<i>n</i> -Butyraldehyde	1.7×10^{-4}	7.4×10
Diallyl ether ^c	9×10^{-5}	4×10
Benzyl alcohol ^c	3×10^{-5}	1×10
Acetic acid	2.3×10^{-6}	1.0

^a From valeryl peroxide (0.23 *M*). ^b Volatile substrate. Curvature obtained in plot. Extrapolated value. ^c Owing to limited solubility, measurements made at only one ratio of [RH]/[Cu(OAc)₂]. Approximate values. ^d Calculated on the basis that k_e is constant. Hydrogen-transfer values relative to acetic acid = 1.

such as isobutyraldehyde and 2-methylbutyraldehyde. Normal aliphatic aldehydes are slightly more reactive than pivalaldehyde. The changeable nature of k_b/k_e with aldehydic structure is mainly attributable to a certain amount of hydrogen abstraction from the α -position.¹⁶

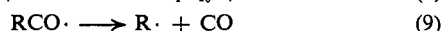
Acyl radical is formed as an intermediate from the reaction of an alkyl radical and an aldehyde as hy-

(16) Such a β -substitution is not expected to enhance greatly the activity of the formyl hydrogen. Contrariwise, steric hindrance should cause a decrease in activity.

Table II. Hydrogen Abstraction from Aldehydes in Competition with Oxidation by Cupric Acetate in 66% Acetic Acid-Water at 57°

Hydrogen abstraction reaction	Peroxide	Aldehyde	k_h/k_e
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	<i>n</i> -Valeryl peroxide	<i>n</i> -Butyraldehyde	1.7×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	<i>n</i> -Valeryl peroxide	<i>n</i> -Butyraldehyde	1.8×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + (\text{CH}_3)_2\text{CHCH}_2\text{CHO}$	<i>n</i> -Valeryl peroxide	Isovaleraldehyde	2.0×10^{-4}
$(\text{CH}_3)_2\text{CHCH}_2\cdot + (\text{CH}_3)_2\text{CHCH}_2\text{CHO}$	<i>n</i> -Valeryl peroxide	Isovaleraldehyde	6.1×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + (\text{CH}_3)_2\text{CHCHO}$	<i>n</i> -Valeryl peroxide	Isobutyraldehyde	4.6×10^{-4}
$(\text{CH}_3)_2\text{CH}\cdot + (\text{CH}_3)_2\text{CHCHO}$	<i>n</i> -Valeryl peroxide	Isobutyraldehyde	2.8×10^{-4}
$(\text{CH}_3)_2\text{CHCH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Isovaleryl peroxide	<i>n</i> -Valeraldehyde	5.3×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Isovaleryl peroxide	<i>n</i> -Valeraldehyde	2.0×10^{-4}
$(\text{CH}_3)_2\text{CHCH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$	Isovaleryl peroxide	2-Methylbutyraldehyde	7.9×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot + (\text{CH}_3)_3\text{CCHO}$	<i>n</i> -Valeryl peroxide	Pivalaldehyde	1.3×10^{-4}
$(\text{CH}_3)_3\text{C}\cdot + (\text{CH}_3)_3\text{C}-\text{CHO}$	<i>n</i> -Valeryl peroxide	Pivalaldehyde	$\leq 9.2 \times 10^{-6}$
$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_3 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$	<i>n</i> -Butyryl peroxide	2-Methylbutyraldehyde	3.9×10^{-4}
$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_3 + \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{HCHO}$	Decanoyl peroxide	2-Methylbutyraldehyde	4.9×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	2-Methylbutyryl peroxide	<i>n</i> -Butyraldehyde	1.6×10^{-4}
$\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	<i>n</i> -Butyryl peroxide	<i>n</i> -Valeraldehyde	1.5×10^{-4}

drogen donor (eq. 8). Subsequent decarbonylation of acyl radicals (eq. 9) presents an alternative source of



alkyl radicals, in addition to those derived from the peroxide. Thus, propyl radicals are generated concomitantly from *n*-butyraldehyde, isobutyl radicals are generated from isovaleraldehyde, *sec*-butyl radicals are generated from 2-methylbutyraldehyde, etc., in addition to *n*-butyl radical generated from valeryl peroxide. Further variations are possible with other peroxides. By these series of reactions, it is possible to generate two (or more) species of alkyl radicals simultaneously: peroxide as a primary source and the aldehyde as a secondary source. *Pairs of alkyl radicals generated in this manner react independently of their origin.* The value of k_h/k_e for *n*-butyl radical derived from valeryl peroxide (primary source) in the presence of *n*-butyraldehyde is the same as that obtained from *n*-valeraldehyde (secondary source) and isovaleryl peroxide (Table II). Furthermore, the values of k_h/k_e for *n*-butyl and isobutyl radicals generated from valeryl peroxide and isovaleraldehyde are substantially the same as those derived from isovaleryl peroxide and *n*-valeraldehyde. The similarity in these values of k_h/k_e in the two sets of reactions of *n*-butyl and isobutyl radicals also indicate that there is, at most, a minor dependency of k_h on the structure of these primary aldehydes.

The homologous *n*-butyl and *n*-propyl radicals are equally prone to reduction and oxidation as shown in Figure 2. Roughly speaking, the value of k_h/k_e is three times larger for isobutyl radical, compared to *n*-butyl radical, in its reaction with primary aldehydes. Secondary radicals, such as isopropyl and *sec*-butyl, have k_h/k_e values only approximately one-half that of normal primary radicals. The *t*-butyl radical appears to have the smallest value of k_h/k_e .

Approximations Pertinent to the Method. The values of the relative rates of reduction and oxidation of alkyl radicals obtainable by the method outlined above are largely devoid of simplifying assumptions. Nonetheless, certain implicit assumptions made in this treatment are worth discussing at this juncture.

(a) Only alkenes arise from the oxidation of alkyl radicals by Cu(II) species. The reaction was closely

scrutinized for other products of oxidation, such as alkyl acetates and other esters. From primary and secondary radicals, no such oxidation was observed. On the other hand, *t*-butyl radical gave evidence of *t*-butyl acetate from pivalaldehyde. However, pivalaldehyde alone in acetic acid yields some *t*-butyl acetate; a quantitative value of k_h/k_e was difficult to make. Pivaloyl peroxide as a source of *t*-butyl radical suffers from facile ionic decomposition.¹⁷ Primary and to a greater extent secondary diacyl peroxides also undergo a certain amount of ionic decomposition in acetic acid solutions.^{10,18} If minor, suitable corrections can be made for the alkyl acetates and alkenes formed by this route. If ionic decomposition was major, only alkyl radicals derived from the secondary source were considered (Table II).

(b) Under conditions of these experiments, no evidence for disproportionation or coupling of alkyl radicals was found. Butene and octane are insignificant in blank runs (no Cu(II) salts) with valeryl peroxide in acetic acid solutions. Constant values of k_h/k_e , independent of the primary or secondary source of alkyl radicals, further reinforce the validity of this assumption. The competitive method, of course, does not depend on total material balance of the alkyl radical, provided it does not yield alkane or alkene by routes other than those considered (eq. 6).

(c) During the course of reaction, the steady-state concentration of Cu(I) is negligible compared to Cu(II). Under most conditions this approximation is valid since Cu(I) could not be detected at concentrations greater than $10^{-5} M$ [0.05% of Cu(II)] by spectrophotometric examination of the biquinoline Cu(I) complex.¹⁹ Reactions carried out in the cavity of an electron spin resonance spectrometer showed no apparent change in the concentration of the paramagnetic Cu(II) species. In an independent series of experiments it can be shown that Cu(I) species react very rapidly and exothermically with diacyl peroxides at 25°. Thus, except at very low peroxide concentrations, the accumulation of Cu(I) species in even low concentrations is quite unfavorable. A further kinetic test is obtained by comparing the butane/butene

(17) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

(18) F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(19) R. V. Subramanian, unpublished results.

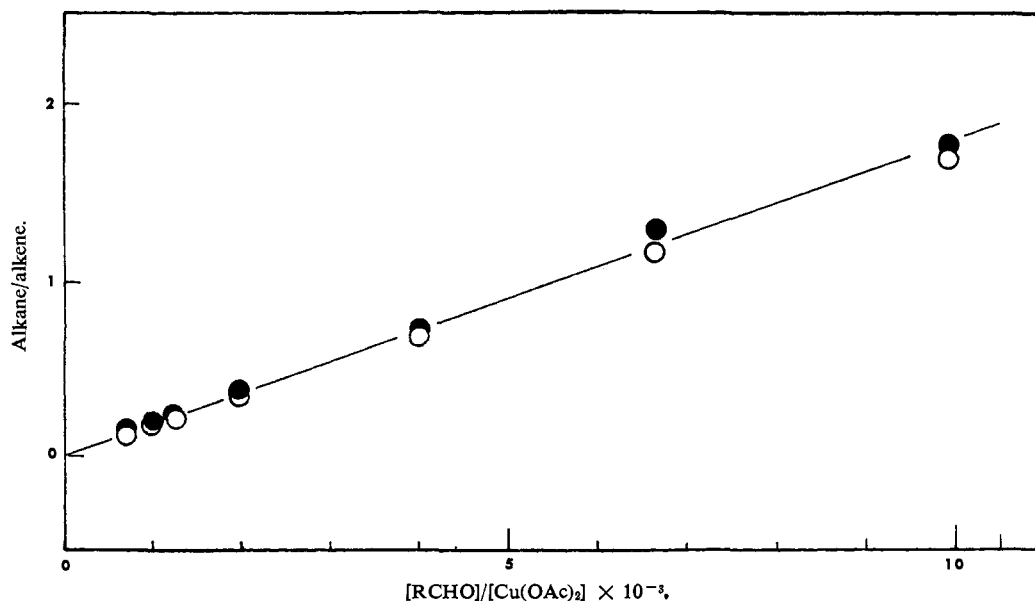
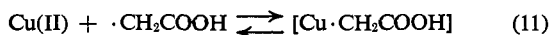


Figure 2. Propane/propene (●) and butane/butene (○) from the decomposition of valeryl peroxide at various cupric acetate and *n*-butyraldehyde concentrations.

ratio in the solvent blank with that in the presence of hydrogen donor. From eq. 6 and 7, the former divided by the latter should be a constant, if the concentration of Cu(II) is the same in each set of experiments. Such a constancy is obtained except at very

$$\frac{\left[\frac{C_4H_{10}}{C_4H_8}\right]_{SH}}{\left[\frac{C_4H_{10}}{C_4H_8}\right]_{RH}} = \frac{k_s[SH]}{k_h[RH]} \quad (10)$$

low Cu(II) concentrations ($< 2 \times 10^{-4} M$).²⁰ In the latter case, a large solvent correction is necessary. Consequently, the radicals derived from the solvent (e.g., $\cdot CH_2COOH$) are important intermediates. Such radicals are only slowly oxidized by cupric acetate (*vide supra*). They may exist in high enough steady-state concentration to affect free Cu(II) by complex formation.²¹



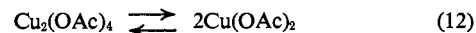
Studies in Glacial Acetic Acid. The decomposition of valeryl peroxide catalyzed by copper salts yields the same products in glacial acetic acid as it does in highly aqueous acetic acid solutions. In general, slightly higher concentrations of Cu(II) salts are required to obviate the formation of butane and to obtain the stoichiometry given by eq. 1. In glacial acetic acid, the competition for the intermediate butyl radicals by Cu(II) and hydrogen donor does not follow the same kinetic relationship (eq. 7) found in aqueous acetic acid. In the anhydrous medium, the ratio, butane/butene, is related to the *square root* of the total copper concentration as shown in Figure 3. The square root dependency is observed with phenylacetaldehyde as donor over a range of cupric acetate and aldehyde concen-

(20) The deviation also occurs at higher Cu(II) when excess pyridine, phenanthroline, or bipyridine is present. With the latter ligands which form strong Cu(I) and Cu(II) complexes, the reaction actually turns pink-red due to the formation of Cu(I) complexes. This is only true at low concentrations of Cu(II) ($< 10^{-4} M$).

(21) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2007 (1961). We imply by eq. 11 that at low concentrations of Cu(II) an appreciable fraction of the cupric species may be tied up as these radical-Cu complexes and materially affect the concentration of the available oxidant.

trations. The value of k_h/k_e is dependent only on the ratio, $[RH]/[Cu(OAc)_2]^{1/2}$. With dichloroacetic acid as donor, the same function applies only at *constant* dichloroacetic acid and *varying* cupric acetate concentrations. On the other hand, if cupric acetate is held constant and the dichloroacetic acid varied, the apparent value of k_h/k_e *decreases* with increasing dichloroacetic acid as shown in Figure 4.

This discordancy can be readily reconciled by considering the dimer-monomer equilibrium (eq. 12) of



cupric acetate in glacial acetic acid.²² In the crystal, cupric acetate monohydrate has been shown to be dimeric $Cu_2(OAc)_4(H_2O)_2$ by X-ray crystallography.²³ Anomalous magnetic moments for Cu(II) carboxylates have been interpreted in terms of an electron-exchange interaction between the closely bonded Cu atoms in the dimer.²⁴

The preservation of the dimeric structure in glacial acetic acid is indicated by the half-order competitive kinetics. In view of the diamagnetic behavior of the cupric acetate dimer,²⁵ it is not surprising that *only the paramagnetic monomeric Cu(II) species are capable of oxidizing alkyl radicals*. The half-order kinetics also implies that the dissociation constant K is sufficiently small, such that the approximation shown in eq. 13

(22) (a) In glacial acetic acid the *ionization* of cupric acetate is several orders of magnitude smaller than the dissociation constant of the dimer.^{22b} Cationic Cu(II) species can, therefore, be neglected from consideration; (b) O. W. Kolling and J. L. Lambert, *Inorg. Chem.*, **3**, 202 (1964).

(23) J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(24) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(25) Actually cupric acetate dimer shows a strongly temperature-dependent magnetic behavior. It is paramagnetic at room temperature, and only diamagnetic below 20°K. (B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London)*, **A214**, 451 (1952); *Phil. Mag.*, **43**, 372 (1952)) due to a low-lying triplet state of the molecule which is partly populated at normal temperature. The singlet-triplet splitting is approximately 300 cm^{-1} , and the triplet state is accessible from merely thermal energies at temperatures used in our studies. Cupric acetate dimer in the triplet state is also largely inactive as an oxidant for alkyl radicals.

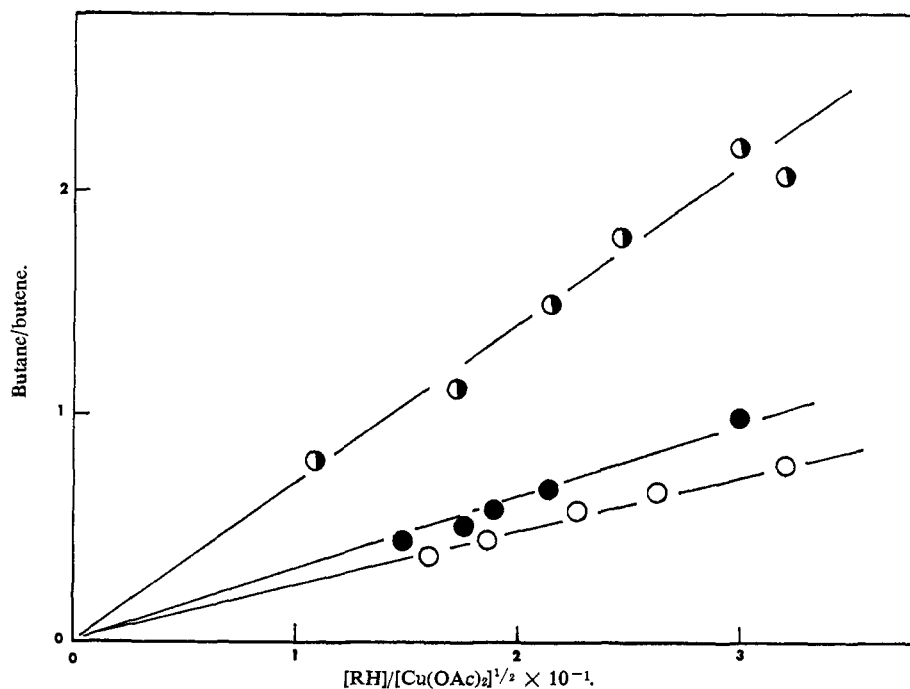


Figure 3. Half-order dependence on cupric acetate of butane/butene in glacial acetic acid with hydrogen donor: ○, phenylacetaldehyde; ●, *n*-butyraldehyde; ○, dichloroacetic acid.

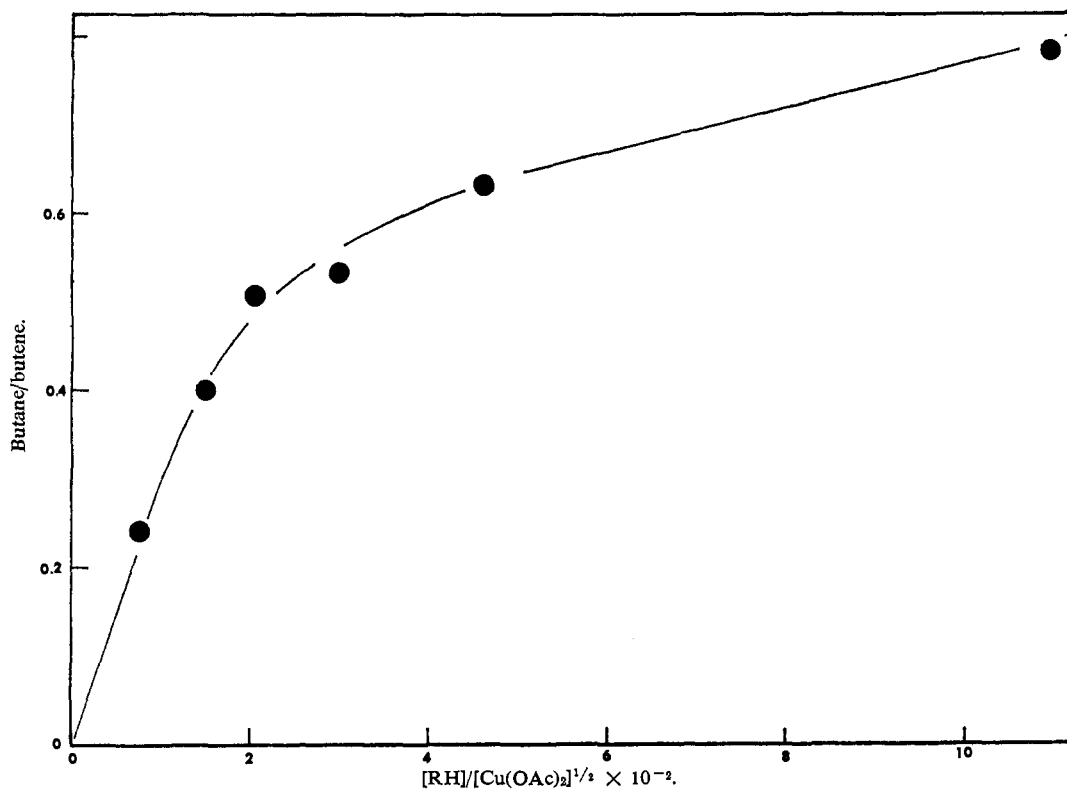


Figure 4. Variation in butane/butene-1 ratio at constant cupric acetate and varying dichloroacetic acid concentrations.

$$[\text{Cu}(\text{OAc})_2] = K^{1/2} [\text{Cu}(\text{OAc})_2]_t^{1/2} \quad (13)$$

is valid, where $[\text{Cu}(\text{OAc})_2]_t$ is the total cupric acetate concentration. Other studies have indeed shown it to be highly dimeric in glacial acetic acid²⁶ ($K = 5.8 \times 10^{-4}$ mole/l. at 57°) as it is in aprotic media.²⁴ Judged by their normal magnetic moments, Cu(II) salts of

(26) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, **4**, 1527 (1965).

strong carboxylic acids such as trichloroacetic acid are monomeric.²⁴ The salt of the weaker chloroacetic acid is subnormal and that of dichloroacetic acid has an intermediate magnetic moment. The latter is presumably a mixture of monomer and dimer; and this readily accounts for the curvature in Figure 4. With increasing dichloroacetic acid, the apparent dissociation constant of the dimer also increases and leads

Table III. Hydrogen-Donor Activities in Glacial Acetic Acid^a

Cupric acetate concn., ^b <i>M</i>	Hydrogen donor	Concn., <i>M</i>	k_h/k_e	-Log <i>K</i>
5.20×10^{-4} - 4.16×10^{-3}	<i>n</i> -Butyraldehyde	0.966	4.4×10^{-4}	3.21
5.20×10^{-4} - 4.16×10^{-3}	Isobutyraldehyde	0.941	9.9×10^{-4}	3.18
5.39×10^{-4} - 3.23×10^{-3}	Dibenzyl ether	0.751	2.6×10^{-4}	3.22
5.32×10^{-4} - 2.65×10^{-3}	Dibenzyl ether	0.451	2.3×10^{-4}	3.30
5.20×10^{-4} - 4.16×10^{-3}	Dichloroacetic acid	1.04	3.4×10^{-4}	3.27

^a In solutions containing 0.07 *M* valeryl peroxide at 57°. ^b Range of Cu(II) concentration examined.

Table IV. Effect of Water on the Oxidation and Reduction of Alkyl Radicals^a

Water, mole %	Hydrogen donor	Concn., <i>M</i>	Cupric acetate concn., ^b <i>M</i>	k_h/k_e	-Log <i>K</i>
0	<i>n</i> -Butyraldehyde	0.966	0.510 - 6.16×10^{-3}	4.4×10^{-4}	3.21
8.6	<i>n</i> -Butyraldehyde	1.61	0.212 - 2.08×10^{-3}	1.3×10^{-4}	3.21
29	<i>n</i> -Butyraldehyde	1.61	0.159 - 1.56×10^{-3}	1.1×10^{-4}	2.27
64	<i>n</i> -Butyraldehyde	2.58	0.260 - 2.60×10^{-3}	1.7×10^{-4}	1.46
				1.8×10^{-4}	1.30 ^c
64	<i>n</i> -Butyraldehyde	1.61	0.260 - 1.95×10^{-3}	1.7×10^{-4}	1.72
				1.8×10^{-4}	1.92 ^c
64	<i>n</i> -Valeraldehyde	1.63	0.260 - 2.60×10^{-3}	1.5×10^{-4}	1.89
64	Dichloroacetic acid	1.04	0.520 - 3.12×10^{-3}	3.1×10^{-4}	0.70

^a In acetic acid solutions containing 0.07 *M* valeryl peroxide at 57°. ^b Range of Cu(II) concentrations employed. ^c Based on C_3H_8/C_3H_6 from aldehyde.

to a progressively higher oxidation rate and smaller apparent values of k_h/k_e . The approximation given by eq. 13 and the half-order dependency on Cu(II) are further invalid at the higher dichloroacetic acid concentrations. As expected, phenylacetaldehyde does not suffer this additional complication at higher concentrations (Figure 3).

Without knowing the value of *K*, the value of k_h/k_e in glacial acetic acid cannot be evaluated from a plot such as Figure 3. The usefulness of this plot is further limited to conditions in which the dissociation constant of cupric acetate dimer is very small and the approximation given by eq. 13 is applicable. It is possible, however, to depict more generally the dependence on total cupric acetate concentration and also to evaluate both k_h/k_e and *K*. The total cupric acetate concentration in terms of monomer and dimer is given by the conservation eq. 14. The simultaneous solution of

$$[\text{Cu}(\text{OAc})_2]_t = 2[\text{Cu}_2(\text{OAc})_4] + [\text{Cu}(\text{OAc})_2] = 2K^{-1}[\text{Cu}(\text{OAc})_2]^2 + [\text{Cu}(\text{OAc})_2] \quad (14)$$

eq. 6, 7, and 14 yields eq. 15. The determination of the

$$\frac{[\text{Cu}(\text{OAc})_2]_t}{[\text{RH}]} \left[\frac{C_4H_{10}}{C_4H_8} \right]_{\text{RH}} = 2K^{-1} \left(\frac{k_h}{k_e} \right)^2 [\text{RH}] \left[\frac{C_4H_8}{C_4H_{10}} \right]_{\text{RH}} + \frac{k_h}{k_e} \quad (15)$$

dissociation constant and the rates of reduction and oxidation by this method has been described.²⁶ Values of *K* and k_h/k_e for various hydrogen donors in glacial acetic acid are summarized in Table III. These values of k_h/k_e only differ by a factor of 2-3 from those obtained in 64 mole % aqueous acetic acid (cf. Tables I and III). Thus, for *n*-butyl radical and *n*-butyraldehyde, k_h/k_e is 4.4×10^{-4} and 1.7×10^{-4} in glacial and aqueous acetic acids, respectively. The corresponding values for *n*-butyl radical and isobutyraldehyde are 9.9×10^{-4} and 4.6×10^{-4} in the two media. It is likely that the hydrogen-transfer constant k_h is the same in

both solvents, and the variation in the ratio is attributed mainly to k_e . It is somewhat surprising that k_e is only slightly greater in a highly aqueous solution compared to glacial acetic acid.

In mixtures of glacial acetic acid and water, there is a progressive and more or less uniform increase in the dissociation constant of the dimer with water content given in Table IV. The relative rates of reduction and oxidation of alkyl radicals, on the other hand, change very rapidly with the addition of small amounts of water to glacial acetic acid. For example, k_h/k_e for butyl radical and butyraldehyde changes from 4.4×10^{-4} in glacial acetic acid to 1.3×10^{-4} on addition of 2.9% v/v. water. Further additions of water bring about only small changes in k_h/k_e . This behavior is most likely attributable to alterations in k_e wrought by changes in the Cu(II) oxidant from $\text{Cu}(\text{OAc})_2 \cdot (\text{HO}_2\text{CCH}_3)_2$ ²⁷ in glacial acetic acid to $\text{Cu}(\text{OAc})_2(\text{H}_2\text{O})_2$ in systems containing water.

The temperature variation of k_h/k_e for *n*-butyl radical from valeryl peroxide in the presence of *n*-butyraldehyde can be obtained from eq. 15 and is illustrated in Figure 5. The difference in energies of activation for hydrogen transfer and oxidation, $E_h - E_e$, is 2.0 ± 0.6 kcal./mole. The ratio of the pre-exponential factors for these reactions A_h/A_e is 6×10^{-3} in glacial acetic acid.

Effect of Nucleophiles. The relative rates of reduction and oxidation k_h/k_e of *n*-butyl radicals were examined in the presence of pyridine and acetate ions as nucleophiles and potential ligands for Cu(II) species.

Pyridine and its effect on cupric acetate in glacial acetic acid can be examined with the aid of eq. 15. The values of k_h/k_e and the dissociation constant at various concentrations of pyridine are presented in Table V. Pyridine as a solute effects dissociation of the cupric acetate dimer. Thus, the dissociation constant of cupric acetate (2×10^{-3} *M*) increases by

(27) D. P. Graddon, *J. Inorg. Nucl. Chem.*, 17, 222 (1961).

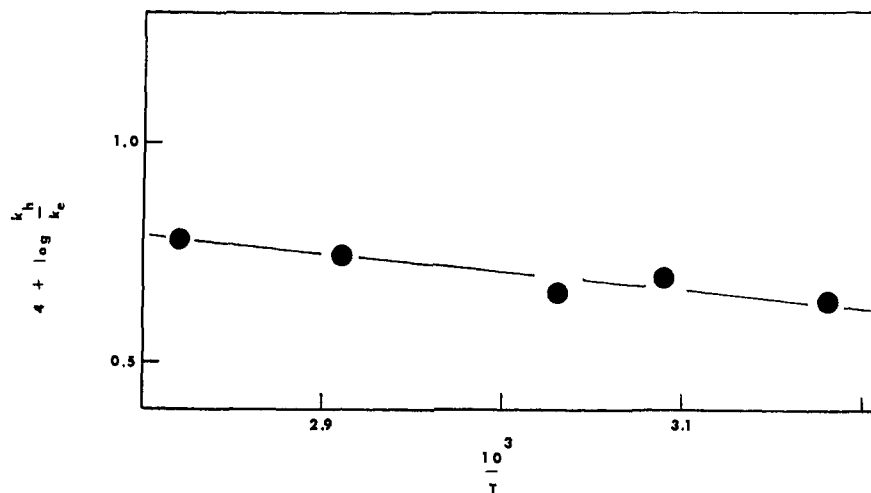


Figure 5. Temperature variation of k_b/k_e from *n*-butyl radicals and *n*-butyraldehyde in glacial acetic acid.

several orders of magnitude from 5.0×10^{-4} mole/l. to 1.9×10^{-2} mole/l. (corresponding to 30 and 85% dissociation, respectively) as pyridine is increased from 0 to 1.06 *M*. The corresponding change in k_b/k_e is relatively minor. Furthermore, in the concentration range 0.01 to 0.10 *M* pyridine, the value of k_b/k_e appears to reach a minimum value. A change in k_b for the reaction between *n*-butyl radicals and dibenzyl ether should not be affected by pyridine in this concentration range. We attribute the change in k_b/k_e to k_e which approaches a maximum value approximately ten times greater than that in glacial acetic acid at 0.2 *M* pyridine.

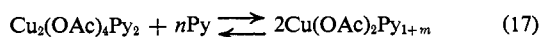
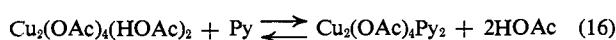
Our data are not sufficient to distinguish among the several mononuclear pyridine-containing Cu(II) species responsible for oxidation of alkyl radicals. The values of k_b/k_e are undoubtedly composite values which include several pyridine Cu(II) complexes. At approximately 1 *M* pyridine, the species are largely indistinguishable from monomeric cupric acetate in their ability to oxidize alkyl radicals. At approximately 0.01 to 0.10 *M* pyridine, species, which are approximately ten times more effective than cupric acetate, are present. We think that such a concentration range may be optimum for the formation of an active diacetate monopyridine Cu(II) complex (eq. 17, $m = 0$).

Table V. Effect of Pyridine and α, α' -Bipyridine on the Oxidation and Reduction of Alkyl Radicals^a

Pyridine concn., <i>M</i>	Hydrogen donor	Concn., <i>M</i>	Cupric acetate concn., <i>M</i>	k_b/k_e	-Log <i>K</i>
0	Dibenzyl ether	0.451	$0.532-2.65 \times 10^{-3}$	2.3×10^{-4}	3.30
0.184	Dibenzyl ether	0.451	$0.534-2.60 \times 10^{-3}$	8.2×10^{-5}	1.89
0.368	Dibenzyl ether	0.451	$0.532-2.12 \times 10^{-3}$	1.0×10^{-4}	2.49
0.736	Dibenzyl ether	0.451	$0.106-1.06 \times 10^{-3}$	1.9×10^{-4}	2.05
1.06	Dibenzyl ether	0.451	$0.534-2.67 \times 10^{-3}$	2.9×10^{-4}	1.72
... ^b	Dibenzyl ether	0.451	$0.512-2.56 \times 10^{-3}$	5.2×10^{-4}	2.38
... ^c	Butyraldehyde	1.61	$0.26-1.30 \times 10^{-3}$	2.9×10^{-4}	2.03

^a In glacial acetic acid solutions containing 0.07 *M* valeryl peroxide at 57°. ^b Using 1:1.1 mole ratio of Cu(II) to α, α' -bipyridine. ^c In 64 mole % aqueous acetic acid with 1:1.1 mole ratio of Cu(II) to bipyridine.

Magnetic moment studies indicate that cupric acetate in pyridine as solvent is largely monomeric.²⁸ Pyridine complexes of copper(II) carboxylates have been isolated.²⁹ However, the monopyridine complex of cupric acetate is *dimeric* and isostructural with the monohydrate.³⁰ These observations, together with the variation of the dissociation constant observed with pyridine as solute, indicates that several equilibria involving cupric acetate are extant in glacial acetic acid.



$$n = 2m = 0, 1, 2, 3$$

(28) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

(29) R. D. Gillard, D. M. Harris, and G. Wilkinson, *J. Chem. Soc.*, 2838 (1964).

(30) F. Hanic, D. Stemplova, and K. Hanicova, *Acta Cryst.*, **17**, 633 (1964).

The bidentate ligands, 1,10-phenanthroline and α, α' -bipyridine, form strong complexes with Cu(II).³¹ The resultant complexes also have higher oxidation potentials.³² The effect of α, α' -bipyridine in stoichiometric amounts on Cu(II) as oxidant was examined quantitatively. By utilizing eq. 15, it was found that at a 1:1 molar ratio bipyridine and cupric acetate formed the characteristic blue complex present in aqueous acetic acid solutions. The value of k_b/k_e determined for *n*-butyl radical and *n*-butyraldehyde was actually slightly more (2.9×10^{-4}) than that obtained for cupric acetate (1.9×10^{-4}). A similar difference was obtained for *n*-butyl radical and dibenzyl ether in glacial acetic acid (bipy copper(II) = 5.2×10^{-4} , Cu(II)(OAc)₂ = 2.3×10^{-4}). Unfortunately at higher molar ratios

(31) L. G. Sillen and A. E. Martell, Special Publication No. 17, The Chemical Society, London, 1964, pp. 440, 664.

(32) B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961); D. D. Perrin, *Rev. Pure Appl. Chem.*, **9**, 257 (1959); C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, 1351 (1962).

Table VI. Effect of Salts on the Oxidation and Reduction of Alkyl Radicals^a

Salt Concn., <i>M</i>	Solvent	Cupric acetate concn., ^c 10 ³ <i>M</i>	RH	<i>k_b/k_e</i>	-Log <i>K</i>
None	HOAc ^b	0.532-2.65	C ₄ H ₁₀	2.3 × 10 ⁻⁴	3.30
0.085 LiClO ₄	HOAc	0.532-2.66	C ₄ H ₁₀	1.4 × 10 ⁻⁴	3.35
0.21 LiClO ₄	HOAc	0.532-2.66	C ₄ H ₁₀	7 × 10 ⁻⁵	3.7
0.085 NaOAc	HOAc	0.520-3.12	C ₄ H ₁₀	4 × 10 ^{-5d}	3.1 ^d
0.23 NaOAc	HOAc	0.532-2.66	C ₄ H ₁₀	1.3 × 10 ⁻⁴	2.70
0.21 LiOAc	HOAc	0.520-2.60	C ₄ H ₁₀	1.4 × 10 ⁻⁴	2.50
1.04 LiOAc	HOAc	0.520-3.12	C ₄ H ₁₀	2.3 × 10 ⁻⁴	<0.5 ^e
None	H ₂ O-HOAc ^f	1.30	C ₄ H ₁₀	1.8 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	1.9 × 10 ⁻⁴	
0.84 LiOAc	H ₂ O-HOAc ^f	1.30	C ₄ H ₁₀	2.0 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	2.4 × 10 ⁻⁴	
1.3 LiOAc	H ₂ O-HOAc ^f	1.30	C ₄ H ₁₀	2.4 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	3.2 × 10 ⁻⁴	
1.7 LiOAc	H ₂ O-HOAc ^f	1.30	C ₄ H ₁₀	2.4 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	3.8 × 10 ⁻⁴	
2.2 LiOAc	H ₂ O-HOAc ^f	1.30	C ₄ H ₁₀	2.8 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	4.9 × 10 ⁻⁴	
None	H ₂ O-HOAc ^h	1.26	C ₄ H ₁₀	4.7 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	2.7 × 10 ⁻⁴	
0.57 LiOAc	H ₂ O-HOAc ^h	1.26	C ₄ H ₁₀	4.8 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	2.9 × 10 ⁻⁴	
1.1 LiOAc	H ₂ O-HOAc ^h	1.26	C ₄ H ₁₀	5.9 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	3.6 × 10 ⁻⁴	
1.4 LiOAc	H ₂ O-HOAc ^h	1.26	C ₄ H ₁₀	7.1 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	4.3 × 10 ⁻⁴	
1.1 LiClO ₄	H ₂ O-HOAc ^h	1.26	C ₄ H ₁₀	5.5 × 10 ⁻⁴	<i>g</i>
			C ₃ H ₈	3.4 × 10 ⁻⁴	

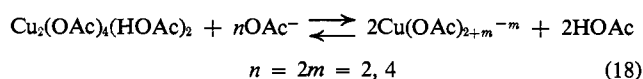
^a In solutions containing cupric acetate, hydrogen donor, and 0.07 *M* valeryl peroxide at 57°. ^b Glacial acetic acid containing 0.451 *M* dibenzyl ether. ^c Where given, range of cupric acetate concentrations studied; others containing water are single-point determinations since Cu(II) is completely monomeric. ^d Approximate value, correction for blank was large. ^e Dimer completely dissociated, none detectable. ^f 34 wt. % aqueous acetic acid containing 1.93 *M* *n*-butyraldehyde. ^g Completely dissociated into monomeric species. ^h 1.53 *M* isobutyraldehyde in 34 wt. % aqueous acetic acid solutions.

of bipyridine/Cu(II) results were not interpretable quantitatively.³³

Previous qualitative results indicated that Cu(II) species present at high pyridine concentrations are less effective oxidants than cupric acetate.³⁴ Similarly, monophenanthroline and monobipyridine Cu(II) complexes oxidize alkyl radicals more effectively than the tris complexes. Extensive coordination of Cu(II) with nitrogen-containing ligands, thus, appears to affect its capacity as an oxidant adversely.

Acetate ion added as an alkali metal salt to solutions of cupric acetate in glacial acetic acid causes extensive breakup of the dimer. The dissociation constant of the dimer in 0.21 *M* LiOAc is 3.2 × 10⁻³ mole/l., which corresponds to 50% dissociation of cupric acetate (4 × 10⁻³ *M*). At 1 *M* LiOAc, cupric acetate (10⁻⁴-10⁻³ *M*) is completely monomeric (Table VI).

Potentiometric and ion-exchange studies have shown that anionic complexes of Cu(II) and acetate ions are readily formed in aqueous solutions.³⁵ Triacetatocuprate (*m* = 1) is the preferred species, though the



tetraacetato complexes (*m* = 2) are formed at high acetate concentrations.

(33) See also footnote 20. Under such circumstances the relative steady-state concentration of Cu(I) relative to Cu(II) is excessive, and the approximation that Cu(II) >> Cu(I) is invalid.

(34) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962).

(35) I. Lundqvist, *Acta Chem. Scand.*, **18**, 858, 1125 (1964).

The values of *k_b/k_e* for *n*-butyl radical and dibenzyl ether fall to a minimum between 0 and 1 *M* LiOAc. This behavior is similar to that observed with pyridine. It is possible that at low acetate concentrations, the formation of the triacetatocuprate is optimum. Such a complex, like the diacetatomonopyridinecopper(II) complex postulated earlier, may be a more active oxidant than species usually found in these solutions. The present results do not eliminate the possibility that the effect of pyridine in acetic acid is to generate acetate ions.³⁶ Pyridine is known to form Cu(II) complexes independently of acetic acid; and we feel that its effect in this medium is also exerted mainly by formation of pyridine Cu(II) complexes (eq. 16 and 17).

The effect of acetate salts is much less pronounced in 64 mole % aqueous acetic acid than it is in the anhydrous medium. The value of *k_b/k_e* for butyl radical is virtually unchanged up to 2.2 *M* lithium acetate as shown in Table VI. For an inexplicable reason the value of *k_b/k_e* for the propyl radicals from the secondary source (butyraldehyde) does increase as acetate salt is increased beyond 1 *M*.

In glacial acetic acid, the addition of neutral lithium perchlorate has very little effect on the dissociation constant of cupric acetate dimer. The value of *k_b/k_e*

(36) Since the conductivity of metal acetates in glacial acetic acid is very low, it is difficult to determine the extent to which an acid-base reaction between pyridine and acetic acid occurs in this medium. There is some evidence for complex formation: I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1014 (1934); L. H. Sutcliffe and J. Proll, *Trans. Faraday Soc.*, **57**, 1078 (1961); Y. T. Deshpande and K. G. Pathki, *ibid.*, **58**, 2134 (1962).

Table VII. Estimated Rate Constants for the Oxidation of Alkyl Radicals by Cu(II) at 57°

Alkyl radical	Ref.	E , kcal./mole	Log A	Log k_h (57°)	k_h/k_e	Log k_e	I.P., e.v.
CH ₃ CH ₂	40	5.9	8.1	4.2	8.80
CH ₃ CH ₂ CH ₂ ·	41	6.7	8.3	3.90	1.8 × 10 ⁻⁴	7.64	8.69
CH ₃ CHCH ₃	42	6.3	8.3	4.15	2.8 × 10 ⁻⁴	7.70	7.90
CH ₃ CH ₂ CH ₂ CH ₂ ·	43	5.4	7.9	4.35	2.0 × 10 ⁻⁴	8.05	8.64
(CH ₃) ₂ CHCH ₂ ·	44	6.5	8.7	4.42	5.3 × 10 ⁻⁴	7.70	8.35
CH ₃ CH ₂ CHCH ₃	45	4.9	7.7	4.47	3.9 × 10 ⁻⁴	7.88	7.93
(CH ₃) ₃ C·	46	4.3	7.5	4.70	9.2 × 10 ⁻⁵	8.74	7.43

falls slightly with increasing lithium perchlorate. Salt effects in anhydrous acetic acid (especially at these high concentrations) are difficult to interpret and other workers have also obtained anomalous results in this medium.^{37a} As shown in Table VI, the values of k_h/k_e in 64 mole % aqueous acetic acid are largely invariant with salt concentrations up to 1 *M*. This probably indicates that both k_h and k_e show little or no salt effect.

Effect of Solvent Deuteration. The oxidation of alkyl radicals by Cu(II) acetate was also examined in 64 mole % deuterium oxide–deuterioacetic acid solutions. These solutions were made by hydrolyzing acetic anhydride with a calculated excess of D₂O with a catalytic amount of D₂O–pre-equilibrated Dowex-50 acid resin as catalyst. For comparison, an equivalent solution of 64 mole % aqueous acetic acid was also prepared from acetic anhydride and duplicate sets of runs were made simultaneously in both solvents. Values of $5.1 \pm 0.1 \times 10^{-4}$ and $2.9 \pm 0.1 \times 10^{-4}$ were obtained for k_h/k_e at 57° for *n*-butyl and isopropyl radicals, respectively, using *n*-valeryl peroxide and isobutyraldehyde as hydrogen donor in 64 mole % H₂O–HOAc. The corresponding values in 64 mole % D₂O–DOAc were approximately 10% larger, being $5.7 \pm 0.1 \times 10^{-4}$ and $3.2 \pm 0.1 \times 10^{-4}$ for *n*-butyl and isopropyl radicals, respectively. No deuterium was incorporated in the products and deuterium exchange into the hydrogen donor or acetic acid was deemed negligible under these conditions. We attribute the small increase in k_h/k_e in deuterated solvent to a decrease of k_e ; k_h is undoubtedly the same in both solvents. However, the decrease of k_e in the deuterated solvent is too small to be meaningfully interpreted as due to effects of changes in solvation^{37b} of the Cu(II) oxidant.

Discussion

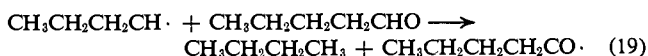
Alkyl radicals derived from the catalytic decomposition of peroxides can be observed simultaneously in reduction and oxidation reactions. Competitive kinetics allow the determination of the relative rates of hydrogen transfer and oxidation by various hydrogen donor substrates and Cu(II) complexes. The ratio of rate constants, k_h/k_e , can be readily determined in aqueous as well as nonaqueous solutions by taking into account partial dimerization of Cu(II) species.

The method allows only the calculation of relative rates of reduction and oxidation of alkyl radicals. A similar type of study of *n*-hexyl radicals was made by DeTar and Wells³⁸ for hydrogen and chlorine abstrac-

tion reactions. They measured relative hydrogen donor properties of various substrates relative to chlorine abstraction from carbon tetrachloride as a monitor reaction. Chloroform is the only substrate we have in common, although it is far from the most desirable. DeTar and Wells³⁸ value for k_h/k_{Cl} for this hydrogen donor is 0.40. Using the value of k_h/k_e listed in Table I, we can calculate k_e/k_{Cl} to be approximately 5×10^2 .

The competitive method allows only the calculation of relative rates of oxidation of alkyl radicals by Cu(II) species. To obtain the absolute rates of these reactions it is necessary to know k_h independently. These hydrogen-transfer rates are only known for reactions in the gas phase. For example, the reduction of *n*-butyl radical by *n*-valeraldehyde has a calculated rate constant of 2.2×10^{-4} l./mole sec. at 57°. If it is assumed that this value is unchanged in solution,³⁹ the second-order rate constant for the oxidation of *n*-butyl radical by Cu(II) in aqueous acetic acid can be evaluated as 1×10^8 l./mole sec. Further, the rates of oxidation of a series of alkyl radicals can be calculated on such a simplifying basis, since the corresponding values of k_h have been determined. The rates of oxidation^{40–46} of several alkyl radicals calculated in this manner are listed in Table VII together with hydrogen-transfer constants at 57°.

The high rates of the oxidation reaction are derived mainly from the low energy of activation. The temperature variation of k_h/k_e yielded the difference in activation energy between hydrogen transfer and oxidation, $E_h - E_e$, as 2.0 kcal./mole. The activation parameters for the transfer reaction 19 in the gas phase are $E_{19} = 5.4$ kcal./mole, $\log A_{19} = 7.9$. The application of these values to solution yields values of E_{20}



$= 3.4 \pm 0.5$ kcal./mole and $\log A_{20} = 10.1 \pm 0.5$ for the oxidation eq. 20. The second-order rate con-

(39) Intuitively this assumption is not badly in error, since alkyl radicals in simple solvents do not appear to be highly solvated. No quantitative comparisons of gas and liquid phase reactions are available, though the problem has been discussed: cf. F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950); F. R. Mayo, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p. 14P.

(40) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1611 (1960).

(41) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572 (1959).

(42) J. A. Kerr and A. F. Trotman-Dickenson, *ibid.*, **55**, 921 (1959).

(43) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602 (1960).

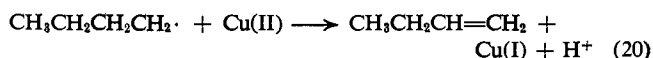
(44) E. L. Metcalfe and A. F. Trotman-Dickenson, *ibid.*, 5072 (1960).

(45) J. T. Gruver and J. G. Calver, *J. Am. Chem. Soc.*, **78**, 5208 (1956).

(46) R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Phys.*, **22**, 678 (1954).

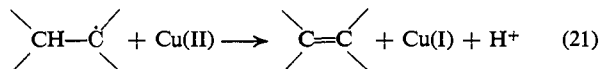
(37) (a) D. Benson and L. H. Sutcliffe, *Trans. Faraday Soc.*, **56**, 246 (1960); (b) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961).

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

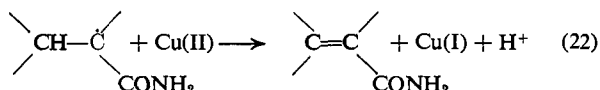


stands for the oxidation of alkyl radicals by Cu(II), thus, are within close approach of the diffusion controlled limit. These large rate constants reflect the versatility of the Cu(II) oxidation reaction in precluding the usual second-order reactions of free alkyl radicals. The use of Cu(II) salts as trapping agents for free alkyl radicals and in synthetic applications is apparent.⁴⁷

From Table II, the second-order rate constants for the oxidation of alkyl radicals by Cu(II) is generally in the range, 10^8 l./mole sec. These values compare with

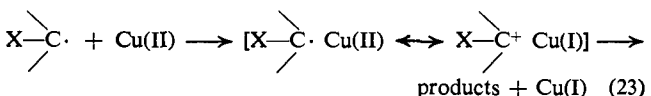


the second-order rate constant of 10^8 l./mole sec. determined by Dainton and co-workers⁶ for the oxidation of an α -carbamido radical by Cu(II) in aqueous



solution. We think that the large difference in rates between these analogous reactions is due to the presence of an electron-withdrawing group (CONH₂) in the α -position of the latter radicals (*vide supra*). Earlier qualitative studies^{7,8} have shown that electron-withdrawing groups, indeed, hinder the oxidation of radicals by electron transfer.⁴⁸ These studies were based on product isolation, which is, at best, a very insensitive tool. The deleterious effect of such substituents has also been observed in the enhanced ionization potentials of the substituted radicals. Thus, the ionization potential (in the gas phase) of alkyl radicals progressively increases with substitution of cyano groups.⁴⁹ The phenomenon is undoubtedly related to the destabilization of the cationic transition state or intermediate by substitution with electron-withdrawing groups.

The oxidation of alkyl radicals by Cu(II) represented by eq. 21 and 22 is considered an electron-transfer process.^{2b} The implication is that a carbonium ion is formed as the first intermediate, followed by a rapid loss of a proton. However, the presence or absence of carbonium ions as discrete intermediates has not been rigorously established to date, although there are abundant qualitative indications^{2-10,47} pointing to a high



degree of carbonium ion character in the activation process.⁵⁰ The fast rates, low energies of activation,

(47) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 1811, 3609 (1965).

(48) Other factors must also be involved since Dainton and co-workers obtained 5.4 ± 1.3 kcal./mole for E_{22} and $A_{22} = 1.1 \times 10^7$ compared to $E_{20} = 3.4 \pm 0.5$ kcal./mole and $A_{20} = 1.3 \times 10^{10}$ for reaction 20. Some of the difference in the pre-exponential terms is perhaps attributable to the difference between large polymeric and simple alkyl radicals.

(49) R. F. Pottie and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 4737 (1961).

(50) The contrary notwithstanding, we assume in subsequent discussions that only the electron is transferred in the rate-determining step.^{2b} Studies directed toward establishing the degree to which the β -carbon-hydrogen bond is simultaneously broken during electron transfer are under investigation.

and large pre-exponential factors as well as the absence of a salt or base effect presented in this study, provide additional support for this contention. The rates of oxidation of alkyl radicals also, qualitatively, correlate with the gas phase ionization potentials⁵¹ of the radicals tabulated in Table VII.

The rapidity of the oxidation of alkyl radicals by Cu(II) is similar to some electron-transfer reactions between inorganic species. The kinetics of fast electron-transfer reactions have been recently measured by relaxation methods. Electron transfer between cationic phenanthroline Fe(II) complexes and anionic Ir(IV) or Ru(IV) complexes have second-order rate constants of the order of 10^9 l./mole sec., or close to the diffusion-controlled limit.⁵² These "outer sphere" electron-transfer reactions in many respects represent optimum examples according to the theory developed by Marcus.⁵³ The second-order rate constant for an electron-transfer process, according to Marcus, is given by the expression

$$k = Z e^{(-W(R) + m^2\lambda)/kT} \quad (24)$$

where Z is the collision frequency between two uncharged reactants in solution, $W(R)$ is the coulombic work term involved in bringing the reactants together in the transition state, and $m^2\lambda$ is related to the work necessary to reorganize the coordination shell around the reactant ion. The reaction between alkyl free radicals and metal ion oxidants should also represent optimum examples of facile electron-transfer reactions. Qualitatively, the electrostatic repulsion between reactants is absent owing to the neutrality of the free radical. Only the reorganization of the coordination shell around the metal oxidant is important since free radicals, by and large, involve minimal changes in solvation in attaining the transition state. The reorganization energy associated with the Cu(I)-Cu(II) transformation does not appear to be large. For example, the less favorable "inner sphere" exchange between Cu(I) chloride and Cu(II) chloride has an estimated second-order rate constant of 5×10^5 l./mole sec.⁵⁴ The low free energy of activation of Cu(II) oxidations of alkyl radicals, in some respects, resembles the facile coupling of these radicals in solution.

Further, it is interesting to compare the oxidation of *alkyl radicals* and the oxidation of *allylic radicals* with respect to variation of the Cu(II) complexes. With the former, the same products are formed irrespective of the Cu(II) oxidant and variations are observed in the *rates* of oxidation. The rates of oxidation of allylic radicals have not been measured, but the *distribution* between allylic isomers (intramolecular competition) can be utilized as a convenient

(51) (a) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959); (b) R. Taubert and F. P. Lossing, *ibid.*, **84**, 1521 (1962). (c) It is surprising that k_6 for both isopropyl and *sec*-butyl radicals are much larger than their primary counterparts in view of their lower ionization potentials, although part of the difference may be due to solvation.

(52) (a) J. Halpern, R. J. Legare, and R. Lumry, *J. Am. Chem. Soc.*, **85**, 680 (1964); (b) P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

(53) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867, 872 (1957); *J. Phys. Chem.*, **67**, 853 (1963); *Trans. Faraday Soc.*, **56**, 21 (1960).

(54) The Cu(I)-Cu(II) exchange is measured in concentrated hydrochloric acid: H. M. McConnell and H. E. Weaver, *J. Chem. Phys.*, **25**, 307 (1956). The mechanism, however, probably involves an inner-sphere chlorine bridge.

probe.^{4a,13,55} The effects of water, pyridine, α,α -bipyridine, as well as common and neutral salts on the rates of oxidation of alkyl radicals are noted in Tables IV, V, and VI. Each of these variables also effects a corresponding change in the allylic isomer distribution of the oxidation products. Pyridine and acetates induce alteration in the distribution of allylic substitution products in marked degree; the effects of water and neutral salt are small but significant.¹³ In each case the rate of oxidation of alkyl radicals and the isomer distribution from the oxidation of allylic radicals can be consistently related to a variation in the structure of the Cu(II) oxidant. In general, variation of the Cu(II) oxidant is reflected in larger changes in the distribution of allylic isomers compared to changes in rates of oxidation of alkyl radicals. The former is, thus, a more sensitive probe for determining the effect of the Cu(II) oxidant on the transition state for oxidation.

Experimental Section

Materials. Anhydrous cupric acetate ($\text{Cu}(\text{OAc})_2$) was from McGean Chemical Co. In glacial acetic acid, it was indistinguishable from the monohydrate from Mallinckrodt Chemical Co. Dichloroacetic acid was Fisher purified reagent. *n*-Valeraldehyde, *n*-butyraldehyde, and isobutyraldehyde (Matheson Coleman and Bell, reagent grade) were redistilled and preserved under argon at 0°. 2-Methylbutyraldehyde and pivalaldehyde were from City Chemical Corp. and redistilled before use. Dibenzyl ether (Eastman Organic, reagent grade) was distilled (*in vacuo*, b.p. 120–130° at 5 mm.) and preserved under argon at 0°. Phenylacetaldehyde was from Givaudan-Delawanna and redistilled before use. Pyridine (Eastman Organic) was refluxed and redistilled from potassium hydroxide pellets. Acetonitrile (Fisher certified reagent) was distilled from phosphorus pentoxide and sodium carbonate. Glacial acetic acid was Du Pont or Baker and Adamson reagent grade. Its water content determined by Karl Fischer titration was less than 0.1%. Argon was from the Linde Co.

n-Valeryl peroxide was prepared from *n*-valeryl chloride and hydrogen peroxide as described earlier.⁹ The other peroxides were also prepared from the corresponding acid chlorides by this procedure. In each case, the isomeric purity of the chlorides was checked by converting them to the methyl esters, which were analyzed by gas chromatography.

Lithium acetate was obtained as the hydrate from Lithium Corp. The water was removed *in vacuo* with heating to approximately 150° for several days. It was obtained as a colorless, free-flowing powder and analyzed potentiometrically for acetate (98.6%). Sodium acetate was anhydrous material from Baker and Adamson Products. Deuterium oxide (99.82 mole % D_2O) was obtained from Bio-Rad Laboratories.

Decompositions. The required amounts of stock solutions of the peroxide, cupric acetate, and hydrogen

donor were pipetted into a 100-ml. reaction flask. Enough solvent was added from a buret so that the volumes of the reactants together with the solvent added up to 35 ml. The reaction flasks were stoppered with self-sealing rubber serum caps and bound with taut rubber bands to maintain a gas-tight seal under pressure. The reaction mixtures were then stirred for 40 min. while being deaerated with a slow stream of argon introduced with hypodermic needles. The flasks were cooled in an ice bath without freezing the contents during deaeration in order to minimize entrainment of the contents. After flushing, the reaction flasks were placed in a thermostated bath ($\pm 0.1^\circ$) for approximately 2 hr. Reaction was terminated by removing the flask from the bath and cooling it in an ice bath. Less than 3 mmoles of peroxide was employed and in most cases it was not completely decomposed. Hence, the concentration of the substrate remained practically unchanged during the reaction. Since the concentration of cupric acetate is not significantly altered, the ratio, $[\text{RH}]/[\text{Cu}(\text{OAc})_2]$ was essentially constant during the decomposition.

Analysis. The reaction flasks were then equilibrated at room temperature and samples of gas were withdrawn and analyzed by gas chromatography (g.c.) on a 15-ft. column of 30% Dowtherm on firebrick at 20° (propane, 5 min.; propylene, 6 min.; butane, 12 min.; butene-1, 15 min.; *trans*-butene-2, 18 min.; *cis*-butene-2, 22 min.) The same analysis was obtained on a 20-ft. column of AgNO_3 -benzyl cyanide on Chromosorb P, 20° (isobutane, 5 min.; butane, 6.5 min.; *trans*-butene-2, 12 min.; isobutylene, 13 min.; butene-1, 17 min.; and *cis*-butene-2, 21 min.).

Known volumes of the pure gases (Matheson Co., or Phillips pure grade) were mixed in various ratios of volumes. They were equilibrated over the solvent used in the reactions, and then analyzed to obtain a calibration factor relating the g.c. area ratios of the gases to their molar ratios. The calibration factor was invariant over the range of molar ratios examined. Reaction mixtures containing glacial acetic acid were diluted with water to 34 vol. % aqueous solutions and equilibrated before removal of gases for analysis. The calibration factor previously obtained for 34% aqueous acetic acid solutions could be used in converting area ratios to molar ratios.

Solutions of acetic acid in deuterium oxide were prepared from the hydrolysis of acetic anhydride (b.p. 134–136°) with a calculated excess of deuterium oxide. Dowex-50 sulfonic acid was preequilibrated five times with D_2O and used as catalyst for the hydrolysis. It was removed by decantation. The solution was used soon after preparation to minimize deuterium exchange with the methyl hydrogens. The butane and butene from the decomposition of valeryl peroxide in the acetic acid/ D_2O solvent was collected and analyzed by infrared and mass spectroscopy. Less than 0.1% deuterium could be detected in either component.

Acknowledgment. We wish to thank the National Science Foundation for generous financial support of this work.

(55) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962).