Tetrahedron. Vol. 24, pp. 5099 to 5113. Pergamon Press 1968. Printed in Great Britain

CATALYTIC REACTIONS OF PEROXIDES
DIRECT INITIATION BY CUPROUS SPECIES

J. K. Kochi and A. Bemis

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

(*Received in USA* 15 *January* 1968; *accepted for publication* 12 *March* 1968)

Abstract—Cuprous acetate complexes are stable in acetonitrile–acetic acid solutions, and procedures for simple preparations of these solutions are described. Cuprous compounds are useful for the direct initiation of copper-catalyzed decompositions of peroxides at the low temperatures often required to obviate competing ionic rearrangements. Thus, these cuprous solutions can be effectively employed at 0° and lower temperatures to catalyze the homolytic chain decomposition of diacyl peroxides and alkyl hydroperoxides. The copper-catalyzed reactions of peresters with alkenes and other substrates can also be initiated at room temperature simply by stirring with a mixture of copper powder and cupric acetate in acetonitrile–acetic acid solutions. The stoichiometries, rates and kinetic chain lengths of these reactions are delineated with regard to a common mechanism which generally prevails in copper catalysis of peroxide reactions.

THE catalytic decompositions of organic peroxides of different structural types lead to a variety of reactions. Metal complexes play important roles in promoting homolytic as well as heterolytic pathways for these reactions.[1] In the former, copper salts are particularly effective catalysts and free radicals are vital intermediates in the chain process.[2] The study of these reactions of peroxides is important both for synthetic purposes as well as serving as models for mechanistic studies of catalysis.[3]

Synthetically, the metal-catalyzed reactions of peresters and alkyl hydroperoxides with various substrates afford products derived by unique substitution patterns.[4] The reaction of peroxides with alkenes and arenes in the presence of copper salts affords adducts in high yields.[5] A variety of intramolecular reactions of peroxides are also catalyzed by metal salts.[6] Furthermore, the decomposition of various peroxides in the presence of copper salts produce alkenes in excellent yields[2,7] and are devoid of the complications usually encountered in thermolysis.[1,8] All of these catalytic reactions appear to proceed in whole or part by similar mechanisms.[9,10]

There are two features common in the mechanism of every one of these catalyzed reactions which are of particular concern: *viz.* the initiation process and the propagation sequence. The decomposition of diacyl peroxides serves as a convenient prototype for these catalyzed reactions because of its relative simplicity. Thus, the autocatalytic decomposition of valeryl peroxide by copper salts has been postulated to proceed via the following chain process:[2,*]

$$(\mathrm{BuCO_2})_2 + \mathrm{Cu^I} \rightarrow \mathrm{Cu^{II}O_2CBu} + \mathrm{BuCO_2\cdot} \tag{1}$$

$$\mathrm{BuCO_2\cdot} \rightarrow \mathrm{Bu\cdot} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{Bu\cdot} + \mathrm{Cu^{II}O_2CBu} \rightarrow \mathrm{C_4H_8} + \mathrm{BuCO_2H} + \mathrm{Cu^I}\ \text{etc.} \tag{3}$$

---

[*] Except where pertinent to the discussion, coordination around $\mathrm{Cu^I}$ and $\mathrm{Cu^{II}}$ species will be omitted.

In the earlier study[2] the reaction was carried out at 55° by using cupric acetate as the catalyst. The induction period was attributed to the slow generation of Cu^I by the limiting thermolysis* of the peroxide (Eq. (4)) followed by facile oxidation of the butyl radicals by Cu^{II} (Eq. (3)). The

$$(BuCO_2)_2 \xrightarrow{\Delta} 2Bu\cdot + 2CO_2 \tag{4}$$

lengthening of the induction period by the addition of either molecular chlorine or bromine was attributed to the destruction of Cu^I by oxidation (Eq. (5)).

$$Cu^I + \tfrac{1}{2}Br_2 \rightarrow Cu^{II}Br \tag{5}$$

since the induction period was proportional to the amount of bromine added.[2]

According to this mechanism (Eqs. (1) to (3)), the catalytic process should be facilitated by the direct use of Cu^I compounds as initiators. This would obviate the undesirable thermal limitations imposed by the homolysis of the peroxide (e.g. Eq. (4)), and also enable other peroxide reactions to be carried out at lower temperatures. It is particularly desirable to develop a method for the catalytic decomposition of peroxides which can be carried out under mild conditions, since a number of peroxides are susceptible to thermal rearrangement[12] and various substrates in the perester reaction are either volatile or liable to heat.

In this study, we wish to show that cuprous species can be efficiently employed in the catalytic decomposition of peroxides at 0°. The perester reaction is also examined briefly to demonstrate the general applicability of cuprous initiation in transfer reactions.

RESULTS AND DISCUSSION

Cuprous complexes in acetonitrile. Cuprous compounds generally disproportionate in solution according to Eq. 6† The stable halide complexes of Cu^I are undesirable

$$2Cu^I \rightarrow Cu^{II} + Cu \tag{6}$$

because of the deleterious effect of halogens on peroxide reactions generally.[13] Cuprous compounds, however, are stabilized in acetonitrile by formation of $Cu^I(NCCH_3)_4$ complexes.[14] The latter are so readily formed that the synproportionation of copper metal and cupric salts in acetonitrile has been used to prepare various Cu (I) complexes such as $Cu^I(NCCH_3)_4X$ ($X = ClO_4, NO_3, BF_4$).[15] We find that the colorless acetonitrile Cu(I) acetate is readily prepared at room temperature simply by stirring a dark green solution of cupric acetate in acetic acid-acetonitrile solutions with copper powder in the absence of air. The rate of syn-proportionation was measured qualitatively by observing the time required for a standard mixture of Cu^{II} and Cu powder to become colorless. As shown in Fig. 1, the rate was optimum between 40–60 %v acetonitrile–acetic acid. Cuprous acetate solutions prepared in this manner were colorless for indefinite periods in the absence of air. Analysis of the cuprous species by titration indicated that the syn-proportionation proceeded quantitatively

---

* We do not wish to imply by Eq. (4) that thermolysis of diacyl peroxides yields two alkyl radicals and CO_2, but only that alkyl radicals are formed in the process. Cage effects are important.[11]

† The virtue of the thermal method of initiation described above is the steady formation of Cu^I species in such low concentrations that disproportionation is not a serious problem, even in solvents in which Cu^I is easily disproportionated. Copper metal has been observed, however, in a number of cases.

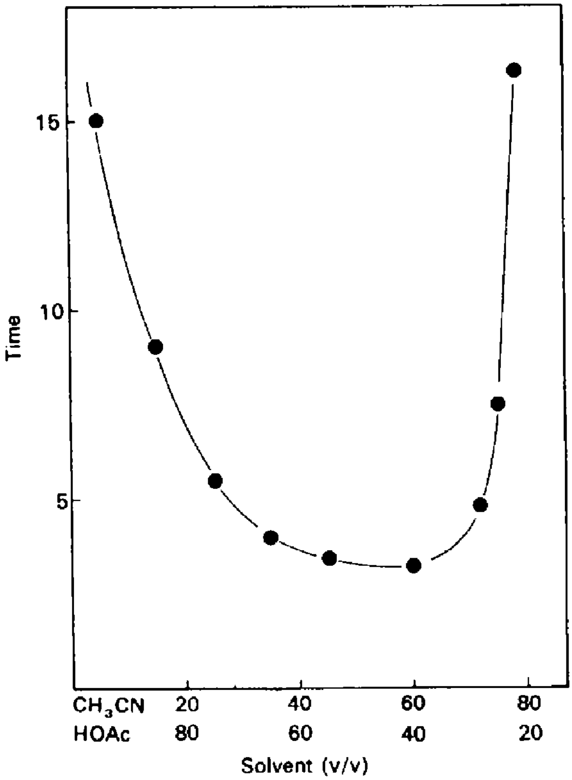


FIG. 1 Rate of syn-proportionation of Cu^{II} acetate and Cu^0 in various acetonitrile-acetic acid solutions (arbitrary time scale).

according to the stoichiometry given in Eq. (7).* Pyridine can also be employed to replace acetonitrile in these reactions. The yellow pyridine Cu (I) acetates similar to the related red α,α'-bipyridine and 1,10-phenanthroline complexes[16] were readily formed.

$$Cu^{II}(OAc)_2 + Cu^0 \xrightarrow[HOAc]{CH_3CN} 2Cu^IOAc \qquad (7)$$

Stable solutions of cuprous complexes can also be readily prepared from precipitated cuprous oxide. The latter was prepared from cupric sulfate and hydrazine sulfate in aqueous solution. After thorough washing and air drying, it was readily soluble in acetic acid–acetonitrile solutions. If care was exercised to remove air from the solvent mixture prior to the addition of cuprous oxide, it was possible to make colorless

$$Cu^I_2O + 2HOAc \xrightarrow[CH_3CN]{} 2Cu^IOAc + H_2O$$

solutions of cuprous acetate containing no cupric species. Solutions of cuprous acetate in acetic acid–acetonitrile prepared by syn-proportionation or methathesis were equivalent for our purposes, and in subsequent studies they were used interchangeably.

Catalytic decomposition of valeryl peroxide at 0°. The decomposition of valeryl peroxide in 40%v acetonitrile-acetic acid solutions containing 0·20M cupric acetate and 0·10M cuprous acetate was complete in less than 15 min at 0°. The stoichiometry

---

* See footnote on page 5099.

of the reaction given by Eq. 8 was determined by measuring carbon dioxide, butene-1 and valeric acid quantitatively by gas chromatography using ethane, *trans*-butene-2 and n-butyric acid, respectively, as internal standards. n-Butane was the only side

$$(\text{n-}C_4H_9CO_2)_2 \xrightarrow{Cu^I\ Cu^{II}} CH_3CH_2CH{=}CH_2 + CO_2 + \text{n-}C_4H_9CO_2H \tag{8}$$

product determined, and in most cases amounted to less than 2%. None (<0·1%) of the butyl acetates could be detected. Pyridine, α,α'-bipyridine and lithium acetate were also added as ligands for the copper species. The stoichiometry was essentially unchanged under these conditions as shown in Table 1.

In the absence of added cuprous salts, a solution of 0·038M valeryl peroxide and 0·20M cupric acetate in 40%v acetonitrile–acetic acid was stable indefinitely at 0°. The rate of decomposition of valeryl peroxide, **P**, increased markedly with added cuprous acetate as shown in Fig. 2. Significantly, no induction period was observed.*

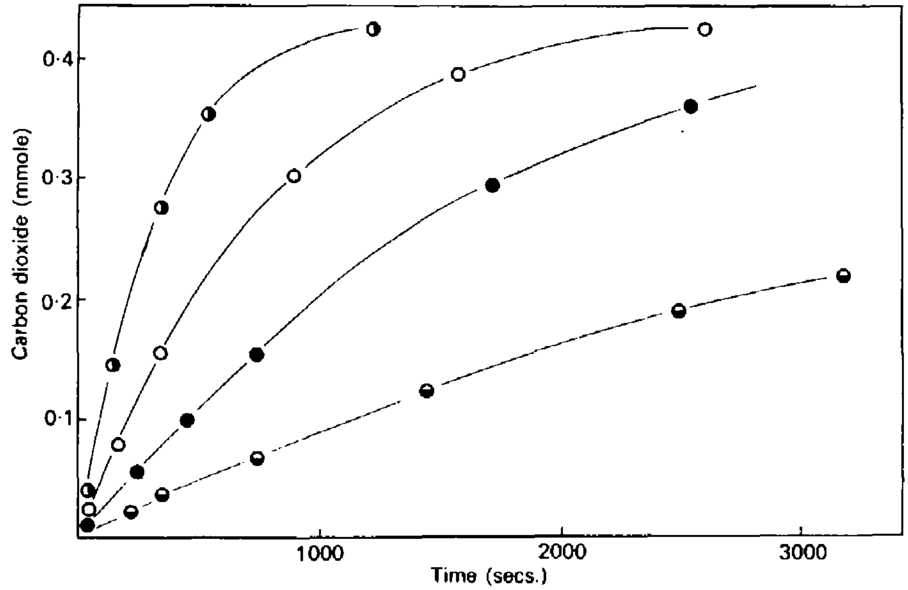


Fig. 2 Copper catalyzed decomposition of 0·038M n-valeryl peroxide in 40%v acetonitrile–acetic acid solutions at 25·5° with 0·80M Cu^{II} acetate and Cu^I acetate: ◐ 0·034M; ○ 0·014M; ● 0·0068M; ⊖ 0·0034M.

The catalytic nature of the reaction could be determined by the amount of cuprous acetate consumed during decomposition of valeryl peroxide. Cuprous acetate added initially and that remaining after reaction were determined titrimetrically. As shown in Table 2, with excess cuprous acetate as catalyst more than 98% was accounted for after completion of the reaction. The absolute amount of cuprous acetate consumed was unchanged at lower concentration. We calculated that the lower limit for the chain length† was 20, and limited primarily by the accuracy of the cuprous titration. The chain length was smaller at lower cupric concentrations.[2]

---

* (*a*) A slight apparent induction period was only observed in the fastest reactions and was due to supersaturation of the CO_2.

[b] Kinetic studies were more conveniently carried out at 25·5 than at 0 where most of the product studies were made. No significant changes in products occurred over this range of temperature.

† The kinetic chain length is defined as the moles of peroxide decomposed per mole of Cu^I consumed.

TABLE 1. CUPROUS INITIATED DECOMPOSITION OF VALERYL PEROXIDE IN 40 %V ACETONITRILE–ACETATE ACID SOLUTIONS AT 0·5°

Run	Valeryl Peroxide	$Cu^{II}(OAc)_2$	$Cu^{I}OAc$	Ligand[a]	Products (mole %)[b]			
	(M)	(M)	(M)	(M)	CO_2	$n\text{-}C_4H_9CO_2H$	$CH_3CH_2CH{=}CH_2$	$n\text{-}C_4H_{10}$
A48A	0·0384	0·20	0·162	—	103	100	98	1·7
A48B	0·0384	0·20	0·158	Py (0·12)	107	98	100	0
A48C	0·0384	0·20	0·142	Bipy (0·12)	101	100	100	0
A48D	0·0384	0·20	0·161	LiOAc(0·14)	99	98	100	1·6
A54A	0·0390	0·20	0·152	—	100	100	98	1·9
A54B	0·0390	0·20	0·209	Py (0·089)	100	105	101	0
A54C	0·0390	0·20	0·095	Bipy (0·11)	109	101	105	0
A54D	0·0390	0·20	0·096	LiOAc(0·16)	104	104	97	1·6
A60A	0·0386	0·20	0·046	—	97	103	100	2·2
A60B	0·0386	0·20	0·075	—	100	100	103	3·3
A60C	0·0386	0·20	0·014	—	104	90	105	2·0
A60D	0·0386	0·20	0·0091	—	112	107	107	1·2
C7A[c]	0·0384	0·040	0·0097	Py (5·1)	117	91	4·5	0
C7B[d]	0·0320	0·033	0·011	Py (5·1)	113	91	4·5	0

[a] Py = pyridine, Bipy = α,α′-bipyridine.

[b] Accuracy of analysis: valeric acid (±4%), butene-1 and n-butane (±5%), CO_2 (±6%).

[c] Saturated with 1,3-butadiene. For other products, see Text.

[d] 1·5M styrene. For other products, see Text.

Table 2. Consumption of cuprous initiator during the catalyzed decomposition of valeryl peroxide[a]

Run[b]	$Cu^{II}(OAc)_2$ (M)	Cu^IOAc[c] (M)	Cu^IOAc Val.Per. (M/M)	Cu^IOAc[d] (M)	Cu^IOAc (% Recovered)
A48A	0·20	0·162	4·22	0·158	97·6
A48B	0·20	0·158	4·12	0·157	99·5
A48C	0·20	0·142	3·70	0·140	98·4
A48D	0·20	0·161	4·20	0·156	97·1
A48E[e]	0·20	0·134	—	0·133	99·6
A54A	0·20	0·152	3·90	0·148	97·1
A54B	0·20	0·209	5·36	0·205	98·1
A54C	0·20	0·095	2·43	0·093	97·9
A54D	0·20	0·096	2·48	0·095	98·8
A54E[e]	0·20	0·128	—	0·126	98·4
A60A	0·20	0·046	1·19	0·044	94·8
A60B	0·20	0·075	1·94	0·076	101
A60C	0·20	0·014	0·37	0·012	85·2
A60D	0·20	0·0091	0·23	0·0082	91·2
A60E[e]	0·20	0·095	—	0·094	99·0

[a] In 40%v acetonitrile–acetic acid solutions at 0°;

[b] See Table 1 for corresponding run.

[c] Concentration of Cu^I determined by weight of cuprous oxide charged.

[d] Cuprous concentration determined by titration after completion of reaction.

[e] No peroxide added, blank.

In the concentration range, 0·034–0·0034M cuprous acetate, the rate of peroxide disappearance followed pseudo first-order kinetics (by evolution of CO_2):

$$-\frac{dP}{dt} = k'(P) \qquad \text{where } k' = k_1(Cu^I)$$

The observed kinetics are consistent with the mechanism presented in Eqs. (1) to (3), in which steps (2) and (3) are rapid compared to the rate-limiting reduction of valeryl peroxide by Cu^I (Eq. (1)). Evidence for the rapidity of the decarboxylation of acyloxy radicals (Eq. (2))[17] and the oxidation of butyl radicals by Cu^{II} (Eq. (3))[18] has been cited previously. The second-order rate constant, k_1, calculated for the reduction of valeryl peroxide by Cu^I in 40%v acetonitrile–acetic acid solution at 25·5°, was 8×10^{-2} l/mole-sec.

The formation of n-butyl radicals from the catalytic decomposition of valeryl peroxide was demonstrated by trapping either with butadiene or styrene (Table 1). Under these conditions only small amounts of butene-1 were formed. Carbon dioxide and valeric acid together with the adducts (octenyl acetate[10] from butadiene and α-phenylhexylacetate and 1-phenylhexene-1 from styrene were formed in molar amounts according to Eq. (9).

$$(n\text{-}BuCO_2)_2 + C_4H_6 + HOAc \xrightarrow[CH_3CN]{Cu^I\text{-}Cu^{II}} n\text{-}Bu{-}C_4H_6{-}OAc + BuCO_2H + CO_2 \qquad (9)$$

These experiments confirm the earlier studies that n-butyl radicals are converted to butene-1 by Cu^{II} quantitatively according to Eq. (10). The second order rate constant,

$$\text{n-}C_4H_9\cdot + Cu^{II} \xrightarrow[\text{HOAc(CH}_3\text{CN)}]{k_e} CH_3CH_2CH{=}CH_2 + H^+ + Cu^I \tag{10}$$

k_e, from Eq. (10) was compared to the rate of hydrogen abstraction from isobutyraldehyde (Eq. (11), second-order rate constant, k_H) by examining butene-1 and butane by the method described earlier.[18] The oxidation (Eq. (13a)) and reduction (Eq. (13b)) of the isopropyl radicals formed by decarbonylation of the attendant 2-formyl-2-propyl radicals (Eq. 11) were studied coincidentally over a range of Cu^{II} and isobutyraldehyde concentrations.

$$\text{n-Bu}\cdot + (CH_3)_2CHCHO \xrightarrow{k_H} \text{n-BuH} + (CH_3)_2CHCO\cdot \tag{11}$$

$$(CH_3)_2CHCO\cdot \longrightarrow (CH_3)_2CH\cdot + CO \tag{12}$$

$$(CH_3)_2CH\cdot \xrightarrow{Cu^{II}} CH_3CH{=}CH_2 + H^+ + Cu^I \tag{13a}$$

$$(CH_3)_2CH\cdot \xrightarrow{(CH_3)_2CHCHO} CH_3CH_2CH_3 + (CH_3)_2CHCO\cdot \tag{13b}$$

The ratio of second-order rate constants, k_H/k_e, for hydrogen abstraction (Eqs. (11) and (13b)) to oxidation (Eqs (10) and (13a)) for n-butyl and isopropyl radicals was found to be $3{\cdot}2 \times 10^{-3}$ and $1{\cdot}0 \times 10^{-3}$, respectively, at 25·5° in 40%v acetonitrile–acetic acid solutions. Consistency in the data could be shown (Fig. 3) by examining the ratio $[(C_4H_{10})(C_3H_6)]/[(C_4H_8)(C_3H_8)]$. It remained invariant at $2{\cdot}85 \pm 0{\cdot}07$ over a wide range of Cu^{II} and isobutyraldehyde concentrations, as shown in Table 3. This consistency provides a convenient method of directly correlating the values of k_H/k_e for a variety of radicals from peroxides by simply employing isobutyraldehyde as the hydrogen donor.[19] The dissociation constant, K_{eq}, for the

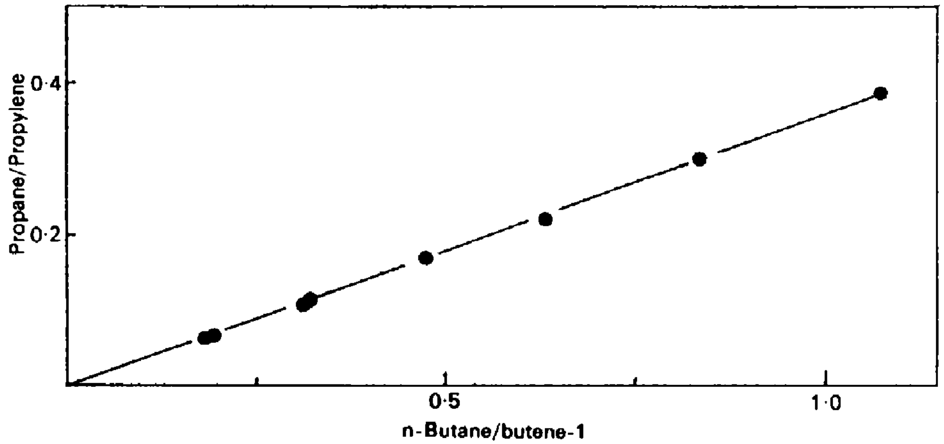


FIG. 3 Hydrogen transfer (alkane) to oxidation (alkene) of isopropyl and n-butyl radicals from the copper-catalyzed decomposition of valeryl peroxide in 40%v acetonitrile–acetic acid acid at 0° in the presence of various amounts of isobutyraldehyde and Cu^{II}.

TABLE 3. RELATIVE RATES OF HYDROGEN TRANSFER AND OXIDATION OF n-BUTYL AND ISOPROPYL RADICALS[a]

$Cu^{II}(OAc)_2$ (M)	Valeryl peroxide (M)	C_3H_8/C_3H_6[b] (mole/mole)	C_4H_{10}/C_4H_8[c] (mole/mole)	$\frac{(C_4H_{10})(C_3H_6)}{(C_4H_8)(C_3H_8)}$
0·0667	0·0277	0·0555	0·194	2·93
0·0330	0·0377	0·108	0·311	2·88
0·0667	0·0377	0·0648	0·184	2·84
0·0330	0·0377	0·108	0·312	2·89
0·0133	0·0344	0·221	0·630	2·85
0·00667	0·0344	0·386	1·075	2·79
0·0133	0·0344	0·288	0·630	2·77
0·00667	0·0344	0·300	0·833	2·78

[a] In solutions of 40%v acetonitrile–acetic acid containing 0·00296 cuprous acetate at 0°.

[b] Propane/propylene.

[c] Butane/butene-1.

cupric acetate dimer (Eq. (14)) in 40%v acetonitrile–acetic acid at 25·5° was determined as $5{\cdot}1 \pm 0{\cdot}3 \times 10^{-2}$ mole/l.[20,*]

$$\mathrm{Cu_2^{II}(OAc)_4 \overset{K}{\rightleftarrows} 2Cu^{II}(OAc)_2} \qquad (14)$$

The absolute rates of oxidation of n-butyl and isopropyl radicals by Cu^{II} acetate in acetonitrile–acetic acid solutions at 25·5° can be obtained from values of k_H/k_e, if gas phase values of k_H can be extrapolated to solution. The activation parameters for reaction of n-butyl radicals with n-valeraldehyde and isopropyl radicals with isobutyraldehyde are: $E_a = 5{\cdot}4$ kcal/mole and $A = 10^{7{\cdot}9}$ l/m-sec and $E_a = 6{\cdot}3$ kcal/mole and $A = 10^{8{\cdot}3}$ l/m-sec, respectively.[21] The extrapolated values for k_H for n-butyl radicals and n-valeraldehyde† and isopropyl radicals and isobutyraldehyde at 25·5° are: $1{\cdot}0 \times 10^4$ and $5{\cdot}0 \times 10^3$ l/mole-sec, respectively. From these, we calculate the second-order rate constants for the oxidation of n-butyl and isopropyl radicals by Cu^{II} in 40%v acetonitrile-acetic acid solutions to be $3{\cdot}1 \times 10^6$ and $4{\cdot}5 \times 10^6$ l/mole-sec, respectively. As discussed previously,[2] these values depend on the assumption that hydrogen transfer rates are the same in solution as in the gas phase.

Catalytic decomposition of 2-methylbutyryl peroxide. In the earlier study,[2] the thermal decomposition of 2-methylbutyryl peroxide in the presence of cupric acetate in glacial acetic acid between 31° and 45° could not be examined without interference from the competing ionic rearrangement of the peroxide. The latter afforded sec-butyl acetate and alcohol in addition to carbon dioxide and 2-methylbutyric acid. The stoichiometry of this rearrangement is not readily distinguished from that of the copper catalyzed decomposition.‡ The formation of butyl acetate via the rearrange-

---

* The value obtained for n-butyl radicals was $4{\cdot}8 \times 10^{-2}$ moles/l. and that for isopropyl radicals was $5{\cdot}5 \times 10^{-2}$ moles/l.

† The value of k_H for n-butyl radical and isobutyraldehyde has not been determined, and we approximate this with n-valeraldehyde.

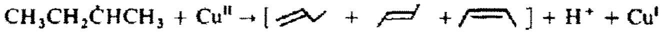
‡ In both reactions a mole of carbon dioxide and acid are formed. Generally, esters (acetates) are formed from the rearrangement reaction carried out in solutions of acetic acid, whereas the catalyzed decomposition affords alkenes (see further for exceptions, however). Alkene and alkyl acetates are in equivalent oxidation states

ment route was particularly troublesome because it also led to ambiguity regarding the products of the oxidation of sec-butyl radicals by Cu^{II} in the presence of acetic acid.

As shown in Table 4, the copper-catalyzed decomposition of 2-methyl-butyryl peroxide by cuprous acetate in 40%v acetonitrile-acetic acid at 0° gave carbon dioxide, 2-methylbutyric acid and butenes according to Eq. (15). sec-Butyl acetate

$$[CH_3CH_2CH(CH_3)CO_2]_2 \xrightarrow[CH_3CN\text{-}HOAc]{Cu^I\ Cu^{II}} C_4H_8 + CO_2 + CH_3CH_2CH(CH_3)CO_2H \qquad (15)$$

formed in the earlier studies was present only in insignificant amounts (<2%). The rearrangement of 2-methylbutyryl peroxide was slow at these temperatures, but may have contributed to the small amount of ester found.* We conclude that sec-butyl radicals were oxidized by Cu^{II} quantitatively† to a mixture of butene-1, *cis*- and *trans*-butene (Eq. (16)) in approximately the same ratio observed earlier at higher temperatures and in a slightly different solvent.



(16)

Pivaloyl peroxide was prepared in pentane solutions at −10°, but all attempts to isolate it were unsuccessful. Even in pentane solution without the aid of copper catalysts, pivaloyl peroxide readily underwent rearrangement presumably via *t*-butyl pivaloyl carbonate and generated isobutylene, carbon dioxide and pivalic acid according to Eq.(17).

$$[(CH_3)_3CCO_2]_2 \rightarrow (CH_3)_2C{=}CH_2 + CO_2 + (CH_3)_3CCO_2H \qquad (17)$$

The facility of peroxides to undergo rearrangement via carboxy inversion (as in Eq. (17)) is largely related to cationic transition states[2, 12, 23] since acyl peroxides which generate tertiary alkyl or benzyl[24] moieties are more prone to undergo such reactions than secondary acyl peroxides, which are in turn more labile than primary acyl peroxides. Since the stoichiometry of these ionic reactions is similar to (and often the same as)‡ that observed by the homolytic route by Cu catalysis, caution must always be exercised in interpreting each.

Catalyzed decomposition of t-amyl hydroperoxide. Tertiary alkyl hydroperoxides are thermally decomposed in the presence of cupric salts at 115° by a process similar to that postulated for diacyl peroxides.[2, 9, 10] Tertiary alkoxy radicals are intermediates (Eq. (18)) which fragment to ketone and alkyl radicals[25] (Eq. 20); the latter

$$CH_3CH_2C(CH_3)_2O_2H + Cu^I \rightarrow CH_3CH_2C(CH_3)_2O\cdot + Cu^{II}OH \qquad (18)$$

are subsequently oxidized by Cu^{II} (cf. Eqs (10) and (13a). We find that t-amyl hydroperoxide is readily decomposed to ethylene and acetone at 0° in 40%v acetonitrile–acetic acid in the presence of 0·080M cupric acetate and 0·010M cuprous acetate (Eq. (19), see Table 5).

$$CH_3CH_2C(CH_3)_2O_2H \xrightarrow[CH_3CN\text{-}HOAc]{Cu^I Cu^{II}} CH_2{=}CH_2 + (CH_3)_2CO + H_2O \qquad (19)$$

---

* (a) The amounts of ester were too small to warrant further investigation of its source.

† (b) Small amounts of esters may have arisen from oxidation of sec-butyl radicals We note that t-alkyl radicals on oxidation with Cu^{II} species afford significant amounts of esters.[22]

‡ The stoichiometry is inferred from previous studies

Table 4. Cuprous initiated decomposition of 2-methylbutyryl peroxide in 40% v acetonitrile–acetic acid at 0·5°

Valeryl Peroxide (M)	$Cu^{II}(OAc)_2$ (M)	$Cu^{I}OAc$ / Val.Per. (M/M)	Ligand[a]	Products (mole %)[b]						
				CO_2	$C_4H_9CO_2H$	C_4H_8-1	t-C_4H_8	c-C_4H_8	C_4H_{10}	s-BuOAc
0·0404	0·040	0·49	—	105	102	38	31	31	0·8	1·9
0·0404	0·040	0·38	—	107	95	39	32	30	-	2·6
0·0303	0·20	0·57	Py (0·51)	103	86	40	30	30	0·3	0·8
0·0404	0·040	0·81	Bipy(0·040)	102	96	42	25	33	0·3	1·3
0·0404	0·20	1·2	Bipy(0·057)	112	91	41	25	34	0·4	1·1

[a] Py = pyridine, Bipy = α,α′-bipyridine.

[b] $C_4H_9CO_2H$ = 2-methylbutyric acid, t-C_4H_8 = *trans*-butene-2, c-C_4H_8 = *cis*-butene-2, s-BuOAc = sec-butyl acetate.

TABLE 5. CUPROUS INITIATED DECOMPOSITION OF t-AMYL HYDROPEROXIDE AT 0°[a]

$Cu^{II}(OAc)_2$ (M)	$[Cu^IOAc]_i$[b] (M)	$[Cu^IOAc]_f$[c] (M)	Ligand	Products (mole %)		
				Ethylene	Acetone	t-Butyl alcohol
0·080	0·014	0·0046 (66)	–	83	—	—
0·080	0·0069	0 (100)[d]	—	55	---	--
0·042	0·049	0·029 (40)	---	61	—	29
0·044	0·048	0·027 (43)	Py (0·11)	55	54	36
0·046	0·043	0·016 (61)	Bipy(0·094)	54	52	43

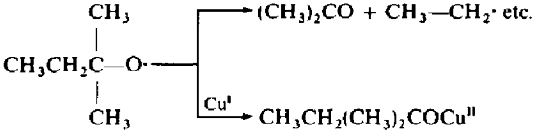
[a] In solutions of 0·0294M t-amyl hydroperoxide in 40%v acetonitrile–acetic acid at 0°.

[b] Cuprous acetate charged (by weight).

[c] Cuprous acetate after completion of reaction. Values in parentheses are percent of cuprous acetate consumed.

[d] Mixture contained unreacted t-amyl hydroperoxide

The amount of t-amyl alcohol which was formed as a side product was related to the cuprous catalyst consumed in the reaction (Table 5). At these low temperatures the unimolecular fragmentation reaction (Eq. (20)) encounters competition from the facile reduction of alkoxy radicals by Cu^I (Eq. (21)*†). The difference between the amounts of cuprous catalyst consumed during decomposition of t-amyl hydroperoxide and valeryl peroxide reflects the relative ease of fragmentation of valeryloxy and t-amyloxy radicals, respectively. The reduction of alkoxy radicals accounts for the less than stoichiometric yields of ethylene and acetone formed under these conditions compared to reactions carried out at higher temperatures.[2,9] It is facilitated by higher concentrations of both Cu^I and alkoxy radicals in the cuprous-initiated reactions.



$$CH_3CH_2C(CH_3)_2O\cdot \longrightarrow (CH_3)_2CO + CH_3{-}CH_2\cdot \text{ etc.} \quad (20)$$

$$CH_3CH_2C(CH_3)_2O\cdot \xrightarrow{Cu^I} CH_3CH_2(CH_3)_2COCu^{II} \quad (21)$$

Copper-perester oxidation of alkenes. The Cu salt catalyzed oxidation of cyclohexene to cyclohexenyl acetate (70–90%) by t-butyl peracetate is usually carried out at 70–80°.[27] A photo-chemical process for carrying out the perester reaction at room temperature (ambient) has been recently proposed.[28] However, the quantum yield is apparently low since initiation is rather inefficient and long periods of illumination are necessitated. After 17 days of irradiation at 30–34°, a 76% yield of cyclohexenyl benzoate was reported from cyclohexene and t-butyl perbenzoate in benzene.

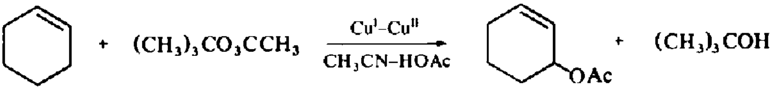
In a modified procedure, a mixture of t-butyl peracetate (2 g), cupric 2-ethylhexanoate (0·05 g) and copper powder (2 g) was stirred magnetically with cyclohexene (10 ml), acetonitrile (40 ml) and acetic acid (3 ml) at room temperature in the absence

---

[*] The second order rate constant for reduction of peroxy radicals by Cu^I in ethanol has recently been estimated to be at least 10^9 l/mole-sec.[26] Alkoxy radicals are generally more reactive than peroxy radicals and their rate of reduction by Cu^I is undoubtedly faster.

[†] The amount of t-amyl alcohol arising via hydrogen abstraction is also, no doubt, important.

of air. The mixture was homogeneous except for the Cu powder and became colorless after stirring for several hours. The color change is a convenient qualitative indication for complete reduction of perester, since the latter reacts rapidly with Cu^{I}. A 70% yield of cyclo-hexenyl acetate (based on t-butyl perester) was obtained. The same



reaction in pyridine as solvent to replace the acetonitrile afforded 45% cyclohexenyl acetate. In 50%v acetonitrile–acetic acid the yield of ester was 35% and in cyclohexene less than 5% cyclohexenyl acetate was found.

A mixture of t-butyl peracetate (3 g), octene-1 (10 ml), cupric 2-ethylhexanoate (0·03 g) and Cu powder (2 g) in a mixture (40 ml) of 95%v acetic acid–acetonitrile was stirred at room temperature for 12 hr. A mixture containing 1-acetoxyoctene-2 (12%) and 3-acetoxyoctene-1 (88%) was obtained in 40% yield. When acetic acid in the solvent was increasingly replaced by acetonitrile the rate of reaction first increased and

$$CH_3(CH_2)_5CH{=}CH_2 + (CH_3)_3CO_3CCH_3 \xrightarrow[HOAc—CH_3CN]{Cu^{0}\text{-}Cu^{II}} C_8H_{15}OAc + (CH_3)_3COH \quad (22)$$

reached a maximum between 50–60%v acetonitrile and then decreased with increasing acetonitrile. The yields of octenyl acetates decreased and increased inversely with the rate.

The yields of substitution products obtainable from alkenes and perester in the presence of a Cu powder–cupric salt combination at room temperature appears to be at least as good as the less convenient photochemical method. Although optimum conditions for reaction were not explored, this method does not afford esters as well as the thermal reaction at higher temperatures. However, there are advantages to conducting reactions at room temperature (or lower) especially when the substrate is volatile or sensitive to heat. The lower yields of products in this system (and based solely on the perester) are mainly due to reduction of the perester by Cu^{I} according to Eq. (23). Thus, t-butyl perbenzoate was reduced to t-butyl alcohol and benzoic acid

$$(CH_3)_3CO_3CC_6H_5 + 2Cu^{I} \rightarrow (CH_3)_3COCu^{II} + C_6H_5CO_2Cu^{II} \quad (23)$$

(after hydrolysis) simply by stirring with Cu powder and cupric acetate in acetonitrile–acetic acid solutions. The reaction was very slow in the absence of acetonitrile. Convenience and the mild conditions inherent in the Cu^{0}–Cu^{II} procedure for the perester reaction more than offset the less than optimum yields obtained at higher temperatures. This is particularly true when substrate is recovered, since products of the reduction of peresters by Cu^{I} are innocuous and t-butyl perester readily available.

The lower yields of substitution product from the Cu^{0}–Cu^{II} method compared to the thermal reaction is directly attributable to the higher Cu^{I} concentration extant in the former.* Earlier, a chain mechanism in which the t-butoxy radical is a key intermediate was proposed:[10]

$$(CH_3)_3CO_3CCH_3 + Cu^{I} \rightarrow CH_3CO_2Cu^{II} + (CH_3)_3CO\cdot \quad (24)$$

$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot \quad (25)$$

$$R\cdot + Cu^{II}O_2CCH_3 \rightarrow R—OAc + Cu^{I} \text{ etc} \quad (26)$$

---

* Provided the activation energy in Eq. (25) is not high and a controlling factor.

The hydrogen transfer step (Eq. (25)) must compete with reduction (Eq. (27); cf. also Eq. (21)) by Cu^I. In both the thermal and photochemical methods the concentration of Cu^I can be maintained at minimal levels by slow homolysis or inefficient

$$(CH_3)_3CO\cdot + Cu^I \rightarrow (CH_3)_3COCu^{II} \tag{27}$$

photolysis of the peroxide (*vide supra*). In the Cu^0–Cu^{II} method of initiation, the rate of production of Cu^I is largely controlled by the solvent (Fig. 1) since Cu^{II} is not a readily adjusted parameter due to its importance in the oxidation step (Eq. (26)). As a consequence, higher levels of Cu^I are maintained in the latter method and lead to shorter chain lengths in the catalytic process.*† These results are in accord with the catalytic decomposition of tertiary alkyl hydroperoxides discussed earlier (*vide supra*), in which competition between fragmentation (unimolecular) and reduction (bimolecular) are competing reactions for the alkoxy intermediate.

Other substrates of potential interest in the perester reaction were not examined extensively. Diethyl ether, tetrahydrofuran and pentene-1 appeared to react readily under these conditions and except for possible complications due to high activation energies for the transfer step (Eq. (25)) with certain substrates, we anticipate no difficulty in carrying out the perester reaction with Cu^0–Cu^{II} at these lower temperatures.

EXPERIMENTAL

Materials. $Cu(OAc)_2 \cdot H_2O$, was analytical reagent grade from Mallinckrodt Chemical Co. Pyridine, from Eastman Organic, was distilled from KOH pellets. 2,2'-Bipyridine was Eastman Organic white label. Lithium acetate hydrate was from Lithium Corporation and dehydrated in a vacuum oven at 110°. Glacial AcOH (0·1 % water) was DuPont reagent grade and was used as such. MeCN (Fisher reagent) was refluxed over P_2O_5 and then distilled through a 3 ft Oldershaw column. Valeryl and 2-methylbutyryl chloride were Eastman Organic white label reagents which were redistilled before use. *t*-Butyl peracetate was from Lucidol Company and was redistilled *in vacuo* (assay, >99 %). Cyclohexene and octene-1 were also redistilled before use.

Cuprous oxide was prepared by reduction of cupric tartrate with hydrazine.[30] n-Valeryl and 2-methylbutyryl peroxides were prepared from their acid chlorides by a method described previously.[2]

General procedure. Cupric acetate, cuprous oxide and pyridine, 2,2'-bipyridine or lithium acetate (as needed) were weighed into a 125 ml Erlenmeyer flask. The flask was cooled to 0° and the required amount of glacial AcOH pipetted into the flask over the weighed-out materials. The AcOH immediately froze; a measured amount of MeCN was added and the flask sealed with a self-sealing rubber septum, washed free of inhibitor. The flask was quickly flushed with argon or nitrogen introduced via a stainless steel needle, inserted through the spectrum and below the liquid surface. After degassing for 10 min, the contents of the flask was stirred magnetically until homogeneous, and allowed to warm to room temp. After recooling to 0° in an ice-water bath, an aliquot of degassed soln of the diacyl peroxide in AcOH–MeCN solvent was introduced into the flask with a hypodermic syringe. A 99·5 % recovery of the cuprous ion could be accomplished, as demonstrated by the Ce^{IV} titration when the diacyl peroxide was omitted. Similarly, no decomposition of the peroxide occurred at 0° in the absence of cuprous ion. Reactions were ordinarily stirred for 2–3 hr, but were checked for completion by CO_2 analysis before removal from the ice bath.

---

* This accounts for lower yields of esters obtained under conditions where the syn-proportionation of Cu^I and Cu^{II} is the fastest, since highest concentrations of Cu^I are extant.

† There also appears to be a direct reaction between peroxide and copper powder. Thus, valeryl peroxide reacts with copper powder suspended in acetonitrile to generate Cu^{II} species. Little carbon dioxide, indicative of valeroxy radicals by one-electron transfer, was formed. This reaction merits further investigation.[29]

Kinetic runs. A similar procedure was used except that stock solns of Cu (II) salts, Cu (I) salts and diacyl peroxides were prepared. In this case the Cu (II) soln as well as additional solvent was added to the flask and degassed. The Cu (I) soln and the peroxide soln were degassed separately. After flushing, the Cu (I) soln was added via syringe and followed by separate addition of the diacyl peroxide soln. In the case of fast reactions, marker gases were added prior to the addition of peroxide.

The reaction flasks were equilibrated at room temp and samples of gas were withdrawn and analyzed by gas chromatography. The hydrocarbons were analyzed on a 15 ft column of 30% Dowtherm A and on a 20 ft column of $AgNO_3$–benzyl cyanide.[2] CO_2 was analyzed on an 8 ft Porapak Q column. Each component was calibrated against an internal marker. CO_2 was monitored (ethane as marker) until evolution ceased. Aliquots of gases used as internal standards were then added, the flasks thoroughly mixed, and the contents analyzed. For calibration, known volumes of pure gases were mixed in various ratios of volumes. They were equilibrated over the solvent used, and analyzed to obtain a calibration factor which was not affected by the presence of Cu^I in soln and did not change over the range of molar ratios of gases studied. After analysis of gaseous products was complete, the flasks were opened and aliquots were removed for analysis of liquid products. Analysis for free carboxylic acids was accomplished by extraction of the acid from an acidified, aqueous aliquot with ether. An isomeric acid was added as an internal standard, and the entire procedure calibrated as described previously. The analysis was performed on a 3 ft column of 20% FFAP (Varian Aerograph) on acid washed Chromosorb W at 142°.

The peroxides were assayed iodometrically[31] and cuprous species were determined by quenching with $FeCl_3$ and titration with standard ceric soln.

Acknowledgement—We wish to thank the National Science Foundation for a generous grant which supported this work. We acknowledge assistance from H. Williams for the studies of the perester reaction.

REFERENCES

[1] E. G. Hawkins, *Organic Peroxides* p. 15 ff. Van Nostrand, New York, N.Y. (1961).

[2] J. Kochi, *J. Am. Chem. Soc.* **85**, 1958 (1963).

[3] J. Kochi, *Records Chem. Progress* **27**, 207 (1966).

[4] [a] M. Kharasch and A. Fono, *J. Org. Chem.* **23**, 324 (1958); **24**, 72 (1959);
[b] G. Sosnovsky and S.-O. Lawesson, *Angew. Chem.* 3, 269 (1964); *Inter. Ed.* for a general review.

[5] J. Kochi, *J. Am. Chem. Soc.* **84**, 2785 (1962); J. Kochi and F. Rust, *Ibid.* **84**, 3946 (1962).

[6] J. Kochi and R. Gilliom, *Ibid.* **86**, 5251 (1964).

[7] S. Goldschmidt, H. Spath and L. Beer, *Liebigs Ann.* **649**, 1 (1962).

[8] D. DeTar and R. C. Lamb, *J. Am. Chem. Soc.* **81**, 122 (1959) and earlier papers.

[9] J. Kochi, *Tetrahedron* **18**, 483 (1962).

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

[11] L. Herk, M. Feld and M. Szwarc, *J. Am. Chem. Soc.* **83**, 2998 (1961); W. Braun, L. Rajenbach and F. Eirich, *J. Phys. Chem.* **66**, 1591 (1962); J. Taylor and J. Martin, *J. Am. Chem. Soc.* **88**, 3650 (1966).

[12] F. D. Greene, H. Stein, C.-C. Chu and F. Vane, *J. Am. Chem. Soc.* **86**, 2081 (1964).

[13] J. Kochi and R. Subramanian, *J. Am. Chem. Soc.* **87**, 1508 (1965); J. Kochi, B. Graybill and M. Kurz, *Ibid.* **86**, 5257 (1964).

[14] **H. Morgan, *J. Chem. Soc.* 2901 (1923); S. Manahan and R. Iwamoto, *Inorg. Chem.* 4, 1409 (1965); I. Kolthoff and J. Coetzee, *J. Am. Chem. Soc.* 79, 1852 (1957).**

[15] B. Hathaway, D. Holah and I. Postlewaite, *J. Chem. Soc.* 3215 (1961); 2444 (1962).

[16] C. Hawkins and D. Perrin, *Ibid.* 1351 (1962); I. Nelson, R. Larson and R. Iwamoto, *J. Inorg. and Nuclear Chem.* **22**, 279 (1961).

[17] M. Szwarc, *Peroxide Mechanisms* (Edited by J. Edwards) p. 153. Interscience, New York, N.Y. (1962).

[18] J. Kochi and R. Subramanian, *J. Am. Chem. Soc.* **87**, 4855 (1965).

[19] Unpublished results, A. Bemis.

[20] J. Kochi and R. Subramanian, *Inorg. Chem.* **4**, 1527 (1965).

[21] J. Kerr and A. Trotman-Dickenson, *Prog. Reaction Kinetics* **1**, 117 (1961).

[22] J. Bacha and J. Kochi, *J. Org. Chem*, in press.

[23] J. Leffler, *Ibid.* **72**, 67 (1950).

[24] P. Bartlett and J. Leffler, *J. Am. Chem. Soc.* **72**, 3030 (1950).

[25] J. Bacha and J. Kochi, *J. Org. Chem.* **30**, 3272 (1965).

[26] A. MacLachlan, *J. Phys. Chem.* **71**, 4132 (1967)
[27] C. Walling and A. Zavitsas, *J. Am. Chem. Soc.* **85**, 2084 (1963).
[28] G. Sosnovsky, *Tetrahedron* **21**, 871 (1965).
[29] cf. R. Razuvaev, *Vistas in Free Radical Chemistry* (Edited by W. Waters) p. 228 f. Pergamon Press, New York (1959).
[30] G. Schlessinger, *Inorganic Preparations*, p. 11. Chemical Publishing, New York (1962).
[31] L. Silbert and D. Swern, *Analyt. Chem.* **30**, 385 (1958).