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THE MECHANISM OF THE COPPER SALT CATALYSED REACTIONS OF PEROXIDES*

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Abstract—The catalytic effect of copper salts on the reactions of peroxides with a variety of hydrogen donor substrates has been described by Kharasch *et al.* The role of copper salts in these reactions is here reinterpreted as one in which they participate in a series of simple redox steps with free radical intermediates. First, reduction of peroxides by cuprous salt to oxy radical and cupric salt. Second, chain transfer reaction between oxy radical intermediates and hydrogen donor substrates. Third, cupric salt oxidation of carbon type radicals formed in the chain transfer step. The rapid rate of the last reaction in most cases precludes complicating side reactions. The behavior of simple alkyl radicals produced from homologous peroxides is shown to be a sensitive function of copper salt concentration. The copper salt catalysis in the reactions of peroxides is compared to those of arene diazonium compounds in the Sandmeyer and Meerwein reactions.

INTRODUCTION

THE discovery by Kharasch *et al.*[1,2] of the facile substitution reactions of peroxides catalysed by copper salts has evoked considerable interest in elucidating the mechanism of these important reactions. We have been engaged in the study of the behavior of organic free radicals towards metal salts, particularly those of the transition series. In this paper we wish to present a unified scheme, based on our investigations, for the peroxide reactions catalysed by copper salts. The proposed mechanism accounts for many of the diverse observations which have been reported in the literature of the catalysed peroxide reactions. The mechanism is further elaborated by a study of the copper salt catalysed decomposition of peroxides derived from the higher homologues of t-butyl peroxides.

Substrates for the peroxides reactions catalysed by copper salts include a variety of compounds possessing hydrogens labile to free radical abstraction processes. Thus, olefins,[2–6] aralkanes,[2] aldehydes,[2] ethers,[2,7,8a,9–12] thioethers,[8b,9,13] esters[2]

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* Part IV, Copper Salt Catalyzed Peroxide Reactions. For previous papers see *J. Amer. Chem. Soc.* **83**, 3162 (1961) and publications in press.
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[1] M. S. Kharasch and A. Fono, *J. Org. Chem.* **23**, 324 (1958).

[2a] M. S. Kharasch and A. Fono, *J. Org. Chem.* **24**, 606 (1959);
[b] M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Amer. Chem. Soc.* **81**, 5819 (1959).
[c] G. Sosnovsky and N. C. Yang, *J. Org. Chem.* **25**, 899 (1960).

[3] M. S. Kharasch and G. Sosnovsky, *J. Amer. Chem. Soc.* **80**, 756 (1958).

[4] P. Story, *J. Amer. Chem. Soc.* **82**, 2085 (1960); *J. Org. Chem.* **26**, 287 (1961).

[5] B. Cross and G. Whitman, *J. Chem. Soc.* 1650 (1961).

[6] J. R. Shelton and J. N. Henderson, *J. Org. Chem.* **26**, 2185 (1961).

[7] S. Lawesson and C. Berglund, *Tetrahedron Letters* No 2, 4 (1960).

[8a] G. Sosnovsky, *J. Org. Chem.* **25**, 874 (1960); *Tetrahedron* **13**, 241 (1961);
[b] G. Sosnovsky, *Ibid.* **26**, 281 (1961).

[9] S. Lawesson, C. Berglund and S. Grönwall, *Acta Chem. Scand.* **15**, 249, (1961).

[10] S. Lawesson and C. Berglund, *Arkiv Kemi* **17**, 475 (1961).

[11a] S. Lawesson and C. Berglund, *Arkiv Kemi* **17**, 465 (1961);
[b] *Angew. Chem.* **73**, 65 (1961).

[12] S. Lawesson and C. Berglund, *Arkiv Kemi* **16**, 287 (1960).

[13] S. Lawesson and C. Berglund, *Acta Chem. Scand.* **15**, 36 (1961).

and alcohols[2,14] react with peresters, dialkyl and diacyl peroxides to yield substitution products. The stoichiometry of the reaction with t-butyl peracetate is described by equation (1). Analogous stoichiometries are applicable to benzoyl peroxide and di-t-butyl peroxide. Thus, benzoates are formed from benzoyl peroxide; and di-t-butyl peroxide under some circumstances yields t-butyl ethers.

$$RH + \text{t-BuOO}_2CCH_3 \xrightarrow{CuX_n} R{-}O_2CCH_3 + \text{t-BuOH} \tag{1}$$

Alkyl hydroperoxides react slightly differently to yield alkyl peroxides[15] according to the stoichiometry (2).

$$RH + 2R'O_2H \xrightarrow{CuX_n} RO_2R' + R'OH + H_2O \tag{2}$$

The apparent dissimilarities among these reactions can be resolved if the following generalized mechanism is evoked.

$$XOOY + Cu^{I} \xrightarrow{\text{I}} XOCu^{II} + YO\cdot \tag{3}$$

$$RH + YO\cdot \xrightarrow{\text{II}} R\cdot + YOH \tag{4}$$

$$R\cdot + XOCu^{II} \xrightarrow{\text{III}} ROX + Cu^{I} \text{ etc.} \tag{5}$$

In reaction (3) the peroxide is reduced by cuprous salt to a cupric salt and an oxy free radical. Step (4) is the well-described chain transfer reaction involving hydrogen abstraction by an oxy free radical. The carbon free radical produced in (4) is oxidized by cupric salt in step (5). In the following discussion each step will be described more fully.

I. *Reduction of peroxides by metal salts*

The mechanism of the catalytic decomposition of hydrogen peroxide by iron salts has been postulated by Haber and Weiss[16] to involve as one of the chain carrying steps an one-electron reduction of the peroxide by ferrous salt:

$$HOOH + Fe^{II} \rightarrow HOFe^{III} + HO\cdot \tag{6}$$

This process has been extended to include the stoichiometric reduction of alkyl hydroperoxides by ferrous and other reducing metal ions to produce alkoxy radicals.[17]

$$ROOH + M^{+n} \rightarrow RO\cdot + MOH^{+n+1} \tag{7}$$

The rates of alkyl hydroperoxide reduction by ferrous, titanous, vanadous, chromous and other salts are rapid even at 0°.

The metal ion catalysed reduction of disubstituted peroxides is less-well documented. Benzoyl peroxide is reduced by antimony[18a], mercury[18b] and iron[19] salts. Ascaridol,

$$(\varphi CO_2)_2 + M^{+n} \rightarrow \varphi CO_2\cdot + \varphi CO_2M^{+n+1}$$

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[14] S. Lawesson and C. Berglund, *Arkiv Kemi* **17**, 485 (1961).

[15] M. S. Kharasch and A. Fono, *J. Org. Chem.* **23**, 324 (1958); **24**, 72 (1959).

[16a] F. Haber and P. Weiss, *Proc. Roy. Soc.* **A147**, 233 (1939).

[b] J. H. Baxendale, M. G. Evans, G. S. Park, *Trans. Faraday Soc.* **42**, 155 (1946); **47**, 462, 591 (1951).

[17a] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.* **15**, 763 (1950);

[b] M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *Ibid.* **16**, 1556 (1951);

[c] A. Tobolsky and R. Mesrobian, *Organic Peroxides* p. 95 ff. Interscience, New York (1954).

[18a] G. Razuvaev, B. Moryganov, E. Olin and Y. Oldekop, *Zh. Obsh. Khim.* **24**, 262 (1954); *Chem. Abstr.* **49**, 4575 (1955);

[b] Y. Oldekop and N. Maier, *Ibid.* **30**, 2274, 2990 (1960) Eng. trans.

[c] G. Razuvaev, *Vistas in Free Radical Chemistry*, p. 224, Pergamon Press, New York (1959).

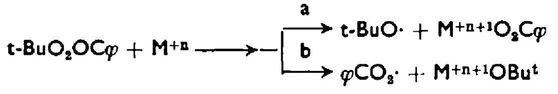
[19a] J. Boeseken and A. Reynhart, *Proc. Acad. Sci., Amsterdam* **29**, 598 (1926).

[b] H. Gelissen and P. Hermans, *Ber. Dtsch. Chem. bes.* **58**, 479 (1925).

[c] W. Kern, *Makromol. Chem.*, **1**, 209 (1947).

a relatively stable peroxide is decomposed by ferrous and titanous salts.[20a] Dibenzene chromium reacts with di-t-butyl peroxide to form tetra-t-butyl chromate at a temperature lower than that required for peroxide homolysis.[20b] The intermediate benzoxy radical from the iron salt catalysed decomposition of benzoyl peroxide has been trapped with styrene (*vide infra*).[21] Other instances of copper salt catalysed decompositions[22] of peroxides have been reported by Kharasch *et al.*[2] and Lawesson and Berglund.[14] Qualitatively, disubstituted peroxides are reduced by metal ions much more slowly than the corresponding hydroperoxides, and reduction often requires some heating.

With unsymmetrical peroxides such as t-butyl perbenzoate two modes of reduction are conceivable:



$$\text{t-BuO}_2\text{OC}\varphi + \text{M}^{+n} \longrightarrow \begin{cases} \xrightarrow{a} \text{t-BuO}\cdot + \text{M}^{+n+1}\text{O}_2\text{C}\varphi \\ \xrightarrow{b} \varphi\text{CO}_2\cdot + \text{M}^{+n+1}\text{OBu}^t \end{cases} \qquad (8)$$

The energetically more favourable reaction producing t-butoxy radicals (8a) is also the one commonly observed.[2c,22] No indication for the alternative cleavage (8b) has been obtained with peracetates and perbenzoates (*vide infra*).

II. *The oxy radical chain transfer step*

The formation of carbon radicals by step (4) [by the reaction of oxy radical with substrate)] proceeds via several competitive paths including chain transfer by hydrogen abstraction and radical addition to unsaturated compounds. With saturated substrates chain transfer by hydrogen abstraction at an activated hydrogen–carbon bond is the preferred route by which oxy radicals formed in step (3) react. Thus, oxy (and related peroxy) radicals such as benzoxy and t-butoxy react with aralkanes to form benzylic radicals (I),[23] with aldehydes to give acyl radicals (II),[24] with ethers to give α-alkoxyalkyl radicals (III),[25] with esters[26] (particularly benzyl or activated) to give α-acyloxy-α-alkoxyalkyl radicals (IV), with primary and secondary alcohols[27a] to give α-hydroxyalkyl radicals (V)[27b,c] with mercaptans to give thiyl radicals (VI),[28] etc.

[20a] H. Paget, *J. Chem. Soc.* 829 (1938); C. G. Moore, *Ibid.* 234 (1951); B. Davis, T. Halsall, A. Hands, *Proc. Chem. Soc.* 83 (1961).

[b] N. Hagihara and H. Yamazaki, *J. Amer. Chem. Soc.* **81**, 3160 (1959); K. Wiberg and G. Foster, *Chem. & Ind.* 108 (1961).

[21] J. Kochi, *J. Amer. Chem. Soc.* **79**, 2942 (1958).

[22a] J. Kochi, *J. Amer. Chem. Soc.* **83**, 3162 (1961).

[b] Publication in press.

[23a] C. Walling, *Free Radicals in Solution* p. 398 ff. Wiley and Sons, New York (1957).

[b] H. Hoch and J. Lang, Ber. *Dtsch. Chem. bes.* **77B**, 257 (1944); **76B**, 169 (1943);

[c] G. Russell, *J. Amer. Chem. Soc.* **78**, 1047 (1956).

[24] H. Bäckström, *Z. Phys. Chem.* **B25**, 99 (1934); C. Walling and E. McElhill, *J. Amer. Chem. Soc.* **73**, 2927 (1951); T. A. Ingles and H. W. Melville, *Proc. Roy. Soc.* **A218**, 163 (1953).

[25] H. Rein and R. Criegee, *Angew. Chem.* **62**, 120 (1950); L. Debiais, M. Niclause and M. Letort, *C. R. Acad. Sci., Paris* **239**, 539 (1954).

[26] J. Allen, J. Cadogan, B. Harris, D. Hey, *Chem. & Ind.* 830 (1961); cf. also Walling, *loc. cit.* p. 414; J. Raley, F. Rust and W. E. Vaughan, *J. Amer. Chem. Soc.* **70**, 3258 (1948).

[27a] Tertiary alcohols react only sluggishly.[14]

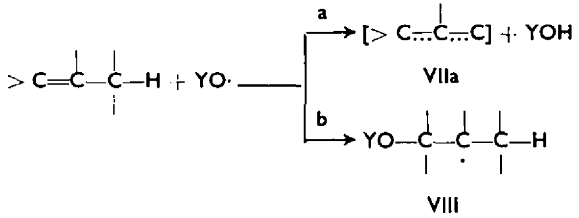
[b] N. Brown, M. Hartig, M. Roedel, A. Anderson, C. Schweitzer, *J. Amer. Chem. Soc.* **77**, 1756, 1760 (1955);

[c] F. Rust, U.S. Patent 2, 871, 104; Harris, 2, 479, 111; W. Urry, F. Stacey, O. Juveland, C. McDonnell, *J. Amer. Chem. Soc.* **76**, 450 (1954).

[28] M. S. Kharasch, W. Nudenberg and G. Mantell, *J. Org. Chem.* **16**, 524 (1951); M. S. Kharasch, A. Read, F. R. Mayo, *Chem. & Ind.* **57**, 752 (1938).

$$\xrightarrow{YO\cdot}\begin{array}{lll} ArCHR_2 & Ar\dot{C}R_2 & I \\ RCHO & R\dot{C}O & II \\ R_2CHOR & R_2\dot{C}OR & III \\ RCO_2CHR_2 & RCO_2\dot{C}R_2 & IV \\ R_2CHOH & R_2\dot{C}OH & V \\ RSH & RS\cdot & VI \end{array} + YOH \qquad (9)$$

Olefins react with oxy radicals by two paths, hydrogen abstraction[22] to yield allylic radicals (VIIa), and oxy radical addition[22] to yield alkyl adduct radicals (VIII).



(10)

Conjugated olefins, such as butadiene, and isoprene, react with oxy radicals primarily by addition to form substituted allylic radicals (VIIb)[22b] similar to (VIIa).

$$\underset{}{YO\cdot + CH_2{=}CH{-}CH{=}CH_2} \rightarrow \underset{VIIb}{[YO{-}CH_2{-}CH{\cdots}CH{\cdots}CH_2]}$$

The stereoselectivity reported earlier[2b,3a,29a] in the reactions off peresters with olefins catalysed by copper salts has been shown[22] not to be a general phenomenon.[29b]

The relative rates of chain transfer and addition with a given olefin is a function of the oxy radical structure. Thus, t-butoxy radicals from t-butyl peresters react with butenes primarily (80–90 per cent)[22] by hydrogen abstraction to yield products from allylic radical intermediates. Benzoxy radicals from benzoyl peroxide react with the same olefins mainly (70–80 per cent)[22b] by addition to form intermediate benzoxy alkyl radicals.

The influence of various structural features of the olefin which determines the competition between radical addition and abstraction reactions has been described by Bolland[30a] and Bateman[30b]. These considerations which were formulated for peroxy radicals, important in autoxidation chains, should also be applicable, in degree, to oxy radicals.

A necessary condition for the chain character of the reaction to be met in these systems is that the chain transfer step (4) be not too highly endothermic. All substrates which have been found reactive in the copper salt catalysed peroxide reactions

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[29a] D. B. Denney, D. Z. Denney and G. Feig, *Tetrahedron Letters* No. 15, 19 (1959).

[b] Since the allylic isomeric olefins were not employed in the early studies[2b,3] the absence of rearrangement was not proved. These workers were apparently misled by the high yields of 3-substituted-1-olefinic products obtained from terminal olefins which usually yield 1-substituted-2-olefinic products in free radical substitution reactions.

[30a] J. Bolland, *Quart. Rev.* **3**, 1 (1949);

[b] L. Bateman, *Ibid.* **8**, 147 (1954).

have met this qualification. In the absence of a suitable chain transfer agent the oxy radical intermediates fragment unimolecularly. The ultimate products in these cases are those which result from the further reactions of the products of thermal fragmentation, methyl radical and acetone from t-butoxy, phenyl radical and carbon dioxide from benzoxy, etc. (*vide infra*).

$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3COCH_3 \tag{11}$$

$$\varphi CO_2\cdot \rightarrow \varphi\cdot + CO_2 \tag{12}$$

III. *Redox reactions between free radicals and cupric salts*

The redox reactions of carbon type free radicals and cupric salts have been delineated into ligand transfer[31] and electron transfer[32] processes. In a ligand transfer process the redox process is accomplished through a transition state[22,32] involving a bridged ligand as in IX. The majority of carbon radical types studied undergo this reaction with facility. The process, however, is particularly sensitive to the nature

$$R\cdot + Cu^{II}X \rightarrow \underset{IX}{[R\cdot\ X{-}Cu^{II} \leftrightarrow R{-}X\ Cu^{I}]} \rightarrow RX + Cu^{I} \tag{13}$$

of the ligand being transferred. Thus the halides, especially bromide and chloride, and thiocyanate are effective bridging ligands. Sulphates and perchlorates give no indication of undergoing this reaction. Of intermediate activity are carboxylates, alkoxides and hydroxide.[22,33]

An electron transfer mechanism is postulated to occur primarily by the transfer of an electron from the free radical to the cupric salt. It generates a transition state[34] X with a high degree of carbonium ion character.

$$R\cdot + Cu^{II}Y \rightarrow \underset{X}{[R^{+}\ YCu^{I} \leftrightarrow R\cdot\ YCu^{II}]} \rightarrow \text{Products} + Cu^{I} \tag{14}$$

Alkyl radicals which possess β-hydrogens may undergo two reactions as a consequence of electron transfer. They are elimination and substitution.[36] The degree to which elimination and substitution reactions compete in electron transfer processes depends on the structure of the alkyl radical. Thus, the importance of elimination reactions progressively decreases in the sequence, ethyl, sec-butyl, and t-butyl radicals.

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[31] J. Kochi, *J. Amer. Chem. Soc.* **78**, 4815 (1956); **79**, 2942 (1957); J. Kumamoto, H. De La Mare, F. Rust, *Ibid.* **82**, 1935 (1960).

[32a] H. De La Mare, J. Kochi, F. Rust, *J. Amer. Chem. Soc.* **83**, 2013 (1961);

[b] To be published.

[33] cf. H. Taube, *Recent advances in Inorganic and Radiochemistry* Vol. 1. p. 1, Academic Press, New York (1959).

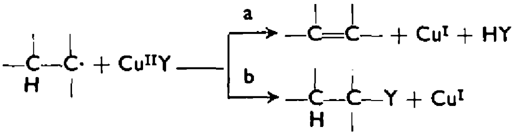
[34] Although in some cases an intermediate free radical-metal ion complex has been postulated,[35] experimental evidence notwithstanding, these complexes have not been invoked in the cupric salt redox reactions.
In the earlier work Kharasch *et al.*[2,15] postulated the existence of various free radical complexes to account for the selectivity of the copper salt reactions. We feel that it is unnecessary to postulate the formation of such complexes if the copper salt redox steps (particularly equation 5) are rapid (*vide infra*).

[35] J. Kochi and F. Rust, *J. Amer. Chem. Soc.* **83**, 2017 (1961).

[36] In many respects these dual processes are akin to the solvolytic merged bimolecular elimination and substitution reactions propounded by Winstein *et al.*[37,32b]

[37] S. Winstein, D. Darwish, N. Holness, *J. Amer. Chem. Soc.* **78**, 2915 (1956); E. Eliel and R. Ro *Tetrahedron* **2**, 354 (1958); D. Kevill, N. Cromwell, *Proc. Chem. Soc.* 252 (1961).

Yields of substitution products increase correspondingly.[32] Acyl, allylic, and benzylic radicals are easily oxidized by this process. In general, the substitution reaction (15b) is favoured with those radicals with low or intermediate ionization potentials, that is, those radicals which yield relatively stable carbonium ions.



(15)

Although the ligand transfer process is not very sensitive to substituent changes in the carbon radical,[32] the electron transfer process is hindered by electron-withdrawing substituents. Thus, radicals possessing α-substituents, such as acyl, cyano or halo groups, react very slowly with cupric perchlorate, sulfate and carboxylates. These results are consonant with the postulate of the importance of carbonium ion character in the transition state of the electron transfer process.

There is no indication that either oxy or thiyl type radicals react with cupric salts by either the ligand transfer or electron transfer processes.

Ligand transfer and electron transfer processes represent, at best, extreme situations in redox processes. In the former, bond making between free radical and ligand is an important part of the driving force of the reaction. In the latter, formation of a carbonium ion is one of the controlling factors. The strict dichotomy of redox reactions into these two categories has been quite arbitrary.[31,32] In a similar manner, the classification of solvolytic mechanisms into S_{N2} or S_{N1} processes fails under close scrutiny because they were found to represent only extreme cases of the importance of bond making or bond breaking processes in the solvolysis transition state.

Halide transfer between metal halides and carbon free radicals at present represent the best models for ligand transfer processes. Similarly the best available paradigms for electron transfer processes are benzylic radicals and metal perchlorates. The gamut of intermediate free radical, ligand, metal salt types cannot be separated distinctly into these classifications. In most of these *intermediate cases* the transition state for redox reactions (13) and (14) can be suitably represented as a resonance hybrid between ligand transfer and electron transfer contributions. The importance of each depends on the nature of the free radical, ligand and metal ion as discussed previously.

$$[\underset{\substack{\text{ligand}\\ \text{transfer}}}{R—XCu^{I}} \longleftrightarrow R\cdot X—Cu^{II} \longleftrightarrow \underset{\substack{\text{electron}\\ \text{transfer}}}{R^{+}\,X—Cu^{I}}]$$

Separate studies of the rates of reaction between carbon type free radicals and cupric salts indicate that the ligand transfer and electron transfer processes are extremely rapid. Even at low cupric salt concentrations, they effectively compete with most active chain transfer reagents for carbon free radical intermediates. The observed modification of free radical reactions by catalytic amounts of copper salts is, therefore, primarily due to the *rapidity of these redox reactions*, which in large part precludes the occurrence of the usual chain transfer reactions characteristic of free radical reactions (*vide infra*). Excessive cupric salt concentrations are often unnecessary. Those cases, however, which involve extremely active chain transfer agents or easily polymerized olefinic monomers benefit by massive cupric salt concentrations.[22b] Selectivity in the copper salt peroxide reactions is observed only in those cases which do not present a multitude of competitive copper salt redox reactions.

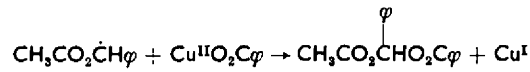
The diverse results observed[1–15] in the copper salt catalysed peroxide reactions are interpretable with this background in mind. Thus, α-cumyl, α-hydroxyalkyl, α-alkoxyalkyl, acyl and similar radicals (from reaction 4) yield the corresponding ester derivatives with cupric carboxylate (formed in reaction 3).

$$R\cdot + Cu^{II}O_2CR' \rightarrow RO_2CR' + Cu^{I} \qquad (16)$$

$$\varphi\dot{C}(CH_3)_2 + Cu^{II}O_2C\varphi \rightarrow \varphi\text{-}C(CH_3)_2O_2C\varphi + Cu^{I}$$

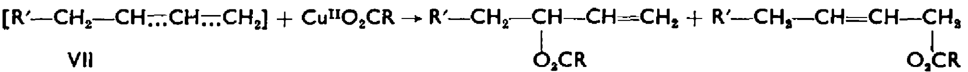
$$CH_3(CH_2)_3\dot{C}O + Cu^{II}O_2C\varphi \rightarrow CH_3(CH_2)_3COO_2C\varphi + Cu^{I}$$

$$\varphi\dot{C}O + Cu^{II}OBu^{t} \rightarrow \varphi COOBu^{t} + Cu^{I}$$



$$CH_3CO_2\dot{C}H\varphi + Cu^{II}O_2C\varphi \rightarrow CH_3CO_2\overset{\varphi}{C}HO_2C\varphi + Cu^{I}$$

Olefins form free radical intermediates, such as allylic radicals VIIa and VIIb and alkyl radicals VIII, which react with cupric carboxylate to yield ester derivatives. Butenyl radicals and 1-t-butoxybutenyl radicals from the reaction of t-butoxy radicals with butene (-1 or -2) and butadiene, respectively, react (equation 16) with cupric carboxylate to yield the same proportion of isomeric allylic esters.[22b] The benzoxybutyl adduct radicals (VIII) from the reaction of butenes with benzoxy radical are oxidized[22b] to ester by the elimination reaction (equation 15a).



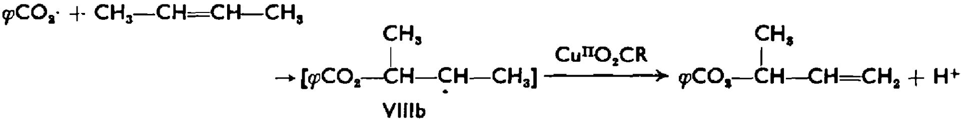
$$[R'{-}CH_2{-}CH{\cdots}CH{\cdots}CH_2] + Cu^{II}O_2CR \rightarrow R'{-}CH_2{-}\underset{O_2CR}{CH}{-}CH{=}CH_2 + R'{-}CH_2{-}CH{=}CH{-}\underset{O_2CR}{CH_2}$$

VII

$R' = H,\ t\text{-}BuO$

$$\varphi CO_2\cdot + CH_2{=}CH{-}CH_2{-}CH_3 \rightarrow [\varphi CO_2{-}CH_2{-}\dot{C}H{-}CH_2{-}CH_3] \xrightarrow{Cu^{II}O_2CR} \varphi CO_2{-}CH_2{-}CH{=}CH{-}CH_3 + H^+$$

VIIIa



$$\varphi CO_2\cdot + CH_3{-}CH{=}CH{-}CH_3 \rightarrow [\varphi CO_2{-}\overset{CH_3}{C}H{-}\dot{C}H{-}CH_3] \xrightarrow{Cu^{II}O_2CR} \varphi CO_2{-}\overset{CH_3}{C}H{-}CH{=}CH_2 + H^+$$

VIIIb

Carbonyl compounds represent interesting examples of the importance of chain transfer (4) and copper salt redox (5) steps. Aldehydes react with oxy radicals primarily by hydrogen abstraction to produce acyl radicals, which are readily oxidized by cupric salt to yield carboxylate derivatives.[32,38] Ketones such as cyclohexanone are moderately active chain transfer agents, in which the α-hydrogens are labile. The α-oxocyclohexyl radical produced, reacts only slowly with cupric carboxylate salts. Consequently, poor yields of α-substituted cyclohexanones (but good yields of benzoic acid) are formed from t-butyl perbenzoate and cyclohexanone.[2c]

Primary and secondary alcohols react with oxy radicals at the α-hydrogen to yield α-hydroxyalkyl radicals. These radicals are known to undergo rapid disproportionation.[39] In the presence of cupric carboxylate they are oxidized to hemiacylals.[2c,14]

$$2R_2\dot{C}OH \rightarrow R_2CHOH + R_2C{=}O \qquad (17)$$

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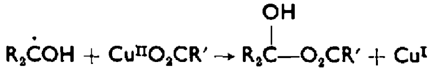
[38] D. D. Coffman, R. Cramer, W. Mochel, *J. Amer. Chem. Soc.* **80**, 2882 (1958).

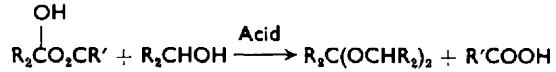
[39] D. Gray and A. Williams, *Chem. Rev.* **59**, 259 (1959); Special Publication *J. Chem. Soc.* **9**, 97 (1957).

In the presence of acid catalysts (RCO_2H or CuX_n) rapid metathesis[8a,19] (19) with alcohol or heterolysis (20) occurs. The carbonyl compounds as well as their acylals

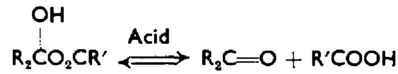


$$R_2\dot{C}OH + Cu^{II}O_2CR' \rightarrow R_2\overset{OH}{\overset{|}{C}}{-}O_2CR' + Cu^{I} \qquad (18)$$

have been observed as products. With alcohols, except for the rate of the reaction (due to copper salt catalysis), the purely thermal and the copper salt catalysed reactions



$$R_2\overset{OH}{\overset{|}{C}}O_2CR' + R_2CHOH \xrightarrow{Acid} R_2C(OCHR_2)_2 + R'COOH \qquad (19)$$

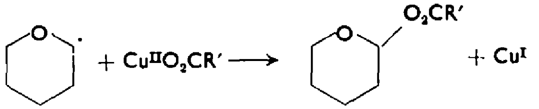


$$R_2\overset{OH}{\overset{|}{C}}O_2CR' \overset{Acid}{\rightleftharpoons} R_2C{=}O + R'COOH \qquad (20)$$

are equivalent. The stoichiometry in both cases [also including equilibria (19) and (20)] is,

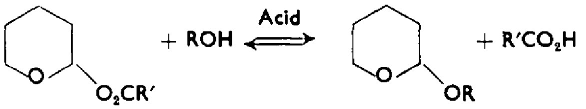
$$R_2CHOH + t\text{-}BuO_2COR' \xrightarrow{(CuX_n)} R_2C{=}O + t\text{-}BuOH + R'CO_2H$$

Ethers are similarly oxidized to mixed ester acylals,[8a] which are isolated together



(21)

with other acylals resulting from alcohol interchange.[10,11a]



(22)

The thiyl radicals produced by abstraction of the acidic hydrogen of mercaptans by oxy radicals are inert to copper salt oxidation. Thiophenoxy radicals from thiophenol thus yield phenyl disulfide.[2c] Similarly oxy radicals produced from the peroxide are unaffected by cupric salts. Both oxy and thiyl radical types, therefore, can be used to initiate these catalysed substitution reactions. In the absence of hydrogen donor substrates thiyl and oxy radicals do not react in a catalytic process (*vide infra*).

The interchangeability of cupric and cuprous salts charged into the reaction has been cited by Kharasch.[2] Although the reaction is catalysed by the cuprous salt reduction (3) of the peroxide, it is not necessary for cuprous salts to be present initially. Since any thermal dissociation of the peroxide will generate oxy radicals, cuprous salts are readily formed from cupric salts by the subsequent reactions (4) and (5). The relative "steady state" concentrations of cuprous and cupric species in solution is dependent on the rates of (3), (4) and (5).

Catalysis of the reaction by copper salts is inoperative if the peroxide reacts with the cuprous salt in the absence of substrates, which can act as hydrogen donors towards oxy radicals. In these cases no carbon type radical is formed (with the exception of fragmentation products of the oxy radical) and no route is available for the regeneration of the cuprous catalyst. The predominant route of the reaction under these circumstances is the thermal decomposition of the peroxide. In order to maintain copper salt catalysis it is necessary to form intermediates which are oxidized by cupric salts. For every radical termination reaction such as radical–radical dimerization or disproportionation which occurs without involving cupric salts, a corresponding peroxide molecule must undergo thermal dissociation. Intermediate cases in which generated radicals are oxidized by cupric salts in *competition* with their mutual (or with oxy radical) annihilation represent *mixed thermal* and *catalytic* processes. The apparent differences in rates of copper salt–perester reactions with various substrates is thus mainly attributed to the different steady state concentrations of cuprous salt.

When t-butyl peresters react with ideal hydrogen donors (e.g. phenols[22b] in the presence of copper salts, no carbon dioxide is liberated. Carbon dioxide observed in some copper salt-catalysed t-butyl perester reactions can be accounted for by the participation of the thermal[40] (and some induced) as well as the catalytic decomposition of the perester. The amount of carbon dioxide liberated from the perester reaction catalysed by copper salt is directly related to the hydrogen donor activity of the substrate.

There are two routes by which foreign nucleophiles can intervene in the substitution process. It is possible for reaction to occur[22b] between the nucleophile and the incipient carbonium ion formed in reaction (14). Alternatively the cupric salt ($\mathrm{Cu^{II}Y}$) can metathesize with foreign nucleophile (HZ) to form other cupric salts which participate in the redox processes (13) and (14).[22b] The formation of cyclohexenyl phthalimide from cyclohexene, t-butyl hydroperoxide and phthalimide, and octenyl benzoate from octene, t-butyl hydroperoxide and benzoic acids are such examples.[2] Other cases have been discussed with butene–perester systems.[22] The solvent effects[2,22] in most of the cited cases are attributable to the metathetical equilibria extant in these solvents.[41]

$$\mathrm{Cu^{II}Y + HZ \rightleftharpoons Cu^{II}Z + HY} \tag{23}$$

$$\mathrm{R\cdot + Cu^{II}Z \longrightarrow RZ + Cu^{I}} \tag{24}$$

Copper salt catalysed reactions of hydroperoxide

The conversion of tertiary hydroperoxides to peroxides in the presence of copper salts[15] is formally analogous to the reactions discussed above. The reaction can be formulated as:

$$\mathrm{t\text{-}BuO_2H + Cu^{I} \longrightarrow t\text{-}BuO\cdot + Cu^{II}OH} \tag{25}$$

$$\mathrm{Cu^{II}OH + t\text{-}BuO_2H \rightleftharpoons Cu^{II}O_2Bu^t + H_2O} \tag{26}$$

$$\mathrm{t\text{-}BuO\cdot + RH \longrightarrow t\text{-}BuOH + R\cdot} \tag{27}$$

$$\mathrm{R\cdot + Cu^{II}O_2Bu^t \longrightarrow RO_2Bu^t + Cu^{I}\ etc.} \tag{28}$$

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[40] A. Blomquist and A. Ferris, *J. Amer. Chem. Soc.* **73**, 3408, 3412 (1951); A. Blomquist and I. Berstein, *Ibid* **73**, 5546 (1951).

[41] The substitution steps originally postulated by Kharasch, *et al.*[1,2,15] varied depending on the nature of the reactants. In many cases an *a priori* determination of the appropriate reaction sequence is a difficult problem.

One of their postulated substitution steps involves a radical induced decomposition of the peroxide. On this basis, however,

$$\mathrm{R{\cdot}Cu^{I} + XOOY \rightarrow ROX + YO\cdot + Cu^{I}}$$

it is difficult to account for the substitution products (benzoates, phthalimides, etc.) obtained in the presence of added nucleophiles (benzoic acid, phthalimide, etc.) since it has been shown that no interchange occurs among products and reactants under the reaction conditions.[22]

If carboxylic acids are present, esters are formed by reactions (29) and (30).

$$\text{Cu}^{\text{II}}\text{OH} + \varphi\text{COOH} \rightleftarrows \text{Cu}^{\text{II}}\text{O}_2\text{C}\varphi + \text{H}_2\text{O} \tag{29}$$

$$\text{R}\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{C}\varphi \longrightarrow \text{RO}_2\text{C}\varphi + \text{Cu}^{\text{I}} \text{ etc.} \tag{30}$$

Steps (25) to (30) are adequate to explain many of the reactions of hydroperoxides reported by Kharasch and Fono[15]. Moreover, the reported differences in reactivities of ketones (cyclohexanones), nitriles,[42] and methyl anilines toward t-alkyl hydroperoxides[15] and toward peresters[2c] may be attributable to the relatively greater ease which cupric t-alkyl peroxide (equation 28) can undergo the necessary ligand transfer reaction (compared to cupric carboxylate, equation 30) with these negatively substituted radicals (*vide supra*). This is consistent with the expected relative stabilities of peroxy and carboxy radicals.

However, the alternative possibility of initially *oxidizing* hydroperoxides with metal ions to peroxy radicals[15,42,43] beclouds, at present, the formulation of a unique mechanism.

$$\text{RO}_2\text{H} + \text{M}^{+\text{n}} \rightarrow \text{RO}_2\cdot + \text{M}^{+\text{n}-1} + \text{H}^+ \tag{31}$$

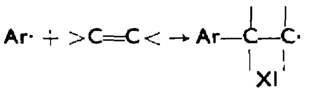
Analogous reactions

The catalysed reaction of peroxides is analogous to the reaction of arene diazonium compounds with copper salts. In the latter, aryl radicals are produced from the cuprous salt reduction[44] of the arene diazonium ion. Subsequent reaction of the aryl radical is by ligand transfer with cupric salts (X = halide) to produce aryl halides (Sandmeyer reaction).[21]

$$\text{ArN}_2{}^+ + \text{Cu}^{\text{I}}\text{X}_\text{n} \rightarrow \text{Ar}\cdot + \text{N}_2 + \text{Cu}^{\text{II}}\text{X}_\text{n} \tag{32}$$

$$\text{Ar}\cdot + \text{Cu}^{\text{II}}\text{X}_\text{n} \rightarrow \text{ArX} + \text{Cu}^{\text{I}}\text{X}_{\text{n}-1} \text{ etc.} \tag{33}$$

In the presence of receptive olefins, aryl radicals add, to yield alkyl adduct radicals



$$\text{Ar}\cdot + {>}\text{C}{=}\text{C}{<} \rightarrow \underset{\text{XI}}{\text{Ar}{-}\overset{|}{\underset{|}{\text{C}}}{-}\overset{|}{\underset{|}{\text{C}}}\cdot} \tag{34}$$

(XI).[21] Similarly sulphur dioxide[45] and carbon monoxide[46] have been found to react with aryl radicals to form other adducts.

$$\text{Ar}\cdot + \text{SO}_2 \rightarrow \text{ArSO}_2\cdot \tag{35}$$

$$\text{Ar}\cdot + \text{CO} \rightarrow \text{ArCO}\cdot \tag{36}$$

Products (Meerwein reaction) are produced for the ligand transfer reaction between the adduct radicals and cupric halide salts.[21,47]

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[42] M. S. Kharasch and G. Sosnovsky, *Tetrahedron* **3**, 97, 105 (1958).

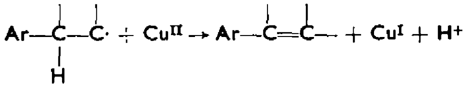
[43a] M. S. Kharasch, A. Fono, W. Nudenberg and P. Bischof, *J. Amer. Chem. Soc.* **17**, 207 (1952); [b] M. Dean and G. Skirrow, *Trans. Faraday Soc.* **54**, 849 (1958).

[44] J. Kochi, *J. Amer. Chem. Soc.* **77**, 5990 (1956); **79**, 2942 (1958); S. C. Dickerman, K. Weiss, A. Ingberman, *Ibid.* **80**, 1904 (1959).

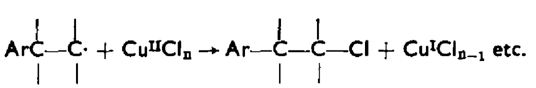
[45] H. Meerwein, G. Dittmar, G. Göllner, R. Hafner, F. Mensch, O. Steinfort, *Chem. Ber.* **90**, 841 (1957).

[46] G. Schrauzer, *Chem. Ber.* **94**, 189 (1961).

[47] The participation of electron transfer processes in the Meerwein reaction has been observed[21] at low chloride ion concentrations.



$$\text{Ar}{-}\overset{|}{\underset{\underset{\text{H}}{|}}{\text{C}}}{-}\overset{|}{\text{C}}\cdot + \text{Cu}^{\text{II}} \rightarrow \text{Ar}{-}\overset{|}{\text{C}}{=}\overset{|}{\text{C}}{-} + \text{Cu}^{\text{I}} + \text{H}^+$$



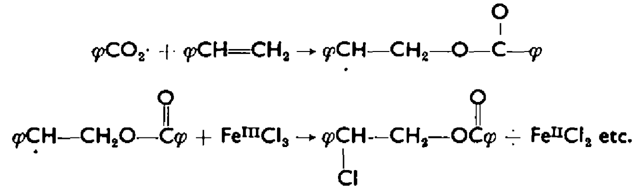
$$\mathrm{ArC{-}C\cdot + Cu^{II}Cl_n \rightarrow Ar{-}C{-}C{-}Cl + Cu^{I}Cl_{n-1}}\ \text{etc.}$$

$$\mathrm{ArSO_2\cdot + Cu^{II}Cl_n \rightarrow ArSO_2Cl + Cu^{I}Cl}$$

$$\mathrm{ArCO\cdot + Cu^{II}Cl_n \rightarrow ArCOCl + Cu^{I}Cl}$$

Chloride ligand transfer in peroxide reactions has also been observed.[21] Thus, benzoyl peroxide and styrene react with iron chlorides to yield products analogous to those obtained in the Meerwein reaction.

$$(\varphi\mathrm{CO_2})_2 + \mathrm{Fe^{II}Cl_2} \rightarrow \varphi\mathrm{CO_2Fe^{III}Cl_2} + \varphi\mathrm{CO_2}\cdot \qquad (37)$$



$$\varphi\mathrm{CO_2}\cdot + \varphi\mathrm{CH{=}CH_2} \rightarrow \varphi\dot{\mathrm{C}}\mathrm{H{-}CH_2{-}O{-}C({=}O){-}}\varphi$$

$$\varphi\dot{\mathrm{C}}\mathrm{H{-}CH_2O{-}C({=}O)}\varphi + \mathrm{Fe^{III}Cl_3} \rightarrow \varphi\mathrm{CH(Cl){-}CH_2{-}OC({=}O)}\varphi + \mathrm{Fe^{II}Cl_2}\ \text{etc.}$$

Results and discussion

Studies of the substitution reactions of peroxides catalysed by copper salts have been primarily conducted with peroxides which contain the t-butylperoxy moiety. Thus, t-butyl peracetate and perbenzoate, di-t-butyl peroxide and t-butyl hydroperoxides, all commercially available compounds, have been used extensively for these reactions. The t-butoxy radical, formed by the reduction of these peroxides by cuprous salt, is relatively stable to unimolecular fragmentation compared to the higher homologues.[22b] Products from the methyl fragment are significant only in the absence of a reactive hydrogen donor.[2c] Because of its stability, t-butoxy radical is the most suitable[48] of the alkoxy radicals with which to carry out substitution reactions of the type discussed earlier.

The success of the copper salt catalysed peroxide substitution reactions is attributed in part to the judicious choice of hydrogen donors which are reactive towards oxy radicals produced in the initiation step. This limits the types of radicals,[49] reacting with cupric salts in a subsequent redox step, to relatively stable moieties, since oxy radicals are known to be reasonably selective in chain transfer processes.[50] Thus, saturated alkyl radicals (particularly primary and secondary) are not readily produced by reaction of alkanes with oxy radicals at the temperature of the copper salt reactions (~80–110°). In fact alkanes, such as n-hexane and n-heptane, often serve as suitable solvents for these copper salt catalysed reactions.[1,22]

Primary and secondary alkyl radicals can be formed in these systems if these chain transfer reactions (equation 4) are avoided and substituted tertiary peresters are employed. The tertiary alkoxy radicals higher than t-butoxy produced from these peresters are more easily cleaved to ketone and alkyl radical.[22b,39] Thus, t-amyloxy radical cleaves (to ethyl radical and acetone) approximately five times faster than

$$\mathrm{R'CO_2CR_3 + Cu^{I} \rightarrow R'CO_2Cu^{II} + R_3CO\cdot} \qquad (38)$$

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[48] However, α-cumyl and related radicals are also akin to t-butoxy radicals in this respect since they undergo only methyl cleavage.

[49] Secondary alkyl radicals can be produced in selected cases if oxy radicals are added to olefins.[22b]

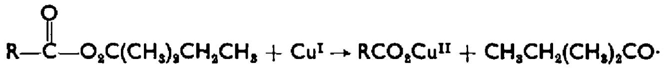
[50a] Reference 39, p. 267 ff;

[b] G. Russell, *J. Org. Chem.* **24**, 300 (1959);

[c] C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.* **82**, 6108, 6113 (1960).

$$R_3CO\cdot \rightarrow R\cdot + R_2C{=}O \tag{39}$$

t-butoxy radical. In this manner ethyl radicals are produced from t-amyl peresters and copper salt catalysts.



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O_2C(CH_3)_2CH_2CH_3 + Cu^I \rightarrow RCO_2Cu^{II} + CH_3CH_2(CH_3)_2CO\cdot \tag{40}$$

$$CH_3CH_2(CH_3)_2CO\cdot \rightarrow CH_3CH_2\cdot + CH_3COCH_3 \tag{41}$$

In benzene solution, gaseous products derived from ethyl radicals are formed in 86–95 per cent yield. The mixture consists of ethylene (95–99 per cent) and ethane (0.2–1 per cent). A small amount of carbon dioxide (1–4 per cent) is also formed.

In the presence of better hydrogen donor solvents, ethylene is still the predominant product. Under these conditions, however, chain transfer of the intermediate t-amyloxy radical with solvent (equation 3, RH = cumene or isopropyl alcohol) competes with its unimolecular fragmentation (equations 24, 26) and the yields of product arising from ethyl radicals are diminished at the expense of t-amyl alcohol formation. Thus, decomposition in isopropyl alcohol gives only a 43 per cent yield of gas, comprised of 97.5 per cent ethylene, 2.0 per cent ethane and 0.5 per cent carbon dioxide. In cumene, 50 per cent gaseous products are formed. They are ethylene (89.0 per cent), ethane (8.8 per cent) and carbon dioxide (2.2 per cent.)

The catalytic decomposition of t-amyl perbenzoate in donor solvents demonstrates the facile oxidation of primary radicals, such as ethyl, by copper salts. The formation of t-amyl alcohol from t-amyloxy radical indicates that hydrogen donor solvents, such as isopropyl alcohol and cumene, effectively compete with unimolecular fragmentation. t-Amyloxy radicals are unaffected by cupric salts. The ethyl radicals

$$CH_3CH_2(CH_3)_2CO\cdot + \varphi CH(CH_3)_2 \left\{ \begin{array}{ll} \xrightarrow{(\sim 50\%)} CH_3CH_2(CH_3)_2COH + \varphi\dot{C}(CH_3)_2 & (42) \\ \xrightarrow{(\sim 50\%)} CH_3CH_2\cdot + CH_3COCH_3 & (43) \end{array} \right.$$

produced in the fragmentation are also subject to two competitive reactions: chain transfer with hydrogen donor to form ethane and oxidation by cupric salt to form ethylene. Although isopropyl alcohol and cumene as hydrogen donors can compete

$$CH_3CH_2\cdot \left\{ \begin{array}{ll} \xrightarrow[(\sim 10\%)]{\varphi CH(CH_3)_2} CH_3CH_3 + \varphi\dot{C}(CH_3)_2 & (44) \\ \xrightarrow[(\sim 90\%)]{Cu^{II}} CH_2{=}CH_2 + Cu^I + H^+ & (45) \end{array} \right.$$

with unimolecular fragmentation of the *t-amyloxy* radicals, these donors are unable to compete with the cupric salt oxidation for the *ethyl* radicals. The low concentrations of cupric salt required for the efficient oxidation of ethyl radicals to ethylene in bulk donor solvents gives some indication of the rapid rate of these cupric salt oxidations. Studies of the effect of cupric salt concentration on the inhibition of olefin polymerizations have given similar results.[22b]

Dialkyl peroxides such as di-t-amyl peroxide are also catalytically decomposed by copper salts. Qualitatively, the temperature required for catalytic decomposition (115–125°) is not widely different from that required for thermal decomposition (130–135°). The product composition, however, is quite sensitive to copper salt concentration. If di-t-amyl peroxide is decomposed in t-butylbenzene solution with catalytic amounts of cuprous bromide at 126–128°, a 78 per cent yield of gaseous products is obtained. This mixture consists of 85–90 per cent *ethane* and only 10–15 per cent ethylene, with small amounts (~5 per cent) of methane. Under these conditions the copper salts are present as an insoluble nondescript brown solid and the solution is colourless, which indicates the presence of little or no *soluble* cupric salts. However, the addition of catalytic amounts of cupric acetate, drastically changes the complexion of the products (75 per cent yield) to *ethylene* (94 per cent), ethane (3 per cent) and methane (3 per cent). The latter effect is also achieved with di-t-amyl peroxide and cuprous bromide if a small amount of acetic acid is added to the reaction. The reactions containing acetate, in one form or another, yield finally solutions which are homogeneous and colored blue. In these catalysed decompositions the evolution of gas coincides with the dissolution of colorless cuprous salt and the appearance of cupric salt in solution (blue). The effect of acetate in altering the product composition can be attributed mainly to the solubility of the cupric salt in t-butylbenzene solution. The initial reduction of di-t-amyl peroxide by cuprous salt is postulated to proceed by the following reaction (compare reactions 3 and 8):

$$(CH_3CH_2(CH_3)_2CO)_2 + Cu^IBr \rightarrow CH_3CH_2(CH_3)_2CO\cdot + Cu^{II}(OC(CH_3)_2CH_2CH_3)Br$$

The cupric bromo t-amyloxide is insoluble in t-butylbenzene solution and does not enter further into the reaction. After the initial consumption of cuprous bromide by this reaction, the decomposition follows the ordinary thermal course. The addition of acetate, either as acetic acid or cupric acetate, to a cuprous bromide–peroxide

$$Cu^{II}(OAm^t)Br + HOAc \rightleftharpoons Cu^{II}(OAc)Br + t\text{-}AmOH \tag{46}$$

$$Cu^{II}(OAc)Br + HOAc \rightleftharpoons Cu(OAc)_2 + HBr \tag{47}$$

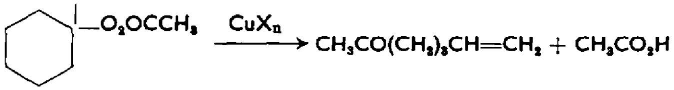
mixture creates a catalytic system since cupric acetate species are sufficiently soluble, albeit in very low concentration, to ensure the redox reaction (27). The effect of copper salt catalysis on the rate of ethylene and ethane formation is shown in Fig. 1 (see Experimental section).

The catalytic decompositions of unsymmetrical dialkyl peroxides were also examined briefly. t-Butyl 4-methyl-4-octyl peroxide reacts with cuprous bromide in t-butylbenzene solution to produce a 32 per cent yield of gas which was comprised of 67 per cent methane, 8 per cent ethylene, 11 per cent propene and 6 per cent butene. Similarly, t-butyl 4-ethyl-4-octyl peroxide yielded a 46 per cent yield of a gaseous mixture containing 41 per cent methane, 40 per cent ethylene, 10 per cent propene and 4 per cent butene. The formation of large amounts of methane in these decompositions indicates that the two modes of reduction represented below are competitive, with the former which produces t-butoxy radicals, predominating.

$$t\text{-}BuOOR^t + Cu^I \longrightarrow \begin{cases} \rightarrow t\text{-}BuO\cdot + Cu^{II}OR^t \\ \rightarrow t\text{-}RO\cdot + Cu^{II}OBu^t \end{cases} \tag{48}$$

R = t-nonyl and t-decyl

By an analogous series of reactions 1-methylcyclohexyl peracetate and catalytic amounts of cuprous chloride forms hepten-6-one-2 in good yield.



(49)

CONCLUSIONS

The mechanism proposed for the reactions of peroxides catalysed by copper salts involves the critical role of the cuprous–cupric couple in a redox capacity with peroxides and intermediate free radicals. This mechanism has been elaborated by the examination of peresters and peroxides other than those derived from t-butyl hydroperoxide. The reduction of these peroxides by cuprous salt has demonstrated the formation of alkoxy radicals (equation 8) as intermediates. The direct formation of carbon type radicals by the fragmentation of alkoxy radicals (rather than chain transfer with hydrogen donor, equation 4) has introduced an alternative method[32] for the study of primary and secondary alkyl radicals in the presence of copper salts.

EXPERIMENTAL

Peroxides

t-Amyl perbenzoate was prepared from t-amyl alcohol and hydrogen peroxide in aqueous sulfuric acid by Milas' procedure.[49] The sodium salt was made by shaking the crude hydroperoxide concentrate with a 40% aqueous NaOH solution at O°. It was washed with ether and n-pentane and dried *in vacuo*. To a suspension of sodium t-amyl peroxide (118 g) in 600 ml ether was added dropwise 120 g benzoyl chloride. The mixture was stirred at room temp for 24 hr and filtered. The ether solution was then stirred with 5% NaOH at room temp to remove unreacted benzoyl chloride. After drying with Na_2SO_4 the ether was vacuum distilled to yield a colourless oil.[50] Yield, 83%; n_D^{25} 1·5132. The infrared spectrum of t-amyl perbenzoate is similar to that of t-butyl perbenzoate. Found: C, 69·4; H, 7·5; Calc. for $C_{12}H_{16}O_3$: C, 69·21; H, 7·74%.

Di-t-amyl peroxide was prepared by Milas' procedure,[49] n_D^{26} 1·4067.

t-Butyl 4-methyl-4-octyl peroxide was prepared from t-butyl hydroperoxide and 4-ethyl-4-octanol as described elsewhere.[51]

t-Butyl 4-ethyl-4-octyl peroxide was prepared from t-butyl hydroperoxide and 4-ethyl-4-octanol in aqueous sulfuric acid.[51]

Copper salt catalyzed decomposition of t-amyl perbenzoate

The peroxide decompositions were carried out at atm press in a 100 ml round bottom flask attached to a gas burette via a spiral water condenser. The system was initially purged with nitrogen and the components introduced. Magnetic stirring was sufficient to insure proper mixing. When the reaction was complete, the gases were distilled into a cold trap (liquid nitrogen) and then expanded into a measured bulb. The gas yields were calculated on the basis of the perfect gas law. The gases were analyzed by GLC (50 ft dimethylsulfolane/firebrick column at 20° and 8 ft silica gel at 0°) and by mass spectral analysis. The solutions were titrated potentiometrically for carboxylic acid. Carbonyl content (acetone) was determined by the standard hydroxylamine method. Benzoic acid was also isolated by extraction.

A solution of 16 g t-amyl perbenzoate in 50 ml benzene and 0·25 g cuprous bromide was heated to 75°, whereupon an exothermic reaction ensued which raised the temp to 85°. Gas (1800 ml, 96%) was liberated which consisted of ethylene (95–99%), ethane (0·2–1%) and carbon dioxide (1–4%). The residual reaction mixture analysed for benzoic acid (94% titration, 75% isolation) and acetone (83%). Neutral esters were also present (approx 10% by saponification).

A solution of 8·6 g t-amyl perbenzoate in 50 ml redistilled isopropyl alcohol and 87 mg cuprous bromide was heated at 68–74° (carefully). Gas evolution was complete in 4 hr. The gas (430 ml, 43%) consisted of 97·5% ethylene, 2·0% ethane, and 0·5 carbon dioxide. The mother liquor contained benzoic acid (94% by titration, 76% by isolation) and acetone (63%).

A solution of 8·6 g t-amyl perbenzoate in 45 ml redistilled cumene and 82 mg cuprous bromide was decomposed at 80–85° in 6 hr. The gas (490 ml, 50%) analyzed for 89% ethylene, 8·8% ethane and 2·2% carbon dioxide. The residual solution contained benzoic acid (85% by titration) and acetone (54%).

Catalysed decomposition of di-t-amyl peroxide

A solution (A) of 3·28 g di-t-amyl peroxide in 25 ml t-butyl benzene and 0·21 g cuprous bromide was heated at 115–120° for 1 hr, but no gas was evolved. At 126–128°, 355 ml (78%) of gas was

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[49] N. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.* **68**, 643 (1946).

[50] Cf. N. Milas and D. Surgenor, *J. Amer. Chem. Soc.* **68**, 642 (1946).

[51] J. K. Kochi, to be published.

liberated in 4 hr. The colorless solution contained a turgid brown precipitate. The gas consisted of methane (~2 %), ethane (90–95 %) and ethylene (5–10 %).

A solution (B) of 4·85 g di-t-amyl peroxide in 25 ml t-butyl benzene and a mixture of 0·19 g cuprous bromide and 0·17 g cupric acetate evolved gas at 122–126° in 3 hr. The gas (465 ml, 81 %) was comprised of methane (1·8 %), ethane (3·0 %), ethylene (92·0 %), butane (2·2 %) and carbon dioxide (1 %). The reaction mixture consisted of a brown precipitate and a light blue solution.

A solution (C) of 3·76 g di-t-amyl peroxide in 25 ml t-butyl benzene, 1·0 g acetic acid and 0·190 g cuprous bromide was decomposed at 127–128° in 1·5 hr. The gas (433 ml, 83 %) was comprised of methane (1 %), ethane (3 %), and ethylene (96 %). The reaction mixture consisted of unreacted cuprous bromide and a clear blue-green solution which analyzed for 81 % alcohol and 75 % ketone.

A solution (D) of 4·13 g di-t-amyl peroxide in 25 ml t-butyl benzene, 0·15 g acetic acid and 0·14 g cuprous bromide yielded 465 ml (81 %) gas in 3 hr at 117–120°. The reaction mixture appeared similar to the previous reaction and analyzed for alcohol (76 %) and ketone (78 %). The gas consisted of methane (2·0 %), ethane (1·4 %), ethylene (93·5 %), butane (2·0 %) and carbon dioxide (0·7 %).

The rates of gas evolution for these reactions is illustrated in Fig. 1. Since heat-up times for the various reactions were not the same only that portion of the graph showing gas evolution is shown. The origin on the time co-ordinate was arbitrarily assigned.

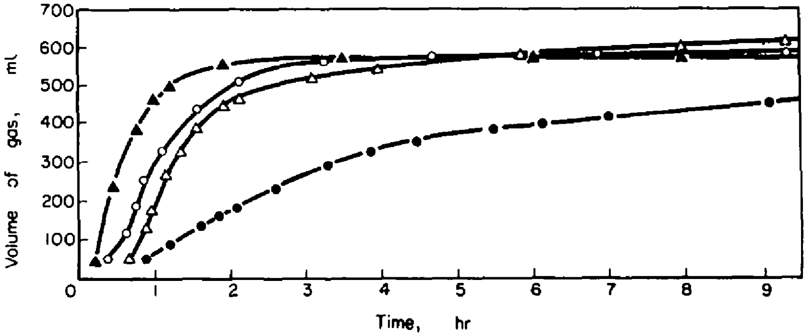

FIG. 1. Copper salt catalysed decomposition of di-t-amyl peroxide. Reaction A = ●, B = △, C = ▲, D = ○ (See text).

Catalysed decomposition of t-butyl, t-nonyl and t-decyl peroxides

A solution of 2·82 g t-butyl 4-methyl-4-octyl peroxide in 25 ml t-butyl benzene, 0·13 g acetic acid and 0·13 g cuprous bromide was heated at 120–121° for 4·5 hr. The evolved gas (100 ml, 32 %) consisted of methane (67 %), ethane (<0·5 %), ethylene (8·1 %), propane (<0·1 %), propylene (17·2 %), butane (<0·6 %), butene (5·5 %) and carbon dioxide (2 %).

A solution of t-butyl 4-ethyl-4-octyl peroxide in 25 ml t-butyl benzene, 0·13 g acetic acid, and 0·13 g cuprous bromide was heated at 120–123°. It liberated 120 ml (46 %) of gas which consisted of methane (41·0 %), ethane (4·0 %), ethylene (39·6 %), propane (<0·3 %), propylene (10·3 %), butane (<0·2 %), butene (3·6 %) and carbon dioxide (1 %).

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