butylperoxy radical if it did not undergo immediate fission into carbon dioxide and *t*-butoxy radical. In order not to be scavenged at all, it must cleave within the time of a very few collisions, faster than the acetoxy radical to which Herk, Feld and Szwarc assign a lifetime of the order of 10^{-9} to 10^{-10} second.[8]

These experiments afford no indication as to possible cage return of the radical pair to which the ester IV dissociates, since the products of such return would be identical with the starting material. However, we have thus far no evidence that pairs of oxygen radicals ever recombine within the solvent cage,[9] although C–O, C–C and C–N couplings do occur under such conditions.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health.

---

[8] L. Herk, M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

[9] A surmise of ours to the contrary (T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **No. 24**, 36 (1960)) has been rendered improbable by further experiments on the autoxidation of cumene to be described in a forthcoming paper.

[CONTRIBUTION FROM EMERYVILLE RESEARCH LABORATORIES, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF., AND DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

Oxidation of Allylic Radicals by Electron Transfer: Effect of Complex Copper Salts[1]

BY JAY K. KOCHI

RECEIVED MARCH 10, 1962

The oxidation of allylic radicals by complex cupric salts of 1,10-phenanthroline and α,α'-bipyridyl affords a mixture of allylic isomers. The composition of the allylic mixture is the same as those obtained from conventional carbonium ion processes. Thus, the specificity previously described for the oxidation of allylic radicals by *simple copper salts* of oxyanions to terminally unsaturated products is destroyed. Oxidation of allylic radicals by copper complexes is postulated to proceed *via* an electron transfer process to produce allylic carbonium ions as intermediates. The role of copper complexes as catalysts in the reactions of peroxides and unsaturated substrates is discussed.

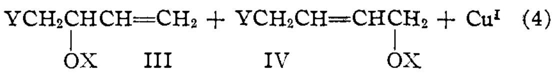
Introduction

Previous studies[2,3] have shown that *t*-butyl peresters, *t*-butyl hydroperoxides and peroxides react with cuprous salts to produce *t*-butoxy radicals (1). In the presence of alkenes these alkoxy radicals produce allylic radicals I by hydrogen abstraction (2); and with conjugated dienes such as butadiene, isoprene and styrene they react by addition (3) to form such adducts as the allylic *t*-butoxybutenyl radicals II. Allylic radicals produced either by hydrogen abstraction or addition react in the same manner with cupric salts of oxyanions, such as carboxylates, alkoxides, sulfates and perchlorates, to afford a mixture of allylic isomers III and IV (reaction 4). The compositions of these mixtures of isomers are strikingly independent of the reaction conditions. Neither the temperature of the reaction nor the constitution of the solvent affects the ratio between these allylic isomers. For example, butenyl radicals produced from any of the normal butene isomers are oxidized by these cupric salts to a mixture of α-methallyl and crotyl derivatives in which the secondary (α-methallyl) isomer is invariably the major constituent (85–95%). The same is true of *t*-butoxybutenyl radicals from butadiene and *t*-butoxy radicals: the secondary or 1,2-adduct (III, Y = *t*-BuO) always predominates (75–85%) over the primary or 1,4-adduct (15–25%).

$$t\text{-BuO}_2\text{X} + \text{Cu}^{\text{I}} \longrightarrow t\text{-BuO}\cdot + \text{Cu}^{\text{II}}\text{OX} \qquad (1)$$

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_8 \longrightarrow t\text{-BuOH} + \underset{\text{I}}{\text{C}_4\text{H}_7\cdot} \qquad (2)$$

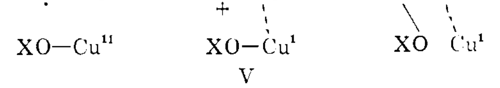
$$t\text{-BuO}\cdot + \text{C}_4\text{H}_6 \longrightarrow \underset{\text{II}}{t\text{-BuOC}_4\text{H}_6\cdot} \qquad (3)$$



$$\text{YC}_4\text{H}_6\cdot + \text{Cu}^{\text{II}}\text{OX} \longrightarrow \underset{\text{III}}{\text{YCH}_2\underset{\text{OX}}{\text{CH}}\text{CH=CH}_2} + \underset{\text{IV}}{\text{YCH}_2\text{CH=CH}\underset{\text{OX}}{\text{CH}_2}} + \text{Cu}^{\text{I}} \qquad (4)$$

X = RCO, H, R; Y = *t*-BuO, H

The study of the products arising from the partitioning of an allylic moiety is a convenient method for studying competitive reactions of reactive intermediates. Thus, the formation of a secondary derivative (III) as a major isomer from allylic free radical or carbonium ion intermediates is an unusual phenomenon. Chain transfer reactions with butenyl radicals usually produce the primary crotyl products.[2] Solvolysis of butenyl halides and esters or the deamination of butenylamines, reactions which proceed *via* carbonium ion or incipient carbonium ion intermediates, produce a mixture of allylic isomers which are approximately evenly distributed between crotyl and α-methallyl derivatives. Neither of these reaction types can be used to account for the predominance of the α-methallyl isomer in the mixture obtained from the oxidation of butenyl radicals by cupric salts of oxyanions. We have interpreted these reactions in valence bond designation as oxidation processes which proceed *via* transition states V comprised of electron transfer and ligand transfer components.[2,3] The importance of the electron transfer or carbonium ion contribution to these transition states has been stressed when copper salts of oxyanions are involved.[3] Implicit



V

---

[1] Part V, The Copper Salt-Catalyzed Reactions of Peroxides.

[2] J. K. Kochi, *J. Am. Chem. Soc.*, **83**, 3162 (1961); **84**, 1572 (1962); *Tetrahedron*, **18**, 483 (1962).

[3] J. K. Kochi, *J. Am. Chem. Soc.*, in press.

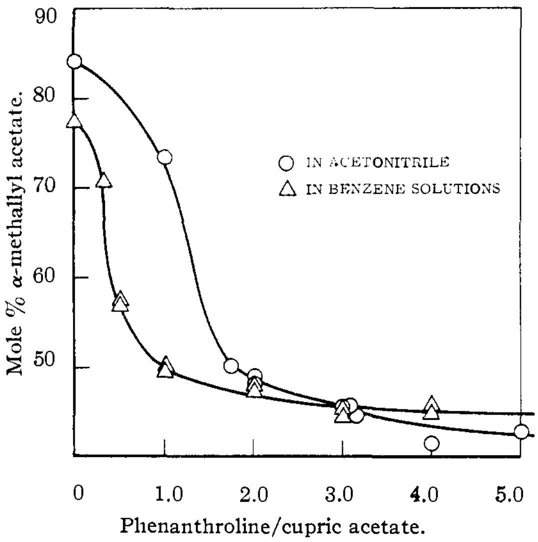


Fig. 1.—The composition of α-methallyl acetate in the butenyl acetate mixture from the oxidation of butenyl radicals by phenanthroline–copper acetate complexes.

in the electron transfer process is the conversion of copper from the cupric valence state to the cuprous valence state. The formation of a coördinative bond between copper and the terminal carbon–carbon π-bond has been used to account for the driving force associated with the formation of the α-methallyl isomers. If the product composition is dependent on this coördinative ability of copper, it is expected that it would change with alterations in the copper moiety, particularly in the direction of other carbonium ion reactions. With this end in mind we have investigated the effects of complexing the copper salts on the oxidation of allylic radicals produced under various conditions, by paying particular attention to the distribution of the allylic products.

Results

***t*-Butyl Peroxides and Olefins.**—In benzene solution butyl peracetate reacts with butene and cuprous chloride to produce in 80–85% yield a mixture of butenyl acetate which consists of 88–92% α-methallyl acetate and 8–12% crotyl acetate. The composition of this mixture is unchanged in *n*-hexane, acetonitrile, methanol or acetic acid–benzene solutions. However, in the presence of excess cupric acetate (8 meq.), in the three latter solvents, the relative proportion of α-methallyl acetate rises slightly to 95–99% and only small quantities (<5%) of crotyl acetate are formed. The over-all yields are also unchanged in acetonitrile (83%) and acetic acid–benzene solutions (87%), but are decreased in *n*-hexane (54%) and methanol (35–45%) due to partial attack on solvent.

The reaction of *t*-butyl peracetate with butene was also examined under the same experimental conditions using a variety of complex copper salts listed in Table I. These ligands are for the most part related to acetylacetonate. Reisolation of these copper complexes after the completion of the reaction was not possible since many of them were partially converted to cupric acetate. Other ligands related to phenol, such as 8-hydroxyquinoline, salicylaldoxime, etc., were oxidized by *t*-butyl peracetate and did not maintain their catalytic integrity. Catalysis in these systems is, thus, due mainly to the copper acetate species.

TABLE I

PRODUCTS FROM *t*-BUTYL PERACETATE AND BUTENE-2 WITH COPPER COMPLEXES OF OXYGEN-TYPE LIGANDS[a]

Run	Acetic[b] acid (% v.)	Copper complex	Over-all butenyl acetate yields, %	α-Methallyl[c] acetate, %
117	0[d]	Cupric acetylacetonate	79	90
116	0[e]	Cupric acetylacetonate	80	93
152	20	Cupric thenoyltrifluoroacetonate[f]	71	76
45	5	Cupric thenoyltrifluoroacetonate[g]	55	79
118	0[h]	Disodium cupric ethylenediamine-tetraacetate	30	87
137	15	Cupric 8-hydroxyquinolate	63	82
136	15	Cupric diphenylthiosemicarbazone	70	92
154	0	Cupric bis-salicylaldoxime	82	83
153	30	Cupric ethylenedinitrilo-o-cresol	52	83

[a] From reaction of *t*-butyl acetate (0.15 mole) and butene-2 (0.8 mole) with copper complex (3 meq.) in benzene solution (100 ml.) containing acetic acid. [b] % v. acetic acid in benzene. [c] % α-methallyl acetate in butenyl acetate mixture, remainder is crotyl acetate. [d] No acetic acid. [e] Acetonitrile. [f] Made *in situ* from cupric acetate (1.5 meq.) and thenoyltrifluoroacetone (7 meq.). [g] From cupric acetate (1 meq.) and thenoyltrifluoroacetone (30 meq.). [h] Acetonitrile solvent.

In contrast, the 1,10-phenanthroline and α,α′-bipyridyl complexes of copper salts affect the relative yields of α-methallyl acetate and crotyl acetate in a marked fashion. The variation in distribution of the two isomers is highly dependent on the mole ratio of these ligands to the copper ion in the complex. In Fig. 1 is illustrated the percentage contribution of α-methallyl isomer in the butenyl acetate fraction as a function of the phenanthroline-to-copper-ion ratio. In benzene solutions the over-all yields of butenyl acetate are independent of the catalyst composition, but in acetonitrile solution these yields fell off with increasing amount of phenanthroline in the copper complex. The results shown in Fig. 1 for the reactions in acetonitrile are not due to the selective destruction of the α-methallyl isomer, since the absolute yields of crotyl acetate also increased with increasing phenanthroline-to-copper ratio. The parallel between overall yield of butenyl acetate and composition of α-methallyl isomer in this mixture with change in the composition of the catalyst is due to the presence of several phenanthroline–copper species of varying degrees of effectiveness. Thus, in Table II it is shown that the over-all yield of butenyl esters is enhanced by an increase in the concentration of the phenanthroline–copper catalyst, especially at relatively high phenanthroline-to-copper ratios. Although the over-all yields of butenyl esters are altered significantly, the distribution between the α-methallyl and crotyl isomers is unchanged by varying the catalyst concentration. Under these conditions added acetic acid serves a beneficial effect on the butenyl acetate yields, whereas with simple copper acetate catalysts it showed no effect.[2] The sensitivity to conditions with the phenanthroline–copper catalysts is also demonstrated by the isomeric normal butenes.

TABLE II

PRODUCTS FROM *t*-BUTYL PERACETATE AND BUTENES WITH PHENANTHROLINE–COPPER COMPLEXES[a]

Run	Butene	Solvent[b]	Cupric acetate, g.	1,10-Phenanthroline, g.	Phen./Cu	Butenyl[c] acetate, %	α-Methallyl[d] acetate, %
130	*cis*	0 A	0.300	0	0	81	92
119	*cis*	5 A	1.500	0	0	85	95
129	*cis*	0 A	0.302	0.302	1.00	80	83
134	But.-1	0 A	.303	.606	2.00	39	59
128	*cis*	0 A	.303	.609	2.01	57	58
28	*cis*	10 A	.301	.634	2.11	67	58
18	*trans*	10 A	.600	1.168	1.95	79	59
39	*trans*	0 A	1.003	2.100	2.10	67	59
151	*trans*	0 A	0.958	2.161	2.26	70	59
148	*trans*	5 A	1.100	2.099	1.91	86	58
26	*trans*	5 A	1.200	2.100	1.75	83	60
7	*trans*	10 A	1.203	2.503	2.08	83	58
8	But.-1	10 A	1.203	2.505	2.08	73	58
10	*cis*	20 A	1.199	2.501	2.08	67	58
38	*trans*	10 A	1.204	3.801	3.16	35	54
31	*trans*	10 B	0.303	0.601	1.98	82	55
47	*trans*	1 B	.302	0.610	2.02	78	58
17	*trans*	10 B	.602	1.168	1.94	76	55
11	*trans*	20 B	1.200	2.502	2.08	82	55
48	*trans*	10 B	1.200	3.694	3.08	52	55
50	*trans*	10 B	1.201	1.803	1.50	87	57
49	*trans*	10 B	1.201	1.201	1.00	84	60
82	*trans*	10 B	1.199	1.202	1.00	88	59
51	*trans*	10 B	1.202	0.603	0.50	82	67
80	*trans*	10 B	0.604	.301	.50	89	67
81	*trans*	10 B	0.602	.201	.33	90	81
52	*trans*	10 B	1.203	0	0	90	89

[a] From reaction of *t*-butyl peracetate (0.15 mole) and butene (0.8 mole) in 100 ml. of solvent. [b] % v. acetic acid in acetonitrile (A) or benzene (B). [c] Over-all butenyl acetate yield. [d] % α-methallyl acetate in mixture, remainder is crotyl acetate.

With the uncomplexed copper acetate catalyst, butene-1 and *cis*- and *trans*-butene-2-all give equivalent results[2]; however, with the phenanthroline–copper catalyst *trans*-butene-2 gave the best yields of butenyl acetates followed by *cis*-butene-2 and butene-1. Each butene, nonetheless, gives mixtures of butenyl acetates of the same composition.

In acetonitrile solutions, bipyridyl is less effective than phenanthroline at equivalent concentrations in altering the composition of the butenyl acetate mixture. Thus, under standard conditions a solution of bipyridyl–copper complex (2:1) yields in 63% a butenyl acetate mixture which consists of 70% α-methallyl isomer. At a mole ratio of 5.0 the yield of butenyl acetate is 44% and the mixture is composed of 68% α-methallyl acetate. However, in benzene solutions the sensitivity of the butenyl acetate composition is less dependent on the concentration and composition of the bipyridyl–copper complex as shown in Table III. Similar differences between acetonitrile and benzene as solvents is shown by the phenanthroline–copper complexes (compare Fig. 1).

When copper–bipyridyl complexes are used as catalysts they are recovered unchanged from the reaction mixture. These reactions are generally so uncontaminated with high boiling materials that the copper complex can be isolated directly after vacuum distillation of the solvent and products. The same is not true of reactions carried out with the phenanthroline–copper complexes. A dark brown viscous material accompanies the formation of product, particularly in those runs which give low yields of butenyl esters (catalyst of high phenanthroline-to-copper ratio in acetonitrile solutions). However, in systems which give good yields of butenyl esters (>75%) the phenanthroline–copper catalysts can be isolated free of tarry materials. Under certain conditions the copper–phenanthroline can be recovered; but more often the complexes are isolated as a dark green viscous oil completely miscible in water. The parent ligand, 1,10-phenanthroline, in the latter cases cannot be isolated as such, but only as a non-crystalline derivative. The ultraviolet and infrared spectra of the amorphous copper complex indicate the presence of a phenanthroline moiety; elemental analysis is compatible with a substituted phenanthroline–copper complex.

TABLE III

REACTION OF *t*-BUTYL PERACETATE AND BUTENE WITH BIPYRIDYL–COPPER COMPLEX[a]

Run	Cupric acetate, g.	α,α′-Bipyridyl, g.	Bipy./Cu	Butenyl[b] acetate, %	α-Methallyl[c] acetate, %
102	0.601	1.445	3.00	88	56
78	.601	0.963	2.00	89	57
103	.301	.483	2.00	89	57
101	.601	.481	1.00	91	59

[a] From reaction of *t*-butyl peracetate (0.15 mole) and butene-2 (0.8 mole) in 100 ml. of 10% v. acetic acid in benzene. [b] Over-all butenyl acetate yield. [c] % α-methallyl acetate in mixture, remainder is crotyl acetate.

In order to demonstrate the generality with which complex copper salts alter the partitioning of the allylic radical, the reactions of several peroxides and olefins listed in Table IV were examined. These include *t*-butyl perbenzoate and *t*-butyl hydroperoxide and butene and pentene-1 in acetic acid–benzene solutions. Butenyl radicals derived from the *t*-butyl hydroperoxide oxidant afford the same distribution of isomeric butenyl acetates as those from *t*-butyl peracetate with a given copper–bipyridyl complex. *t*-Butyl perbenzoate and butene-2 with phenanthroline–copper catalysts in 5% v. acetic acid–benzene solutions produce a mixture of butenyl acetates (30%) and butenyl benzoates (48%) which both have the same composition, that of the α-methallyl isomer (56% acetate, 57% benzoate). The pentenyl radical from pentene-1 is oxidized by cupric acetate or benzoate to mixtures (68%) of pentenyl esters in which the 3-acyloxypentene-1 isomer predominates (88–91%). The same radical is oxidized by phenanthroline–copper complex to a mixture of pentenyl esters comprised of equal amounts of each isomer. If either α-methallyl or crotyl acetate is charged into the reaction of *t*-butyl peracetate or *t*-butyl hydroperoxide and pentene-1 in the presence of phenanthroline or bipyridyl complexes of copper, they are recovered unchanged. Neither is isomerized to the other isomer, nor is there any evidence of solvolysis of the butenyl acetate charged. The

TABLE IV

PRODUCTS FROM *t*-BUTYL PERBENZOATE AND HYDROPEROXIDE AND BUTENE-2 AND PENTENE-1 WITH COMPLEX COPPER CATALYSTS[a]

Run	Olefin	Solvent[b]	Peroxide[c]	Cupric acetate	Ligand[d]	Lig./Cu	Over-all[e] ester yield	Secondary[f] isomer
147	*t*-But.	25	*t*BHP	0.601	0	0	59a	89
14	*t*-But.	25	*t*BHP	.603	0	0	62a	89
148	*t*-But.	25	*t*BHP	.602	0.482B	1.0	62a	56
15	*t*-But.	25	*t*BHP	.603	.481B	1.0	60a	56
64	*t*-But.	5	*t*BPB	.302	.610P	2.0	30a 48b	56a 57b
49	Pent-1	0	*t*BPB	.202	0	0	68b	88b
50	Pent-1	100	*t*BPB	.203	0	0	66a 5b	91a ..
67	Pent-1	10	*t*PBP	.301	0.615P	2.0	39a 28b	51a 52b
84	Pent-1	10	*t*BPB	1.201	1.201P	1.0	43a 31b	62a 63b

[a] From peroxide (0.15 mole) and olefin (0.7 mole) in acetic acid–benzene solutions (100 ml.). [b] % v. acetic acid in benzene. [c] *t*BHP, *t*-butyl hydroperoxide; *t*BPB, *t*-butyl perbenzoate. [d] P, 1,10-phenanthroline; B, α,α'-bipyridyl. [e] Over-all butenyl or pentenyl ester yield; a, acetate; b, benzoate. [f] % secondary isomer (α-methallyl from butene-2 and 1-pentene-3-yl from pentene-1).

changes in the isomer composition of the butenyl ester fractions by the use of complex copper catalysts are, therefore, not due to the rearrangement of the products by catalysts. In a similar manner, the butene was recovered from the reaction mixture and reanalyzed. In no instance was any rearrangement observed.

***t*-Butyl Peroxides and Butadiene.**—*t*-Butyl peracetate reacts with butadiene in the presence of cupric acetate to produce a mixture of 1:1 adducts which consists of 1-*t*-butoxy-2-acetoxybutene-3 and 1-*t*-butoxy-4-acetoxybutene-2.[3] The effect of copper complexes of bipyridyl and 1,10-phenanthroline on the yields of 1:1 adducts and the distribution between the two isomers is shown in Table V. The same effect is obtained from either *t*-butyl peracetate or *t*-butyl hydroperoxide with a given copper catalyst. In both cases it has been shown that *t*-butoxy radicals are intermediates which add to butadiene to produce the allylic radical, *t*-butoxybutenyl.[3] Oxidation of this radical by either cupric acetate or complexed copper catalysts proceeds in the same manner as that of the simple butenyl radicals. Phenanthroline or bipyridyl complexes of copper ion effect alteration of the isomer ratios from mainly 1,2-addition to more 1,4-addition.

TABLE V

ADDUCTS FROM BUTADIENE AND PEROXIDES WITH COMPLEX COPPER CATALYSTS[a]

Run	Solvent[b]	Peroxide[c]	Cupric acetate	Ligand[d]	Lig./Cu	Yield 1:1 adducts, %	1,2[e] adduct
120	25–0	*t*BPA	0.603	0	0	83	80
113	25–0	*t*BPA	.604	0.484B	1.0	73	39
141	25–0	*t*BPA	.602	.481B	1.0	77	39
114	25–25	*t*BPA	.600	.481B	1.0	53	39
121	25–25	*t*BPA	1.205	.960B	1.0	60	39
105	25–0	*t*BHP	0.602	0	0	41	80
106	25–25	*t*BHP	.602	0	0	36	82
107	25–0	*t*BHP	.602	0.602P	1.0	45	37
108	25–25	*t*BHP	.601	.603P	1.0	42	41
111	25–0	*t*BHP	.600	.484B	1.0	42	35
112	25–25	*t*BHP	.603	.482B	1.0	38	38
121	25–25	*t*BHP	1.205	.960B	1.0	58	39

[a] From reactions of peroxide (0.15 mole) and butadiene (0.7 mole) in benzene solutions containing acetic acid and methanol. [b] % v. acetic acid–% v. methanol. [c] *t*BPA, *t*-butyl peracetate; *t*BHP, *t*-butyl hydroperoxide. [d] B, α,α'-bipyridyl; P, 1,10-phenanthroline. [e] % 1-*t*-butoxy-2-acetoxybutene-3 in mixture, remainder is 1,4-isomer.

Discussion

t-Butyl peracetate, perbenzoate and hydroperoxide all react with copper acetate catalysts in the presence of butenes to produce the same mixture of butenyl esters in which the α-methallyl isomer predominates (85–95%). Pentene-1 reacts with these peroxides to afford an analogous mixture which contains mainly 3-acyloxypentene-1 (88–91%) and some 1-acyloxypentene-2. Similar results are obtained from butadiene as substrate, which yields a mixture of allylic adducts rich in the 1,2-adduct (1-*t*-butoxy-2-acyloxybutene-3, 75–85%). An allylic radical intermediate has been proposed as an intermediate in each of these systems: butenyl radical from normal butenes,[2] pentenyl-1 radical from pentene-1 and 1-*t*-butoxybutenyl radical from butadiene.[3] If a complex copper salt containing either 1,10-phenanthroline or α,α'-bipyridyl is substituted for the simple copper acetate salts, the distribution of allylic isomers obtained under equivalent conditions is drastically altered. The degree of alteration in the isomer distributions is highly dependent on the composition of the copper complex and to a lesser degree on the solvent. *With fully coördinated copper catalysts the composition of the isomeric mixture attains a value which is independent of the solvent and the copper complex (either phenanthroline or bipyridyl).* The composition of this mixture is more evenly distributed between the two allylic isomers than that obtained from the simple copper acetate catalyst. For example, from butenes a butenyl ester mixture is obtained which is composed of 55% α-methallyl isomer and 45% crotyl isomer; from pentene-1 it is 50% of 3-acyloxypentene-1 and 50% 1-acyloxypentene-2; from butadiene it is 35% 1,2-adduct and 65% 1,4-adduct. *The specificity of forming terminally unsaturated derivatives from allylic radical intermediates by simple copper salts is lost by the use of copper phenanthroline or related complexes.*

The sequence of reactions from *t*-butyl peroxides and olefins which is brought about by complex copper salts is analogous to those catalyzed by simple copper salts. The solvation or neutralization of the intermediate allylic carbonium ion[4] formed in reaction 7 is the factor which determines the distribution between the two allylic isomeric products (*vide infra*).

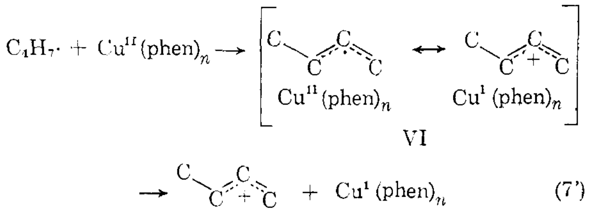
$$t\text{-BuOOX} + \text{Cu}^{\text{I}}(\text{phen})_n \longrightarrow t\text{-BuO}\cdot + \text{Cu}^{\text{II}}(\text{phen})_n + \text{XO}: \quad (5)$$

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_8 \longrightarrow t\text{-BuOH} + \text{C}_4\text{H}_7\cdot \quad (6)$$

$$\text{C}_4\text{H}_7\cdot + \text{Cu}^{\text{II}}(\text{phen})_n \longrightarrow \text{C}_4\text{H}_7^+ + \text{Cu}^{\text{I}}(\text{phen})_n \text{ etc.} \quad (7)$$

The compositions of the mixtures of allylic isomers which result from the oxidation of allylic radicals by fully complexed copper salts correspond quite closely to those obtained from other carbonium ion type reactions. Thus, the silver ion-assisted acetolysis of α-methallyl or crotyl halides gives a mixture of butenyl acetates which resembles the mixture obtained from the deamination of α-methallylamine and crotylamine; and it is the same mixture that is obtained from the oxidation of butenyl radicals by phenanthroline–copper complexes.[2] A similar correlation exists between the composition of the mixture of *t*-butoxyacetoxybutenes obtained from the acetolysis of *t*-butoxybutenyl chlorides and the oxidation of *t*-butoxybutenyl radicals by copper complexes in the presence of acetic acid.[3]

We propose that the oxidation of allylic radicals by cupric–phenanthroline and related complexes is representative of an electron transfer process in which a carbonium ion is formed as an intermediate. These oxidations in valence bond terminology are distinguished from those by simple cupric salts of oxyanions by the minimal role played by ligand transfer contributions in the transition state VI for oxidation.



VI

(7′)

The partitioning of the allylic radical as a consequence of oxidation by cupric species is the criterion on which we base the distinction between an *electron transfer process* represented by a transition state such as VI and an *electron transfer–ligand transfer hybrid process* represented by a transition state such as V.[2,3]

Cupric ion is known to form at least three complexes with phenanthroline.[5] These differ from one another mainly by the number of ligands coördinated to the copper ion as indicated in reaction 8. Copper species as catalysts for the reaction of peroxides and olefins can be examined

$$\text{Cu}^{\text{II}} + n\text{C}_{12}\text{H}_6\text{N}_2 \rightleftarrows \text{Cu}^{\text{II}}(\text{C}_{12}\text{H}_6\text{N}_2)_n \quad n = 1,2,3 \quad (8)$$

by two criteria: their efficiency in the *cuprous* state in carrying out the reduction of the peroxide (eq. 1 and 5) and their ability in the *cupric* state in promoting electron transfer type reactions (eq. 4 and 7). The *over-all* catalytic efficiency of a given copper salt is dependent on the rates of both of these reactions since the former is responsible for generating free radicals by catalyzing the decomposition of the peroxide and the latter is involved in the product-determining step. Each reaction is dependent on the other for the production of the copper species in the appropriate oxidation state. The steady state concentration of cuprous and cupric species is, therefore, a measure of the relative rates of each of these oxidation–reduction reactions. These concentrations have not yet been ascertained, but experiments based on final concentrations of copper species do give qualitative information on the rates of these reactions. Thus, on this basis it is found that the fully complexed copper–phenanthroline or bipyridyl complexes are not as effective as either the simple copper salts or the copper–monophenanthroline compounds as catalysts. From a practical standpoint the lower rates of reactions and yields of butenyl esters shown by the higher copper complexes can be partially offset by increasing the catalyst concentration. When copper complexes are used as catalysts, the steady state concentration of species in the cupric valence state is lower than when simple copper acetate salts are employed. In comparative experiments it can be shown (by examination of the visible spectra and by autoxidation of the solutions that the intermediate and the final reaction mixtures contain appreciable amounts of cuprous complex, whereas when copper acetate is employed there is very little evidence for the presence of cuprous salts.[6] Since neither phenanthroline nor bipyridyl ligands become detached from the copper moiety during the oxidation–reduction cycle,[7] the differences in catalytic rates of various copper species, complexed and otherwise, is attributed to the variations in rates of the reduction step (1 and 5). This is also consistent with the ability of phenanthroline type ligands to stabilize the

---

[4] The possibility of an ion-pair as the actual intermediate is neither discounted nor rejected.

[5] J. Bjerrum, *Rec. trav. chim.*, **76**, 658 (1956); C. K. Jorgensen, *Acta Chem. Scand.*, **7**, 1362 (1955); C. V. Banks and R. I. Bystroff, *J. Am. Chem. Soc.*, **81**, 6153 (1959).

[6] This statement is applicable in our studies only to butenes as substrates. When butadiene is used both copper acetate and copper complexes end up primarily as cuprous compounds.[3] The higher final concentrations of cuprous species in the presence of butadiene can be accounted for by the formation of cuprous–butadiene complexes between uncomplexed copper salts and butadiene (see also footnote 19) much like the cuprous–acetonitrile complexes (*vide infra*). At present it is difficult to speculate on the reactivity of these stable cuprous–diene complexes. In both the copper–phenanthroline and the copper acetate–butadiene systems the preponderance of the cuprous species in solution can be attributed to the stabilization of the lower valence state of copper by complex formation (see ref. 8).

[7] R. T. Pflaum and W. W. Brandt, *J. Am. Chem. Soc.*, **76**, 6215 (1954); **77**, 2019 (1955), have demonstrated that in the course of either the reduction of cupric phenanthroline salts or the oxidation of cuprous phenanthroline salt, the phenanthroline moiety is not detached from the copper nucleus.

cuprous state.[8] At present we have no evidence to indicate that allylic radicals are oxidized at grossly different rates by the various complex cupric species.[9]

Although different copper complexes may show varying catalytic behavior, they all oxidize allylic radicals by essentially the same mechanism. In benzene solution a 1:1 phenanthroline–copper complex produces the same mixtures of butenyl acetate by the oxidation of butenyl radicals as does a tris-phenanthroline complex. In acetonitrile solutions a 1:1 phenanthroline or bipyridyl–copper complex affords a mixture of allylic isomers more akin to that produced by simple copper salts than it does in benzene solutions. Part of this difference is attributable to the dissociation of the copper complex in acetonitrile by the competitive formation of a cuprous–acetonitrile complex[10] during the oxidation–reduction cycle. The effect of solvent is also shown by the copper–bipyridyl complexes; at the same mole ratio of bipyridyl to copper the butenyl acetate mixture is richer in the α-methallyl component in acetonitrile than in benzene. The formation of butenyl acetate mixtures which are intermediate between those resulting from copper acetate catalysts and from fully complexed copper catalysts results from the concomitant oxidation of allylic radicals by both simple copper salts and complex copper salts (particularly 1:1 complexes). The coexistence in solution of these simple copper salts and 1:1 copper complexes is especially noticeable when the mole ratio of phenanthroline to copper ion is less than 2 in acetonitrile and approximately 1 in benzene. With bipyridyl as ligand, the ratio is between 1 and 2 in benzene and greater than 5 in acetonitrile. The formation constants of bipyridyl copper complexes are known to be smaller than the corresponding phenanthroline complexes.[11] Since all complexed copper species oxidize butenyl radicals to the same mixture of butenyl isomers, we believe that each oxidation is represented by the equivalent transition states VI (n = 1, 2, 3).

The difference between simple cupric salts of oxyanions and complex cupric salts of phenanthroline-type ligands as oxidants can also be interpreted qualitatively by considering changes in the copper moiety. The oxidation of allylic radicals by cupric species is accompanied by the change in the geometry of the copper from a square planar cupric[12a] to a tetrahedral cuprous configuration. The transition state for this transformation probably involves copper in a configuration intermediate between these extremes. For purposes of simplification[12] the transition state can be approximated as tetrahedral, and with simple copper salts the transition state is one in which the incipient olefinic linkage of the butenyl fragment occupies a corner of the tetrahedral complex. The bonding is expected to be of the type encountered in stable olefin complexes of cuprous and argentous salts.[13] In these complexes σ-bonding between the olefin and metal involves the use of the empty metal 4s and $4p_x$, $4p_y$ and $4p_z$ orbitals and the bonding π-orbital of the olefin and π-bonding between the filled metal $3d_{x^2-y^2}$ and $3d_{z^2}$ or $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals and the antibonding π-orbitals of the olefin. Unlike the olefin complexes of the square planar[14] Pt^{+2} and Pd^{+2}, the structures of the tetrahedral olefin complexes of copper have not been determined and it is not possible to state at present which orbitals are actually involved in these complexes.

Cupric compounds generally do not form olefin complexes and the driving force for the olefin-copper interactions in the case of allylic radicals and cupric ion is associated with the unpaired electrons on both the free radical and the cupric salt.[15] The effect of complexing the cupric ion with π-bonding ligands such as 1,10-phenanthroline and α,α'-bipyridyl is to decrease the π-interaction between the allylic and copper moieties.

---

[8] J. V. Quagliano and R. L. Robertus, "Chemistry of Coordination Compounds," J. C. Bailar, Editor, Reinhold Publ. Corp., New York, N. Y., 1956, p. 398 ff.

[9] From the energetics (the copper half-cell potentials) *alone* it may be expected that the fully (tris) coördinated cupric complexes would also react faster than either the bis- or mono-coördinated cupric complexes. In each case the oxidation is postulated to proceed *via* an electron transfer mechanism to produce an allylic carbonium ion intermediate (*vide infra*). Such comparisons between complexed and uncomplexed copper species are difficult to make since equivalent processes (eq. 4 and 7) are not involved.

[10] N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950, p. 134f.

[11] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Chemical Society Special Publication No. 9, London, 1957.

[12] (a) The classical square planar structure for Cu^{II} compounds has been largely replaced by either a six coördinate tetragonal or a tetrahedral arrangement; see R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961). (b) Studies[12a,c] of the crystal structure of cupric acetate monohydrate indicate that it exists as a binuclear complex, $Cu_2(AcO)_4(H_2O)_2$. The copper atoms are held together by four acetate bridges and a weak *d*-bond. In solvents of relatively low dielectric constant and solvating power such as benzene and acetic acid, it is not inconceivable that the copper species also exist in part as dimers. At the present stage of development we are not able to choose between the monomer or dimer (or both) as the species involved in the oxidation step (eq. 4). A case can be made for the effect of such complexing agents as phenanthroline and bipyridyl to destroy the dimer. However, the contrary notwithstanding, we prefer to base our arguments, at present, on the reactions as given in eq. 4 and 7. We hope to pursue these points more rigorously with kinetic measurements. (c) J. Van Niekerk and F. Schoening, *Acta Cryst*, **6**, 227 (1953); R. L. Martin, *et al.*, *J. Chem. Soc.*, 3837 (1956); 2545 (1957); 1359, 2960 (1959).

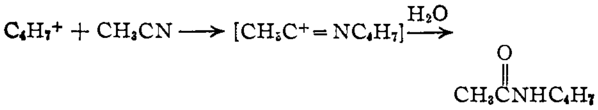
[13] J. Chatt, in "Cationic Polymerization and Related Complexes," P. H. Plesch, Editor, Heffer, Cambridge, 1953, pp. 40–56; F. S. Mathews and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 4745 1958).

[14] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954); **8**, 57 (1955); J. R. Baenziger, *et al.*, *J. Am. Chem. Soc.*, **77**, 4984, 4987 (1955).

[15] (a) The cupric ion-butenyl radical interaction bears *formal* resemblance to the isolable π-allyl complexes such as butenyl cobalt tricarbonyl (Co°) (R. F. Heck and D. S. Breslow, *ibid.*, **82**, 4438 (1960)), and butenylchloronickel tris-triphenyl phosphine (Ni^{I}) (R. F. Heck and D. S. Breslow, "Advances in Chemistry of Coördination Compounds," S. Kirschner, ed., The Macmillan Co., New York, N. Y., 1961, p. 281), compounds which are all isoelectronic. Such interactions may also account for the cuprous salt assisted acetolysis of butenyl esters.[3] (b) The butenyl radical–cupric ion interaction can be alternatively viewed as a butenyl carbonium ion–cuprous interaction. Cationic complexes of the latter type recently have been isolated from unsaturated carbonium ions and metal carbonyls (see H. J. Dauben, *et al.*, *J. Am. Chem. Soc.*, **80**, 5570 (1958), **83**, 497 (1961); E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960); J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **84**, 1511 (1962)). In these complexes the bonding is formulated as involving the donor properties of the olefin π-bond with the vacant metal 3d orbitals, and back donation from the filled metal 3d orbitals to the vacant p orbital of the carbonium ion. Since the 3d orbitals of cuprous ion are completely filled this necessitates promotion of an electron pair into an antibonding orbital.

Phenanthroline-type ligands resemble olefins in their synergic bonding with metals of low valence,[16] but they involve at least two filled 3d orbitals of the metal in the π-bonding. It has been asserted[17] that a maximum of only two strong π-bonds is possible in tetrahedral complexes of this type; this conclusion has been seriously queried,[18] however. In either case, it is apparent that olefin complexes of simple copper salts are more stable than those derived from phenanthroline-type copper complexes.[19] With the latter complexes of copper, π-interaction between the butenyl fragment and the cupric oxidant is minimal and the oxidation proceeds *via* essentially an electron transfer mechanism.

The formation of allylic carbonium ion intermediates by such a process is indicated by the attack on acetonitrile solvent, especially at high phenanthroline-to-copper ratios. In the absence of added acetic acid or other nucleophiles, the intermediate nitrilium ion partially undergoes condensation to tarry by-products. However, in acetonitrile solutions containing small amounts of added water it is possible to trap the intermediate as N-butenylacetamide in a manner reminiscent of the Ritter reaction.[20]



$$C_4H_7^+ + CH_3CN \longrightarrow [CH_3C^+{=}NC_4H_7] \xrightarrow{H_2O} CH_3\overset{\overset{\displaystyle O}{\|}}{C}NHC_4H_7$$

Copper-phenanthroline complexes do not always survive the treatment with peroxide unaltered. However, the isolation of copper compounds which still have the phenanthroline nuclei attached indicates that the catalyst has maintained its integrity. The ultraviolet and infrared spectra of these isolated complexes indicate the presence of phenanthroline moieties. The main alteration in the structure of the complex appears to be substitution by either a butenyl or butoxy group. The survival of copper-bipyridyl complexes intact as catalysts is consistent with the more facile substitution into the nuclei of polynuclear aromatic compounds.

Experimental

The cupric complexes were prepared *in situ* by dissolving cupric acetate in either acetonitrile or acetic acid with heat and adding a solution of phenanthroline in benzene or acetonitrile. The formation of the cupric complex was immediate and apparent from the change in color from a blue-green mixture to a clear blue solution. Care was exercised so that it was certain that the formation of the complex was complete. Those reactions which employed less than a stoichiometric amount of phenanthroline or bipyridyl in benzene solutions were not homogeneous at room temperatures due to the insolubility of the cupric acetate. The catalyst solution was chilled to 0° and the peroxide and olefin charged in the usual manner.[3] The reactions were conducted in heavy wall polymerization bottles previously described. After heating, the crude reaction mixture in many cases consisted of a homogeneous solution of cuprous and cupric compounds. For example, those from copper–bipyridyl complexes varied from yellow-green to medium green. On exposure to air the solutions autoxidized rapidly to the clear blue solution characteristic of the cupric–bipyridyl complex. The visible spectra of these solutions before aeration showed little cupric complex.

The crude solutions were also analyzed by g.l.c. for butenyl esters. *n*-Butyl acetate was employed as a marker and a calibration factor of 0.90 was used to determine the yields of α-methallyl and crotyl acetate. The esters were also separated by distillation and compared with authentic samples. Each isomer was further separated from the crude reaction mixture directly, by a preparative gas chromatograph (Beckman Megachrom) in a quantitative manner to be certain that the chromatographic peaks were homogeneous. Finally, the crude reaction mixture was vacuum distilled to separate the copper catalyst, and the distillate was hydrogenated over 5% Pd-on-charcoal or 5% Rh-on-charcoal to a mixture of *sec*-butyl acetate and *n*-butyl acetate. In this manner there was no question of the identity and relative yields of the butenyl ester products.

The oily copper residues from the vacuum distillation were washed once with pentane. That from bipyridyl–copper complex crystallized on standing and after drying *in vacuo* the unpurified solid was analyzed. The visible spectrum in water was the same as complex isolated from the original catalyst solution. *Anal.* Calcd. for $CuC_{14}H_{14}N_2O_4$: Cu, 18.8; C, 49.8; H, 4.2; N, 8.29. Found (from run 101, Table III): Cu, 18.2; C, 48.9, 49.3; H, 4.5, 4.5; N, 7.6; (from run 102, Table III, after vacuum drying): Cu, 18.4; C, 50.2, 50.2; H, 4.3, 4.3; N, 8.1. The bipyridyl–copper complex (3:1) from run 102 on vacuum drying underwent dissociation so that two moles of bipyridyl were sublimed. The remaining 1:1 complex was treated with aqueous sodium cyanide and the bipyridyl ligand was extracted and compared with the authentic sample.

The copper complexes from phenanthroline runs were not easily isolated consistently. When high concentrations of 1:1 complex were employed, the catalyst was reisolated unchanged by a method similar to that used for the bipyridyl complexes. The 1:1 complex was isolated as a crystalline solid and analyzed directly without further purification. *Anal.* Calcd. for $C_{16}H_{14}N_2O_4$: Cu, 17.5; C, 53.1; H, 3.9; N, 7.7. Found (run 82, Table II): Cu, 16.8; C, 51.6, 51.7; H, 4.2, 4.2; N, 7.3. The infrared and visible spectra were the same as for a 1:1 phenanthroline–cupric acetate solution. The copper phenanthroline complexes obtained from other runs were not the unaltered phenanthroline complexes. Although the infrared spectrum of the isolated ligand was definitely that of a phenanthroline moiety (bands at 6.68, 7.07, 8.80, 11.69, 11.90) and the visible and ultraviolet spectra indicated a phenanthroline–copper complex, there were present impurities which could not be removed. The dark green oils were analyzed directly. *Anal.* Calcd. for $CuC_{47}H_{56}N_4O_4$: Cu, 7.06; C, 62.8; H, 6.28; N, 6.22. Found (from run 55, Table II): Cu, 6.7; C, 62.7, 62.8; H, 6.11, 6.07; N, 6.6; (from run 56, Table II): Cu, 7.4; C, 62.8, 62.8; H, 6.09, 6.11; N, 6.1. In all cases the sample though completely soluble in water had to be combusted before reproducible copper values could be obtained. These complexes were not degraded by fuming nitric–sulfuric acid mixtures.

N-Butylacetamide was isolated from the reaction of *t*-butyl peracetate and butene in 5% v. water in acetonitrile. Vacuum distillation of the products left a dark brown viscous residue which was diluted with water and extracted with ether several times. The ether solution was washed with sodium cyanide, dried and hydrogenated with 5% Pd-on-charcoal. The ether was distilled and the residual liquid collected on a cold finger *in vacuo*. The infrared spectrum was very similar to that of *n*-butylacetamide. *Anal.* Calcd. for $C_6H_{13}NO$: C, 62.5; H, 11.4; N, 12.2. Found: C, 62.9; H, 11.3; N, 12.3.

Acknowledgment.—I wish to thank Mr. Fred Rodgers for valuable technical assistance and Dr. Dennis Barnum for helpful discussions.

---

[16] L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen, New York, N. Y., 1960, p. 144.

[17] W. S. Fyfe, *J. Chem. Phys.*, **28**, 907 (1958); L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959); J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[18] F. A. Cotton, *ibid.*, 5269 (1960).

[19] Values for the formation constants of mixed olefin and phenanthroline-type complexes are incomplete. There are indications, however, that multiple π-bonding between olefins and metal ion are unfavored (see, *e.g.*, K. B. Yatsimirskii, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, ed., Macmillan Co., New York, N. Y., 1961, p. 96 ff.; and R. Hogg, G. A. Nelson and R. O. Wilkins, *ibid.*, p. 391).

[20] J. J. Ritter and P. R. Minieri, *J. Am. Chem. Soc.*, **70**, 4045, 4048 (1948).