56613-17-3; acetone, 67-64-1; (*Z,Z*)-2-(7-hexadecenyl)-11-eicosenoic acid methyl ester, 66587-44-8.

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Role of Silver(II) in Silver-Catalyzed Oxidations by Peroxydisulfate[1]

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In Ag^+-catalyzed oxidations of organic substrates by peroxydisulfate, both $SO_4^{-}\cdot$ and Ag(II) are present as oxidants and may show quite different selectivity patterns, yielding quite different products. Ag(II) is shown to oxidize alcohols to alkoxy radicals, but at a slower rate than its known decarboyxlation of acids. Contrary to some previous reports, rates of acid decarboxylation appear quite sensitive to acid structure and also to pH. In the oxidation by Ag(II) of aromatic molecules with side-chain -OH or -COOH functions, reaction may involve either side-chain attack or ring oxidation to a radical cation, the relative importance of the two paths depending on structure. The contribution of Ag(II) to the overall oxidation is shown to increase with the Ag/substrate ratio and to vary inversely with the rate of the $SO_4^{-}\cdot$ substrate reaction. The rate of the reaction $SO_4^{-}\cdot + Ag^+ \rightarrow SO_4^{2-} + Ag(II)$ is estimated as $\sim 3 \times 10^9$.

Silver ion is a well-known catalyst for peroxydisulfate ($S_2O_8^{2-}$) oxidations, the first report being by Marshall in 1900,[2] and a number of reveiws covering earlier work are available.[3-5] The initial steps usually postulated for such oxidations are the one-electron redox processes

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^{-}\cdot + Ag(II) \qquad (1)$$

$$SO_4^{-}\cdot + RH \rightarrow SO_4^{2-} + R\cdot + H^+ \qquad (2)$$

$$SO_4^{-}\cdot + Ag^+ \rightarrow SO_4^{2-} + Ag(II) \qquad (3)$$

although in some interpretations Ag(III) has also been proposed as an intermediate. Reactions 1 and 2 are quite analogous to the initial steps in the Fenton's reagent oxidation of organic substrates by Fe^{2+}–H_2O_2 or Fe^{2+}–$S_2O_8^{2-}$ [6] but differ in that while Fe^{3+} is able to oxidize intermediate substrate radicals, Ag(II) is a considerably stronger oxidizing agent and capable of oxidizing suitable substrates as well. As a conse-

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Table I. Oxidation of 2-Methyl-2-butanol[f]

Conditions[a]	Products, % 2-Methyl-2,3-butanediol	Acetone	Ethanol
Fe[b,c]	45, 48	3, 6	2
60 °C	48, 38	0, 5	5, 2
60 °C, 10^{-4} M Ag^+	16	23	2
60 °C, 10^{-3} M Ag^+	6	35	2
Fe,[b] H_2O_2[d]	54	0	*e*
Fe,[b,c] H_2O_2[d]	38	2	*e*

[a] All experiments used ~1 M substrate, ~0.04 M $S_2O_8^{2-}$ (or H_2O_2), and 0.1 M Cu^{2+}. [b] Fe^{2+} initiation in 0.1 M $HClO_4$ at room temperature. [c] "Inverse addition," Fe^{2+} was added slowly to the system. [d] H_2O_2 was used in place of $S_2O_8^{2-}$. [e] Other diols were present (~10%). [f] Registry no.: 2-methyl-2-butanol, 75-85-4.

quence, it is rapidly reduced back to Ag^+ to reenter the cycle, thus accounting for the catalytic effect of traces of Ag^+ on the overall oxidation rate.

Since a different oxidant is present in the Ag^+-catalyzed reactions, different products might be expected. The first clearly documented case of such a difference is in the oxidation of glycols, where in 1954 Greenspan and Woodburn[7] reported that 1,2-diols are cleaved in good yield by Ag^+–$S_2O_8^{2-}$ but not by $S_2O_8^{2-}$ alone. Subsequently, Anderson and Kochi[8] have shown that Ag^+ also changes the course of $S_2O_8^{2-}$ oxidation of aliphatic acids, leading to smooth decarboyxlation (eq 4), while $SO_4^{-}\cdot$ radicals from peroxydisulfate alone predominantly attack C–H bonds in the rest of the molecule.

$$RCOOH + Ag(II) \rightarrow R\cdot + CO_2 + Ag^+ + H^+ \qquad (4)$$

The thermal oxidation of alcohols by $S_2O_8^{2-}$ is consistent with a chain reaction involving the propagation steps[9]

$$SO_4^{-}\cdot + R_2CHOH \rightarrow SO_4^{2-} + R_2\dot{C}OH \qquad (5)$$

$$R_2\dot{C}OH + S_2O_8^{2-} \rightarrow R_2C{=}O + SO_4^{-}\cdot + SO_4^{2-} + H^+ \qquad (6)$$

Reaction 6 is relatively slow, and in Fe^{2+}–$S_2O_8^{2-}$ systems it is replaced[6] by

$$R_2\dot{C}OH + Fe^{3+} \rightarrow R_2C{=}O + Fe^{2+} + H^+ \qquad (7)$$

or if Cu^{2+} is present by

$$R_2\dot{C}OH + Cu^{2+} \rightarrow R_2C{=}O + Cu^+ + H^+ \qquad (8)$$

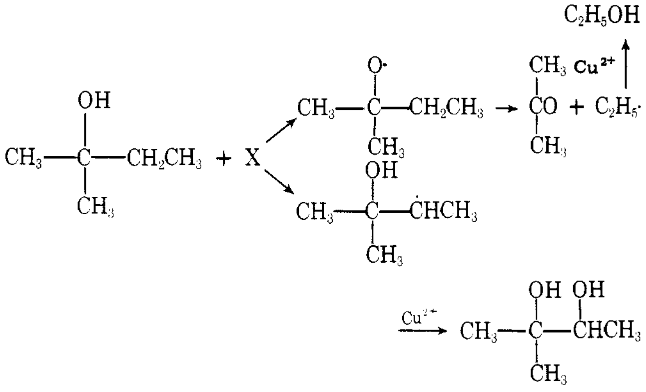
Our interest in the problem was aroused by the report by Ledwith[10] that he had been able to trap alkoxy radicals in the oxidation of alcohols by $S_2O_8^{2-}$, both in the presence and absence of Ag^+, a result quite at variance with the above formulation. We find that typical reactions of alkoxy radicals are indeed observed during the oxidation of alcohols by $S_2O_8^{2-}$, *but they are important only in the presence of* Ag^+, indicating that alcohols react with Ag(II) in the same manner as do carboxylic acids.

$$ROH + Ag(II) \rightarrow RO\cdot + Ag^+ + H^+ \qquad (9)$$

While this work was in progress,[11] a similar conclusion was reported by Caronna et al. using quite a different technique.[12] This paper presents our findings together with some results on the oxidation of carboxylic acids and aromatic molecules which provide a more comprehensive view of Ag^+-catalyzed $S_2O_8^{2-}$ oxidations and the relative rates of reaction of Ag(II) with different functional groups.

Results

Alcohol Oxidations. Our initial experiments were carried out with 2-methyl-2-butanol, using Cu^{2+} as an oxidant for intermediate radicals, with conditions under which O–H and C–H attack should lead to clearly different products as shown.



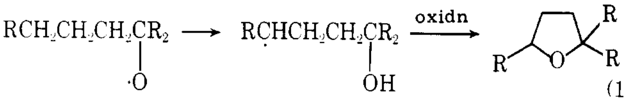
$X = SO_4^{-}\cdot$ or Ag(II) (10)

The oxidation of the β-hydroxyalkyl radical shown probably leads initially to an epoxide,[13] which, however, rapidly opens to a diol in acid solution. Results with several oxidizing systems are listed in Table I which clearly show the large effect of Ag^+ on product distribution. In the presence of Ag^+, acetone is the predominant product, consistent with reaction 9. The small yield of diol probably results either from some attack by $SO_4^{-}\cdot$, reaction 2, or attack by an intermediate alkoxy radical on another molecule of alcohol. With $S_2O_8^{2-}$ in the absence of Ag^+, the chief product is 2-methyl-2,3-butanediol, while with H_2O_2 some isomeric diols are also formed by attack on CH_3 groups by the less selective HO· radical. Interestingly, small yields of acetone are also observed in the absence of Ag^+, pointing to detectable O–H attack even by $SO_4^{-}\cdot$ and HO·.

Differentiation between C–H and O–H attack is more difficult with primary and secondary alcohols because of the facile interconversion

$$R_2CHO\cdot + R_2CHOH \rightarrow R_2CHOH + R_2\dot{C}OH \qquad (11)$$

Here, advantage can be taken of the even more facile intramolecular abstraction of δ hydrogens by long chain alkoxy radicals, as in the Barton reaction, intramolecular chlorination with hypochlorites, and lead tetraacetate oxidations, which in the presence of a suitable oxidant lead to tetrahydrofurans.[14]



(12)

Results on the oxidation of 1- and 2-pentanol appear in Table II, employing thermal $S_2O_8^{2-}$ oxidations in the presence of Cu^{2+} with and without Ag^+. With 1-pentanol and no Ag^+ the product is chiefly pentanal, although a small amount of 2-methyltetrahydrofuran is also formed. With increasing Ag^+ the furan yield rises substantially. Similar results are obtained with 2-pentanol, except that here intramolecular reaction requires attack on a primary C–H bond and is slower, so β scission to acetaldehyde (and presumably an *n*-propyl radical) takes place as well.

Aliphatic Acids. Since the decarboxylation of carboxylic acids by Ag(II) is well established, our chief interest was in comparing the rates of reaction of Ag(II) with acids and alcohols. To this end, products (CO_2 and acetone) were determined for the oxidation of mixtures of 2-methyl-2-butanol and three aliphatic acids. Results, expressed as $k_{CO_2}/k_{acetone}$ (i.e., the ratio of CO_2 to acetone formed corrected for the concentrations of acid and alcohol present), are listed in Table III. While the results are reproducible and consistent (see Experimental Section), yields of CO_2 from acid oxidations are in general higher than those of acetone from the alcohol. Ac-

Table II. Oxidation of Pentanols[a]

			Products, %		
Substrate	Registry no.	[Ag$^+$], M	Pentanal	2-Pentanone	2-Me-THF
1-Pentanol (4)	71-41-0	0	42 ± 2		9.8 ± 0.5
1-Pentanol (2)		0.01	16 ± 2		40 ± 2
1-Pentanol (2)		0.05	9.7 ± 2		55 ± 3
2-Pentanol (2)	6032-29-7	0		92 ± 4	2.2 ± 0.1
2-Pentanol (2)		0.05		26 ± 1	17[b] ± 1

[a] Conditions for all runs: 3–6 h at 60 °C; [ROH] = 0.5 M; [$S_2O_8^{2-}$] = 0.05 M; [Cu^{2+}] = 0.05 M; in 26% by volume acetonitrile (1-pentanol) or 20% (2-pentanol). The indicated uncertainty is the standard deviation of the mean of the number of runs indicated in parentheses. [b] Plus 37% of acetaldehyde.

Table III. Competitive Oxidations of Acids and 2-Methyl-2-butanol[a]

Acid	Registry no.	pH	$k_{CO_2}/k_{acetone}$
n-Butyric	107-92-6	1.0	1.42 ± 0.13 (2)
n-Butyric		2.7	2.63 ± 0.04 (4)
n-Butyric		4.7	3.96 ± 0.05 (2)
Isobutyric	79-31-2	1.0	5.13 ± 0.08 (2)
Isobutyric		2.7	12.2 ± 0.05 (2)
Pivalic	75-98-9	1.0	196 ± 16 (6)

[a] Conditions for all experiments: 4 h at 60 °C; [$S_2O_8^{2-}$] = 0.05 M; [Cu^{2+}] = 0.05 M; [Ag^+] = 0.01 M. The indicated uncertainty is the standard deviation of the mean of the number of runs indicated in parentheses.

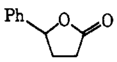
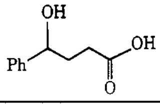
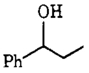
cordingly, the actual relative rates of oxidation of acid to alcohol could be smaller by a factor of as much as 2. Nevertheless, their variations with conditions and acid structure should be significant.

The most notable feature of the table is the large change in reactivity with acid structure in the order butyric < isobutyric < pivalic. This is in marked contrast to Anderson and Kochi's[8] finding for the same acids. Second, relative reactivities are evidently pH dependent, with the relative reactivity of the acid increasing as the acidity decreases. The results are qualitative only, since the table reports initial pH, and additional acid is generated during reaction (cf. eq 4). However, it seems likely that the change is in the rate of reaction of Ag(II) with the acid (see below).

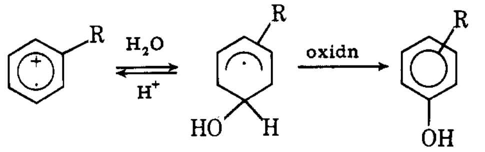
Because of the difference between Anderson and Kochi's findings and our own, we also carried out direct competitive oxidations of pivalic and butyric acids in the presence of Cu^{2+} and 0.1 M $HClO_4$, analyzing the reaction mixtures for CO_2, propene and *tert*-butyl alcohol. (Any isobutene formed would be hydrated in the acid medium.) Four experiments at average butyric/pivalic acid ratios of 14.3 gave 87 ± 2% of CO_2, 8.2 ± 0.5% of propene, and 66 ± 3% of *tert*-butyl alcohol. The *tert*-butyl alcohol/propene ratio corresponds to a relative reactivity for pivalic/butyric acids of 115 compared with 138 from the data of Table III.

Aromatic Substrates. As we have discussed in detail elsewhere,[15,16] the major path by which $SO_4^{-}\cdot$ attacks aromatic molecules is by oxidizing them to radical cations which can either react with water to yield hydroxycyclohexadienyl radicals (capable of subsequent oxidation to phenols) or undergo some species of side-chain fragmentation, giving side-chain oxidation products.

Table IV. Oxidation of γ-Phenylbutyric Acid[a]

	Yield, %			
[Ag^3], M				
0 (2)	46.1 ± 2	5.1 ± 0.2	12.5 ± 0.2	2.9 ± 0.2
1 × 10^{-3} (2)	38.3 ± 2	5.2 ± 0.6	17 ± 0.2	3.2 ± 1
1 × 10^{-2} (5)	14.2 ± 1.4	2.2 ± 0.5	24.0 ± 0.6	1.4 ± 0.2
5 × 10^{-2} (4)	7.7 ± 1.4	1.5 ± 0.4	33.5 ± 2.4	3.3 ± 1

[a] Conditions for all experiments: [phenylbutyric acid] = 0.1 M; [Cu^{2+}] = 0.05 M; [$S_2O_8^{2-}$] = 0.01 M; [H^+] = 0.1 M; CH_3CN, 20–30 vol %; *T* = 60 °C (90 °C without Ag$^+$). Experimental errors are the standard deviations of the mean of the number of experiments shown in parentheses. Registry no.: γ-phenylbutyric acid, 1821-12-1.



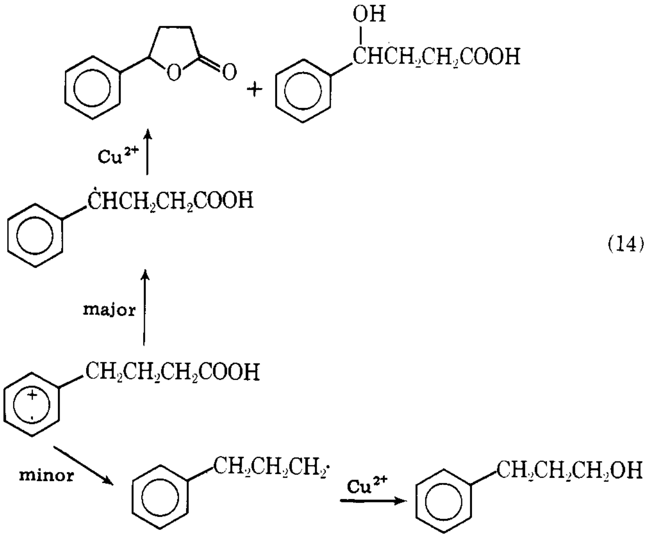
(13)

fragmentation → side-chain oxidation products

Simple aromatics are apparently also oxidized to radical cations by Ag(II)[17] and should yield similar products. However, when the aromatics contain side-chain –OH or –COOH groups, attack may occur there as well, and the problem is to choose molecules where the two paths predict significantly different products.

Table IV shows results with γ-phenylbutyric acid, carried out in the presence of Cu^{2+} to efficiently trap radical intermediates and 0.1 M acid to suppress the formation of phenolic products.[6,16] A complex mixture of products is obtained, but one which plainly varies with the concentration of Ag$^+$.

In the absence of Ag$^+$, the major reaction path is evidently fragmented by loss of a benzylic proton.



(14)

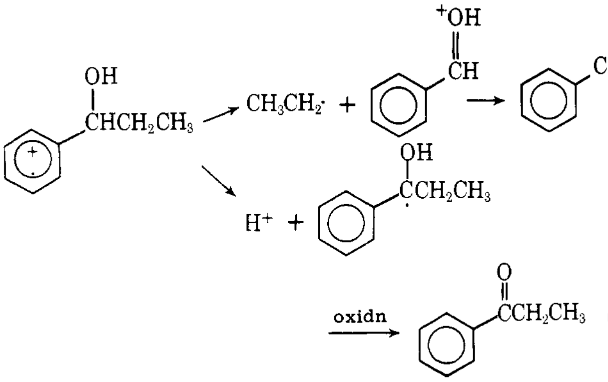
With increasing Ag$^+$, the yields of products expected from 3-phenylpropyl radicals increase. If at 0.05 M Ag$^+$ all oxidation is occurring through Ag(II), some 75% of its reaction with phenylbutyric acid must be by decarboxylation.

A similar case is provided by 1-phenylpropanol (Table V). Here data in the absence of Ag$^+$ indicates that the radical cation fragments by two paths to give propiophenone and benzaldehyde, as had been previously reported by Snook and Hamilton.[18]

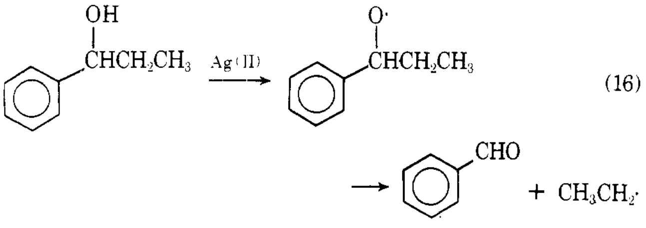
Table V. Oxidation of 1-Phenylpropanol[a]

$[Ag^+]$, M	$[Cu^{2+}]$, M	Yield, % Benzaldehyde	Yield, % Propiophenone
0 (2)	0.01	30.3 ± 0.5	65.9 ± 0.4
0.001 (2)	0.01	31.5 ± 1.4	56.9 ± 0.6
0.01 (2)	0.01	45.7 ± 1.8	38.0 ± 2.7
0.1 (2)	0.01	64.8 ± 0.1	27.7 ± 0.1
0	0	28.7	64.5
0.1 (4)	0	88.0 ± 15	44.5 ± 8
0.2 (2)	0	91.5 ± 5	39.2 ± 24

[a] In all runs $[S_2O_8^{2-}]$ = 0.01 M, [phenylpropanol] = 0.1 M, and CH_3CN = 30 vol % at T = 60 °C. Experimental errors are the standard deviations of the mean of the number of experiments shown in parentheses. Registry no.: 1-phenylpropanol, 93-54-9.


(15)

In the presence of Ag^+ the yield of benzaldehyde rises, suggesting that -OH attack is now important.


(16)

The cleanest experiments are those in the presence of Cu^{2+}, which efficiently oxidizes intermediate radicals. Assigning "excess" benzaldehyde yield to reaction 16 and assuming that at the highest Ag^+ concentration the reaction is going entirely through Ag(II), we calculate that 56% of the reaction is via reaction 16. Analysis of the data in the absence of Cu^{2+} leads to a similar result. Here it will be noted that at high Ag^+ concentrations the total product yields (calculated on the basis of 1 mol of product/mol of $S_2O_8^{2-}$) exceed 100%. This is stoichiometrically acceptable if some ethyl radicals escape further oxidation.

Agreement between the phenylpropanol and phenylbutyric acid systems is plausible. Somewhat more side-chain attack occurs with the acid, consistent with the indications of Table III.

With some substrates side-chain cleavage of the radical cation and initial side-chain attack lead to the same products. Here we might expect to determine the reaction path by carrying out oxidations under conditions (high Cu^{2+} and low acid) where the radical cations give substantial yields of phenols. Phenylacetic acid and 2-phenylethanol are two such examples. Tables VI and VII show that phenol yields are significantly reduced in the presence of Ag^+, implying chiefly side-chain attack on -COOH or -OH. However, the results are a bit equivocal since blank experiments show that phenols are rapidly oxidized further by Ag^+–$S_2O_8^{2-}$ at high Ag^+ levels, a previously known reaction;[19] so phenols are probably lost.

Table VI. Oxidation of Phenylacetic Acid[a]

$[Ag^+]$, M	Yield, % Benzyl alcohol	Yield, % Phenols (*o*–*m*–*p*)
0	42	21 (36–25–39)
5.9×10^{-4}	48	20 (36–24–40)
3.5×10^{-3}	47	12 (35–25–40)
6.1×10^{-3}	49	9 (33–26–41)
1.4×10^{-2}	47	4 (32–26–42)

[a] All runs used [phenylacetic acid] = 0.06 M and $[Cu^{2+}]$ = 0.20 M at T = 60 °C. Registry no.: phenylacetic acid, 103-82-2.

Table VII. Oxidation of 2-Phenylethanol[a]

$[Ag^+]$, M	Yield, % Benzyl alcohol	Yield, % Phenols (*o*–*m*–*p*)
0	17	38 (40–15–45)
3.6×10^{-3}	16	31 (42–15–45)
3.5×10^{-2}	16	6 (53–16–31)
7.6×10^{-4} [b]	32	19 (49–18–33)
3.6×10^{-2} [b]	27	3

[a] All runs used [phenylethanol] = 0.08 M and $[Cu^{2+}]$ = 0.24 M at T = 60 °C. Styrene glycol (1–3%) was also detected in the products. Registry no.: 2-phenylethanol, 60-12-8. [b] $HClO_4$ (0.05 M).

Discussion

In planning and interpreting our experiments, we have assumed that $SO_4^{-}\cdot$ and Ag(II) are the two species involved in the initial attack on substrates in our systems, but other intermediates have been proposed in the past and we should give our reasons for discarding them. Hydroxyl radicals, formed by oxidation of water by either Ag(II)[20] or Ag(III),[21] have been proposed as the intermediates which actually attack substrates. However, the marked difference in products found in Ag^+–$S_2O_8^{2-}$ and HO· radical systems and the fast bimolecular reactions observed between Ag(II) and typical substrates (see below) make their role here unlikely.

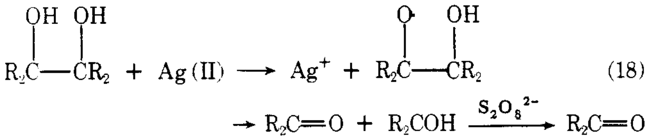
The possible intervention of Ag(III) is more complicated, and the problem has been clearly discussed by Wilmarth and Haim.[4] There is evidence that the equilibrium

$$2\mathrm{Ag(II)} \rightleftarrows \mathrm{Ag}^+ + \mathrm{Ag(III)} \qquad (17)$$

is fast but lies far to the left and also that Ag(III) may be involved in the oxidation of water by higher valence Ag. The role of Ag(III) has usually been invoked in order to account for the complex overall kinetics of Ag^+–$S_2O_8^{2-}$ oxidations.[22] Perhaps the best reason to exclude it is the observation that the kinetics of those Ag(II)–substrate reactions which have been studied[23] appear to be cleanly second order, inconsistent with Ag(III) being the active oxidant if equilibrium 17 is in fact rapid and unfavorable.

Our conclusion that alkoxy radicals are the major products in the oxidation of alcohols by Ag(II) is consistent not only with the results of Caronna et al.[12] (who employed protonated quinoline as a trapping agent for cleavage products) but also with earlier reports of cleavage products from *tert*-butyl alcohol[24] and 1,3-diols.[25] The possibility that oxidation and β scission might be concerted so that alkoxy radicals do not in fact exist as discrete intermediates seems ruled out by the formation of tetrahydrofurans from long-chain alcohols (cf. Table II) and Carona et al.'s trapping of intermediate δ-hydroxyalkyl radicals.

With these observations it seems likely that the better-known cleavage of 1,2-diols should also be formulated as a stepwise process,



$$R_2C(OH)\text{—}C(OH)R_2 + Ag(II) \longrightarrow Ag^+ + R_2C(O\cdot)\text{—}C(OH)R_2 \quad (18)$$
$$\rightarrow R_2C{=}O + R_2\dot{C}OH \xrightarrow{S_2O_8^{2-}} R_2C{=}O$$

particularly since *cis*- and *trans*-cyclohexanediols[7] and *cis*- and *trans*-cyclopentanediols[26] behave very similarly. Taken overall, our results suggest that Ag^+–$S_2O_8^{2-}$ may provide a convenient route for generating alkoxy radicals to bring about the cleavage of C–C bonds or the formation of tetrahydrofurans, particularly since the reactions occur smoothly in H_2O–acetonitrile mixtures for substrates of low water solubility.

Three conclusions of interest emerge from our results with carboxylic acids. First, contrary to Anderson and Kochi's report[8] but consistent with direct measurement of carboxylic acid oxidations by Ag(II),[23] rates vary with acid structure, consistent with rapid reversible complex formation followed by slow concerted oxidation and R–CO_2 bond scission,

$$RCOOH + Ag(II) \rightleftarrows RCOOH\cdot Ag(II) \rightarrow R\cdot + CO_2 + Ag^+ + H^+ \quad (19)$$

paralleling the behavior of Pb(IV), Co(III), and Mn(III).[27] If so, the discrepancy with Anderson and Kochi's results could arise because in their much less aqueous medium the first step in eq 19 is less completely reversible. Second, the rate of decarboxylation is apparently pH dependent. This has been discussed by Mentasti et al.[23] in terms of the $Ag^{2+} \rightleftarrows AgOH^+$ equilibrium,[28] but it could also arise from a series of complexes, e.g.,

$$RCOOH + Ag(II) \rightleftarrows RCOOH\cdot Ag(II) \rightleftarrows RCOO^-\cdot Ag(II) + H^+ \quad (20)$$

Third, our competitive experiments indicate that at low acidities even unreactive straight-chain acids react more readily with Ag(II) than do alcohols, implying that in the oxidation of complex molecules containing –OH and –COOH groups preferential decarboxylation by Ag^+–$S_2O_8^{2-}$ can be achieved.

Our results with aromatic systems are complex, but in general they show that Ag(II) oxidations occur by two competing paths: oxidation of the ring to a radical cation and attack on side-chain –OH or –COOH groups. The balance evidently depends on the particular structure involved, but both processes must be taken into consideration in accounting for product distributions.

The oxidation of γ-phenylbutyric acid with and without Ag^+ has also been examined by Clerici, Minisci, and Porta[29] with results qualitatively similar to our own. However, in the absence of Cu^{2+} and at relatively low substrate/$S_2O_8^{2-}$ ratios, benzaldehyde was reported as a major product and attributed to β scission of 3-phenylpropyl radicals. We also obtained benzaldehyde under these conditions, but since we find no benzyl alcohol or bibenzyl we suggest that it arises instead from further oxidation of 1-phenylpropanol (cf. Table V).

A further consideration is the point at which substrate oxidation by Ag(II) takes over in Ag^+–$S_2O_8^{2-}$ systems. This obviously depends upon the relative rates of reaction of $SO_4^-\cdot$ with Ag^+ and substrate, reactions 2 and 3. As far as we are aware of, the rate constant for reaction 3 has not been reported, but it can be estimated from our data. From the yields of acetaldehyde plus 2-methyltetrahydrofuran and 2-pentanone from 2-pentanol (Table II), $k_3/k_2 \cong 21$. Taking k_2 the same as for 2-propanol (8.5×10^7)[29] gives $k_3 = 1.8 \times 10^9$. A similar calculation for the two pieces of data on 1-pentanol, taking $k_2 = 4.8 \times 10^7$, the same as for 1-propanol,[29] gives k_3 = 3 and 6×10^9. The geometric mean of the three would be 3×10^9 and indicates that reaction 3 is close to a diffusion-controlled process. Since rates of reaction of primary and secondary alcohols with $SO_4^-\cdot$ in general lie between 10^7 and 10^8, oxidation by Ag(II) becomes the dominant process at Ag^+/substrate ratios greater than 10^{-2}, but with tertiary alcohols even lower ratios should be effective. Relatively low concentrations of Ag^+ should also be effective in decarboxylating acids (k_2 for acetic acid is 8.8×10^4,[30] and we obtain 85–90% of CO_2 at Ag^+/substrate = 0.01). On the other hand, k_2 for $SO_4^-\cdot$ attack on aromatics is in general greater than 10^9.[31] From Tables IV and V, Ag^+/substrate ratios approaching unity are necessary to insure that almost all of the reaction involves Ag(II).

Finally, we can comment briefly on the overall rate of oxidation in Ag^+–$S_2O_8^{2-}$ systems, a topic discussed at length by Wilmarth and Haim, but where the various steps involved are now better understood. The slow thermal decomposition of $S_2O_8^{2-}$ is accelerated by reaction 1, the Ag(II) returning to Ag^+ by oxidation of water or attack on substrates. If intermediate radicals do not participate in the chain processes, substrates should have little further effect on the rate of $S_2O_8^{2-}$ decomposition. If substrates yield radicals capable of attacking $S_2O_8^{2-}$ (alcohols provide the best studied case, cf. reactions 5 and 6, but the range of substrates participating in such chains is not well defined at present), a chain decomposition of $S_2O_8^{2-}$ is superimposed on reaction 1. However, the situation is complicated since Ag(II) can also provide a termination step by oxidizing radical intermediates to stable products or by generating different intermediates, e.g., alkoxy radicals in the case of alcohols. It is not surprising that such systems have not proved very amenable to purely kinetic analysis.

The addition of Cu^{2+} ion has been sometimes observed to produce a further acceleration of $S_2O_8^{2-}$ consumption, and here it is plausible that an alternate chain process is introduced.

$$R\cdot + Cu^{2+} \rightarrow \text{product} + Cu^+ \quad (21)$$

$$Cu^+ + S_2O_8^{2-} \rightarrow Cu^{2+} + SO_4^{2-} + SO_4^-\cdot \quad (22)$$

Since reaction 21 occurs readily with most carbon radicals, such induced chains should be quite general in Cu^{2+}–Ag^+–$S_2O_8^{2-}$ systems.

Experimental Section

Reagents. Potassium peroxydisulfate was recrystallized from water, purity by titration >98%. Reagent grade perchloric acid, cupric perchlorate, ferrous perchlorate, cupric sulfate, and silver nitrate were used as received. The purity of organic reagents was checked by gas–liquid chromatography (GLC), and they were distilled or sublimed if necessary. 1-Phenylpropanol was synthesized from phenylmagnesium bromide and propionaldehyde. Reference compounds were either purchased or synthesized by known methods.

Reactions. Thermal reactions were carried out in stoppered flasks by mixing standard solutions, flushing the mixtures with N_2, and placing the flasks in a thermostat. In experiments where CO_2 was determined, the flasks containing weighed amounts of $K_2S_2O_8$ were closed with a serum cap and evacuated through a syringe needle, N_2-flushed solutions of other reagents were added via syringes, and the mixtures were stirred to solution and placed in the bath. Reactions employing ferrous ion were carried out by the dropwise addition of peroxydisulfate or ferrous ion solution to the other components of the system as described previously.[16]

Analyses of reaction mixtures were by GLC, using previously calibrated internal standards and reference materials. For CO_2 and propene, ethane, introduced via syringe after the reaction was complete, was used as an internal standard. The CO_2 that dissolved in the aqueous phase was corrected for using Henry's Law using a constant measured on similar reaction mixtures containing known amounts of CO_2. In determining aromatic acids and phenols, products were silylated as described previously.[16]

Registry No.—Ag(II), 15046-91-0; $S_2O_8^{2-}$, 15092-81-6.

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Thermolysis of *tert*-Butyl Cubanepercarboxylate. The Cubyl Radical

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The rate and activation parameters for the thermal decomposition of *tert*-butyl cubanepercarboxylate have been measured in cumene. The cubyl radical is formed about 4600-fold less rapidly than the *tert*-butyl radical under the same conditions. The selectivity of the cubyl radical in halogen atom abstraction reactions has also been investigated. The competition constant, *r*, for the reactions of the radical with bromotrichloromethane and carbon tetrachloride is 80. This value is larger than the competition constants of other bridgehead radicals. These results may be rationalized on the basis of the novel hybridization of the carbon atoms of cubane.

The stereochemistry of tricoordinate carbon radicals has been actively investigated for some time.[1] Recent studies indicate that simple alkyl radicals are not strictly planar and that *tert*-butyl radicals are distinctly pyramidal.[2-5] However, the energy difference between the planar and pyramidal forms of the simple carbon free radicals is apparently quite small.[5]

Bridgehead radicals can neither undergo inversion nor become planar. The radicals of this class are readily formed and their chemistry has also been actively investigated. Two lines of investigation, the thermal decomposition of the peresters[6-9] and the selectivity of the radicals in halogen atom abstractions,[9-11] have received special attention. The rates of decomposition of the peresters depend on the structure of the radical importantly with norbornyl radical formed about 1000-fold less rapidly than the *tert*-butyl radical.[6-9] The selectivity of the bridgehead radicals in reactions with carbon tetrachloride and bromotrichloromethane at 80 °C decrease in the order: 3-homocubyl > 1-bicyclo[2.2.1]heptyl > 1-bicyclo[2.2.2]octyl > 1-adamantyl.[9-11] We have undertaken a complementary investigation of the related reactions of the more highly strained cubane derivatives.

Results and Discussion

Cubanecarboxylic acid was prepared by a well known procedure.[12,13] The acid was converted to the perester through reaction of the acid chloride with *tert*-butyl hydroperoxide. The *tert*-butyl perester of adamantane carboxylic acid was also prepared for study of the procedures used in this work.

Kinetic Observations. The rates of decomposition of the peresters of adamantane and cubane are presented in Table I.

First-order reactions were observed in all the kinetic experiments. The rate constant for the decomposition of adamantane is within experimental error of the constants reported in prior work.[6-9] The relative rates and activation parameters for the *tertiary* acyclic and bridgehead peresters are summarized in Table II.

Analyses of the data for the homolytic decomposition reactions of peresters indicate that such reactions occur by several different mechanisms which range from simple oxygen–oxygen bond homolysis to two-bond fragmentation reactions with varying degrees of polar character. Several experimental approaches have been used to distinguish between these two extremes. The entropy of activation has frequently been used as one of these criteria.[15] Generally, two-bond concerted decomposition reactions which proceed with rotational restriction exhibit more positive entropies of activation. From this viewpoint, the results presented in Table II suggest that the thermolysis of the bridgehead peresters may not all occur by the same mechanism. However, the experimental errors are relatively large and the reaction solvents differ. Further, Traylor and his students investigated the decomposition of 1-bicyclo[2.2.1]heptanecarboxy, cubanecarboxy, and 4-homocubanecarboxy radical in hydrocarbon solvents.[16] They report that even the relative rates of decarboxylation are immeasurably fast and that there is a quantitative evolution of carbon dioxide. These results do not require that the thermolysis reactions of the peresters proceed by two-bond fragmentation processes. However, these observations and

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