Silver(I)-Catalyzed Oxidative Decarboxylation of Acids by Peroxydisulfate. The Role of Silver(II)

James M. Anderson and Jay K. Kochi

*Contribution from the Department of Chemistry, Case Western Reserve University,
Cleveland, Ohio, and Indiana University, Bloomington, Indiana.
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Abstract: Silver(I) is involved in an efficient catalysis of the oxidative decarboxylation of acids by peroxydisulfate ion in aqueous solutions. The rate of decarboxylation is first order in silver(I) and peroxydisulfate, but zero order in carboxylic acid. The formation of alkane, alkene, alcohol, and ketone as products are attributed to alkyl radical intermediates. The synergistic effect of copper(II) as a cocatalyst occurs at low concentrations, and is associated with the efficient trapping of alkyl radicals. The product distribution and the stoichiometry of the oxidative decarboxylation can be deliberately altered by considering the mechanistic effects of silver(I), copper(II), and carboxylic acid concentrations. A mechanism is proposed in which the silver(II) species is formed as a metastable intermediate and it plays an important role in the specific and efficient oxidation of the carboxylic acid function.

The readily available peroxydisulfate ion, $S_2O_8{}^{2-}$, is an excellent and versatile oxidant for a variety of organic and inorganic compounds.[1-3] Despite the relatively high oxidation potential for the half-reaction (eq 1), many oxidations by peroxydisulfate do not pro-

$$S_2O_8{}^{2-}(aq) + 2e \longrightarrow 2SO_4{}^{2-}(aq) \qquad E_0 = 2.01 \text{ V} \qquad (1)$$
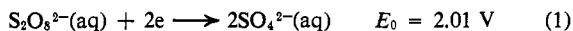
ceed at a convenient rate at ambient temperatures. The latter can be largely attributed to the rate-limiting homolysis given by eq 2,[1,4] which has an activation energy

$$S_2O_8{}^{2-} \longrightarrow 2SO_4\cdot{}^- \qquad (2)$$
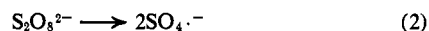
of approximately 30 kcal/mole. The decomposition of the peroxydisulfate ion, however, is accelerated by strong mineral acids as well as by trace-metal ions.[1,2] Among the latter, catalysis by silver and copper species has been studied extensively.

We have been interested in the various roles which metal ions perform as catalysts in the oxidation and reduction of organic compounds.[5] The oxidative decarboxylation of acids given by eq 3 is a convenient

$$RCO_2{}^- \longrightarrow RCO_2\cdot + e \qquad (3)$$

probe for the investigation of the mechanism of such oxidations.[6]

The noncatalyzed decarboxylation of salts of carboxylic acids by peroxydisulfate was originally investigated by Fichter and coworkers.[7] Recently Tanner and Osman[8] have evaluated the relative rates of electron transfer (eq 4) from various ring-substituted phenyl-

$$RCO_2{}^- + SO_4\cdot{}^- \longrightarrow RCO_2\cdot + SO_4{}^{2-} \qquad (4)$$

acetates to the sulfate ion-radical persumed to be the active species in these oxidations.[9]

We have found that the oxidative decarboxylation of a series of acids by peroxydisulfate ion is markedly accelerated by silver ion. The mechanism of this silver-catalyzed oxidative decarboxylation of acids by peroxydisulfate is, no doubt, related to the extensive studies carried out with oxalate and to a certain extent formate ions.[1] The problem, however, extends beyond these two unique examples to carboxylic acids generally.[10]

In this paper we present our investigation of the mechanism of the catalysis by silver species and delineate the role of alkyl radicals and silver(II) complexes as reactive intermediates. Our conclusions regarding the mechanism of the silver catalysis will be applied in subsequent studies.

Results

The Stoichiometry of Oxidative Decarboxylation with a Silver Catalyst. The oxidation of three representative aliphatic carboxylic acids was examined in detail: pivalic (tertiary), isobutyric (secondary), and *n*-butyric (primary) acids. The products from the silver-catalyzed oxidation of these acids were obtained from homogeneous reactions in solution carried out at 60° in degassed and sealed vessels. All three acids were examined initially in aqueous dimethyl sulfoxide (DMSO) solutions to provide a common basis for comparison. The principal products were carbon dioxide and products derived from the alkyl moiety: alkane, alkene, and alcohol (see Experimental Section). The stoichiometry of the oxidation was slightly better in the absence of DMSO, since the latter is known to be oxidized by peroxydisulfate.[11] In the presence of a large excess of carboxylic acid in aqueous solution, car-

(1) For reviews see (a) D. A. House, *Chem. Rev.*, **62**, 185 (1962); (b) E. J. Behrman and J. E. McIssac, Annual Reports on Mechanisms of Reactions of Sulfur Compounds, Vol. 2, Intra-Science Research Foundation, Santa Monica, Calif., 1968, p 235.

(2) W. K. Wilmarth and A. Haim, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 175 ff.

(3) (a) R. G. R. Bacon, W. J. W. Hanna, and D. Stewart, *J. Chem. Soc., C,* 1384, 1388 (1966); (b) *ibid.,* 1332, 1339 (1960); (c) *ibid.,* 2275 (1954); *Proc. Chem. Soc.,* 113 (1962); (d) G. D. Menghani and G. V. Bakore, *Bull. Chem. Soc. Japan,* **41**, 2574 (1968).

(4) The problem is complicated by the ready induced decomposition of peroxydisulfate and the chain character of many of these reactions.

(5) J. K. Kochi, *Rec. Chem. Progr.,* **27**, 207 (1966).

(6) J. K. Kochi, J. D. Bacha, and T. W. Bethea, *J. Am. Chem. Soc.,* **89**, 6538 (1967).

(7) (a) F. Fichter and H. Lapin, *Helv. Chim. Acta,* **12**, 993 (1929); **15**, 996 (1932); **16**, 338 (1933); (b) R. H. Thomson and A. G. Wylie, *J. Chem. Soc., C,* 321 (1966); 842 (1968).

(8) D. D. Tanner and S. A. A. Osman, *J. Am. Chem. Soc.,* **90**, 6572 (1968).

(9) There is ambiguity, however, as to whether the oxidant is $SO_4\cdot{}^-$ or $HO\cdot$ under these conditions. See H. N. Po and T. L. Allen, *J. Am. Chem. Soc.,* **90**, 1127 (1968), and L. Dogliotti and E. Hayon, *J. Phys. Chem.,* **71**, 2511 (1967).

(10) (a) The oxidative decarboxylation of phenylacetic acid has also been reported [R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.,* 1632 (1960)]. (b) A preliminary study of pivalic and isobutyric acids has not been fulfilled [R. G. R. Bacon and R. W. Bott, *Chem. Ind.* (London), 1285 (1953)].

(11) E. Howard, Jr., and L. S. Levitt, *J. Am. Chem. Soc.,* **75**, 6170 (1953).

Table I. Stoichiometry of the Silver-Catalyzed Oxidative Decarboxylation by Peroxydisulfate[a]

| RCO₂H acid (M) | Products, mmole | | | | | $CO_2/S_2O_8^{2-}$ | R_{ox}^{b}/RH | $\Sigma R \cdot c$/CO₂ |
	CO₂	RH	R(-H)	ROH	>C=O			
Acetic (8.7)	1.49	0.59	0.32[h]	0.10	0	1.49	0.7	0.68
Isobutyric (5.5)[d]	1.65	1.03	0.09[e]	0.10	0.10	1.65	0.4	0.80
(0.33)	1.03	0.05	0.64	0.08	0.08	1.03	16	0.85
(0.66)	1.05	0.10	0.67	0.07	0.11	1.05	8.5	0.90
(0.99)	1.10	0.14	0.52	0.14	0.15	1.10	5.8	0.86
n-Butyric (5.5)[f]	1.82	1.21	0.13	0.07	+[g]	1.82	0.17	0.78
(5.5)	1.97	1.31	+	+	+	1.97	0.01	0.67
(0.33)	0.95	0.06	0.55	0.01	0.05	0.95	11	0.70
(0.66)	0.95	0.12	0.52	0.08	+	0.95	5	0.76
(0.99)	1.08	0.26	0.45	0.09	+	1.08	2.1	0.74

[a] In 10 ml of degassed aqueous solution containing 0.01 M silver nitrate and 0.10 M ammonium peroxydisulfate at 60° for 4 hr. [b] Sum of alkene, alcohol, ester, and twice ketone (aldehyde). [c] Includes all alkyl fragments (R_{ox} + RH). [d] Contains 10 vol % acetonitrile. [e] Includes 0.05 mmole of isopropyl isobutyrate. [f] Eight-hours. [g] Trace. [h] Methyl acetate.

**Table II.** Products from the Silver-Catalyzed Oxidative Decarboxylation by Peroxydisulfate Cocatalyzed by Copper[a]

| Acid[b] RCO₂H | Products, mmole | | | $CO_2/S_2O_8^{2-}$ | R_{ox}^{c}/RH | $\Sigma R \cdot d$/CO₂ |
	CO₂	R(-H)	ROH			
Acetic	0.92		0.74[e]	0.92	100	0.81
n-Butyric (5.5)	1.00	0.85	Trace[f]	1.00	14	0.91
n-Butyric (0.33)	0.78	0.45	0.03[g]	0.78	500	0.62
Isobutyric (5.5)	1.17	0.66[h]	0.30[i]	1.17	14	0.89
Isobutyric (0.33)	0.85	0.44	Trace	0.85	500	0.55

[a] In 10 ml of aqueous solution containing 0.01 M silver nitrate, 0.01 M copper sulfate, and 0.10 M ammonium peroxydisulfate at 60° for 4 hr. [b] Value in parentheses is molarity of acid. [c] Sum of alkene, alcohol, ester, and twice ketone (aldehyde). [d] Includes all alkyl fragments (R_{ox} + RH). [e] Includes 0.50 mmole of methyl acetate. [f] Trace amounts (0.01 mmole) of isopropyl alcohol and acetone. [g] Includes 0.01 mmole of acetone. [h] Includes 0.06 mmole of isopropyl isobutyrate. [i] Includes 0.08 mmole of acetone.

bon dioxide and alkane were the major products (Table I). The stoichiometry of oxidative decarboxylation under these conditions approached that given in eq 5.[12]

$$2RCO_2H + S_2O_8^{2-} + 2HY \xrightarrow{Ag(I)}$$
$$2RH + 2CO_2 + 2H^+ + 2SO_4^{2-} + Y_2 \quad (5)$$
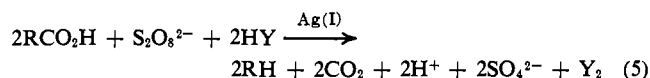
The stoichiometry of the oxidation changed as the concentration of the acid decreased, and it approached that given in eq 6 at the lower limit. The principal

$$RCO_2H + S_2O_8^{2-} \xrightarrow{Ag(I)} [R^+]_{ox} + H^+ + CO_2 + 2SO_4^{2-} \quad (6)$$
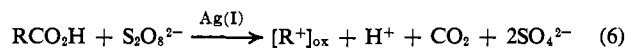
products were now those derived from the oxidation of the alkyl group represented as $[R^+]_{ox}$, since they corresponded to those derived from the carbonium ion, i.e., alkene, alcohol, ester or from further oxidation (ketone, aldehyde) of these products (see Tables I and VIII).

Control experiments were also carried out on the peroxydisulfate oxidation of n-butyric acid in the absence of silver catalyst. The disappearance of the peroxydisulfate was followed iodometrically until its titer dropped to nil. The half-life of the peroxydisulfate in the presence of 0.01 M silver nitrate was 11 min, whereas it was 600 min in the absence of silver(I). Under these conditions the yields of carbon dioxide diminished from 1.95 to 0.36 mmole/mmole of $S_2O_8^{2-}$, respectively. In the latter instance, only traces (<0.01 mmole) of propane and propylene were found.

Synergistic Effects by a Copper Cocatalyst. Catalytic amounts of cupric sulfate had a dramatic effect on the products of the silver-catalyzed oxidation of acids by peroxydisulfate. In the presence of Cu(II), oxidations carried out under the variety of conditions

(12) (a) HY-hydrogen donor; (b) dimers and disproportionated products derived by attack on the alkyl group of the carboxylic acid as solvent was presumed, cf. ref 3.

described above afforded only carbon dioxide and *alkene* as the major products (Table II). Alkane under these conditions was a minor component and the stoichiometry of the oxidation could be represented by eq 7.

$$RCO_2H + S_2O_8^{2-} \xrightarrow{Ag(I)-Cu(II)} R(-H) + CO_2 + 2H^+ + 2SO_4^{2-} \quad (7)$$
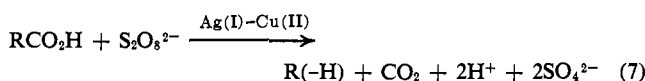
The Relationship between Carbon Dioxide Evolution and Peroxydisulfate Disappearance in the Ag(I) and the Ag(I)–Cu(II) Catalyzed Reactions. Since silver as well as copper specific catalyzed the decomposition of peroxydisulfate without necessarily effecting oxidative decarboxylation, it was necessary to distinguish the decomposition of peroxydisulfate from oxidative decarboxylation. The extent of oxidative decarboxylation was measured directly by following the amount of liberated carbon dioxide by gas chromatography.

The **evolution of carbon dioxide** during oxidation of n-butyric acid by peroxydisulfate alone was quite slow ($t_{1/2}$ = 600 min) as shown in Figure 1. The rate of carbon dioxide evolution was essentially unaffected by the addition of cupric sulfate. On the other hand, the presence of 0.01 M silver nitrate markedly catalyzed the decarboxylation ($t_{1/2}$ = 11 min). Under these conditions the reaction liberated 2 moles of carbon dioxide for each mole of peroxydisulfate. The synergistic effects of Cu(II) and Ag(I) were also apparent in the slightly increased rate of decarboxylation ($t_{1/2}$ = 6 min). Furthermore, in the presence of the Cu(II)–Ag(I) cocatalyst oxidative decarboxylation led to 1 mole of carbon dioxide for each mole of peroxydisulfate (Figure 1, dotted line).

The **disappearance of the peroxydisulfate** was also followed independently under the same conditions by
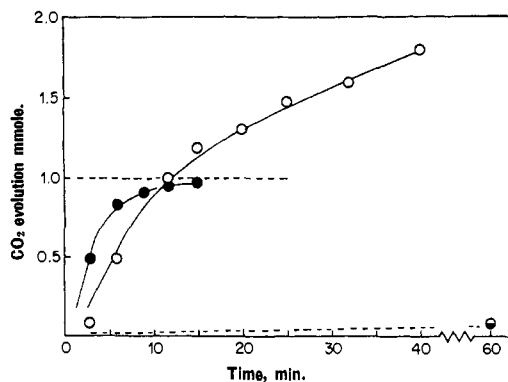
Figure 1. Carbon dioxide evolution at 60°: 10 ml of 50 vol % aqueous n-butyric acid with 1.0 mmole of ammonium peroxydisulfate: O, 0.01 M silver nitrate; ●, 0.01 M silver nitrate, 0.01 M cupric sulfate; ◒, 0.01 M cupric sulfate and the uncatalyzed reaction.

Figure 3. Evolution of carbon dioxide $vs.$ decomposition of peroxydisulfate at 60°: 10 ml of 50 vol % aqueous n-butyric acid with 1.0 mmole of ammonium peroxydisulfate; ◒, 0.01 M silver nitrate; ●, 0.01 M cupric sulfate; O, uncatalyzed reaction.
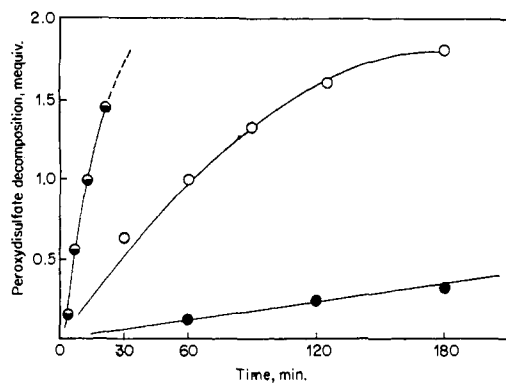

Figure 2. Peroxydisulfate decomposition at 60°: 10 ml of 50 vol % aqueous n-butyric acid with 1.0 mmole of ammonium peroxydisulfate: ◒, 0.01 M sulver nitrate; O, 0.01 M cupric sulfate; ●, uncatalyzed reaction.

Figure 4. Evolution of carbon dioxide at 60°: ◒, 0.005 M silver nitrate in n-PrCOOH-H₂O-CH₃CN, 50/40/10, v/v/v; O, 0.005 M silver nitrate and 0.018 M cupric sulfate in n-PrCOOH-H₂O-CH₃CN, 50/40/10, v/v/v; ●, 0.01 M silver nitrate, 0.66 M n-PrCOOH.

iodometric titration. The decomposition of peroxydisulfate in aqueous n-butyric acid in the absence of any metal catalyst was slow and the rate ($t_{1/2} = 500$ min, Figure 2) approximated the rate of evolution of carbon dioxide (see above). Silver nitrate (0.01 M) effectively catalyzed the rate of peroxydisulfate disappearance, and the increased rate ($t_{1/2} = 11$ min) coincided with the rate of carbon dioxide evolution determined independently. Cupric sulfate (0.01 M) was slightly less effective ($t_{1/2} = 50$ min) than silver nitrate as a catalyst for the decomposition of peroxydisulfate but was distinguished from the latter, of course, by its inability to effect oxidative decarboxylation.

The relationship between oxidative decarboxylation (carbon dioxide liberated) and the decomposition of peroxydisulfate (iodometric titration) is definitely established in Figure 3. Under conditions of high carboxylic acid concentrations, it is clear that the silver-catalyzed reaction produced approximately 2 moles of carbon dioxide for every mole (2 equiv) of peroxydisulfate decomposed. Copper(II) alone, despite its effectiveness as a catalyst for the decomposition of peroxydisulfate, is ineffective in the oxidative decarboxylation process, unless it is coupled with a silver catalyst. Moreover, the uncatalyzed oxidative decarboxylation of acids by peroxydisulfate appeared to be unpromising from both a kinetic as well as stoichiometric objective. We conclude, therefore, that both the copper-catalyzed and
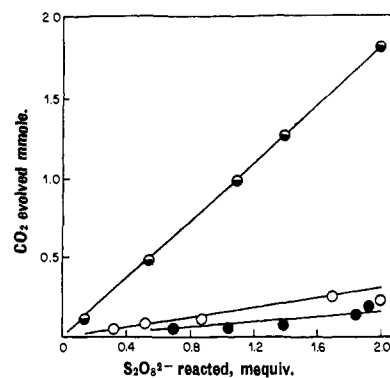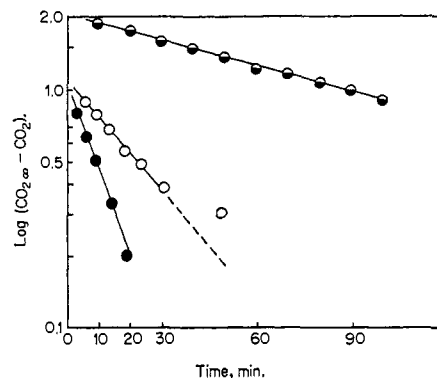
the uncatalyzed reactions of peroxydisulfate proceed largely via nondecarboxylative pathways ($i.e.$, processes which afford no carbon dioxide[12]) and that silver catalyst is necessary for oxidative decarboxylation. Hereafter we shall limit our results and subsequent discussion only to the oxidative decarboxylation reactions, $i.e.$: (a) decarboxylations which are catalyzed by silver(I) alone and (b) silver-catalyzed decarboxylations which are cocatalyzed by copper(II).

Kinetics of the Silver-Catalyzed Oxidative Decarboxylation of Acids. The stoichiometric formation of carbon dioxide in the silver-catalyzed oxidative decarboxylations by peroxydisulfate (given in Tables I and II and shown in Figure 3) enabled us to examine the kinetics of the reaction by following the carbon dioxide evolution. The carbon dioxide evolution was plotted as the function log ($CO_{2\alpha}$ − CO_2) $vs.$ time. The infinity value for carbon dioxide ($CO_{2\alpha}$) at high concentrations of carboxylic acid was 2 according to eq 5. At low concentrations of carboxylic acid the infinity value for carbon dioxide was 1 (eq 6). Most of the kinetic plots showed excellent linearity to more than 75% of the reaction. Some typical examples are illustrated in Figure 4. First-order rate constants extracted in this manner were easily reproducible to within 10%.

The observed first-order rate constants listed in Table III for the evolution of carbon dioxide during the silver-catalyzed decarboxylation of isobutyric and n-butyric

acids by peroxydisulfate were largely independent of the structure and the concentration (0.33–0.99 M) of the acid. The rate of carbon dioxide formation was also independent of the structure of the carboxylic acid at higher concentrations (5.5 M) as also shown in Table III. Acetonitrile was added as cosolvent in the latter

Table III. Pseudo-First-Order Rate Constants for the Silver-Catalyzed Decarboxylation with Peroxydisulfate[a]

RCO_2H	Concn, M	Ag(I), M	$k_1 \times 10^3$, sec^{-1}
Isobutyric	0.33	0.01	2.05 ± 0.06
n-Butyric	0.33	0.01	2.12 ± 0.14
n-Butyric	0.66	0.01	2.04 ± 0.07
n-Butyric	0.99	0.01	2.55 ± 0.05
Isobutyric[b]	5.5	0.01	0.23 ± 0.02
Isobutyric[b]	5.5	0.005	0.12 ± 0.015
n-Butyric[b]	5.5	0.01	0.22 ± 0.02
n-Butyric[b]	5.5	0.005	0.11 ± 0.01

[a] In 10 ml of aqueous solution containing 0.10 M ammonium peroxydisulfate at 60°. [b] Contains 10 vol % acetonitrile.

studies to maintain homogeneity, particularly of isobutyric acid.

The observed first-order rate constants for the evolution of carbon dioxide showed a first-order dependence on the silver salt concentration in the range 10^{-2} to 10^{-3} M (see Experimental Section, Table IX). Moreover the rate was independent of the particular anion employed with the silver(I) species as well as the cation associated with the peroxydisulfate anion (Table IV).

Table IV. Effect of Ag(I) and the Counterions on the First-Order Rate Constant[a]

AgX X =	AgX, M	$(Y)_2S_2O_8$, mmoles Y =	$k_1 \times 10^3$, sec^{-1}
NO_3^-	0.001	NH_4^+, 1.0	0.10
NO_3^-	0.0025	NH_4^+, 1.0	0.25
NO_3^-	0.005	NH_4^+, 1.0	0.64
NO_3^-	0.01	NH_4^+, 1.0	1.23
CF_3COO^-	0.01	NH_4^+, 1.0	1.28
ClO_4^-	0.01	NH_4^+, 1.0	1.28
NO_3^-	0.01	K^+, 1.0	1.14
$LiNO_3$	0.01	NH_4^+, 1.0	No reaction[b]

[a] In 10 ml of 5.5 M aqueous n-butyric solutions at 60°. [b] 0.04 mmoles of CO_2 detected after 90 min.

Finally, when lithium nitrate was substituted for silver nitrate, only trace amounts of carbon dioxide (0.04 mmole) were observed in the first 90 min of the reaction.[13] Product studies also showed (see Experimental Section) that at increasing concentrations of silver nitrate the yield of propylene increased at the expense of propane and the reaction approached the stoichiometry given by eq 6.

The temperature dependence of the observed first-order rate constant for the silver-catalyzed decarboxylation of a concentrated solution of n-butyric acid led to an enthalpy of activation of 15.2 kcal/mole and an entropy of acitivation of -26.4 eu. The latter value should be modified to -28.4 eu if the observed rate constant is treated as a pseudo-first-order constant to include the silver catalyst. The same study at low con-

(13) This time period corresponded to 10 half-lives for the silver-catalyzed reaction.

centrations of n-butyric acid showed appreciable scatter. The activation parameters were, however, within experimental error the same as those obtained in more concentrated acid solutions.

The Effect of Cu(II) on the Kinetics of the Ag(I)-Catalyzed Decarboxylation by Peroxydisulfate. The addition of catalytic amounts of cupric sulfate accelerated the silver-catalyzed decarboxylation of n-butyric acid by peroxydisulfate (Table V). With the concen-

Table V. Effect of Copper(II) Sulfate on the Pseudo-First-Order Rate Constant for the Silver(I) Catalyzed Oxidative Decarboxylation[a]

$CuSO_4$, M	$[Cu^{II}]$-$[Ag^+]$	$k_1 \times 10^3$, sec^{-1}	$t_{1/2}$, min	$C_3H_6/$ C_3H_8
0		0.125	92.4	<0.1
0.001	0.2	0.37	31.5	0.8
0.0025	0.5	0.69	16.9	1.8
0.005	1	0.68	17.0	4.6
0.01	2	0.61	18.9	
0.018	3.6	0.68	17.0	23
0.035[b]	7	0.55	21	

[a] In aqueous solution of 5.5 M n-butyric acid containing 10 vol % acetonitrile and 0.005 M silver nitrate and 0.10 M ammonium peroxydisulfate at 60°. [b] Cupric nitrate.

tration of the silver catalyst at 5×10^{-3} M, the effect was marked at low concentrations ($<10^{-3}$ M) of cupric sulfate. The rate of carbon dioxide evolution, however, became *independent of cupric sulfate* at concentrations greater than 2.5×10^{-3} M. The sensitivity to cocatalysis by Cu(II) paralleled the formation of high yields of propylene relative to propane (see Table V, columns 4 and 5), i.e., the pseudo-first-order rate constant reached a limiting value only when high yields of propylene were achieved. In the kinetic treatment the infinity value of one for carbon dioxide ($CO_{2\,\infty}$) was necessitated by the stoichiometry (cf. eq 7).

Competitive Decarboxylations of Acids by Peroxydisulfate. The effect of the structure of the acid on the decarboxylation step was probed by competitive methods, since the gross kinetics of oxidative decarboxylation were found to be zero order in the carboxylic acid. The silver-catalyzed reaction was examined in solutions containing a large excess of equimolar mixtures of pivalic and isobutyric or n-butyric acids. The relative rates were calculated by quantitatively accounting for the t-butyl and isopropyl or n-propyl fragments, respectively, by a method described previously.[14] The relative rates of oxidation given by the expression [ΣC_4-$(C_3H_7CO_2H)/\Sigma C_3(C_4H_9CO_2H)$] in the last column of Table VI increased only slightly on proceeding from n-butyric acid (relative rate = 1.0) to isobutyric acid (1.2) and pivalic acid (2.0). The addition of cupric sulfate did not affect the order of these relative rates of decarboxylation, despite the significant change in product composition effected by the cocatalyst (vide supra).

Silver(II) Species as Metastable Intermediates. The detection of a silver(II) species as a transient intermediate during the silver(I)-catalyzed decarboxylation with peroxydisulfate was attempted by electron spin resonance (esr) and absorption spectral techniques. These physical methods were used in conjunction with product studies in which the decarboxylation of acids

(14) S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 5196 (1968).

Table VI. Competitive Decarboxylation of (A) Pivalic Acid and (B) Isobutyric or n-Butyric Acid by Silver(I) and Peroxydisulfate[a]

Cu(II), M	CO$_2$	PrH	Pr$_{ox}$[b]	i-BuH	Bu$_{ox}$[c]	Pr$_{ox}$/PrH	Bu$_{ox}$/t-BuH	ΣC_4(B)[d]/ΣC_3(A)
			B = Isobutyric Acid					
0	1.03	0.20	0.16	0.31	0.11	0.8	0.3	1.2
0.01	0.98	+[e]	0.41	0.03	0.39	50	13	1.0
			B = n-Butyric Acid					
0	0.99	0.15	0.06	0.28	0.14	0.4	0.5	2
0.01	0.95	0	0.26	+	0.47	50	50	1.8

[a] In 10 ml of aqueous solution containing 33% by volume DMSO, 1.8 M pivalic acid and 1.8 M isobutyric or n-butyric acid, 0.10 M ammonium peroxydisulfate and 0.01 M silver nitrate at 60°. [b] Pr$_{ox}$ includes all propyl oxidation products. [c] Bu$_{ox}$ includes all t-butyl oxidation products. [d] ΣC_4 and ΣC_3 includes Bu$_{ox}$ + BuH and Pr$_{ox}$ + PrH, respectively. [e] Trace amounts (<0.01 mmole).

by the silver–peroxydisulfate procedure was compared with that employing well-characterized silver(II) complexes.

The esr spectra of a number of stable Ag(II) complexes have been determined,[15] and we have been able to reproduce these spectra. However, the concentration of any paramagnetic d^9 silver(II) complexes formed during the silver-catalyzed decarboxylation of n-butyric acid by peroxydisulfate was too low (<10^{-6} M) for us to detect.

Silver(II) complexes were generated in solution separately by the oxidation of 0.01 M silver(I) nitrate and perchlorate with 0.1 M peroxydisulfate in concentrated (3–5 M) mineral acid solutions. Ag(II) species formed in nitric acid absorbed at 381 nm whereas those formed in perchloric acid absorbed at 461 nm. The visible absorption spectra were the same as those obtained by ozonolysis of silver(I) complexes.[16] The variation in the spectra obtained for Ag(II) species in the presence of various counterions (e.g., nitrate and perchlorate) has been attributed to the formation of rather stable inner-sphere complexes. The peroxydisulfate oxidation of silver(I) under these conditions did not generate silver(II) in quantitative yields, based on extinction coefficients reported by Kirwin, et al.[16]

Although Ag(II) species could be prepared by peroxydisulfate (0.12 M) oxidation of silver(I) salts (0.05 M) in 5 M aqueous nitric acid, no Ag(II) could be observed when the reaction was carried out in the presence of 0.5 M n-butyric acid. Furthermore, the addition of a 0.1 M aqueous solution of n-butyric to Ag(II) generated in a manner described above led to an instantaneous decoloration of the Ag(II) solution. We conclude that Ag(II) species in strong mineral acid solutions are highly unstable in the presence of carboxylic acids. Product studies of the decarboxylation under these conditions unfortunately did not afford acceptable material balances.[17,18]

Attempts to observe Ag(II) species spectrally in the absence of concentrated solutions of mineral acids were unsuccessful. Thus, solutions containing Ag(I), peroxydisulfate, and n-butyric acid remained colorless whereas the same reaction mixture in the absence of n-butyric produced a dark grey precipitate of silver oxide (AgO).

Nitrogen-containing ligands such as α-picolinic acid and α,α^1-bipyridine, however, are known to stabilize Ag(II) species. The formation of the bisbipyridine-silver(II) complex from the oxidation of the silver(I) complex with peroxydisulfate can be examined kinetically.[19] This silver(II) complex was not a sufficiently strong oxidant to oxidize readily n-butyric acid at 25° and the kinetics of its formation under these conditions were unaffected by the presence of n-butyric acid.

Carboxylic acids, however, could be oxidatively decarboxylated by these amine silver(II) complexes in a stoichiometric manner at higher temperatures. The products obtained were essentially the same as those formed by the catalytic decomposition of peroxydisulfate with silver(I) described above.[20] Furthermore, the same trend toward higher yields of oxidation products (alkenes, alcohols, and esters) from the tertiary acid compared to the secondary or primary acids (found

$$RCO_2H + 2Ag(II) \longrightarrow [R^+] + CO_2 + H^+ + 2Ag(I)$$
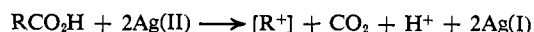
earlier in the catalytic peroxydisulfate decarboxylation) was reproduced in these stoichiometric reactions of amine silver(II) complexes.

Discussion

The efficiency with which the decarboxylation of acids occurs during the silver(I)-catalyzed reaction with peroxydisulfate is unique. The utilization of peroxydisulfate in these reactions is close to quantitative and indicates the existence of an exceedingly efficient process for the specific oxidation of the carboxylic acid function.[21]

Kinetic studies show that the rates of carbon dioxide evolution and peroxydisulfate disappearance are first order in silver(I) and first order in peroxydisulfate but zero order in carboxylic acid (eq 8).

$$\frac{dCO_2}{dt} = -n\frac{dS_2O_8{}^{2-}}{dt} = k_2[Ag(I)](S_2O_8{}^{2-})(RCO_2H)^0 \quad (8)$$

The kinetic expression given by eq 8 follows a general pattern for the silver-catalyzed oxidation by peroxydisulfate of a diverse variety of other reducing agents including oxalate, thiosulfate, cerium(IV), ammonia and ammonium ion, arsenious acid, and hydrogen peroxide.[1,2] Furthermore, the activation enthalpy ($\Delta H^{\pm}$ = 15.2 kcal/mole) and entropy ($\Delta S^{\pm}$ = −28.5 eu) for the

(15) J. A. McMillan and B. Smaller, J. Chem. Phys., 35, 1698 (1961).
(16) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, J. Phys. Chem., 67, 1617 (1963).
(17) The problem is related to the rapid oxidation of alkenes by metal oxidants in the presence of strong mineral acids.[18]
(18) J. K. Kochi, R. A. Sheldon, and S. S. Lande, Tetrahedron, 25, 1197 (1969).
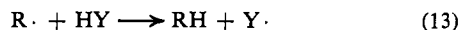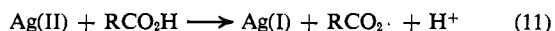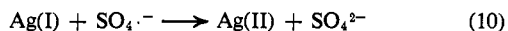
(19) J. D. Miller, J. Chem. Soc., A, 1778 (1968).
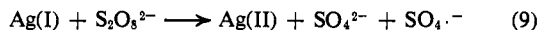(20) J. M. Anderson and J. K. Kochi, J. Org. Chem., in press.
(21) The relationships among the yields of carbon dioxide, the consumption of oxidant and the nature of the alkyl products in oxidative decarboxylation of acids has been delineated.[18]

silver-catalyzed decarboxylation is strikingly similar to values found for those systems. These results clearly indicate that the rate-limiting step involves peroxydisulfate and silver(I) to afford one or more reactive intermediates capable of rapidly oxidizing the carboxylic acid groups.

Our results are best fitted by the catalytic mechanism given in Scheme I. Various facets of this mechanism

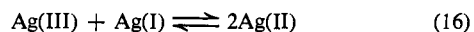**Scheme I.** Silver(I)-Catalyzed Decarboxylation[a]

$$Ag(I) + S_2O_8^{2-} \longrightarrow Ag(II) + SO_4^{2-} + SO_4 \cdot^- \quad (9)$$

$$Ag(I) + SO_4 \cdot^- \longrightarrow Ag(II) + SO_4^{2-} \quad (10)$$

$$Ag(II) + RCO_2H \longrightarrow Ag(I) + RCO_2 \cdot + H^+ \quad (11)$$

$$RCO_2 \cdot \longrightarrow R \cdot + CO_2 \quad (12)$$

$$R \cdot + HY \longrightarrow RH + Y \cdot \quad (13)$$

$$R \cdot + Ag(II) \longrightarrow [R^+]_{ox} + Ag(I) \text{ etc.} \quad (14)$$
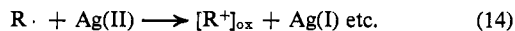
[a] $[R^+]_{ox}$ = alkene, alcohol, ester

will be taken into account in the following discussion.

Initiation and the Formation of Silver(II) Species. The rate-limiting oxidation of silver(I) by peroxydisulfate (eq 9) followed in quick succession by a second oxidation by the sulfate ion-radical (eq 10) has been considered at length.[1,2]

Sequence (9) and (10) cannot be kinetically distinguished from the formation of a silver(III) species by a two-equivalent oxidation (eq 15), which undergoes rapid *syn* proportionation (eq 16).[22] The equilibrium constant for the latter reaction lies far to the right, although it has only been studied in concentrated solu-

$$Ag(I) + S_2O_8^{2-} \longrightarrow Ag(III) + 2SO_4^{2-} \quad (15)$$

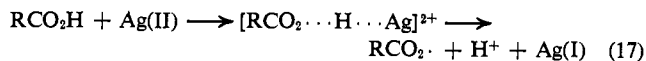$$Ag(III) + Ag(I) \rightleftharpoons 2Ag(II) \quad (16)$$

tions of mineral acids,[23] the only medium in which these high oxidation states of silver are stable.
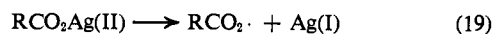
The activation process for the silver(I)-catalyzed oxidative decarboxylation by peroxydisulfate is largely associated with the formation of silver(II) species. Support for successive one equivalent steps (9) and (10) are obtained from the kinetic study of the peroxydisulfate oxidation of the related bisbipyridinesilver(I).[19] The isolable bisbipyridinesilver(II) complex may not be an unreasonable model for the aquosilver(II) species postulated in our system, since the catalytic properties of the bipyridine complex also parallels the behavior of the aquo complex in the catalytic decomposition of hydrogen peroxide.[24]

Silver(II) Species and the Decarboxylation of Acids. We propose that it is the silver(II) species which is the agent directly responsible for the decarboxylation of the acid. The latter, as pointed out earlier (eq 3), has been shown to be a reliable probe for the one-equivalent oxidation of acids since alkyl radicals result from decarboxylations of the acyloxy radical. At this juncture it is a moot point whether such an oxidation occurs *via* hydrogen atom transfer directly from the acid (eq 17), or *via* prior incorporation of the acid into the Ag(II) species as a ligand (eq 18)[25] followed by homol-

$$RCO_2H + Ag(II) \longrightarrow [RCO_2 \cdots H \cdots Ag]^{2+} \longrightarrow$$
$$RCO_2 \cdot + H^+ + Ag(I) \quad (17)$$

ysis of the silver–oxygen bond (eq 19). In either case

$$RCO_2H + Ag(II) \rightleftharpoons RCO_2Ag(II) + H^+ \quad (18)$$

$$RCO_2Ag(II) \longrightarrow RCO_2 \cdot + Ag(I) \quad (19)$$

the acyloxy radical is known to undergo rapid fragmentation with liberation of carbon dioxide and an alkyl radical (eq 20).[26]

$$RCO_2 \cdot \longrightarrow R \cdot + CO_2 \quad (20)$$

The absence of significant differences in the rates of decarboxylation of pivalic, isobutyric, and *n*-butyric acids militates against the simultaneous fission of the alkyl–carbonyl bond in the decarboxylation step such as that for-

$$RCO_2H + Ag(II) \longrightarrow R \cdot + CO_2 + H^+ + Ag(I) \quad (21)$$

mulated in (eq 21).[25] When multibond changes of acids are important, pivalic, isobutyric, and *n*-butyric acids show large differences in rates of decarboxylation.[18] The selectivity shown in the oxidative carboxylation of these acids by a variety of metal oxidants is compared in Table VII. If we assume that the homolysis of the silver–oxygen bond is involved in the decarboxylation process, comparison with other metal oxidants can then be related to the differences in the activation energy for homolysis and the resultant change in the extent to which bonds are stretched in the transition state.[26] Qualitatively, acids are decarboxylated more readily by the silver–peroxydisulfate method than by Pb(IV). The latter effects decarboxylation at lower temperatures than Co(III), and decarboxylation by Mn(III) is carried out at the highest temperatures and shows the greatest selectivity. Decarboxylation by Ce(IV) is induced photochemically and shows no selectivity. In the latter case sufficient energy is provided by irradiation at 3500 Å to effect simple homolysis to acyloxy radicals, and driving force obtainable by multibond cleavage is presumably not required.[27b] A similar photochemical process probably pertains to decarboxylation with Tl(III) complexes.[27c] On this basis, we postulate that the decarboxylation of acids by Ag(II) is highly exothermic[28] as already indicated by the facility with which it takes place.

The instability of Ag(II) species under these experimental conditions precludes the direct test of this hypothesis. However, we can demonstrate that Ag(II) formed in strong mineral acid solutions is capable of rapid decarboxylation of acids, although the stoichiometry of the oxidation is not yet clear. Moreover, even those Ag(II) complexes stabilized with α,α'-bipyridine and α-picolinato ligands are capable of facile oxidative decarboxylation of acids.[20,29,30]

Ag(III). (b) We consider the alternative possibility of the rate-determining and essentially irreversible incorporation of the carboxylate ligand into the silver species as unlikely.

(26) M. Szwarc, ref 2, p 153 ff.

(27) (a) Co(III), S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 5196 (1968); (b) Mn(III), J. M. Anderson and J. K. Kochi, to be published; (c) Ce(IV), R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 6688 (1968); (d) Tl(III), T. W. Bethea and J. K. Kochi, *J. Org. Chem.*, **33**, 75 (1968).

(28) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(29) Oxidations with Ag/S₂O₈²⁻ system has been compared with those involving authentic Ag(II) complexes. See ref 3 and 20.

(30) For Ag(II) complexes as oxidants, see (a) R. G. R. Bacon and W. J. W. Hanna, *J. Chem. Soc.*, 4692 (1965); (b) J. A. McMillan, *Chem. Rev.*, **62**, 65 (1965); (c) J. B. Lee and T. G. Clarke, *Tetrahedron Letters*, 415 (1967); (d) J. M. Anderson, unpublished studies.

(22) (a) B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958); (b) F. Jirsa, *Z. Anorg. Allgem. Chem.*, **148**, 130 (1925); **158**, 33, 61 (1926).

(23) A. A. Noyes, K. S. Pitzer, and C. L. Dunn, *J. Am. Chem. Soc.*, **57**, 1229, 1238 (1935); **59**, 1326 (1937).

(24) A. Malaguti, *Ann. Chim.* (Rome), **42**, 138 (1952).

(25) (a) The carboxylato ligand may also be incorporated into Ag(II) *via* the substitution labile Ag(I) followed by *syn* proportionation with

Table VII. Relative Rates of Decarboxylation of Acids by Metal Oxidants

Oxidant $M(O_2CR)_n$	Temp, °C	Method[a]	Relative rate[b] Pivalic/i-butyric	Relative rate[b] Pivalic/n-butyric	Decarboxylation mechanism	Ref
Ag(II)	60	Δ	1.7	2.0	Acyloxy	This work
Pb(IV)	30	$h\nu$	5	90	Multibond	18
Pb(IV)	80	Δ	3	20[c]	Chain	18
Co(III)	80	Δ	10	100[c]	Multibond	14
Mn(III)	105	Δ	25	500[d]	Multibond	27b
Ce(IV)	30	$h\nu$	1.2	1.1	Acyloxy	27c

[a] $h\nu = 3500$ A, Δ = thermal. [b] By competition studies. [c] At 100°. [d] At 120°.

Finally, Ag(III) species have been widely invoked as intermediates in the silver(I) catalyzed reactions of peroxydisulfate,[2,31] and it is conceivable that Ag(III) is directly involved in the two-equivalent oxidation of the acid such as in eq 22. Such a postulate, however, does
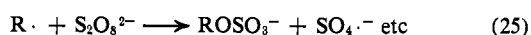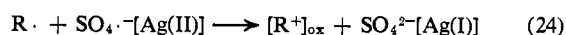
$$RCO_2H + Ag(III) \longrightarrow [R^+]_{ox} + CO_2 + H^+ + Ag(I) \quad (22)$$
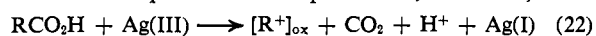
not allow for a ready explanation (*vide infra*) of the critical role played by alkyl radicals and the catalysis by Cu(II).

Alkyl Radicals as Intermediates. The mechanism proposed involving the one-equivalent oxidation of acids by Ag(II) demands that alkyl radicals are intermediates. Direct observation of alkyl radicals by their electron spin resonance spectra have been reported in the related decarboxylations by Pb(IV)[6] and Ce(IV),[32] and studies directed toward that end in the silver–peroxydisulfate system are in progress. Chemical and kinetic evidence can be used to support alkyl radicals as intermediates in these reactions.
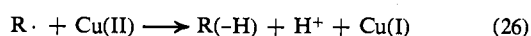
Product Formation. The increase in the production of alkane with increasing concentrations of carboxylic acid as shown in Table I is related to hydrogen abstraction (predominantly from the α position) from the acid (eq 23). As the concentration of the carboxylic acid

$$R \cdot + HO_2C\overset{|}{C}H \longrightarrow RH + HO_2C\overset{|}{C} \cdot \quad (23)$$
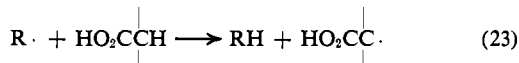
acid is lowered, the alkyl radical increasingly suffers oxidation. Alkenes and alcohols become predominant products. It is not clear at this point whether further oxidation of the alkyl radical is effected by Ag(II) or sulfate ion radical (eq 24) or by induced decomposition of the peroxydisulfate (eq 25).

$$R \cdot + SO_4 \cdot ^-[Ag(II)] \longrightarrow [R^+]_{ox} + SO_4{}^{2-}[Ag(I)] \quad (24)$$

$$R \cdot + S_2O_8{}^{2-} \longrightarrow ROSO_3^- + SO_4 \cdot ^- etc \quad (25)$$

Catalysis by Copper(II). The effect of copper(II) species on the stoichiometry and the kinetics of the silver-catalyzed decarboxylation by peroxydisulfate provides strong evidence for the formation of alkyl radicals as prime intermediates. Cu(II) is an exceedingly efficient scavenger of alkyl radicals.[33] Oxidation to alkenes (eq 26) occurs quantitatively under most circumstances, since reaction 26 has a second-order rate constant of 10^8–10^9 M^{-1} sec^{-1}.

$$R \cdot + Cu(II) \longrightarrow R(-H) + H^+ + Cu(I) \quad (26)$$

The dramatic change in the stoichiometry of the decarboxylation with the addition of copper(II) follows from the formation of alkyl radicals as intermediates. Even at high concentrations of carboxylic acid, excellent yields of alkene are produced from the copper(II) cocatalyst, despite competition from the hydrogen transfer reaction (eq 23).

There are a variety of paths by which Cu(I) produced in the oxidation step (eq 26) regenerates Cu(II). It can be shown independently that Cu(I) is readily oxidized by peroxydisulfate.[34] The latter represents the route by which we account for the catalytic role of copper(II) in the decarboxylation.

Cocatalysis by Copper(II). A number of steps in this mechanism are common with that proposed for the silver-catalyzed reaction (eq 9–14).

$$Cu(I) + S_2O_8{}^{2-} \longrightarrow Cu(II) + SO_4{}^{2-} + SO_4 \cdot ^- \quad (27)$$

$$SO_4 \cdot ^- + Ag(I) \longrightarrow Ag(II) + SO_4{}^{2-} \quad (10)$$

$$Ag(II) + RCO_2H \longrightarrow Ag(I) + R \cdot + CO_2 + H^+ \quad (11, 12)$$

$$R \cdot + Cu(II) \longrightarrow R(-H) + H^+ + Cu(I) \quad (26)$$

The scheme presented for the cocatalysis by copper(II) correctly predicts[35] a ceiling in the rate, which becomes independent of the copper(II) at very low concentrations shown in Figure 5. The latter is related to the facile oxidation of alkyl radicals by Cu(II). The region in which the rate is dependent on Cu(II) (*i.e.*, $<10^{-3}$ M) also coincides with the production of alkane as shown in Table VII. Under these conditions the oxidation of alkyl radicals by Cu(II) is competing with hydrogen transfer and other oxidation reactions (23–25).

The Role of Sulfate Ion Radicals. Sulfate ion radicals, $SO_4 \cdot ^-$, have been included as intermediates in a variety of catalyzed as well as uncatalyzed reactions of peroxydisulfate.[1,2] They have been invoked in alkaline media for the oxidation of acids by the Fichter procedure.[8] However, it is well established that the behavior of the sulfate ion radical is highly sensitive to pH, especially with respect to electron-transfer processes (28) and (29).[9]

$$RCO_2^- + SO_4 \cdot ^- \longrightarrow RCO_2 \cdot + SO_4{}^{2-} \quad (28)$$

$$SO_4 \cdot ^- + OH^- \longrightarrow SO_4{}^{2-} + HO \cdot \quad (29)$$

Under our conditions there is no necessity of involving sulfate ion radicals directly in decarboxylative processes such as eq 30, since sulfate ion radicals generated

$$RCO_2H + SO_4 \cdot ^- \longrightarrow RCO_2 \cdot + HSO_4^- \quad (30)$$

(31) (a) H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, 7, 244 (1968). (b) However, in the oxidation of oxalate, Ag(II) is considered to be the oxidant of choice [A. J. Kalb and T. L. Allen, *J. Am. Chem. Soc.*, 86, 5107 (1964)].

(32) (a) Ce(IV): D. Greatorex and T. J. Kemp, *Chem. Commun.*, 383 (1969); (b) Pb(IV): K. Heusler, H. Labhart, and H. Loeliger, *Tetrahedron Letters*, 2847 (1965); *Helv. Chim. Acta.*, 52, 1495 (1969).
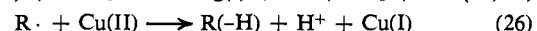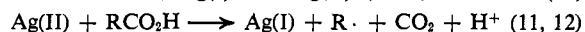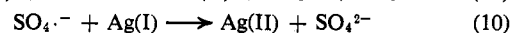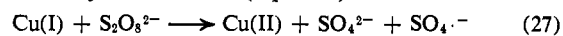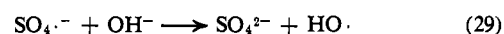
(33) (a) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, 87, 4855 (1965); (b) J. K. Kochi, C. L. Jenkins, and A. Bemis, *ibid.*, 90, 4616 (1968).

(34) O. A. Chaltykyan and N. M. Beileryan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauk*, 11, No. 1, 13 (1958).

(35) Wilmarth and Haim correctly anticipated such a catalytic behavior (see ref 2, p 203–205).
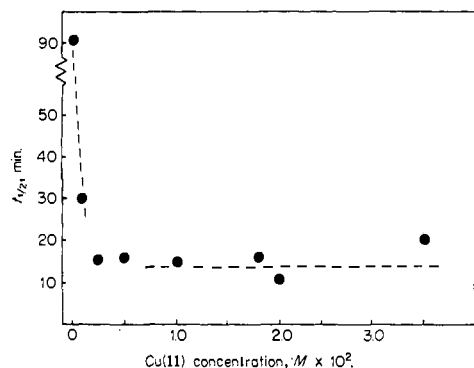
Figure 5. Effect of added Cu(II) on the half-life of the carbon dioxide evolution at 60°: 0.005 M silver nitrate and 1.0 mmole of ammonium peroxydisulfate in 10 ml of n-PrCOOH-H$_2$O-CH$_3$CN, 50/40/10, v/v/v.

by thermolysis of peroxydisulfate (eq 2) are ineffective in carrying out decarboxylations in the absence of silver(I). Furthermore, the mechanism of the copper-catalyzed oxidation of oxalate[36,37] and other reducing agents by peroxydisulfate are not applicable to carboxylic acids in general since the latter undergo oxidation under comparable conditions *via* nondecarboxylative pathways.

Summary

The silver(I)-catalyzed decarboxylation of acids by peroxydisulfate proceeds *via* a series of one-equivalent oxidation–reduction cycles. Products studies and kinetic comparisons point directly to the involvement of Ag(II) species and not sulfate radical anions, or hydroxyl radicals, as the prime reactive intermediates. Ag(II) species are formed by the rate-limiting oxidation of Ag(I) by peroxydisulfate. Direct and facile oxidation of the carboxylic acid group by Ag(II) in a fast follow-up step generates an acyloxy radical, which subsequently fragments to an alkyl radical and carbon dioxide. Products are derived by oxidation of the alkyl radical by silver species as well as by hydrogen transfer to solvent. These routes to products can be circumvented by the addition of copper(II) salts which intercept all alkyl radicals. Efficient cocatalysis by copper(II) is associated with the oxidation of alkyl radicals to alkenes. The resulting copper(I) species are involved in the further one-equivalent reduction of peroxydisulfate and are indirectly involved in the regeneration of silver(II). A ceiling rate in the synergistic effects of copper(II) and silver(I) catalysts is attained at low concentration of copper(II). The Cu(II)–Ag(I) cocatalyzed oxidative decarboxylation of acids by peroxydisulfate affords alkenes in excellent yields.

Experimental Section

Materials. All carboxylic acids were purified by distillation. Pivalic acid was generously donated by the Enjay Chemical Co.
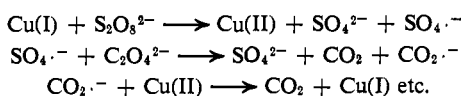
Esters were either prepared by standard procedures or purchased from commercial sources and redistilled before use. Dimethyl sulfoxide, DMSO, was distilled from calcium hydride under vacuum. Acetonitrile was distilled from phosphorus pentoxide.

Ammonium peroxydisulfate, potassium peroxydisulfate, silver nitrate, silver trifluoroacetate, silver perchlorate, lithium nitrate, cupric sulfate, and cupric nitrate, all reagent grade, were obtained from commercial sources. Rubber septa were washed repeatedly with acetone until the solvent was colorless.

General Procedure for the Study of Products. The required amount of the peroxydisulfate salt was added gravimetrically to a 50-ml long-necked, round-bottomed flask. The flask was sealed with a gas-tight rubber septum and degassed *in vacuo* for at least 15 min. The aqueous carboxylic acid solution, with or without the desired additive or cosolvent, was degassed by bubbling helium through it for 15 min. A 10-ml aliquot of this solution was added to the degassed flask with a hypodermic syringe. The flask was shaken until the peroxydisulfate salt dissolved. It was then placed in a thermostated oil bath and the contents were stirred magnetically.

The reaction was carried out for extended times to ensure completion since there was no color change to provide a visual indication. After completion of the reaction, the flask was removed from the bath, cooled to room temperature, and markers were added.

Analytical Procedures. All products were quantitatively analyzed by gas chromatography using the internal standard method. To obtain calibration factors, mixtures containing known amounts of products and markers were analyzed under reaction conditions.

After the markers had been added, gaseous products were analyzed on a gas chromatograph using thermal conductivity detectors. When the analysis of gaseous products was complete, the pressure was released and internal standards were added for the analysis of the liquid products. Analyses of esters were carried out using the following work-up procedure. After addition of the marker, the reaction solutions were taken up in ether and washed three times with water, three times with a saturated solution of sodium bicarbonate to remove excess carboxylic acid, and finally twice with water. The ether solution was analyzed for the ester products. Analyses on the FFAP (Varian-Aerograph) column were conducted directly from the reaction solution without prior work-up. The analysis of liquid products was carried out on a Varian-Aerograph Model 200 with a flame ionization detector.

The following conditions were used in determining yields of products (internal standard, column, temperature, products): ethane, 2-ft Poropak Q, room temperature, carbon dioxide, methane; n-butane, 15-ft 30% Dowtherm on firebrick, room temperature, propane, propylene, isobutane, isobutylene; n-butyl acetate, 10-ft FFAP (Varian-Aerograph), 80°, methanol, n-propyl alcohol, isopropyl alcohol, t-butyl alcohol, acetone methyl acetate, isopropyl isobutyrate; n-butyl acetate, 6-ft Morflex, 85°, t-butyl pivalate; n-butyl acetate, 8-ft DEGS, 85°, n-propyl n-butyrate, isopropyl n-butyrate.

The disappearance of the peroxydisulfate salt was followed iodometrically using Allen's procedure.[38] Iodometric titrations of standard peroxydisulfate solutions showed that silver iodide did not interfere with the visual end point.

The stoichiometry for oxidative decarboxylations of pivalic, isobutyric and n-butyric acids in the presence and absence of a copper-(II) cocatalyst in DMSO is given in Table VIII. The last column in the table shows that greater than 70% of the alkyl fragment from the decarboxylation could be accounted for by these products. The alkane and alkene yields showed a reciprocal relationship as the carboxylic acid was changed from primary to secondary to tertiary. Thus the yield of alkene was the highest with pivalic acid and the lowest with n-butyric acid, whereas the alkane yield varied in the opposite manner.

The increase in products of oxidation (R_{ox}) from n-butyric acid with increasing concentration of silver(I) catalyst are shown in Table IX.

Kinetic Procedure. Kinetic runs were prepared in the same manner as the product studies. After degassing and addition of the approprirate carboxylic acid solution, a known volume of the ethane marker was added. Helium was then added to increase the internal pressure; the flask was shaken to dissolve the contents and placed in the thermostated oil bath. The evolution of carbon dioxide was followed by extracting a gas sample at an appropriate

(36) E. Ben-Zvi and T. L. Allen, *J. Am. Chem. Soc.*, 83, 4352 (1961).
(37) Oxalate is a significantly stronger reducing agent than carboxylates and electron transfer by SO$_4 \cdot^-$ may be more important. It is possible to formulate an analogous mechanism for copper catalysis without invoking Cu(III).[34]

$$Cu(I) + S_2O_8{}^{2-} \longrightarrow Cu(II) + SO_4{}^{2-} + SO_4 \cdot^-$$
$$SO_4 \cdot^- + C_2O_4{}^{2-} \longrightarrow SO_4{}^{2-} + CO_2 + CO_2 \cdot^-$$
$$CO_2 \cdot^- + Cu(II) \longrightarrow CO_2 + Cu(I) \text{ etc.}$$

(38) T. L. Allen, *J. Am. Chem. Soc.*, 73, 3589 (1951).

Table VIII. Products from the Silver-Catalyzed Oxidative Decarboxylation by Peroxydisulfate[a]

| RCO₂H acid | Add[b] | Products, mmole | | | CO₂/S₂O₈²⁻ | RH/CO₂ | R$_{ox}$[c]/RH | ΣR·[d]/CO₂ |
		CO₂	Alkane	Alkene				
Pivalic	0	1.11	0.26	0.23[e]	1.11	0.23	2	0.71
Pivalic	Cu(II)	0.98	+[f]	0.43[g]	0.98	0.01	130	0.68
Isobutyric	0	1.10	0.58	0.16[h]	1.10	0.53	0.6	0.76
Isobutyric	Cu(II)	1.08	+	1.01	1.08	0.01	200	0.94
n-Butyric	0	1.10	0.69	0.08	1.10	0.63	0.1	0.70
n-Butyric	Cu(II)	1.02	+	0.96	1.02	0.01	200	0.94

[a] In 10 ml of degassed solution containing 0.01 M silver nitrate and 0.10 M ammonium peroxydisulfate in 33% by volume RCO₂H, DMSO, and water at 60° for 4 hr. [b] Additive at 10^{-2} M. [c] Sum of alkene, alcohol, ester, and twice ketone. [d] Includes all alkyl fragments (R_{ox} + RH). [e] Plus 0.30 mmole of t-butyl alcohol. [f] Trace amounts (<0.01 mmole). [g] Plus 0.24 mmole of t-butyl alcohol. [h] Plus 0.10 mmole of acetone.

Table IX. Effect of Ag(I) Concentration on the Products of Oxidative Decarboxylation by Peroxydisulfate[a]

| AgNO₃, M | Products, mmole | | | ΣPr[b]/CO₂ | C₃H₆/C₃H₈ |
	CO₂	C₃H₈	C₃H₆		
0.01	1.97	1.31	Trace	0.67	0.01
0.05	1.62	1.14	0.18	0.82	0.16
0.10	1.29	0.72	0.39	0.86	0.54
0.50	1.09	0.39	0.44	0.76	1.1

[a] In 10 ml of aqueous solutions of 5.5 M n-butyric acid, 0.10 M ammonium peroxydisulfate for 4 hr at 60°. [b]ΣPr = C₃H₈ + C₃H₆.

Table X. Temperature Dependence of the Pseudo-First-Order Rate Constant[a]

n-Butyric acid, M	Temp, °C	$k_1 \times 10^3$, sec⁻¹
5.5	60	1.25 ± 0.04
5.5	50	0.60 ± 0.02
5.5	40	0.28 ± 0.02
0.33	60	2.12 ± 0.14
0.33	50	1.81 ± 0.15
0.33	40	1.30 ± 0.06
0.33	30	0.45 ± 0.01

[a] In aqueous solutions containing 0.10 M ammonium peroxydisulfate and 0.01 M silver nitrate.

time interval, after inverting the flask twice for equilibration of the gaseous product and marker. The gas sample was immediately analyzed for carbon dioxide. No more than eight gas samples, 0.5 ml each, were withdrawn from the flask (65 ml total free volume) for each kinetic run.

In order to follow the disappearance of the peroxydisulfate, runs were prepared in the same manner. However, each kinetic point was obtained from reaction mixtures prepared individually. For the slow kinetic runs, the amount of carbon dioxide and the concentration of peroxydisulfate were determined from the same reaction flask.

For the faster kinetic runs, separate determinations of the evolution of carbon dioxide and the disappearance of the peroxydisulfate

salt were made to ensure accuracy. Both the evolution of carbon dioxide and the disappearance of the peroxydisulfate salt were reproducible to within 10%.

The temperature dependence of the pseudo-first-order rate constant for the oxidation of n-butyric acid at high and low acid concentrations is given in Table X.