Silver(II) Complexes in Oxidative Decarboxylation of Acids

JAMES M. ANDERSON AND JAY K. KOCHI

*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106,
and Department of Chemistry, Indiana University, Bloomington, Indiana 47401*

Silver(II) picolinate, bis(α,α'-bipyridine)silver(II) nitrate, and silver oxide have been employed directly in the oxidative decarboxylation of acids. Excellent yields of carbon dioxide, isobutylene, and t-butyl derivatives are obtained from pivalic acid by oxidation with all three silver(II) oxidants under a variety of conditions. The t-butyl cation is the precursor for the butyl products. The decarboxylation is postulated to occur *via* two successive 1-equiv processes, in which the oxidation of the carboxylate moiety by silver(II) yields carbon dioxide and an alkyl radical followed by further oxidation of the alkyl radical to the cation by a second silver(II) species.

Silver(II) species are among the most powerful oxidants available for organic chemistry.[1-4] In aqueous solutions, Ag^{2+} is viable only in highly acidic media[5] in which it is in equilibrium with Ag^{3+}. Even under

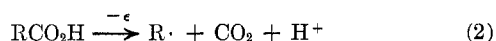$$2Ag^{2+} \rightleftharpoons Ag^+ + Ag^{3+} \quad (1)$$
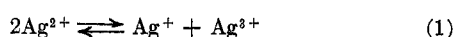
these conditions Ag^{2+} is coordinated with such weakly complexing ions as perchlorate.[6] Aqueous solutions of Ag^{2+} are, moreover, relatively unstable and oxidize water to oxygen at room temperature.[7]

We found that silver(II) species were formed as metastable intermediates in the silver(I)-catalyzed reactions of peroxodisulfate ion and were highly effective in the oxidative decarboxylation of acids.[8] Several stable silver(II) complexes have been reported: silver-(II) picolinate (1), bisbipyridinesilver(II) nitrate (2),

1   2
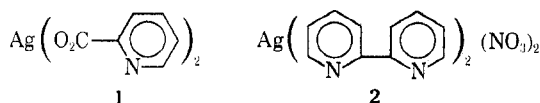
and silver oxide (AgO). In this paper we sought to determine the effectiveness of these silver(II) complexes in the direct oxidative decarboxylation of acids. The liberation of carbon dioxide and the formation of alkyl radicals are diagnostic of the transformation of silver(II) to silver(I) in common with the behavior of other 1-equiv oxidants.[9]

$$RCO_2H \xrightarrow{-e} R\cdot + CO_2 + H^+ \quad (2)$$

All three silver(II) complexes listed above were employed in comparative studies of the oxidative decarboxylation of pivalic, isobutyric, butyric, and acetic acids, which served as representative examples.

Results

Studies of oxidative decarboxylation of acids by silver(II) complexes were all carried out using a common

procedure. The silver(II) compound was weighed into a flask which was sealed with a rubber septum and degassed *in vacuo*. The carboxylic acid was added with a hypodermic syringe after thorough degassing to remove oxygen. The reaction mixture was stirred magnetically and decomposed thermally.

Oxidative Decarboxylation with Silver(II) Picolinate.—Decarboxylations with silver(II) picolinate were carried out in carboxylic acid as solvent to avoid complications from water. The reduction of silver(II) proceeded readily at 90° and could be followed visually by the disappearance of the orange silver(II) species to the colorless silver(I) picolinate. The reaction times listed on Table I were a qualitative yet reliable measure of the complete reduction of silver(II).

Carbon dioxide and alkene and alkyl esters were formed in excellent yields in most cases. Thus pivalic acid afforded carbon dioxide, isobutylene, and t-butyl pivalate according to the stoichiometry given in eq 3. Isobutyric, n-butyric, and even acetic acid under-

$$(CH_3)_3CCO_2H + 2Ag^{II} \longrightarrow [(CH_3)_3CO_2C(CH_3)_3 +$$
$$(CH_3)_2C{=}CH_2] + CO_2 + 2H^+ + 2Ag^I \quad (3)$$
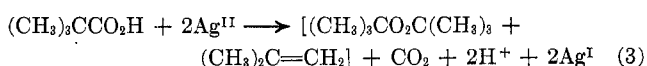
went decarboxylation in an analogous manner. With the exception of isobutyric acid, alkanes were generally minor products. It should be noted that the principal product from the oxidative decarboxylation of n-butyric acid was the unrearranged n-propyl n-butyrate. The isopropyl isomer was only a minor constituent.

Oxidative decarboxylation by silver(II) picolinate was accelerated by trifluoroacetic acid and even more so by pyridine. Neither of these additives, however, significantly affected the stoichiometry of the decarboxylation (Table I). Copper(II) acetate, on the other hand, retarded the decarboxylation induced by silver(II) picolinate. The addition of as little as 1% copper(II) acetate [based on silver(II)] increased the reaction time from 1 hr to >20 hr. Under these conditions, *alkane* was the major product, although at higher copper(II) concentrations alkene predominated. In the latter cases, the extent of oxidative decarboxylation was minor. These reactions were not homogeneous and we are unable to draw any conclusions regarding the inhibitory effect of copper(II) on the decarboxylation. The inhomogeneity of the reaction may also reflect the otherwise inexplicable observation that the relative rates of decarboxylation (gross overall) by silver(II) picolinate appeared to

(1) For a review of the higher oxidation states of silver, see J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

(2) J. B. Lee and T. G. Clarke, *Tetrahedron Lett.*, 415 (1967).

(3) L. Syper, *ibid.*, 4193 (1967).

(4) R. G. R. Bacon and D. J. Munro, *J. Chem. Soc.*, 1339 (1960); R. G. R. Bacon and W. J. W. Hanna, *ibid.*, 4692 (1965); R. G. R. Bacon and D. Stewart, *ibid.*, C, 1384 (1966).

(5) (a) A. A. Noyes, J. L. Hoard, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **57**, 1221 (1935); *J. Chem. Phys.*, **59**, 1316 (1937); (b) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 713, 1645 (1964); **12**, 479 (1965).

(6) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, *J. Phys. Chem.*, **67**, 1617 (1963).

(7) H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, **7**, 244 (1968).

(8) J. M. Anderson and J. K. Kochi, to be published.

(9) (a) Pb^{IV}: J. K. Kochi, J. D. Bacha, and T. W. Bethea, *J. Amer. Chem. Soc.*, **89**, 6538 (1967). (b) Ce^{IV}: R. A. Sheldon and J. K. Kochi, *ibid.*, **90**, 6688 (1968). (c) Co^{III}: S. S. Lande and J. K. Kochi, *ibid.*, **90**, 5196 (1968).

TABLE I

DECARBOXYLATION OF ACIDS BY Ag(PICOLINATE)₂ AT 90°[a]

Acid	Additive	Additive/ Ag^{II}	Reacn time, min	CO₂	2CO₂/ Ag^{II}	RH	R(-H)	Ester	Ester	R$_{ox}$[b]/ alkane	ΣR[c]/ CO₂
Pivalic	...	...	600	0.53	1.06	0[d]	0.34[e]	0.10[f]	0	>100	0.83
	TFA	5	120	0.51	1.02	0	0.31	+	0	>100	0.61
	C₅H₅N	5	30	0.48	0.96	+	0.28	+	0	>60	0.59
Isobutyric	...	...	120	0.60	1.20	0.19[g]	0.13[h]	0.09[i]	0	1.1	0.68
[j]	...	...	420	0.50	1.00	0.16	0.12	0.10	0	1.4	0.75
	TFA	5	150	0.54	1.08	0.12	0.13	0.11	0	2.0	0.67
	C₅H₅N	5	15	0.52	1.04	0.10	0.14	0.13	0	2.7	0.71
[j]	Cu(OAc)₂	1	1440	0.13	0.26	+	0.14	<0.03	0	>40	1.00
n-Butyric	...	...	60	0.52	1.04	0.05[g]	0.08[h]	0.02[k]	0.27[l]	7.4	0.81
[j]	...	...	120	0.45	0.90	0.05	0.07	0.02	0.17	5.2	0.67
	TFA	5	30	0.46	0.92	0.05	0.07	0.02	0.13	4.4	0.59
	C₅H₅N	5	15	0.50	1.00	0.05	0.05	+	0.24	5.8	0.68
[j]	Cu(OAc)₂	1	1440	0.26	0.52	+	0.16	<0.03	0	>33	0.70
Acetic	...	...	60	0.50	1.00	0.09[m]	...	0.43[n]	0	4.7	1.00
	...	...	30	0.47	0.94	+	...	0.32	0	80	0.68
	TFA	5	15	0.47	0.94	+	...	0.13	0	>26	0.28
	C₅H₅N	5	15	0.46	0.92	+	...	0.38	0	>78	0.83

[a] 1.0 mmol of Ag(picolinate)₂ in 10 ml of carboxylic acid. [b] R$_{ox}$ includes alkene and esters. [c] ΣR· includes all products derived from alkyl moiety (alkene, alkane, and ester) and represents material balance. [d] Isobutane. [e] Isobutylene. [f] t-Butyl pivalate. [g] Propane. [h] Propylene. [i] Isopropyl isobutyrate. [j] 80°. [k] Isopropyl n-butyrate. [l] n-Propyl n-butyrate. [m] Methane. [n] Methyl acetate.

TABLE II

DECARBOXYLATION OF ACIDS BY Ag(C₁₀H₈N₂)₂(NO₃)₂ AT 60°[a]

Acid	Reacn time, min	CO₂	2CO₂/ Ag^{II}	RH	R(-H)	ROH	Ester	ΣR·[b]/ CO₂
Pivalic[c]	20	0.24	0.75	0	0.08[d]	0.15[e]	0	0.96
Isobutyric	3	0.33	1.02	0	0.12[f]	0.10[g]	0.05[h]	0.82
n-Butyric	10	0.28	0.86	0	0.11[f]	+[g]	0.06[i]	0.63

[a] 0.65 mmol of Ag(C₁₀H₈N₂)₂(NO₃)₂ in 5 ml of 50% aqueous carboxylic acid. [b] ΣR· includes all products (alkene, alkane, ester, and alcohol) derived from alkyl moiety. [c] 0.65 mmol of Ag(C₁₀H₈N₂)₂(NO₃)₂ in 10 ml of pivalic acid–water–DMSO (33:33:33, v/v/v). [d] Isobutylene. [e] t-Butyl alcohol. [f] Propylene. [g] Isopropyl alcohol. [h] Isopropyl isobutyrate. [i] Isopropyl n-butyrate.
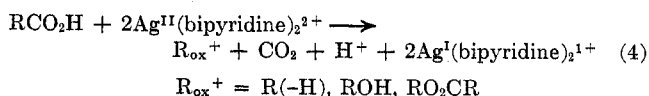
TABLE III

DECARBOXYLATION OF ACIDS BY AgO AT 90°[a]

Acid	Additive	Additive/ AgO	Reacn time, hr	CO₂	2CO₂/ AgO	RH	R(-H)	Ester	Ester	R$_{ox}$[b]/ alkane	ΣR·[c]/ CO₂
Pivalic[d]	...	...	3	1.54	1.00	0	1.10[e]	0.22[f]	0.08[g]	>200	0.91
	AgOAc	1.0	3	1.55	1.01	0	1.08	0.23	0.08	>200	0.90
	TFA	1.0	1	1.43	0.92	0	0.35	0.51	0.10	>200	0.67
	TFA	2.0	1	1.46	0.96	0	0.31	0.52	0.08	>200	0.62
Isobutyric	...	...	24	0.72	0.48	+	0.08[h]	0.02[i]	+[i]	20	0.14
	TFA	1.0	1	0.78	0.52	+	0.10	0.08	+	36	0.24
n-Butyric	...	...	24	0.86	0.57	+	0.05[k]	+[k]	0	10	0.05
	AgOAc	1.0	14	0.34	0.23	+	0.06	+		10	0.18
	TFA	1.0	1	0.65	0.43	+	0.05	+	0	10	0.10
	TFA	2.0	3	0.85	0.57	+	0.10	+	0	10	0.12

[a] 3.0 mmol of AgO in 10 ml of carboxylic acid. [b] R$_{ox}$ includes alkene and esters. [c] ΣR·includes all products (alkene, alkane, and esters) derived from alkyl moiety. [d] t-BuCOOH–HOAc (96:4, w/w). [e] Isobutylene. [f] t-Butyl pivalate. [g] t-Butyl acetate. [h] Propylene. [i] Isopropyl isobutyrate. [j] Isopropyl acetate. [k] Trace amounts of n-propyl n-butyrate, isopropyl n-butyrate, and isopropyl acetate.

decrease in the order acetic > n-butyric > isobutyric > pivalic acid.[10]

Oxidative Decarboxylation with Bis(α,α′-bipyridine)-silver(II) Nitrate.—Oxidative decarboxylation of acids with bis(α,α′-bipyridine)silver(II) was carried out in solutions containing 50% by volume aqueous carboxylic acid (Table II). Water was added as a cosolvent to provide an homogeneous medium. The reduction of silver(II) was complete within a few minutes at 60° under these conditions. Excellent yields of carbon dioxide, alkene, alcohol, and ester were obtained according to the stoichiometry given by eq 4.

$$RCO_2H + 2Ag^{II}(bipyridine)_2{}^{2+} \longrightarrow$$
$$R_{ox}{}^+ + CO_2 + H^+ + 2Ag^{I}(bipyridine)_2{}^{1+} \quad (4)$$
$$R_{ox}{}^+ = R(-H), ROH, RO_2CR$$

The yield of alkane was unimportant (<0.01 mmol). It is noteworthy that oxidative decarboxylation of n-butyric acid produced significant amounts of the rearranged isopropyl alcohol and isopropyl n-butyrate.

Oxidative Decarboxylation with Silver Oxide.—Carboxylic acids were decarboxylated with silver oxide by vigorous stirring in the neat acid at 90° (Table III). The silver(I) carboxylate products were not soluble under these conditions. On heating the reaction mixtures, the finely divided black suspension of silver oxide was gradually replaced by a flocculent white precipitate. Silver(I) carboxylates were readily iso-
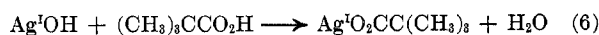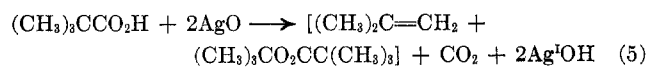
TABLE IV

EFFECT OF ACETONITRILE ON OXIDATIVE DECARBOXYLATIONS WITH SILVER OXIDE[a]

| Acid RCO$_2$H	CH$_3$CN, vol. %	Reacn time, min	CO$_2$	RH	Products, mmol R(-H)	RNHAc	Ester	ΣR·/CO$_2$
Pivalic	10	15	0.98	0	0.62	0.11	0.12	0.87
Pivalic	25	15	1.01	0	0.54	0.19	0.10	0.82
Pivalic	50	15	0.95	0	0.36	0.31	0.08	0.79
Pivalic	50[b]	720	0.82	0	0.71	0	...	0.86
Isobutyric	25	3[c]	0.41	0	0.04	+[d]	+	0.10
n-Butyric	25	4[c]	0.42	0	0.03	+	+	0.07

[a] In solutions containing 2.0 mmol of AgO in 10 ml of solvent at 85°.   [b] N,N-Dimethylacetamide.   [c] 110°.   [d] Trace, <0.01 mmol.

lated by filtration and the procedure could be conveniently employed to prepare these silver(I) salts.

The oxidation of pivalic acid (with 4% by volume acetic acid to facilitate handling) by silver oxide afforded high yields of carbon dioxide. Greater than 90% of the t-butyl moiety could be accounted for as isobutylene and t-butyl pivalate. A small amount of acetate ester was derived from the acetic acid.

$$(CH_3)_3CCO_2H + 2AgO \longrightarrow [(CH_3)_2C{=}CH_2 +$$
$$(CH_3)_3CO_2CC(CH_3)_3] + CO_2 + 2Ag^IOH \quad (5)$$

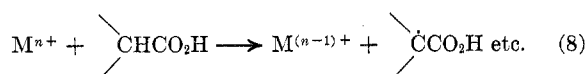$$Ag^IOH + (CH_3)_3CCO_2H \longrightarrow Ag^IO_2CC(CH_3)_3 + H_2O \quad (6)$$

Oxidative decarboxylations with silver oxide proceeded significantly faster when acetonitrile was employed as a cosolvent. The silver(I) carboxylates formed soluble complexes in acetonitrile and on complete reduction the reaction mixture consisted of a homogeneous solution. In the presence of acetonitrile an additional product, N-alkylacetamide, was also found in yields proportional to the concentration of

$$(CH_3)_3CCO_2H + 2AgO \xrightarrow{CH_3CN}$$
$$(CH_3)_3CNHCOCH_3 + CO_2 + Ag^I_2O(CH_3CN)_n \quad (7)$$
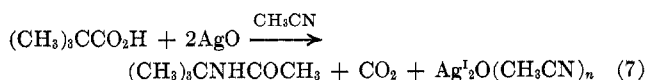
acetonitrile (Table IV). The rate of reduction of silver oxide was also accelerated by trifluoroacetic acid. N,N-Dimethylacetamide had little effect and pyridine a retarding one.

The yields of carbon dioxide from the oxidation of isobutyric, n-butyric, and acetic acid by silver oxide were not as good as those from pivalic acid. Acids with available α hydrogens are also susceptible to side-chain oxidation which consumes oxidant but does not lead directly to decarboxylation.[11] These processes may also play a role in these oxidations. The

$$M^{n+} + \diagdown{C}HCO_2H \longrightarrow M^{(n-1)+} + \diagdown{C}CO_2H \text{ etc.} \quad (8)$$

cesses may also play a role in these oxidations. The use of silver oxide was further limited by the rather poor material balance between the carbon dioxide liberated and the alkyl products produced (Table IV, last column). Part of this problem may have been due to scavenging of alkyl radicals by the oxygen produced in the acid-catalyzed decomposition of silver oxide.[12]
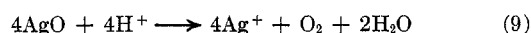
$$4AgO + 4H^+ \longrightarrow 4Ag^+ + O_2 + 2H_2O \quad (9)$$

Discussion

Silver picolinate, bis(bipyridine)silver nitrate, and silver oxide represent silver(II) complexes of three different structural types. Silver picolinate is a well-characterized silver(II) compound in which the silver atom exhibits *trans* square dsp^2 hybridization.[13] Burstall and Morgan[14] characterized the silver complex isolated from the oxidation of bis(α,α-bipyridine)-silver(I) nitrate with peroxodisulfate as the tris(bipyridine)silver(II) nitrate. Analysis of the compound which we isolated using their procedure indicates that it is the bis(bipyridine)silver(II) nitrate. The latter is in accord with the coordination number of 4 generally associated with the silver(II) species.[1] It is, moreover, consistent with the stoichiometry observed in oxidative decarboxylations (*cf.* Table II). In the crystal lattice of silver oxide, the silver atoms occupy two different sites[15] characteristic of silver(I) and silver(III) oxidation states. Silver oxide does produce silver(II) species, however, on dissolution in strong mineral acids, albeit in low yields.[16]

Despite the diversity of structural types, these silver(II) compounds exhibit common oxidizing properties in the decarboxylation of acids. Difficulties with solubility preclude a detailed comparison of their chemical properties and a quantitative kinetic examination at this time. Certain characteristic features of oxidative decarboxylation by these three silver(II) complexes are, however, clearly brought out with pivalic acid.

The essential stoichiometry of the oxidative decarboxylation of pivalic acid by all three silver(II) oxidants is given by eq 10. One mole of carbon dioxide is

$$(CH_3)_3CCO_2H + 2Ag^{II} \longrightarrow$$
$$[(CH_3)_3C^+] + CO_2 + H^+ + 2Ag^I \quad (10)$$
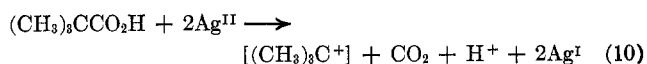
formed from 2 mol of Ag^{II}. The fate of the t-butyl cation is dependent on the medium. It gives rise to isobutylene by proton loss and t-butyl alcohol or t-butyl ester by solvation in the protic solvents. Furthermore, in the presence of acetonitrile, the cation affords N-alkylacetamide.[17]

(11) *Cf.* the oxidation of acetic acid with Mn^{III}: R. E. Van der Ploeg and E. C. Kooyman, *J. Catal.*, **10**, 52 (1968); E. I. Heiba, R. E. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 138 (1969); **90**, 5905 (1968); J. B. Bush, Jr., and H. Finkbeiner, *ibid.*, **90**, 5903 (1968).

(12) (a) Oxygen was detected by gas chromatography after completion of the reduction; (b) T. P. Dirkse and B. Wiers, *J. Electrochem. Soc.*, **106**, 284 (1959).
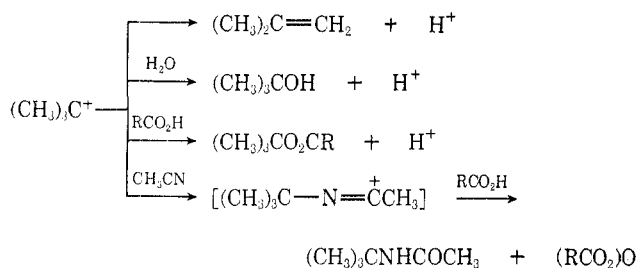
(13) E. G. Cox, W. Wardlow, and K. C. Webster, *J. Chem. Soc.*, 775 (1936).

(14) (a) G. T. Morgan and F. H. Burstall, *ibid.*, 2594 (1930); (b) see also S. Sugden, *ibid.*, 161 (1932).
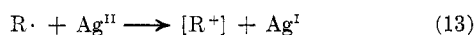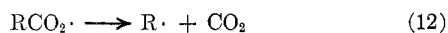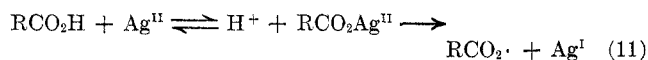
(15) (a) J. A. McMillan, *J. Inorg. Nucl. Chem.*, **13**, 28 (1960); (b) V. Scatturin, P. L. Bellon, and R. Zannetti, *Ric. Sci.*, **30**, 1034 (1960); *J. Electrochem. Soc.*, **108**, 819 (1961).

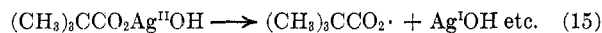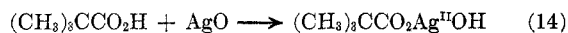(16) D. H. Huchital, N. Sutin, and B. Warnqvist, *Inorg. Chem.*, **6**, 839 (1967).

(17) *Cf.* J. K. Kochi and A. Bemis, *J. Amer. Chem. Soc.*, **90**, 4038 (1968).

$$(CH_3)_3C^+ \begin{cases} \xrightarrow{\quad} (CH_3)_2C{=}CH_2 + H^+ \\ \xrightarrow{H_2O} (CH_3)_3COH + H^+ \\ \xrightarrow{RCO_2H} (CH_3)_3CO_2CR + H^+ \\ \xrightarrow{CH_3CN} [(CH_3)_3C{-}N{=}\overset{+}{C}CH_3] \xrightarrow{RCO_2H} \end{cases}$$

$$(CH_3)_3CNHCOCH_3 + (RCO_2)O$$

We tentatively suggest[18] that oxidative decarboxylation by silver(II) proceeds by two discrete 1-equiv oxidations. First, oxidation of the carboxylate group by silver(II) occurs followed by further oxidation of the alkyl radical by a second silver(II) species (eq 11 and 13).

$$RCO_2H + Ag^{II} \rightleftharpoons H^+ + RCO_2Ag^{II} \longrightarrow$$
$$RCO_2\cdot + Ag^I \quad (11)$$

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

$$R\cdot + Ag^{II} \longrightarrow [R^+] + Ag^I \quad (13)$$

The metastability of aquosilver(II) species in the presence of carboxylic acids and the formation of alkyl radicals has been described.[8] A similar role is ascribed to silver(II) complexes in these studies, but the rates are no doubt slower. The high efficiency with which silver oxide effects oxidative decarboxylation can be formulated in an analogous manner.

$$(CH_3)_3CCO_2H + AgO \longrightarrow (CH_3)_3CCO_2Ag^{II}OH \quad (14)$$

$$(CH_3)_3CCO_2Ag^{II}OH \longrightarrow (CH_3)_3CCO_2\cdot + Ag^IOH \text{ etc.} \quad (15)$$

The formation of alkanes represents indirect evidence for alkyl radicals as intermediates, although further work is necessary to establish this point. Yields of alkanes from the decarboxylation of pivalic, isobutyric, n-butyric, and acetic acid by silver(II) species are significantly lower than those obtained from decarboxylation induced by other metal oxidants such as cobalt(III), lead(IV), manganese(III), cerium(IV), and thallium(III).[9,19] Esters and alkenes predominate as products, and even acetic acid produces high yields of methyl·acetate. We interpret this to indicate that silver(II) complexes carry out efficient oxidation[20] of alkyl radicals (eq 13) in a manner similar to the structurally related copper(II) species.[21]

Carbonium ions appear to be intermediates in the decarboxylation of pivalic acid by silver(II) species. Similarly, the products from the oxidation of isopropyl and n-propyl radicals are consistent with the formation of an isopropyl cation. However, the oxidation of n-butyric acid by silver(II) picolinate afforded n-propyl n-butyrate when carried out in the neat acid as solvent. The formation of this unrearranged ester

in such relatively high yields is rather unique.[9] It may arise directly from solvolysis of an alkylsilver intermediate under these rather poorly ionizing conditions.[22]

$$R\cdot + Ag^{II} \longrightarrow [R{-}Ag]^{2+} \xrightarrow{RCO_2H} RO_2CR + Ag^I + H^+ \quad (16)$$
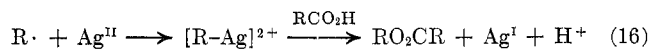
Experimental Section

Materials.—The carboxylic acids were redistilled before use. Pivalic acid was generously donated by the Enjay Chemical Co. Pyridine was distilled from barium oxide. Esters were obtained from commercial sources or prepared by esterification and redistilled before use.

Silver(II) picolinate was prepared by oxidation of silver(I) picolinate by peroxodisulfate in the presence of excess picolinic acid.[13,23] The total silver content was determined by reduction followed by Volhard determination of silver(I).

Anal. Calcd for $C_{12}H_{10}O_4N_2Ag$: Ag, 30.6. Found: Ag, 30.1.

Silver oxide was prepared by oxidation of silver nitrate with peroxodisulfate in an alkaline medium.[24] The silver(II) content was determined by reduction with an excess of a standard ferrous solution and back titration with standard ceric ammonium sulfate. The total silver content was also determined gravimetrically by electrodeposition.

Anal. Calcd for AgO: Ag, 87.1. Found: Ag, 87.1 (titration), 87.5 (electrodeposition).

Bis(α,α'-bipyridine)silver(II) nitrate was prepared in poor yields from the oxidation of bis(α,α'-bipyridine)silver(I) nitrate with ammonium peroxodisulfate.[14,25] The melting point (176°) and solubility characteristics paralleled those described by Morgan and Burstall. Elemental analysis, however, indicated that it was the bisbipyridine complex.

Anal. Calcd for $Ag(C_{10}H_8N_2)_2(NO_3)_2$: C, 44.11; H, 2.95; N, 15.44. Calcd for $Ag(C_{10}H_8N_2)_3(NO_3)_2$: C, 51.5; H, 3.4; N, 16.0. Found: C, 42.5; H, 2.86; N, 15.3. Further analysis of this complex is in progress.

Procedure.—The silver(II) compound was weighed into a long-neck, round-bottom flask and sealed with a gas-tight rubber septum. The flask was evacuated *in vacuo.* A degassed solution of the carboxylic acid was added with a hypodermic syringe and the mixture was stirred magnetically. Decarboxylations were carried out thermally in a thermostated bath.

The carbon dioxide was sampled directly from the reaction flask and analyzed by gas chromatography (Varian Aerograph, Porapak Q) using ethane as an internal standard. The gaseous hydrocarbons were analyzed in a similar manner to isomeric analogs as internal standards (15 ft, 30% Dowtherm on firebrick). Calibration curves were prepared by adding known amounts of gases to a system which simulated reaction conditions as closely as possible.

The reaction mixture was diluted with ether, washed with water, and extracted with sodium carbonate solution. The esters were analyzed by gas chromatography using isomeric esters as internal standards. Calibration curves were always constructed by subjecting known mixtures to the same work-up procedure. Reactions carried out in aqueous solution were analyzed directly without work-up. The following columns were used in the analyses: 8-ft diethylene glycol succinate at 85°, 6-ft Morflex at 85°, and 10-ft FFAP at 80° (Varian Aerograph Co.). Oxygen was analyzed on a 6-ft molecular-sieve 5A column at room temperature.

(18) Largely by analogy with other oxidants.[9]

(19) J. K. Kochi and T. W. Bethea, *J. Org. Chem.,* **33,** 75 (1968).

(20) Alternatively, the high yields of esters and alkenes can mean that a direct 2-equiv oxidation pertains. Such an oxidation can occur *via* a binuclear Ag^{II} species or a Ag^{III} species: $RCO_2H - 2e \longrightarrow R^+ + CO_2 + H^+$. (b) *Cf.* D. Sen, *J. Chem. Soc., A,* 1304 (1969).

(21) (a) J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.,* **87,** 4855 (1965); (b) J. K. Kochi, C. L. Jenkins, and A. Bemis, *ibid.,* **90,** 4616 (1968); (c) *cf.* G. W. A. Fowles, R. W. Mathews, and R. A. Walton, *J. Chem. Soc., A,* 1108 (1968).

(22) Analogous alkylcopper species have been postulated in related oxidations with copper(II).[21b]

(23) R. G. R. Bacon and W. J. W. Hanna, *J. Chem. Soc.,* 4962 (1965).

(24) R. N. Hammer and J. Kleinberg, *Inorg. Syn.,* **4,** 12 (1953).

(25) *Cf.* also the kinetics of the formation of bipyridinesilver(II): J. D. Miller, *J. Chem. Soc., A,* 1778 (1968).