Manganese(III) complexes in oxidative decarboxylation of acids

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ml of ether and 500 ml of water. The ether was removed under reduced pressure to yield a solid which on crystallization from methanol yielded 14 g (84%) of product, mp 75–76°; $[\alpha]^{23}$D −10° (c 1.0, methanol). The (±) nitrile gave mp 65–66°; nmr (CCl₄) δ 7.25–7.1 (m, 10 H), 3.92 (d, 1 H, J = 9.5), 3.33 (m, 1 H), 1.21 (d, 3 H, J = 7.0).

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.60; H, 6.91; N, 6.59.

The 1-deuterio-2-methyl-3,3-diphenylpropionitrile was prepared by exchange in methanol-*d* with 1.0 *N* sodium methoxide, nmr (CCl₄) δ 7.25–7.1 (m, 10 H), 3.91 (s, 1 H), 1.19 (s, 3 H).

1-Tritio-1-methyl-2,2-diphenylcyclopropylnitrile. To an ether solution of 2.0 g (0.009 mol) of 2,2-diphenylcyclopropylnitrile was added an equivalent amount of lithium diisopropyl amide dissolved in ether. The deep red solution was hydrolyzed with 1.0 ml of tritiated water (250 μCi/ml) to yield 1.2 g of nitrile with 114 dec/min/mg.[30] Table VII is typical of the rate data for tritium–hydrogen exchange. Straight lines were obtained in all cases and the average of ten runs gave an average slope of 8.0×10^{-3} min^{-1}.

(30) Scintillation counting was performed using PPO (4 g/l.) and POPOP (50 mg/l.) in toluene-counting solution in conjunction with a Packard Tricarb liquid scintillation counter.

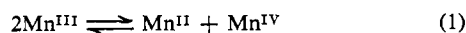# Manganese(III) Complexes in Oxidative Decarboxylation of Acids

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Contribution from the Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio, and Indiana University, Bloomington, Indiana 47401. Received August 11, 1969

Abstract: Manganese(III) effects oxidative decarboxylation of a variety of acids in nonaqueous solutions. The products and stoichiometries of the decarboxylation are examined. The reduction of Mn^{III} follows first-order kinetics. Autoretardation by the Mn^{II} formed in the reaction is attributed to mixed valence complexes between Mn^{III} and Mn^{II}. Alkyl radicals (and carbon dioxide) formed by multibond homolysis of the Mn^{III} carboxylates are oxidized by a second Mn^{III} to alkenes and esters. The enhanced rate of decarboxylation and oxidation of alkyl radicals by Mn^{III} in the presence of strong acids is ascribed to cationic Mn^{III} species. Copper(II) effectively traps alkyl radicals from the decarboxylation. The autoxidative decarboxylation of pivalic acid in the presence of oxygen is catalyzed by Mn^{III} and produces high yields of *t*-butyl alcohol and di-*t*-butyl peroxide.

A variety of transition metal compounds have been employed to catalyze the autoxidation of hydrocarbons.[1] In many cases, these autoxidations involve a rather complex set of reactions and metastable intermediates. In particular, the role of free radicals and their interaction with the metal species are not clear. Manganese(III) complexes have been used to oxidize a number of types of organic functional groups.[2] When manganese compounds are employed in a catalytic capacity, the metal species is thought to alternate between the II and III oxidation states. Mn^{III} in aqueous solutions, however, is especially prone to disproportionate (eq 1).[3] The latter does not

$$2Mn^{III} \rightleftharpoons Mn^{II} + Mn^{IV} \qquad (1)$$

appear to be as severe a limitation in nonaqueous solutions, since Mn^{III} complexes are relatively stable in these media.

In this report, we demonstrate the use of Mn^{III} complexes in the oxidative decarboxylation of acids. Products and kinetic studies are coupled in order to clarify the mechanism of the oxidation, the catalysis by strong acids, the retardation by Mn^{II} and the inter-

mediacy of alkyl radicals. The abilities of Mn^{III} and Cu^{II} to oxidize alkyl radicals are also compared.

Results

All oxidative decarboxylations by Mn^{III} were studied thermally in homogeneous and degassed solutions. Manganese(III) carboxylates were generated *in situ* (eq 1) by dissolving manganese(III) acetate in the carboxylic acid as solvent. The products, the stoichiometry, and the kinetics of the oxidation of three acids, chosen to be representative of tertiary (pivalic), sec-

$$Mn^{III}(OAc)_3 + 3RCO_2H \rightleftharpoons Mn^{III}(O_2CR)_3 + 3HOAc \qquad (2)$$

ondary (isobutyric), and primary (*n*-butyric) acids, were examined in detail. Qualitatively, the rates of reduction could be followed visually, since the color of the solution changed from deep burgundy to colorless as Mn^{III} was converted to Mn^{II}.

Products and Stoichiometry of Oxidative Decarboxylation by Mn^{III}. Pivalic Acid. The oxidative decarboxylation of pivalic acid was carried out in solutions of the neat acid containing 4% by wt acetic acid to maintain fluidity and facilitate handling at room temperature. From each mole of Mn^{III}, 0.5 mole each of carbon dioxide and isobutylene were formed together with smaller amounts of *t*-butyl pivalate and acetate. Excellent material balances based on eq 3 (where

$$2Mn^{III} + (CH_3)_3CCO_2H \longrightarrow 2Mn^{II} + [t\text{-}Bu^+]_{ox} + H^+ + CO_2 \qquad (3)$$

$[t\text{-}Bu^+]_{ox} = (CH_3)_2C{=}CH_2$, $t\text{-}BuO_2CC(CH_3)_3$, etc.) were obtained (Table I).

(1) For a review, see (a) N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967; (b) "Oxidation of Organic Compounds," Advances in Chemistry Series, No. 76, Vol. 2, American Chemical Society, Washington, D. C., 1968; (c) *Angew. Chem. Intern. Ed. Engl.*, **8**, 97 (1969).

(2) W. A. Waters and J. S. Littler, "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 3.

(3) Except where it is pertinent to the discussion, the ligands associated with the manganese species will not be included. Octahedral coordination generally pertains.

Table I. Decarboxylation of Pivalic Acid by Mn(III) at 125° [a]

Mn(III),[b] mmoles	Additive	Add./ Mn(III)[c]	Reaction time, min	Products, mmoles							
				CO_2	$2CO_2/$ Mn(III)[c]	i-C_4H_{10}	C_4H_8	t-BuO_2C- t-Bu	t-Bu- O_2CCH_3	t-Bu$_{ox}$[c,d]/ C_4H_{10}	Σt-Bu[c]/ CO_2
2.72			90	1.37	1.01	0.01	0.89	0.15	0.11	54	0.80
2.76[e]			120	1.37	0.99	0.02	0.79	0.11	0.23	58	0.84
2.77	$Cu(OAc)_2$	0.05	90	1.40	1.01	t[h]	1.19	0.07	0.04	>250	0.93
2.76	$Mn(OAc)_2$	1.0	150	1.38	1.00	0.04	0.78	0.13	0.09	25	0.75
2.76[e]	$Mn(OAc)_2$	1.0	150	1.40	1.01	0.02	0.85	0.09	0.23	60	0.85
2.80	$Mn(OAc)_2$	2.0	150	1.42	1.01	0.05	0.79	0.13	0.10	21	0.75
2.74[e]	$Mn(OAc)_2$	2.0	150	1.40	1.03	0.02	0.82	0.13	0.21	58	0.85
2.74	TFA[f]	1.0	15	1.35	0.99	t	1.00	0.12	0.05	>250	0.87
2.71	TFA[f]	1.0	10	1.36	1.01	t	0.90	0.10	0.15	>250	0.85
2.84	TFA,[f] Cu^{II} [g]	1.0	15	1.34	0.95	0	1.00	0.13	0.05	>250	0.88
2.76	TFA[f]	2.0	10	1.39	1.01	t	0.88	0.12	0.16	>250	0.84
2.77	TFA[f]	3.0	10	1.37	0.99	t	0.91	0.18	0.04	>250	0.83
2.80	TFA,[f] Cu^{II} [g]	3.0	10	1.32	0.95	0	0.83	0.22	0.05	>250	0.83
2.70	H_2SO_4	1.0	20	1.26	0.93	t	0.76	0.24	0.02	>200	0.81
2.78	H_2SO_4	3.0	15	1.29	0.93	t	0.55	0.23	0.05	>150	0.64
2.72	$HClO_4$	1.0	10	1.33	0.98	t	0.47	0.20	t	>120	0.50
2.78	$HClO_4$	3.0	10	1.33	0.96	t	t	0.04	0.06		0.08

[a] In 10 ml of pivalic acid–acetic acid (96:4 wt/wt). [b] $Mn(OAc)_3 \cdot 2H_2O$. [c] Mmoles/mmole. [d] t-Bu$_{ox}$ includes isobutylene and esters. [e] In 10 ml of pivalic acid–acetic acid (80:20 v/v). [f] Trifluoroacetic acid. [g] 5 mole % $Cu(OAc)_2$ based on Mn(III). [h] Trace amounts (<0.01 mmole).

The reduction of Mn^{III} was complete in less than 90 min at 125°. The rate, however, was retarded by Mn^{II}, but markedly accelerated by the addition of such strong acids as trifluoroacetic, sulfuric, or perchloric acid. The rate of decarboxylation was unaffected by Cu^{II}.

Effect of Oxygen. The oxidative decarboxylation of pivalic acid by Mn^{III} took an entirely different course in the presence of oxygen. Except for the oxygen atmosphere (40 psig, 150 mmoles), the decarboxylation was carried out for 10 hr in the same manner as described above. Under such conditions, isobutylene was no longer a product. Instead the products from each millimole of Mn^{III} were t-butyl alcohol (7.04 mmoles), acetone (0.97 mmole), and di-t-butyl peroxide (0.42 mmole) together with 8.9 mmoles of carbon

$$(CH_3)_3CCO_2H + O_2 \xrightarrow{\ Mn^{III}\ } CO_2 +$$
$$[(CH_3)_3COH + (CH_3)_2CO + (CH_3)_3CO_2C(CH_3)_3] \quad (4)^4$$
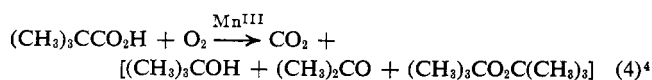
dioxide. The length of time the reaction was heated was quite arbitrary since it was apparent that Mn^{III} was not materially reduced under these conditions.

Isobutyric Acid. Propane was the major alkyl product derived from the oxidative decarboxylation of isobutyric acid by Mn^{III} at 115°. Propylene was a minor

$$2Mn^{III} + (CH_3)_2CHCO_2H \longrightarrow$$
$$2Mn^{II} + C_3H_7 + CO_2 + H^+ + S_{ox}^+ \quad (5)^5$$
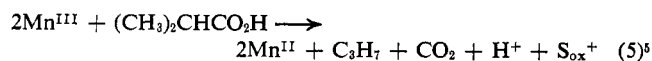
product, and the material balance given in Table II (columns 6 and 12) was not as good as that obtained from pivalic acid. On the addition of Cu^{II}, however, propylene was the major product and the stoichiometry given by eq 6 pertained.

$$2Mn^{III} + (CH_3)_2CHCO_2H \xrightarrow{\ Cu^{II}\ } 2Mn^{II} + C_3H_6 + CO_2 + 2H^+ \quad (6)$$
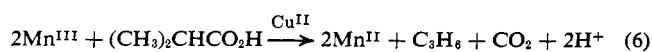
Trifluoroacetic acid also improved the stoichiometry of oxidative decarboxylation given by eq 7 ($[i$-Pr$^+]_{ox}$

$$2Mn^{III} + (CH_3)_2CHCO_2H \longrightarrow$$
$$2Mn^{II} + [i\text{-}Pr^+]_{ox} + CO_2 + H^+ \quad (7)$$
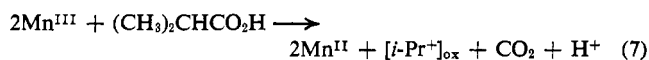
$= C_3H_6$, i-PrO$_2$CCH(CH$_3$)$_2$, etc.). The effects of such additives as sulfuric acid, pyridine, and lithium acetate are also given in Table II.

n-Butyric Acid. The reduction of Mn^{III} in n-butyric acid proceeded slowly at 125° and produced carbon dioxide and propane in poor yields, together with minor amounts of propylene, n-propyl, and isopropyl butyrates (Table III). The rate of Mn^{III} reduction and the amount of decarboxylation were markedly increased by the addition of trifluoroacetic acid. Similar effects were shown by sulfuric and perchloric acids.

The generally poor material balances for the decarboxylations of n-butyric and isobutyric acids by Mn^{III} were attributed to side reactions involving nondecarboxylative processes. Hydrogen loss from the α-position of the acid to form carboxyalkyl radicals is one such oxidation which has been carefully delineated with acetic acid.[6-8]

$$Mn^{III} + CH_3CO_2H \longrightarrow \cdot CH_2COOH + Mn^{II} + H^+ \quad (8)$$

Competitive Decarboxylation of Acids by Mn^{III}. Mixtures of pivalic acid and n-butyric or isobutyric acid were decarboxylated with Mn^{III} in the absence and presence of varying amounts of trifluoroacetic acid (Table IV). Yields of carbon dioxide, alkane (isobutane, propane), and alkene (isobutylene and propylene) were measured quantitatively. The yields of the accompanying esters were obtained by simple extrapolation of the detailed data for the decarboxylation of the separate acids presented in Tables I, II, and III. The validity of this extrapolation was cross checked with competition studies in the presence of Cu^{II}, since decarboxylations under the latter conditions generated only alkene (vide supra).

(4) The reaction is not stoichiometric and the equation is not balanced.

(5) The products derived from the carboxylic acid solvent were not examined (vide infra).

(6) R. E. van der Ploeg, R. W. de Korte, and E. C. Kooyman, J. Catal., 10, 52 (1968).

(7) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., J. Am. Chem. Soc., 91, 138 (1969); 90, 5905 (1968); Discussions Faraday Soc., 46, 189 (1968).

(8) See, however, J. B. Bush, Jr., and H. Finkbeiner, J. Am. Chem. Soc., 90, 5903 (1968); Discussion Faraday Soc., 46, 150 (1968).

Table II. Decarboxylation of Isobutyric Acid by Mn(III) at 115° a

| Mn(III),b mmoles | Additive | Add./ Mn(III)c | Reaction time, min | Products, mmoles | | | | | | | |
				CO2	2CO2/ Mn(III)c	C3H8	C3H6	i-PrO2C- i-Pr	i-Pr- O2CCH3	i-Prox c,d/ C3H8	Σi-Prc/ CO2
2.66			300	1.28	0.90	0.55	0.15	0.13	0	0.5	0.65
2.70			300	1.28	0.95	0.57	0.15	0.12	0	0.5	0.66
2.65	Cu(OAc)2	0.5	300	1.12	0.85	t^h	0.85	t	0.04	>250	0.80
2.72	Mn(OAc)2	0.5	880	1.29	0.95	0.63	0.09	0.11	0.11	0.5	0.73
2.72	Mn(OAc)2	1.0	1020	1.29	0.95	0.62	0.05	0.07	0.05	0.3	0.61
2.70	Mn(OAc)2	2.0	990	1.30	0.96	0.63	t	0.02	0.06	0.1	0.55
2.72	TFA e	0.5	120	1.34	0.99	0.57	0.23	0.19	0.07	0.8	0.79
2.64	TFA e	1.0	120	1.34	1.02	0.47	0.34	0.28	0.12	1.6	0.90
2.72	TFA e	2.0	90	1.42	1.04	0.38	0.43	0.23	0.06	1.9	0.77
2.78	TFA,e CuII f	1.0	120	1.14	0.82	t	0.88	0.03	t	>250	0.80
2.72	TFA e	3.0	60	1.31	0.96	0.59	0.45	0.30	t	1.3	1.02
2.73	TFA e, CuII f	3.0	60	1.24	0.91	0.11	0.86	0.11	t	8	0.87
2.62	H2SO4	2.1	30	1.48	1.13	0.08	0.32	0.57	0.08	12	0.71
2.65	H2SO4	2.0	30	1.60	1.21	0.07	0.42	0.71	0.11	18	0.82
2.65	H2SO4	1.4	30	1.50	1.13	0.07	0.49	0.38	0.11	13	0.70
2.62	H2SO4	1.4	30	1.56	1.19	0.10	0.55	0.42	0.11	11	0.76
2.70	C5H5N g	0.5	760	1.23	0.93	0.60	0.11	0.17	0	0.5	0.72
2.71	C5H5N g	1.0	780	0.91	0.67	0.61	0.10	0.12	0.04	0.4	0.94
2.71	C5H5N g	2.0	780	1.34	0.99	0.67	0.07	0.10	0.07	0.4	0.68
2.67	LiOAc	1.0	180	1.26	0.94	0.56	0.08	0.12	0.05	0.5	0.64
2.70	LiOAc	1.0	240	1.27	0.94	0.65	0.10	0.11	0.07	0.4	0.73
2.69	LiOAc	2.1	180	1.01	0.75	0.64	0.07	0.09	0.09	0.4	0.88
2.70	LiOAc	2.6	120	0.98	0.73	0.66	0.08	0.09	0.05	0.3	0.90

a In 10 ml of isobutyric acid. b Mn(OAc)3·2H2O. c Mmoles/mmole. d i-Prox includes propylene and esters. e Trifluoroacetic acid f 5 mole % Cu(OAc)2 based on Mn(III). g Pyridine. h Trace amounts (<0.01 mmole).

Table III. Decarboxylation of n-Butyric Acid by Mn(III) at 125° a

| Mn(III),b mmoles | Additive | Add./ Mn(III)c | Reaction time, min | Products, mmoles | | | | | | | |
				CO2	2CO2/ Mn(III)c	C3H8	C3H6	n-PrO2C- n-Pr	i-PrO2C- n-Pr	Prox c,d/ C3H8	ΣPrc/ CO2
2.77			720	0.67	0.48	0.27	0.04	0.03	t g	0.3	0.51
2.78	Cu(OAc)2	0.05	900	0.50	0.36	t	0.19	0	0	38	0.38
2.79	Mn(OAc)2	1.0	780	0.58	0.42	0.19	0.03	0.02	t	0.3	0.41
2.92	Mn(OAc)2	2.0	780	0.64	0.43	0.20	0.03	t	t	0.2	0.36
2.73	TFA e	1.0	180	0.79	0.58	0.43	0.06	0.02	t	0.2	0.65
2.77	TFA,e CuII f	1.0	240	0.73	0.53	0.02	0.50	t	0	25	0.71
2.74	TFA e	3.0	60	0.93	0.68	0.50	0.09	0.03	t	0.2	0.67
2.72	TFA e, CuII f	3.0	90	0.94	0.69	0.02	0.67	0.02	t	35	0.76
2.72	H2SO4	1.0	60	0.83	0.61	0.25	0.10	0.14	0.08	1.3	0.69
2.75	H2SO4	3.0	60	0.78	0.57	0.10	t	0.24	0.18	4.2	0.67
2.77	HClO4	1.0	60	0.76	0.55	0.27	0.11	0.04	0.02	0.6	0.58

a In 10 ml of n-butyric acid. b Mn(OAc)3·2H2O. c Mmoles/mmole. d Prox includes propylene and esters. e Trifluoroacetic acid. f 5 mole % Cu(OAc)2 based on.Mn(III). g Trace amounts (<0.01 mmole).

From these competition studies, it was possible to obtain the relative rates of overall decarboxylation of pivalic, isobutyric, and n-butyric acids. These values (given in the last column of Table X) depended highly on the accuracy of the product analysis and small variations should be overlooked.

The competition method also allowed us to assess the amounts of oxidation products (alkene and ester) produced relative to hydrogen abstraction product (alkane) for n-propyl, isopropyl, and t-butyl radicals (columns 8 and 9, Table IV) when they were generated in the same environment.

Kinetics of the Reduction of Mn[III] in Pivalic Acid. The rate of reduction of Mn[III] in pivalic acid (containing 1% of acetic acid) was followed by monitoring the absorption band at 462 nm spectrophotometrically. The rate of disappearance of Mn[III] followed first-order kinetics for approximately 60% of the reaction, and then decreased as the concentration of Mn[II] built up (Figure 1). The deviation from first-order kinetics became more severe at lower temperatures (compare

Figures 1 and 2). Pseudo-first-order rate constants given in Table V cover only the initial phases of the reduction and were readily reproducible to within 10%. The kinetic behavior of anhydrous manganese(III) trisacetate was essentially indistinguishable from its dihydrate or manganese(III) tris-n-butyrate.

Effect of Manganese(II). Deliberate addition of Mn[II] bisacetate caused a reduction in the rate of reduction of Mn[III] as shown in Figure 1 and listed in Table VI. Mn[II] had the further effect of increasing the linear portion of the first-order plot.

Effect of Acid. Trifluoroacetic acid, on the other hand, accelerated the reduction of Mn[III] (Figure 2 and Table VII). The dependence of the first-order constant (k_1) on the concentration of trifluoroacetic acid followed a linear relationship and could be expressed by eq 9.

$$k_M = k_1 + k_H(CF_3CO_2H) =$$

$$[4.63 + 1.35(CF_3CO_2H)] \ sec^{-1} \quad (9)$$

The addition of trifluoroacetic acid also reduced the

Table IV. Competitive Decarboxylation of (A) Pivalic Acid and (B) Isobutyric or n-Butyric Acid by Mn(III)[a]

B^b/A	$TFA^{b,c}/$ Mn(III)	CO_2	C_3H_8	$C_3H_7^+$	C_4H_{10}	$C_4H_9^+$	$C_3H_7^{+d,e}/$ C_3H_8	$C_4H_9^{+/d,e}/$ C_4H_{10}	$\Sigma C_4B^{b,f}/$ ΣC_3A
				B = Isobutyric Acid[g]					
5	0	1.46	0.21	0.02	0.06	0.62	0.2	13	17
5[h]	0	1.48	0.02	0.20	0.01	1.17	10	128	28
10	0	1.54	0.20	0.04	0.04	0.55	0.3	18	28
10[h]	0	1.65	t^i	0.35	t	0.72	>70	>150	21
5	1	1.57	0.20	0.20	0.03	0.80	0.6	31	16
5[h]	1	1.39	t	0.14	t	0.68	>28	>140	25
10	1	1.45	0.12	0.08	0.05	0.55	1.4	13	25
10[h]	1	1.49	t	0.39	t	0.75	>80	>170	21
5	3	1.57	0.10	0.06	0.07	0.69	1.0	12	23
5[h]	3	1.53	t	0.18	t	0.82	>40	>200	25
10	3	1.47	0.07	0.15	0.01	0.61	3.0	75	24
10[h]	3	1.45	t	0.72	t	0.67	>150	>130	11
				B = n-Butyric Acid[i]					
10	0	1.28	0.005	0.009	0.05	0.48	4	13	240
10[h]	0	1.46	0	0.02	t	0.82	>4	>190	460
50	0	1.00	0.03	0.02	0.05	0.31	1.3	10	400
50[h]	0	0.97	t	0.04	t	0.43	>8	>100	650
10	1	1.42	0.01	t	0.01	0.83	<0.5	>100	500
10[h]	1	1.40	0	0.02	t	0.90	>4	>220	530
50	1	1.11	0.05	0.01	t	0.51	<0.4	>120	490
50[h]	1	1.06	t	0.04	t	0.51	>8	>120	900
10	3	1.55	0.009	t	0.007	0.83	<0.5	>150	1040
10[h]	3	1.48	0	0.014	0	0.76	>4	>200	500
50	3	1.33	0.07	0.02	t	0.65	<0.3	>170	500
50[h]	3	1.33	t	0.09	t	0.68	>18	>180	500

[a] In solutions containing ca. 2.7 mmoles of $Mn(OAc)_3 \cdot 2H_2O$ in 10 ml of carboxylic acid (component A = pivalic acid and component B = isobutyric or n-butyric acid). [b] Moles/mmole. [c] Trifluoroacetic acid. [d] $C_3H_7^+$ includes propylene and propyl esters; $C_4H_9^+$ includes isobutylene and t-butyl esters. [e] To closest significant figure. [f] ΣC_3 includes all propyl products; ΣC_4 includes all butyl products. [g] 105°. [h] 5 mole % $Cu(OAc)_2$ based on $Mn(OAc)_3 \cdot 2H_2O$ added. [i] 120°. [j] Trace amounts.

retarding effect exerted by Mn^{II} in relation to its concentration. For example, when a 5 molar excess (relative to Mn^{II}) of trifluoroacetic acid was employed, the disappearance of Mn^{III} followed first-order kinetics to beyond 90% reduction.
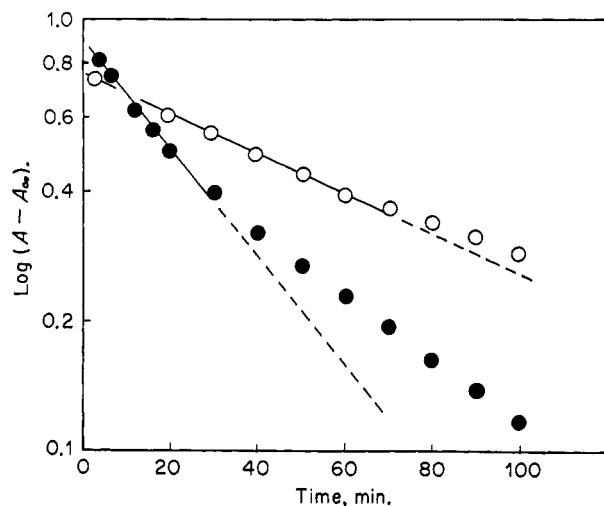

Figure 1. Kinetics of Mn(III) reduction in pivalic acid at 80°. Effect of Mn^{III}: ●, 2.60×10^{-3} M $Mn(OAc)_3$; O, 2.60×10^{-3} M $Mn(OAc)_3$, 5.26×10^{-3} M $Mn(OAc)_2$.

Solvent Isotope Effect. The deuterium isotope effect was studied by comparing the reduction of Mn^{III} in pivalic acid and pivalic acid-d under equivalent conditions. The reduction of Mn^{III} was 1.3 ± 0.1 times faster in the protic medium at 70°.

The Effect of Metal Carboxylates. The effect of various metal carboxylates on the rate of reduction of Mn^{III} by pivalic acid is given in Table VIII. These
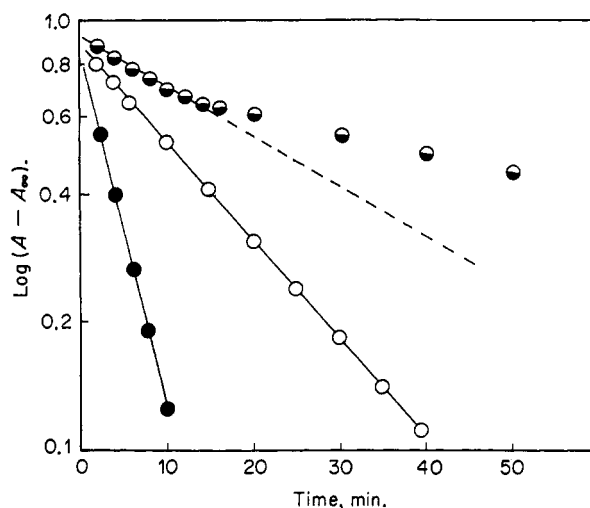
Figure 2. Kinetics of Mn(III) reduction in pilvalic acid at 70°. Effect of trifluoroacetic acid: ◓, 2.60×10^{-3} M $Mn(OAc)_3$; O, 2.60×10^{-3} M $Mn(OAc)_3$, 2.63×10^{-3} M $Mn(OAc)_2$, 13.82×10^{-3} M TFA; ●, 2.60×10^{-3} M $Mn(OAc)_3$, 13.82×10^{-3} M TFA.

first-order rate constants (k_M) are compared with that k_1 obtained in the absence of additives in the last column of the table.

The effects of metal carboxylates on the reduction of Mn^{III} by pivalic acid were also studied in the presence of added trifluoroacetic acid. Under these conditions, the metal carboxylates underwent metathesis according
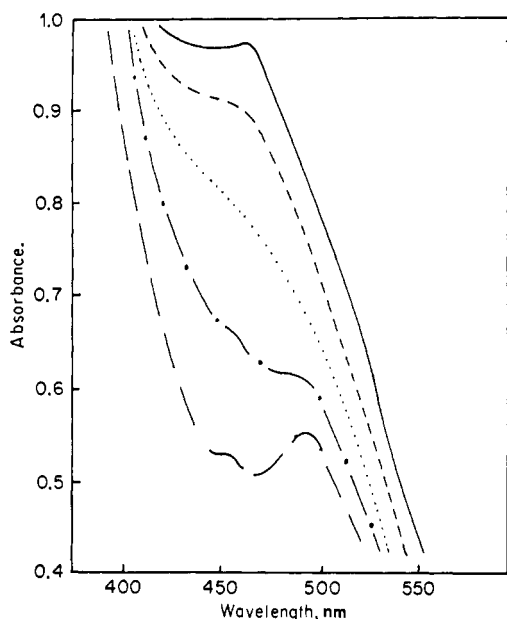
Figure 3. Visible absorption spectra of $Mn(OAc)_3 \cdot 2H_2O$ with added $Mn(OAc)_2$ in 80 vol % pivalic acid–acetic acid: ——, 2.58 × 10^{-3} M Mn(III); - - - - - -, 2.58 × 10^{-3} M Mn(III), 5.20 × 10^{-3} M Mn(II); ...., 2.58 × 10^{-3} M Mn(III), 7.80 × 10^{-3} M Mn-(II); — · — · —, 2.58 × 10^{-3} M Mn(III), 13.0 × 10^{-3} M Mn(II); — — —, 2.58 × 10^{-3} M Mn(III), 20.8 × 10^{-3} M Mn(II).

to eq 10. Since trifluoroacetic acid is significantly

$$M^{n+}(OAc)_n + nCF_3CO_2H \rightleftharpoons M^{n+}(O_2CCF_3)_n + nHOAc \quad (10)$$

stronger than acetic acid, we assumed that the free trifluoroacetic acid $(CF_3CO_2H)_{eff}$ remaining after neutralization was given by eq 11, where $(CF_3CO_2H)_0$ was

$$(CF_3CO_2H)_{eff} = (CF_3CO_2H)_0 - n[M(OAc)_n] \quad (11)$$

Table V. First-Order Rate Constants for the Reduction of Mn(III)[a]

Mn(III), 10^3 M	k_1,[b] 10^4 sec^{-1}
5.22[c]	8.6 ± 0.3
5.20[d]	10.0 ± 0.1
3.92[c]	8.4 ± 0.3
3.90[d]	9.2 ± 0.2
2.61[c]	8.9 ± 0.6
2.60[d]	9.7 ± 0.5
1.31[c]	8.3 ± 0.2
1.30[d]	9.9 ± 0.4

[a] In 99 wt % pivalic acid–acetic acid solution at 80°. [b] Average of at least two runs. [c] Dihydrate. [d] Anhydrous.

Table VI. Effect of Mn(II) on the Reduction of Mn(III) by Pivalic Acid[a]

Mn(III),[b] 10^3 M	Mn(II),[c] 10^3 M	Mn(II)/ Mn(III)[d]	k_1,[e] 10^4 sec^{-1}
2.61[f]	0		8.9 ± 0.6
2.60[g]	0		9.7 ± 0.5
2.62[f]	1.32	0.5	4.24 ± 0.03
2.60[g]	1.32	0.5	3.3 ± 0.2
2.62[f]	2.64	1.0	2.94 ± 0.02
2.60[g]	2.63	1.0	2.37 ± 0.07
2.62[f]	5.28	2.0	1.8 ± 0.1
2.60[g]	5.26	2.0	1.9 ± 0.1

[a] In 99 wt % pivalic acid–acetic acid solution at 80°. [b] Manganese(III) trisacetate. [c] Manganese(II) bisacetate. [d] Molar ratio. [e] Average of at least two runs. [f] Dihydrate. [g] Anhydrous.

Table VII. Effect of Trifluoroacetic Acid on the Reduction of Mn(III) in Pivalic Acid[a]

CF_3CO_2H, 10^3 M	$CF_3CO_2H/$ Mn(III)[b]	k_1,[c] 10^4 sec^{-1}
0[d]		4.3 ± 0.2
0[e]		5.0 ± 0.5
2.76[d]	1.05	7.5 ± 0.1
2.76[e]	1.05	7.8 ± 0.4
5.52[d]	2.11	13.1 ± 0.1
5.52[e]	2.11	11.1 ± 0.7
8.3[d]	3.17	14.9 ± 0.3
8.3[e]	3.17	14 ± 1
11.04[d]	4.23	19.5 ± 0.6
11.04[e]	4.23	20 ± 1
13.82[d]	5.28	28.9 ± 0.2
13.82[e]	5.28	27 ± 1

[a] In 99 wt % pivalic acid–acetic acid solutions containing 2.60 × 10^{-3} M manganese(III) trisacetate at 70°. [b] Molar ratio. [c] Average of at least two runs. [d] Dihydrate. [e] Anhydrous.

the amount of acid charged and n was the oxidation state of the metal. The experimental first-order rate constant was corrected for the amount of trifluoroacetic acid lost by neutralization according to (eq 9 and 11). The corrected rate constant k_c was compared with the experimentally determined rate constant k_M in the presence of various metal carboxylates. The validity of this assumption was demonstrated by comparing the effects of lithium and sodium acetate with lithium and sodium trifluoroacetate at corrected concentrations of trifluoroacetic acid. A slight positive kinetic salt effect was noted in these cases.

The results in Table VIII show that Mn^{II} and Co^{II} are unique in their retarding effect on the reduction of Mn^{III} by pivalic acid in the presence as well as in the absence of trifluoroacetic acid.

Activation Parameters. The temperature dependence of the first-order rate constant for the reduction of anhydrous Mn^{III} trisacetate and its dihydrate in pivalic acid was the same within experimental error. These results are found in Table IX, together with those obtained in the presence of trifluoroacetic acid.

The Absorption Spectra of Mn^{III} and Mn^{II} Systems. The visible absorption spectrum of manganese(III) trisacetate in pivalic–acetic acid solutions showed an absorption maximum at 462 nm (ϵ 360 M^{-1} cm^{-1}), which followed the Beer–Lambert relationship to within 5% in the concentration range 3 × 10^{-3} to 3 × 10^{-4} M. Manganese(II) bisacetate showed no appreciable absorption in this region.

The absorption maximum of 2.58 × 10^{-3} M Mn^{III} at 462 nm diminished with increasing amounts of added Mn^{II} (Figure 3), and at high ratios of Mn^{II}/Mn^{III}, a new maximum appeared at 494 nm (ϵ 250 M^{-1} cm^{-1}, Mn^{II} = 1.30 × 10^{-2} M). No clear isosbestic points were noted. However, when a solution containing 2.58 × 10^{-3} M Mn^{III} and 2.08 × 10^{-2} M Mn^{II} (i.e., Mn^{II}/Mn^{III} = 8) was diluted, the apparent extinction coefficient in the region between 450 and 500 nm increased. Finally, at the dilution of Mn^{III} of less than 10^{-4} M, Mn^{II} (10^{-3} M) exerted no noticeable effect on the absorption spectrum of Mn^{III}. The effect of Mn^{II} on the spectrum of Mn^{III} at a given concentration also increased with decreasing temperatures.

A variety of other metal carboxylates including lithium, sodium, and magnesium acetates and trifluoro-

Table VIII. Kinetics of the Reduction of Mn(III) at 70°.[a–c] The Effect of Salts as Bases

Added salt	Added salt, $M \times 10^3$	TFA,[d] $M \times 10^3$	TFA$_{eff}$,[e] $M \times 10^3$	TFA$_{eff}$/ Mn(III)	$k \times 10^4$, sec^{-1} k_M[f]	k_c[g]	k_M/k_c
LiOAc[h]	2.54	13.2	10.7	4.1	23.2	19.0	1.2
LiOAc[i]	2.54	13.2	10.7	4.1	22.0	19.0	1.2
NaOAc[h]	2.58	13.2	10.6	4.1	20.3	19.0	1.1
NaOAc[i]	2.58	13.2	10.6	4.1	21.4	19.0	1.1
Mg(OAc)₂[h]	2.61	13.8	8.6	3.3	16.9	15.2	1.1
Mg(OAc)₂[h]	2.61	0	0		3.3	4.3	0.8
Mg(OAc)₂[i]	2.61	13.8	8.6	3.3	15.6	15.2	1.0
Mg(OAc)₂[i]	2.61	0	0		3.2	5.0	0.7
Cu(OAc)₂[h]	2.62	13.2	8.0	3.0	15.3	15.2	1.1
Cu(OAc)₂[i]	2.62	13.2	8.0	3.0	17.5	14.0	1.2
Mn(OAc)₂[h]	2.63	13.8	8.6	3.3	8.5	15.2	0.56
Mn(OAc)₂[h]	2.63	0	0		1.5	4.3	0.34
Mn(OAc)₂[i]	2.63	13.8	8.6	3.3	9.1	15.2	0.60
Mn(OAc)₂[i]	2.63	0	0		1.1	5.0	0.21
Co(OAc)₂[h]	2.63	13.8	8.6	3.3	5.6	15.2	0.37
Co(OAc)₂[h]	2.63	0	0		Ca. 1.0	4.3	0.22
Co(OAc)₂[i]	2.63	13.8	8.6	3.3	5.2	15.2	0.34
Co(OAc)₂[i]	2.63	0	0		Ca. 1.0	5.0	0.20
LiTFA[h]	2.5	10.6	13.1	5.0	25.6	19.0	1.4
LiTFA[i]	2.5	10.6	13.1	5.0	21.0	19.0	1.1
NaTFA[h]	2.5·	10.6	13.1	5.0	21.0	19.0	1.1
NaTFA[i]	2.5	10.6	13.1	5.0	25.0	19.0	1.3

[a] 2.60×10^{-3} M Mn(III). [b] 99 wt % pivalic acid–acetic acid. [c] Molar ratio; added salt/Mn(III) = 1.0. [d] Trifluoroacetic acid, TFA/ Mn(III) = 5.0 when applicable. [e] Effective TFA concentration = initial TFA concentration − n[M(OAc)$_n$]. [f] Average of at least two runs. [g] k_c was determined from plots of k_1 vs. TFA concentration (data in Table VII). [h] Dihydrate. [i] Anhydrous.

Table IX. Temperature Dependence of the Reduction of Mn(III) in Pivalic Acid. Effect of Acetic Acid and Trifluoroacetic Acid

HOAc, M	CF₃-COOH, 10^2 M	Temp, °C	$k_1 \times 10^4$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$,[d] eu
0.2	0	80	8.9 ± 0.6[b]		
0.2	0	80	9.7 ± 0.5[c]		
0.2	0	70	4.3 ± 0.2[b]	17.1	−24
0.2	0	70	5.0 ± 0.5[c]		
0.2	0	60	2.0 ± 0.3[b]		
0.2	0	60	2.1 ± 0.1[c]		
0.2	13.8	70	28.9 ± 0.2[c]		
0.2	13.8	70	27 ± 1[c]		
0.2	13.8	60	16.7 ± 1.4[b]	14.3	−18
0.2	13.8	60	17.9 ± 0.4[c]		
0.2	13.8	50	7.4 ± 0.2[b]		
0.2	13.8	50	7.7 ± 0.4[c]		
3.5	0	80	13.8 ± 0.8[b]		
3.5	0	70	3.0 ± 0.2[b]	34.6	+26
3.5	0	60	0.7 ± 0.03[b]		
3.5	13.8	70	22.8 ± 1.0[b]		
3.5	13.8	60	11.3 ± 0.4[b]	16.7	−22
3.5	13.8	51	4.6 ± 0.4[b]		

[a] Average of at least two runs. [b] Mn(OAc)₃·2H₂O. [c] Mn-(OAc)₃. [d] Calculated at 70°.

acetates as well as lead(II) and cobalt(II) acetates were also examined. None of these, with the exception of cobalt(II) acetate, showed an effect comparable to manganese(II) acetate.[9] We tentatively ascribe the behavior of the latter to the formation of Mn^{III}-Mn^{II} mixed valence complexes with rather low forma-

$$Mn^{III}(O_2CCH_3)_3 + Mn^{II}(O_2CCH_3)_2 \rightleftharpoons$$
$$Mn^{III}(O_2CCH_3)_5Mn^{II} \quad (12)$$
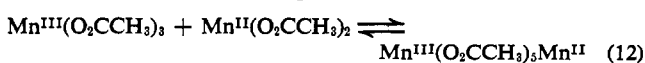
tion constants and extinction coefficients. The carboxylato ligands associated with these metal species, however, can act as *bases* and their effect in this capacity

(9) (a) Changes in the absorption spectrum of Mn^{III} in acetic acid solutions of alkali metal acetates at higher concentrations have been reported;[7] (b) W. J. de Klein, Thesis, Leiden, 1967.

cannot be excluded.[7,9] Further work is necessary to establish this point.

Spectral Studies of the Disproportionation of Mn^{III} by Electron Spin Resonance. At low concentrations, the amplitudes of the first derivative of the hyperfine lines (at constant line width) of Mn^{II} in aqueous solutions are proportional to the concentration.[10] We found that standard solutions of 1×10^{-4} to 3×10^{-4} M Mn^{II} acetate in acetic acid showed the same behavior quantitatively.

The disproportionation of 10^{-2} M Mn^{III} in acetic acid was assumed to be similar to that observed in aqueous acid solutions. The disproportionation constant K_d is then given by eq 13, where (Mn^{III})₀ is the concentration of Mn^{III} charged. It was further

$$2Mn^{III} \xrightleftharpoons{K_d} Mn^{II} + Mn^{IV} \quad (1)$$
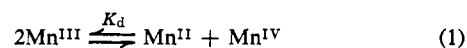
$$K_d = \frac{(Mn^{II})^2}{[(Mn^{III})_0 - 2(Mn^{II})]^2} \quad (13)$$

assumed that Mn^{IV} had no effect on the esr spectrum of Mn^{II}. Measurements of Mn^{II} were made at various concentrations of Mn^{III} and temperatures. Reversibility in eq 1 was shown by the addition of Mn^{II} and repeatedly recycling the temperature. Values of K_d obtained in this manner increased from 2.03 ± 0.06 × 10^{-4} at 30°, 2.43 ± 0.13 × 10^{-4} at 50° to 3.08 ± 0.24 × 10^{-4} at 70°. These values were essentially the same for anhydrous manganese(III) acetate and its dihydrate in acetic acid solutions.[7,11] The value of K_d increased from 2.0 × 10^{-4} to 4.1 × 10^{-4} on the addition of trifluoroacetic acid (6.5 × 10^{-2} M) at 44°.

(10) G. G. Guilbault and G. Lubrano, *Anal. Letters*, 1, 725 (1968); *Anal. Chem.*, 41, 1100 (1969).

(11) *Cf.* also values in aqueous acid solutions: H. Diebler and N. Sutin, *J. Phys. Chem.*, 68, 174 (1964); R. G. Selim and J. J. Lingane, *Anal. Chim. Acta*, 21, 536 (1959).

Discussion

Manganese(III) species oxidize carboxylic acids by two competing and largely independent paths: oxidative decarboxylation and alkyl oxidation. For example, the half-reactions for acetic acid are represented by eq 14 and 15, respectively. For a given carboxylic acid,

oxidative decarboxylation

$$CH_3COOH \xrightarrow{-e} CH_3 \cdot + CO_2 + H^+ \qquad (14)$$

alkyl oxidation

$$CH_3COOH \xrightarrow{-e} \cdot CH_2COOH + H^+ \qquad (15)$$
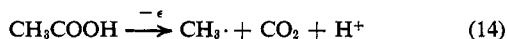
the relative importance of these reactions depends on the availability of the α-hydrogens. Thus carboxymethyl radicals are the prime intermediates in the oxidation of acetic acid by Mn^{III} and their reactions have been examined extensively.[6-8] On the other hand, we find that pivalic acid which has no α-hydrogen reacts with Mn^{III} solely via oxidative decarboxylation. Primary and secondary acids, such as n-butyric and isobutyric acids, react via both routes,[12] the relative importance of which can be controlled by the addition of strong acids.

We are primarily concerned here with the mechanism of oxidative decarboxylation summarized in eq 16–20. In the following discussion, we will focus our

oxidative decarboxylation by Mn^{III}

$$Mn^{III} + RCO_2H \rightleftharpoons Mn^{III}O_2CR + H^+ \qquad (16)$$

$$MnO_2^{III}CR \longrightarrow Mn^{II} + R \cdot + CO_2 \qquad (17)$$

$$Mn^{II} + Mn^{III}O_2CR \rightleftharpoons Mn^{II}(O_2CR)Mn^{III} \qquad (18)$$

$$Mn^{III} + R \cdot \longrightarrow Mn^{II} + R_{ox}^+ \qquad (19)$$

$$R \cdot + SH \longrightarrow RH + S \cdot \text{ etc.} \qquad (20)$$

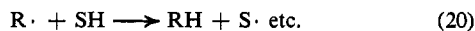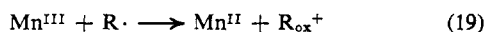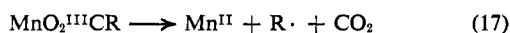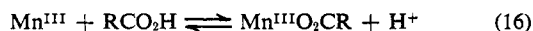attention on several pertinent features of this mechanism: the Mn^{III} species in solution, the retarding effect of Mn^{II}, the catalysis by strong acids, the effect of oxygen and Cu(II), and alkyl radicals as intermediates.

Manganese(III) in Solution. Manganese(III) acetate has been described in an hydrated form as manganese-(III) trisacetate dihydrate[13] and as an anhydrous material manganese(III) trisacetate.[14] Hessel and Romers[15] have carried out careful studies on the preparation and the structure of the anhydrous form, and they have concluded on the basis of an X-ray crystallographic investigation that it is a trinuclear μ-oxo species, $Mn_3O(OAc)_6^+OAc^- \cdot HOAc$. Variable amounts of acetic acid persist as solvate, and the anhydrous material in our hands is better characterized as $Mn(OAc)_3$ (see Experimental Section). Be that as it may, in pivalic acid solutions we find that the chemical and kinetic behavior of the anhydrous form and the dihydrate of manganese(III) trisacetate are practically indistinguishable (vide supra).

The metathesis of manganese(III) acetate in a carboxylic acid medium is extensive. A solution of manganese(III) acetate in pivalic acid behaves the
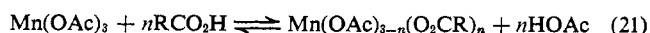
same as manganese(III) n-butyrate under the same

$$Mn(OAc)_3 + nRCO_2H \rightleftharpoons Mn(OAc)_{3-n}(O_2CR)_n + nHOAc \qquad (21)$$

conditions. Furthermore, proton transfer is not kinetically important since the reduction of pivalic acid shows no significant solvent (deuterium) isotope effect.

We attribute the reduction of Mn^{III} in pivalic acid to the homolysis of Mn^{III} pivalate directly to Mn^{II} with the liberation of t-butyl radicals and carbon dioxide.[16]

$$Mn^{III}O_2CC(CH_3)_3 \longrightarrow Mn^{II} + CO_2 + (CH_3)_3C \cdot \qquad (22)$$
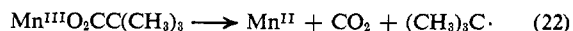
A variety of pivalatomanganese(III) species are, no doubt, extant in these solutions. We attribute the observed first-order kinetics to reduction of monomeric Mn^{III} species.[17,18]

The addition of varying amounts of acetic acid to a solution of Mn(III) in pivalic acid does not alter the products of oxidation (cf. Table I). There is, however, a marked increase in the overall enthalpy of activation for the reduction of Mn^{III} from 17.1 kcal/mole (-24 eu at 70°) in a solution of 0.2 M acetic acid to 34.6 kcal/mole ($+26$ eu) in 3.5 M acetic acid in pivalic acid.[19] The latter is comparable to values ($\Delta H^{\pm} = 32.5$ kcal/mole, $\Delta S^{\pm} = +15$ eu) previously measured for the decarboxylation of pivalic acid by Co^{III}. We attribute these differences to the various acetato-(pivalato)manganese(III) species extant in solution. Interestingly, the activation parameters become independent of the concentration of acetic acid when trifluoroacetic acid is present. Under these conditions the facility of ligand exchange, the presence of cationic Mn^{III} species and the dissociation of polynuclear Mn^{III} complexes are important factors. We cannot at present assess the importance of polynuclear manganese(III) species in solution. Any formulation, however, must be consistent with the first-order kinetics observed for the reduction of Mn^{III} by pivalic acid.[19]

Retardation by Manganese(II). The negative deviation from first-order kinetics observed after 60% reduction of Mn^{III} can be attributed to the retarding influence by the Mn^{II} formed in the reaction. This is supported by the diminished rate obtained when manganese(II) acetate is deliberately added to a solution of Mn^{III} in pivalic acid initially. Mn^{II} carboxylates exert an effect on the rate of reduction of Mn^{III} in excess of that produced by other metal carboxylates listed in Table VIII. Thus, the alkali metal trifluoroacetates evoke a small positive salt effect, while the corresponding acetates retard the rate slightly.

(12) Owing to the poor stoichiometry obtained in the reduction of Mn^{III} by these acids, it is doubtful whether the kinetic study of the reduction of Mn^{III} in caproic acid is meaningful (V. M. Gol'dberg and L. K. Obukhova, Izvest. Akad. Nauk SSR, 1419 (1967)).

(13) O. T. Christiansen, Z. Anorg. Chem., 27, 325 (1901).

(14) L. W. Hessel, Thesis, Leiden, 1968.

(15) L. W. Hessel and C. Romers, Rec. Trav. Chim., 88, 545 (1969).

(16) (a) The initiation of vinyl polymerization by thermolysis of Mn^{III} acetylacetonate has been reported [C. H. Bamford and D. J. Lund, Proc. Roy. Soc. (London), 302A, 145 (1968)]; (b) see, however, an alternative mechanism [M. A. Suwyn and R. E. Hamm, Inorg. Chem.- 6, 142 (1967)]; (c) C. F. Wells and C. Barnes [Discussions Faraday Soc., 46, 193 (1968)] suggest that oxidation of acids by Mn^{III} in aqueous solutions occurs by an outer-sphere mechanism.

(17) This would be contrary to Hessel's conclusion concerning the trimeric nature of Mn^{III} in acetic acid,[14] unless (a) extensive dissociation occurs in pivalic acid or (b) all polynuclear Mn^{III} species undergo homolysis at the approximately same rate.

(18) (a) This observation also makes it unlikely that Mn^{IV} formed by disproportionation is the species responsible for decarboxylation; (b) glycol oxidation with alleged Mn^{IV} acetate has been carried out [S. A. Zonis and A. G. Pesina, J. Gen. Chem. USSR, 20, 1223 (1950)].

(19) Such large changes in the activation parameters caused by the addition of acetic acid probably reflect a change in mechanism. Studies of Mn^{III} species in acetic acid and in pivalic acid are, therefore, not always comparable.

None of these alkali metal carboxylates perturb the absorption spectrum of Mn^{III} in pivalic acid significantly at the concentrations employed in the kinetic studies. Mn^{II} acetate, however, interacts with a Mn^{III} species in pivalic acid sufficiently strongly to replace the absorption band at 462 nm with a new band at 494 nm (Figure 3). The effect in pivalic acid is much more pronounced than that observed earlier by de Klein.[20] He also attributed the retarding effect of Mn^{II} in the reduction of Mn^{III} by acetic acid to the formation of an "interaction complex."
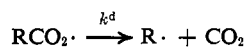
The absorption band at *ca.* 460 nm of Mn^{III} species in solution has been ascribed to a d–d transition (assigned as $^5B_{1g} \rightarrow {}^5E_g$ assuming D_{4h} symmetry).[21] Doubtlessly, Mn^{II} affects this transition in the Mn^{III} species although the mechanism of the interaction is not understood. Co^{II} acetate produces similar changes in the absorption spectrum of Mn^{III} and also exerts a retarding influence on the reduction of Mn^{III}.

We attribute the effect of Mn^{II} on the properties of Mn^{III} to the formation of a mixed valence complex[22] $Mn^{III}(O_2CR)_xMn^{II}$ which is less prone to undergo homolysis (eq 23) than the parent Mn^{III} carboxylates.

$$Mn^{III}(O_2CR)Mn^{II} \longrightarrow 2Mn^{II} + R\cdot + CO_2 \qquad (23)$$

We also attribute the effects of the Co^{II} additive to the formation of an analogous $Mn^{III}\cdot Co^{II}$ binuclear complex. We sought direct evidence for the $Mn^{III}\cdot Mn^{II}$ mixed valence complex by examination of the electron spin resonance spectrum in a manner similar to that recently employed in the $Cu^{I}\cdot Cu^{II}$ mixed valence complex.[23] No further splitting of the Mn^{II} sextet was observed in the presence of excess Mn^{III}. A slight line broadening was obtained which led to diminution of the peak-to-peak heights of the derivative signal of Mn^{II}. The results are ambiguous, however, since such line broadening may arise in alternative ways such as exchange due to bimolecular reactions between Mn^{II} and Mn^{III}.[24]

An alternative explanation involving *reversibility* in the reduction step (17) is highly unlikely because of the transient nature of the alkyl radical. The same objection applies to the reversible decomposition of the Mn^{III} complex *via* acyloxy radicals since it is well known that the lifetime of the acyloxy radical is very

$$Mn^{III}O_2CR \rightleftharpoons Mn^{II} + RCO_2\cdot$$

$$RCO_2\cdot \xrightarrow{k^d} R\cdot + CO_2$$

short ($k_d > 10^9$ sec^{-1} at 60°).[25] The retarding effect of Mn^{II} in the oxidation of arenes by Mn^{III} has been attributed by Dewar and coworkers[26] to reversibility

in the electron-transfer step (eq 24). However, aro-

$$Mn^{III} + ArH \rightleftharpoons Mn^{II} + ArH\cdot^+ \qquad (24)$$

matic cation-radicals are appreciably more stable than alkyl radicals and reversibility may very well pertain in the latter instance although the importance of mixed valence complexes as a factor in the retardation has not been fully assessed.[26,27]

Catalysis by Strong Acids. The addition of strong acids, such as perchloric, sulfuric, and trifluoroacetic acids, affect the reduction of Mn^{III} by carboxylic acids in several fundamental ways. First, the rate of reduction of Mn^{III} increases linearly with acid concentration (Table VIII and eq 9). The reaction also follows first-order kinetics to much higher conversions than obtained otherwise (*cf.* Figure 2). Second, the ability of the Mn^{III} species to oxidize alkyl radicals formed in the reduction of the Mn^{III} carboxylates is greatly enhanced (*cf.* R_{ox}/R_H ratios in Tables I, II, and III).

Metal carboxylates act as general bases in carboxylic acid media as shown earlier (eq 10). Similarly, Mn^{III} carboxylate can participate in ligand exchanges leading to a series of trifluoroacetato(carboxylato)manganese-(III) complexes. Trifluoroacetato ligands are less strongly complexing than acetato and related car-

$$Mn^{III}(O_2CR)_3 + nCF_3CO_2H \rightleftharpoons$$
$$Mn^{III}(O_2CR)_{3-n}(O_2CCF_3)_n + nRCO_2H \qquad (25)$$
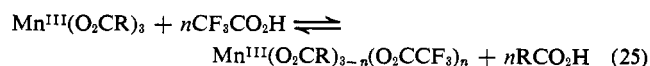
boxylato ligands, and both ion-pair formation (eq 26) as well as dissociation (eq 27) of these mixed carboxylatomanganese(III) complexes to cationic species is facilitated,[28,29] *e.g.*

$$Mn^{III}(O_2CR)_2(O_2CCF_3) \rightleftharpoons Mn^{III}(O_2CR)_2^+(O_2CCF_3)^- \quad (26)$$

$$Mn^{III}(O_2CR)_2^+(O_2CCF_3)^- \rightleftharpoons Mn^{III}(O_2CR)_2^+ + O_2CCF_3^- \quad (27)$$

We propose that these cationic manganese(III) species are responsible for the increased reactivity of Mn^{III} in the presence of strong (and noncomplexing) acids. Cationic transition metal species which exhibit coordinatively unsaturated behavior have been previously suggested for increased reactivity of Co^{III},[30] Ce^{IV},[31] and Ag^{II}[32] complexes in related oxidative decarboxylations. A similar phenomenon has been recently noted in the enhanced reactivity of cationic binuclear rhodium, ruthenium, and molybdenum carboxylates as hydrogenation catalysts when they are prepared by protonolysis of the transition metal carboxylates with strong acids.[33]

(20) In acetic acid Mn^{II} perturbs the spectrum of Mn^{III} slightly[9b] and no new maximum is observed as it is in pivalic acid.

(21) T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, 7, 1944 (1968).

(22) A variety of mixed valence complexes are known and the subject has been recently reviewed, M. B. Robin and P. Day, *Advan. Inorg. Radiochem.*, 10, 248 (1967); and N. S. Hush, *Progr. Inorg. Chem.*, 8, 391 (1967).

(23) (a) C. Sigwart, P. Hemmerich, and J. T. Spence, *Inorg. Chem.*, 7, 2545 (1968); (b) we wish to thank Dr. J. A. Heslop for suggesting this experiment.

(24) The difference between Cu^{II} and Mn^{II} in this regard may be due to much slower (on the esr time scale) exchange rates of the latter.

(25) (a) W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962); (b) M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p 153 ff.

(26) P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, 88, 5473 (1966).

(27) Mn^{II} also retards the oxidation of formic acid by Mn^{III} in sulfuric acid. Kemp and Waters [*J. Am. Chem. Soc.*, 64, 339 (1942)] attributed the retardation to disproportionation and suppression of the active oxidant Mn^{IV}. However, formic acid differs from other carboxylic acids in that it is susceptible to *two*-equivalent oxidants [J. Halpern and S. M. Taylor, *Discussions Faraday Soc.*, 29, 174 (1960)].

(28) (a) Metal acetates are generally very poorly dissociated in glacial acetic acid; (b) O. W. Kolling and J. E. Lambert, *Inorg. Chem.*, 3, 202 (1964); (c) P. J. Proll and L. H. Sutcliffe, *Trans. Faraday Soc.*, 57, 1078 (1961); (d) K. Heymann and H. Klaus, "Chemistry in Nonaqueous Ionizing Solvents," Vol. 4, G. Lander, H. Spandau, and C. C. Addison, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 88 ff.

(29) A similar effect of acids has been noted[30] with Co^{III}. Dissociation of Co^{III} carboxylates by trifluoroacetic acid is supported by cryoscopic measurements (to be published, S. S. Lande). Studies of Mn^{III} were discouraged by poor solubility.

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

(31) R. A. Sheldon and J. K. Kochi, *ibid.*, 90, 6688 (1968).

(32) J. M. Anderson and J. K. Kochi, *J. Org. Chem.*, 35, 986 (1970).

(33) P. Legzdins, G. L. Rempel, and G. Wilkinson, *Chem. Commun.*, 825 (1969).

Cationic manganese(III) carboxylates undergo homolysis readily and are less likely to form mixed valence complexes with Mn^{II} which retard reduction. The

$$Mn^{III}(O_2CR)_2^+ \longrightarrow Mn^{II}(O_2CR)^+ + R\cdot + CO_2 \quad (28)$$

marked increase in alkenes and esters under strong acid conditions also indicates that alkyl radicals are more readily oxidized by cationic Mn^{III} species than their neutral counterparts (vide infra).[34]

$$Mn^{III}(O_2CR)_2^+ + R\cdot \longrightarrow Mn^{II}(O_2CR)_2 + [R^+]_{ox} \quad (29)$$

Alkyl Radicals as Intermediates. Alkanes, alkenes, and esters are derived from the alkyl moiety as a result of oxidative decarboxylation. Alkanes arise from alkyl radicals by hydrogen abstraction from the solvent. Alkenes and esters are products of oxidation $[R^+]_{ox}$ of

$$R\cdot + SH \xrightarrow{k_H} RH + S\cdot \quad (30)$$

the alkyl radical by Mn^{III}, and are *formally* derived from the alkyl cation by loss of a β-proton or solvation by the carboxylic acid.[35] The relative rates of these

$$R\cdot + Mn^{III} \xrightarrow{k_{ox}} [R^+]_{ox} + Mn^{II} \quad (31)$$

two process (k_{ox}/k_H) are proportional to the ratio R_{ox}/RH in Tables I, II, and III for the t-butyl, isopropyl, and n-propyl radicals, respectively. We attribute the increased magnitudes of these values in the presence of strong acids to the more efficient oxidation of the alkyl radicals by cationic Mn^{III} species extant under these conditions (vide supra).

A more direct comparison of the rates of oxidation and hydrogen transfer of a pair of alkyl radicals can be obtained from the competitive decarboxylations in which a common solvent (hydrogen donor) is employed. Under these conditions (Table IV) k_{ox}/k_H for t-butyl radical is approximately 50 times greater than the value for isopropyl radical and at least 100 times greater than the value for n-propyl radical. Unfortunately, it is not possible by this procedure to make a quantitative and direct comparison between n-propyl and isopropyl radicals since they afford some products in common.

These relative values of k_{ox}/k_H reflect approximate differences in rates of oxidation since the rates of hydrogen abstraction of alkyl radicals generally do not vary widely.[36] On this basis, we conclude that the rate of oxidation of t-butyl radical by Mn^{III} is faster than that of isopropyl radical and much faster than that of n-propyl radical. We attribute this ordering of reactivities to the importance of carbonium ion character in the transition state for oxidation. Without further study it is difficult to say whether carbonium

ions are actually intermediates. The observation of isopropyl products from the oxidation of n-propyl radicals, however, does support such a formulation.[37]

Effect of Copper(II). When Cu^{II} is added to the reaction, the values of R_{ox}/RH increases dramatically and alkenes become the dominant products. Copper(II) does not materially affect the rate of reduction of Mn^{III} and must be involved subsequent to the rate-limiting homolysis. Previous studies have established that Cu^{II} is an exceedingly efficient trap for t-butyl, isopropyl, and n-propyl radicals. Isobutylene and propylene, respectively, are exclusive products of oxidation[38] which proceeds with a second-order rate constant of 10^8–$10^9 M^{-1} sec^{-1}$. The rapid reoxidation of Cu^I by Mn^{III} (which can be shown independently)

$$R\cdot + Cu^{II} \longrightarrow R(-H) + H^+ + Cu^I \quad (32)$$

enables the use of catalytic amounts of Cu^{II}. Comparisons show that Cu^{II} is significantly more efficient

$$Cu^I + Mn^{III} \longrightarrow Cu^{II} + Mn^{II} \quad (33)$$

than Mn^{III} in the oxidation of alkyl radicals despite its lower oxidation potential.

Effect of Oxygen. Alkyl radicals formed in the decarboxylation can also be intercepted by molecular oxygen. Thus, the decarboxylation of pivalic acid by Mn^{III} in the presence of an oxygen atmosphere leads to high yields of t-butyl alcohol, di-t-butyl peroxide, and acetone which can be directly attributed to the t-butylperoxy intermediate.[39]

$$(CH_3)_3C\cdot + O_2 \longrightarrow (CH_3)_3CO_2\cdot \quad (34)$$

$$2(CH_3)_3CO_2\cdot \left[\begin{array}{l} \longrightarrow 2(CH_3)_3CO\cdot + O_2 \text{ etc.} \quad (35) \\ \longrightarrow (CH_3)_3CO_2C(CH_3)_3 + O_2 \quad (36) \end{array} \right.$$

The yield of carbon dioxide is in large excess of the Mn^{III} actually reduced. Such a catalytic decarboxylation requires that Mn^{III} be regenerated from Mn^{II} under reaction conditions. Since oxygen is incapable of reconverting Mn^{II}, it is likely that alkoxy and alkylperoxy radicals are involved. Evidence for the latter has been recently presented by de Klein and Kooyman.[40] A formulation for the catalytic process is given by eq 37–39.

autoxidative decarboxylation catalyzed by Mn^{III}

$$(CH_3)_3CCO_2H + Mn^{III} \longrightarrow (CH_3)_3C\cdot + CO_2 + H^+ + Mn^{II} \quad (37)$$

$$(CH_3)_3C\cdot + O_2\cdot \longrightarrow [(CH_3)_3CO_2] \longrightarrow$$
$$(CH_3)_3CO\cdot + 0.5O_2 \quad (38)$$

$$(CH_3)_3CO\cdot + Mn^{II} + H^+ \longrightarrow (CH_3)_3COH + Mn^{III}, \text{etc.} \quad (39)$$

Competitive Decarboxylation. Competition studies presented in Table IV indicate that pivalic acid is decarboxylated 25 times faster than isobutyric acid and at least 500 times faster than n-butyric acid. These rela-

(34) An examination of the data in Tables III and IV suggests that the effect of trifluoroacetic acid on the oxidation and competitive oxidation of n-propyl radicals is marginal. However, we feel that the tabulation of R_{ox}/R_H in this case should be interpreted liberally due to the poor yields of R_{ox} obtained and the higher relative errors in these values due to limitations of the analysis.

(35) J. K. Kochi, R. A. Sheldon, and S. S. Lande, Tetrahedron, 25, 1197 (1969); (b) J. D. Bacha and J. K. Kochi, J. Org. Chem., 33, 83 (1968).

(36) (a) J. A. Kerr and A. F. Trotman-Dickenson, Progr. Reaction Kinetics, 1, 107 (1961); (b) a quantitative comparison between rates of oxidation of n-propyl and isopropyl cannot be made by this method since a change in solvent changes donor properties. Thus, it appears from Table IV that n-propyl radical is oxidized faster than isopropyl radicals on the basis of k_{ox}/k_H. This conclusion is unwarranted since isobutyric acid is a much better hydrogen donor than n-butyric acid.

(37) (a) Phenylacetic acid also yields benzyl acetate in high yields;[6] (b) n-propyl esters do not rearrange to isopropyl ester under reaction conditions; (c) an alternative suggestion has been proposed by Professor Kooyman that n-propyl esters arise by addition of n-propyl radical to the carbonyl group of Mn^{III} carboxylate followed by displacement of Mn^{II} (private communication).

(38) J. K. Kochi and R. V. Subramanian, J. Am. Chem. Soc., 87, 4855 (1965); J. K. Kochi, C. L. Jenkins, and A. Bemis, ibid., 90, 4616 (1968).

(39) P. D. Bartlett and T. G. Traylor, ibid., 85, 2407 (1963); A. Factor, C. A. Russell, and T. G. Traylor, ibid., 87, 3692 (1965).

(40) W. J. deKlein and E. C. Kooyman, J. Catal., 4, 626 (1965).

tive rates of decarboxylation include the preequilibrium formation of the respective carboxylatomanganese(III) species (eq 21). Since the decarboxylation of isobutyric acid by Mn^{III} acetate and Mn^{III} isobutyrate proceed at the same overall rates we conclude that the preequilibrium metathesis (eq 21) cannot be rate limiting. The rates of ligand exchange (carboxylato) on the Mn^{III} nucleus may vary significantly from pivalic to isobutyric or n-butyric acid.[41] Steric factors, however, should cause a *decrease* in the formation constants of various Mn^{III} carboxylates in the order n-butyric > isobutyric > pivalic acid. If this is correct the observed relative rates of decarboxylation must represent lower limits to rates of homolysis. These relative rates correlate with the stability of the alkyl radical $[(CH_3)_3C \cdot > (CH_3)_2CH \cdot > CH_3CH_2CH_2 \cdot]$ and suggest that the stretching of the alkyl–carbonyl bond in the transition state is simultaneous with the reduction of Mn^{III}. Multibond cleavage of the carboxylate

$$RCO_2Mn^{III} \longrightarrow [R \cdots CO_2 \cdots Mn] \neq \longrightarrow$$
$$R \cdot + CO_2 + Mn^{II} \quad (40)$$

moiety is also observed in decarboxylations effected by Co^{III}[30] and to a lesser extent Pb^{IV} oxidants.[35] On the other hand, the facile thermal decarboxylations induced by Ag^{II}[32] and photochemical decarboxylations by Ce^{IV}[31] show no selectivity. Acyloxy radicals have been proposed as intermediates which decarboxylate in a fast subsequent step.

$$RCO_2Ce^{IV} \xrightarrow{h\nu} Ce^{III} + RCO_2 \cdot \longrightarrow R \cdot + CO_2 \quad (41)$$
$$(1) \qquad\qquad (2)$$
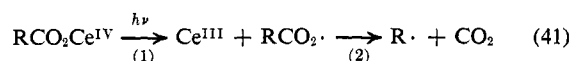
Multibond decarboxylations of acids by metal oxidants are associated with processes requiring a relatively high activation energy and derive driving force from the liberation of carbon dioxide. Stabilization of the alkyl radical also helps the concerted process, and t-alkyl radicals contribute the most and primary radicals the least toward lowering the barrier.[42]

Oxidative decarboxylation must compete with the alkyl oxidation of acids (eq 15) which depends on the availability of α-hydrogens. Tertiary acids, thus, represent optimum examples for oxidative decarboxylation whereas acetic and other primary acids are constructed for alkyl oxidation. The results presented in Tables I, II, and III are consistent with this trend. It is interesting to note that those oxidations (Ag^{II} and photochemical Ce^{IV}[43]) which proceed *via* acyloxy radicals are much less sensitive to the competiting alkyl oxidations, and high efficiency is achieved in the decarboxylation process even with acetic acid.

Summary. The oxidative decarboxylation of acids by Mn^{III} proceeds by multibond homolysis of a Mn^{III} carboxylate and simultaneously generates Mn^{II}, carbon

(41) The foregoing statements can be reconciled if one considers that the effects of minor differences in rates (especially of preequilibria) are highly magnified in a competitive situation. The discrepancy is especially serious when the homolysis of the Mn^{III} carboxylate is only slightly slower than the metathesis. The possibility that at least three carboxylato ligands in the Mn^{III} monomer and six in the trimer[14] can exchange serially complicates the issue further, especially since each of these Mn^{III} species probably decarboxylates at a different rate.

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

(43) The thermal decarboxylation of acids by Ce^{IV} is slow[31] except in the presence of strong acids, and recently Heiba and Dessa have shown that carboxymethyl radicals are formed in high yields from acetic acid. (We wish to thank these authors for kindly communicating these results to us prior to publication.)

dioxide, and an alkyl radical. The rate of reduction of Mn^{III} follows first-order kinetics but is retarded by the Mn^{II} formed during the reaction. Kinetic and spectral studies allude to a mixed valence complex between Mn^{III} and Mn^{II} carboxylates. The formation of these binuclear complexes is inhibited by strong acids which also accelerate the reduction of Mn^{III} by formation of cationic Mn^{III} species. The latter also oxidize alkyl radicals more efficiently than their neutral counterparts. Neither Mn^{III} species can compete, however, with the efficient Cu(II) scavenger which converts alkyl radicals clearly to alkenes. Pivalic acid undergoes catalytic decarboxylation in the presence of oxygen. The mechanism of this autoxidation follows directly from the mechanism of oxidative decarboxylation by Mn^{III}.

Experimental Section

Materials. Manganese(III) acetate dihydrate was prepared from potassium permanganate and manganese(II) acetate in glacial acetic acid.[26] It was dried *in vacuo* over potassium hydroxide for 3 days at room temperature. The electron spin resonance spectra showed the presence of less than 2 mole % Mn^{II}.

Anhydrous manganese(III) acetate was prepared by a modified method[6,14] and dried in the same manner after washing several times with anhydrous ether. The manganese(III) content was determined by treatment with a known excess ferrous solution followed by back-titration with a standard ceric solution. The analyses are given in Table X and compared with other data.

Manganese(III) n-butyrate dihydrate was prepared by metathesis of manganese(III) acetate dihydrate and n-butyric acid. The acetic acid was removed under vacuum. *Anal.* Calcd for $C_{12}H_{25}O_8Mn$: 15.6% Mn^{III}. Found: 15.1% Mn^{II}.

Table X. Elemental Analyses of Mn^{III} Complexes

| | Calcd, % | | | Found, % | | |
	Mn^{III}	C	H	Mn^{III}	C	H
$Mn(OAc)_3 \cdot 2H_2O$	20.5	26.87	4.85	20.9	27.34	4.95
$Mn(OAc)_3$	23.67	31.05	3.91	23.6	30.12	4.10
$Mn_3(OAc)_8OH^a$	25.3	29.36	3.82	25.2[a]	29.40[a]	

[a] See ref 15.

All acids were purified by distillation. The Enjay Chemical Co. generously donated the pivalic acid. The esters, whether obtained from commercial sources or prepared by standard procedures, were distilled before use. The metal acetates and trifluoroacetates used in our studies were dried at 100° *in vacuo* for 24 hr. Pivalic acid-*d* and acetic acid-*d* were prepared as described previously.[30]

Product Studies. General Procedure. Approximately 2.7 mmoles of manganese(III) acetate and other salts as required were weighed into a 50-ml round-bottom flask. A 10-ml sample of the appropriate carboxylic acid was added by pipet and the flask sealed with a gas-tight rubber septum. All rubber septa were washed with toluene and acetone to remove inhibitors. The flask was degassed *in vacuo* for 30 min. Acid catalysts when needed were dissolved in the carboxylic acid, degassed, and added to the reaction vessel *via* a hypodermic syringe. The flask was then placed in a thermostated oil bath and the contents were stirred magnetically.

The completion of the reaction in most cases was determined visually by a change in color from dark red-brown to colorless. Cupric acetate obscured the visual end point and these reactions were allowed to run for approximately one and one-half times as long as the uncatalyzed reaction to ensure completion. The oxygen-bomb experiment was carried out using a procedure previously described.[30]

Analytical Procedure. When the reaction was complete, the reaction flask was immediately cooled in a carbon dioxide–isopropyl alcohol bath and known volumes of reference gases were added with a hypodermic syringe. The reaction flask was warmed

to room temperature, helium added to increase the pressure to slightly above atmospheric, and the flasks were vigorously shaken. The gases were then analyzed by gas chromatography. Mixtures of known volumes of products and reference gases were analyzed under reaction conditions to obtain calibration factors.

After the gas analysis, a reference ester was added to the reaction solution and the solution brought to a volume of 50 cc with glacial acetic acid. A 15-ml aliquot of the solution was then added to 15 ml of diethyl ether. The ether solution was washed three times with water and three times with saturated sodium bicarbonate solution to remove the excess carboxylic acid. The ether solution was analyzed for ester products by gas chromatography. Solutions containing known concentrations of product and reference esters were analyzed in the same manner to obtain calibration factors.

Gas chromatographic analyses of gaseous products were performed on instruments equipped with thermal conductivity detectors. Carbon dioxide was analyzed on a 2-ft Poropak Q column at room temperature using ethane as a reference gas. Propane, propene, isobutane, and isobutene were analyzed on a 15-ft 30% Dowtherm on firebrick column at room temperature using n-butane as a marker.

Esters were analyzed on instruments employing flame-ionization detectors (Varian Aerograph, Model 1200, and Varian Aerograph, Model 200). An 8-ft DEGS column was used to analyze n-propyl n-butyrate, isopropyl n-butyrate, isopropyl isobutyrate, and isopropyl acetate with n-butyl acetate as the marker. A 6-ft Morflex column was used to analyze t-butyl pivalate and t-butyl acetate with n-butyl acetate as the marker.

Kinetic Procedure. Kinetics were followed on a Beckmann DB-G spectrophotometer equipped with a Sargent Model SRLG recorder. Temperature control was within $\pm 0.4°$ in the thermostated compartment. The manganese(III) acetate concentrations were determined spectrophotometrically at 462 nm (shoulder).

Stock solutions of $ca.$ 1.3×10^{-2} M manganese(III) acetate in pivalic acid were used and diluted by a factor of 5 with pivalic acid for the kinetic studies. Added acids and bases were dissolved in pivalic acid and added as required.

After the reaction solution had been made up, a portion was transferred to a 1-cm cell which was sealed with a rubber septum. The solution was then degassed with helium introduced through a hypodermic needle for 10–15 min. The cell was preheated with shaking to within 10° of the desired temperature before being placed in the spectrophotometer.

Epr Method. All spectra were run on a Varian E-3 epr spectrometer. The same sample tube was used for the sample Mn^{III} and standard Mn^{II} solutions. The temperature was controlled to within 1.0°.

Organoboranes. IX. Structure of the Organoboranes Formed in the Reaction of 1,3-Butadiene and Diborane in the Stoichiometric Ratio. An Unusual Thermal Isomerization of These Organoboranes

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Abstract: The hydroboration of 1,3-butadiene with diborane in the stoichiometric ratio at 0° produces predominantly the dumbbell-shaped structures, 1,3- and 1,4-bis(1-boracyclopentyl)butanes. Although the ratio of the two major isomers varies somewhat with the reaction conditions, the 1,3 isomer is the preferred product, $\sim 70\%$, under kinetically controlled conditions. Under isomerization conditions (140–170°), this isomer rapidly vanishes and the product is converted into 75% 1,1- and 25% 1,4-bis(1-boracyclopentyl)butanes. Independent syntheses of 1,1- and 1,4-bis(1-boracyclopentyl)butanes was achieved by treating 1-butyne and 1,3-butadiene with B-methoxyboracyclopentane and lithium aluminum hydride. The structure of the 1,4 isomer was confirmed by treatment with carbon monoxide to form 1,1'-tetramethylenedicyclopentanol. In marked contrast to the behavior of simple trialkylboranes, the boracyclopentane ring is readily opened by solvolysis with water or alcohol. Deuterolysis with heavy water, followed by oxidation, provides a convenient synthesis of 1-butanol-4-d_1. The present understanding of the reaction products and the chemistry of "bisborolane" permits postulation of a reaction mechanism for the hydroboration of 1,3-butadiene.

T he cyclic hydroboration of dienes with thexylborane[2] followed by carbonylation provides a convenient new synthetic route to cyclic and polycyclic ketones.[3,4] Hydroboration with diborane, followed by carbonylation, has been successfully applied

to trienes[5] and to one diene, 1,5-cyclooctadiene.[6] However, extension of this promising new synthetic approach to dienes generally has been handicapped by the confused state of our knowledge as to the structure of the products formed from the reaction of diborane with dienes.[7]

(1) Postdoctorate Research Associate on a research grant, DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

(2) H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967).

(3) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

(4) For a general review of this development with complete literature references, see H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

(5) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5478 (1967); H. C. Brown and W. C. Dickason, *ibid.*, **91**, 1226 (1969); H. C. Brown and E. Negishi, *ibid.*, **91**, 1224 (1969).

(6) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280, 5281, 5283 (1968).

(7) The hydroboration-oxidation of dienes has been subjected to detailed study. However, for such production of enols or diols, the precise structure of the boron intermediates is not of major importance and