τ 7.79 for the methyl ketone protons, a sharp six-proton singlet at τ 8.34 for the *gem*-dimethyl group, and a methyl doublet (J = 7.0 Hz) at τ 8.79.

The infrared spectrum (CCl_4) of **12** showed absorbances indicative of an α,β-unsaturated ketone at 1680 ($\nu_{C=O}$) and 1625 cm^{-1} (ν_{C-C}). The nmr spectrum (CCl_4) showed three singlets at τ 7.95, 8.17, and 8.27 in the area ratio 1:2:1. The two high-field resonances were slightly broadened due to long-range coupling.

A separate experiment showed that treatment of 1.0 g (0.0066 mol) of **11** with a 20% solution of sodium carbonate (20 ml, 4 g, 0.04 mol) for 15 min at reflux in 15 ml of carbon tetrachloride led to a clean conversion to 0.67 g (0.0060, 91%) of **12**.

Acetylation of Methylcyclopropane. Since methylcyclopropane is a gas (bp 4°) this acetylation was run using the procedure outlined for the normal acetylation of cyclopropane. Methylcyclopropane (Chemical Procurement Laboratories) was purified by slowly passing it through a trap containing saturated, neutral potassium permanganate solution, then through a trap containing anhydrous calcium sulfate (Drierite) and collecting the gas in a vessel cooled in a Dry Ice–acetone bath. The resultant material showed only a single vpc peak and was free of alkenes. A 0.10 M scale reaction (5.5 g of methylcyclopropane) in 50 ml of methylene chloride was carried out at 0° for 1 hr. The reaction was monitored by vpc using a 5-ft QF-1 column at 130° with a helium flow rate of 70 cc/min. Three major products with retention times of 0.70, 3.0, and 4.0 min were observed.

The compound with the retention time of 0.70 min, formed in 12% yield, was a clear, colorless liquid. It was identical with the unsaturated ketone formed in the acetylation of 2-butene, *i.e.*, 3-methyl-3-penten-2-one (**9**). The ir spectrum (CCl_4) had principal bands at 1670 ($\nu_{C=O}$) and 1640 cm^{-1} ($\nu_{C=C}$). The nmr spectrum (C_6D_6 solution) showed a quartet of quartets (J_{gem} = 7.0 Hz, J_{vic} = 1.4 Hz) at τ 3.68 for the vinyl proton, a singlet at τ 8.00 for the methyl ketone protons, a three-proton multiplet centered at τ 8.25 (C-3 methyl group), and an eight-line resonance at τ 8.58 for the remaining methyl group.

The second product, retention time 3.0 min, was formed in 18% yield. The structure was shown to be 4-chloro-3-methyl-3-pentanone (**8**) on the basis of its ir and nmr spectra. The carbonyl band in the ir spectrum (CCl_4) appeared at 1710 cm^{-1}. The nmr spectrum (CCl_4) consisted of a one-proton multiplet centered at τ 5.80 (C-4 proton), a one-proton multiplet at τ 7.32 (C-3 proton), a singlet for the methyl ketone protons at τ 7.82, a doublet (J = 6.5 Hz) at τ 8.50 (C-4 methyl), and a doublet (J = 7.0 Hz) at τ 8.87 (C-3 methyl).

The major product, formed in 65% yield, had a retention time of 4.0 min. It was shown to be 5-chloro-2-hexanone (**7**) by its ir and nmr spectra. The ir spectrum (CCl_4) had the carbonyl stretch at 1710 cm^{-1}. The nmr spectrum (CCl_4) showed a one-proton multiplet centered at τ 6.02 (methine proton), a triplet (J = 7.0 Hz) at τ 7.38 for the two protons adjacent to the carbonyl function, a singlet at τ 7.92 for the methyl ketone protons, a complex multiplet centered at τ 8.08 for the C-4 methylene protons, and a doublet (J = 6.5 Hz) at τ 8.48 for the C-6 methyl protons.

Formation and Oxidation of Alkyl Radicals by Cobalt(III) Complexes

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Abstract: The homolysis of Co^{III} carboxylates, formed by metathesis of Co^{III} acetate in a carboxylic acid medium, follows first-order kinetics. The products derived from the decarboxylation of the acid arise from an alkyl radical precursor. Primary and secondary propyl radicals from n-butyric and isobutyric acids, respectively, afford principally propane by hydrogen transfer from solvent. Oxidation by Co^{III} is a minor reaction. These radicals are, however, readily intercepted by catalytic amounts of Cu^{II} salts and propylene is generated in quantitative yields. On the other hand, t-butyl radicals from the decarboxylation of pivalic acid are readily oxidized by Co^{III}. t-Butyl radicals are trapped efficiently by oxygen, and the regeneration of Co^{III} from Co^{II} by reaction with t-butylperoxy and t-butoxy radicals allows for the catalytic oxidative decarboxylation of pivalic acid. Strong acids markedly enhance the rates of both decarboxylation and oxidation of alkyl radicals by Co^{III}. Cationic carboxylatocobalt(III) complexes, proposed as the reactive species responsible for facile homolysis, are also capable of the oxidation of primary and secondary alkyl radicals as well as alkenes. Carboxylate salts also promote decarboxylation by Co^{III} *via* anionic carboxylatocobaltate(III) complexes. The latter, however, are ineffective toward primary and secondary alkyl radicals. A mechanism for the oxidation of alkyl radicals by various Co^{III} complexes is proposed.

A variety of transition metal complexes catalyze the autoxidation of organic compounds in nonaqueous media by an oxidation–reduction process.[1] Prominent among these are cobalt compounds, which function between the Co^{II} and Co^{III} oxidation states. In order to examine the mechanisms of these complex and interesting catalytic processes, it is desirable to elucidate some fundamental reactions between the metal species and the organic substrate.

Co^{III} complexes have been utilized as oxidants for a number of types of functional groups.[2] The decarboxylation of aliphatic acids induced by cobaltic ion in aqueous perchloric acid solutions has been examined by Waters and coworkers,[3] who found an inverse acid dependence of rate. They proposed a mechanism which involves the reversible replacement of water on the Co^{III} nucleus by carboxylato ligands, and subsequent homolysis to Co^{II}, carbon dioxide, and alkyl radical. The latter participated in the induced oxidation of toluene.

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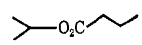
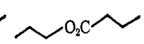
[1] (a) For a review see E. Denisov and N. Emanuel, *Russ. Chem. Rev.*, **29**, 645 (1960); also "Liquid Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967; (b) "Oxidation of Organic Compounds," Vol. II, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968.

[2] (a) W. Waters and J. Littler, "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 186 ff.

[3] (a) A. Clifford and W. Waters, *J. Chem. Soc.*, 2796 (1965); (b) T. Cooper, A. Clifford, D. Mills, and W. Waters, *ibid.*, *B*, 793 (1966).

Table I. Decarboxylation of *n*-Butyric Acid by Co^{III} at 100° [a]

Co^{III}-$(OAc)_3$, mmol	Additive	Add./Co^{III} [e]	Time [f]	Products, mmol: CO_2	$2CO_2$/Co^{III}					R_{ox}/∧ [b]	$\Sigma R\cdot$/CO_2 [c]
2.92	None		360	1.41	0.96	0.74	0.06	0.00	0.07	0.2	0.61
3.54	H_2SO_4	1.1	~1	0.74	0.43	0.33	0.07	<0.01	0.03	0.3	0.58
2.77	H_2SO_4	1.9	~1	0.48	0.34	0.04	0.03	0.12	0.05	0.5	0.50
2.79	H_2SO_4	5.8	~1	0.49	0.33	0.04	0.01	0.05	0.02	2.0	0.25
3.66	CH_3SO_3H	0.8	30	1.01	0.61	0.63	0.16	0.03	0.05	0.4	0.86
2.91	CH_3SO_3H	1.5	19	0.94	0.64	0.54	0.06	0.04	0.10	0.4	0.89
2.93	CH_3SO_3H	7.0	2.5	0.52	0.34	0.08	0.05	0.03	0.08	2.0	0.46
2.88	$HClO_4$	0.8	52	1.28	0.88	0.94	0.05	0.03	0.05	0.1	0.83
2.89	$HClO_4$	2.5	17	0.75	0.52	0.29	0.04	0.13	0.08	0.9	0.72
2.90	$HClO_4$	4.2	6	0.78	0.54	0.31	0.01	0.12	0.07	0.7	0.66
2.88	BF_3		30	1.65	1.13	1.16	0.05	0.09	0.07	0.2	0.82
2.93	BF_3		20	1.37	0.94	1.05	0	0.12	0.06	0.2	0.90
2.89	BF_3		35	1.76	1.19	1.22	0.03	0.07	0.05	0.1	0.78
2.95	CF_3CO_2H	1.1	65	1.62	1.09	0.95	0.17	0.04	0.10	0.3	0.78
2.96	CF_3CO_2H	3.1	19	1.60	1.09	1.21	0.16	0.04	0.09	0.2	0.93
2.91	CF_3CO_2H	5.4	16	1.72	1.17	1.26	0.20	0.04	0.08	0.3	0.92
2.93	CF_3CO_2H/Cu^{II}	3.1/0.08	13	1.47	1.02	0.04	1.09	0.00	t [g]	>10	0.77
2.97	H_2O	49	140	0.58	0.39	0.08	0.14	0.00	<0.01	1.8	0.38
5.25 [d]	C_5H_5N	1.0	100	2.21	0.84	1.08	0.05	...	...	<0.01	0.51

[a] In solutions containing 10 ml of *n*-butyric acid. [b] R_{ox} include propylene and isopropyl and *n*-propyl butyrate. [c] $\Sigma R\cdot$ includes propane and R_{ox}. [d] Reaction at 140°. [e] mmol/mmol. [f] For completion. [g] t = trace.

Studies of Co^{III} species in aqueous solution suffer from some severe limitations. Cobaltic ions, partly dimeric, also oxidize water at a rate inversely proportional to the concentration of acid.[4] High acidities are limited by the leveling effect of water. Furthermore, alcohols as products of oxidation of alkyl radicals in water are highly prone to further oxidation and, thus, obscure the primary reactions.[5]

In this study we have examined the formation and oxidation of alkyl radicals from the decarboxylation of aliphatic acids by Co^{III} as a part of a continuing study of the mechanism of oxidation processes induced by metal species.[6] Reactions were carried out in nonaqueous solutions in order to obviate problems dealing with the stability of the products and to relate Co^{III} with other oxidants.[7,8] More importantly, the use of carboxylic acid media allowed us to employ catalysis by strong acids in order to examine effects unobservable in aqueous solution. The mechanism of the decarboxylation of acids and subsequent oxidation of alkyl radicals by Co^{III} species is the pertinent objective.

Related studies involve the decarboxylation of aromatic acids to aryl radicals induced by cobalt salts in the presence of peroxides and oxygen by Starnes,[9] as well as the cobalt-catalyzed oxidation of butyric acid.[10] The reduction of Co^{III} acetete in aqueous solution by addition of dilute mineral acids has been noted.[11]

Results

Decomposition of Cobalt(III) Carboxylates. Product Studies. Cobalt(III) acetate was soluble[12] in a variety of carboxylic acids, which were employed as solvent. The rate of solution of Co^{III} acetate in acetic acid was especially slow, but solutions were stable at room temperature and allowed for complete dissolution without decomposition. The thermal decomposition of Co^{III} acetate was examined in three representative aliphatic carboxylic acids: *n*-butyric (primary), isobutyric (secondary), and pivalic (tertiary) acids. The reactions were carried out in a constant temperature bath in the absence of air. The rates were followed throughout the course of decomposition by monitoring the evolution of gas, which could be done reproducibly to ±3%. However, for analytical purposes, it was much more convenient to conduct reactions in closed evacuated vessels and follow the disappearance of the green color of Co^{III} species. The end of the reaction was marked by a distinct color change. We found this more convenient method to be as reliable as gas evolution for qualitative but meaningful indications of rates of Co^{III} disappearance. The total lapsed time for the reaction, measured by this method, was reproducible to within 10%. In the following, the products of reduction of Co^{III} in *n*-butyric, isobutyric, and pivalic acids will be discussed separately.

Reduction of Co^{III} in *n*-Butyric Acid. The thermolysis of Co^{III} in butyric acid proceeded slowly at 100° to produce Co^{II}, carbon dioxide, and propane (eq 1),[13,14] together with minor amounts of propylene and

$$Co^{III} + CH_3CH_2CH_2CO_2H \longrightarrow Co^{II} + CH_3CH_2CH_3 + CO_2 \quad (1)$$

propyl esters given in Table I. The rate of production of carbon dioxide coincided with the reduction of Co^{III}. Both rates could be markedly accelerated by the addition of a variety of strong acids, including sulfuric, methanesulfonic, perchloric, and trifluoroacetic acids, as well as boron trifluoride (*cf.* column 4 in Table I). The rates increased with acid concentration, but the

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(4) (a) M. Anbar and I. Pecht, *J. Am. Chem. Soc.*, **89**, 2553 (1967); (b) C. Bawn and A. White, *J. Chem. Soc.*, 331 (1951).

(5) D. Hoare and W. Waters, *ibid.*, 965 (1962); 2552, 2560 (1964).

(6) J. Kochi, *Record Chem. Progr.*, **27**, 207 (1966).

(7) (a) J. Kochi, *J. Am. Chem. Soc.*, 87, 3609 (1965); (b) J. Kochi, J. Bacha, and T. Bethea, *ibid.*, **89**, 6538 (1967).

(8) J. Kochi and T. Bethea, *J. Org. Chem.*, **33**, 75 (1968).

(9) W. Starnes, *ibid.*, **31**, 1436 (1966).

(10) R. Van Helden, A. Bickel, and E. Kooyman, *Rec. Trav. Chim.*, **80**, 1257 (1961).

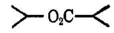
(11) (a) J. Sharp, *J. Chem. Soc.*, 2030 (1957); (b) M. Mori, E. Kyuno, and M. Shibata, *J. Chem. Soc. Japan*, 77, 1434 (1956).

(12) S. Lande and J. Kochi, to be published.

(13) In the following presentation the coordination around cobalt will not be included unless it is required for discussion. Generally octahedral coordination pertains.

(14) The reaction is not balanced since the reaction was not stoichiometric.

Table II. Decarboxylation of Isobutyric Acid by Co^{III} at 80° [a]

Co^{III}-$(OAc)_3$, mmol	Additive	Add./Co^{III} [i]	Time,[j] min	Products, mmol CO_2	$2CO_2/(Co^{III})$				$R_{ox}/\wedge$ [b]	$\Sigma R\cdot/CO_2$ [c]
2.91	None		800	1.93	1.33	1.40	0.17	0.20	0.3	0.92
3.00[d]	None		800	2.12	1.41	1.48	0.13	0.22	0.3	0.87
2.94	CF_3CO_2H	1.4	170	2.04	1.39	1.12	0.35	0.29	0.7	0.86
2.98	CF_3CO_2H	4.1	100	1.66	1.11	0.48	0.67	0.37	2.2	0.92
2.94	CF_3CO_2H	7.0	80	1.52	1.07	0.26	0.87	0.35	4.7	0.98
2.94	CF_3CO_2H/Cu^{II}	1.4/0.10	110	1.58	1.07	0.06	1.53	0.08	27	1.02
2.94	CF_3CO_2H/Cu^{II}	1.4/0.08	95	1.51	1.02	0.06	1.50	0.09	27	1.03
2.97	CH_3SO_3H	1.6	130	1.51	1.02	0.56	0.36	0.28	1.1	0.80
2.96	CH_3SO_3H	4.7	6	0.85	0.58	0.04	0.29	0.21	>20	0.64
2.94	CH_3SO_3H	7.8	6	0.72	0.49	0.05	0.23	0.19	>20	0.65
2.95	H_2SO_4	0.3	520	1.80	1.22	1.32	0.22	0.18	0.3	0.95
2.95	H_2SO_4	0.6	350	1.66	1.12	0.85	0.25	0.16	0.5	0.76
2.74	H_2SO_4	1.0	180	1.21	0.88	0.29	0.32	0.19	1.8	0.66
2.94	H_2SO_4	1.3	15	0.83	0.56	0.03	0.35	0.15	>20	0.61
2.95	H_2SO_4	1.9	5	0.88	0.60	0.03	0.25	0.14	>20	0.48
2.94	H_2SO_4	5.7	5	0.74	0.51	0.01	0.09	0.17	>20	0.42
2.96	$HClO_4$	1.2	180	1.45	0.98	0.47	0.41	0.40	1.7	0.88
2.95	$HClO_4$	2.4	40	0.90	0.61	0.11	0.13	0.48	5.5	0.80
2.97	$HClO_4$	3.7	9	0.91	0.61	0.11	0.08	0.61	6.3	0.88
2.95	BF_3		25	1.68	1.34	0.43	0.42	0.89	3.0	1.03
2.98	BF_3		35	1.83	1.23	0.54	0.63	0.60	2.3	0.97
4.80[e]	C_5H_5N	1.2	1400	1.98	0.83	1.96	0.12	...	<0.1	1.05
2.91	NaIB[f]	5.1	50	1.73	1.19	0.92	0.19	0.24	0.5	0.78
2.95	NaIB[f]	1.0	300	1.82	1.23	0.77	0.32	0.11	0.6	0.66
2.95	NaTF[g]	4.7	50	1.84	1.24	1.19	0.20	0.18[h]	0.3	0.85
2.95	NaTF[g]	1.0	300	1.70	1.15	0.94	0.19	0.16	0.4	0.76

[a] Reaction in 10 ml of isobutyric acid. [b] R_{ox} includes propylene and isopropyl isobutyrate. [c] Sum of R· includes propane and R_{ox}. [d] Co^{II} isobutyrate. [e] Reaction at 100°. [f] Sodium isobutyrate. [g] Sodium trifluoroacetate. [h] Includes isopropyl trifluoroacetate. [i] mmol/mmol. [j] For completion.

yields of carbon dioxide generally fell with acid, the exceptions being trifluoroacetic acid and boron trifluoride (columns 5 and 6). In the same manner, the amounts of propylene and esters relative to propane also increased with added acid (column 11).

Catalytic amounts (~5%) of Cu^{II} altered the reaction dramatically. Propylene was formed in excellent yields according to eq 2. Propane and esters were minor products, which disappeared entirely at slightly higher Cu^{II} concentrations. The rate of decarboxylation was increased approximately 50% by Cu^{II}, but beyond a lower limit (3%), the rate was independent of Cu^{II}.

$$2Co^{III} + CH_3CH_2CH_2CO_2H \xrightarrow{Cu^{II}} 2Co^{II} + CH_3CH{=}CH_2 + 2H^+ + CO_2 \quad (2)$$

Reduction of Co^{III} in Isobutyric Acid. The decarboxylation of isobutyric acid by Co^{III} occurred more readily than that of *n*-butyric acid, and studies could be carried out readily at 80°. Furthermore, the yields of carbon dioxide and products derived from the isopropyl moiety were significantly higher (see columns 5 and 11, Table II). Propane was the major product.

$$Co^{III} + (CH_3)_2CHCO_2H \longrightarrow Co^{II} + CH_3CH_2CH_3 + CO_2 \quad (3)^{14}$$

Minor amounts of propylene and isopropyl isobutyrate were also formed, in addition to small yields of methacrylic, tetramethylsuccinic, and α-isobutyroxyisobutyric acids.

The rate of decarboxylation of isobutyric acid by Co^{III} could also be enhanced by addition of strong acids (see column 4, Table II). Propylene and isopropyl esters were formed in relatively high proportions. Sulfuric, methanesulfonic, and perchloric acids, followed by boron trifluoride and trifluoroacetic acid, were the most effective acids in optimizing these oxidation products relative to propane (Table II, column 10). These strong acids, however, materially affected the amount of decarboxylation. Yields of carbon dioxide fell with increasing concentrations of acid (Table II, columns 3 and 6). The effects which strong acids created on the rates and products of decomposition of *n*-butyric acid were accentuated in the isobutyric isomer. Under equivalent conditions, the amounts of propylene (and ester) produced relative to propane were approximately half again to twice as large from the decarboxylation of isobutyric compared to *n*-butyric acid.

Salts such as sodium isobutyrate and trifluoroacetate also increased the rate of decarboxylation of isobutyric acid by Co^{III}. The products and their relative yields, however, were singularly unaffected (Table II).

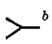
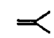
When catalytic amounts of Cu^{II} were added, propylene was generated in almost quantitative yields according to eq 4. The rate of decarboxylation also increased by roughly 60%.

$$2Co^{III} + (CH_3)_2CHCO_2H \xrightarrow{Cu^{II}} 2Co^{II} + CH_3CH{=}CH_2 + 2H^+ + CO_2 \quad (4)$$

Decarboxylation of Pivalic Acid by Co^{III}. The decarboxylation of pivalic acid by Co^{III} was examined at 60°. It occurred much more readily than that of isobutyric acid. The reduction of Co^{III} proceeded with complete oxidation of the *t*-butyl moiety to isobutylene and *t*-butyl pivalate according to eq 5. Only traces of isobutane were formed even in the absence of either strong mineral acid or Cu^{II} salts required with isobutyric and *n*-butyric acids (Table III).

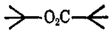
$$(CH_3)_3CCO_2H + 2Co^{III} \longrightarrow [(CH_3)_2C{=}CH_2 + (CH_3)_3CO_2CC(CH_3)_3] + CO_2 + 2Co^{II} + 2H^+ \quad (5)$$

Table III. Decarboxylation of Pivalic Acid by Co^{III} at 60° [a]

Co^{III}-$(OAc)_3$, mmol	Additive	Add.[e]/Co^{III}	Time,[f] min	Products, mmol: CO_2	$2CO_2/Co^{III}$	 [b]		+OAc	$+O_2C+$	$\Sigma R\cdot/CO_2$[c]
2.98	None	. . .	900	1.65	1.10	t	1.37	0.04	0.14	0.94
2.97[d]	None	. . .	120	1.70	1.15	t	1.23	0.04	0.21	0.87
2.98	CH_3SO_3H	0.3	500	1.72	1.15	t	1.17	0.04	0.19	0.82
2.97	CH_3SO_3H	0.5	350	1.70	1.15	t	1.11	0.07	0.38	0.91
2.88	CH_3SO_3H	1.6	300	1.41	0.98	t	0.38	0.08	0.67	0.82
2.89	CH_3SO_3H	4.8	10	0.84	0.58	0	0.05	0.02	0.10	0.22
2.98	CF_3CO_2H	1.4	500	1.69	1.13	t	1.30	0.04	0.15	0.78
2.98	CF_3CO_2H	4.1	130	1.76	1.10	t	1.10	0.03	0.25	0.88
2.99	CF_3CO_2H	6.8	70	1.76	1.18	t	0.80	0.03	0.33	0.66
2.94[d]	CF_3CO_2H	0.9	70	1.66	1.13	t	1.38	0.02	0.11	0.91
2.94[d]	CF_3CO_2H/Cu^{II}	0.9/0.067	50	1.49	1.01	0	1.56	0.04	0.13	0.94
2.97	H_2SO_4	0.6	600	1.53	1.03	t	0.67	0.02	0.57	0.81
2.97	H_2SO_4	1.3	160	1.24	0.84	t	0.15	0.03	0.57	0.61
2.94	$HClO_4$	2.5	400	1.31	0.88	0	0.21	0.02	0.65	0.67

[a] Solutions in 10 ml of pivalic acid containing 4 wt % acetic acid. [b] Traces (~0.01 mmol); 0 indicates <0.005 mmol. [c] ΣR· includes isobutane, isobutylene, and *t*-butyl esters. [d] Reactions at 80°. [e] mmol/mmol. [f] For completion.

Table IV. Effect of Oxygen and Peroxide on Decomposition of Co^{III} in Pivalic Acid[a]

Cobalt acetate, mmol	Additive	O_2 (psig)	Time,[g] min	Products, mmol: CO_2		 [h]	+OH		$(t\text{-}BuO)_2$
Co^{III} (2.97)	None	0	120	1.70	1.23	0.21	0	0	0
Co^{III} (2.97)	None	40	1200[f]	>10	<0.01	0	8.28	1.82	0.52
Co^{III} (2.97)	CF_3CO_2H[b]	0	80	1.67	1.36	0.25	0	0	0
Co^{III} (2.97)	CF_3CO_2H[b]	40	1200[f]	>15	<0.01	0	13.83	2.19	0.96
Co^{II} (3.12)	None	40	1200[f]	~15	<0.01	0	11.56	2.52	0.80
Co^{III} (2.97)	DTBP[c]	0	720	1.68	1.37	. . .	0	0	0.71
Co^{III} (2.97)	None	0	120	1.70	1.23	. . .	0	0	0
Co^{II} (3.12)	DTBP[c]	0	720		0	0	0	0	0.68
Co^{II} (3.12)	DTBP[d]	0	720[e]	0.85	0.19	. . .	0.43	0	0.79
None	DTBP[d]	0	720[e]	0.14	0	. . .	0.16	0.48	1.15

[a] Reactions at 80° in 10 ml of pivalic acid contained in 150-ml, glass bomb reactor. [b] CF_3CO_2H/Co^{III} = 1.4. [c] 0.71 mmole of di-*t*-butyl peroxide. [d] 1.73 mmol of di-*t*-butyl peroxide. [e] Reactions at 105–110°. [f] Co^{III} not exhausted. [g] For completion. [h] Includes acetate.

The rate of decarboxylation of pivalic acid by Co^{III}, like isobutyric and butyric acids, was enhanced by strong acids. Since isobutylene was the major product in the absence of acid, the latter had no effect on the course of oxidation other than decreasing the amount of decarboxylation at high acid concentrations (*vide infra*). Cu^{II} exerted little or no effect on either the course or the rate of reaction.

Since the stoichiometry of the decarboxylation of pivalic acid by Co^{III} could be represented uniformly by eq 5 under a variety of conditions, we chose this system to probe the mechanism of decarboxylation further. Three principal objectives were pursued: (a) effect of oxygen, to delineate the role of alkyl radicals as intermediates, (b) competition involving several acids, to determine rates of decarboxylation and to ascertain rates of oxidation of alkyl radicals by Co^{III}, (c) general acid and base catalysis, to provide information about the nature of the Co^{III} oxidant.

Effect of Oxygen on the Decarboxylation of Pivalic Acid with Co^{III}. A solution of 0.29 *M* Co^{III} in pivalic acid was heated with oxygen in a glass bomb reactor stirred at 80°. Except for the oxygen atmosphere (40 psig), the reaction was carried out in the same manner as described previously. The green color of Co^{III} persisted even after heating for 20 hr. The reaction mixture was removed from the bath and analyzed (Table IV). It was apparent that the yield of carbon dioxide (340%) far exceeded the Co^{III} charged. The normal products of oxidation were singularly absent, and instead large yields of *t*-butyl alcohol (280%) and acetone (61%), together with di-*t*-butyl peroxide (36%), were found. Equivalent results were obtained when trifluoroacetic acid was added. Moreover, when Co^{II} was charged in the reactor, the reaction mixture turned from pink to green. It remained so until the oxygen was exhausted and extensive decarboxylation had occurred. In the absence of oxygen, Co^{II} in the latter reaction was unchanged after prolonged heating.

It is apparent from these experiments that Co^{II} and Co^{III} were interconverted, and that the decarboxylation of pivalic acid was catalytic. Optimum conditions for decarboxylation were not explored since we were somewhat limited to reactions in small sealed systems. The efficient scavenging of *t*-butyl radicals readily accounts for the products obtained (*vide infra*). The over-all transformation given by eq 6[14] can be considered as an autoxidative decarboxylation. A chain mechanism

$$(CH_3)_3CCO_2H + O_2 \xrightarrow{Co^{II}-Co^{III}} CO_2 + [(CH_3)_3COH + (CH_3)_3COOC(CH_3)_3 + (CH_3)_2CO] \quad (6)$$

for such a process requires a route for the reoxidation of Co^{II}.

The possible oxidation of Co^{II} with *t*-butoxy radicals was examined by carrying out the decomposition of di-

Table V. Competitive Decarboxylation of (A) Pivalic Acid and (B) Isobutyric or *n*-Butyric Acid by Co^{III} [a]

B/A[b]	CF_3CO_2H[b]/Co^{III} [b]	Cu^{II}, mmol	Products, mmol[c]					$C_3H_7^+$/C_3H_8[c, d]	$C_4H_9^+$/C_4H_{10}[c, d]	ΣC_4B/ΣC_3A[d, e]
			CO_2	C_3H_8	$C_3H_7^+$	C_4H_{10}	$C_4H_9^+$			
					B = Isobutyric Acid					
5	0	0	1.5	0.40	0.11	0.38	0.41	0.3	1	8
5	0	0.16	1.5	0.02	0.40	0.05	0.94			10
10	0	0	1.5	0.33	0.11	0.28	0.38	0.3	1	10
10	0	0.16	1.4	0.05	0.68	0.03	0.68			10
5	1	0	1.5	0.48	0.36	0.13	0.46	0.8	4	4
5	1	0.17	1.4	0.03	0.59	0.04	0.73			6
10	1	0	1.2	0.50	0.42	0.06	0.34	0.8	5	4
10	1	0.19	1.4	0.04	0.89	0.03	0.59			7
5	3	0	1.4	0.30	0.60	0.02	0.45	2	20	3
5	3	0.20	1.4	0.02	0.70	0.02	0.63			5
10	3	0	1.4	0.24	0.50	0.03	0.61	2	20	9
10	3	0.22	1.1	0.01	0.73	0.0	0.35			5
					B = *n*-Butyric Acid					
10	0	0	1.4	0.04	0.04	0.18	0.27	~1	2	70
10	0	0.23	1.7	0.0	0.06	0.0	1.22			100
50	0	0	1.3	0.10	0.07	0.15	0.26	~0.7	2	100
50	0	0.22	1.4	0.0	0.34	0.0	0.69			100
10	1	0	1.4	0.05	0.04	0.06	0.94	~0.8	20	100
10	1	0.19	1.5	0.0	0.13	0.0	1.34			100
50	1	0	1.5			0.06	0.86		20	
50	1	0.20	1.4	0.0	0.31	0.0	0.68			100
10	3	0	1.3	0.08	0.04	0.01	0.84	~0.5	80	70
10	3	0.21	1.4	0.0	0.14	0.0	1.29			90
50	3	0	1.3	0.21	0.08	0.02	0.92		50	
50	3	0.21	1.4	0.0	0.33	0.0	0.53			80

[a] In solutions containing 3.0 mequiv of Co(III) in 10 ml of carboxylic acid (component A = pivalic acid and component B = isobutyric or *n*-butyric acid), solution at 80°. [b] Molar ratio. [c] $C_3H_7^+$ includes propylene and propyl esters; $C_4H_9^+$ includes isobutylene and *t*-butyl esters. [d] To closest significant figure only. [e] ΣC_3 includes all propyl products; ΣC_4 includes all butyl products.

t-butyl peroxide in pivalic acid solution. The formation of Co^{III} was readily determined by evolution of carbon dioxide and isobutylene. At 80° the decomposition of di-*t*-butyl peroxide was negligible, and it was recovered quantitatively from a charge consisting of either Co^{III} or Co^{II} in pivalic acid solutions. Furthermore, the decomposition of Co^{III} in pivalic acid was unaffected by di-*t*-butyl peroxide at these temperatures.

At 110°, however, the half-life of di-*t*-butyl peroxide is 50–60 hr.[15] Solutions containing Co^{II} in pivalic acid were converted to Co^{III} by visual indication of a change in color from pink to green. A 91% yield of carbon dioxide was obtained based on the peroxide decomposed.[16] *t*-Butyl alcohol was formed in major amounts, but little acetone was in evidence. In the absence of Co^{II}, the decomposition of di-*t*-butyl peroxide in pivalic acid afforded much smaller amounts (<20%) of carbon dioxide.[16b] The yield of acetone was commensurate with the peroxide decomposed, and approximately three times greater than *t*-butyl alcohol. The slightly faster rate of decomposition of di-*t*-butyl peroxide in the presence of cobalt salts indicated that some induced decomposition may have occurred (eq 7).

$$(CH_3)_3COOC(CH_3)_3 + Co^{II} \longrightarrow (CH_3)_3COCo^{III} + (CH_3)_3CO\cdot \text{ etc.} \quad (7)$$

Competitive Decarboxylation of Pivalic and Isobutyric (*n*-Butyric) Acids. Mixtures of pivalic and isobutyric acids as well as mixtures of pivalic and *n*-butyric acids were treated with Co^{III} acetate. These reactions were also studied in the absence and presence of various amounts of trifluoroacetic acid (Table V). To simplify analysis, only the yields of carbon dioxide, alkane (isobutane, propane) and alkene (isobutylene, propylene) were measured quantitatively. The yields of the accompanying esters were obtained by simple extrapolation of the detailed data of the decarboxylation of the separate acids presented in Tables I–III. The essential validity of this assumption was checked with competition studies in the presence of Cu^{II}. Alkenes were shown earlier to be the only significant products of decarboxylation in the presence of Cu^{II} (*cf.* Tables I–III). The consistency of these two sets of studies is given in the last column of Table V.

From these competition studies it was possible to obtain the relative rates of over-all decarboxylation of pivalic, isobutyric, and *n*-butyric acids (column 11, Table V). Moreover, we could also determine the amounts of alkene (and ester) produced relative to alkane when *n*-propyl, isopropyl, and *t*-butyl radicals were generated under more or less equivalent conditions of solvent (*cf.* columns 9 and 10, Table V).

Kinetics of the Reduction of Co^{III} in Pivalic Acid. Acid and Base Catalysis. The kinetics of the decarboxylation of pivalic acid by Co^{III} was determined spectrophotometrically. The pivalic acid used as solvent contained 4 wt % of glacial acetic acid to maintain fluidity at room temperature and to facilitate handling. The disappearance of Co^{III} was followed directly in a thermostated compartment of a Cary 14 spectrophotometer. This method yielded rate constants which were easily reproducible to ± 10% and were comparable to those obtained serially with sealed ampoules (Table VI). The disappearance of Co^{III} followed first-order

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[15] (a) In dilute solutions of benzene. (b) O. Mageli, S. Bukata, and D. Bolton, Bulletin 30.30, Wallace and Tiernan Co., Lucidol Div., Buffalo, N. Y., 1965.

[16] (a) Based on a stoichiometry of 2 mol of Co^{II} oxidized per mol of peroxide. (b) The decarboxylation of acids induced by di-*t*-butyl peroxide has been discussed.[9]

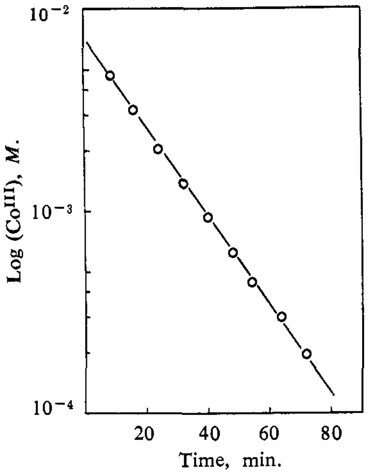

Figure 1. Reduction of cobalt(III) acetate in pivalic acid at 80°.

Table VI. Kinetics of Reduction of Co^{III} in Pivalic Acid. Effect of Salts[a]

Co^{III},[b] $M \times 10^3$	Temp, °C	Salt	Concn, $M \times 10^2$	$k_1 \times 10^4$ [c] sec^{-1}
2.0	71.0	None		0.81
8.0[d]	71.0	None		0.78
8.0	71.0	None		0.88
8.6[d]	71.0	None		0.78
20.0[d]	71.0	None		0.75
20.0	71.0	None		0.75
21.0[d]	71.0	None		0.79
4.0	71.0	None		0.76
4.0	71.0	$Co^{II}(OAc)_2$	3.7	0.58
4.0	71.0	$Co^{II}(OAc)_2$	5.0	0.52
4.0	71.0	$Pb^{II}(OAc)_2$	6.2	0.76
4.0	71.0	$Mg^{II}(OAc)_2$	5.5	0.97
4.0	61.5	None		0.18
4.0	61.3	LiO_2CCF_3	8.6	0.62
4.0	61.3	NaO_2CCF_3	4.7	0.32
4.0	61.5	LiO_2CCH_3	9.1	0.33

[a] Co^{III} was monitored in the thermostated cell of the spectrophotometer (±0.3°). [b] Initial concentration of Co^{III}. [c] Apparent first-order rate constant. [d] Co^{III} was followed serially by the sealed-ampoule technique.

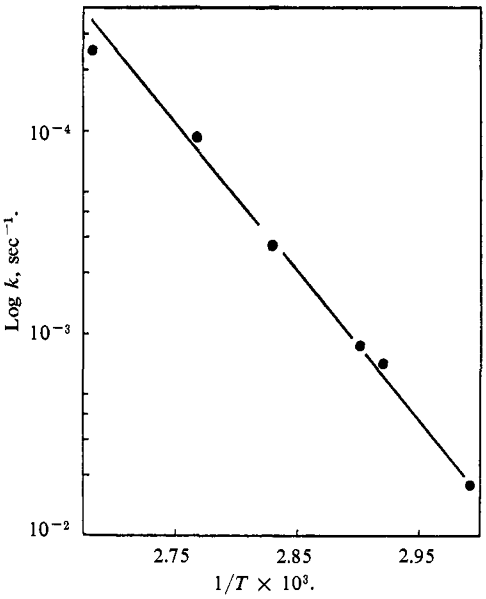

Figure 2. Temperature dependence of the first-order rate constant for reduction of cobalt(III) acetate in pivalic acid. $\Delta H^{\ddagger} = 30$ kcal/mol, $\Delta S^{\ddagger} = 8$ eu (75°).

Table VII. Kinetics of Reduction of Co^{III} in Pivalic Acid. Effect of Trifluoroacetic Acid[a]

Co^{III},[b] $M \times 10^3$	CF_3CO_2H, $M \times 10^3$	Added salt	Concn, $M \times 10^2$	$k_1 \times 10^4$, sec^{-1} [c]
2.00	9.26	None		0.75
4.00	9.26	None		0.63
8.00	9.26	None		0.45
4.00	9.26	$Co^{II}(OAc)_2$	4.98	0.33
4.00	92.6	None		3.64
7.90	92.6	None		2.25
39.5	92.6	None		0.74
4.00	92.6	$Co^{II}(OAc)_2$	0.52	3.53
4.00	92.6	$Co^{II}(OAc)_2$	1.03	2.61
4.00	92.6	$Co^{II}(OAc)_2$	1.55	1.71
4.00	92.6	$Co^{II}(OAc)_2$	2.58	0.73
4.00	92.6	$Co^{II}(OAc)_2$	4.98	0.45
4.00	92.6	$Mg^{II}(OAc)_2$	6.10	0.37
4.00	92.6	$Pb^{II}(OAc)_2$	5.78	0.10
4.00	92.6	LiOAc	19.0	0.33
4.00	92.6	LiO_2CCF_3	8.8	2.21
4.00	92.6	LiO_2CCF_3	10.2	1.85
4.00	92.6	LiO_2CCF_3	16.8	1.83
4.00	92.6	NaO_2CCF_3	4.7	2.02

[a] Runs carried out at 61.4°, followed spectrophotometically. [b] Initial Co^{III} concentration. [c] Apparent first-order rate constant for at least 30% of reaction.

kinetics for at least three half-lives (Figure 1), and the first-order rate constants were invariant over a tenfold range in concentrations. The apparent activation energy determined between 61 and 100° was 30 kcal/mol [$\Delta H^{\ddagger} = 29$ kcal/mol, $\Delta S^{\ddagger} = 8$ eu (75°)] (Figure 2).

The addition of metal carboxylates did not alter the apparent first-order kinetics. Addition of a tenfold excess of Co^{II} acetate only depressed the rate by approximately 30%. Magnesium and lithium acetates as well as lithium and sodium trifluoroacetates accelerated the rate, but Pb^{II} acetate had little effect (Table VI).

The disappearance of Co^{III} was accelerated by trifluoroacetic acid in a manner consistent with the earlier qualitative observations based on gas evolution. The effect diminished with increasing Co^{III} concentration, as shown in Table VII. Furthermore, addition of Co^{II} acetate depressed the rate, in contrast to the effect observed in the absence of trifluoroacetic acid. In the presence of trifluoroacetic acid, first-order kinetics were observed only over a limited portion (30–40%) of the reaction. The negative deviation from first-order kinetics could be attributed to retardation by the products of the reaction, since deliberate addition of Co^{II} acetate achieved the same effect. In the latter case, first-order kinetics, although diminished in magnitude, were observed over a longer portion of the decomposition with increasing concentrations of Co^{II} acetate. Finally, an eightfold excess of Co^{II} acetate negated the effect of trifluoroacetic acid in enhancing the rate of Co^{III} decomposition.

The effect of Co^{II} acetate on reactions induced by trifluoroacetic acid was not restricted, since Li, Mg, and Pb^{II} acetates exerted similar retarding effects. However, Li and Na trifluoroacetates caused only mild rate depressions, which did not change significantly even at high salt concentrations (Table VII).

It was apparent from these data that the effect of trifluoroacetic acid (at a given concentration) was largely related to the amount of Co^{III} acetate present, and not necessarily to the absolute concentration of this acid. The behavior of metal acetates [$M(OAc)_n$ generally] in the presence of trifluoroacetic acid could be ascribed (*vide infra*) to the acid–base equilibria given by eq 8, since metal trifluoroacetates exerted only minor effects.

$$M(OAc)_n + CF_3CO_2H \rightleftarrows M(OAc)_{n-1}{}^{+}O_2CCF_3{}^{-} + HOAc \quad (8)$$

Cobalt(III) acetate was employed in these studies, largely for convenience. In order to show that a preequilibrium exchange process was not rate limiting, we compared the rates of reaction of Co^{III} acetate and Co^{III} isobutyrate in isobutyric acid. The disappearance of Co^{III} in isobutyric acid did not follow clean first-order kinetics, due largely to the multiplicity of reactions (*vide supra*, and Table II). However, the rate of decrease of Co^{III} was monotonic and, within 5%, the same for Co^{III} acetate as it was for Co^{III} isobutyrate. Equivalent rates were also found in the presence of trifluoroacetic acid.

The decarboxylations of pivalic acid and pivalic acid-*d* by Co^{III} were compared under identical conditions, in order to examine possible equilibrium or kinetic isotope effects. To obviate problems associated with the preparation of pivalic acid-*d* by exchange with deuterium oxide, pivalic acid used in the comparative studies was also prepared by the same procedure using water. The rate of decarboxylation of the protio acid by Co^{III} was 1.28 ± 0.10 times faster than that of pivalic acid-*d* at 68.6°.

Discussion

The examination of the mechanism of the reduction of Co^{III} acetate in carboxylic solvents can be dissected into studies of products, transient intermediates, and kinetics of the reaction. In order to facilitate discussion, we will anticipate certain conclusions and present a framework for a general discussion of the mechanism, in terms of the formation of alkyl radicals from Co^{III} species and their subsequent reactions.

Co^{III} Complexes as Reactants. Co^{III} acetate exists in glacial acetic acid largely as dimeric species.[12,17] For kinetic purposes, the metathesis (eq 9) of Co^{III} acetate

$$Co^{III}{}_2(OAc)_6 + 6RCO_2H \rightleftarrows Co^{III}{}_2(O_2CR)_6 + 6HOAc \quad (9)$$

with the carboxylic milieu under our conditions is rapid and complete,[18] since Co^{III} isobutyrate and Co^{III} acetate decarboxylate isobutyric acid at the same rate. Furthermore, the products observed in both cases are those derived from the decarboxylation of isobutyric acid. No significant deuterium isotope effect is observed with pivalic acid-*d*, and a rate-limiting hydrogen transfer from the acid to Co^{III}, as in eq 10, is not involved.[19] We conclude that decomposition of Co^{III} carboxylate represents the rate-determining process. Apparent first-order kinetics observed in the disappearance of Co^{III} is related to the homolysis of dimeric Co^{III} complexes. The concentration of any monomers formed on dissociation (eq 11) is probably too small to greatly affect these kinetics.[20] Ionization is not a significant process under these conditions, since the equivalent conductivity of 7.2 × 10^{-3} *M* Co^{III} solutions is 3.93 × 10^{-3} mhos/*M*.[21] This corresponds to a degree of ionization of 4.3 × 10^{-3}.[22]

$$(CH_3)_3CCO_2H + Co^{III} \longrightarrow (CH_3)_3C\cdot + CO_2 + Co^{II} + H^+ \quad (10)$$

$$Co^{III}{}_2(O_2CR)_6 \rightleftarrows 2Co^{III}(O_2CR)_3 \quad (11)$$

Competitive Decarboxylation of Acids by Co^{III}. The reduction of Co^{III} by carboxylic acids involves two separate and independent processes: (a) the decarboxylation of the carboxylic function *via* a carboxylatocobalt(III) intermediate, and (b) the oxidation of the resultant alkyl radical. Homolysis of Co^{III} pivalate proceeds with an apparent activation energy of 30 kcal/mol; the decarboxylation is accompanied by the liberation of *t*-butyl radicals according to eq 12.[23]

$$(CH_3)_3CCO_2Co^{III} \longrightarrow (CH_3)_3C\cdot + CO_2 + Co^{II} \quad (12)$$

Competition studies presented in Table V show that pivalic acid is decarboxylated approximately ten times faster than isobutyric acid by Co^{III}, and approximately 100 times faster than *n*-butyric acid. These relative rates of decarboxylation were obtained by accounting for all the alkyl fragments from the *t*-butyl and isopropyl (*n*-propyl) radicals derived from these acids. The molar ratio of these material balances divided by the molar ratio of the reactant acids yields a quantity which is related to the relative rates of over-all decarboxylation. It is apparent from an inspection of Table V that this quantity does not remain absolutely constant on changing the relative concentrations of a given pair of acids. We feel that part of this variation in apparent relative rates of decarboxylation is attributable to experimental difficulties inherent in quantitative product analysis.

We should also consider the preequilibrium metathesis (eq 13) of Co^{III} acetate [20] with each acid. Since the

$$Co^{III}{}_2(OAc)_6 + nRCO_2H \rightleftarrows Co^{III}{}_2(OAc)_{6-n}(O_2CR)_n + nHOAc \quad (13)$$

decarboxylations of isobutyric acid by Co^{III} acetate and Co^{III} isobutyrate proceed at the same over-all rates, we conclude that reactions such as eq 13 cannot be rate limiting. The rates of ligand exchange (carboxylato) on the Co^{III} nucleus, however, may vary significantly from pivalic to isobutyric or *n*-butyric acid.[18] The two statements can be reconciled if one considers that in a competitive situation, the effects of minor differ-

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(17) Co^{III} acetate is principally a mixture of $Co_2(OAc)_6$, $Co_2(OAc)_5OH$, and $Co_2(OAc)_4(OH)_2$.[12] In the following discussion we will represent it as $Co_2(OAc)_6$ as a matter of convenience.

(18) (a) Co^{III} species are generally substitution inert, but exchange with the labile Co^{II} may obscure any rate effects; (b) N. Bonner and J. Hunt, *J. Am. Chem. Soc.*, 82, 3826 (1960); (c) J. Shanker and B. de Souza, *J. Inorg. Nucl. Chem.*, 24, 187, 693 (1962); (d) H. Habib, *J. Am. Chem. Soc.*, 88, 1668 (1966).

(19) The absence of a significant deuterium isotope effect, strictly speaking, does not preclude a rate-determining hydrogen transfer as in eq 18. Other investigators[9,10] have suggested this possibility, but we consider it unlikely.

(20) (a) Molecular weight studies in glacial acetic acid indicate that the dissociation constant for Co^{III} acetate dimer is small. We *assume* that the same situation prevails for Co^{III} carboxylates dissolved in other carboxylic acids. (b) Mixed valence Co^{II}–Co^{III} binuclear species must also be considered. (c) In the subsequent discussion, we consider Co^{III} dimers and monomers interchangeably since we cannot at this juncture rigorously distinguish between them. For expediency, Co^{III} monomer is represented in reactions.

(21) J. Sharp and A. White, *J. Chem. Soc.*, 110 (1952).

(22) (a) The ionization of metal acetate is generally low in glacial acetic acid solutions; (b) O. Kolling and J. Lambert, *Inorg. Chem.*, 3, 202 (1964); (c) L. Sutcliffe and J. Proll, *Trans. Faraday Soc.*, 57, 1078 (1961); (d) S. Bruckenstein and I. Kolthoff, *J. Am. Chem. Soc.*, 78, 2974 (1956).

(23) We assume that the enthalpy change in the preequilibrium step is negligible.

ences in rates (especially of preequilibria) are highly magnified.[24a,b]

The relative rates of decarboxylation cited above include the preequilibrium formation (eq 13) of the respective carboxylate and thus do not measure the rate-determining homolysis (eq 14), exclusively. Steric

$$RCO_2Co^{III} \longrightarrow R\cdot + CO_2 + Co^{II} \tag{14}$$

factors, however, should cause a decrease in the formation constants of various Co^{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. Multibond cleavage of Co^{III} carboxylates is indicated by the order and magnitude of this reactivity sequence of acids.[24c] It is also consistent with analogous homolyses of Pb^{IV}[7] and Tl^{III}[8] carboxylates. A similar homolysis of aquo Co^{III} carboxylates has been postulated by Waters and Clifford.[3a]

The rates of decarboxylation can be measured either by evolution of carbon dioxide or disappearance of Co^{III}. These rates do not necessarily coincide, since the latter depends on the fate of alkyl radicals subsequent to homolysis. If alkyl radicals are completely oxidized by Co^{III}, the rate of disappearance of Co^{III} will be twice the rate of evolution of carbon dioxide. This is observed in the decarboxylation of pivalic acid. On the other hand, if alkyl radicals[25a] are not affected by Co^{III}, and ultimately disappear by second-order processes (dimerization, disproportionation, etc.), these rates will be identical. The decarboxylation of *n*-butyric acid and, to a degree, isobutyric acid follows this relationship. On the other hand, the decarboxylation of these acids by Co^{III} in the presence of Cu^{II} leads to complete oxidation of the propyl radicals. The observed increase in the rate (Tables I and II) is consistent with this formulation.[25b]

Alkyl Radicals as Intermediates. Trapping experiments show that *t*-butyl, isopropyl, and *n*-propyl radicals are direct precursors in the decarboxylation of pivalic, isobutyric, and butyric acids, respectively, by Co^{III}. Thus, the addition of catalytic amounts of Cu^{II} complexes is sufficient to intercept all of the isopropyl and *n*-propyl radicals and convert them to propylene (eq 15).[26] The yield of propane under these conditions

$$\begin{aligned} CH_3CH_2CH_2\cdot + Cu^{II} \longrightarrow CH_2{=}CHCH_3 + H^+ + \\ Cu^{I} \longleftarrow Cu^{II} + (CH_3)_2CH\cdot \end{aligned} \tag{15}$$

drops precipitously. The concentration of Cu^{II} remains invariant throughout the course of reaction be-

$$Cu^{I} + Co^{III} \longrightarrow Cu^{II} + Co^{II} \tag{16}$$

cause Cu^{I} is oxidized by Co^{III} much more readily than the latter undergoes decomposition.[27,25b]

The efficiency with which Cu^{II} complexes act as scavengers of alkyl radicals has been demonstrated quantitatively in other studies.[28] The rate of decarboxylation of acids by Co^{III} in the presence of Cu^{II} is not dependent on the concentration of the latter (beyond a small lower limit). Copper species in any form (*e.g.*, as Cu^{III}), therefore, cannot be directly responsible for the *generation* of radicals by decarboxylation.

Cu^{II} salts also aid in the oxidation of *t*-butyl radicals from the decarboxylation of pivalic acid by Co^{III}, but the effect is marginal (Table III) due to the facility with which Co^{III} itself acts in this capacity. However, the interception of *t*-butyl radicals by oxygen eliminates the alternative possibility that isobutylene arises by an independent ionic (2-equiv) process. The normal products of oxidation (isobutylene, *t*-butyl esters) are absent from the decomposition of Co^{III} in pivalic acid under an oxygen atmosphere. In their place, *t*-butyl alcohol, acetone, and di-*t*-butyl peroxide (DTBP) are formed, which are symptomatic of the presence of *t*-butylperoxy radicals.[29]

$$(CH_3)_3C\cdot + O_2 \longrightarrow (CH_3)_3CO_2\cdot \tag{17}$$

$$2(CH_3)_3CO_2\cdot \longrightarrow \left\{ \begin{array}{ll} (CH_3)_3COOC(CH_3)_2 + O_2 & (18) \\ O_2 + 2(CH_3)_3CO\cdot \ \text{etc.} & (19) \end{array} \right.$$

Even more striking is the formation of a large excess of these products (together with carbon dioxide) beyond the Co^{III} actually charged.[30] No doubt the latter is involved in a catalytic process in which Co^{III} is regenerated from Co^{II}. It is possible that either *t*-butylperoxy or *t*-butoxy radicals, or both, can effect such a transformation. The high yields of *t*-butyl alcohol and

$$Co^{II} + (CH_3)_3CO_2\cdot \longrightarrow Co^{III}OOC(CH_3)_3 \ \text{etc.} \tag{20}$$

$$Co^{II} + (CH_3)_3CO\cdot \longrightarrow Co^{III}OC(CH_3)_3 \ \text{etc.} \tag{21}$$

the oxidation of Co^{II} by DTBP support the latter. Kooyman has recently presented evidence for the oxidation of Co^{II} by peroxy radicals.[31] Direct autoxidation of Co^{II} to Co^{III} has also been observed and measured in a number of complexes.[32]

Oxidation of Alkyl Radicals by Co^{III}. The fate of the alkyl radical generated in the homolysis (eq 14) is dependent on its structure. Thus, *t*-butyl radicals are

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(24) (a) The discrepancy is serious when the homolysis of the Co^{III} carboxylate is only slightly slower than the metathesis. (b) The possibility that at least three carboxylato ligands in the Co^{III} monomer and six in the dimer can exchange complicates the issue further, especially since each of these Co^{III} species probably decarboxylates at a different rate. (c) The mechanisms of decarboxylation of a variety of related metal carboxylates have been compared (J. Kochi, R. Sheldon, S. Lande, submitted for publication).

(25) (a) Radicals formed secondarily by hydrogen transfer to the first-formed alkyl radicals are equivalent in this regard. (b) If *none* of the alkyl radicals were oxidized by Co^{III}, the rate of reduction of Co^{III} theoretically should be doubled on the addition of Cu^{II} (since the latter scavenged all the alkyl radicals). The extent to which the rate is not doubled is an indication of the effectiveness of Co^{III} as an oxidant.

(26) H. DeLaMare, F. Rust, and J. Kochi, *J. Am. Chem. Soc.*, 85 1437 (1963).

(27) The oxidation of a variety of metal acetates by Co^{III} has been examined: (a) Ce^{III}, L. Sutcliffe and J. Weber, *Trans. Faraday Soc.*, **55**, 1892 (1959); (b) Fe^{II}, L. Bennett and J. Sheppard, *J. Phys. Chem.*, **66**, 1275 (1962); (c) Cr^{II}, L. Sutcliffe and J. Weber, *Trans. Faraday Soc.*, **57**, 91 (1961); (d) D. Rosseinsky and W. Higginson, *J. Chem. Soc.*, 31 (1960); (e) Ag^{I}, J. Haugen and H. Habib, *J. Inorg. Nucl. Chem.*, **30**, 225 (1968).

(28) (a) J. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); (b) J. Kochi and R. Subramanian, *ibid.*, **87**, 4855 (1965).

(29) (a) A. Factor, C. Russell, and T. Traylor, *ibid.*, **87**, 3692 (1965); (b) P. Bartlett and T. Traylor, *ibid.*, **85**, 2407 (1963); (c) P. Bartlett and P. Grunther, *ibid.*, **88**, 3288 (1966).

(30) The catalytic effect of cobalt salts in autoxidative decarboxylation has been noted previously by J. Pasky [U. S. Patent 3,251,878 (May 1966)]. We thank Dr. Pasky for a copy of this patent.

(31) (a) W. deKlein and E. Kooyman, *J. Catalysis*, **4**, 626 (1965). (b) The role of cobalt species in the catalyzed decomposition of alkyl hydroperoxides also relates to this problem. (c) W. Richardson, *J. Am. Chem. Soc.*, **87**, 246, 1096 (1965); *J. Org. Chem.*, **30**, 2804 (1965). (d) M. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958).

(32) (a) J. Simplicio and R. Wilkins, *J. Am. Chem. Soc.*, **89**, 6092 (1967); (b) M. Mori, J. Weil, and M. Ishiguro, *ibid.*, **90**, 615 (1968); (c) U. Thewalt and R. Marsh, *ibid.*, **89**, 6364 (1967); L. Zompa, C. Sokol, and C. Brubaker, *Chem. Commun.*, 701 (1967).

completely converted by Co^{III} to a mixture of isobutylene and *t*-butyl pivalate (eq 22 and 23), and isobutane

$$\begin{array}{l} (CH_3)_3C\cdot \\ + \\ Co^{III} \end{array} \left\{ \begin{array}{ll} \xrightarrow{\hspace{2em}} (CH_3)_2C{=}CH_2 + H^+ + Co^{II} & (22) \\ \xrightarrow[(CH_3)_3CCO_2H]{} (CH_3)_3CCO_2C(CH_3)_3 + H^+ + Co^{II} & (23) \end{array} \right.$$

is only a minor product. The analogous oxidation of the secondary isopropyl or the primary *n*-propyl radicals is much less effective, since products of oxidation, propylene, and propyl esters are minor. Propane is the major product, which is formed by hydrogen abstraction from the solvent (eq 24).

$$CH_3CH_2CH_2\cdot + SH \longrightarrow CH_3CH_2CH_3 + S\cdot \longleftarrow (CH_3)_2CH\cdot + SH \quad (24)$$

The amounts of oxidation products relative to alkane represent a measure of the relative rates of oxidation and hydrogen transfer of alkyl radicals. The comparison of *t*-butyl, isopropyl, and *n*-propyl radicals from the decarboxylation of pivalic, isobutyric, and *n*-butyric acids by this procedure, however, is limited by the variation of the structure of the hydrogen donor (carboxylic acid as solvent).

Radicals generated by the competitive decarboxylation of acids obviate this difficulty. In solutions of pivalic acid and *n*-butyric or isobutyric acid, the primary or secondary acid represents the hydrogen donor since pivalic acid is not only the minor component (Table V), but it is also a much poorer hydrogen donor

$$(CH_3)_3C\cdot + (CH_3)_2CHCO_2H \xrightarrow{k_H} (CH_3)_3CH + (CH_3)_2\dot{C}CO_2H \quad (25)$$

$$(CH_3)_2CH\cdot + (CH_3)_2CHCO_2H \xrightarrow{k_H} CH_3CH_2CH_3 + (CH_3)_2\dot{C}CO_2H \quad (26)$$

toward alkyl radicals. Alkene and esters are the products of oxidation of alkyl radicals by Co^{III}, for which the second-order rate constant is represented by k_{ox}. The values of k_{ox} are not readily obtainable from these

$$(CH_3)_3C\cdot + Co^{III} \xrightarrow[RCO_2H]{k_{ox}} [(CH_3)_2C{=}CH_2 + (CH_3)_3CO_2CR] + H^+ + Co^{II} \quad (27)$$

$$(CH_3)_2CH\cdot + Co^{II} \xrightarrow[RCO_2H]{k_{ox}} [CH_3CH{=}CH_2 + (CH_3)_2CHO_2CR] + H^+ + Co^{II} \quad (28)$$

data. However, the ratios R^+/RH (R = *t*-butyl, isopropyl, and *n*-propyl) given in columns 9 and 10 of Table V provide a qualitative measure of the relative ease of oxidation of these radicals. It is interesting that the differences among *t*-butyl, isopropyl, and *n*-butyl are not large. We hope to provide more quantitative data on the rates of oxidation of alkyl radicals by Co^{III} at a later time.[33]

Acid Catalysis in the Decarboxylation and Oxidation Steps Involving Co^{III}. Strong (usually mineral) acids effect two fundamental changes on the course and rates of reduction of Co^{III} in carboxylic media. The rates of decomposition of Co^{III} carboxylates and the capacity of Co^{III} to carry out subsequent oxidation of alkyl radicals are enhanced markedly by strong acids. Thus, the addition of sulfuric, methanesulfonic, perchloric, or trifluoroacetic acids, as well as boron trifluoride, to a solution of Co^{III} dissolved in carboxylic acids lowers the temperature and decreases the time required for decarboxylation by several hundredfold, depending on the concentration and the acid (*cf.* Tables I–III and VII). Furthermore, under these conditions the fraction of alkyl radicals, which are oxidized to alkene and ester, also increases with the strength and concentration of the acid (Tables I–III and V).

The direct dependence of the rate on the acid is diametrically opposed to the effect observed in aqueous solutions.[34] In the latter case, metathesis between aquo Co^{III} and carboxylic acid was postulated to account for the inverse acid dependence of the rate.[3a] Inclusion of dimeric Co^{III} species in this kinetic scheme,

$$Co^{III}(H_2O)_6{}^{3+} + RCO_2H \rightleftharpoons Co^{III}(H_2O)_5(O_2CR)^{2+} + H_3O^+$$

however, is necessary, since recent studies show that dimers are present even at high acid concentrations.[4,35]

Exchange between ligands of such different basic properties as water and carboxylic acids on the Co^{III} nucleus, in part, seriously limits the effect of strong acids on the reduction of Co^{III} carboxylates in aqueous solutions. The latter, of course, is not as serious a problem in nonaqueous solutions.

We postulate that strong acids affect the properties of Co^{III} carboxylates in nonaqueous solutions largely by *ionization*. For example, trifluoroacetic acid can be used to investigate the cryoscopic behavior of Co^{III} in acetic acid since it is highly dissociated.[12,36] Addition of sodium acetate to this mixture caused a very

$$CF_3CO_2H + HOAc \rightleftharpoons AcOH_2{}^+O_2CCF_3{}^- \rightleftharpoons AcOH_2{}^+ + O_2CCF_3{}^- \quad (29)$$

slight elevation of the melting point, despite the fact that sodium acetate alone in glacial acetic acid caused a molar depression characteristic of a highly associated ion pair.[22] This suggests that the following equilibria were extant.

$$Na^+OAc^- + AcOH_2{}^+O_2CCF_3{}^- \rightleftharpoons Na^+O_2CCF_3{}^- + 2HOAc \quad (30)$$

$$Na^+O_2CCF_3{}^- \rightleftharpoons Na^+ + O_2CCF_3{}^-$$

When Co^{III} acetate was added to a solution of trifluoroacetic acid, the melting point of the mixture was raised. Co^{III} acetate itself in glacial acetic acid showed a cryoscopic behavior in acetic acid characteristic of the dimer. We conclude that the following equilibria pertain to Co^{III} acetate in the presence of trifluoroacetic acid. An alternative, but less likely, explanation of the

$$Co^{III}{}_2(OAc)_6 + AcOH_2{}^+O_2CCF_3{}^- \rightleftharpoons Co_2(OAc)_5{}^+O_2CCF_3{}^- + 2HOAc \quad (31)$$

$$Co_2(OAc)_5{}^+O_2CCF_3{}^- \rightleftharpoons Co_2(OAc)_5{}^+ + O_2CCF_3{}^-$$

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[33] R. Sheldon, unpublished studies.

[34] In aqueous solutions, the reduction of Co^{III} acetate shows linear acid dependence.[11] In contrast, reduction of aquoCo^{III} by carboxylic acids in aqueous solution is inversely related to acid.[3]

[35] (a) L. Sutcliffe and J. Weber, *J. Inorg. Nucl. Chem.*, **12**, 281 (1960); (b) J. Baxendale and C. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).

[36] (a) See K. Heyman and H. Klaus, "Chemistry in Lower Fatty Acids," G. Jander, Ed., Interscience Publishers, New York, N. Y., 1963, for a discussion of the properties of glacial acetic acid as a solvent for metal acetates. (b) The crystal structure of the related acetic acid–sulfuric acid complex has been determined (P. G. Jönson and I. Olovsson, *Acta Cryst.*, 824, 559 (1968)).

Table VIII. Effect of Strong Acids and Co^{III} on Alkenes[a]

Co^{III}-$(OAc)_3$, mmol	Added acid	>= mmol	Time, min	Products, mmol						
				CO_2	⋀	⋀=	ΣiPr·[b]	>= recovd	>—O_2C—<[c]	Σ>=
0	H_2SO_4[d]	0.89	20	0	0	0	...	0.26	0.67	0.93
0	H_2SO_4[d]	2.66	20	0	0	0	...	0.51	1.76	2.27
2.97	H_2SO_4[d]	0	20	0.91	0.03	0.28	0.46	...	...	...
2.97	H_2SO_4[d]	0.89	20	0.46	0.02	0.16	0.25	0.11	0.31	0.49
3.00	H_2SO_4[d]	3.66	20	0.45	0.02	0.17	0.26	0.74	1.34	1.88
0	CF_3CO_2H[e]	0.89	50	...	...	...	...	0.56	0.18	0.74
2.95	CF_3CO_2H[e]	0	50	1.86	0.79	0.57	1.68	...	...	...
2.93	CF_3CO_2H[e]	0.89	50	1.35	0.70	0.72	1.76	0.28	0.18	0.46
0	None	0.89[f]	1500	...	...	...	...	0.92[f]	0	0.92[f]
0	$HClO_4$	0.89[f]	30	...	...	...	...	0.59[f]	0.23[g]	0.82[f]
0	BF_3	0.89[f]	30	...	...	...	...	0.93[f]	0.02[g]	0.95[f]
0	BF_3	0.89[f]	180	...	...	...	...	0.86[f]	0.04[g]	0.90[f]

[a] Reactions at 80° conducted in 10 ml of isobutyric acid. [b] Includes propane, propylene, and propyl ester. [c] Includes *t*-butyl acetate. [d] $H_2SO_4/Co^{III} = 1.27$. [e] $CF_3CO_2H/Co^{III} = 2.14$. [f] Propylene. [g] Isopropyl isobutyrate.

effect of trifluoroacetic acid is dissociation of the Co^{III} dimer to monomeric species (eq 32 etc.).

$$Co^{III}_2(OAc)_6 + AcOH_2^+O_2CCF_3^- \rightleftharpoons Co^{III}(OAc)_3H^+Co^{III}(OAc)_3O_2CCF_3^- + HOAc \quad (32)$$

The spectral characteristics of Co^{III} in the ultraviolet–visible region were different in glacial acetic acid and trifluoroacetic acid. The difference closely resembled spectral changes of Co^{III} in aqueous solutions on the addition of perchloric acid, which have been attributed to dissociation of the Co^{III} dimer by acid[34a] and ion-pair formation.[37] Equilibria analogous to eq 29–32 can also be considered between other Co^{III} carboxylates and strong acids.[38a]

On the basis of the foregoing evidence, we attribute the enhanced reactivity of Co^{III} species in strong acid solutions to the formation of cationic Co^{III} species, such as $Co^{III}(O_2CR)_5^+$ or $Co^{III}(O_2CR)_2^+$. At this juncture we cannot distinguish among these species, and until further evidence is forthcoming, we will consider them interchangeably. The important conclusion is that these cationic Co^{III} complexes are more potent oxidants than their neutral counterparts.[38b,c] They undergo homolysis (eq 33) more readily than neutral

$$Co^{III}(O_2CR)_2^+ \longrightarrow Co^{II}O_2CR^+ + R\cdot + CO_2 \quad (33)$$

Co^{III} species, as indicated by the enhanced rate of decarboxylation. Furthermore, the subsequent oxidation of alkyl radicals (eq 34) is also facilitated (*cf.* R^+/

$$Co^{III}(O_2CR)_2^+ + R\cdot \longrightarrow Co^{II}(O_2CR)_2 + [R^+] \quad (34)$$

RH in Tables I–III with acid). The yields of alkanes are diminished and alkenes and esters are more dominant products when decarboxylation is induced by strong acids (columns 9 and 10, Table V). Lastly, alkenes are prone to further oxidation by these cationic Co^{III} species and account for the diminished yields of carbon dioxide liberated in the presence of strong acid (see Experimental Section). Alkenes can be formed and recovered quantitatively from carboxylic acid solutions containing Co^{III}. However, in the presence of strong acids (Table VIII), alkenes are oxidized by Co^{III} and cannot be accounted for quantitatively.[39] The problem is more severe with perchloric and sulfuric acids than it is with trifluoroacetic acid, and is related to the strength of the acid. Similar observations have been noted by Bawn and Sharp.[40]

The Effect of Bases. The addition of metal carboxylates causes no observable changes in the electronic spectrum of Co^{III} acetate in acetic acid. These results differ from the effects of sodium acetate observed on the spectrum of the more substitution-labile Co^{II} acetate.[35] The properties of Co^{III} carboxylate under reaction conditions, however, are modified by alkali metal acetates and trifluoroacetates (Tables II and VI), since the rate of decarboxylation of isobutyric acid by Co^{III} is accelerated. We attribute this effect to the formation of carboxylatocobaltate(III) complexes such as in eq 35.[41]

$$Co_2^{III}(O_2CR)_6 + 2Na^+O_2CR^- \rightleftharpoons 2Co^{III}(O_2CR)_4^-Na^+ \quad (35)$$

These anionic Co^{III} complexes are also more prone to undergo homolysis much like carboxylatoplumbate(IV) complexes formed from Pb^{IV} carboxylates and a variety of bases.[6] However, unlike the cationic Co^{III} species formed in strong acids, the anionic Co^{III} complexes are not particularly potent oxidants toward alkyl radicals. Alkyl radicals generated under the latter circumstances primarily suffer reduction to alkanes[27] (Table II).

Summary

Oxidation of Alkyl Radicals by Co^{III}. The study of the decarboxylation of acids by Co^{III} is illustrative of Co^{III} species as oxidants. Three principal types of Co^{III} species, which are primarily distinguished from

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(37) (a) L. Sutcliffe and J. Weber, *Trans. Faraday Soc.*, 57, 91 (1961). (b) *Cf.* also the dimerization of the related Co^{II} acetate. (c) P. Proll, L. Sutcliffe, and J. Walkley, *J. Phys. Chem.*, 65, 455, 1993 (1961).

(38) (a) According to this formulation, the quantitative effect of various strong acids is related to changes in ion-pair and ionization equilibria (*e.g.*, eq 31). (b) The most important feature which distinguishes cationic Co^{III} and the neutral species is probably the extent of ligand coordination. We suggest tentatively that cationic Co^{III} complexes are coordinatively unsaturated. Carboxylato ligands are often bidentate. Protonation of such a carboxylato ligand (as a bridge in Co^{III} dimer or intramolecularly in the monomer) could lead to severing of one bond without actually causing dissociation. (c) For equilibria in nonaqueous solutions see L. Katzin, *Transition Metal Chem.* 3, 56 (1966), and J. Lagowski, "Chemistry of Non-Aqueous Solvents," Vol. I, Academic Press Inc., New York, N. Y., 1966.

(39) (a) The amount of alkene converted to ester by acid-catalyzed addition of carboxylic acid is taken into account. (b) The acid-catalyzed reactions of alkenes with acetic acid further complicates the problem (*cf.* Y. Pocker and A. Miller, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April, 1968, Abstract P195).

(40) C. Bawn and J. Sharp, *J. Chem. Soc.*, 1854, 1866 (1957).

(41) (a) Evidence for acetatocobaltate(III) ions has been presented by D. Benson, P. Proll, L. Sutcliffe, and J. Walkley, *Discussions Faraday Soc.*, **29**, 60 (1960); (b) see also D. Benson and L. Sutcliffe, *Trans. Faraday Soc.*, **56**, 246 (1960).

one another by the extent of coordination of the Co^{III} moiety, are postulated. In the presence of strong acid, cationic species, such as $Co^{III}_2(O_2CR)_5^+$ and $Co^{III}(O_2CR)_2^+$, are possible. In the presence of bases, anionic carboxylatocobaltate(III) complexes, such as $Co^{III}_2(O_2CR)_7^-$ or $Co^{III}(O_2CR)_4^-$, can be formed. In the absence of additives, the cobalt species is present in solution primarily as the neutral dimer, $Co^{III}_2(O_2CR)_6$.[17] Both of the charged species undergo homolysis more readily than the neutral Co^{III} complex, and enhanced rates of decarboxylation are observed.

The rates of oxidation of alkyl radicals formed during decarboxylation generally follow their ionization potential and decrease in the order: tertiary > secondary > primary. The cationic Co^{III} species completely oxidize *t*-butyl radicals, whereas secondary radicals are oxidized partially and primary radicals less readily. The anionic or neutral Co^{III} complexes, on the other hand, are unable for the most part to oxidize primary and secondary radicals. In view of the wide advantage in the oxidation potential, it is somewhat surprising that none of these Co^{III} complexes is a more effective oxidant than Cu^{II} toward alkyl radicals.[42]

The relative reactivity of these Co^{III} species toward alkyl radical leads us to postulate that oxidation occurs by an inner-sphere complex (eq 36), which undergoes subsequent heterolysis (eq 37).[43a] According to this formulation, the rate of formation of the alkylcobalt

$$R\cdot + Co^{III} \rightleftharpoons [RCo] \qquad (36)$$

$$[RCo] \longrightarrow Co^{II} + [R^+] \qquad (37)$$

intermediate is related to the state of coordination of the Co^{III} species, and occurs fastest with the cationic complexes.[43b] The extent to which the formation of the alkylcobalt intermediate is reversible obscures the rate-limiting process.

A similar mechanism has been proposed for the facile oxidation of alkyl radicals by Cu^{II} complexes[43c] and has been employed with Pb^{IV} oxidations.[43d]

Experimental Section

Materials. Acids. Glacial acetic acid was either Du Pont or Baker and Adamson reagent; *n*-butyric acid (bp 163-164°, lit.[44] 164°) and isobutyric acid (bp 153-154°, lit.[44] 154°) were obtained from Fisher Scientific Company; pivalic acid (bp 162-164°, lit.[44] 164°) was from Enjay Chemical Co.; trifluoroacetic acid and *n*-decanoic acid were from Matheson Coleman and Bell; α-bromoisobutyric acid was from Columbia Organic Chemical Co.; methacrylic acid was from Rohm and Haas Co.; crotonic acid was from Aldrich Chemical Co. All acids were redistilled before use.

Sulfuric acid (98%) and aqueous perchloric acid (70%) were from Baker and Adamson; methanesulfonic acid was from Matheson Coleman and Bell. Pyridine, Matheson Coleman and Bell, was dried over barium oxide and distilled; di-*t*-butyl peroxide was supplied by Shell Development Co.; azobis(isobutyronitrile) was from Du Pont.

Esters. *sec*-Butyl acetate, *n*-butyl acetate, and *t*-butyl acetate were from Matheson Coleman and Bell; isopropyl isobutyrate, *n*-propyl *n*-butyrate, and isopropyl *n*-butyrate were prepared from the corresponding carboxylic acids and alcohols in ether with sulfuric acid and distilled.

Gases. Ethane, carbon dioxide, *n*-butane, propane, and propylene and isobutane were from the Matheson Company.

Salts. Cobaltous acetate [$Co(OAc)_2 \cdot 4H_2O$] and lithium acetate, anhydrous (LiO_2CCH_3), were from Matheson Coleman and Bell; copper acetate [$Cu(OAc)_2 \cdot H_2O$] was from Mallinckrodt Chemical Co.; sodium acetate (NaOAc) and lead acetate [$Pb(OAc)_2 \cdot 3H_2O$] were from the Fisher Scientific Co.; lead(IV) acetate [$Pb(OAc)_4$] was from G. Frederic Smith; magnesium acetate [$Mg(OAc_2) \cdot 4H_2O$] was from J. T. Baker Chemical Co. Lithium trifluoroacetate and lithium isobutyrate were prepared from lithium carbonate (Mallinckrodt Chemical Co.) and the corresponding acid; sodium trifluoroacetate and sodium isobutyrate were prepared from sodium carbonate (Fisher Chemical Co.) and the corresponding acid. The preparation and characterization of cobaltic(III) acetate has been described elsewhere.[12]

Preparation of Cobaltic Isobutyrate. Cobaltous isobutyrate was prepared by adding 88 g (0.5 mol) of cobaltous acetate (anhydrous) to 274 g of *n*-butyric acid in a two-necked, round-bottomed flask equipped with a Trubore stirrer, and vigorously stirring it for 2 hr at room temperature. The acetic acid was stripped from solution by distillation and the remaining cobaltous isobutyrate diluted with isobutyric acid to a total volume of 400 ml. Ozonation was carried out by the procedure described earlier.[12] Titration indicated a solution that was 1.2 *M* in cobalt(III).

α-Carboxyisobutyric Acids. α-Isobutyroxy-, α-acetoxy-, and α-trifluoroacetoxybutyric acids were prepared from α-bromoisobutyric acid and the corresponding silver carboxylate by the procedure of Mosher and Kehr.[45] Silver isobutyrate was prepared from silver nitrate, isobutyric acid, and sodium hydroxide;[46] silver acetate was from Mallinckrodt Chemical Co.; and silver trifluoroacetate was from City Chemical Co. α-Isobutyroxy- and α-acetoxyisobutyric acids were colorless crystals, melting at 78-79°, lit.[45] 76-77°, and 49-55°, lit.[47] 59-60°, respectively. α-Trifluoroacetoxyisobutyric acid was a yellowish crystalline material which decomposed between 165 and 170°.

Tetramethylsuccinic acid and tetramethylsuccinic anhydride were prepared by hydrolyzing tetramethylsuccinonitrile. The nitrile was prepared by heating azobis(isobutyronitrile) in refluxing carbon tetrachloride overnight.[48] The carbon tetrachloride was stripped and the nitrile was hydrolyzed in 60% sulfuric acid[49] to tetramethylsuccinic anhydride. After two recrystallizations from benzene-petroleum ether (bp 30-60°), white crystals were obtained, mp 153-155°, lit.[50] mp 157°. Ir bands were observed at 5.55, 5.83, 8.24, and 8.50 μ characteristic of acid anhydrides.[51]

Tetramethylsuccinic acid was prepared by hyrolyzing the anhydride in 10% aqueous sodium hydroxide. The solution was carefully acidified with sulfuric acid and the resulting mass collected and recrystallized from ethanol. White needles melting at 198-199°, lit.[52] 200°, resulted, with infrared bands at 6.00, 7.50, 7.78, and 8.10 μ.

Oxidative Decarboxylation of Acids with Cobalt(III) Acetate. General Procedure—Sealed System. Approximately 3 mmol of cobalt(III) acetate and other salts as required were weighed into a ₸ 14/20 long-necked, round-bottomed flask. The appropriate carboxylic acid (10 ml) was added by pipet and the flask sealed with a 6-in. ₸ sleeve capped with a gas-tight rubber septum. The flask was degassed with a hypodermic needle inserted through the septum.

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[42] Part of this difference can be attributed to oxidative elimination processes which are particularly facile with Cu^{II} complexes. Quantitative determination of effects of structure on rate of oxidation are under investigation.

[43] (a) The heterolysis of an alkylcobalt intermediate to a carbonium ion poses certain problems. The ester derived from *n*-butyric acid is predominantly the *n*-propyl isomer rather than the isopropyl ester, which one would expect from the rearrangement of the *n*-propyl cation. Ligand transfer processes may also be involved. The isopropyl *n*-butyrate observed arises partly by acid-catalyzed addition of butyric acid to propylene (see Table IX). This point is under further investigation. (b) Reaction of an alkyl radical with an octahedrally coordinated Co^{III} species presumably can only occur by an outer-sphere mechanism.[38] (c) J. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, **90**, 4616 (1968). (d) J. Kochi and J. Bacha, *J. Org. Chem.*, **33**, 2746 (1968).

[44] "Handbook of Physics and Chemistry," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

[45] W. Mosher and C. Kehr, *J. Am. Chem. Soc.*, **75**, 3173 (1953).

[46] E. Hornung, Ed., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 578.

[47] F. K. Beilstein, "Handbuch der organischem Chemie," Vol. III, 4th ed, Springer-Verlag, Berlin, 1961, p 595.

[48] N. Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 273.

[49] A. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc,, New York, N. Y., 1966, p 410.

[50] I. Heilbron, Ed., "Dictionary of Organic Chemicals," Vol. 5, 4th ed, Oxford University Press, New York, N. Y., 1965, p 3029.

[51] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 45.

[52] Reference 50, p 1128.

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 stirred magnetically.

The completion of the reaction was readily determined visually by a change in color from deep green to reddish pink or blue depending upon the added Lewis acid. The time of reaction determined in this manner compared to within 10% of that found by following evolution of gas (*vide infra*). Titration for $\mathrm{Co^{III}}$ confirmed the complete conversion to $\mathrm{Co^{II}}$.

General Procedure—Gas Evolution. The rate of disappearance of $\mathrm{Co^{III}}$ could be readily followed by gas evolution. The vessel, equipped with a side arm capped with a gas-tight septum for flushing, was connected to a gas buret. The decarboxylation was conducted at atmospheric pressure as described previously.[7]

Analytical Procedures. Gases were identified by gas–liquid partition chromatography (glpc) and determined quantitatively by the internal standard method. Carbon dioxide was determined with ethane as marker on a 2-ft Porapak Q column (Varian Aerograph) at room temperature. Propane, propylene, isobutane, butane, and isobutylene were analyzed on a 15-ft column consisting of Dowtherm A (30%) or silver nitrate with benzyl cyanide on Firebrick.

After the reaction was complete, the flask was removed from the bath and cooled in a Dry Ice bath. Known volumes of reference gases were injected through the septum with a gas-tight syringe. The flask was then warmed quickly and the contents thoroughly shaken. Helium was introduced carefully to increase the pressure slightly above atmospheric pressure, and the gases were sampled and analyzed. In each case, parallel runs were made and the reaction mixture analyzed qualitatively prior to quantitative analysis. Calibration curves were constructed by using various molar volumes of gases under conditions which matched the reactions as closely as possible.

The reaction mixture was transferred and diluted to 40 ml with glacial acetic acid. A 10-ml aliquot was analyzed qualitatively for esters by adding excess water and repeated extraction with pentane, followed by glpc on a column of diethylene glycol succinate or morpholex on Firebrick. The procedure was adapted for quantitative analysis by adding an aliquot of a standard solution of marker (isomeric ester) prior to work-up. The method was calibrated to obviate difficulties introduced by fractionation during work-up. Methacrylic acid was determined by direct analysis of the reaction mixture on a 2.5-ft column of 20% FFAP (Varian Aerograph) on Chromosorb W. The α-acyloxyisobutyric acids could not be analyzed quantitatively in this manner due to decomposition.

Decarboxylation of $\mathrm{Co^{III}}$ Isobutyrate. A solution of $\mathrm{Co^{III}}$ isobutyrate (100 ml of 1.1 *M*) in isobutyric acid was added to 50 ml of isobutyric acid at 140–150° over a period of 4 hr under a nitrogen atmosphere. Periodic sampling of the gas showed that the molar ratio of propane to propylene remained between 9.0 and 9.5 to 1. The mixture was poured into benzene and extracted with 5% aqueous perchloric acid. The extract was dried and distilled to remove acids and low-boiling esters. The residual oil was recrystallized from a benzene–petroleum ether solution and yielded tetramethylsuccinic anhydride as a crystalline solid melting at 154–157°.

Effect of Oxygen on the Decomposition of $\mathrm{Co^{III}}$ Carboxylates. The appropriate cobalt carboxylate was weighed into a heavy-walled glass bomb described previously.[7] Pivalic acid (10 ml) and the solution of the catalyst in pivalic acid were added, and the bomb was pressured with 40 psi oxygen by a standard procedure. The mixture was heated at 80° while being stirred magnetically until the solution changed in color from green to pink. After cooling, the gases were vented into a gas buret and analyzed by gas chromatography.

Kinetic Studies. Reactions in sealed tubes were examined with ampoules made from 6-in. test tubes filled with stock solutions of cobaltic acetate in solutions of pivalic and acetic acids. They were degassed by the freeze–thaw method, sealed under vacuum, and placed into a constant temperature bath at 71 ± 1°. The reactions were quenched by plunging the ampoules into a Dry Ice bath and left until analyzed. The cobalt(III) concentrations were determined spectrophotometrically at 550 and 610 mμ with a Beckman DU spectrophotometer. The extinction coefficient of $\mathrm{Co^{III}}$ at 610 mμ was 245 l./mol cm in pivalic acid and decreased to 198 l./mol cm in pivalic acid solutions containing 9.3×10^{-2} *M* trifluoroacetic acid.

Direct measurement of rates was followed in degassed, 10-mm cells placed in a thermostated compartment of a Cary 14 spectophotometer. Temperature regulation was within ±0.3°. Solvent consisting of pivalic acid and containing 4% by weight acetic acid was liquid at room temperature. It was used to make stock solutions of 4.0×10^{-2} *M* cobalt(III) acetate, 5.0×10^{-1} *M* cobalt(II) acetate, and 9.3×10^{-1} *M* trifluoroacetic acid. These solutions were diluted serially. The reaction mixture was made up in a 25-ml erlenmeyer flask (capped with a gas-tight rubber septum) and degassed with a stream of purified nitrogen introduced with a hypodermic needle. It was transferred with a hypodermic syringe to a 10-mm spectrophotometric cell previously capped and flushed. The rubber septa were washed with toluene and acetone to remove inhibitors. In use the septum was protected from the reaction mixture with a 0.2-mil Teflon liner. Before placing the cell into the compartment, it was quickly preheated with shaking to within 2° of the desired temperature. Absorption was followed for at least three half-lives. After the kinetic order of the reaction was established, the absorption was followed for only one half-live.

Pivalic Acid-*d*. Pivalic acid (0.2 mol) and deuterium oxide (2 mol, >99.8% D) were stirred for 30 min and the $\mathrm{D_2O}$ removed *in vacuo*. The residue was recharged with additional deuterium oxide (2 mol) and the procedure repeated. Pivalic acid was finally distilled and a fraction boiling at 160–162° collected, mp 34.0–34.5°, lit. 36°. The infrared and nuclear magnetic resonance spectra showed no hydroxy absorptions. As a blank, the procedure was repeated with water. The pivalic acid and its deuterated analog were used in direct comparisons of rate.

The Effect of Strong Acids on Alkenes in the Presence of $\mathrm{Co^{III}}$. In the series of *n*-butyric, isobutyric, and pivalic acids, we consistently observed that the presence of strong acids caused a decrease in the amount of decarboxylation observed. The latter was related to the loss of $\mathrm{Co^{III}}$ *via* a route which did not involve carboxylic acid. The effect of strong acids on alkenes was suspect. In the following study we examined this problem in the presence and absence of $\mathrm{Co^{III}}$.

Propylene could be recovered quantitatively from a solution of cobalt(II) acetate in isobutyric acid under conditions of these reactions (Table VIII). In the presence of perchloric acid or boron trifluoride, however, it was slowly converted to isopropyl isobutyrate. Since the latter and recovered propylene accounted for all of the propylene charged, we concluded that addition was the only significant reaction occurring under these conditions. In a similar manner, isobutylene was converted to *t*-butyl isobutyrate in the presence of sulfuric acid, and the material balance was unequivocal.

In the presence of $\mathrm{Co^{III}}$, however, isobutylene was consumed by an additional reaction. Isobutylene was added to pivalic acid in the presence of $\mathrm{Co^{III}}$ and sulfuric acid. After the $\mathrm{Co^{III}}$ was completely reduced, the mixture was reexamined. Only 47% of the isobutylene was accounted for as *t*-butyl isobutyrate and unreacted isobutylene. Furthermore, the amounts of propane, propylene, and propyl esters normally obtained under these conditions from the isobutyric acid (in the absence of isobutylene) were diminished by the same amount.

The oxidation of isobutylene by $\mathrm{Co^{III}}$ under the influence of sulfuric acid was not as severe when trifluoroacetic acid was employed. The course of the decarboxylation of isobutyric acid by $\mathrm{Co^{III}}$ in the presence of trifluoroacetic acid was not materially affected by the addition of isobutylene. The latter was accounted for (after reaction) in good yields as a mixture of *t*-butyl isobutyrate and trifluoroacetate and unreacted isobutylene.

Acknowledgment. We wish to thank the National Science Foundation and the Air Force Office of Scientific Research for generous grants which made this work possible, and the Enjay Chemical Co. for generous gifts of pivalic acid.