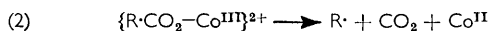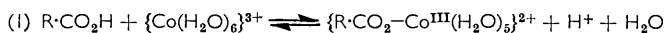**502.** *Oxidations of Organic Compounds by Cobaltic Salts. Part VI.*[1] *Kinetic and Product Studies of the Oxidations of Some Carboxylic Acids*

By A. A. CLIFFORD and WILLIAM A. WATERS

Evidence is presented to show that the oxidation of aliphatic carboxylic perchlorate follows the mechanism

(1) $R \cdot CO_2H + \{Co(H_2O)_6\}^{3+} \rightleftharpoons \{R \cdot CO_2 - Co^{III}(H_2O)_5\}^{2+} + H^+ + H_2O$

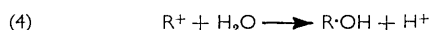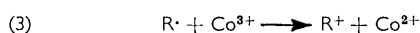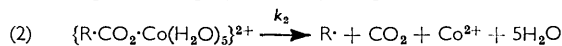(2) $\{R \cdot CO_2 - Co^{III}\}^{2+} \longrightarrow R \cdot + CO_2 + Co^{II}$

in which the slow fragmentation of the cobaltic–carboxylate complex is a concerted process, the energy available from carbon dioxide formation assisting in the liberation of the free alkyl radical. The oxidations of propionic and phenylacetic acids show Michaelis–Menten kinetics, thus establishing the rapid equilibrium process (1), whilst product studies show that end-products are entirely derived from free radicals, $R \cdot$, and cannot be formed from α-hydroxy-acids.

In the case of β-phenylisovaleric acid, $Ph \cdot CMe_2 \cdot CH_2 \cdot CO_2H$, the oxidation products ($Ph \cdot CHO$ and Me_2CO) are formed by the expected molecular rearrangement of neophyl radicals:

$$Ph \cdot CMe_2 \cdot CH_2 \cdot \longrightarrow Ph \cdot CH_2 \cdot CMe_2 \cdot$$
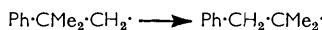
SATURATED aliphatic acids, in general, are highly resistant to chemical oxidation except by reagents which can also attack paraffins, but we have found that many of them can be oxidised by aqueous cobaltic perchlorate at rates comparable to those for oxidation of alcohols or ketones (see previous Parts [1-4]). We now give details of kinetic and product studies, previously outlined in a lecture,[5] to show that the oxidation of carboxylic acids by cobalt(III) takes place by an inner-sphere mechanism involving (1) the rapid reversible formation of a cobaltic complex which then (2) breaks down slowly with liberation of free alkyl radicals; these then undergo further rapid reactions (*e.g.*, 3 and 4).

(1) $R \cdot CO_2H + Co(H_2O)_6^{3+} \overset{K_1}{\rightleftharpoons} \{R \cdot CO_2 \cdot Co(H_2O)_5\}^{2+} + H^+ + H_2O$

(2) $\{R \cdot CO_2 \cdot Co(H_2O)_5\}^{2+} \overset{k_2}{\longrightarrow} R \cdot + CO_2 + Co^{2+} + 5H_2O$

(3) $R \cdot + Co^{3+} \longrightarrow R^+ + Co^{2+}$

(4) $R^+ + H_2O \longrightarrow R \cdot OH + H^+$

This mechanism is similar to that deduced in Parts I,[2] IV,[4] and V[1] for the oxidation of alcohols, and we attribute the relative ease of oxidation of acids to the fact that equilibrium constants, K_1, for complex formation with acids are definitely much higher than those (K_5) for the corresponding reactions with alcohols, since these, as yet, have proved to be too small for evaluation

(5) $R \cdot OH + Co(H_2O)_6^{3+} \overset{K_5}{\rightleftharpoons} R \cdot O \cdot Co(H_2O)_5 + H_2O + H^+$
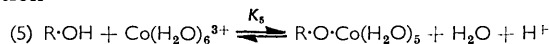
Kinetic Studies.—All kinetic measurements were made spectrophotometrically in aqueous perchloric acid–sodium perchlorate mixtures of constant total ionic strength (3·14M) using cobalt(III) concentrations varying between 3×10^{-4} and 10^{-3}M. Tests (Table 1) showed that cobaltous ions, even in excess, had no effect on the reaction velocity. The organic acid was taken in such big excess that (*a*) negligible secondary oxidation of stable molecular products, *e.g.*, $R \cdot OH$, occurs (see " Product studies," p. 2800) and (*b*) the measured rate was at least 10 times that of the spontaneous reduction of cobaltic ions by

[1] Part V, D. G. Hoare and W. A. Waters, *J.*, 1964, 2560.
[2] Part I, D. G. Hoare and W. A. Waters, *J.*, 1962, 965.
[3] Part II, D. G. Hoare and W. A. Waters, *J.*, 1962, 971.
[4] Part IV, D. G. Hoare and W. A. Waters, *J.*, 1964, 2552.
[5] International Symposium on Reaction Mechanisms, Cork, 1964; W. A. Waters, *Chem. Soc., Special Publ.*, No. 19, 1965.

TABLE 1

Effect of cobaltous ions on the rate of oxidation of organic acids by cobaltic perchlorate in 1·10M-perchloric acid at 15°

Series A: $[NaClO_4] = 2·04M$; Initial $[Co(ClO_4)_2] = 1·5 \times 10^{-3}M$
Series B: $[NaClO_4] = 1·99M$; Initial $[Co(ClO_4)_2] = 1·5 \times 10^{-2}M$

Substrate	Concn. (M)	$10^3k'$ (Series A)	$10^3k'$ (Series B)
Et·CO$_2$H	1·00	4·2	4·2
Me$_2$CH·CO$_2$H	0·0095	7·1	7·1
Me$_3$C·CO$_2$H	0·0045	7·6	7·9
Ph·CH$_2$·CO$_2$H	0·0077	18·4	19·2

(k' = measured first-order rate constant (sec.$^{-1}$) for the disappearance of Co^{III})

TABLE 2

Reaction order with respect to [cobalt(III)]

$[HClO_4] = 2·12M$; $[NaClO_4] = 1·02M$; Temp. 15°

	Propionic acid (1·00M)		Isobutyric acid (9·5 × 10^{-3}M)		Pivalic acid (4·5 × 10^{-3}M)		Phenylacetic acid (5·7 × 10^{-3}M)	
Time (min.)	$[Co^{III}]_0 =$ 3 × 10^{-4}M X *	$10^3k'$ (sec.$^{-1}$)	$[Co^{III}]_0 =$ 1·0 × 10^{-3}M X	$10^3k'$ (sec.$^{-1}$)	$[Co^{III}]_0 =$ 1·0 × 10^{-3}M X	$10^3k'$ (sec.$^{-1}$)	$[Co^{III}]_0 =$ 1·0 × 10^{-3}M X	$10^3k'$ (sec.$^{-1}$)
3	0·215	2·75	0·283	3·62	0·289	3·80	0·604	7·71
4	0·293	2·81	0·383	3·63	0·387	3·72	0·794	7·45
5	0·365	2·80	0·472	3·62	0·466	3·57	0·995	7·64
6	0·437	2·80	0·568	3·63	0·577	3·68	1·197	7·64
7	0·516	2·83	0·637	3·49	0·638	3·49	1·491	8·17
8	0·574	2·76	0·752	3·61	0·736	3·53		
9	0·637	2·72	0·843	3·60	0·838	3·57		
10	0·723	2·77	0·938	3·60	0·934	3·57		
12	0·854	2·73	1·129	3·61	1·129	3·61		

* X: $\log_{10} ([Co^{III}]_0/[Co^{III}]_t)$.

TABLE 3

Oxidations of isobutyric and pivalic acids at 15°

	10^3[Acid] (M)	$[HClO_4]$ (M)	$10^3k'$ (sec.$^{-1}$)	k_{II}	$k_{II}[HClO_4]$
Isobutyric acid	9·5	1·10	7·1	0·74	0·82
,,	19·5	1·10	14	0·73	0·81
,,	29·5	1·10	22	0·75	0·82
,,	9·5	2·12	3·6	0·38	0·81
,,	9·5	3·14	2·4	0·25	0·80
Pivalic acid	2·0	1·10	3·4	1·68	1·85
,,	4·5	1·10	7·6	1·72	1·91
,,	9·5	1·10	16·3	1·70	1·87
,,	4·5	2·12	3·6	0·80	1·87
,,	4·5	3·14	2·5	0·58	1·81

water. For the latter reason the rate of oxidation of acetic acid by cobaltic perchlorate was too slow for accurate study. Under the conditions chosen the rate of disappearance of cobalt(II) was accurately of the first order for 3—4 half-lives. Typical figures are given in Table 2.

To within experimental error the rates of oxidation of isobutyric and pivalic acids were found to be of the first order with respect to the concentrations of the organic acid and inversely proportional to the concentration of the perchloric acid (Table 3). With propionic acid, which had to be examined at a much higher molarity, the first-order rate constants at 15° could be fitted to Michaelis–Menten reciprocal plots, as shown by Figure 1, and so could be used for the separate evaluation of K_1 and k_2, since from equation (1) it can be deduced for a rapid equilibrium that

$$[R·CO_2·Co^{III}] = [Total Co^{III}]. \quad K_1[R·CO_2H]/([H^+] + K_1[R·CO_2H])$$

whence $-d[Co^{III}]/dt = k'[Co^{III}] = k_2[Co^{III}]. \quad K_1[R·CO_2H]/([H^+] + K_1[R·CO_2H])$

or

$$1/k' = 1/k_2 + [H^+]/k_2K_1[R·CO_2H]$$

If the equilibrium (1) were slow then the oxidations would not be strictly of the first order with respect to [cobalt(III)].

Table 4 shows that the experimental data can be fitted to the expression

$$k' = 0.0076\ [Et \cdot CO_2H]/[HClO_4] + 0.72\ [Et \cdot CO_2H]$$

whence $K_1 = 0.72$ and $k_2 = 1.05 \times 10^{-2}$ (sec.$^{-1}$), and that for phenylacetic acid the corresponding equation

$$k' = 2.9\ [Ph \cdot CH_2 \cdot CO_2H]/[HClO_4] + 26\ [Ph \cdot CO_2H])$$

is satisfactory. In this case the errors in K_1 (2%) and k_2 0.11 sec.$^{-1}$) are much greater since to obtain suitable measurements the phenylacetic acid had to be used at *ca.* 10^{-3}M, and the deviation from the simpler equation

$$-d[Co^{III}]/dt = k[Co^{III}][R \cdot CO_2H][HClO_4]$$

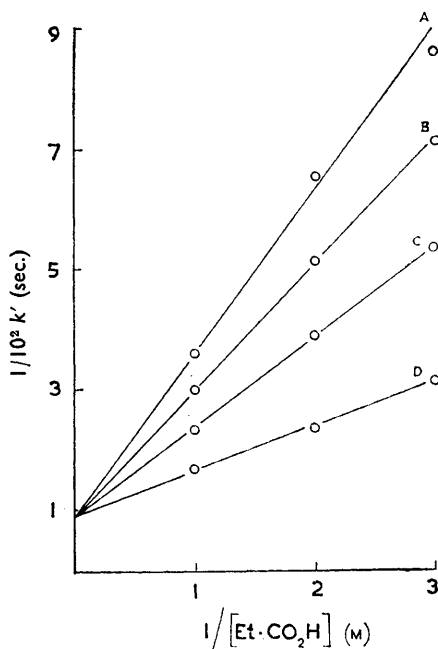
FIGURE 1. Michaelis–Menten plot for the oxidation of propionic acid by cobaltic perchlorate at 15°

A, [HClO$_4$] = 2.12M
B, [HClO$_4$] = 1.61M
C, [HClO$_4$] = 1.10M
D, [HClO$_4$] = 0.59M

TABLE 4

Oxidation of propionic acid (15°)			Oxidation of phenylacetic acid (15°)			
[Et·CO$_2$H]	$10^3 k'$ (sec.$^{-1}$)		[HClO$_4$]	10^3[Ph·CH$_2$·CO$_2$H]	$10^3 k'$ (sec.$^{-1}$)	
M	Found	Calc.*	M	M	Found	Calc.*
0·33	3·2	3·1	0·59	3·0	14·4	13·1
0·50	4·2	4·0	0·59	4·7	21	19·2
1·00	5·9	5·8	0·59	9·7	35	33
0·33	1·86	1·87	1·10	3·7	8·4	9·0
0·50	2·6	2·6	1·10	5·7	14·0	13·4
1·00	4·2	4·2	1·10	9·7	22	21
0·33	1·40	1·35	1·61	3·7	6·1	6·3
0·50	1·94	1·93	1·61	5·7	9·2	9·4
1·00	3·3	3·3	1·61	9·7	15·6	15·1
0·33	1·17	1·06	2·12	3·7	4·9	4·8
0·50	1·56	1·53	2·12	5·7	7·6	7·3
1·00	2·7	2·7	2·12	7·7	9·3	9·5
—	—	—	2·12	9·7	12·0	11·7
—	—	—	2·12	11·7	13·7	14·0
—	—	—	2·12	13·7	15·6	16·1

* See text for the rate equations.

is small.   Actually if isobutyric and pivalic acids really do follow similar oxidation kinetics to propionic acid the deviation from the simpler kinetics of Table 3 would have been undetectable for K_1 values less than 5.   Table 5, for propionic acid, shows

TABLE 5

Temperature-dependence of propionic acid oxidation

$[HClO_4] = 1\cdot10M;$ $[NaClO_4] = 2\cdot04M$

$10^3k'$ (sec.$^{-1}$)

Temp.	[Et·CO$_2$H] (M)	Found	Calc.	10^3k_2 (sec.$^{-1}$)	K_1
10°	0·50	1·17	1·21		
10	0·67	1·28	1·50	4·9	0·72
10	1·00	1·73	1·94		
15	0·33	1·86	1·93		
15	0·50	2·6	2·6	10·5	0·72
15	1·00	4·2	4·2		
20	0·50	5·5	5·7		
20	0·67	7·3	7·1	24	0·68
20	1·00	8·8	9·2		
25	0·50	13·0	13·4		
25	0·67	16·0	16·4	51	0·77
25	1·00	19·8	21		

TABLE 6

Temperature-dependence of rate constants

Acid	Values of $K_1 . k_2$ [HClO$_4$] (Found)						ΔE (kcal.)	A	ΔS^* (e.u.)$^{298°}$
	10°	15°	20°	25°	30°	35°			
Propionic	3·4	7·6	16·3	39·0	(all × 10^{-3})	—	26·7	7·6 × 10^{17}	+21·4
Isobutyric......	0·33	0·81	1·42	2·6	5·2	10·5	22·6	1·12 × 10^{17}	+16·1
Pivalic	0·68	1·84	3·1	4·4	8·0	14·7	18·7	2·9 × 10^{14}	+4·1
Phenylacetic ...	1·25	2·9	5·1	8·7	—–	—–	21·4	5·0 × 10^{16}	+13·1

For propionic and phenylacetic acids K_1k_2[HClO$_4$] has been evaluated from the slopes of the Michaelis–Menten plots.   For propionic, isobutyric, and pivalic acids the reaction velocities and A values approximately correspond to the stoicheiometry 1 [Acid] $\equiv$ 2[Co^{III}], and for phenylacetic acid to 1 [Acid] $\equiv$ 4[Co^{III}] (see " Product studies," p. 2800), but ΔS^* has been calculated to correspond to the initial reaction, R·CO$_2$H + Co^{III} $\longrightarrow$ Primary products.

TABLE 7

Oxidation of propionic acid in methyl cyanide–water at 15°

$[HClO_4] = 1\cdot10M;$ $[NaClO_4] = 2\cdot04M;$ Initial [Co^{III}] *ca.* 3 × 10^{-4}M

MeCN (%) (v/v) = x	[EtCO$_2$H] M	$10^3k'$ Found	Calc.	$10^3K_1k_2$	10^2k_2	K_1	10^2k_2 (calc.) ^{a}	$10^3K_1k_2$ (calc.) ^{b}
0	(see Tables 4 and 5)			7·6	1·05	0·72	1·00	7·4
10	0·33	2·7	2·7					
10	0·50	3·7	3·7	11·3	1·38	0·82	1·44	11·2
10	1·00	5·9	5·9					
20	0·33	4·1	4·1					
20	0·50	5·5	5·6	17·2	1·95	0·88	2·1	18·2
20	1·00	8·7	8·7					
30	0·33	7·8	7·3					
30	0·50	10·3	10·3	32	3·5	0·92	3·0	29
30	1·00	17·0	15·8					

^{a} Calc. from $k_2 = 1\cdot00$ exp $3\cdot7x$. ^{b} Calc. from $K_1k_2 = 7\cdot4$ exp $4\cdot5x$.

that the equilibrium constant K_1 varies little with temperature.   Thus the heat of complex formation must be small and the temperature-dependence of the oxidation closely indicative of the activation energy needed for the slow decomposition process (2).

The evaluation of other thermodynamic data is given in Table 6.   Table 7 shows that

propionic acid oxidises more rapidly in methyl cyanide–water mixtures than in water alone and that the effect of the methyl cyanide can be represented by the empirical equation $R_{soln} = R_{water} \exp (Mx)$ (where R is the reaction velocity constant, x is the volume fraction of methyl cyanide, and M is a constant) previously found by Hoare and Waters [4] to be satisfactory for the oxidation of alcohols and by Cooper and Waters [6] for the oxidation of aromatic aldehydes. The changes of solvent affect the velocity constant k_2 far more than the equilibrium constant K_1.

Product Studies.—Further kinetic and analytical measurements have been carried out with each acid mentioned in the preceding section and also with β-phenylisovaleric acid, $Ph \cdot CMe_2 \cdot CH_2 \cdot CO_2H$. In each case evidence has been obtained to show that reactions (1) and (2) represent the initial oxidative route. The reasoning however differs somewhat in each case.

(a) *Phenylacetic acid.* This gave benzaldehyde as a major oxidation product; previously Mr. T. A. Cooper (Part III [6]) had shown that this is oxidised very slowly by cobaltic perchlorate even in aqueous methyl cyanide. Two oxidative routes are thus possible:
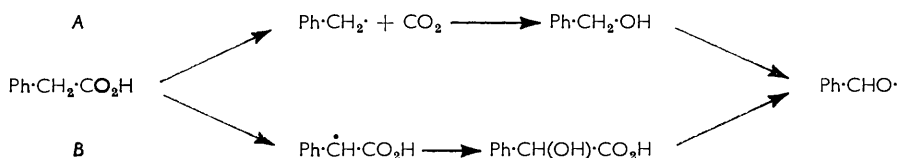
The following bimolecular rate constants (l. mole^{-1} sec.$^{-1}$) measured at 15° in 1·10M-perchloric acid show that route A should yield benzaldehyde much more rapidly than route B: $Ph \cdot CH_2 \cdot CO_2H$, 2·8; $Ph \cdot CH_2 \cdot OH$, *ca.* 400; $PhCH(OH) \cdot CO_2H$, 1·93; $Ph \cdot CHO$, 0·02. Solutions containing $3·0 \times 10^{-2}$ mole phenylacetic acid and $2·6 \times 10^{-2}$ mole cobaltic perchlorate in 1·10M-perchloric acid were allowed to interact completely; the percentage yields of benzaldehyde, measured by a slight modification (see Experimental section) of that of Part IV,[4] were 90, 87, and 91. The calculated yields (1 $Ph \cdot CH_2 \cdot CO_2H$ requires 4 Co^{III}) are: Route A, 92%; Route B, 5%.

The products from another oxidation on a larger scale of phenylacetic acid, taken in excess, were extracted into ether, washed with alkali, concentrated, and examined by vapour-phase chromatography through firebrick coated with a polyadipate ester: the chromatogram gave large overlapping peaks corresponding to benzaldehyde and benzyl alcohol and a small peak corresponding to bibenzyl (under 1%), indicative of the transient formation of benzyl radicals.

$[\alpha\alpha^{-2}H_2]$Phenylacetic acid, $Ph \cdot CD_2 \cdot CO_2H$, was then prepared and its oxidation rate compared with that of the protio-acid (Table 8).

TABLE 8

The deuterium isotope effect for the oxidation of phenylacetic acid at 15°

$[HClO_4] = 2·12M$; $[NaClO_4] = 1·02M$; Initial organic acid = $9·7 \times 10^{-3}M$

$10^3k'$ (sec.$^{-1}$) for $Ph \cdot CH_2CO_2H$	$10^3k'$ (sec.$^{-1}$) for $Ph \cdot CD_2 \cdot CO_2H$	k_H/k_D
12·0, 12·5, 11·9	9·8, 10·1, 9·6	1·24, 1·25, 1·25

The low figure (*ca.* 1·1^2) for k_H/k_D is consistent only with a secondary kinetic isotope effect; had a C–H (C–D) bond been the site of direct attack of cobalt(III) a much larger kinetic isotope effect would have been found (cf. 2·3 for the oxidation of *m*-nitrobenzaldehyde [6]).

(b) *Isobutyric acid.* This was oxidised to acetone but in low yield.

---

[6] Part III, T. A. Cooper and W. A. Waters, *J.*, 1964, 1538.

The alternative reaction paths are
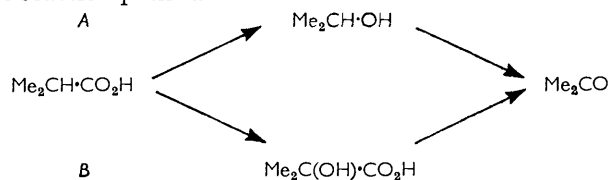
and the following bimolecular rate constants (1. mole⁻¹ sec.⁻¹) were measured * in 1.57M perchloric acid at 15°: $Me_2CH\cdot CO_2H$, 0.23; $Me_2CH\cdot OH$, 0.037; $Me_2C(OH)\cdot CO_2H$, 1.44; Me_2CO, 1.2×10^{-4}. In similar acid, with $2.3 \times 10^{-2}\text{M}$-cobalt(III), the percentage yields of acetone,* calculated for 1 mole acetone being equivalent to 4 moles cobalt(III) consumed were those of Table 9. Clearly the main oxidation product must be isopropyl alcohol, which oxidises so slowly that when isobutyric acid is taken in large excess over cobalt(III) as

TABLE 9

Percentage yields of acetone from the oxidation of isobutyric acid

$Me_2CH\cdot CO_2H$ taken (M)	Calc. for Route A	Calc. for Route B	Found
0·036	3·6	65	3·2
0·072	2·0	36	2·6

in the measurements of Tables 3 and 6 the stoicheiometry of the oxidation is closely $1 \ Me_2CO\cdot CO_2H \equiv 2Co^{III}$.

(c) *Pivalic and propionic acids.* The course of an oxidation of pivalic acid with an excess of cobaltic perchlorate is shown in Figure 2. The sharp fall in [cobalt(III)] ends when 1·88 moles of cobalt(III) have been used per mole of pivalic acid initially present and
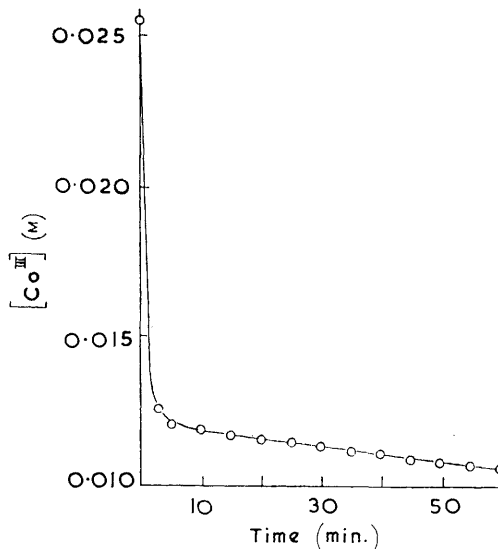

FIGURE 2. The oxidation of pivalic acid by an excess of cobaltic perchlorate at 15°

$[HClO_4] = 1.65\text{M}$. Initial $[Co^{III}] = 2.56 \times 10^{-2}\text{M}$. Initial $[Me_3C\cdot CO_2H] = 7.28 \times 10^{-3}\text{M}$

the subsequent oxidation rate is less than 6.5×10^{-3} 1. mole⁻¹ sec.⁻¹. Possible oxidation products of pivalic acid are $Me_3C\cdot OH$ or $Me_2C(CO_2H)\cdot CH_2OH$. The following rate data (in 1. mole⁻¹ sec.⁻¹) at 15° in 1·1M-perchloric acid show that only t-butanol is sufficiently resistant to oxidation to be the first molecular oxidation product of pivalic acid for all primary alcohols oxidise 100 times more easily: $Me_3C\cdot OH$, 2.2×10^{-3}; $Me_2CH\cdot CH_2OH$, 0.72; EtOH, 0.51; $MeCH(OH)\cdot CO_2H$, 0.46; $Me\cdot CHO$, 0.64.

From propionic acid the formation of a little acetaldehyde was established by the

* These measurements were made by Dr. D. G. Hoare, and in part have been reported in previous Parts.

isolation of its 2,4-dinitrophenylhydrazone, but the rates of oxidation of the possible products (ethanol and lactic acid) are so similar that the postulated oxidative route *via* ethyl radicals remains inferential.

(d) β-*Phenylisovaleric acid*, $Ph \cdot CMe_2 \cdot CH_2 \cdot CO_2H$. According to the mechanism of equations (1—3) the first oxidation product of this acid should be the neophyl radical, $Ph \cdot CMe_2CH_2 \cdot$, and the second the corresponding cation, but it is well known [7,8] that both these active particles rapidly undergo intramolecular phenyl transfer to give the much more stable radical $Ph \cdot CH_2 \cdot CMe_2 \cdot$ or cation $Ph \cdot CH_2CMe_2^+$. There is, however, some evidence to indicate that the unrearranged radical does have a separate existence and may need an activation energy not exceeding 8 kcal. for its isomerisation.[9] Since the activation energy for the oxidation of all aliphatic acids by cobalt(III) greatly exceeds this figure it follows that if the oxidation of β-phenylisovaleric acid accords with equations (1—2) then the easily detectable reaction products should be almost exclusively the further oxidation products of 2-benzylpropan-2-ol, $Ph \cdot CH_2CMe_2 \cdot OH$, *i.e.*, benzaldehyde and acetone (cf. Part IV), whereas oxidation by direct attack at C–H should give the hydroxy-acid $Ph \cdot CMe_2 \cdot CH(OH) \cdot CO_2H$ and thence the aldehyde $Ph \cdot CMe_2 \cdot CHO$. Benzaldehyde and acetone, but no other aldehyde or ketone, were indeed produced by the oxidation of β-phenylisovaleric acid in 30% aqueous methyl cyanide and the rate and product data of Tables 10 and 11 show that the carboxylic acid oxidation occurs with virtually complete molecular rearrangement.

TABLE 10

Rates of oxidation of β-phenylisovaleric acid and of 2-benzylpropan-2-ol

$[HClO_4] = 3 \cdot 14M$; Initial $[Co^{III}]$ *ca.* $10^{-3}M$; Solvent = 30% MeCN (v/v). Temp. 15°.

	$10^3[substrate]$	$10^3k'$ (sec.$^{-1}$)	k_{II} (l. mole^{-1} sec.$^{-1}$)
$Ph \cdot CMe_2 \cdot CH_2CO_2H$	3·5	1·38	0·39
,, ...	5·5	2·0	0·38
,, ...	7·5	2·7	0·37
,, ...	9·5	3·7	0·39
$Ph \cdot CH_2CMe_2 \cdot OH$	18	2·1	0·107
,, ...	23	2·6	0·110
,, ...	28	3·2	0·112
,, ...	33	3·7	0·112
,, ...	38	4·8	0·126

TABLE 11

Quantitative product yields from oxidation of 2-benzylpropan-2-ol and β-phenylisovaleric acid

Solvent = 30% MeCN (v/v); $[HClO_4] = 3 \cdot 14M$; $[Co^{III}] = 1 \cdot 03 \times 10^{-2}M$; Temp. 15°

(a) $Ph \cdot CH_2 \cdot CMe_2OH$ oxidations (0·041M)

Percentage yields found: Ph·CHO = 96, 98, 95; Me_2CO, 98, 101, 100 (calc. for both products, 100, assuming 1 ROH ≡ 4 Co^{III}).

(b) $Ph \cdot CMe_2 \cdot CH_2CO_2H$ oxidations

$10^2[Acid]$	PhCHO (%)	Me_2CO (%)	Calc. (%) *
2·0	41	44	43
3·0	36	39	36
4·0	30	30	31

* Assuming 1 mole acid requires 6 moles Co^{III} and complete rearrangement.

The above work decisively establishes that the oxidation of β-phenylisovaleric acid passes through the radical $Ph \cdot CMe_2 \cdot CH_2 \cdot$ but not necessarily that this radical rearranges before it is oxidised to the corresponding cation. We consider that the rearrangement probably does occur at the radical stage because test oxidations of n-butyric acid $Me \cdot CH_2 \cdot CH_2 \cdot CO_2H$ failed to give detectable amounts of acetone. n-Propyl radicals have

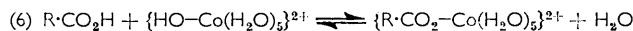[7] W. H. Urry and M. S. Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438.
[8] W. H. Saunders and R. H. Paine, *J. Amer. Chem. Soc.*, 1961, **83**, 882.
[9] F. H. Seubold, *J. Amer. Chem. Soc.*, 1953, **75**, 2532.

been shown not to rearrange at low temperatures, but n-propyl cations do rearrange under the conditions of the Friedel–Crafts reaction.[10]
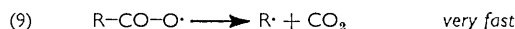
DISCUSSION

Previous Parts have suggested that in aqueous perchloric acid the chemically active ion of cobalt(III) is $\{HO-Co(H_2O)_5\}^{2+}$ since all measured oxidations have shown an inverse acidity dependence. For the oxidations of carboxylic acids the complex-forming reaction may be represented equally well as (6) or (7)
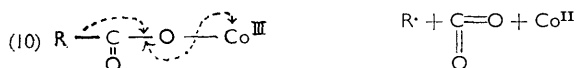
$$(6) \quad R \cdot CO_2H + \{HO-Co(H_2O)_5\}^{2+} \rightleftharpoons \{R \cdot CO_2-Co(H_2O)_5\}^{2+} + H_2O$$

$$(7) \quad R \cdot CO_2- + \{Co(H_2O)_6\}^{3+} \rightleftharpoons \{R \cdot CO_2-Co(H_2O)_5\}^{2+} + H_2O$$

and from the kinetic data ions such as $\{R \cdot CO_2-Co(H_2O)_4-OH\}^+$ and $\{(R \cdot CO_2)_2=Co(H_2O)_4\}^+$

$$\left\{ \begin{array}{c} CH_2 \cdot CO_2 \\ | \\ CH_2 \cdot CO_2 \end{array} \middle\rangle Co(H_2O)_4 \right\}^+$$

(I)

can both be excluded. In accordance with the latter conclusion oxalic acid is not oxidised by cobaltic perchlorate in perchloric acid and the oxidation of succinic acid which also could form a chelate complex (I) was just detectable, though adipic acid which cannot form chelate complexes can be oxidised somewhat faster $(k[H \cdot ClO_4] = 1 \cdot 3 \times 10^{-2})$ than propionic acid.

Table 6 shows that the ease of oxidation of aliphatic acids follows the sequence $Me \cdot CO_2H < Me \cdot CH_2 \cdot CO_2H < Me_2CH \cdot CO_2H < Me_3C \cdot CO_2H$, and that the activation energy decreases by about 4 kcal. for each replacement of an α-hydrogen by a methyl group. This would not be expected for a 2-stage decomposition:

$$(8) \quad R-CO-O-Co^{III} \longrightarrow R-CO-O \cdot + Co^{II} \quad slow$$

$$(9) \quad R-CO-O \cdot \longrightarrow R \cdot + CO_2 \quad very \; fast$$

for the mere inductive effect of a distant alkyl group on the homolysis of an O–Co bond should be small.

Radical stability, however, increases significantly in the sequence $Me < Et < Pr^i < Bu^t$, as shown for instance by the activation energies needed for the homolysis of alkyl iodides.[11] We therefore suggest that the decomposition of cobaltic–carboxylate complexes is a concerted fragmentation (10)

$$(10) \quad R \overset{\cdots}{-} \underset{\underset{O}{\|}}{C} \overset{\cdots}{-} O \overset{\cdots}{-} Co^{III} \qquad \qquad R \cdot + \underset{\underset{O}{\|}}{C} = O + Co^{II}$$

whereby the large amount of energy made available by the formation of carbon dioxide in the exothermic partial reaction (9) can supplement the external activation energy needed to liberate a free radical when one election enters the inert d shell of cobalt in the valency change from cobalt(III) to cobalt(II). The overall result of this concerted fragmentation is thus that there can be produced an organic free radical which is chemically more reactive than the original oxidant. To some extent the positive entropy of activation helps in the release of the energy-rich free radical, but this is a common feature of all oxidations by cobaltic perchlorate.

EXPERIMENTAL

Materials.—All liquids were dried (Na_2SO_4) and fractionated using a 10 : 1 reflux ratio. Solid acids were recrystallised.

[$\alpha\alpha$-$^2H_2$]*Phenylacetic Acid.*[12]—1·0 g. of dry sodium phenylacetate and a solution of 0·1 g. sodium in 2 ml. deuterium oxide (99·8% D_2O) were heated together in a sealed tube at 150° for 6 days. The contents were then evaporated to dryness at 100° in carbon dioxide free air; the

[10] H. S. A. Douwes and E. C. Kooyman, *Rec. Trav. chim.*, 1964, **83**, 276.

[11] E. W. R. Steacie, " Atomic and Free Radical Reactions," vol. I, p. 97, Reinhold Publ. Co., New York, 1954.

[12] Cf. D. J. G. Ives, *J.*, 1938, 81.

exchange process was repeated twice by addition of fresh 2 ml. portions of deuterium oxide to the dried mixture. The solution was then acidified, the acid was crystallised once from water and then dried at 130° in a vacuum. Analysis by n.m.r. and by infrared spectroscopy after combustion gave 1·92 and 1·88 atoms D per mol., respectively (we thank Mrs. E. Richards and Dr. F. B. Strauss for these analyses).

β-*Phenylisovaleric Acid*.—ββ-Dimethylacrylic acid [13] and benzene were condensed using aluminium chloride and the product was crystallised from light petroleum to the authentic [14] m. p. (59°) (Found: C, 74·0; H, 8·1. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 8·1%). 2-Benzylpropan-2-ol was prepared by the Grignard reaction between benzylmagnesium bromide and acetone). After low-temperature crystallisation from light petroleum it had m. p. 23—24° (lit.,[15] 24° (Found: C, 80·2; H, 9·3. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·3%).

The aqueous cobaltic perchlorate was made electrolytically as described in Part I and used on the day of preparation. The kinetic measurements were made spectrophotometrically as in Parts I—V, the absorption of cobalt(III) at 230 mμ being used, except for 2-benzylpropan-2-ol (594 mμ).

Product Analyses.—The method of Part IV [4] was used for 10^{-2} mole quantities of reactions. Cyclohexanone dinitrophenylhydrazone was used as the reference standard and the chromatoplates were eluted with benzene–cyclohexane (3/2). The acetone yields were always slightly high and a blank value of 5×10^{-5} mole found even with purified reagents had to be subtracted. In the test oxidation 0·1 mole of n-butyric acid gave less than 10^{-4} mole acetone.

[13] L. I. Smith, W. W. Pritchard, and L. J. Spillane, *Org. Syntheses*, 1943, **23**, 27.
[14] M. A. Saboor, *J.*, 1945, 922.
[15] I. M. Heilbron and H. M. Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.