490. *Oxidations of Organic Compounds by Cobaltic Salts. Part IV.*[1]
Kinetic Product Studies of Oxidations of Tertiary Alcohols.[*]

By D. G. HOARE and WILLIAM A. WATERS.

Oxidations of tertiary alcohols by cobaltic perchlorate yield mixtures of ketones. These have been analysed quantitatively by thin-layer chromatography of their dinitrophenylhydrazones followed by absorptiometric analysis. Evidence is given that the reaction probably involves the formation of an alkoxy-radical which then loses an alkyl group. .

Relative rates of cobalt(III) consumption by a series of alcohols have been measured in methyl cyanide–water mixtures. Ease of oxidation of an alcohol $R'CR_2 \cdot OH$ bears some relationship to the ease of fission of an alkyl group, $R \cdot$ or R', from the radical $R'CR_2$–O.
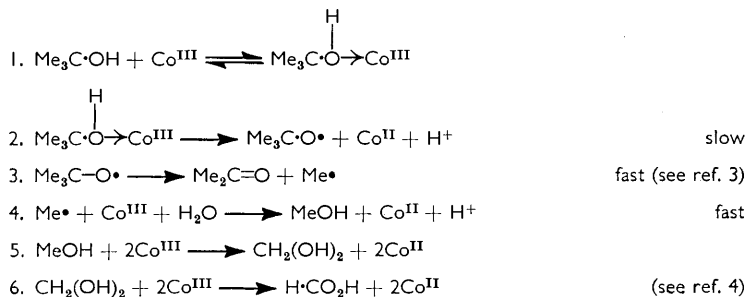
PART I[2] described the kinetics of the slow oxidation of t-butyl alcohol with aqueous cobaltic perchlorate. Initially the reaction is of the first order with respect to both the alcohol and Co^{III} and can be represented as the scheme shown since acetone, which is highly resistant to further oxidation, is a major reaction product. According to this

* Presented at the XIXth Congress of I.U.P.A.C., London, 1963.
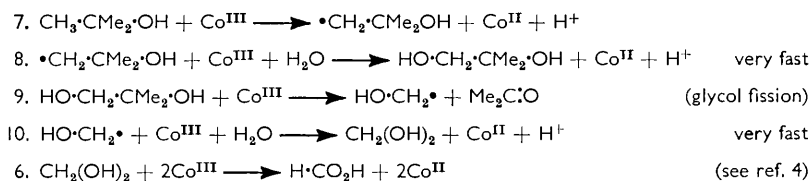[1] Part III, Cooper and Waters, *J.*, 1964, 1538.
[2] Hoare and Waters, *J.*, 1962, 965.

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complete scheme one should find in the reaction products 1 mole of acetone per 6 equivalent of cobalt(III) consumed, provided that there was no secondary oxidation of the acetone and that the composite oxidations (5) and (6) were both faster than reaction (2).   At very high $[Me_3C-OH] : [Co^{III}]$ ratios reaction (2) would become relatively more rapid,

$$1.\ Me_3C \cdot OH + Co^{III} \rightleftharpoons Me_3C \cdot \overset{\overset{\displaystyle H}{|}}{O} \rightarrow Co^{III}$$

$$2.\ Me_3C \cdot \overset{\overset{\displaystyle H}{|}}{O} \rightarrow Co^{III} \longrightarrow Me_3C \cdot O\bullet + Co^{II} + H^+ \qquad\qquad slow$$

$$3.\ Me_3C-O\bullet \longrightarrow Me_2C{=}O + Me\bullet \qquad\qquad fast\ (see\ ref.\ 3)$$

$$4.\ Me\bullet + Co^{III} + H_2O \longrightarrow MeOH + Co^{II} + H^+ \qquad\qquad fast$$

$$5.\ MeOH + 2Co^{III} \longrightarrow CH_2(OH)_2 + 2Co^{II}$$

$$6.\ CH_2(OH)_2 + 2Co^{III} \longrightarrow H \cdot CO_2H + 2Co^{II} \qquad\qquad (see\ ref.\ 4)$$

and the observed stoicheiometry should drop to the limiting value of 1 molecule of acetone per 2 equivalents of cobalt(III), corresponding to reactions (1)—(4) only.

Another oxidative route, however, merits consideration since it is known that the oxidation of t-butyl alcohol by both acetoxy [5] and hydroxy [6] free radicals effects homolysis of C–H and not O–H bonds.   This route would be

$$7.\ CH_3 \cdot CMe_2 \cdot OH + Co^{III} \longrightarrow \bullet CH_2 \cdot CMe_2OH + Co^{II} + H^+$$

$$8.\ \bullet CH_2 \cdot CMe_2 \cdot OH + Co^{III} + H_2O \longrightarrow HO \cdot CH_2 \cdot CMe_2 \cdot OH + Co^{II} + H^+ \qquad very\ fast$$

$$9.\ HO \cdot CH_2 \cdot CMe_2 \cdot OH + Co^{III} \longrightarrow HO \cdot CH_2\bullet + Me_2C\overset{\cdot\cdot}{O} \qquad (glycol\ fission)$$

$$10.\ HO \cdot CH_2\bullet + Co^{III} + H_2O \longrightarrow CH_2(OH)_2 + Co^{II} + H^+ \qquad very\ fast$$

$$6.\ CH_2(OH)_2 + 2Co^{III} \longrightarrow H \cdot CO_2H + 2Co^{II} \qquad (see\ ref.\ 4)$$

If reactions (9) and (6) were much faster than (7), then this reaction sequence would produce 1 mole of acetone per 6 equivalents of cobalt(III) consumed, assuming that there was no secondary oxidation of acetone.   However, at high $[Bu^tOH] : [Co^{III}]$ ratios, the

TABLE 1.

Acetone yields from the oxidation of t-butyl alcohol in water.

$[HClO_4] = 1\cdot57M$; initial $[Co^{III}]$ *ca.* $0\cdot03M$; temp. $15°$.

$[Bu^tOH]$ (M)	$10^6 \times [Co^{III}]$ consumed	$10^6 \times [Acetone]$ formed	$[Co^{III}]/$ $[Acetone]$	$[Bu^tOH]$ (M)	$[10^6 \times Co^{III}]$ consumed	$10^6 \times [Acetone]$ formed	$[Co^{III}]/$ $[Acetone]$
0·102	24·6	2·78	8·8	0·824	24·6	6·77	3·6
0·125	24·1	3·76 *	6·4	0·910	25·0	7·25 *	3·4
0·205	24·6	3·70	6·7	0·943	24·8	6·31	3·9
0·250	24·1	4·55 *	5·3	1·28	19·2	6·22	3·1
0·417	24·6	4·91	5·0	1·28 †	19·2	5·44 (6·0)	3·5 (3·2) †
0·500	24·1	5·20 *	4·6	1·65	24·6	7·74	3·2
0·750	25·2	6·91 *	3·6	2·46	24·6	5·96	4·1

* Average of two results.   † With addition of $1\cdot0M$-acrylamide.   The value in brackets has been corrected for loss of Co^{III} by direct attack on acrylamide.

yield of acetone would tend to fall to zero; this is the opposite of the trend shown by the reaction sequence (1)—(6).   Comparison of these predictions with the results shown in Table 1 shows that the reaction sequence (1)—(6) is correct.

[3] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.
[4] Kemp and Waters, *Proc. Roy. Soc.*, 1963, *A*, **274**, 480; Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **57**, 786.
[5] Kharasch, Rowe, and Urry, *J. Org. Chem.*, 1951, **16**, 905.
[6] Dixon and Norman, *J.*, 1963, 3119.

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The rates of oxidation of the compounds involved in these reaction sequences are shown in Table 2. The actual yield of acetone from the reaction sequence (1)—(6) can be calculated from the particular concentration of t-butyl alcohol present, and the relative rates of oxidation of t-butyl alcohol, methyl alcohol, and formaldehyde; predicted values of this type are in fair agreement with the data in Table 1.

TABLE 2.

Rates of oxidation at 15° (k_2 in l. mole⁻¹ sec.⁻¹).

$Me_3C \cdot OH$, $2 \cdot 16 \times 10^{-3}$; $HO \cdot CH_2 \cdot CMe_2 \cdot OH$, $1 \cdot 42$; $MeOH$, $0 \cdot 118$; $CH_2(OH)_2$, *ca.* 5 (ref. 4); $COMe_2$, $0 \cdot 5 \times 10^{-3}$.

Further experimental evidence supports this conclusion, for carbon radicals can be trapped by polymerisable olefins even in the presence of strong oxidants and, as Table 1 shows, the addition of acrylamide makes no difference to the [Acetone] : [Co^{III}] ratio
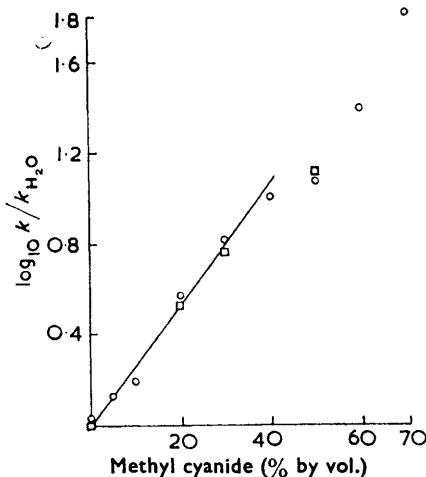
The relation of oxidation rate to solvent composition for oxidation of t-butyl alcohol.

     O in 0·375M-perchloric acid at 10°.
     □ in 1·57M-perchloric acid at 15°.

though polymerisation does occur to give a viscous solution which fortunately did not cause undue trouble in the subsequent analysis for acetone. Presumably the polymer is of fairly low molecular weight since the chain-ending reaction (11) would be fairly rapid.

11. $R \cdot [CH_2 \cdot CH(CO \cdot NH_2)] \cdot + Co^{III} \longrightarrow R \cdot [CH_2 \cdot CH(CO \cdot NH_2)]_n \cdot OH + Co^{II}$
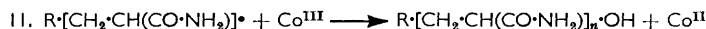
The validity of the acrylamide method for deducing the reaction path, which is known to give excellent results with cerium(IV) oxidations,[7] is well shown by Table 3 which gives data for oxidations of α-hydroxyisobutyric acid and of 3-methylacetoin.

TABLE 3.

Acetone yields from Co^{II} oxidations.

| Substrate [M]	$10^6 \times$ mole Co^{III} consumed	$10^6 \times$ mole acetone formed	Yield (%) *
α-Hydroxyisobutyric acid (0·0535M)	19·2	7·2	75
,, ,, + 1·0M-acrylamide	19·2	2·2	23
3-Methylacetoin (0·0577M)	19·2	7·44	77
,, ,, + 1·0M-acrylamide	19·2	7·03	73

* Yields calculated from 4 Co$^{III} \longrightarrow$ 1 Acetone.

Previous studies in this laboratory have shown that the 1-electron oxidations of α-hydroxy-acids take the route $HO \cdot CR_2 \cdot CO_2H \longrightarrow HO \cdot CR_2 \cdot \longrightarrow$ products in which

[7] Mino, Kaizermann, and Rasmussen, *J. Amer. Chem. Soc.*, 1959, **81**, 1494.
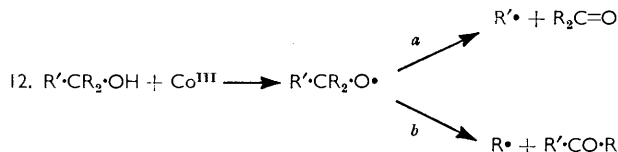
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carbon dioxide is lost in the initial reaction.[8]   As Table 3 shows the radical $HO \cdot CMe_2 \cdot$ can be trapped by acrylamide before it is all oxidised to acetone.

Conversely with 3-methylacetoin the study by Jones and Waters [9] of its 1-electron oxidation by vanadium(v) indicated that the oxidative path was

$$Me_2C(OH) \cdot COMe \longrightarrow Me_2C(O\bullet) \cdot COMe \longrightarrow Me_2CO + \bullet COMe$$
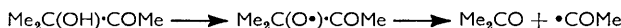
molecular acetone being produced together with the radical $\cdot COMe$.   Here radical trapping with acrylamide does not significantly affect the yield of acetone.

Having this confirmation that the oxidation of a tertiary alcohol by cobaltic perchlorate involves the liberation of an alkyl radical it is now possible to depict the oxidation of higher alcohols as (12),

$$12.\ R' \cdot CR_2 \cdot OH + Co^{III} \longrightarrow R' \cdot CR_2 \cdot O\bullet$$

$$\begin{array}{c} a \nearrow R'\bullet + R_2C{=}O \\ b \searrow R\bullet + R' \cdot CO \cdot R \end{array}$$

in which the transient alkyloxy-radical undergoes simultaneous fission into two pairs of products, *viz.* two ketones which should both be reasonably stable and two alkyl radicals which would be oxidised very rapidly to lower alcohols.   We have extended our study to the examination of a number of higher tertiary alcohols and find that they can all be

TABLE 4.

Oxidations of tertiary alcohols: analysis of ketonic products.

Solvent = methyl cyanide–water 1 : 1; $[HClO_4]$ = 1·57M;   [alcohol] shown below;   initial $[Co^{III}]$ ca. 0·03M;   temp. 15°.

Alcohol, $R \cdot CEtR' \cdot OH$		Concn. (M)	Product ratio	Notes
Groups R and R'			$RCOR'$: $EtCOR'$	
Me	Me	0·24	98·0 * : 1·97 * ± 0·18	Me·CHO also found
Bu^i	Me	0·35	85·2 † : 14·8 * ± 1·1	,, ,,
Pr^n	Me	0·31	74·7 † : 25·3 * ± 0·4	,, ,,
Bu^n	Me	0·27	77·9 † : 22·1 * ± 4·0	,, ,,
n-C$_5$H$_{11}$	Me	0·34	75·6 † : 24·4 * ± 2·0	,, ,,
Pr^i	Me	0·25	4·16 * : 95·8 * ± 0·26	,, ,,
MeO·CH$_2$	Et	0·11	3·07 * : 96·9 ‡ ± 0·02	CH$_2$O also found
MeO·CO	Me	0·18	45·4 * ‡ : 9·9 * ± 0·5	Unidentified product (44·8) ¶ also found
1-Methylcyclohexanol		0·17	Hydroxy-ketone § : Cyclo-hexanone ca. 5 : 1	

* Identified by comparison of R_F value with authentic dinitrophenylhydrazone.   † Identified by comparison of R_F value with estimated value.   ‡ Dinitrophenylhydrazone identified by m. p. and mixed m. p. with authentic sample.   ¶ Dinitrophenylhydrazone as pale yellow needles, m. p. 153—154°; *not* formaldehyde (mixed m. p.).   § The dinitrophenylhydrazone has a low R_F value, and presumably the product is $MeCO \cdot [CH_2]_5 \cdot OH$.

oxidised much more easily than t-butyl alcohol.   Since they are very sparingly soluble in water it has been necessary to use a mixed solvent to ensure homogeneity in our reactions. Fortunately we have found that methyl cyanide, if purified carefully, is attacked extremely slowly by cobaltic perchlorate for which it is a good solvent and that methyl cyanide–water mixtures containing up to 40% of methyl cyanide affect the rates of oxidation of tertiary alcohols, and indeed of organic compounds of other types in a systematic manner. Both kinetic and product studies have been carried out.

Product Studies.—Equation (12) shows that an unsymmetrical tertiary alcohol should give a mixture of two ketones in relative amounts corresponding to the ease of fission of alkyl groups, $R\bullet$ or $R'\bullet$, from the intermediate alkyloxy-radical $R \cdot CR_2 \cdot O\bullet$ provided that the alcohol is taken in sufficiently large excess over the cobalt(III) to minimise the secondary oxidations of the ketones.   To analyse our ketone mixtures we have converted the

[8] Levesley and Waters, *J.*, 1955, 217; Kemp and Waters, *J.*, 1964, 1192.
[9] Jones and Waters, *J.*, 1962, 1629.

reaction products into their 2,4-dinitrophenylhydrazones, extracted these and separated them, together with a known marker substance, by thin-plate chromatography, and then estimated colorimetrically the yields of pure products.

Table 4 summarises our experimental data, whilst Table 5, calculated from it, gives the relative ease of oxidative elimination of various alkyl radicals. The great ease of elimination of ethyl groups compared with methyl so soon became evident that alcohols of the type $R \cdot CMeEt \cdot OH$ proved to be the most suitable for our study since they yielded comparable amounts of the two ketones $RCOMe$ and $EtCOMe$ together with traces of acetaldehyde formed by the oxidative sequence $Et \cdot \longrightarrow Et \cdot OH \longrightarrow Me \cdot CHO$.

The sequence of Table 5, *viz.* $Me_2CH \cdot > Et \cdot > R \cdot CH_2 \cdot CH_2 \cdot > Me \cdot$, corresponds to the order of stabilities of alkyl radicals (or to the number of β-hydrogens that can be concerned in hyperconjugation, $[(R \cdot CH_2 \cdot CH_2 \cdot) \longleftrightarrow (H \cdot RCH=CH_2)]$ and parallels the order of elimination of alkyl groups in the Fe^{II}-catalysed decomposition of hydroperoxides,[10] and in the homolysis of tertiary alkyl hypochlorites [11] (see Table 5). These reactions are both considered to involve intermediate alkyloxy-radicals. The very great ease of elimination of $MeO \cdot CH_2 \cdot$ is of particular interest, for it supports recent explanations of the ease of 1-electron oxidation of pinacol monomethyl ether.[12]

TABLE 5.

Relative rates of elimination of radicals from tertiary alcohols by cobaltic perchlorate.

Radical	Rel. rate of removal	Lit. values	Radical	Rel. rate of removal	Lit. values
Me	$1 \cdot 06 \pm 0 \cdot 1$	$0 \cdot 3$ (ref. 11), 10(ref. 11a)	n-C_5H_{11} ...	$32 \cdot 3 \pm 2 \cdot 5$	
Et	100 (standard)	100 (standard)	Pr^i	2300 ± 140	2000 (ref. 11a),
Pr^n	$33 \cdot 9 \pm 0 \cdot 5$	65 (ref. 10)	Bu^i	$17 \cdot 4 \pm 1 \cdot 2$	3200—4500 (ref. 11b)
Bu^n	$28 \cdot 0 \pm 6 \cdot 0$	43 (ref. 10)	$MeO \cdot CH_2 \cdot$	6310 ± 40	
			$MeO \cdot CO \cdot$ ...	$21 \cdot 7 \pm 1 \cdot 0$ (?10·9 *)	

* This figure should be used if the unknown product has also been formed by loss of an ethyl radical.

Table 5 thus accords with our view that the oxidation of tertiary alcohols occurs (equation 1) by the formation of an alkyloxy-radical which (equation 2) eliminates an alkyl group, though our kinetic evidence (below) indicates that reactions (1) and (2) are to a high degree concerted processes, as we have suggested in Part I.

Kinetic Studies.—Organic compounds are more rapidly oxidised by cobaltic perchlorate in methyl cyanide–water than in water alone and the Figure shows that for mixtures containing up to 40% of methyl cyanide by volume the reaction velocities can be correlated by the empirical equation $R_{soln} = R_{water} \exp(Mx)$, where x is the volume fraction of methyl cyanide and M is a constant depending on the compound oxidised.

Part I showed that the reactivity of aqueous cobaltic perchlorate depended on the equilibrium

$$13. \quad \{Co(H_2O)_6\}^{3+} + H_2O \rightleftharpoons \{HOCo(H_2O)_5\}^{2+} + H_3O^+$$
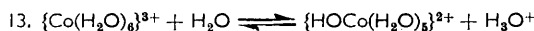
the stronger oxidant being $\{HOCo(H_2O)_5\}^{2+}$, and the general effect of methyl cyanide, in the low concentration range could well be attributed to a shift of this equilibrium, for the addition of the methyl cyanide would lower the dielectric constant of the solvent and so favour charge separation. Table 6 shows that the general form of the acidity dependence for t-butyl alcohol oxidation, which at 10° in water is given by

$$-d[Co^{III}]/dt = 10^{-3}[Co^{III}][Bu^tOH]\{1 \cdot 82/[HClO_4] + 0 \cdot 07/[HClO_4]^2\}$$

is not altered in 30% methyl cyanide and also that the neutral-salt effect rises very steeply at high ionic strengths in this mixed solvent. (Compare Table 4 of Part I.) Only at high

[10] Kochi, *J. Amer. Chem. Soc.*, 1962, **84**, 1193.
[11] (*a*) Green, Savitz, Lau, Osterholtz, and Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 2196; (*b*) Green, Savitz, Lau, Osterholtz, Smith, and Zanet, *J. Amer. Chem. Soc.*, 1963, **88**, 55.
[12] Littler and Waters, *J.*, 1960, 2767.

concentrations of methyl cyanide, well beyond those used for any of our kinetic work, is it rational to suppose that methyl cyanide molecules replace water molecules as ligands of

TABLE 6.

The effect of acid and salt concentrations on oxidation rates in aqueous methyl cyanide.

(a) *Variation of acid concentration*

$[Bu^tOH] = 0.20M$; $[HClO_4] + [NaClO_4] = 2.0M$; in 30% methyl cyanide at 15°; initial $[Co^{III}] \simeq 0.002M$.

$[HClO_4]$, M	0.17	0.30	0.50	1.00	1.50	2.00
10^3k (l. mole^{-1} sec.$^{-1}$)	162	79.3	45.8	19.8	13.0	9.70
10^3k (calc.)	165	81.1	44.1	20.3	13.2	9.73

Calc. values from $10^3k = 18.6/[HClO_4] + 1.72/[HClO_4]^2$ l. mole^{-1} sec.$^{-1}$.

b) *Variation of salt concentration*

$[Bu^tOH] = 0.4M$; $[HClO_4] = 0.375M$; in 30% methyl cyanide at 15°; initial $[Co^{III}] \simeq 0.002M$.

$[NaClO_4] + [HClO_4]$, M	0.375	1.02	1.98	2.30	2.95	3.59
10^3k (l. mole^{-1} sec.$^{-1}$)	42.4	49.5	70.4	89.5	124.4	205.8

cobalt(III), for the absorption of the blue colour of aqueous cobaltic perchlorate remains unaltered in 40% methyl cyanide: in the presence of 0.17M-perchloric acid the colour changes to a deep purple with 95% methyl cyanide, but with 3M-perchloric acid the colour change is evident with 60% methyl cyanide.

TABLE 7.

Rate constants for oxidation of tertiary alcohols.

$(-d[Co^{III}]/dt = k[Co^{III}][ROH]$; k in l. mole^{-1} sec.$^{-1}$). $[HClO_4] = 1.57M$; initial $[Co^{III}] \simeq 0.002M$; temp. 15°; the percentage of methyl cyanide in the solvent is given in each case in brackets after the rate constant.

Alcohol	$10^2 \times$ [Alcohol], M		Rate constants (10^3k)			
CMe$_3$·OH	64.8	found	2.16(0)	7.41(20)	12.6(30)	28.2(50)
		calc.	2.16	7.11	12.9	43
CMe$_2$Et·OH	2.81	found	60.1(4)	104(20)	164(30)	228(50)
		calc.	58.1	107	157	335
CMe$_2$Pr^i·OH	2.53	found	80.6(4)	99.0(20)	119(30)	158(50)
		calc.	79.3	101	117	159
CMe$_2$Bu^t·OH	2.42	found	12.1(20) *	12.2(25) *	11.6(30)	13.2(50)
		calc.	12.0	12.2	12.4	13.2
CMeEtPr^n·OH	2.08	found	68.7(4)	108(20)	126(30)	
		calc.	71.0	104	132	
n-C$_5$H$_{11}$·CMeEt·OH ...	1.74	found	99.0(10) *	104(20)	131(30)	
		calc.	94.1	107	122	
MeO·CO·CMeEt·OH...	5.90	found	10.7(4)	21.1(20)	35.2(30)	
		calc.	10.0	21.6	34.2	
MeO·CH$_2$·CEt$_2$·OH ...	1.84	found	177(4)	267(20)	339(30)	
		calc.	177	263	337	

* Specified [alcohol] reduced by half to avoid an inhomogeneous system. Calculated values from $k_{solv} = k_{water} \exp (Mx)$, with values of k_{water} and M from Table 8.

Table 7 lists our measurements of oxidation rates of tertiary alcohols in aqueous methyl cyanide whilst Table 8 gives comparative rate constants extrapolated for aqueous solution and also values for the factor M in the empirical equation given above. It may be noted that M depends on the alcohol concerned, which suggests that the solvent shift of the initial equilibrium (1) may well be more important than its effect on equilibrium (13).

Comparison of Tables 5 and 8 shows that alcohols with easily-liberated groups, *e.g.*, Me$_2$CH and MeO·CH$_2$ are oxidised much more easily than is t-butyl alcohol. This may indicate that stages (2) and (3) of the reaction process are concerted. Quantitative comparisons, however, should not be made because the overall stoichiometry differs for each alcohol. Thus the isopropyl radical would oxidise only to acetone, consuming but 3 equivalents of cobalt(III) whilst the oxidation of the ethyl radical beyond the stage of

acetaldehyde again cannot be very fast and the $Me_3C \cdot$ radical would produce t-butyl alcohol with only one equivalent of cobalt(III). The difficulty of release of methyl radicals accords with our finding that t-butyl alcohol is much more difficult to oxidise than any

TABLE 8.

Extrapolated rate data for tertiary alcohols.

[Alcohol] specified in Table 7; $[HClO_4] = 1.57M$; initial $[Co^{III}] \simeq 0.002M$; temp. 15°; k_0 extrapolated to water from aqueous methyl cyanide; x = volume fraction of methyl cyanide in the solvent.

$$-1/k_0 \times d[Co^{III}]/dt = [Co^{III}][\text{alcohol}] \exp (Mx).$$

Alcohol	$10^3 \times k_0$ (l. mole^{-1} sec.$^{-1}$)	M
$CMe_3 \cdot OH$	2·16	6·0
$CMe_2Et \cdot OH$	50·1	3·8
$CMe_2Pr^i \cdot OH$	74·8	1·5
$CMe_2Bu^t \cdot OH$	11·3	0·32
$CMeEtPr^n \cdot OH$	64·6	2·38
$n\text{-}C_5H_{11} \cdot CMeEt \cdot OH$	82·6	1·31
$MeO \cdot CO \cdot CMeEt \cdot OH$	8·59	4·61
$MeO \cdot CH_2 \cdot CEt_2 \cdot OH$	160	2·49

homologue. Indeed t-butyl alcohol is not typically representative of tertiary alcohols in regard to chemical stability.

EXPERIMENTAL

Materials.—The tertiary alcohols used were either fractionated samples of commercial compounds or substances prepared by conventional Grignard reactions. Since mere traces of ketones considerably reduce the accuracy of the product analyses, Table 4, still further purification was essential. Usually the alcohol was shaken for 30 min. at 30—40° with 10 times its volume of 0·1M-potassium carbonate saturated with potassium permanganate (*ca.* 7%). The excess of oxidant was then destroyed ($Na_2S_2O_5$), and the alcohol separated in ether, dried, and fractionated under diminished pressure. Compounds sensitive to permanganate, *e.g.*, 2-methylpropane-1,2-diol were purified by the use of Girard's reagent P.

Distilled methyl cyanide usually shows some absorption at 250—285 mμ due to aldehydes or ketones which are readily oxidised by cobalt(III) and had to be removed by an initial oxidation. To methyl cyanide (325 ml.) was slowly added concentrated sulphuric acid (40 ml.) and then, portionwise with stirring, solid potassium permanganate (50 g.). The initial reaction

TABLE 9.

Solvent decomposition rates.

$[Co^{III}]$, (M)	$10^4 \times k$ (sec.$^{-1}$)	Conditions			
0·01	0·30	$[HClO_4] = 0.35M$;	$[NaClO_4] = 3.05M$;	10°	
0·01	0·48	,, 0·35M	,, 4·95M;	,,	
0·002	0·32	,, 1·57M	,, nil;	15°	
0·006	0·38	,, 1·57M	,, ,,	,,	
0·003	1·06	,, 1·35M;	,, ,,	,,	70% MeCN
0·003	0·70	,, 0·50M;	,, ,,	,,	70% MeCN

needed watchful control by cooling, but thereafter the mixture was refluxed for $3\frac{1}{2}$ hr. The methyl cyanide was then decanted, made neutral (solid K_2CO_3), and refluxed for 1 hr. over phosphorus pentoxide.[13] The latter treatment was repeated 6—7 times until the phosphorus pentoxide was scarcely discoloured by several hours reflux. The final material, b. p. 81·5—81·7° (*ca.* 200 ml.) then contained less than a $10^{-4}M$ of carbonyl compounds.

The convention used in describing water–methyl cyanide mixtures is volume fraction, x, of methyl cyanide = volume of methyl cyanide added to mixture/total volume of all components in mixture. Since the volume change on mixing of water and methyl cyanide is small, this approximates closely to the v/v composition of the mixture. In Table 3 the percentages of methyl cyanide = $100x$.

[13] " The Technique of Organic Chemistry," Vol. VIII, ed. Weissberger, Interscience Publ., New York, p. 435.

Nitroethane (for chromatographic use; 50 ml.) was shaken with dinitrophenylhydrazine (2 g.) and aqueous sulphuric acid (5M.; 1 ml.). After separation, the nitroethane was neutralised, dried (K_2CO_3), and fractionated at 10—20 mm. pressure. Acrylamide was crystallised from benzene and dried in a vacuum.

Kinetic Procedure.—Aqueous cobaltic perchlorate solutions were prepared as described in Part I. The spectrophotometric measurements were made at selected frequencies in the 235—280 mμ absorption band of cobalt(III), the exact wavelength being chosen so as to avoid interference from possible products. The measurements of Table 9 were used to correct for self-decomposition of cobaltic perchlorate solutions. It was essential to use all-glass apparatus in preparing solutions; if stainless-steel needles were used on micrometer syringes significant reduction of cobalt(III) always occurred. Effects of dissolved oxygen were negligible.

Product Analysis.—It was necessary to analyse for aldeydes or ketones in the 10^{-3}—10^{-2}M concentration range to an accuracy of 2—3%. Our method, which resembles that published by Fürst and Feustel [14] while our work was in progress, has attained considerably higher accuracy by employment of the chromatoplate technique. Our procedure was as follows: (i) A 0·1M-solution (0·5 ml.) of 2,4-dinitrophenylhydrazine in 5M-sulphuric acid, chloroform (1·0 ml.), and a small amount of a standard solution of a known dinitrophenylhydrazone in 1,1,2,2-tetrachloroethane, were added to an oxidised reaction mixture (1·3 ml.) and thoroughly admixed. (ii) The chloroform layer was transferred with a small pipette to a conical centrifuge tube (20 ml.) in which it was twice shaken with 1·0 ml. portions of 5M-sulphuric acid to remove unchanged dinitrophenylhydrazine. The aqueous layers were carefully removed each time with a small pipette. (iii) The chloroform layer was decanted through a little solid potassium carbonate into a small tube; the chloroform and any other liquids present were then removed by careful evaporation in a vacuum. (iv) The solid dinitrophenylhydrazones were then dissolved in chloroform (0·2 ml.), and a portion of this solution was applied, in a thin band, across the base of a chromatoplate (20 × 5 cm.) coated with a 0·25 mm. layer of unbaked silica gel containing 13% of plaster of Paris. (v) The plates were then placed vertically in a tank so that the top 3 cm. of each plate protruded through a slit in the tank lid. This allowed of continued development of the chromatogram after the solvent front had reached the top of the plate. Upward development of the chromatogram was effected by using a 5—10 mm. deep mixture of light petroleum (b. p. 30—40°) with 4% of nitroethane. (vi) When the dinitrophenylhydrazones had separated into distinct bands the plates were removed and allowed to dry in the air. The material comprising each band was carefully scraped, with a spatula and a small dry brush, into a separate conical funnel the base of which had been drawn out to a capillary (*ca.* 0·5 mm. diam.) and blocked by a small plug of cotton wool. The solid was pressed into a compact layer above this filterpad. Each dinitrophenylhydrazone was then extracted by running distilled tetrachloroethane through the powder in the funnel into a 2-ml. standard flask. (vii) The solutions were made up to 2·0 ml. and then estimated colorimetrically by their absorptions at their $\lambda_{max.}$ values (*ca.* 365 mμ); the requisite $\varepsilon_{max.}$ values have already been published.[15] From the absorption found for the standard solution of the known dinitrophenylhydrazone which had been added at stage (i) it was possible to calculate the concentrations of aldehyde or ketone in the original oxidation mixture. The following figures indicate the attainable accuracy: Taken: $1·34 \times 10^{-5}$ mole of cyclohexanone, together with $0·487 \times 10^{-5}$ mole of isopropyl methyl ketone dinitrophenylhydrazone; Found 1·336 and $1·342 \times 10^{-5}$ mole of cyclohexanone. The accuracy was of course less for mixtures of ketones in molar ratios of over 20 : 1, but the standard marker could then be adjusted to be comparable in concentration to the minor component. Table 10 below gives R_F' values (R_F' values are R_F values relative to isopropyl methyl ketone dinitrophenylhydrazone) for substances which we have seaparated by this method.

Oxidation Procedure for Product Analysis.—A weighed amount of the tertiary alcohol was made up to a total volume of 1·3 ml. in 50% aqueous methyl cyanide containing the requisite amount of perchloric acid. Nitrogen was bubbled through this for 5 min. through a short capillary tube. A stock solution of cobaltic perchlorate was standardised by addition to ferrous sulphate and back-titration with ceric sulphate. Nitrogen was bubbled through 0·30 ml. portions of this in a small tube, 1·0 ml. of the air-free alcohol solution was added, and after

[14] Fürst and Feustel, *Z. Chem.*, 1962, **2**, 106.
[15] Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 2720; " Organic Electronic Spectral Data," ed. Kamlet, Interscience Publ., New York, 1960.

TABLE 10.

R_F' Values of dinitrophenylhydrazones on unbaked silica plates.

Developing solvent; light petroleum (b. p. 30—40°) + 4% of nitroethane. $R_F' = R_F$ values relative to isopropyl methyl ketone dinitrophenylhydrazone.

Ketone	R_F'	Ketone	R_F'	Aldehyde	R_F'
$C_6H_3(NO_2)_2 \cdot NH \cdot NH_2$	0·03	$Me_2C(OH) \cdot CO \cdot Me$	0·05	CH_2O	0·27
$MeCO \cdot CO_2Me$	0·35	$MeO \cdot CH_2 \cdot CO \cdot Me$	0·43	MeCHO	0·37
Cyclopentanone	0·31	$COMe_2$	0·52	EtCHO	0·57
Cyclohexanone	0·65	$EtCO \cdot Me$	0·75		
$COEt_2$	0·92	Pr^nCOMe	0·82		
Bu^nCOMe	0·93	Pr^iCOMe	1·00 *		
Bu^iCOMe	0·94	Bu^tCOMe	1·12		
$n \cdot C_5H_{11} \cdot COMe$	1·05	Pr^i_2CO	1·40		

* Reference standard.

20 sec. the nitrogen stream was stopped and the tube corked and placed in a thermostat until at least 6 half-lives of the oxidation had elapsed. The contents of the tubes were then analysed at once. Each oxidation was conducted in duplicate. In general ketone yields were found to be 70—80% of that calculated for $2 \, Co^{III} \longrightarrow 1$ ketone. The difference can be due to secondary oxidations (compare Table 3).