180. *Oxidations of Organic Compounds by Cobaltic Salts. Part I. The Mechanism of Oxidation of Cyclohexanol and t-Butyl Alcohol.*

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The oxidations by aqueous cobaltic perchlorate of cyclohexanol, 1-deuterocyclohexanol and t-butyl alcohol have been examined kinetically. In all cases the main reaction has a rate that varies inversely with the acid concentration. With cyclohexanol there is a small primary isotope effect, $k_H/k_D = 1{\cdot}72$ at 10°, and it is suggested that this may be due to the concerted breaking of a C–H group whilst the cobalt(III) atom removes an electron from the oxygen atom of the alcohol.

AQUEOUS solutions of cobaltic salts are powerful oxidisers of organic compounds of many types [1] but, though the compounds decompose spontaneously, probably producing free hydroxyl radicals,[2] Bawn and White [3] have concluded that the fast oxidation of alcohols by cobaltic sulphate is essentially due to a direct reaction (1) between alcohol molecules and cobaltic ions, rather than to the oxidation of alcohols by the more slowly formed hydroxyl radicals.

$$(1)\quad R{\cdot}CH_2{\cdot}OH + Co^{3+} \longrightarrow R{\cdot}CH_2{\cdot}O{\cdot} + Co^{2+} + H^+$$

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[1] Swann and Xanthakos, *J. Amer. Chem. Soc.*, 1931, **53**, 400.
[2] Bawn and White, *J.*, 1951, **331**.
[3] Bawn and White, *J.*, 1951, **343**.

Recent studies in this laboratory [4,5] of the oxidation of cyclohexanol by the 1-electron-abstracting oxidants $V(OH)_3^{2+}$ and Ce^{4+} have indicated that C–H bonds of $CH_2{\cdot}OH$ groups, rather than their O–H bonds as indicated in equation (1), may be involved in alcohol oxidations of this type, but for oxidation by cobaltic sulphate the view that the initial electron-removal takes place at the hydroxyl group receives support from the fact that this oxidant, unlike most others, attacks even tertiary alcohols directly.[6] An interesting contrast between oxidations effected by cobalt(III) and those effected by vanadium(V) or cerium(IV) is that alcohols in general are more easily oxidised than are ketones. With the oxidants previously studied in this laboratory the reverse is the case.

The Oxford work cited above, in common with many recent kinetic studies of inorganic oxidations,[7] shows that the nature and the stereochemistry of the ligand groups which invariably surround, in solution, the cations of transition-metal ions of variable valency are important controllers of the mechanisms of their oxidation and reduction. For this reason a more detailed study of oxidations involving cobalt(III) has been begun: use is being made of kinetic isotope effects to assist the elucidation of reaction mechanisms. In the present study cobaltic perchlorate, rather than cobaltic sulphate, has been used as the oxidant, to avoid the complicating kinetic effects due to the formation of sulphate complexes.[8,9] These rather fast reactions have been carried out at 10°; both titrimetric and spectrophotometric methods of analysis have been used concurrently.

Results.—Table 1 shows that for both cyclohexanol and t-butyl alcohol, when the alcohol is present in at least five-fold excess, the oxidation is of first order with respect to cobalt(III). Table 2 shows that it is also of first order with respect to the alcohol.

TABLE 1.

(C_0 and C = [Co^{III}] at times t_0 and t)

(*a*) Reduction of cobaltic perchlorate by an excess of cyclohexanol at 10°.

[Cyclohexanol] = 0·0517M; initial [Co^{III}] = 0·00948M; [H$^+$] = 1·3M.

Time (sec.)	38	92	180	247	300	360	420
$\log_{10} C_0/C$	0·0178	0·046	0·085	0·121	0·140	0·178	0·210
10^3k (sec.$^{-1}$).........	1·08	1·13	1·09	1·13	1·08	1·14	1·15

[Cyclohexanol] = 0·138M; initial [Co^{III}] = 0·00826M; [H$^+$] = 1·3M.

Time (sec.)	60	120	190	240	300	360
$\log_{10} C_0/C$	0·079	0·156	0·243	0·300	0·386	0·461
10^3k (sec.$^{-1}$).........	3·03	2·99	2·95	2·88	2·96	2·95

(*b*) Reduction of cobaltic perchlorate by an excess of t-butyl alcohol at 10°.

[Bu^{t}OH] = 0·239M; initial [Co^{III}] = 0·0103M; [H$^+$] = 3·25M.

Time (min.)	10	23·5	31·5	44·5	58	72	91·5	116
$\log_{10} C_0/C$	0·031	0·084	0·112	0·155	0·198	0·245	0·312	0·401
10^3k (sec.$^{-1}$).........	0·119	0·137	0·137	0·134	0·131	0·131	0·131	0·133

[Bu^{t}OH] = 0·239M; initial [Co^{III}] = 0·00553M; [H$^+$] = 0·65M; [NaClO$_4$] = 2·60M.

Time (min.)	5·25	10	14·3	19	23·3	31·5
$\log_{10} C_0/C$	0·102	0·179	0·239	0·334	0·418	0·589
10^3k (sec.$^{-1}$).........	0·75	0·69	0·64	0·68	0·69	0·72

This gives a much simpler kinetic picture of the oxidations than that found by Bawn and White [3] for oxidation of ethanol and propan-1-ol by cobaltic sulphate. Table 3 shows that oxidation in perchloric acid–sodium perchlorate solutions of constant ionic strength (3·4M) is slower in the solutions of higher acid concentration, in which incidentally cobalt(III) becomes more stable,[2] and that for cyclohexanol and 1-deuterocyclohexanol

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[4] Littler and Waters, *J.*, 1959, 4046.

[5] Littler, *J.*, 1959, 4135; 1962, 832.

[6] Bawn and Sharp, *J.*, 1957, 1854.

[7] Halpern, *Quart. Rev.*, 1961, **15**, 207.

[8] Ashurst and Higginson, *J.*, 1956, 343; see also following paper.

[9] Sutcliffe and Weber, *Trans. Faraday Soc.*, 1961, **57**, 91.

the results closely fit the equations (*A*) and (*B*), respectively (rates in mole l.^{-1} sec.^{-1}; *t* in sec.).

$$(A)\ -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][\text{Cyclohexanol}]\{53{\cdot}3/[\mathrm{HClO_4}] + (10/[\mathrm{HClO_4}]^2)\}$$

$$(B)\ -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][1\text{-}^2\text{H-Cyclohexanol}]\{32/[\mathrm{HClO_4}] + (3/[\mathrm{HClO_4}]^2)\}$$

These results can also be expressed in terms of h_0, a Hammett acidity function [*i.e.*, antilog $(-H_0)$], as in equations (*C*) and (*D*). (As in related work from this laboratory,[10] Paul and Long's H_0 data [11] for 6M-mixtures of perchloric acid and sodium perchlorate have been used.)

$$(C)\ -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][\text{Cyclohexanol}]\ (6 + 1740/h_0)$$

$$(D)\ -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][1\text{-}^2\text{H-Cyclohexanol}](3{\cdot}4 + 1040/h_0)$$

The kinetic isotope effect $k_\mathrm{H}/k_\mathrm{D}$ at 10° varies between 1·65 and 1·75 in the range of acid concentrations studied, giving an average value of 1·7.

Table 3 shows that at a fixed ionic strength the product (Reaction velocity) × (Acid concentration) is nearly constant. The value of this constant, however, depends on the ionic strength of the solution in a manner shown in Table 4, which gives results for the oxidation of cyclohexanol in 0·325M-perchloric acid in the presence of various amounts of sodium perchlorate. The extrapolated value for $k[\mathrm{HClO_4}] = 30{\cdot}6 \times 10^{-3}$ (sec.^{-1}) at zero ionic strength.

TABLE 2.

(*a*) Order of reaction in respect to cyclohexanol.

Initial $[\mathrm{Co^{III}}]$ 0·01M; $[\mathrm{HClO_4}]$ = 1·30M; μ = 1·30M.

[Cyclohexanol] (M)...	0·0517	0·0862	0·138	0·173	0·224
10^3k (l. mole^{-1} sec.^{-1})	21·8	22·8	21·0	22·0	20·8

(*b*) Order of reaction in respect to t-butyl alcohol.

Initial $[\mathrm{Co^{III}}]$ 0·01M; $[\mathrm{HClO_4}]$ = 0·325M; $[\mathrm{NaClO_4}]$ = 2·93M.

$[\mathrm{Bu^tOH}]$ (M)	0·0717	0·143	0·239
10^3k (l. mole^{-1} sec.^{-1})	6·37	6·55	6·36

TABLE 3.

Influence of acid concentration on the rate of oxidation of cyclohexanol and 1-deuterocyclohexanol.

(*a*) [Cyclohexanol] = 0·052M; μ = 3·40M; initial $[\mathrm{Co^{III}}]$ = *ca.* 0·01M.

$[\mathrm{HClO_4}]$ (M)	0·325	0·488	0·650	1·30	2·08	2·28	2·93	3·40
10^3k (l. mole^{-1} sec^{-1})	232 *	145 *	117	50·5	30·0	25·4	19·7	16·2
$10^3k[\mathrm{H^+}]$ (sec.^{-1}) (found)	75·4	70·6	75·8	65·6	57·7	57·8	57·8	55·2
$10^3k[\mathrm{H^+}]$ (sec.^{-1}) (calc. from *A*)	84·1	73·8	68·7	61·0	58·1	57·7	56·7	56·2
kh_0 (found)	1·84	1·83	2·08	1·92	2·12	2·07	2·54	2·95
kh_0 (calc. from *C*)	1·79	1·82	1·85	1·97	2·17	2·23	2·50	2·81

* [Cyclohexanol] = 0·0345M; initial $[\mathrm{Co^{III}}]$ 0·005M.

(*b*) $[1\text{-}^2\text{H-Cyclohexanol}]$ = 0·054M; μ = 3·40M; initial $[\mathrm{Co^{III}}]$ = 0·001M.

$[\mathrm{HClO_4}]$ (M)	0·65	1·45	2·10	3·4
10^3k (l. mole^{-1} sec.^{-1}).....................	64·8	25·9	17·5	9·4
$10^3k[\mathrm{H^+}]$ (sec.^{-1}) (found)	42·1	37·6	36·7	31·9
$10^3k[\mathrm{H^+}]$ (sec.^{-1}) (calc. from *B*)	39·7	35·5	34·4	33·5
kh_0 (found)	1·15	1·13	1·24	1·67
kh_0 (calc. from *D*)	1·10	1·19	1·28	1·64

TABLE 4.

Effect of the ionic strength on the rate of oxidation of cyclohexanol.

[Cyclohexanol] = 0·0345M; $[\mathrm{HClO_4}]$ = 0·325M; initial $[\mathrm{Co^{III}}]$ = 0·005M.

Ionic strength (M)	0·325	1·63	2·28	3·40	4·22	5·52
10^3k (l. mole^{-1} sec.^{-1})...............	103	147	182	232	302	653

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[10] Jones, Waters, and Littler, *J.*, 1961, 630.

[11] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

t-Butyl alcohol was oxidised in a similar manner, but much more slowly; acetone was identified as a product. The reaction velocities at 10° in solutions of 3·25M-ionic strength (see Table 5) fit equation *E* (units as above).

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

TABLE 5.

Influence of acid concentration on the rate of oxidation of t-butyl alcohol.

$[\mathrm{Bu^tOH}] = 0{\cdot}293\mathrm{M}$; $\mu = 3{\cdot}25\mathrm{M}$; initial $[\mathrm{Co^{III}}] = 0{\cdot}01\mathrm{M}$.

$[\mathrm{HClO_4}]$	0·325	0·65	1·95	3·25
10^3k (l. mole^{-1} sec.$^{-1}$)	6·38	2·95	0·97	0·60
10^3k $[\mathrm{HClO_4}]$ (sec.$^{-1}$) (found)	2·07	1·92	1·89	1·95
,, ,, (calc. from *E*)	2·04	1·93	1·86	1·84

Thus, by using the results in Table 4 to make the comparison of the rates of oxidation in solutions of identical ionic strength we have:

(Rate of oxidation of Cyclohexanol)/(Rate of oxidation of $\mathrm{Bu^tOH}$) = 38·6;

this ratio varies only slightly with acid concentration in the range 0·3—3·0M.

In these experiments the cobalt(III) solutions, prepared electrolytically, were of the order of 1—5 × 10^{-3}M and contained cobalt(II) ions in a similar order of concentration. However, the presence of cobalt(II) ions is of no mechanistic significance, for the concentration of these ions could be increased some 200-fold (with compensatory adjustment of ionic strength by using zinc ions), *i.e.*, to 0·4M, and then effected only a 7% increase of oxidation rate for cyclohexanol. Consequently it is most unlikely that any reversible redox equilibrium is involved.

Discussion.—(a) *The nature of the oxidant ion.* It is a characteristic feature of oxidations effected by aqueous solutions of cobalt(III) that they are faster at lower acid concentrations. For oxidations of alcohols Bawn and White[3] have suggested that protonation, *i.e.*, $\mathrm{RO^- + H^+ \rightleftharpoons ROH}$, and $\mathrm{ROH + H^+ \rightleftharpoons ROH_2^+}$, would reduce the ease of electron loss from oxygen (cf. reaction 1) and the same view was advanced by Hargreaves and Sutcliffe[12] for oxidation of formaldehyde. However, oxidations of inorganic ions ($\mathrm{Tl^+}$, $\mathrm{Ce^{3+}}$, $\mathrm{Co^{2+}}$, $\mathrm{V^{3+}}$, $\mathrm{V^{4+}}$)[8,9,13-15] by cobalt(III) solutions generally follow the kinetic equation $k = a + b/[\mathrm{H^+}]$. Sutcliffe and Weber[13] have obtained spectroscopic evidence of a rapid equilibrium, which they represent as:

$$(2)\ \mathrm{Co(H_2O)_6^{3+} \rightleftharpoons Co(OH)(H_2O)_5^{2+} + H^+} \quad (K = 7{\cdot}5 \times 10^{-3}\ \text{mole l.}^{-1}\ \text{at } 10^\circ).$$

Baxendale and Wells[16] have published similar data. $\mathrm{Co(OH)(H_2O)_5^{2+}}$ is the more reactive species and our kinetic findings accord with this view, for equations (*A*)—(*E*) all contain large terms in $[\mathrm{HClO_4}]^{-1}$ or h_0^{-1}, and it is doubtful whether the small terms in these equations have any mechanistic significance.

For the much slower oxidations of alcohols by vanadium(V) and cerium(IV) there is definite spectroscopic evidence[4,5] for the rapid reversible formation of a complex, $\mathrm{RHO \longrightarrow M^{n+}}$, with the transition-metal ion. Similar rapid pre-equilibria probably involving exchange of co-ordinated water may be involved with cobalt(III), for even in 4M-perchloric acid the exchange of water molecules between the hydration shell and the free solvent is complete in less than 2 minutes at 10°.[17] However, such exchanges are probably slow[18] with a low-spin cobalt(III) complex such as $\mathrm{Co(H_2O)_6^{3+}}$, and the suggestion

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[12] Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 786.

[13] Sutcliffe and Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225; 1959, **55**, 1892.

[14] Bonner and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 3826.

[15] Rosseinsky and Higginson, *J.*, 1960, 31.

[16] Baxendale and Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

[17] Friedman, Taube, and Hunt, *J. Chem. Phys.*, 1950, **18**, 759.

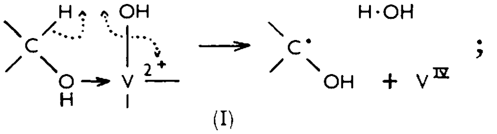
[18] Taube, *Chem. Rev.*, 1952, **50**, 69.

(due to Dr. R. J. P. Williams) that $Co(OH)(H_2O)_5^{2+}$ may well be principally a high-spin complex would account for rapid exchange of a ligand group with a water or alcohol molecule. On this view the rate-determining reaction occurs within a cobalt(III)-alcohol complex. The hydrogen-atom transfer reaction (3) could account for the observed

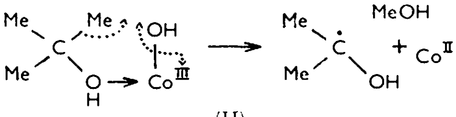
$$(3)\ ROH + (HO)Co(H_2O)_5^{3+} \xrightarrow{\text{Slow}} RO\cdot + Co(H_2O)_6^{2+}$$

kinetics even more simply, but, as shown below, it does not account for the kinetic isotope effect.

(b) *The mechanism of oxidation of alcohols.* Few oxidants attack tertiary alcohols directly. Thus, with chromic acid the slow oxidation of a tertiary alcohol involves prior dehydration to an olefin, whereas oxidations of primary and secondary alcohols involve esterification and base-catalysed, or cyclic, decomposition of the ester by slow rupture of C–H bonds.[19] For oxidation by cobalt(III), in contrast, our results indicate that the oxidations of cyclohexanol and t-butyl alcohol are kinetically similar, though there is a marked rate difference. Hence the cyclic mechanism (I) suggested for the oxidation of cyclohexanol by vanadium(V), in view of the similarity of the deuterium isotope effect $k_H/k_D = 4{\cdot}5$ at 50° to that found for oxidation by chromic acid,[4] cannot hold for oxidation of t-butyl alcohol by cobalt(III) unless direct removal of an alkyl group is postulated, as in (II).



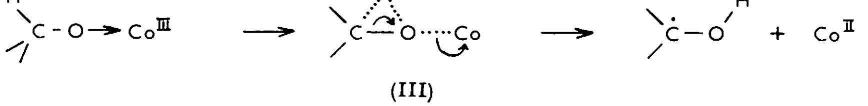
(I)



(II)

Though mechanism (II) could account for oxidation of some primary and secondary alcohols by C–C bond fission, as has been observed for vanadium(V),[20] postulation of a cyclic mechanism (I) for oxidation of cyclohexanol by cobalt(III) does not adequately account for the low primary isotope effect ($k_H/k_D = 1{\cdot}7$ at 10°). If one assumes that kinetic isotope effects for carbon–hydrogen bonds are due to differences in activation energy alone, then all kinetic isotope effects, even if measured at different temperatures, can rationally be compared in terms of energy ratios, $\Delta E'/\Delta E$, where k_H/k_D (observed) = exp $(\Delta E'/\boldsymbol{R}T)$ and ΔE is the energy difference calculated for C–H and C–D bonds, from zero-point energy differences for linear stretching; the latter have been computed by Wiberg.[21]

For the oxidation under consideration, $\Delta E'/\Delta E = 0{\cdot}27$, and it is difficult to believe that this small ratio could be ascribed entirely to differences in activation entropy. However, as Bell has pointed out,[22] $\Delta E'$ may be much lower than ΔE for a transition state involving transverse vibrations of a comparatively high frequency. Now no kinetic isotope effect should be discernible if the oxidation of cyclohexanol by cobalt(III) involved pure O–H bond fission, as proposed by Bawn and White[3] (reactions 1 and 3), but if an electron movement mainly of this type were to some extent concerted with migration of hydrogen from carbon to oxygen, as in (III), then the observed $\Delta E'/\Delta E$ value has a rational magnitude, since in the transition state (III) the hydrogen atom can have a considerable degree of transverse vibrational energy.



(III)

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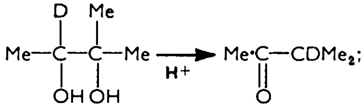
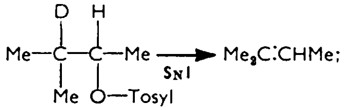
[19] Waters, *Quart. Rev.*, 1958, **12**, 277.
[20] Jones and Waters, *J.*, 1960, 2772.
[21] Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[22] Bell, "The Proton in Chemistry," Methuen, London, 1960.

Hydride migration between two adjacent carbon atoms involves a movement spatially similar to (III), and the associated kinetic isotope effect has been measured in several instances, *e.g.*:

(4) 

$$\mathrm{Me{-}\overset{D}{\underset{OH}{C}}{-}\overset{Me}{\underset{OH}{C}}{-}Me \xrightarrow[H^+]{} Me{\cdot}\underset{O}{\overset{\|}{C}}{-}CDMe_2};\quad \Delta E'/\Delta E = 0{\cdot}3 \text{ (ref. 23)}$$

(5) 

$$\mathrm{Me{-}\overset{D}{\underset{Me}{C}}{-}\overset{H}{\underset{O{-}Tosyl}{C}}{-}Me \xrightarrow[S_N1]{} Me_2C{:}CHMe};\quad \Delta E'/\Delta E = 0{\cdot}26 \text{ (ref. 24)}$$

and, as will be seen, has given isotope effects of similar magnitude. Fission of C–H bonds by consecutive reactions, *e.g.*:

$$(1)\ \mathrm{R_2CH{\cdot}OH + Co^{III} \longrightarrow R_2CH{\cdot}O{\cdot} + Co^{II} + H^+}$$

$$(6)\ \mathrm{R_2CH{\cdot}O{\cdot} + Co^{III} \longrightarrow R_2C{:}O + Co^{II} + H^+}$$

can be excluded from consideration, since if the steady-state condition, $[\mathrm{R_2CH{\cdot}O{\cdot}}] =$ Constant, holds for the radical concentration during the oxidation of the alcohol to the ketone the consumption of cobalt(III) would be given by the equation

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 2k_1[\mathrm{R_2CH{\cdot}OH}][\mathrm{Co^{III}}]$$

which does not involve at all the reaction (6) in which the C–H bond is broken.

Since tertiary alkyloxy-radicals have an appreciable free life, reactions analogous to (1) and (6) may be involved in the oxidation of t-butyl alcohol, but for this slow oxidation again the concerted migration of a methyl group from carbon to oxygen, by mechanism (III) or the concerted elimination (7) is also possible.

$$(7)\ \mathrm{Me_3C{\cdot}OH + Co^{III} \longrightarrow Me_2CO + Co^{III} + Me{\cdot} + H^+}$$

EXPERIMENTAL

Fresh cobaltic perchlorate solutions were prepared each day by the electrolysis of ~0·2M-cobaltous perchlorate [12] in stirred solutions at 0°. About 20% of cobalt(II) remained at the end of the electrolysis. These solutions were analysed, allowed to reach 10° in a thermostat bath, and then added in aliquot amounts to previously prepared mixtures of all the other reagents already at 10° ± 0·05°. The reaction was followed by adding portions to standard ferrous sulphate solution to which an equal volume of 90% phosphoric acid had previously been added. The excess of ferrous ion was then back-titrated with 0·0015M-ceric sulphate with barium anilinobenzenesulphonate as indicator. An automatic glass syringe (A. R. Horwell, London) was used as " pipette " for the rapid reactions. Control tests showed that in 0·35M-perchloric acid the spontaneous decomposition rates of cobalt(III) at 10° in 3·4M- and 5·3M-ionic strengths were $0{\cdot}3 \times 10^{-6}$ and $0{\cdot}48 \times 10^{-6}$ mole $\mathrm{l.^{-1}\,sec.^{-1}}$; these were less than 2% of the rate of consumption of cobalt(III) by either alcohol.

When t-butyl alcohol was used it was added to perchloric acid–sodium perchlorate mixtures immediately before the cobalt(III) solution, so as to minimise the risk of acid-catalysed dehydration to isobutene.

Experiments with 1-deuterocyclohexanol were performed in a Unicam spectrophotometer, the change of light absorption at 260 mμ being measured. A quartz cell was used inside a copper block through which water at 10° was circulated and a current of dry air was blown around the block to prevent condensation of moisture. In this case the solutions were measured by means of glass micropipettes or of an all-glass syringe fitted with a micrometer screw; the volumes in each case were reproducible to $<10^{-3}$ ml. 1-Deuterocyclohexanol was prepared as described by Littler and Waters [4] (yield 70%). Cyclohexanol and t-butyl alcohol were

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[23] Smith, Bowman, and Kmet, *J. Amer. Chem. Soc.*, 1959, **81**, 997.

[24] Cram and Tadanier, *J. Amer. Chem. Soc.*, 1959, **81**, 2737.

distilled from freshly prepared quicklime, through a 12″ fractionating column; their solutions were made up by weight in distilled water. 60% " AnalaR " perchloric acid was used and, from this, sodium perchlorate was made, by means of " AnalaR " sodium carbonate; it was recrystallised and dried to constant weight before dissolution.

From solutions resulting from the oxidations of cyclohexanol and t-butyl alcohol it was easy to obtain the 2,4-dinitrophenylhydrazones of cyclohexanone and acetone, respectively.

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