551. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part IV.*[1] *The Oxidation of Some α-Glycols.*

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The oxidations by quinquevalent vanadium in sulphuric acid of eight α-glycols have been compared with the oxidations of pinacol and cyclohexanol. From kinetic measurements it is concluded that mono- and di-tertiary glycols are oxidised by C–C bond fission and that primary and secondary glycols are oxidised like monohydric alcohols by $:CH(OH) \longrightarrow :CO$ conversion. Comparison of the relative rates of oxidation of a number of glycols and alcohols by a series of different oxidants indicates that pinacol can be oxidised by one-electron-abstracting agents and by chromium(VI) with exceptional ease. It is suggested that the determination of the relative rates of oxidation of pinacol and of another α-glycol and alcohol might be used to decide whether an oxidant effects one-electron or two-electron removal.

IN Part I (a) [2] it was reported that acid solutions of quinquevalent vanadium oxidise α-glycols with production of free radicals, and that immediate colour changes indicate that labile glycol–vanadium complexes are formed. To study the structural requirements for C–C bond fission by vanadium(V) in aqueous sulphuric acid the acid dependence of the rates of oxidation of the following glycols has been examined: *cis*- and *trans*-cyclohexane-1,2-diol, *cis*- and *trans*-1,2-dimethylcyclohexane-1,2-diol, butane-2,3-diol, 2-methylbutane-2,3-diol, propane-1,2-diol, ethane-1,2-diol. Further comparative measurements, when necessary, were made with both pinacol and cyclohexanol.

Results.—Table 1 gives the initial rates of consumption of vanadium(V), at various acidities, by the compounds that have been examined. Since the ionic strengths and $(HSO_4)^-$ concentrations of the solutions were not kept constant, the rates of oxidation of

TABLE 1. *Oxidations of diols by vanadium*(V) *in aqueous sulphuric acid.*

[Substrate] = 0·1M; $[V^V]$ = 0·04M. Temp. = 60·0°. First-order rate constants, $k_1 \times 10^4$ (sec.$^{-1}$).

	$[H_2SO_4]$ (M)							
Substrate *	0·0935	0·374	0·50	1·00	1·50	2·0	2·5	5·0
1	—	0·2	—	0·48	1·15	1·77	2·93	—
2	—	0·0439	—	0·140	0·291	0·533	0·809	—
3	—	0·281	—	0·576	0·833	1·41	2·84	—
4	0·524	—	—	1·083	1·648	—	4·49	—
5	—	0·047	—	—	0·26	—	0·654	—
6	—	—	0·052	—	0·391	—	0·951	—
7	—	—	—	0·38	—	1·15	—	—
8	—	1·82	—	2·56	3·25	4·44	6·00	—
9	—	—	—	0·082	—	—	0·378	1·199
10	—	*ca.* 160	—	—	—	—	—	—

* Substrates: (1) *cis*-Cyclohexane-1,2-diol. (2) *trans*-Cyclohexane-1,2-diol. (3) *trans*-1,2-Dimethylcyclohexane-1,2-diol. (4) *cis*-1,2-Dimethylcyclohexane-1,2-diol. (5) Ethane-1,2-diol. (6) Propane-1,2-diol. (7) Butane-2,3-diol. (8) 2-Methylbutane-2,3-diol. (9) Cyclohexanol. (10) Pinacol.

TABLE 2. *Rates of oxidation of diols by vanadium*(V).

Substrate *	1	2	3	4	5	6	7	8	9	10
Rate of acid-dependent oxidation, relative to that of cyclohexanol	6·9	2·05	3·9	7·3	1·7	2·45	4·4	10·0	1·00	—
Rate of oxidation by VO_2^+, 10^4k (sec.$^{-1}$)	0	0	0·21	0·47	0	0	0	1·63	0	*ca.* 160

* As for Table 1. With substrates (3), (4), and (8) the acid-dependent rate only refers to the range 0—1·5M-acid; with the others it refers to the whole range (0—2·5M).

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[1] Part III, Littler and Waters, *J.*, 1959, 4046.

[2] Part I, Littler and Waters, *J.*, 1959, 1299; Part II, Littler and Waters, *J.*, 1959, 3014.

TABLE 3.

1,2-Diol	Moles of V^V consumed per mole of diol	End products
trans-Cyclohexane-	10	Formic and glutaric acids
cis-Cyclohexane-	10	Formic and glutaric acids
trans-1,2-Dimethylcyclohexane-	2 *	Mixture of ketones
cis-1,2-Dimethylcyclohexane-	2 *	Mixture of ketones

* Increasing on long reaction.

the compounds were not proportional to the acidity. However, for the majority of the glycols, the ratio (rate of oxidation) : (rate of oxidation of cyclohexanol at the same acidity) was constant. For the remaining glycols, which evidently resemble pinacol in being oxidised by the ion VO_2^+ as well as by $V(OH)_3^{2+}$ and $(VO,OH_2,SO_4)^+$, the rates of oxidation do not extrapolate to zero rate at zero acidity (see Fig. 1). Table 2 gives, for the latter glycols, the relative rates of the acid-dependent and acid-independent oxidation processes.

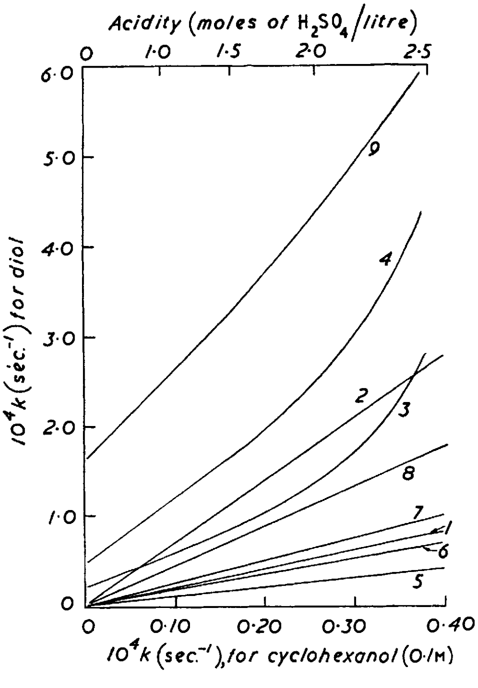


FIG. 1. *Rate of oxidation of diols compared with that of cyclohexanol at the same acidity.*

TABLE 4.

(*a*) Optical density per cm. (*D*) at 300 mμ of solution of *trans*-cyclohexane-1,2-diol containing 0·10M-V^V and 1·87M-H_2SO_4. Quartz cell.

[Diol] (M)	*D*	*D*/[diol]	[Diol] (M)	*D*	*D*/[diol]	[Diol] (M)	*D*	*D*/[diol]
0	0	—	0·08	1·28	16·0	0·14	2·33	16·6
0·04	0·60	15	0·10	1·61	16·1	0·16	2·65	16·5
0·06	1·01	16·8	0·12	1·98	16·5	0·20	3·22	16·6
							Mean	16·3

(*b*) Optical density per cm. (*D*) at 300 mμ of solution of 0·2M-*trans*-cyclohexane-1,2-diol containing 0·10M-V^V and various amounts of acid.

[H_2SO_4] (M)	*D*	Rate of oxidation of cyclohexanol 10^4k (sec.$^{-1}$)	$D/(k \times 10^4)$
0·93	0·98	0·075	13·1
1·4	1·85	0·14	13·2
1·87	3·32	0·225	14·7
2·35	5·7	0·33	17·2
2·8	10·7	0·46	23·2

Table 3 gives the final equivalent consumption of vanadium(V) when the oxidations of some of the glycols have been carried out to completion.

Table 4 gives the initial optical density at 300 mμ of solutions of *trans*-cyclohexane-1,2-diol containing 0·10M-vanadium(V) in 1·87M-sulphuric acid, together with the optical density of 0·20M-solutions of the diol and 0·10M-vanadium(V) in sulphuric acid of varying concentration. This Table, when correlated with Table 1, clearly shows that the extent of formation of a red 1 : 1 glycol–vanadium(V) complex is proportional, at moderate acidities, to the rate of oxidation of the *trans*-cyclohexanediol, which follows that of cyclohexanol.

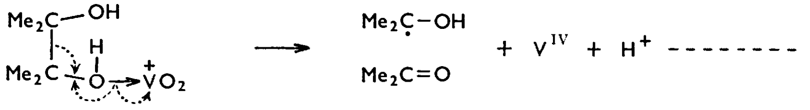
DISCUSSION

Any interpretation of diol oxidation by vanadium(V) must provide an explanation for (i) the distinction between those diols which are oxidised by VO_2^+ and those which are not; (ii) the remarkable ease of oxidation of pinacol, compared with that of other diols which have been examined, and (iii) the differences between the rates of oxidation of cyclohexanol and the cyclohexane-1,2-diols.

(1) The diols which are oxidised to a detectable extent by VO_2^+ are those which contain a tertiary hydroxyl group. For these glycols which must be oxidised by C–C bond fission, the graph of oxidation velocity against that of cyclohexanol is not linear at acidities above 1·5M, and consequently a different reaction mechanism must operate. This plot can only be linear if the substrate and cyclohexanol are oxidised at the same relative rates by both $V(OH)_3^{++}$ and the corresponding sulphate complex (see Part III [1]), and if the salt effect is identical in both reactions. Neither of these conditions can be expected to be fulfilled when the mechanism of oxidation differs from that of cyclohexanol.

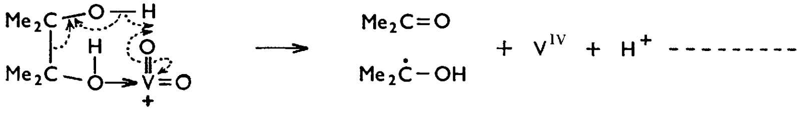
The great difference of oxidation rates (*ca.* 100-fold) between pinacol and the isomeric 1,2-dimethylcyclohexane-1,2-diols must be due to stringent steric requirements in the transition state of the reaction. Three different mechanisms can be written for C–C fission by vanadium(V).

(I)



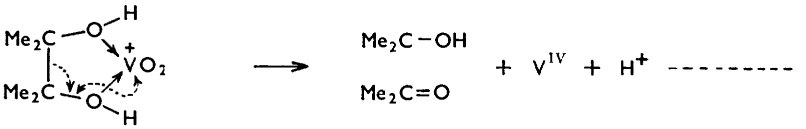
(1)

(II)



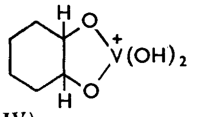
(2)

(III)

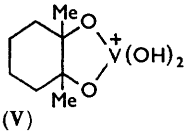


(3)

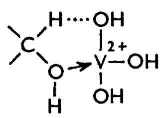
Mechanism (1), proceeding *via* an acyclic transition state (I), has no steric limitations, whilst the requirements for mechanism (2), proceeding *via* a



(IV)



(V)



(VI)

hydrogen-bonded seven-membered structure (II) are not stringent. Mechanism (3) involyes the formation of a nearly planar five-membered chelate ring (III), and will be greatly hindered if this ring is fused to a six-membered ring. Models, in which the V–O distance[3] is taken as 1·86 Å, show that while bicyclic structures such as (IV) are nearly strainless in the case of cyclohexane-1,2-diol, yet structures (V) for the dimethyl-diols are considerably strained in comparison with both (IV) and (III). Consequently the stability constant K for the complex formation,

$$\text{diol} + \text{V}^{\text{V}} \overset{K}{\rightleftharpoons} \text{complex}$$

would be lower for structure (V) than for (IV), and this would reduce the oxidation rate.

(2) Models of the di-tertiary glycol complexes (III), (IV), and (V) also show that, if the five-membered chelate ring is to be strainless, then it must be planar or almost so. Hence, the methyl groups in the pinacol complex (III) must be considerably occluded. This proximity of groups will impose a considerable strain on the C–C bond which is to be split in the ensuing oxidation, for the Me–Me interaction barrier can be estimated[4] at approximately 4·8 kcal./mole. In this way it is possible to account for the considerable ease of oxidation of pinacol as compared with that of butane-2,3-diol which, though it may form an analogous complex, is not oxidised by C–C bond fission (see below). Other reasons for the faster oxidation of pinacol than of 2,3-butanediol, by C–C bond fission, are (*a*) the inductive effect of the two methyl groups which will operate so as to increase the stability constant K of the more methylated diol complexes, and (*b*) the stability of the 2-hydroxy-2-propyl radical formed by the oxidation.

With *cis*- and *trans*-cyclohexanediols the two hydroxyl groups can achieve coplanarity more easily in the *cis*-isomer.[5] If this difference is not affected by the extra methyl groups, then the stability of complex (V) will be greater when formed from the *cis*-1,2-dimethylcyclohexane-1,2-diol than from its isomer. Infrared measurements of *trans*-cyclohexane-1,2-diol and *trans*-1,2-dimethylcyclohexane-1,2,-diol in carbon tetrachloride (0·01M-solution) show that the former has a sharp OH peak at 3637 cm.$^{-1}$ and a broad (hydrogen bonded) one at 3603 cm.$^{-1}$, while the latter has a sharp peak at 3634 cm.$^{-1}$ and a broad one at 3595 cm.$^{-1}$. In the di-secondary diol the hydrogen-bonded peak is the more intense, while in the di-tertiary diol the peaks are of equal intensity. The broad peaks indicate that intramolecular hydrogen bonding occurs in both molecules. Consequently, their hydroxyl groups are normally in the di-equatorial conformation which is required for formation of a chelate complex.

(3) Fig. 1 indicates that the *cis*- and *trans*-cyclohexane-1,2-diols and also ethane-1,2-diol, propane-1,2-diol, and butane-2,3-diol are all oxidised by the same mechanism as is cyclohexanol, *i.e.*, CH(OH) ⟶ C=O (see Part III[1]). For *trans*-cyclohexane-1,2-diol the more stable conformation is that having the two hydroxyl groups equatorially oriented.[6] In these circumstances the environment of each hydroxyl group is very similar to that of the hydroxyl group in cyclohexanol itself. Therefore with the diol the statistical expectation is that the oxidation rate should be about twice that of cyclohexanol. Since each hydroxyl group may inductively affect the rate of oxidation of the other, the observed rate factor of 2·05 is rational.

The oxidation of the *cis*-diol is faster than that of the *trans*- by a factor of 3·36. Now in both the *trans*-diol and cyclohexanol the hydrogen atom which is removed in the oxidation is axially oriented; the *cis*-diol has one equatorial hydrogen atom on a carbinol group. C–H bond fission is the rate-determining process of cyclohexanol oxidation, and, as Winstein and Holness[7] have pointed out in the case of chromic acid oxidations, the breakage of an axial C–H bond is hindered with respect to that of an equatorial C–H. For this reason *cis*-cyclohexane-1,2-diol should, and in fact does, react more rapidly.

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[3] Chemical Society Special Publication No. 11, 1958; Interatomic Distances.
[4] Klyne, " Progress in Stereochemistry," Vol. 1, p. 36, Butterworths, London, 1954.
[5] Angyal and Macdonald, *J.*, 1952, 686.
[6] Cole and Jefferies, *J.*, 1956, 4391.
[7] Winstein and Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562.

Though the *cis*-diol could well form the reaction complex (VI) less easily with the vanadium(V) species at the axial hydroxyl group, it appears that this does not greatly reduce the oxidation rate, and indeed Kwart and Francis [8] have suggested the opposite.

The relative oxidation rates of ethylene, propene, and butene glycols can be ascribed to the $I+$ inductive effect of the additional methyl groups.

The kinetics of the oxidation of 2-methylbutane-2,3-diol show features of both pinacol and monohydric alcohol types, in that it is oxidisable by VO_2^+, while the acid dependence does not depart greatly from that of alcohol oxidation. Evidently both mechanisms are operative concurrently.

Further Implications.—We have shown above that oxidation of diols by a typical 1-electron oxidant, vanadium(V), can be explained in terms of (*a*) alcohol-type oxidation of secondary and primary hydroxyl groups and (*b*) C–C fission *via* a chelate complex when tertiary hydroxyl is present. Table 5 shows that pinacol is oxidised considerably more easily than less methylated glycols by vanadium(V) and manganese(III), and, to a less marked extent, by cerium(IV), which are all one-electron oxidants, and also very rapidly by chromium(VI). No such effect is observed with the known two-electron oxidants, lead tetra-acetate and periodic acid, which oxidise *cis*-cyclohexane-1,2-diol or racemic butane-2,3-diol much faster than pinacol. On this basis one can tentatively correlate the easy oxidation of pinacol with a one-electron mechanism; if so, then chromium(VI) may in this case be behaving as a one-electron oxidiser. A five-membered ring is not the essential

TABLE 5.

				Cr^{VI}	
Oxidant and conditions	$Pb(OAc)_4$; HOAc; 20°	H_5IO_6; 0°		35—40°; $[H^+] = 0{\cdot}2$—$0{\cdot}22$M	25°; $[H^+] = 2{\cdot}8$M
Substrate	k''	k'	K	k''	k''
1	840	3300	400	—	3470
2	35·5	165	1000	—	611
7	1465 (racemic)	308	8000 (—)	$68 \times [H^+]^2$	—
	61·7 (*meso*)	182	373 (*meso*)	($[H^+] = 0{\cdot}22$M) 40°	
10	90	$k'' = 4 \times [H^+]$		$1500 \times [H^+]$ $[H^+] = 0{\cdot}22$M 40°	—
Monohydric alcohols	v. slow	Not attacked		$13{\cdot}3 \times [H^+]^2$ $[H^+] = 0{\cdot}20$M 35° (Pr^iOH)	579
References	12	9, 13, 14		15, 16	17

	Mn^{III}	V^V	Ce^{IV}		
Oxidant and conditions	0·12M-pyrophosphate; pH 0·19—0·20M; $[Mn^{III}] = 1{\cdot}8 \times 10^{-2}$M	Aqueous H_2SO_4; 60°	H_2SO_4; 50°	$HClO_4$; 25°	
Substrate	k''	k'', related to cyclohexanol	k''	k'	K
1	*ca.* 0·75 (40°)	6·9	—	—	—
2	*ca.* 0·05 (40°)	2·05	—	—	—
7	—	4·4	210	225	17 (*meso*)
10	*ca.* 48 (35°)	*ca.* 160	620	—	
Monohydric alcohols	Not attacked	1·00 (cyclohexanol)	k' 1·38 K 13 (cyclohexanol)	66	8·8 (EtOH)
References	10, 18		19, 20, 21	22, 23	

k'', in units (mole^{-1} sec.$^{-1}$ $\times 10^4$), refers to $-(d/dt)$ [oxidant] $= k''$ [substrate][oxidant].
K, in units (mole^{-1}), is the stability constant of the oxidant–substrate complex.
k', in units (sec.$^{-1}$ $\times 10^4$), is the first-order constant for the decomposition of any complex. In dilute solution, or when K is small, $k'K = k''$ (approx.).

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[8] Kwart and Francis, *J. Amer. Chem. Soc.*, 1959, **81**, 2116.
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[10] Levesley, Waters, and Wright, *J.*, 1956, 840.

requirement for C–C bond fission of a glycol, since periodic acid does not oxidise pinacol particularly easily, and does form a cyclic complex.[9] The rapidity of oxidation of pinacol by one-electron oxidants is considered further in the following paper.

EXPERIMENTAL

Materials.—The vanadium solutions, cyclohexanol, and pinacol were prepared by the methods of Parts I—III.[1,2] *cis*- and *trans*-Cyclohexane-1,2-diol and *cis*- and *trans*-1,2-dimethylcyclohexane-1,2-diol were prepared by the methods described by Levesley, Waters, and Wright.[10] The butane-2,3-diol, b. p. 184°, was a fractionated sample of commercial material (*i.e.*, a mixture of stereoisomers). 2-Methyl-2,3-butanediol, b. p. 177°, was prepared by dehydrating t-pentyl alcohol and oxidising the resulting pentene with performic acid, and propane-1,2-diol, b. p. 189°, was prepared by hydrolysis of propene oxide.

Kinetic Measurements.—These were carried out at 60° ± 0·1° as in Part II.[2] Good first-order plots were obtained when neutral diol solutions were added to vanadium(v) solutions of the required acidity so that pinacol–pinacolone rearrangements of the diols were minimised. Fig. 2 shows the effect of pre-treating *trans*-1,2-dimethylcyclohexane-1,2-diol for 1 hr. with 2·8M-sulphuric acid to form some dimethylcyclohexanone before the oxidation was allowed to commence. The observed reaction velocities were unchanged when the reactant solutions were air-freed by sweeping out with nitrogen.

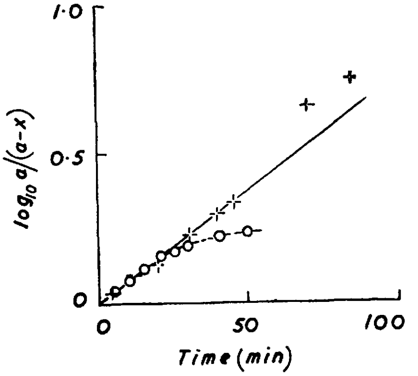

FIG. 2. *Effect of pinacol–pinacolone reaction.*
+ Diol added to V^V acid mixture.
○ V^V added to diol–acid mixture after 1 hr.
Final acidity = 2·5M-H_2SO_4.

Stoicheiometry of the Reactions.—Diol solutions were kept for several days at 60° with a known large excess of vanadium(v) and were titrated at intervals. Formic acid, when formed, was identified by the chromotropic acid test,[11] and glutaric acid by its m. p. and mixed m. p. Ketones were identified as 2,4-dinitrophenylhydrazones but were not separated.

The infrared measurements were carried out on a Unicam S.P. 100 double-beam grating spectrophotometer, and the ultraviolet measurements on a Unicam S.P. 500 spectophotometer.

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