552. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part V.*[1] *A Comparative Study of the Oxidation of Alcohols and Glycols by Cerium*(IV), *Vanadium*(V), *and Chromium*(VI).

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The rates of oxidation of a number of glycols have been measured in both water and deuterium oxide using as oxidants vanadium(V), cerium(IV), and chromium(VI) in sulphuric acid. Differences between the mechanisms of oxidation by these reagents are discussed.

IN Part IV,[1] from studies of the rates of oxidation of a series of α-glycols by vanadium(V), it was concluded that two mechanisms, *viz.*, oxidation of :CH(OH) to :C=O as in alcohols, and fission of the C–C bond as in pinacol, operate. The latter mechanism appeared to require the formation of a vanadium–glycol chelate complex. By the method of Chang and Westheimer,[2] in which are compared (*a*) the rates of oxidation of pinacol in water and deuterium oxide, and (*b*) the rates of oxidation of pinacol and its monomethyl ether, further evidence for chelate formation has been obtained. The oxidation of 2,3-dideuterobutane-2,3-diol has been shown to occur by CH(OH) ⟶ C=O conversion, since there is a definite isotope effect with vanadium(V) and chromium(VI) though this is uncertain with cerium(IV).

TABLE 1. (A) *Oxidations by vanadium*(V) *at* 50° (*except where indicated*).

Substrate *	[Substrate] (M)	[Oxidant] (N)	[H+] (M)	Solvent	Rate, 10^4k (sec.$^{-1}$)	$\frac{10^4k}{[\text{Substrate}]}$	k_H/k_D
1	0·149	0·049	2·9	H_2O	11·7 †	78·5	0·89
1	0·152	0·051	2·9	D_2O	13·4 †	88·0	
1	0·149	0·049	0·5	H_2O	5·96 ‡	40·0	0·81
1	0·152	0·051	0·5	D_2O	9·0 ‡	59·2	
2	0·105	0·049	5·3	H_2O	1·0	9·52	0·68
2	0·095	0·051	5·3	D_2O	1·36	14·3	
3	0·134	0·049	5·3	H_2O	2·56	19·1	0·74
3	0·134	0·051	5·3	D_2O	3·45	25·8	
3	0·176	0·049	5·3	H_2O	3·15	17·9	
4	0·171	0·049	5·3	H_2O	0·96	5·6	
5	0·124	0·049	5·3	H_2O	1·58	12·7	
6	0·0426	0·05	5·9	H_2O	2·37	57	2·7
7	0·0169	0·05	5·9	H_2O	0·356	21·1	
8	0·032	0·05	1·06	H_2O	1·28	37·6	
1	0·053	0·05	1·06	H_2O	32	604	
9	0·073	0·05	5·9	H_2O	too fast	—	
10	0·058	0·05	5·9	H_2O	<0·075	<1·3	

* Substrates: (1) Pinacol. (2) Cyclohexanol. (3) Ethane-1,2-diol. (4) Ethanol. (5) 2-Methoxyethanol. (6) Butane-2,3-diol. (7) 2,3-Dideuterobutane-2,3-diol. (8) Pinacol monomethyl ether. (9) Acetoin. (10) t-Butyl alcohol.

† Carried out at 25°. ‡ Carried out at 30°.

(B) *Oxidations by* 0·049N-*chromium*(VI) *at* 50° *in water* (*except where indicated*).

Substrate	6	7 †	9
[Substrate]	0·0426	0·0169	0·073
[H+]	0·25	0·25	0·25
10^4k	3·5	0·354	2·51
10^4k/[Substrate]	82·1	20·9	34·4
k_H/k_D	3·93		

(C) *Oxidations by* 0·0044N-*cerium*(IV) *at* 50° *in water* (*except where indicated*).

Substrate	6	7	7	8	1 ‡	8 *	1 *	1 *†	10
[Substrate]	0·0682	0·0169	0·0338	0·032	0·10	0·032	0·053	0·053	0·058
[H+]	0·272	0·272	0·272	0·112	0·112	0·096	0·096	0·096	0·272
10^4k	13·6	3·5	5·9	24	—	1·23	5·37	5·25	0·05
10^4k/[Substrate]	198	192	175	750	618	37·2	101	99	0·86
k_H/k_D							1·02		

* Oxidations at 25°. † D_2O solvent. ‡ Calculated from ref. 15.

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[1] Part IV, Littler, Mallet, and Waters, preceding paper.

[2] Chang and Westheimer, *J. Amer. Chem. Soc.*, 1960, **82**, 1401.

Results.—Table 1 gives the rate of consumption of oxidant by the different compounds, and the ratios k_H/k_D which express the effect of replacing hydrogen by deuterium either in the compound or in the solvent, as indicated. In a few cases it was necessary to confirm that the reaction was of first order with respect to the organic substrate: Table 2 gives the relevant data for butane-2,3-diol, which shows that there is no detectable complex formation between the reactants. From Table 1 it can be seen that the oxidation of pinacol by vanadium(v) is slightly faster in deuterium oxide, and the oxidations of cyclohexanol and ethylene glycol are rather more affected.

TABLE 2. *Reaction orders with respect to the organic substrate.*

Temperature = 50°; k'' = second-order rate constant.

Substrate 6;	[Substrate] (M)	0·0852	0·0682	0·0511	0·0341
$[V^V]$ = 0·05N;	10^4k	0·92	0·70	0·54	0·39
$[H^+]$ = 3·46M	10^4k/[Substrate]	10·7	10·3	10·5	11·5
Mean value of $k'' = (10{\cdot}8 \pm 0{\cdot}4) \times 10^{-4}$ mole^{-1} sec.$^{-1}$.					
Substrate 6;	[Substrate] (M)	0·119	0·0852	0·0511	0·0170
$[Cr^V]$ = 0·049N;	10^4k	28·8	21·4	13·2	4·1
$[H^+]$ = 0·48M	10^4k/[Substrate]	241	251	258	241
Mean value of $k'' = (248 \pm 7) \times 10^{-4}$ mole^{-1} sec.$^{-1}$.					
Substrate 6;	[Substrate] (M)	0·1278	0·0852	0·0682	0·0426
$[Ce^{IV}]$ = 0·004N;	10^4k	28	18	13·6	9·9
$[H^+]$ = 0·272M	10^4k/[Substrate]	219	211	198	232
Mean value of $k''_H = (215 \pm 12) \times 10^{-4}$ mole^{-1} sec.$^{-1}$.					
Substrate 7;	[Substrate] (M)	0·0169	0·0338		
$[Ce^{IV}]$ = 0·0044N;	10^4k	3·25	5·9		
$[H^+]$ = 0·272M	10^4k/[Substrate]	192	175		
Mean value of $k''_D = (183 \pm 9) \times 10^{-4}$ mole^{-1} sec.$^{-1}$.					
Substrate 4;	[Substrate] (M)	0·300	0·200	0·100	
$[Ce^{IV}]$ = 0·0044N;	10^4k	2·03	2·27	2·57	
$[H^+]$ = 0·272M	10^4k/[Substrate]	6·77	11·35	25·7	
Substrate 3;	[Substrate] (M)	0·300	0·200	0·100	
$[Ce^{IV}]$ = 0·044N;	10^4k	2·20	2·16	2·08	
$[H^+]$ = 0·272M	10^4k/[Substrate]	7·33	10·8	20·8	
Substrate 5;	[Substrate] (M)	0·304	0·203	0·101	
$[Ce^{IV}]$ = 0·044N;	10^4k	1·4	1·86	2·03	
$[H^+]$ = 0·272M	10^4k/[Substrate]	4·6	9·16	20·1	

When ceric sulphate is the oxidant pinacol is oxidised at the same rate in both water and deuterium oxide. Methylation of one hydroxyl group of pinacol very markedly decreases the rate of oxidation by vanadium(v) (*ca.* 16 : 1) but it has much less effect (*ca.* 3 : 1) on the rate of oxidation by cerium(IV). The rates of oxidation of ethylene glycol, ethylene glycol monomethyl ether, and ethanol by vanadium(v) and cerium(IV) differ so little that polar effects may suffice to explain the difference. It is noteworthy that the rate of oxidation of these substrates by cerium(IV) decreases with increasing substrate concentration. This would be consistent with the formation of a cerium(IV)–substrate complex which resists oxidation. Since we assume that the 1 : 1 complexes are those which take part in the oxidation, the inert complexes must contain a higher proportion of substrate molecules.

The oxidation of butane-2,3-diol by vanadium(v) is faster than that of the deuterated compound by a factor of 2·7; this is a smaller factor than that observed[3] in the oxidation of cyclohexanol (k_H/k_D = 4·5). An isotope effect of 3·9 was observed when chromium(VI) was the oxidant (Westheimer and Nicolaides[4] found k_H/k_D = 6 for isopropyl alcohol), but no evident isotope effect has been observed with cerium(IV).

A trace of impurity in the 2,3-dideuterobutane-2,3-diol gave an initial rapid reduction of part of the vanadium(v), but this was not noticed when chromium(VI) or cerium(IV) was used. As shown in the Table, this is consistent with the presence of acetoin in the diol, as

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

[4] Westheimer and Nicolaides, *J. Amer. Chem. Soc.*, 1949, **71**, 25.

its oxidation rate was too fast to be measured when vanadium(V) was used though it was of the same order of magnitude with chromium(VI). Attempted oxidations of t-butyl alcohol confirmed that simple tertiary alcohols are very resistant to oxidation.

TABLE 3. *Reaction orders with respect to acidity.*

(A) Substrate 8; 0·032M; $[V^V]$ = 0·05N; 50°.

$[H^+]$	1·06	1·54	2·02	2·50	2·98	3·94
10^4k	1·20	2·54	4·4	7·45	11·1	29
$10^4k/[H^+]$	1·13	1·65	2·18	2·98	3·72	7·36
10^4k * for oxidation of substrate 2	0·09	0·165	0·25	0·38	0·51	0·81
∴ k_8/k_2	13·3	15·4	17·6	19·6	21·8	35·8

(B) Substrate 1; 0·053M, $[Ce^{IV}]$ = 0·0044N; 25°; constant ionic strength; $[HSO_4^-]$ = 0·24M.

$[H^+]$	0·48	0·114	0·240
10^4k	2·92	2·76	3·2
$10^4k/[H^+]$	55	52	60

Mean value $k'' = (56 \pm 3) \times 10^{-4}$ mole^{-1} sec.$^{-1}$

* Interpolated from Part IV.

Table 3 shows the acid dependence of the oxidation of pinacol monomethyl ether by vanadium(V). A plot of these figures passes through the origin, showing that there is no detectable oxidation by the species VO_2^+ (contrast Fig. 1 in Part I [5]). The increase of oxidation rate with acidity is also rather more rapid than that of secondary alcohols under similar conditions (Part IV [1]). There are also recorded three experiments which show that in the range 0·05—0·25M-acid, the oxidation of pinacol by ceric sulphate solutions is not noticeably hydrogen-ion dependent.

DISCUSSION

From the fact that only secondary isotope effects are observed when pinacol is oxidised by chromium(VI) in deuterium oxide, and that pinacol monomethyl ether is oxidised considerably more slowly than is pinacol itself, Chang and Westheimer [2] have deduced that the oxidation of pinacol proceeds by a mechanism involving a chelate complex of glycol and chromium(VI) (II), which then decomposes. The secondary isotope effects arise from the acid–base equilibria between various forms of the oxidising agent, as a protonated species is a weaker acid in deuterium oxide than in water [6] by a factor which is often about 2. This means that if $V(OH)_3^{++}$ [or $V(OD)_3^{++}$] is the oxidant (as with cyclohexanol) the reaction should be faster in deuterium oxide than in water, as is observed, for there is a greater concentration of oxidant present at any particular acidity. On the other hand pinacol, which is oxidised by both VO_2^+ and $V(OH)_3^{++}$, should not show so large an effect. When ceric sulphate is used, there is no appreciable acid dependence in the range studied, and so the secondary isotope effect which should be small is in fact negligible. So in neither case is it necessary to postulate a *primary* isotope effect involving fission of the deuterium-replaceable O–H bonds of the pinacol. Now, pinacol monomethyl ether is easily oxidised by cerium(IV) but not at all by VO_2^+ and rather slowly by $V(OH)_3^{++}$ or its sulphate complex. Thus, it would appear that vanadium(V) oxidises pinacol by decomposition of a chelate complex (I), while cerium(IV) does not [cf. (III)].

The mechanism suggested in Part I involving a complex of type (III) must therefore be amended, as shown above, but it appears to be applicable, *mutatis mutandis*, to the oxidation of pinacol or its monomethyl ether by ceric sulphate. The data on ethanol derivatives show that ethylene glycol is not oxidised by vanadium(V) by this cyclic mechanism. Correspondingly the oxidation of 2,3-dideuterobutane-2,3-diol is undoubtedly that of an alcohol, *i.e.*, $\colon CD(OH) \longrightarrow \colon C{=}O$. Since there is an isotope effect with butane-2,3-diol when chromium(VI) is used, it is evident that this oxidant preferentially oxidises secondary alcohols at the $\colon CH(OH)$ group rather than by C–C fission.[7] In the oxidation of glycols by cerium(IV), however, the absence of a pronounced

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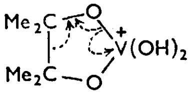
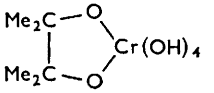
[5] Littler and Waters, *J.*, 1959, 1299.

[6] Moelwyn-Hughes and Bonhoeffer, *Z. Electrochem.*, 1934, **40**, 469.

[7] Slack and Waters, *J.*, 1949, 594; Chatterji and Mukherjee, *Z. phys. Chem.*, 1958, **208**, 281.

isotope effect implies that butane-2,3-diol may be oxidised primarily by C–C fission. This is confirmed by examination of the volatile products of this reaction: C–C fission would be expected to give acetaldehyde, as found; if it did not occur, the first oxidation product would be acetoin, which on further oxidation gives considerable quantities of biacetyl.


(I)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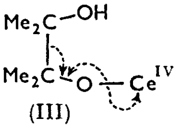
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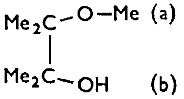

(IV)

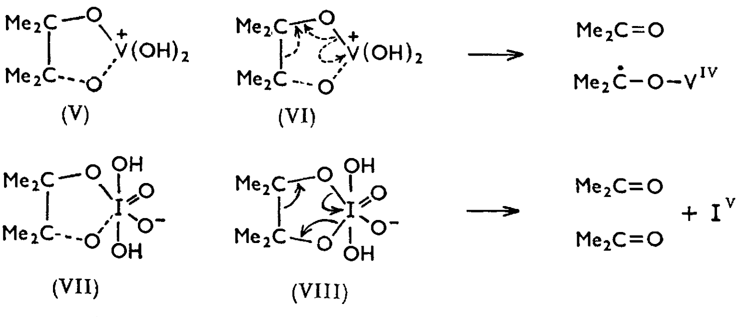
Since complex formation between butane-2,3-diol and cerium(IV) was not kinetically detectable, the oxidation of this diol resembles that of pinacol rather than that of ethylene glycol. That C–C bond fission of glycols is not a general reaction of cerium(IV) is indicated by the similarity of the oxidation rates of ethylene glycol, ethanol, and ethylene glycol monomethyl ether.

The rates of oxidation of t-butyl alcohol by all three oxidants are very small. This shows that the methoxy-group (*a*) in pinacol monomethyl ether (IV) is having a profound effect on the stability of the tertiary alcohol group (*b*) quite apart from the fact that ether (IV) cannot form a complex of type (I). In oxidations with both cerium(IV) and vanadium(V) the radical product of C–C bond fission, *i.e.*, $\cdot CMe_2\cdot OH$ or $\cdot CMe_2\cdot OMe$, is much more stable than the radicals $CH_3\cdot$ which could be produced by a similar oxidation of t-butyl alcohol. This probably accounts for the ease of oxidation of the ether (IV).

The acid dependence of the oxidation of the ether (IV) by vanadium(V) is not identical with that of a normal secondary alcohol but increases rather more rapidly with acidity (Table 3). This indicates that the two species $V(OH)_3^{++}$ and $(VO,OH_2,SO_4)^+$ responsible for oxidation of alcohols in sulphuric acid solutions (Part III [3]) may oxidise this ether (IV) at different relative rates.

The mechanisms of oxidation of glycols and pinacol by vanadium(V) put forward in Part IV of this series are therefore confirmed, but cannot be extended to the somewhat more powerful oxidant cerium(IV). This may be due to the reduced selectivity that would be expected with the use of a more powerful oxidant, evidently capable of oxidising pinacol without the formation of a cyclic complex. In an acyclic mechanism the conformation of the glycol can remain in the most stable (staggered) position, but with the weaker vanadium(V) as oxidant it is necessary to strain or stretch the central C–C bond to form the much more eclipsed structure of the cyclic complex (I). If, as inferred, cerium(IV) oxidises both pinacol and butane-2,3-diol by the same acyclic mechanism, it is clear why their rates of oxidation only differ by a factor of 3 (cf. Table 5, Part IV) and why both rates are considerably greater than the rates of oxidation of cyclohexanol, ethanol, or ethylene glycol.

The structures of the complexes (V), (VII) and of the transition states (VI), (VIII) for oxidation of pinacol by a one-electron oxidant (VO_2^+) and by a two-electron oxidant (IO_4^-) [8] have different steric requirements:


(V) (VI) (VII) (VIII)

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[8] Buist, Bunton, and Miles, *J.*, 1959, 743.

Both (V) and (VII) can have a puckered five-membered ring that relieves the Me–Me interaction. The transition state (VI) retains this conformation, as the electron movement involves only one of the oxygen atoms. However, in (VIII) the cyclic electron-switch involves the whole ring, which must therefore be coplanar. Thus there will be an energy of activation in passing from (VII) to (VIII) which has no parallel in the transition from (V) to (VI). It is generally observed that a reaction involving a cyclic electron shift, as in (VIII), is easy. In this way one can explain why the relative ease of oxidation of glycols by periodic acid depends entirely on the steric requirements of complex formation and decomposition,[8] and not at all on whether the glycol contains a tertiary hydroxyl group. There is no similar facilitation in any one-electron oxidation of a glycol, though steric effects and the increased stability of tertiary radicals do favour C–C fission of glycols containing one or two tertiary hydroxyl groups.

EXPERIMENTAL

Materials.—Vanadium(V) solutions were prepared as in Part II.[9] Ceric sulphate was made up from B.D.H. ceric sulphate " low in other rare earths."

The deuterium oxide, supplied by Norske Hydro, was of 99·8% purity. Deuterosulphuric acid was prepared from this by treatment with sulphur trioxide; its concentration was checked by titration.

Cyclohexanol was purified as described in Part III.[3]

Acetoin (B.D.H.) was washed first with alcohol, then with ether, and sucked dry.

t-Butyl alcohol (B.D.H.) was used as supplied.

Pinacol monomethyl ether was prepared by Lindner's method.[10] The relative oxidation rates and vapour-phase chromatogram peak areas of two fraction, b. p. 147—148° and 149—150°, that contained only the pinacol mono- and di-methyl ethers were compared. On the assumption that pinacol dimethyl ether was not oxidised, the linear relationship between vapour-phase chromatogram peak area and composition indicated that the fractions contained 60 ± 5 and 75 ± 5% of the monomethyl ether respectively. The fraction of b. p. 149—150° was used, without further purification, for kinetic studies.

2,3-Dideuterobutane-2,3-diol was prepared by lithium aluminium deuteride reduction of biacetyl [11] (cf. preparation of 1-deuterocyclohexanol [3]). The protium compound used for comparison was prepared in an identical manner, and had an infrared spectrum identical with that of fractionated commercial butane-2,3-diol. It presumably is a mixture of the *meso*- and DL-isomers. For the product studies the latter material (b. p. 180°, m. p. 19—21°) was used.

Kinetic Measurements.—All reactions were carried out in a 2-mm. quartz cell mounted in an Adkins thermostatically controlled cell holder, giving temperature control to ±0·2°. This fitted into a Unicam S.P. 500 spectrophotometer. For oxidations by vanadium the increase in concentration of vanadium(IV) was observed at 750 mμ; [12] for those by cerium(IV) the decrease in concentration of cerium(IV) was observed at 380 mμ,[13] and for those by chromic acid the decrease in concentration of chromium(VI) was observed at 350 mμ.[14] Solutions of the reactants were prepared by adding to weighed material, in test-tubes closed by serum caps, measured volumes of solvent from an " Agla " micrometer syringe. By using the micrometer syringe, reaction mixtures (1 ml.) were made up by volume in test-tubes closed by serum caps, shaken, and then rapidly transferred by syringe to the spectrophotometer cell. For vanadium(V) oxidations in deuterium oxide the stock of oxidant solution was made up from solids so that the final water was still 98·8% in deuterium oxide, but in the ceric oxidations, as only 0·05 ml. of cerium(IV) solution was used per 1 ml. of reaction mixture, ceric sulphate dissolved in ordinary water was used, so the final solution contained 95% of deuterium oxide.

Examination of Volatile Products.—Butane-2,3-diol or acetoin (1 g.) was dissolved in 2N-sulphuric acid (50 ml.) at 100° and solid ceric sulphate was added.[15] A brisk current of carbon

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[9] Littler and Waters, *J.*, 1959, 3014.

[10] Lindner, *Monatsh.*, 1911, **32**, 403.

[11] Loewus, Westheimer, and Vennesland, *J. Amer. Chem. Soc.*, 1953, **75**, 5018.

[12] La Salle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

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

[14] Hepler, *J. Amer. Chem. Soc.*, 1958, **80**, 6181; Cohen and Westheimer, *ibid.*, 1952, **74**, 4387; Cardone and Compton, *Analyt. Chem.*, 1952, **24**, 1903.

[15] Mino, Kaizerman, and Rasmussen, *J. Amer. Chem. Soc.*, 1959, **81**, 1494.

dioxide was passed through the liquid, up a reflux condenser, and then into solutions of (*a*) saturated aqueous dimedone, and (*b*) 2,4-dinitrophenylhydrazine sulphate in methanol. The volatile products from the oxidation of the diol gave a dimedone derivative, m. p. 140° (cf. acetaldehyde derivative, m. p. 140°), and a 2,4-dinitrophenylhydrazine derivative, m. p. 144° (cf. acetaldehyde derivative, m. p. 148°). The products from oxidation of acetoin gave a small quantity of dimedone derivative, m. p. 140°, and a 2,4-dinitrophenylhydrazine derivative which softened at 144° and melted at *ca.* 250° (cf. biacetyl bisdinitrophenylhydrazone, m. p. 315°). Hence the volatile product of the diol oxidation is substantially pure acetaldehyde, whilst those of oxidation of acetoin contain a little acetaldehyde but mainly consist of biacetyl. This was also evident from the odour of the vapour.

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