812. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part III.*[1] *The Oxidation of Cyclohexanol.**

By J. S. Littler and William A. Waters.

The oxidations of cyclohexanol and 1-deuterocyclohexanol by quinquevalent vanadium in sulphuric acid solutions are of the first order with respect to both $[V^V]$ and the alcohols. The acidity dependence in perchloric acid solution is indicative of oxidation by the cation $\{V(OH)_3\}^{2+}$; in sulphuric acid the more active oxidant is $[VO(H_2O)SO_4]^+$ or a similar complex ion. Optical measurements indicate that in perchloric acid solution all alcohols combine rapidly and reversibly with quinquevalent vanadium to form reddish complexes of composition $\{ROH,V(OH)_3\}^{2+}$. The oxidations of cyclohexanol and 1-deuterocyclohexanol proceed *via* these complexes and, since there is a kinetic isotope effect, C–H (or C–D) bond fission is involved in the rate-determining step. Evidence for a radical mechanism is put forward and discussed.

In Part I[2] it was indicated that primary and secondary alcohols were oxidised by acid solutions of quinquevalent vanadium with formation of free radicals. We have now studied kinetically the oxidations of cyclohexanol and 1-deuterocyclohexanol by quinquevalent vanadium, using perchloric and sulphuric acid solutions, and have been better able to elucidate the natures of the oxidising species in these two solutions.

Results.—Table 1 shows that the rate of consumption of vanadium(v) is of first order with respect to alcohol concentration. In this and the remaining Tables k is the first-order rate constant determined graphically from plots of log $[V^V]$ against time. Oxidations carried out in the presence of excess of the alcohol all give good first-order reaction plots with respect to $[V^V]$ (the total concentration of all vanadium(v) species) for at least 50% of the reaction (cf. Part II[1]).

Table 1. *Order with respect to alcohol of the oxidation of cyclohexanol in aqueous sulphuric acid.*

$[V^V]$ = 0·05N, $[H_3O^+]$ = 3·5M, ionic strength = 3·6M.

[Alcohol] (M)	0·0417	0·1038	0·125	0·166	0·2076
10^4k (sec.$^{-1}$)	0·121	0·268	0·328	0·447	0·537
10^4k/[alcohol]	2·88	2·58	2·62	2·69	2·59

Mean value of k/[alcohol] = (2·65 ± 0·08) × 10^{-4} mole^{-1} sec.$^{-1}$.

Tables 2 and 3 show that in both perchloric and sulphuric acid the oxidation rate is linearly dependent on the hydrogen-ion concentration $C_{H_3O^+}$, provided that the ionic strength is held constant by the addition of a salt of the same acid.

Table 2. *Order with respect to hydrogen-ion concentration of the oxidation of cyclohexanol in aqueous perchloric acid.*

$[V^V]$ = 0·05N, ionic strength = 6·0M.

$C_{H_3O^+}$ (M)	1·04	3·32	4·20	4·68	5·59
[Alcohol] (M)	0·104	0·104	0·083	0·083	0·104
10^4k	0·137	0·337	0·375	0·414	0·608
10^4k/[alcohol]	1·32	3·24	4·52	4·98	5·85
10^4k/[alcohol] . $C_{H_3O^+}$	1·26	0·98	1·07	1·06	1·05

Mean value of k/[alcohol] . $C_{H_3O^+}$ = (1·08 ± 0·09) × 10^{-4} mole^{-2} sec.$^{-1}$.

In order to investigate the nature of the deep red complex of vanadium(v) formed in sulphuric acid solutions,[2] oxidations were carried out in solutions of almost constant

---

* The substance of this paper was presented to a Symposium on Oxidation held at Queen Mary College, London, on April 14th, 1959.

[1] Part II, Littler and Waters, *J.*, 1959, 3014.

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

acidity and constant ionic strength in which perchlorate ions had been progressively replaced by bisulphate ions. Table 4 shows that until about two thirds of the perchlorate has been replaced the oxidation rate increases linearly with bisulphate concentration.

TABLE 3. *Order with respect to hydrogen-ion concentration of the oxidation of cyclohexanol in aqueous sulphuric acid.*

$[V^V] = 0{\cdot}05$N, $[HSO_4^-] = 6{\cdot}0$M, ionic strength = 6·0M, [alcohol] = 0·104M.

$C_{H_3O^+}$ (M)	2·7	4·3	5·9
10^4k	0·494	0·802	1·10
$10^5k/C_{H_3O^+}$	1·83	1·86	1·87

Mean value of $k/C_{H_3O^+} = (1{\cdot}85 \pm 0{\cdot}02) \times 10^{-5}$ mole^{-1} sec.$^{-1}$.

TABLE 4. *Effect of bisulphate ion on the oxidation of cyclohexanol in aqueous perchloric acid.*

$[V^V] = 0{\cdot}05$N, [alcohol] = 0·104M, ionic strength = 6·0M.

$[HSO_4^-]$ (M)	0	1·2	2·4	3·6	4·8	6·0
$[H_3O^+]$ (M)	5·6	5·65	5·7	5·8	5·85	5·9
10^4k	0·608	0·750	0·895	0·995	1·06	1·10
$10^5k/[H_3O^+] = 10^5k'$	1·09	1·33	1·57	1·72	1·81	1·87
$10^5(k' - k'_0)$	0	0·24	0·48	0·63	0·72	0·78
$10^6(k' - k'_0)/[HSO_4^-]$	—	2·0	2·0	1·9	1·5	1·3

Mean value $(k' - k'_0)/[HSO_4^-] = 2{\cdot}0 \times 10^{-6}$ mole^{-2} sec.$^{-1}$ in range 0—4M-H_2SO_4.

TABLE 5. *Effect of sodium perchlorate on the rate of oxidation in perchloric acid.*

$[V^V] = 0{\cdot}05$N, [alcohol] = 1·04M, $[H_2O^+] = 1{\cdot}04$M.

Ionic strength (M)	3·6	6
10^5k	0·34	1·37

Table 5 shows that the addition of sodium perchlorate increases the rate of oxidation in perchloric acid solution.

The addition of vinyl cyanide leads to the production of insoluble polymers that contain both carbonyl and hydroxyl groups, but the addition does not greatly affect the rate of oxidation. The reacting mixtures absorb some oxygen, but this has but slight effect on the rate of disappearance of quinquevalent vanadium (Table 6).

TABLE 6. *Effect of addition of vinyl cyanide and of oxygen on the rate of reduction of vanadium*(V).

$[V^V] = 0{\cdot}05$N, [alcohol] = 0·104M.

$[H_2SO_4] = 5{\cdot}9$M, ionic strength = 6·0M.

Atmosphere	air	O_2	N_2
10^4k	1·10	1·08	1·19

$[HClO_4] = 3{\cdot}5$M, ionic strength = 3·6M.

[Vinyl cyanide] (M)	0	0·31
10^5k	2·7	2·8

Consecutive reactions occur after the initial attack. Adipic acid is eventually formed, in almost quantitative yield, with consumption of eight equivalents of vanadium(V). In contrast to cyclohexanone, which is rapidly oxidised, up to five days are needed to ensure the complete oxidation of cyclohexanol at 50° in 4·2M-sulphuric acid. This could indicate that a relatively resistant intermediate, such as cyclohexyl adipate,[3] may be formed. Under similar conditions diphenylmethanol was oxidised only to benzophenone; benzoic acid could not be detected.

Samples of 1-deuterocyclohexanol and cyclohexanol, prepared by the same method, have been oxidised under identical conditions in both perchloric and sulphuric acid solutions. Table 7 shows that there are kinetic isotope effects of moderate magnitude.

A red-brown solution is formed immediately on admixture of yellow acid solutions of

---

[3] Milas, *J. Amer. Chem. Soc.*, 1928, **50**, 493.

quinquevalent vanadium with all alcohols. With cyclohexanol and 1-deuterocyclohexanol this colour persists until it is obscured by the blue colour of the vanadium(IV) resulting from the oxidation of the alcohol. As this oxidation is very slow at room temperature it has been possible to investigate the relationship between the intensity of the reddish colour and the concentrations of acid, cyclohexanol, and quinquevalent vanadium (see Experimental), and to establish that the intensity of the colour is proportional to the product $[H_3O^+][V^V][\text{alcohol}]$. The colour is dependent on ionic strength; use of the deutero-alcohol makes no difference to its intensity.

TABLE 7. *Isotope effects on the oxidation of cyclohexanol by vanadium*(V).

$[V^V] = 0{\cdot}05$, ionic strength $= 6$M, (*a*) $[H_2SO_4] = 5{\cdot}9$M, (*b*) $[HClO_4]_4 = 5{\cdot}59$M.

Isotope	[alcohol] (M)	10^4k	10^4k/[alcohol]	H/D rate ratio
(*a*) H	0·0857	0·932	10·88	4·5
D	0·0824	0·199	2·41	
(*b*) H	0·104	0·608	5·85	3·6
D	0·0824	0·133	1·61	

Cyclohexyl orthovanadate $(C_6H_{11}{\cdot}O)_3VO$, which is stable to distillation under diminished pressure,[4,5] was prepared by the method of Prandtl and Hess.[4] It is not catalytically decomposed to vanadium(IV) in toluene solution by addition of the bases water, ammonia, or pyridine, or by anhydrous hydrogen chloride or acetic and chloroacetic acid, but the Lewis acids aluminium trichloride and boron trifluoride do promote formation of vanadium(IV). However all these acids and bases catalyse the reduction of the vanadate ester by ketones and olefins. Although t-butyl alcohol is not oxidised by vanadium(V), these catalysed oxidations could also be effected by t-butyl orthovanadate. The reduction of trialkyl orthovanadates in contact with moist air reported by Prandtl and Hess,[4] and the slow decomposition of these esters to vanadium(IV) compounds in storage, have been found to be photochemical decompositions. Prandtl and Hess reported that the isopropyl and the isopentyl ester are photosensitive; the phenomenon seems to be quite general.

DISCUSSION

(1) *Nature of the Reactive Oxidants.*—In Part II [1] the oxidation of ketones by acid vanadium(V) was ascribed to the cation $V(OH)_3^{2+}$ in perchloric acid solutions, and to a sulphate complex in sulphuric solutions. The form of the acid-dependence of the oxidation rate of cyclohexanol in perchloric acid is identical with that observed for the oxidation of cyclohexanone, and so can be ascribed to the same ions (eqns. 1). The kinetic data on bisulphate-dependence (Table 4) indicate that the transition state formed during oxidation by the sulphuric acid complex contains both hydrogen and bisulphate ions; the marked colour of sulphuric acid solutions of vanadium(V) indicates that this extra bisulphate ion is present in the red vanadium(V) species. The additional reactions (2) and (3) must therefore be occurring. Bobtelsky and Glasner [6] found that the oxidation of ethanol depended on the concentration of alcohol and of vanadium(V), but they did not explain the acid-dependence that they observed.

$$VO_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+}$$

$$ROH + V(OH)_3^{2+} \underset{\text{fast}}{\rightleftharpoons} [\text{complex}]^{2+} \underset{\text{slow}}{\longrightarrow} \text{products} \qquad \ldots\ldots \quad (1)$$

$$V(OH)_3^{2+} + HSO_4^- \underset{\text{fast}}{\rightleftharpoons} \{V(OH)_3HSO_4\}^+ \qquad \ldots\ldots\ldots \quad (2)$$

$$\{V(OH)_3HSO_4\}^+ + ROH \underset{\text{fast}}{\rightleftharpoons} [\text{complex}] \underset{\text{slow}}{\longrightarrow} \text{products} \qquad \ldots\ldots \quad (3)$$

---

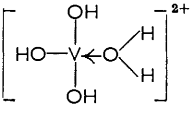
[4] Prandtl and Hess, *Z. anorg. Chem.*, 1913, **82**, 103.

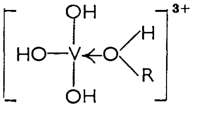
[5] Funk, Weiss, and Zeising, *Z. anorg. Chem.*, 1958, **296**, 36.

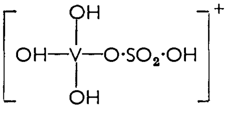
[6] Bobtelsky and Glasner, *J. Amer. Chem. Soc.*, 1942, **64**, 1462.

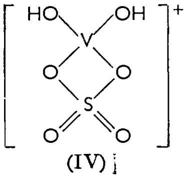
Our spectrophotometric measurements in perchloric acid confirm the existence of a relatively stable alcohol complex, and indicate that it has the composition $\{ROH,V(OH)_3\}^{2+}$. A similar intensification of colour occurs immediately on mixing alcohols with sulphuric solutions of vanadium(v), so the bisulphate complex $\{ROH,V(OH)_3,HSO_4\}^+$ must also be formed rapidly. Similar complex formation was shown by Ardon to occur between cerium(IV) and alcohols.[7]

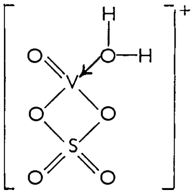
If these complexes are co-ordination compounds, in which vanadium(v) is tetrahedrally co-ordinated as in $VOCl_3$,[8] VO_4^{3-},[9] VO_3^-,[10] V_2O_5,[11] and orthoesters $(RO)_3VO$, then the yellow doubly charged cation of vanadium(v) may be (I) (a hydrated entity), the alcohol complex in perchloric acid (II), the bisulphate complex (III), (IV), or (V), and the bisulphate–alcohol complex (VI) or (VII).

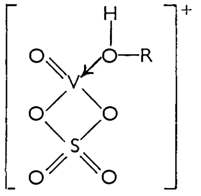

(I)

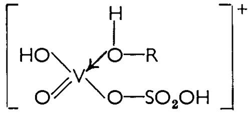

(II)

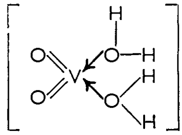

(III)


(IV)


(V)


(VI)


(VII)


(VIII)

The immediate formation of the alcohol complexes suggests that a direct substitution of a co-ordinated R–OH for a co-ordinated H–OH may occur, possibly with inversion about the vanadium centre, rather than a displacement by RO of an OH. Again V–O–R bonds are very easily hydrolysed, and so under these aqueous conditions an ester is not likely to remain formed. The simple substitution of $-O{\cdot}SO_2{\cdot}OH$ for $-OH$ (III) would not be expected to produce the marked difference in colour between perchlorate and sulphuric solutions of vanadium(v); formulæ in which the sulphate group is a chelating ligand [(IV) and (V)] can explain this difference. Chelating sulphate groups are present in the ceric complexes $(CeSO_4)^{2+}$, $Ce(SO_4)_2$, and $\{Ce(SO_4)_3\}^{2-}$.[12] The structure (V) is to be preferred to (IV) since it more easily indicates the ease of replacement of H_2O by ROH. Similarly the ion VO_2^+, which is probably not linear,[13] may be weakly hydrated as in (VIII), which is of the type of (V) and (VI).

Further evidence for the existence of the ion $V{:}O(OH_2)SO_4^+$ comes from the work of Lanford and Kiehl,[14] who isolated the solid $V_2O_5,4SO_3,4H_2O$ from 18M-sulphuric acid. Ramsey, Colichman, and Pack[15] interpreted this compound as $\{V(OH)_2^{3+}\}_2(SO_4^{2-})_3,H_3O^+,HSO_4^-$ but it could be equally well written as $\{VO{\cdot}OH_2{\cdot}SO_4\}^+HSO_4^-,\frac{1}{2}H_2O$, *i.e.*, a salt of structure (V). It does not contain sufficient water to be a derivative of the non-chelated ion (III). Rates of oxidations involving active ions such as $V(OH)_2^{3+}$ or VO^{3+} would have depended on $[C_{H_3O^+}]^2$ and not on $[C_{H_3O^+}][HSO_4^-]$. The lack of any departure from first-order dependence on $C_{H_3O^+}$ in either

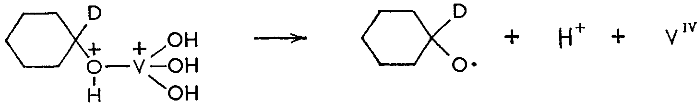
[7] Ardon, *J.*, 1957, 1811.
[8] Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.
[9] Mulligan and Vernon, *J. Phys. Chem.*, 1952, **56**, 145.
[10] Wells, " Structural Inorganic Chemistry," 2nd edn., Oxford Univ. Press, 1950, p. 499.
[11] Keletaar, *Z. Krist.*, 1939, **95**, 9; Byström, Wilhelmi, and Brotzen, *Acta Chem. Scand.*, 1950, **4**, 1119.
[12] Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 828.
[13] LaSalle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.
[14] Lanford and Kiehl, *J. Amer. Chem. Soc.*, 1940, **62**, 895.
[15] Ramsey, Colichman, and Pack, *J. Amer. Chem. Soc.*, 1946, **68**, 1695.

sulphuric or perchloric acid solutions shows that at no time were the complex-forming equilibria (1,2,3) displaced sufficiently to the right to invalidate the assumption that $[VO_2^+] \equiv$ [Total of all species of V^V].

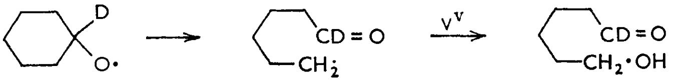
(2) *Mechanism of Oxidation of Primary and Secondary Alcohols.*—The catalysis of the polymerisation of vinyl cyanide shows that organic free radicals are formed during the oxidation of alcohols. Whilst some of these may be formed in the oxidation of subsequently formed ketones or aldehydes, isolated dry polymers from cyclohexanol had an absorption band at 3400 cm.$^{-1}$ which indicated that they contain hydroxyl groups. Since the polymers from cyclohexanone do not exhibit this absorption it can be inferred that hydroxyl-containing radicals are formed in the initial steps of the alcohol oxidation. The relative resistance to oxidation of alcohols compared with ketones [2] is consistent with the behaviour of other one-electron oxidisers.[16]

The isotope effect observed indicates that the C–H or C–D bond of the carbinol group is involved in the rate-determining step of the oxidation. If oxidation proceeds by O–V bond fission to leave an alkoxy-radical and vanadium(IV), then the C–D bond would not be involved (eqn. 4). Fission and oxidation (eqn. 5) would then be expected to follow.[17] This mechanism would not explain the resistance of t-butyl alcohol to oxidation or the absence of any benzoic acid among the products of oxidation of diphenylmethanol.

(IX)

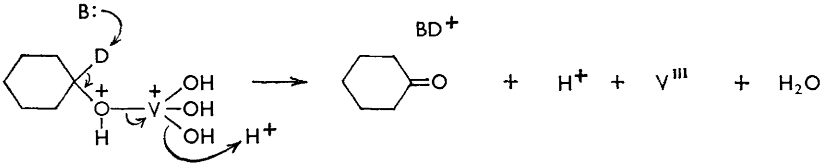


(4)

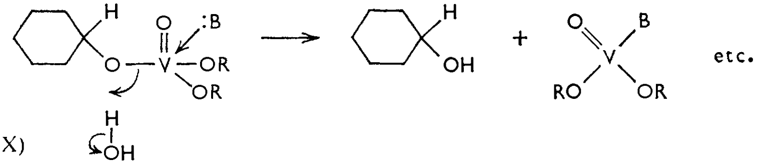


(5)

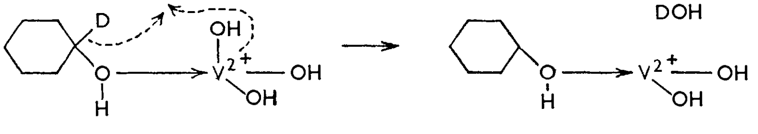
An acid–base catalysed two-electron redistribution (6) such as that proposed by Westheimer [18] for the oxidation of alcohols by chromium(VI) would account for the isotope effect but is not consistent with resistance of the orthovanadate esters to acid–base-catalysed reduction, or the formation of $R_2C{\cdot}OH$ radicals. The hydrolysis of orthovanadate esters can be represented as in (7), in which electron movement is of a different type from that in (6).



(IX) . . (6)



(X) . . . (7)



(IX) (8)

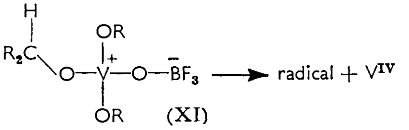
---

[16] Waters, *Quart. Rev.*, 1958, **12**, 277.

[17] Hawkins, *J.*, 1950, 2801.

[18] Westheimer, *Chem. Rev.*, 1949, **45**, 419.

A mechanism which fits all the evidence is a cyclic one-electron decomposition of the complex (8) in which bond formation between D from C–D and OH from V–OH participates in the rate-determining stage. The difference between the isotope effects in perchloric and sulphuric acid can be accounted for by the difference between the H, or D, abstracting species;[19] in one case $\{V(OH)_3\}^{2+}$ and in the other $(VOSO_4)^+$. This radical decomposition (8) of the complex (IX) would not be acid- or base-catalysed and the resistance of ortho-esters (X) may be due to the inability of the vanadium atom to acquire a sufficiently large positive charge to pull off the hydrogen atom in non-aqueous solution, except when co-ordinated (*e.g.*, XI) with an extremely strong electron-withdrawing group such as $AlCl_3$ or BF_3.



$$R_2CH{-}O{-}\overset{+}{V}(OR)_2{-}O{-}\overset{-}{B}F_3 \longrightarrow \text{radical} + V^{IV}$$

(XI) . . . . (9)

Either the bisulphate ligand is sufficiently strongly electron-withdrawing in comparison with the groups it replaces to overcome the effect of the reduced overall charge of the complex or the concentration of the bisulphate complex (VI) is larger than that of (II). The photochemical decomposition of orthovanadate esters (X) including t-butyl orthovanadate must proceed by a mechanism different from (8).

EXPERIMENTAL

Materials.—Vanadium(v) solutions were made up as described in Part II.

Cyclohexanol (commercial, 1% maximum ketone), after being washed with ferrous sulphate and water, was distilled under nitrogen over 2,4-dinitrophenylhydrazine up a short fractionating column. After removal of any water as the azeotrope, the alcohol was collected at 159·5°. After a further fractionation the alcohol showed no absorption at 1700 cm.$^{-1}$ (C=O bond).

1-*Deuterocyclohexanol.*—Lithium aluminium deuteride (0·80 g.) (Metal Hydrides Inc., 97·5%) and 5 ml. of pure (see Part II) cyclohexanone in dry ether were refluxed for ½ hr. Excess of deuteride was decomposed with wet ether, and dilute hydrochloric acid was added. The ethereal layer was separated and the aqueous layer extracted three times with further quantities of ether. The combined extracts were dried ($MgSO_4$). Under diminished pressure the ether was removed and the residue was distilled over quicklime into a receiver protected from moisture ($CaCl_2$ tube). A sample of the protio-compound, made in the same way from lithium aluminium hydride, was used in the comparative experiments. The rate of oxidation of this sample did not differ by more than 2% from the rate calculated from the experiments with the bulk cyclohexanol purified as described above. The spectra of the alcohols prepared by reduction of cyclohexanone showed no carbonyl absorption at 1700 cm.$^{-1}$. The deuterium compound had a moderately strong C–D absorption at 2100 cm.$^{-1}$, and its spectrum differed considerably from that of the protio-compound in the 750—1400 cm.$^{-1}$ region.

Kinetic measurements, polymerisations, and studies of oxygen uptake were carried out at 50·0° ± 0·2° as described in Part II.

Spectrophotometric measurements were carried out on a Hilger " Spekker " absorptiometer using " spectrum violet " gelatine filters (601) to isolate the wavelength region 3900 Å to 4700 Å, in which the alcohol complex absorbed more strongly than the other vanadium(v) ions present.

Solutions of the complex in perchloric acid were compared with the relevant solutions of vanadium(v) in perchloric acid. The absorption was found to be proportional to: (1) the concentration of alcohol (0·0—0·14M) at constant acidity (5·5M), ionic strength (5·8M), and $[V^V]$ (0·2N); (2) $[H_3O]^+$ (0—4·5M) at constant concentration of alcohol (0·104M) and vanadium(v) (0·05N), and at constant ionic strength (6·0M); (3) $[V^V]$ (0—0·15N) at constant ionic strength (3·6M), acidity, and alcohol concentration (0·104M) when balanced against corresponding solutions containing no alcohol. Also, when the acidity and ionic strength were increased together [as in (2), but ionic strength 1·2M—6M] the increase in absorption was greater than

[19] Swain, Stivers, Reuwer, and Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.

when acidity alone was increased. Replacement of cyclohexanol by 1-deuterocyclohexanol did not alter the absorption. The absorption of vanadium(v) in alcohol-free solutions did not alter with acidity.

Complete Oxidation of Cyclohexanol.—10 ml. of alcohol solution (0·415M) and 200 ml. of 0·2N-vanadium(v) solution in 4·4M-sulphuric acid were mixed and left at 50° for 5 days. Titration of the solution showed that each mole of cyclohexanol had reduced 7·97 equivalents of vanadium(v) (Calc. for $C_6H_{11}\cdot OH + 4O \longrightarrow (CH_2)_4(CO_2H)_2$: 8 equiv.). Ether-extraction yielded the expected quantity of adipic acid, m. p. and mixed m. p. 151°.

One of us (J. S. L.) thanks the Salters' Company for a Scholarship.

DYSON PERRINS LABORATORY, SOUTH PARKS ROAD, OXFORD. [*Received, May* 19*th*, 1959.]