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Kinetic Acidity Dependence in Certain Oxidation Reactions. Part II.¹ Oxidation of Propane-1,3- and Butane-1,4-Diols by Quinquevalent Vanadium Ion

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The oxidation of propane-1,3- and butane-1,4-diols by quinquevalent vanadium ion has been studied in the presence of sulphuric and perchloric acids. The reaction, which is acid-catalysed, depends on the activity of water for the entire range of acid concentration used. The tentative reactive vanadium(v) species is discussed, and the experimental evidence in support of an acyclic mechanism of oxidation has been put forward.

WATERS and LITTLER² observed that the correlation of the rate with the acidity in the oxidation of organic compounds by vanadium(v) could be used as a mechan-

istic tool to characterise the nature of the intermediate complex. The dependence of the oxidation rate on h_0 , the Hammett acidity function,³ is considered to indicate the formation of a chelate complex, and an acyclic complex is preferred if the rate depends on

¹ Part I, Raj Narain Mehrotra, *J. Chem. Soc. (B)*, 1968, 642.

² W. A. Waters and J. S. Littler, 'Oxidation in Organic Chemistry, ed. Kenneth B. Wiberg, Academic Press, New York, 1965, Part A, p. 185.

³ L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

$C(H_3O^+)$. These two correlations of the rate with acidity are known as Hammett relations.⁴

This study of the oxidation of primary glycols other than 1,2-glycols is intended to test the hypothesis of Waters and Littler² in the present reactions.

EXPERIMENTAL AND RESULTS

The reacting solutions were brought to the required temperature ($\pm 0.1^\circ$), before mixing. At suitable intervals 5 ml. of the mixture were withdrawn and quenched in 5 ml. of standard ferrous ammonium sulphate solution. The excess of the ferrous solution was titrated with a standard solution of vanadium(v), barium *NN*-diphenylsulphamate in the presence of phosphoric acid being used as indicator.

The reaction was followed under pseudo-first-order conditions, with the organic substrate in large excess. The first-order rate constant, k_1 , was calculated from the slope of the straight line obtained on plotting the logarithm of the titre changes against time. The reproducibility is better than 3%.

The results, obtained on varying the substrate concentration more than twelve-fold in 2M-sulphuric acid, are in Table 1. The plot of rate constants against respective substrate concentrations is a straight line passing through the origin, showing that no intermediate complex is formed and that the order with respect to the substrate concentration is unity.

TABLE 1

First-order dependence on substrate concentration in 2M-sulphuric acid at 50°

[Vanadium(v)] = 0.025M

[Propane-1,3-diol] (M)	0.13	0.25	0.5	0.75	1.0	1.4	1.8
$10^3 k_1$ (min. ⁻¹)	0.93	1.75	3.49	5.27	7.16	10.1	13.0
$10^3 k_1$ /[Substrate]	7.15	7.00	6.98	7.02	7.16	7.21	7.22

Average $10^3 k_1$ /[Propane-1,3-diol] = 7.11 ± 0.11 l. mole⁻¹ min.⁻¹.

[Butane-1,4-diol] (M)	0.14	0.25	0.50	0.75	1.0	1.4	1.8
$10^3 k_1$ (min. ⁻¹)	0.74	1.30	2.62	3.94	5.48	7.60	9.94
$10^3 k_1$ /[Substrate]	5.30	5.20	5.24	5.25	5.48	5.42	5.52

Average $10^3 k_1$ /[Butane-1,4-diol] = 5.34 ± 0.11 l. mole⁻¹ min.⁻¹.

Similar results are obtained when the substrate concentration is varied in the perchloric acid medium. The average value of $10^3 k_1$ /[Substrate] in 3M-perchloric acid is 5.34 ± 0.11 and 5.00 ± 0.15 l. mole⁻¹ min.⁻¹ respectively for propane-1,3- and butane-1,4-diols.

TABLE 2

Variation of the rate constant with concentration of n-propyl alcohol

[Vanadium(v)] = 0.017M; [sulphuric acid] = 2M; temp. = 50°

[n-Propyl alcohol] (M)	0.21	0.44	0.67	0.89	1.20	1.73
$10^3 k_1$ (min. ⁻¹)	0.64	1.31	2.08	2.94	3.91	5.34
$10^3 k_1$ /[n-Propyl alcohol]	3.05	3.00	3.10	3.30	3.26	3.09

Average $10^3 k_1$ /[n-Propyl alcohol] = 3.13 ± 0.1 l. mole⁻¹ min.⁻¹.

The effect of the acid concentration on the rate has been investigated in 2M—10M-sulphuric and 2M—8M-perchloric acids. The results (Table 3) indicate that for the same molar

concentration of the acid, the rate is faster in sulphuric than in perchloric acid.

TABLE 3

Effect of increasing acid concentration on the reaction rate at 50° *

[Vanadium(v)] = 0.025M; [propane-1,3-diol] = 0.25M									
[Acid] (M) ...	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
$10^3 k_1$ (min. ⁻¹)
(H ₂ SO ₄) ...	1.75	4.13	8.06	14.7	22.0	28.8	31.6	30.0	27.8
$10^3 k_1$ (min. ⁻¹)
(HClO ₄) ...	0.46	1.34	3.01	6.11	13.1	27.8	39.3	—	—
[Vanadium(v)] = 0.025M; [butane-1,4-diol] = 0.25M									
[Acid] (M) ...	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
$10^3 k_1$ (min. ⁻¹)
(H ₂ SO ₄) ...	1.30	3.24	7.13	13.5	21.5	31.6	42.4	57.5	73.3
$10^3 k_1$ (min. ⁻¹)
(HClO ₄) ...	0.45	1.22	2.41	5.27	12.0	29.3	46.0	—	—

TABLE 4

Effect of adding sodium perchlorate and sodium hydrogen sulphate on reaction rate at 50°

[Vanadium(v)] = 0.025M; [sulphuric acid] = 2M; [substrate] = 0.25M

[NaHSO ₄] (M)	0.0	2.5	2.0	1.5	1.0	0.5	0.0
[NaClO ₄] (M)	0.0	0.0	0.5	1.0	1.5	2.0	2.5
$10^3 k_1$ (min. ⁻¹) (Propane-1,3-diol)	1.75	5.67	5.17	4.68	4.40	4.17	3.84
$10^3 k_1$ (min. ⁻¹) (Butane-1,4-diol)	1.30	5.22	4.76	4.37	4.00	3.74	3.37

The addition of sodium perchlorate and sodium hydrogen sulphate enhances the rate. However, the increase in the rate is greater in the case of sodium hydrogen sulphate than of sodium perchlorate (Table 4).

The activation parameters for the reaction in sulphuric and perchloric acids, calculated by measuring the rate constants from 30° to 60°, are in Table 5.

TABLE 5

Activation parameters for n-propyl alcohol and propane-1,3- and butane-1,4-diols calculated for 30°

	2M-Sulphuric acid		2M-Perchloric acid	
	$\Delta H^\ddagger \pm 0.5$ (kcal./mole)	$\Delta S^\ddagger \pm 1.7$ (e.u.)	$\Delta H^\ddagger \pm 0.5$ (kcal./mole)	$\Delta S^\ddagger \pm 1.7$ (e.u.)
Propyl alcohol	22.5	-10.4	19.6	-21.2
Propane-1,3-diol	22.3	-9.7	26.3	0.0
Butane-1,4-diol	20.9	-14.4	23.4	-8.8

DISCUSSION

This investigation was aimed to test the empirical theory of Waters and Littler² to distinguish between a cyclic and an acyclic mechanism, for the oxidation of organic compounds by quinquivalent vanadium ion, by correlating the rate with the acidity.

* Footnote added by Professor W. A. Waters.—The criterion for diagnosis of mechanism put forward by Littler and Waters (refs. 2 and 9) should not be applied to data of Table 3 because these measurements have not been carried out in solutions of constant ionic strength. Table 4 shows the magnitude of the ionic strength effect in the weakest acid used (2M) and so in the 4M—8M range it is not surprising that the plots of $\log k_1$ against $\log [HClO_4]$ have slopes of about 4.

Bunnett's correlations (ref. 8) however are cogent for measurements made in solutions of different ionic strengths, when $\alpha(H_2O)$ varies. Consequently the author's conclusion must be judged with reference to Bunnett's theories.

⁴ L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, Publ. Co., New York, 1940, ch. IX.

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Though no kinetic evidence for the formation of a complex between vanadium(v) and the diols could be ascertained (see Table 1), yet an indication of the complex formation is provided by the change in the colour of vanadium(v) solution on the addition of these diols.

The rate of oxidation of these diols has been measured in deuterium oxide at 50° in 2M-sulphuric acid. The mean of two runs in D₂O has given a value of k_{D_2O} , the second-order rate constant, as 0.0108 and 0.0102 for

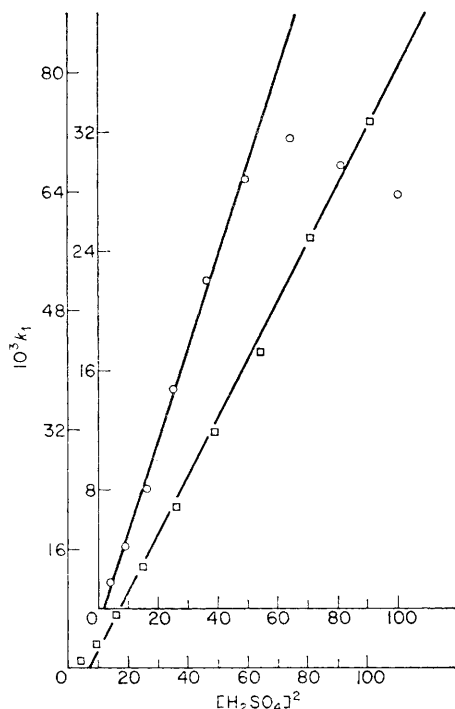


FIGURE 1 Dependence of rate on the square of the concentration of sulphuric acid. The inner scale is for propane-1,3-diol and the outer for butane-1,4-diol. The former shows a linear dependence from 2M- to 7M-H₂SO₄; the latter from 3M to 10M

○ Propane-1,3-diol
□ Butane-1,4-diol

propane-1,3- and butane-1,4-diols respectively. The ratio of $k_{D_2O} : k_{H_2O}$ is 1.5 and 1.9 for propane-1,3- and butane-1,4-diols respectively. This is certainly greater than the observed ratio of 1.3 in the oxidation of acetoin⁵ and much nearer to the solvent isotope effect ($k_{D_2O} : k_{H_2O} = 2-2.5$) expected for an acid-catalysed reaction.⁶

The plots of two Hammett relations which could be drawn with the data given in Table 3 do not give straight lines for the complete range of acid concentrations used. The slope of the straight-line component, when $\log k_1$ is plotted against $\log[HClO_4]$, is 3.8 and 4.2 for the propane-1,3- and butane-1,4-diols respectively. The corresponding slope in sulphuric acid is 2.2 and 2.4 respectively.

⁵ J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 1962, 1629.

⁶ P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 1962, 822.

⁷ M. A. Paul and F. A. Long, *Chem. Revs.*, 1957, 57, 1.

The slope of the straight-line component, when $\log k_1$ is plotted against $-H_0$, is 0.6 and 0.65 for propane-1,3- and butane-1,4-diols respectively in perchloric acid. Simi-

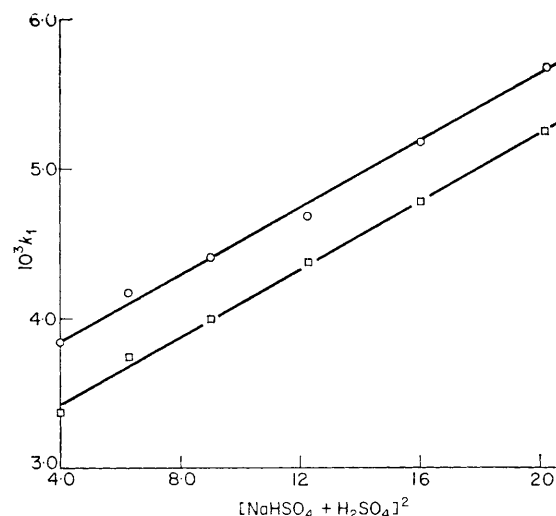


FIGURE 2 Linear dependence of rate on the square of total concentration of bisulphate ions, i.e., the total of H₂SO₄ + NaHSO₄ at any time

○ Propane-1,3-diol
□ Butane-1,4-diol

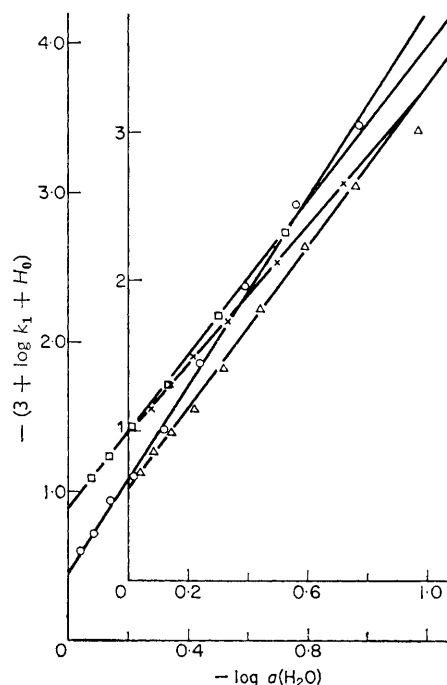


FIGURE 3 Linear dependence of $\log k_1 + H_0$ on $\log a(H_2O)$
Outer scale: propane-1,3-diol; ○ H₂SO₄, □ HClO₄
Inner scale: butane-1,4-diol; △ H₂SO₄, × HClO₄

larly the slopes of the straight line in sulphuric acid are 0.64 and 0.7. The slope in each case is significantly less than the ideal slope of unity in such plots. The value of $-H_0$, the Hammett acidity function,³ has been taken from Paul and Long's review.⁷

The slope of almost 2 when $\log k_1$ is plotted against \log [sulphuric acid] indicates that the order of the reaction with respect to sulphuric acid is 2. The plot of the rate constant against the square of sulphuric acid concentration (up to 7M in propane-1,3-diol and up to 10M in butane-1,4-diol) produces a straight line confirming that the order of the reaction with respect to sulphuric acid within this range is 2 (Figure 1).

The plot based on Bunnett's correlation of the rate with the activity of water is shown in Figure 3. The value of the activity of water in different concentrations of the respective acid is taken from the values reported by Bunnett.⁸ The value of Bunnett parameter, w , is 3.3 and 2.6 for propane-1,3- and butane-1,4-diol respectively in sulphuric acid. The corresponding values of w in perchloric acid are 2.7 and 2.3.

According to Bunnett's hypothesis, the w values, 2.6, 2.3, or 2.7, which are less than 3.0 indicate that a water molecule acts as nucleophile in the rate-determining step. The w value of 3.3 for propane-1,3-diol in sulphuric acid indicates that water molecule acts as a proton-abstracting agent (base) in the rate-controlling step. This different behaviour of the water molecule in the mechanism helps to explain the observed fall in the oxidation rate of propane-1,3-diol beyond 8M-sulphuric acid. It is not difficult to visualise that the proton transfer from the intermediate complex to the water molecule will gradually become difficult in the presence of increased concentration of sulphuric acid beyond a certain concentration. The rate is, therefore, expected to show a fall as observed.

Acyclic Mechanism.—Structurally each hydroxyl group in these diols is similar to the hydroxyl group in *n*-propyl alcohol. It is, therefore, expected that the rate of oxidation of these diols might be nearly twice the rate of oxidation of *n*-propyl alcohol. The observed ratio of $k_{\text{diol}} : k_{\text{n-propyl alcohol}}$ where k is the second-order rate constant, in 2M-sulphuric acid and at 50° for propane-1,3- and butane-1,4-diols is 2.2 and 1.7 respectively, which is rational. The smaller rate ratio obtained for butane 1,4-diol is understandable in view of the relative distance of the two hydroxyl groups in these diols.

The acyclic mechanism for the oxidation of these diols is indicated by the similar values of the activation parameters for these diols and that of *n*-propyl alcohol (Table 5) which being a primary alcohol should be oxidised by an acyclic mechanism.⁹

Other evidence for the acyclic mechanism for the oxidation of propane-1,3-diol is obtained from the analysis of the intermediate product, which has been characterised as 2-hydroxypropionaldehyde. The formation of this intermediate makes it clear that no cyclic chelate is formed and that the oxidation takes place at only one hydroxyl group.

⁸ J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

⁹ J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1959, 4046.

¹⁰ H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 1962, 4411.

¹¹ R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Canad. J. Chem.*, 1966, **44**, 1197.

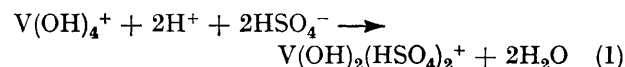
Reactive Vanadium(v) Species.—The nature of vanadium(v) compounds in 100% sulphuric acid and dilute oleum has attracted interest. Mishra and Symons¹⁰ excluded the formation of species such as $\text{V}(\text{OH})_4^+$ and VO_2^+ , but have suggested the formation of such species as $\text{VO}(\text{HSO}_4)_3$ and $\text{VO}(\text{OH})(\text{HSO}_4)_2$.

Gillespie, Kapoor, and Robinson¹¹ suggested the formation of $\text{VO}(\text{HSO}_4)_3$ or $\text{H}[\text{VO}(\text{HSO}_4)_4]$, the latter differing from the former only by a solvent molecule. However, there is no report on the nature of vanadium compounds in such concentrations of sulphuric acid as used in the present investigation.

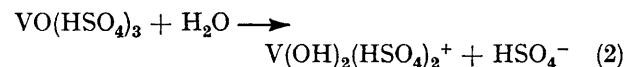
A tentative conclusion, however, could be adduced from our kinetic results. The vanadium(v) species such as VO_2^+ or $\text{V}(\text{OH})_4^+$, the latter having been considered as the correct representation of the former¹² in conformity with the tetrahedral structure of the vanadium compounds,¹³ could be excluded. The straight line, when rate is plotted against [sulphuric acid]² shown in Figure 1, cuts the sulphuric acid axis for zero rate. This indicates that the rate is zero even in the presence of smaller concentrations of sulphuric acid, the condition under which VO_2^+ or $\text{V}(\text{OH})_4^+$ are supposed to exist. It has been noted that there was hardly any change in vanadium(v) concentration worth measuring even after 6–8 hr. in the presence of *N*-sulphuric acid.

The linear dependence of the rate on the square of (1) sulphuric acid concentration and (2) bisulphate ion plus the concentration of sulphuric acid (Figure 2) kinetically indicates that the reactive vanadium(v) species should contain some sort of sulphate or bisulphate group.

The presence of $\text{V}(\text{OH})_2(\text{HSO}_4)_2^+$ as the reactive vanadium(v) species would be consistent with the assumption of reaction (1), which could be rationalised by



considering the hydrolysis of $\text{VO}(\text{HSO}_4)_3$, the species present in concentrated sulphuric acid,^{10,11} in dilute sulphuric acid medium as shown in reaction (2).



Although reaction (1) is consistent with the observed second-order dependence on sulphuric acid and bisulphate ion (Figures 1 and 2), yet it is based on the assumption that sulphuric acid dissociates to bisulphate ions only (or behaves as monobasic acid). Nevertheless, there is a strong evidence¹⁴ that sulphuric acid is significantly ionised to SO_4^{2-} in the lower range of concentration of sulphuric acid used here. (We thank a Referee

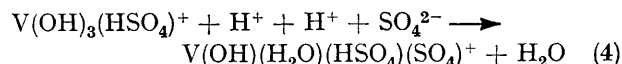
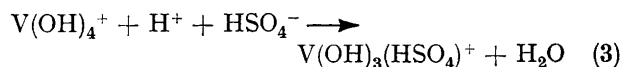
¹² C. D. Coryell and D. M. Yost, *J. Amer. Chem. Soc.*, 1933, **55**, 1909.

¹³ (a) W. O. Mulligan and L. W. Vernon, *J. Phys. Chem.*, 1952, **56**, 145; (b) K. J. Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.

¹⁴ R. H. Stokes and R. A. Robinson, 'Electrolyte Solutions,' Butterworths, 1959, p. 381.

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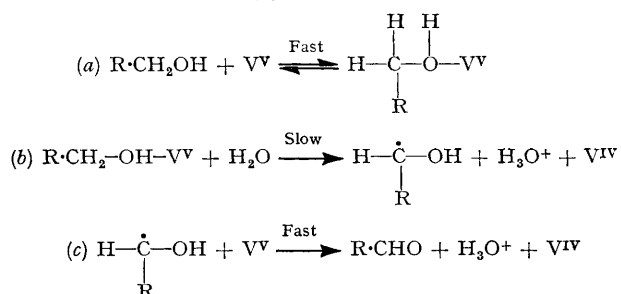
for this suggestion.) Reaction (1) could, therefore, be represented by (3) and (4).



These reactions, though consistent with the observed second-order dependence in sulphuric acid, give rise to a different reactive species of vanadium(v). It is difficult to distinguish between the two species $\text{V}(\text{OH})_2(\text{HSO}_4)_2^+$ and $\text{V}(\text{OH})(\text{H}_2\text{O})(\text{HSO}_4)(\text{SO}_4)^+$ present in the sulphuric acid solution because the maximum absorption of the complexes present in sulphuric acid occurs below 2000 Å.¹⁵ At best it could be concluded that the observed faster rate in sulphuric acid might be due to vanadium(v) complexes with sulphate species (as a Referee suggested), the nature of which is not yet completely known.

Mechanism.—The *w* values, 2·6 and 2·3 for butane-1,4-diol in sulphuric and perchloric acids respectively and 2·7 for propane-1,3-diol in perchloric acid, indicate that water molecule acts as a nucleophile in the rate-determining step. It is difficult to visualise the participation of the water molecule as a nucleophile in the strict Bunnett sense in such reactions. Lambert and Mason¹⁶ suggested the direct attack by the water molecule to overcome this difficulty. The similar course, to denote the water molecule behaving as nucleophile, is also sought here. The mechanism is, therefore, represented as in Scheme 1.

SCHEME 1

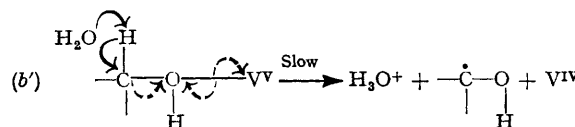


However, in the case of propane-1,3-diol in sulphuric acid, where water molecule acts as a proton-transfer agent (base) the mechanism could be represented by the step (b') (Scheme 2)

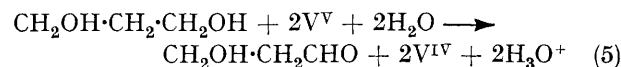
But in the case of propane-1,3-diol, where water acts as a proton transfer agent the step (b') would be as given as

in Scheme 2, to be followed by (c), where full arrows indicate 2-electron movements and dotted ones show single-electron movements, R and V^V are the Groups of the diol and the vanadium(v) reactive species respectively.

SCHEME 2



Stoichiometry and Oxidation Product.—Propane-1,3- and butane-1,4-diols consumed almost two equivalents of vanadium(v) in 1 week at room temperature (30°) in 2M-sulphuric acid. West and Skoog¹⁷ have reported that 10 eqvs. of vanadium(v) are used per mole of propane-1,3-diol in 9·9M-sulphuric acid during 1 hr. at 100°, and predicted the formation of 3 moles of formic acid per mole of the diol. The reaction could be represented as (5).



The oxidised solution after 1 week was treated with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone, washed and dried, had m.p. 150° (2,4-dinitrophenylhydrazone of 2-hydroxypropionaldehyde¹⁸). The oxidised mixture of butane-1,4-diol also gave a derivative, m.p. 90°, but m.p. of the corresponding hydroxyaldehyde is not known.

The oxidised solution of propane-1,3-diol after 3 months gave a positive test for formaldehyde with chromotropic acid.¹⁹

Materials.—Ammonium metavanadate was a Thomas Tyrer product. Propane-1,3-diol was a pure Fluka product, butane-1,4-diol was a gift from General Aniline and Film Corporation, U.S.A. AnalaR sulphuric acid was used. 70% Perchloric acid was a Riedel product. Other chemicals were AnalaR products. Deuterium oxide was supplied by the Bhabha Atomic Research Centre and is claimed to have deuterium content of 99·9%. The vanadium(v) solution in D₂O was prepared by using solid ammonium metavanadate and concentrated sulphuric acid.

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[8/063 Received, January 17th, 1968]

¹⁵ J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1959, 3014.

¹⁶ D. G. Lambert and J. G. Mason, *J. Amer. Chem. Soc.*, 1966, **88**, 1633, 1637.

¹⁷ D. M. West and D. A. Skoog, *Analyt. Chem.*, 1959, **31**, 583.

¹⁸ Ian Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds, Eyre and Spottiswoode, London, p. 817.

¹⁹ F. Feigl, 'Spot Tests in Organic Chemistry,' Elsevier Publishing Co., Amsterdam, 6th English edn., 1960, p. 349.