

The Mechanism of Oxidation of α -Glycols by Periodic Acid. Part VI.* Oxidation of Pinacol at pH 0—6

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The oxidation of pinacol by periodic acid has a second-order kinetic form in the region pH 0—6, with a rate maximum at pH 1. The variation of rate with pH is consistent with a mechanism involving the formation of a pinacol-periodate monoester which cyclises to a diester which decomposes to the reaction products. At pH > 2 the reactants and monoester are in equilibrium, but at pH < 2 the formation of the monoester becomes slow. A large kinetic salt effect observed in the range pH 2—4 is probably caused by the salt effect on the dissociation of periodic acid. The reaction rate in the region of the maximum is about 30% slower in D₂O than in H₂O. There is no appreciable deuterium isotope effect on the apparent first dissociation of periodic acid.

THERE is good evidence that the periodate oxidation of 1,2-diols involves the formation of a cyclic periodate ester of the diol which decomposes to the products.¹⁻³

* Part V, G. J. Buist, C. A. Bunton, and J. H. Miles, *J. Chem. Soc.*, 1959, 743.

¹ F. R. Duke, *J. Amer. Chem. Soc.*, 1947, **69**, 3054; F. R. Duke and V. C. Bulgrin, *ibid.*, 1954, **76**, 3803.

² G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1954, 1406; 1957, 4580; G. J. Buist, C. A. Bunton, and J. H. Miles, *ibid.*, 1957, 4567.

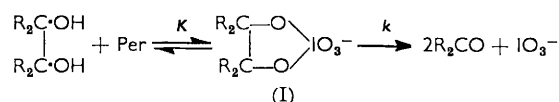
Periodic acid and its salts do not oxidise those 1,2-diols which cannot form cyclic esters^{4,5} suggesting that (I),

³ (a) G. J. Buist, C. A. Bunton, and J. H. Miles, *J. Chem. Soc.*, 1957, 4575; (b) C. A. Bunton, "Oxidation in Organic Chemistry," Part A, ed. K. B. Wiberg, Academic Press Inc., New York, 1965, ch. VI.

⁴ R. Criegee, *Sitzber. Ges. Befoerder. Ges. Naturw. Marburg*, 1934, **69**, 25 (*Chem. Abs.*, 1935, **29**, 6820).

⁵ S. J. Angyal and R. J. Young, *J. Amer. Chem. Soc.*, 1959, **81**, 5251, 5467; J. Honeyman and C. J. G. Shaw, *J. Chem. Soc.*, 1959, 2455; C. A. Bunton and M. D. Carr, *ibid.*, 1963, 770.

written here as the dehydrated form of the monoanion, is a key intermediate in the oxidation.



(Per is any species formed by ionisation or dehydration of periodic acid, H_5IO_6 .)

For the simple 1,2-diols, kinetic^{1,2} and spectroscopic³ evidence shows that the cyclic ester is formed rapidly and reversibly from the reactants, and decomposes slowly to the products. The kinetic form of the reaction is:

$$k_\psi' = kK[\text{G}]/(1 + K[\text{G}]) \quad (1)$$

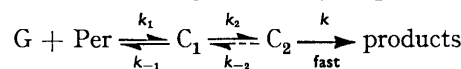
(where the diol, G, is in large excess over periodate, and k_ψ' is the observed first-order rate constant with respect to periodate). This rate equation predicts that the reaction will be of first order with respect to each reactant when the diol concentration is very low, and that the second-order rate constant k_ψ'' will be given by:^{1,2}

$$k_\psi'' = kK \quad (1a)$$

However, for many diols, *e.g.*, most cyclic or highly substituted 1,2-diols, the oxidation has a second-order kinetic form over a wide range of reagent concentration^{1,2,5-7} which could arise because $K[\text{G}] \ll 1$ in equation (1), but in many cases does not, because the overall variation of rate with pH cannot be explained in these terms. Therefore most workers have concluded that for these highly substituted diols the rate-limiting step is formation of the cyclic ester. It has been reported that the oxidation of some of these highly substituted diols is general acid-base catalysed.⁷ We show in the following paper that the oxidation of ethanediol is not general acid-base catalysed, but that the oxidation of pinacol is, and that this general catalysis follows the Brønsted catalysis law. There is no general catalysis on the decomposition of the cyclic intermediate to products, as shown by the oxidation of ethanediol, therefore the general catalysed step must be formation of the cyclic intermediate. In this Paper we discuss the oxidation of pinacol in unbuffered solutions of pH 0–6 only, and show that the variation of rate with pH can be explained by a chemically plausible mechanism in which formation of an ester intermediate is rate-limiting. In the following Paper we discuss the general acid-base catalysed reaction, the reaction in unbuffered alkaline solutions, and details of the mechanism.

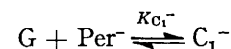
In the region pH 0–2, the rates are similar in sulphuric and perchloric acids, and are slower in deuterium oxide than in water. In general we have used perchloric acid as catalyst, in order to avoid the uncertainties which arise from the ionisation of sulphuric acid to hydrogen sulphate and sulphate ions, and the possibility of general

catalysis by these ions. For the purpose of the kinetic treatment we assume that pinacol and periodate can form reversibly an open-chain ester C_1 which can cyclise reversibly to C_2 , but that C_2 decomposes to products so rapidly that the rate of reaction is formation of C_2 , and therefore in the following scheme $k \gg k_{-2}$:



We could derive the same rate equations by assuming that C_1 decomposes irreversibly to products in a reaction involving a cyclic transition state. Because the oxidation is of first order with respect to both pinacol and periodate we assume that the concentrations of C_1 and C_2 are low, and that we can apply the stationary-state approximation.

The following symbols are employed: k_ψ' and k_ψ'' are the experimental first- and second-order rate constants; superscripts 0, –, and = denote the charge on the reactive species; and for the catalytic constants superscripts denote the active catalyst, *e.g.*, OH and W relate to the hydroxide ion- and the water-catalysed reactions, respectively. For the equilibrium constants involving complex formation the subscript C is always used, with the numeral 1 to indicate formation of the monoester, as in:



As in previous papers we use K without subscripts for the overall equilibrium constant between the reactants and the cyclic ester.^{2,3a} For the rate constant for decomposition of the cyclic ester to products, the symbol k will be used with a superscript as above when it is necessary to denote the charge (this differs slightly from the convention we used previously²).

The stationary-state approximation gives:

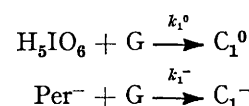
$$1/k_\psi'' = 1/k_1 + k_{-1}/k_1k_2 \quad (2)$$

$$= 1/k_1 + 1/k_2K_{\text{C}_1} \quad (3)$$

Equation 3 will be used for the analysis of reaction rates in unbuffered and buffered solutions. In the range pH 0–6.5 only undissociated molecules and monoanions need be considered. For convenience we write $K_{\text{C}_1} = k_1/k_{-1}$ in equation (3), but this does not imply that C_1 and the reactants are necessarily in equilibrium in all experimental conditions.

In order to analyse the effect of pH on reaction rate we must consider its effect on the three constants in equation (3).

k_1 . Both H_5IO_6 and its monoanions (IO_4^- and H_4IO_6^-) can react with the diol:



and $k_1[\overline{\text{Per}}] = k_1^0[\text{H}_5\text{IO}_6] + k_1^-[\text{Per}^-]$ where $\overline{\text{Per}}$ = total periodate).

⁷ P. Zuman, J. Sicher, J. Krupicka, and M. Svoboda, *Nature*, 1956, **178**, 1407.

⁶ C. C. Price and T. J. Kroll, *J. Amer. Chem. Soc.*, 1938, **60**, 2727; C. C. Price and M. J. Knell, *ibid.*, 1942, **64**, 552; V. C. Bulgrin and G. Dahlgren, *ibid.*, 1958, **80**, 3883; V. C. Bulgrin, *J. Phys. Chem.*, 1957, **61**, 702.

If \bar{K}_1 is the first dissociation constant of periodic acid expressed in terms of concentrations, then:

$$k_1 = \frac{k_1^0[H^+]/\bar{K}_1 + k_1^-}{1 + [H^+]/\bar{K}_1} \quad (4)$$

k_2 . In unbuffered solutions of pH < 6 we assume that cyclisation of the monoester occurs *via* a spontaneous or water-catalysed reaction, and that C_1^0 and C_1^- cyclise at different rates:

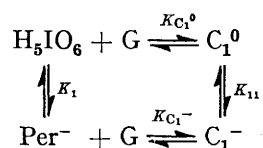
$$\text{then } k_2[\bar{C}_1] = (k_2^w)^0[C_1^0] + (k_2^w)^-[C_1^-] \quad (5)$$

(where \bar{C}_1 = total monoester).

For the acid dissociation of the monoester:

$$C_1^0 \xrightleftharpoons{K_{11}} C_1^- + H^+, \text{ hence:} \\ k_2 = \frac{(k_2^w)^0[H^+]/K_{11} + (k_2^w)^-}{1 + [H^+]/K_{11}} \quad (6)$$

K_{C1} . The equilibria involving reactants and C_1 are:



and therefore

$$K_{C1} = \frac{K_{C1}^-(1 + [H^+]/K_{11})}{1 + [H^+]/\bar{K}_1} \quad (7)$$

From equations (6) and (7):

$$1/k_2K_{C1} = \frac{1 + [H^+]/\bar{K}_1}{K_{C1}^-\{(k_2^w)^0[H^+]/K_{11} + (k_2^w)^-\}} \quad (8)$$

Because we cannot separate all the equilibrium and rate constants in equation (8), we combine some of them as follows:

$$(k^w)^0 = (k_2^w)^0K_{C1}^0 = (k_2^w)^0K_{C1}^-\bar{K}_1/K_{11}; \\ (k^w)^- = (k_2^w)^-K_{C1}^-;$$

and then:

$$1/k_2K_{C1} = \frac{1 + [H^+]/\bar{K}_1}{(k^w)^0[H^+]/\bar{K}_1 + (k^w)^-} \quad (9)$$

From equations (3), (4), and (9):

$$1/k_\psi'' = (1 + [H^+]/\bar{K}_1) \left\{ \frac{1}{k_1^0[H^+]/\bar{K}_1 + k_1^-} + \frac{1}{(k^w)^0[H^+]/\bar{K}_1 + (k^w)^-} \right\} \quad (10)$$

An alternative form of equation (10), more suitable for analysis of the kinetics at high hydrogen-ion concentrations, is:

$$1/k_\psi'' = (1 + \bar{K}_1/[H^+]) \left\{ \frac{1}{k_1^0 + k_1^-\bar{K}_1/[H^+]} + \frac{1}{(k^w)^0 + (k^w)^-\bar{K}_1/[H^+]} \right\} \quad (10a)$$

As we shall show, these equations fit the experimental results very well. The following procedure was used. For small $[H^+]$ equation (10) reduces to:

$$k_\psi'' = (k^w)^0[H^+]/\bar{K}_1 + (k^w)^- \quad (11)$$

and plotting k_ψ'' against $[H^+]$ gives first approximations to $(k^w)^0$ and $(k^w)^-$; the linear relationship is obeyed well up to $[H^+] = 10^{-3}M$, justifying neglect of k_1^- . For large $[H^+]$ we use equation (10a) to calculate first approximations to k_1^0 and k_1^- . The latter is used in the calculation of the final values of $(k^w)^0$ and $(k^w)^-$ from the results at low acid concentrations. Then it is possible to calculate the final values of k_1^0 and k_1^- , and to test the fit between theory and experiment.

In treating the results we use values of \bar{K}_1 , the apparent first dissociation constant of periodic acid, expressed in terms of concentrations. They were determined spectrophotometrically at various ionic strengths (see Experimental section). Two sets of values of the rate constant k_ψ'' were used to test equation (10). In the first (Table 1) the ionic strength is 0.2 or higher, and the range of acid concentration is 3×10^{-6} to 1.4M. In the second (Table 2) the effect of altering the ionic strength is shown for various acid concentrations below 0.1M.

Some details of the procedure used to fit equation (10) are as follows. First approximations to $(k^w)^0$ and $(k^w)^-$ were calculated using equation (11) and values of k_ψ'' from Table 1 with $[H^+] < 0.002M$, giving $(k^w)^0 = 0.527$ l. mole⁻¹ sec.⁻¹, and $(k^w)^- = 3.38 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹. The results for $[H^+] > 0.04M$ were used next, in equation (12), a rearrangement of (10a):

$$\frac{1}{k_1^0 + k_1^-\bar{K}_1/[H^+]} = \frac{1}{k_\psi''(1 + \bar{K}_1/[H^+])} - \frac{1}{(k^w)^0 + (k^w)^-\bar{K}_1/[H^+]} \quad (12)$$

From the experimental values of k_ψ'' and \bar{K}_1 , and the first approximations to $(k^w)^0$ and $(k^w)^-$, we calculated the term on the left-hand side of (12), and from its variation with $\bar{K}_1/[H^+]$ obtained $k_1^0 = 0.10$ l. mole⁻¹ sec.⁻¹ and $k_1^- = 2.8$ l. mole⁻¹ sec.⁻¹. The latter result enabled the contribution of k_1^- at the lower acidities to be allowed for, and hence the second approximations to $(k^w)^0$ and $(k^w)^-$ to be calculated. Equation (13) was used, this being a rearrangement of (10) with the omission of the k_1^0 term which is negligible at low acidities:

$$\frac{1}{(k^w)^0[H^+]/\bar{K}_1 + (k^w)^-} = \frac{1}{k_\psi''(1 + [H^+]/\bar{K}_1)} - \frac{1}{k_1^-} \quad (13)$$

The last six results of Table 1 were used, and the values $(k^w)^0 = 0.544$ l. mole⁻¹ sec.⁻¹ and $(k^w)^- = 3.36 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹ obtained for the ionic strength of 0.20. These values were used in equation (12) to obtain the second approximations to k_1^0 and k_1^- . The function $k_1^0 + k_1^-\bar{K}_1/[H^+]$ plotted against $\bar{K}_1/[H^+]$ gave a straight line from which we estimated $k_1^0 = 0.127$ l. mole⁻¹ sec.⁻¹ and $k_1^- = 2.53$ l. mole⁻¹ sec.⁻¹. Although

TABLE 1
Reactions in perchloric acid solutions at 25.3°, $I \geq 0.20$

[H ⁺] (M)	1.444	0.768	0.480	0.433	0.230	0.0971 *
k_{ψ}'' (obs.) (l. mole ⁻¹ sec. ⁻¹)	0.158	0.181	0.197	0.205	0.235	0.267
k_{ψ}'' (calc.) ,,	0.156	0.181	0.202	0.207	0.237	0.263
[H ⁺] (M)	0.0487 *	0.0210 *	0.0105 †	0.00417 †	0.00126 †	
k_{ψ}'' (obs.) (l. mole ⁻¹ sec. ⁻¹)	0.242	0.181	0.113	0.0545	0.0203	
k_{ψ}'' (calc.) ,,	0.243	0.174	0.113	0.0548	0.0203	
[H ⁺] (M)	$6.32 \times 10^{-4} \dagger$	$3.16 \times 10^{-4} \dagger$	$1.25 \times 10^{-4} \dagger$	$3.5 \times 10^{-6} \dagger \ddagger$		
k_{ψ}'' (obs.) (l. mole ⁻¹ sec. ⁻¹)	0.0122	0.00779	0.00507	0.00343		
k_{ψ}'' (calc.) ,,	0.0120	0.00773	0.00507	0.00340		

* NaClO₄ added to give $I = 0.200$. † KCl added to give $I = 0.200$. ‡ Equilibrium water, [H⁺] calculated from measured pH.

these values differ somewhat from the first approximations, they lead to third approximations to $(k^w)^0$ and $(k^w)^-$ which are identical with the second approximations. Hence the second approximations are taken as the final values:

$$\begin{aligned} k_1^0 &= 0.127 \quad \text{l. mole}^{-1} \text{ sec.}^{-1}, I = 0.2-1.4 \\ k_1^- &= 2.53 \quad \text{,, ,, ,, } I = 0.2-1.4 \\ (k^w)^0 &= 0.544 \quad \text{,, ,, ,, } I = 0.200 \\ (k^w)^- &= 3.36 \times 10^{-3} \quad \text{,, ,, ,, } I = 0.200 \end{aligned}$$

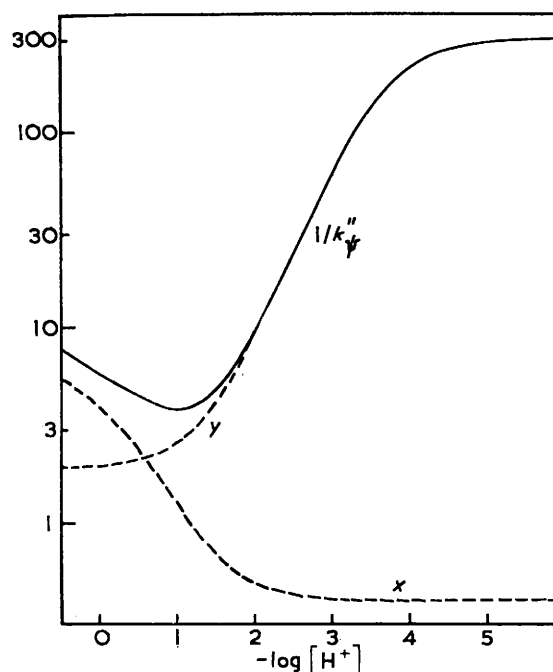
Table 1 lists values of k_{ψ}'' calculated from the above constants using equations (10) or (10a). Equation (10) contains two terms on the right-hand side, each multiplied by $(1 + [H^+]/\bar{K}_1)$. The first includes the rate constants for attack of H₅IO₆ and Per.⁻, respectively on pinacol, and the second includes the rate constants for spontaneous cyclisation of the monoester and its monoanion. In the Figure these two terms, multiplied by $(1 + [H^+]/\bar{K}_1)$, are plotted against [H⁺] on logarithmic scales to show their relative importance in determining $1/k_{\psi}''$.

Equation (10) fits the results accurately. The rate maximum at [H⁺] = 0.1M may be explained qualitatively as follows. According to our treatment the increase in rate with increasing acidity below 0.1M is due either to an increase in the total monoester concentration, or to the rate of cyclisation of undissociated monoester being greater than that of its monoanion (because the concentration of monoester is very low we cannot distinguish between these possibilities). At [H⁺] < 10⁻²M the monoester and the reactants are in equilibrium, but at higher acidities the formation of the monoester becomes partially rate-limiting. Because the major path of formation of the monoester is reaction between pinacol and a periodate monoanion (probably IO₄⁻) the reaction rate decreases as the monoanion is replaced by undissociated periodic acid. We discuss details of the mechanism in the following Paper.

Salt Effect, pH 1—6.—The salt effects on the rate constants k_1^0 , k_1^- , $(k^w)^0$, and $(k^w)^-$ are expected to be small because they all refer to reactions in which at least one of the reactants is uncharged. Therefore the theory predicts that the salt effect on the overall reaction is caused mainly by the effect on \bar{K}_1 , the classical first dissociation constant of periodic acid. Comparison of Tables 1 and 2 shows that at [H⁺] = 0.097M there is

no salt effect, whereas in the range 10⁻⁴ to 10⁻²M [H⁺] there is a marked *negative* effect, and at a higher pH, in equilibrium water, there is a small *positive* effect. The quantitative treatment of these effects is as follows.

The last three results of Table 2 extrapolated to zero [H⁺] using equation (13) give $(k^w)^- = 3.14 \times 10^{-3}$ l.



Dependence of reciprocal of second-order rate constant, and functions X and Y on hydrogen ion concentration

$$X = \frac{1 + [H^+]/\bar{K}_1}{k_1^0[H^+]/\bar{K}_1 + k_1^-}; \quad Y = \frac{1 + [H^+]/\bar{K}_1}{(k^w)^0[H^+]/\bar{K}_1 + (k^w)^-}$$

mole⁻¹ sec.⁻¹ at the mean ionic strength of 3×10^{-4} , compared with 3.36×10^{-3} at $I = 0.20$. This small salt effect is reasonable for a reaction involving an ion and a water molecule. The calculated values of k_{ψ}'' in Table 2 were obtained using equation (10), assuming the low ionic strength result for $(k^w)^-$ and the values obtained above for the other rate constants at $I \geq 0.2$. For each ionic strength we used the appropriate \bar{K}_1 value. The agreement between calculated and observed k_{ψ}'' is good, showing that there is little or no salt effect on $(k^w)^0$, the rate constant making the major contribution to k_{ψ}'' in the range 3×10^{-4} to 10⁻²M [H⁺].

Reaction in Sulphuric Acid and the Solvent Deuterium Isotope Effect.—Table 3 shows that the reaction rate in sulphuric acid is similar to that in perchloric acid, suggesting that catalysis by HSO_4^- or SO_4^{2+} is not important, but the hydrogen-ion concentration is uncertain in sulphuric acid solutions, so we have not analysed these results quantitatively. Table 3 also shows results for the rate in D_2SO_4 ; the kinetic solvent deuterium isotope

TABLE 2

Salt effect in perchloric acid solutions at 25.3° ; $[\text{H}^+] < 0.1\text{M}$

$10^3[\text{H}^+]$ (M)	97.1	10.50	1.261	1.261	0.632
$10^2 I$	58.8 *	1.06	2.58 †	0.497 †	0.072
$10^2 k_{\psi''}$ (obs.) (l. mole ⁻¹ sec. ⁻¹)	27.0	14.8	2.60	2.95	1.81
$10^2 k_{\psi''}$ (calc.) (l. mole ⁻¹ sec. ⁻¹)	26.1	15.1	2.69	3.07	1.87
$10^3[\text{H}^+]$ (M)	0.316	0.125	0.0035 ‡		
$10^2 I$	0.041	0.022	0.018		
$10^2 k_{\psi''}$ (obs.)	1.10	0.629	0.322		
$10^2 k_{\psi''}$ (calc.)	1.14	0.644	0.325		

* Ionic strength adjusted with NaClO_4 . † Ionic strength adjusted with KCl. ‡ Equilibrium water.

TABLE 3

Reaction rate in H_2SO_4 and D_2SO_4 solutions

$[\text{H}_2\text{SO}_4]$ (mole l. ⁻¹)	1.746	1.007	0.303	0.101	0.0303	0.0101
$k_{\psi''}$ (l. mole ⁻¹ sec. ⁻¹)	0.130	0.176	0.229	0.243	0.197	0.118
$[\text{D}_2\text{SO}_4]$ (mole l. ⁻¹)	1.75	0.395	0.0989	0.00946		
$k_{\psi''}$ (l. mole ⁻¹ sec. ⁻¹)	0.103	0.154	0.154	0.0722		
$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$	1.26	1.43	1.58	1.55		

effect is about 1.5 ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$) in the range 0.01–1.8M- D_2SO_4 . This is not due to an isotope effect on the first dissociation of periodic acid as measurements show this to be negligible (see Experimental Section). Because the reaction is complex, and there is uncertainty regarding the states of hydration of the periodate species in H_2O and D_2O , we cannot draw mechanistic conclusions from this relatively small isotope effect. However, it is reasonable to expect a small primary kinetic isotope effect for the attack of pinacol upon periodic acid to give the monoester, which will be opposed by an inverse isotope effect on the dehydration of H_4IO_6^- to IO_4^- .

EXPERIMENTAL

Materials.—Sodium metaperiodate, NaIO_4 , prepared in the usual way from the orthoperiodate,⁸ was recrystallised from slightly acidified water (0.02M-perchloric acid) to prevent precipitation of the orthoperiodate. Pinacol (B.D.H.) was dissolved in water, the solution extracted with carbon tetrachloride to remove impurities, and the hydrate recrystallised from water. Sodium perchlorate and potassium chloride (AnalaR) were recrystallised from water and dried at 130° . AnalaR perchloric and sulphuric acids were used.

Kinetics.—The reaction was followed titrimetrically² or spectrophotometrically. Since periodate absorbs strongly near 2200Å ,^{3,9} the spectrophotometric method is convenient and accurate. A Unicam S.P. 500 spectrophotometer was used with a jacketed 1 cm. silica cell maintained

⁸ E. L. Jackson, "Organic Reactions," ed. R. Adam, vol. II, Wiley, New York, 1944, ch. 8.

at 25.3° by circulating water. The reaction was started by adding a small amount of periodate solution to the other reactants, and optical density readings were taken for *ca.* two half-lives. The residual periodate was then decomposed by the addition of propane-1,2-diol in order to determine an infinity reading. A large excess of pinacol was used, and the first-order rate constants, $k_{\psi'}$, were calculated using the integrated form of the first-order rate equation or Guggenheim's modification of it.¹⁰ The second-order rate constants, $k_{\psi''}$, were calculated from the $k_{\psi'}$ values using pinacol concentrations at 50% reaction. Table 4 shows the agreement between observed and calculated optical densities. Variation of [pinacol] did not change

TABLE 4

No. 77 $[\text{HClO}_4] = 1.261 \times 10^{-3}\text{M}$; $I = 0.0101$ (KCl added); [pinacol] = 0.01490M ; [per.] = $9 \times 10^{-5}\text{M}$. Optical density, D , measured at 2220Å

Time (min.)	0	4	8	12	16
$D_t - D_\infty$ (obs.)...	0.683	0.610	0.558	0.501	0.455
$D_t - D_\infty$ (calc.)...	0.683	0.617	0.557	0.503	0.454
Time (min.)	20.5	24.5	28.0	32.5	36
$D_t - D_\infty$ (obs.)...	0.403	0.367	0.332	0.297	0.271
$D_t - D_\infty$ (calc.)...	0.404	0.365	0.334	0.298	0.272
Time (min.)	40	44.5	48.0	52.0	56.0
$D_t - D_\infty$ (obs.)...	0.243	0.219	0.199	0.181	0.161
$D_t - D_\infty$ (calc.)...	0.246	0.219	0.200	0.181	0.163

First order rate constant $k_{\psi'} = 4.26 \times 10^{-4}\text{ sec.}^{-1}$.

the values of $k_{\psi''}$. For the titrimetric method equal concentrations of pinacol and periodate were used, and the results from this method agreed well with those obtained spectrophotometrically.

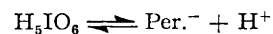
First Dissociation Constant of Periodic Acid.—The apparent classical first dissociation constant, \bar{K}_1 , was determined spectrophotometrically at 25.3° using the S.P. 500 spectrophotometer at wavelengths in the range 2150 – 2300Å . Three values of ionic strength were used, and in each case the optical density of periodate in various HClO_4 – NaClO_4 mixtures was determined. Values of \bar{K}_1 , calculated from the variation of optical density with $[\text{H}^+]$, are given in Table 5. Values of \bar{K}_1 for other ionic strengths

TABLE 5

Values of $10^2 \bar{K}_1$ for periodic acid

λ (Å)	$I = 0.0517$	$I = 0.294$	$I = 0.985$
2150	—	—	5.42
2180	3.01	—	—
2220	3.01	4.25	5.33
2260	2.98	4.25	—
2300	2.96	4.20	5.85
Mean	2.99	4.23	5.5

were obtained by interpolation or extrapolation of a graph of $\log \bar{K}_1$ against \sqrt{I} . The Davies equation¹¹ was used for the extrapolation down to zero ionic strength. Note that \bar{K}_1 is an apparent dissociation constant referring to the equilibrium



where Per.^- refers to all monoanions, irrespective of their state of hydration.^{9b}

⁹ (a) C. E. Crouthamel, H. V. Meek, D. S. Martin, and C. V. Banks, *J. Amer. Chem. Soc.*, 1949, **71**, 3031; (b) C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *ibid.*, 1951, **73**, 82.

¹⁰ E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

¹¹ C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

The apparent first dissociation constant was also measured by determining the pH with a glass electrode of a $\text{NaIO}_4/\text{HClO}_4$ mixture (ionic strength 0.12) both in H_2O and in D_2O . A Pye "Dynacap" pH meter with a calomel reference electrode and a ceramic plug liquid junction was used. For the determination in D_2O , a perchloric acid solution was prepared from 72% acid and 99.7% D_2O , and solid NaIO_4 was then added. The pD value was obtained by adding 0.40 to the meter reading.¹² Thermodynamic dissociation constants were determined using activity coefficients calculated from the Davies equation (for D_2O the value 0.515 was used for the Debye-Hückel constant¹³):

$$(\bar{K}_1)_\text{H} = 2.3 \times 10^{-2}; (\bar{K}_1)_\text{D} = 2.4 \times 10^{-2}$$

This results for $(\bar{K}_1)_\text{H}$ agrees exactly with that obtained by Crouthamel *et al.*,^{9a} but the extrapolation of our spectrophotometric results to $I = 0$ gives 2.0×10^{-2} . The discrepancy is probably due to the different ways in which the calculated activity coefficients enter the results, and to the assumptions inherent in the pH measurements.

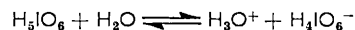
The value of $(\bar{K}_1)_\text{H}/(\bar{K}_1)_\text{D}$ is unity within experimental error, whereas a value of about two is generally found for acids as strong as periodic.¹⁴ The constant \bar{K}_1 includes dehydration as well as ionisation, and assuming the normal isotope effect on the ionisation step, our result indicates that K_H/K_D for the dehydration of H_4IO_6 to IO_4^- is less than unity, as predicted qualitatively by the treatment of solvent deuterium isotope effects due to Bunton and Shiner.¹⁵ The treatment cannot be applied quantitatively because

¹² P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Amer. Chem. Soc.*, 1964, **86**, 1; R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 1964, **68**, 3806.

¹³ R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 1964, **68**, 1186.

the state of hydration of the monoanion is uncertain. However we can make quantitative predictions for two limiting situations:

(i) No dehydration of the monoanion:



Calculation¹⁵ gives $K_\text{H}/K_\text{D} = 2.0$ (using pK values given in refs. 9b and 16).

(ii) Complete dehydration of the monoanion:



Calculation gives $K_\text{H}/K_\text{D} = 0.42$ (assuming that IO_4^- is such a weak base that it will not compete with water as a hydrogen-bonding acceptor). Therefore if the monoanion existed wholly as IO_4^- the calculated net solvent isotope effect would be $K_\text{H}/K_\text{D} = 2.0 \times 0.42 = 0.8$, which is in good, but probably fortuitous, agreement with experiment, because there is evidence that the monoanion is partially hydrated.^{9b}

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¹⁴ C. K. Rule and V. K. LaMer, *J. Amer. Chem. Soc.*, 1938, **60**, 1974; D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1939, 1366; K. Wiberg, *Chem. Rev.*, 1955, **55**, 713.

¹⁵ C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42.

¹⁶ H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 1962, 1194.