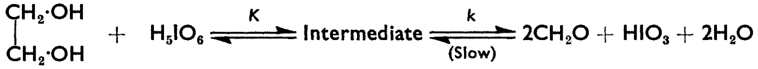
918. *The Mechanism of Oxidation of α-Glycols by Periodic Acid. Part II.* Propane-1 : 2-, 2-Methylpropane-1 : 2-, Butane-2 : 3- and 2-Methylbutane-2 : 3-diol.*

By G. J. Buist, C. A. Bunton, and J. H. Miles.

The kinetics of oxidation of propane-1 : 2-, 2-methylpropan-1 : 2-, (−)- and *meso*-butane-2 : 3-, and 2-methylbutane-2 : 3-diol by periodic acid, in water at 0°, have been followed over a wide pH range. An intermediate is formed from periodic acid and the glycol, and decomposes to the products. For a given glycol the variations of the equilibrium constant, *K*, for the formation of the intermediate, and the rate constant, *k*, for its decomposition to products, can be observed and understood.

The general effect of methyl-substitution in the α-glycol is to increase the rate constant, *k*. The effect on the equilibrium constant, *K*, is two-fold: electron-release increases the equilibrium constant, but steric effects may decrease it. The latter depend on the stereochemistry of the glycol, *e.g.*, there is a steric repulsion between one of the methyl groups and an oxygen atom in the intermediate formed between *meso*-butane-2 : 3-diol and periodic acid, but not in that from the (−)-isomer.

In Part I of this series * the oxidation of ethanediol by periodic acid was studied over a wide range of pH. We now describe an extension of this work to some methyl-substituted α-glycols. From the kinetic form for the oxidation of ethanediol (in large excess) Duke [1] showed that an intermediate was formed rapidly, and in high concentration, and that it slowly decomposed to the products, *viz.*:



$$\begin{matrix}CH_2\cdot OH\\ | \\ CH_2\cdot OH\end{matrix} + H_5IO_6 \overset{K}{\rightleftharpoons} \text{Intermediate} \underset{\text{(Slow)}}{\overset{k}{\rightleftharpoons}} 2CH_2O + HIO_3 + 2H_2O$$

This reaction sequence requires the kinetic law:

$$1/k' = 1/kK[G] + 1/k \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where *k'* is the first-order rate constant with respect to periodic acid, and [G] the glycol concentration. The oxidation of ethane- and other diols [2] was found to fit this kinetic form, and values of the constants *k* and *K* were determined. No effect of acidity on rate was considered, and for all the reactions in which the kinetic law (1) was obeyed it was assumed that the intermediate and the reactants were in equilibrium, *i.e.*, that the rates

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* Part I, *J.*, **1954**, 1406.

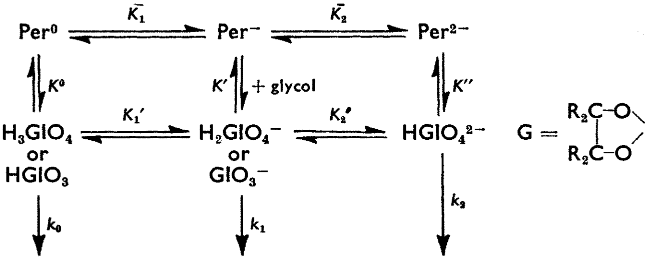
[1] Duke, *J. Amer. Chem. Soc.*, **1947**, **69**, 3054.

[2] Duke and Bulgrin, *ibid.*, **1954**, **76**, 3803.

of formation of the intermediate, and of decomposition to the reactants, were much faster than the rate of decomposition to the products. For certain of the reactions studied this assumption is incorrect, as is shown in our subsequent papers.

Any interpretation of the kinetic data must take into account the equilibrium between the various species of periodic acid,[3] and between the various intermediates formed by co-ordination of a glycol molecule with periodic acid or its ions (Part I).

The equilibrium and rate constants can be related, as shown in the annexed scheme,



where Per^0, Per^-, and Per^{2-} represent the totality of the various periodate species, for the charges represented.

In Part I it was shown that to a good approximation k_0 and k_2 could be neglected, *i.e.*, only the singly negatively charged intermediate decomposes to products. With this simplification the rate constant, k, takes the forms:

$$\text{pH} > 5,\ k = k_1/(1 + K_2' f_{i^-}/a_{H^+} f_{i^{2-}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\log K_2' + \text{pH} + \log f_{i^-}/f_{i^{2-}} = \log(k_1/k - 1) \quad . \quad . \quad . \quad . \quad (2a)$$

$$\text{pH} < 5,\ 1/k = 1/k_1 + f_{i^-} a_{H^+}/K_1' k_1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a_{H^+} is the hydrogen-ion activity determined with a glass electrode, and f_{i^z} are the activity coefficients of the z-charged ions. The assumptions involved in the deduction of these equations are discussed in Part I.

The equilibrium and apparent dissociation constants can be similarly related; *e.g.*, for solutions of pH <5:

$$K = \frac{\bar{K}_1(K' - K)}{f^- a_{H^+}} + \frac{K'\bar{K}_1}{K_1'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These relations were deduced from observations on the oxidation of ethanediol (Part I). They apply equally to the oxidations of propane-1 : 2-, 2-methylpropane-1 : 2-, and *meso*-butane-2 : 3-diol over the whole pH range, and to the oxidations of (—)-butane-2 : 3- and 2-methylbutane-2 : 3-diol over certain pH ranges,[4] and in this paper we restrict our attention to systems in which intermediate and reactants come into equilibrium. These relations do not apply to the oxidation of pinacol; this will be the subject of a later communication.

As an example of the results we show a plot of eqn. (2*a*) (Fig. 1). The slope should be, and is, independent of glycol structure, and close to unity. Values of the equilibrium constants are given in Table 1, and those of the rate constants for the breakdown of the single negatively charged intermediates in Table 2.

There are certain omissions from Table 1. These, which apply to the oxidations of (—)-butane-2 : 3- and 2-methylbutane-2 : 3-diol at pH 4—5, arise because the underlying assumption of equation 1, that both the conversion of the reactants into the intermediate and its breakdown to regenerate the reactants are much faster than decomposition to the products, is not always correct. If the reactants and intermediate are not in equilibrium the numerical values of K and k [equation (1)] may be incorrect. There are several methods

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[3] Crouthamel *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 3031; 1951, **73**, 82.

[4] Buist, Bunton, and Shiner, *Research*, 1953, **6**, 45.

by which this equilibrium requirement can be tested. It may be possible to verify by physical measurements, *e.g.*, electrochemical (Part I) or spectrophotometric (subsequent paper), that the formation of the intermediate is an equilibrium reaction. Further evidence can sometimes be obtained by a careful study of the kinetic form. In the oxidations of (—)-butane-2 : 3- and 2-methylbutane-2 : 3-diol at pH 4—5 an induction period can be observed: this corresponds to a slow build up of the intermediate. Here also equation (1) is not obeyed, *i.e.*, a plot of $1/k'$ against $1/[G]$ may not give a straight line. There are, however, cases where equilibrium is not maintained, but the above discrepancies are not observed.

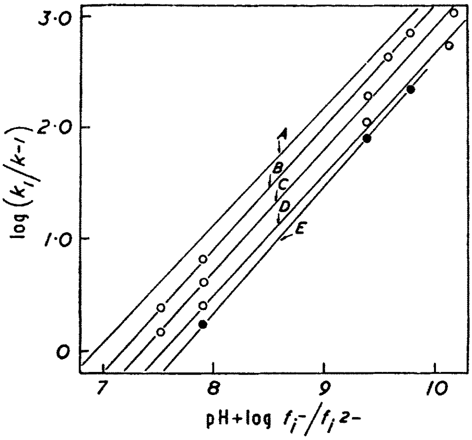

FIG. 1. *Relation between rate constant and* pH. *Diols*: *A, ethane-*; *B, propane-*1 : 2- *and* meso-*butane-*2 : 3-; *C,* (—)-*butane-*2 : 3-; *D,* 2-*methylpropane-*1 : 2-; *E,* 2-*methylbutane-*2 : 3-.

TABLE 1. *Equilibrium and dissociation constants* (*mole*$^{-1}$ *l.*) *of the intermediates.*

Diol	K^0	K'	K''	$10^2K_1'$	$10^7K_2'$
Ethane- [a]	10	189	1800	17·4	1·1
Propane-1 : 2-	39	500	2800	5·0	0·65
meso-Butane-2 : 3-	19 [b]	68 [b]	373	2·6	0·50
(—)-Butane-2 : 3-	270	—	8000	3·4	0·42
2-Methylpropane-1 : 2-	16	101	360	2·6	0·28
2-Methylbutane-2 : 3-	60	—	940	1·4	0·19

[a] Part I. [b] It is difficult to verify the equilibrium conditions here. The first and second dissociation constants of periodic acid are: by direct measurement, $3·6 \times 10^{-3}$ and $1·2 \times 10^{-8}$ respectively, and by analysis of the kinetic data, $4·0 \times 10^{-3}$ and $1·2 \times 10^{-8}$.

TABLE 2. *Rate constants for decomposition of single negatively charged intermediate.*

Diol	Ethane- *	Propane-1 : 2-	*meso*-Butane-2 : 3-	(—)-Butane-2 : 3-	2-Methyl-propane-1 : 2-	2-Methyl-butane-2 : 3-
10^4k_1 (sec.$^{-1}$) ...	45·7	120	182	302	607	244

* Part I.

A more sensitive test comes from rate studies in which the concentrations of reactants are sufficiently low for the concentration of the intermediate to become negligible in comparison with them. On these conditions the stationary-state approximation can be used and then for the reaction:

$$\text{Glycol} + \text{Periodate} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{Intermediate} \xrightarrow{k} \text{Products}$$

we can write:

$$v = k_s[G][Per] = kk_f[G][Per]/(k_b + k) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

i.e.,

$$k_s = k_f/(1 + k_b/k) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

where k_s is the limiting second-order rate constant, and k_f and k_b are second- and first-order rate constants for the forward and back reactions involved in formation of the intermediate. For equilibrium $k_b/k \gg 1$, and $K = k_f/k_b$, and so $k_s = kK$; *i.e.*, the reciprocal of k_s should equal the slope of the line obtained by plotting $1/k'$ against $1/[G]$ [equation (1)].[2] If equilibrium conditions are not maintained, *i.e.*, if k_b/k is not much greater than 1, then $1/k_s$ will be greater than the slope of the " reciprocal plot " (eqn. 1). The conditions in which this test can be applied are discussed in a subsequent paper.

If reactant and intermediate are in equilibrium, the limiting second-order rate constant is:

$$k_s = kK = \frac{k_1K'}{(f^-a_{H^+}/\bar{K}_1) + 1 + (f^-\bar{K}_2/f^{2-}a_{H^+})} \propto \frac{[\text{Per}^-]}{[\text{Per}]} \quad . \quad . \quad . \quad (6)$$

This equation is derived by multiplying equations (7) and (9) of Part I, and assuming that $k_1 \gg k_0$ and k_2. The variation of k_s with pH will therefore follow the relative concentration of the singly negatively charged periodate ions, and hence of IO_4^-, and be independent of the nature of the glycol; observation of this correlation can give no evidence for the mechanism of reaction between the glycol and periodic acid (cf. ref. 5). This relation between k_s and $[IO_4^-]$ will not necessarily be true if the reactants and intermediate are not in equilibrium.

Recently the periodate oxidations of several α-glycols have been followed by a polarographic method.[6] The reagent concentrations were so low that the kinetic form of equation (1) was not found, and a second-order rate law applied [equation (5*a*)]. Such an observation of itself gives no evidence about the mechanism of oxidation.

Summary of Kinetic Data.—It was arbitrarily assumed that the equilibrium conditions were satisfied when $k_b/k > 10$. This was so for the oxidations of propane-1 : 2-, 2-methylpropane-1 : 2-, and *meso*-butane-2 : 3-diol at all acidities examined (and for ethanediol; Part I). Equilibrium conditions were not satisfied for the oxidation of (—)-butane-2 : 3- and 2-methylbutane-2 : 3-diol in the region pH 4—5. Deviation from equilibrium is particularly marked for the latter compound. The equilibrium and rate constants of Tables 1 and 2 were calculated by the methods outlined in Part I. These constants, unlike those derived from equation (1), are independent of pH.

Discussion of Variations of Equilibrium and Rate Constants.—*Dissociation constants of the intermediates.* With increasing methyl-substitution K_1' and K_2' (the apparent first and second dissociation constants of the intermediate) decrease regularly. This could be due to inductive electron-release by the methyl groups. The effect of two methyl groups on the same carbon atom is greater than that of two methyl groups on different carbon atoms. As would be expected, the intermediates are stronger acids than periodic acid itself, the acid strength decreasing with increase in the number of methyl groups.

Equilibrium constants for formation of the intermediate. It is not easy to relate structural changes with K^0 and K' (the constants relating the reactants and the neutral and singly negatively charged intermediates respectively), because these two intermediates may exist in hydrated or dehydrated forms (Part I), as may periodic acid itself.[3] This difficulty does not arise if we restrict our attention to the doubly negatively charged intermediate, because this must exist in the hydrated form (this is probably, but not certainly also true of the neutral intermediate).

The equilibrium constants follow the sequence: ethane- < propane-1 : 2- < (—)-butane-2 : 3- > *meso*-butane-2 : 3- ≈ 2-methylpropane-1 : 2- < 2-methylbutane-2 : 3-diol. This requires the effect of methyl-substitution to be, at least, two-fold. We suggest that inductive electron-release by the methyl groups increases the stability of the intermediate (relatively to that of the reactants) by increasing the electron-availability at the oxygen bonds. There is also an obvious steric effect: this can be seen by comparing the

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[5] Taylor, *J. Amer. Chem. Soc.*, 1953, **75**, 3912.

[6] Zuman, Sicher, Kmpicka, and Svoboda, *Nature*, 1956, **178**, 1407.

values for 2-methylpropane-1 : 2- and butane-2 : 3-diol. Inspection of molecular models shows that there may be steric pressure between the methyl groups and one or more of the oxygen atoms in the intermediate. Molecular models of the hypothetical cyclic intermediate were constructed, using the dimensions of the Stuart models for carbon, oxygen, and hydrogen and the dimensions of ammonium trihydrogen paraperiodate, $(NH_4)_2H_3IO_6$, as determined by *X*-ray crystallography.[7] In this compound iodine is octahedral with iodine–oxygen distances of 1·93 Å.

It is improbable, from consideration of molecular geometry, that the five-membered ring of the presumed intermediate is planar. If the carbon–carbon distance and the carbon bond angles are assumed to be unchanged in the intermediate, such a planar ring would require the oxygen–oxygen distance to be smaller, and the oxygen–iodine–oxygen bond angle to be greater than in ammonium trihydrogen paraperiodate. It seemed probable therefore that the strain of such a ring would be reduced by puckering, as shown in Fig. 2, where the plane through the iodine and the carbon atoms of the ring is at right angles to the plane of the paper, the two carbon atoms are in the plane of the paper, and the iodine atom and the " glycol " oxygen atoms are above it. Two of the oxygen atoms attached to the octahedral iodine atom are omitted (for clarity); they lie towards the observer, in positions equivalent to *P* and *P'*. Methyl groups may occupy any of the four positions, *F* and *F'*, and *H* and *H'*. Examination of molecular models shows that the two equivalent positions *F* and *F'* (free positions) are not near to any of the oxygen atoms, but that there is some compression between the oxygen atoms and methyl groups in the equivalent positions, *H* and *H'* (hindered positions). If we consider methyl-substitution in the intermediate formed between ethanediol and periodic acid, we find that for both propane-1 : 2-, and (—)-butane-2 : 3-diol the methyl groups may be in free positions, *F* and *F'*. But 2-methylpropane-1 : 2-, *meso*-butane-2 : 3-, and 2-methylbutane-2 : 3-diol must have one methyl group in a hindered position, *H* or *H'*, with consequent compression, and a lowering of the equilibrium constant. Pinacol must have two methyl groups in hindered positions, and the equilibrium constants for formation of its intermediates would therefore be low.

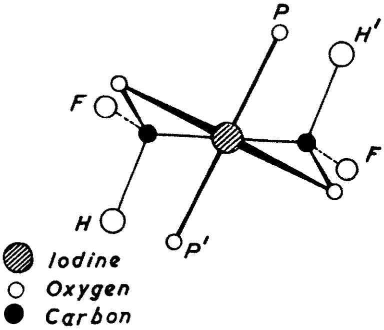

FIG. 2. *Model of the intermediate complex* (*two oxygen atoms omitted*).

Structures other than this cyclic form have been proposed for the intermediates between glycols and glycol-splitting reagents (see, for example, Criegee *et al.*[8]). In most of these only one of the hydroxyl-oxygen atoms is bonded directly to the iodine atom, the other being bonded through a hydrogen atom, to an oxygen atom of the oxidising agent or to some other entity. Such structures may well exist, particularly with reagents such as lead tetra-acetate which are used in non-aqueous solutions and are less specific in their reactivity than is periodic acid. However the five-membered cyclic intermediate seems to us to be the only formulation which will explain the effects of changes in the

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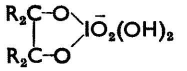
[7] Helmholtz, *J. Amer. Chem. Soc.*, 1937, **59**, 2036.

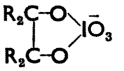
[8] Criegee, Höger, Huber, Kruck, Marktscheffel, and Schellenberger, *Annalen*, 1956, **599**, 81.

glycol structure on the formation and breakdown of the intermediate, and the fact that only the singly negatively charged intermediate decomposes to the products.

We can therefore analyse the experimental sequence for the equilibrium constant, K'', in terms of the two sequences. (*a*) Increasing polar effect, no hindered methyl groups: ethane- $<$ propane-1 : 2- $<$ (—)-butane-2 : 3-diol. (*b*) Increasing steric compressions: (—)-butane-2 : 3- $>$ *meso*-butane-2 : 3- $\approx$ 2-methylpropane-1 : 2-diol. 2-Methylbutane-2 : 3-diol, with three methyl groups, one in a hindered position, shows these opposing steric and polar effects. Comparison between K'' for *meso*- and (—)-butane-2 : 3-diol (Table 1) shows that a hindered methyl group in the intermediate reduces the equilibrium constant *ca.* 20-fold. Thus the expected value of K'' for pinacol would be much less than that of 2-methylbutane-2 : 3-diol, particularly because steric effects are intensified with increased overcrowding. It seems unlikely that this equilibrium constant can be determined experimentally for pinacol (cf. ref. 2).

Rate constant for decomposition of the intermediate to the products. The values of k_1 (Table 2) increase with increasing methyl-substitution in the glycol (except for *meso*-butane-2 : 3- and 2-methylbutane-2 : 3-diol). The rate of breakdown of the intermediate to the products should be assisted by hyperconjugation between the methyl groups and the partially formed carbonyl groups. This does not explain the different rates of breakdown of the intermediates formed from the three butanediols. If one carbon–oxygen double bond began to be formed before the other the faster decomposition of the intermediate of 2-methylpropane-2 : 3-diol than of the butane-2 : 3-diols would be explained, as in the first case two methyl groups would be hyperconjugated with the forming double bond. However, all such considerations are complicated by the possibility that the singly negatively charged intermediate may exist in hydrated (*a*) and dehydrated (*b*) forms:

(*a*) 

 (*b*)

It has been suggested that only the dehydrated form (*b*) decomposes to the products (Part I). If this is so, the rate of decomposition will depend on the relative amounts of these two forms, and this in turn, to an extent at present unknown, on the groups present.

The results described here are in complete agreement with the demonstration that only the singly negatively charged intermediate decomposes to the reaction products (Part I). On this hypothesis it is possible to calculate the equilibrium constants for formation of the intermediate, its acid dissociation constants, and its rate constant for decomposition, provided it is known, from experiment, that in any given reaction the reactant and intermediate are in equilibrium. Examples of the kinetic form of oxidations in which this equilibrium condition does not hold will be given in a subsequent paper.

EXPERIMENTAL

Materials.—Propane-1 : 2- and (—)-butane-2 : 3-diol were purified by vacuum-distillation of commercial samples. Propane-1 : 2-diol had n_D^{25} 1·4315; (—)-butane-2 : 3-diol had m. p. 19°, n_D^{25} 1·4310, 1·4312, $[\alpha]_D^{20}$ $-12·84°$, $-12·68°$.

meso-Butane-2 : 3-diol was isolated from a commercial sample of butane-2 : 3-diol by fractionation under reduced pressure and recrystallisation of the hydrate; after dehydration it had m. p. 33·6—34·4°, n_D^{25} 1·4371 (supercooled), and no optical activity.

2-Methylpropane-1 : 2- and 2-methylbutane-2 : 3-diol were prepared by the osmium tetroxide-catalysed oxidation of the corresponding olefin with *tert.*-butyl hydroperoxide.[9] 2-Methylpropane-1 : 2-diol had b. p. 84—85°/14 mm., n_D^{25} 1·4330. 2-Methylbutane-2 : 3-diol hydrate had m. p. 22·0—22·7° (unchanged by further recrystallisation). Dehydration gave the glycol with b. p. 84—85°/19 mm., n_D^{25} 1·4363. A sample of this glycol obtained in poor yield by oxidation of trimethylethylene with peracetic acid had physical properties identical with those given above, and was oxidised at the same rate as the other sample.

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[9] Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302.

The periodate and buffer solutions were prepared and used as described in Part I. Here, and subsequently, the concentration of glycol is that at half reaction, except for runs in which reactant concentrations are similar.

Rate Measurements.—Most reactions were followed by the general methods described in Part I. However, some oxidations were too fast for conventional sampling methods to be used. An automatic pipette, based on the well-known "self-filling" pipette, was therefore made. It was kept at a constant temperature by circulating ice-water through its jacket. It could be filled, and its contents expelled, by compressed air, and could deliver up to 11 samples per min. Faster runs with pH < 4 were quenched in alkali to stop the reaction rapidly, the pH was then adjusted to 8, with saturated aqueous sodium hydrogen carbonate, for analysis of periodate. In one case, that of (−)-butane-2 : 3-diol at pH 5, it was necessary to use a spectrophotometric method for following the first part of the run.

First-order rate constants were calculated graphically, from the usual integrated form. Second-order rate constants were calculated graphically from the equation $k_2t(b - a) = 2{\cdot}3 \log\{a(b - x)/b(a - x)\}$, where a and b are the initial concentrations of the reactants, and x is the extent of reaction, in the same units. When a and b were of similar magnitude the second-order rate equation was used in its expanded approximate form. In one case [oxidation of (−)-butane 2 : 3-diol], the limiting second-order rate constant, k_s, could not be obtained with reactant concentrations sufficiently high for determination by titration; the concentration of periodate was therefore obtained spectrophotometrically.[3] All first-order rate constants are in sec.$^{-1}$, and all second-order are in sec.$^{-1}$ mole^{-1} l.

Summary of Kinetic Results.—No departure from equilibrium behaviour was found for the oxidations of propane-1 : 2-, 2-methylpropane-1 : 2-, and *meso*-butane-2 : 3-diol, but there were marked deviations from equilibrium in the region pH 4—5 for both (−)-butane-2 : 3- and 2-methylbutane-2 : 3-diol.

In general the value of the limiting second-order rate constant, k_s (equation 5*a*), was determined at pH 1 and *ca.* 5. This was done by progressively decreasing the reactant concentrations until a constant value of the second-order rate constant was reached. Observation of a straight line for a plot of $\log (b - x)/(a - x)$ against time is not a sensitive test for a second-order kinetic form (cf. ref. 2): it is in general impossible to determine kinetic order from the results of a single run.

Propane-1 : 2-*diol*. The evidence for equilibrium is: At pH 1·0, the limiting second-order rate constant $k_s = 0{\cdot}214$ (for 10^4[G] = 3·70M and 10^4[Per] = 5·99M, the value kK calculated from equation 1 = 0·234). At pH 5·4, 8·8, and 9·12 spectrophotometric measurements show that k_f and $k_b \gg k$.

pH	0·99	1·37	1·76	1·94	4·48	5·58	7·20	7·53	9·19	9·41
I *	0·130	0·054	0·148	0·01	0·021	0·055	0·087	0·129	0·130	0·102
10^4k	43·7	72·5	102	102	120	112	35·7	16·1	0·282	0·170
K	56	59	109	110	500	490	850	—	—	—

* Ionic strength in mole l.$^{-1}$.

2-*Methylpropane*-1 : 2-*diol*. The evidence for equilibrium is: pH 1·0, $k_s = 0{\cdot}280$ (the value of kK calculated from equation 1 is 0·302). At higher pH values spectrophotometric measurements show that k_f and $k_b \gg k$.

pH	0·99	1·37	5·44	7·53	9·04	9·78
I	0·130	0·054	0·104	0·129	0·100	0·100
10^4k	149	270	596	177	5·54	1·12
K	20·7	20·4	103	232	350	360

meso-*Butane*-2 : 3-*diol*. The evidence for equilibrium is: pH 1·4, $k_s = 0{\cdot}80$ sec.$^{-1}$ mole^{-1} l. (from equation 1, $kK = 0{\cdot}82$). At pH 4·48, $k_s = 1{\cdot}23$ and $kK = 1{\cdot}25$ (this is not a sensitive test because K is low). At pH 7·13, $k_s = 0{\cdot}943$, and $kK = 0{\cdot}833$.

pH	0·99	4·48	7·13	9·17
I	0·130	0·021	0·123	0·100
10^4k	44·0	182	70·9	0·568
K	18·6	68·2	118	373

(−)-*Butane* 2 : 3-*diol.* At pH 1·0, $k_s = 3{\cdot}2$ and $kK = 3{\cdot}2$. At pH > 9 spectrophotometric measurements (following paper) show that k_f and $k_b \gg k$, *i.e.*, at both high and low pH reactants and intermediate are in equilibrium. This is not so for reaction at pH 5·44. Here the initial part of the reaction was followed spectrophotometrically (Fig. 3). There is a slow build up of the intermediate, and k_b does not greatly exceed k. The value of $k_s = 26$, but the slope of the " reciprocal " plot (equation 1) = 5·9, *i.e.*, reactants and intermediate are not in equilibrium. The initial reactant concentrations of *ca.* 10^{-5}M were too low for chemical methods of analysis, and therefore spectrophotometric methods were used.

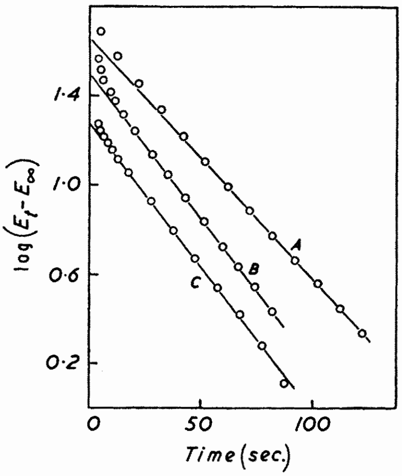

FIG. 3. *Oxidation of* (−)-*butane*-2 : 3-*diol at* pH 5·4.

A, [G] = 3 × 10^{-3}M. *B*, [G] = 10^{-2}M. *C*, [G] = 3 × 10^{-2}M.

pH	0·99	1·37	5·44	7·20	7·53	9·04	9·79
I	0·130	0·054	0·104	0·087	0·129	0·100	0·121
10^4k	94	151	300	126	61·5	1·58	0·282
K	370	320	*	*	—	*ca.* 10^5	*ca.* 8 × 10^4

* The " apparent " value of K, from the slope of the " reciprocal " plot (equation 1), is *ca.* 2000.

2-*Methylbutane*-2 : 3-*diol.* The kinetic form of the oxidation was not determined in detail over the whole pH range. At pH 1·0, $k_s = 0{\cdot}245$ and $kK = 0{\cdot}247$. At pH > 9, spectrophotometric measurements (following paper) showed that the reactants and intermediate are in equilibrium. Therefore equilibrium conditions are satisfied, at high and low values of pH. The results at pH 4·5 provided an excellent example of a periodic acid oxidation in which the reactants and intermediate are not in equilibrium. The breakdown of the intermediate to the products is in fact *ca.* 3 times as fast as to the reactants; this kinetic form will be discussed in detail in a subsequent paper.

pH	0·99	1·37	4·48	7·53	9·04	9·41
I	0·130	0·054	0·021	0·129	0·100	0·102
10^4k	38·9	64·8	244	91·2	3·04	*ca.* 1
K	67	78	(250 *)	(400 *)	940	—

* These are " apparent " values from the slope of the " reciprocal " plot.

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