920. *The Mechanism of Oxidation of α-Glycols by Periodic Acid. Part IV.* The Oxidation of 2-Methylbutane-2 : 3-diol at* pH 4·5.

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In the oxidation of 2-methylbutane-2 : 3-diol at pH 4·5 the cyclic intermediate is formed at a rate comparable with that of its breakdown to the products. The complex kinetic form of the oxidation can be analysed; the rates of formation of the intermediate from, and its decomposition to, the glycol and periodic acid, and the rate of decomposition to the products, are calculated.

In a kinetic study of the periodic acid oxidation of open-chain α-glycols it was found that the kinetic form could be interpreted by assuming that the reactants were in equilibrium with an intermediate, C[1a,b,2] (cf. Part III *). There were, however, certain exceptions, *e.g.*, the oxidation of pinacol,[1a,b,3] where no evidence could be found for the formation of an intermediate. Another deviation was in the oxidations of (—)-butane- and 2-methylbutane-2 : 3-diol, with glycol in excess,[4] where in the pH range 4—5 the first-order plots of log periodate *versus* time, instead of being linear, showed an initial downward curvature whose extent decreased with increasing glycol concentration (Fig. 1). This deviation from the usual simple first-order kinetics shows that there is an initial slow build-up of the intermediate. An increase in glycol concentration increases the rate of formation of the intermediate, and therefore decreases the extent of the induction period.

The kinetic form of this " non-equilibrium " system was investigated in detail for the oxidation of 2-methylbutane-2 : 3-diol at pH 4·5. A mathematical solution for reversible consecutive, first-order reactions is available.[5] Its use restricts our study to cases in which glycol is in large excess, and k_f[G] (where [G] is the concentration of glycol) is then the first-order rate constant for formation of the intermediate.

When the initial concentrations of the intermediate, C, and the products are zero, the solutions of the equation are:

$$[\mathrm{Per}]_t = \frac{[\mathrm{Per}]_0}{k(\phi_1 - \phi_2)}\left\{\phi_1(k - \phi_2)\exp(-\phi_2 t) - \phi_2(k - \phi_1)\exp(-\phi_1 t)\right\} \quad . \quad (1)$$

$$[\mathrm{C}]_t = \frac{[\mathrm{Per}]_0\phi_1\phi_2}{k(\phi_1 - \phi_2)}\left\{\exp(-\phi_2 t) - \exp(-\phi_1 t)\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

and

$$\overline{[\mathrm{Per}]}_t = [\mathrm{Per}]_0 - [\mathrm{Products}]_t = \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\frac{[\mathrm{Per}]_0}{\phi_1 - \phi_2}\left\{\phi_1\exp(-\phi_2 t) - \phi_2\exp(-\phi_1 t)\right\} \quad . \; . \; . \quad (3a)$$

where the quantities in square brackets are the concentrations at times $t = 0$ and t, and $\overline{[\mathrm{Per}]}$ = the stoicheiometric periodate concentration, *i.e.*, $\overline{[\mathrm{Per}]} = [\mathrm{Per}] + [\mathrm{C}]$. ϕ_1 and ϕ_2 are the positive and the negative roots respectively of a quadratic equation, *i.e.*,

$$\left.\begin{matrix}\phi_1\\ \phi_2\end{matrix}\right\} = \frac{k_f[\mathrm{G}] + k_b + k \pm \sqrt{\{(k_f[\mathrm{G}] + k_b + k)^2 - 4kk_f[\mathrm{G}]\}}}{2} \quad . \; . \quad (4)$$

Kinetic Analysis.—The rate constants k_f, k_b, and k were calculated from the experimental results by two independent methods. In the first they were calculated from the

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* Part III, preceding paper.

[1] Duke *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 3054; 1954, **76**, 3803; (*b*) Buist, Bunton, and Shiner, *Research*, 1953, **6**, 45; Buist and Bunton, *J.*, 1954, 1406.

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

[3] Price *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 2726; 1942, **64**, 552.

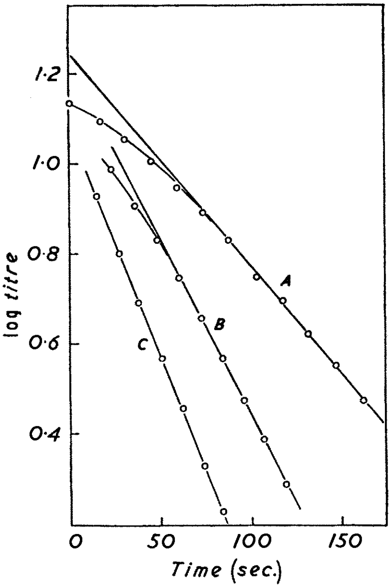
[4] Buist, Bunton, and Miles, *J.*, 1957, 4567.

[5] Rakowski, *Z. phys. Chem.*, 1907, **57**, 321.

values of ϕ_1 and ϕ_2, obtained from the curved first-order plot (Fig. 1). In the second, and more accurate, method they were evaluated from the variation of ϕ_2 with glycol concentration, and the limiting second-order rate constant, k_S.

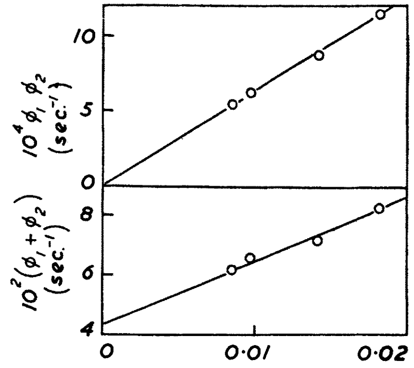
Method 1. The stoicheiometric concentration of periodate is given by the difference between the two exponential terms of equation 3*a*. The positive root ϕ_1 is greater than the negative root ϕ_2, and so the term $\phi_2 \exp(-\phi_1 t)$ decreases much more rapidly than does the term $\phi_1 \exp(-\phi_2 t)$, and soon becomes negligible. Hence the initial curvature of the "first-order plot" (Fig. 1) of log titre against time is due to the difference between these two exponential terms, but the later, linear portion is due to the term $\phi_1 \exp(-\phi_2 t)$ only.

FIG. 1. *Oxidation of 2-methylbutane-2 : 3-diol at* pH 4·5 *and* 0°.



A, [G] = 0·851 × 10^{-2}M; $\phi_2 = 106$. *B*, [G] = 1·82 × 10^{-2}M; $\phi_2 = 176$. *C*, [G] = 7·38 × 10^{-2}M; $\phi_2 = 228$. (ϕ_2 in 10^{-4} sec.$^{-1}$.)

FIG. 2. *Method* 1. *Determination of* k, k_f, *and* k_b *from the roots* ϕ_1 *and* ϕ_2.



Values of ϕ_2 can therefore be calculated from the linear slope of the curve: this linear portion can be extrapolated back to zero time, and the equation of this straight line is:

$$\log X_t = \log \{[\mathrm{Per}]_0/(\phi_1 - \phi_2)\}\phi_1 \exp(-\phi_2 t) \quad . \quad . \quad . \quad . \quad (5)$$

Then from equations 3 and 5, we have:

$$\log (X_t - \overline{[\mathrm{Per}]}_t) = \log \frac{[\mathrm{Per}]_0\phi_2}{\phi_1 - \phi_2} - \frac{\phi_1 t}{2{\cdot}3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The quantity $X_t - \overline{[\mathrm{Per}]}_t$ is given by the difference between the extrapolated straight portion of Fig. 1 and the experimental curve of log titre against time. Equation (6) requires that a plot of $\log (X_t - \overline{[\mathrm{Per}]}_t)$ should be linear with time. This linear relation is obeyed and the values of ϕ_1, calculated from the curved part of Fig. 1 by using equation (6), are given with values of ϕ_2, calculated from the straight portion of Fig. 1, in Table 1. (At the higher glycol concentrations, the initial curvatures are too small for ϕ_1 to be calculated.) The rate constants k_f, k_b, and k can be calculated from the relations for the roots of a quadratic:

$$\phi_1 + \phi_2 = k_f[\mathrm{G}] + k_b + k$$

and

$$\phi_1\phi_2 = k_f k[\mathrm{G}]$$

TABLE 1. *Analysis of the kinetics of oxidation. Method* 1.

$10^3[\text{Per}]_0$ (M)	0·76	0·69	0·68	0·98	0·64	0·68	0·94	1·03	0·94
$10^3[\text{G}]$ * (M)	8·51	9·47	9·64	10·47	14·10	18·20	29·8 [b]	53·5	73·8
$10^4\phi_1$ (sec.$^{-1}$)	490	—	540	500 [a]	560	650	—	—	—
$10^4\phi_2$ (sec.$^{-1}$)	106	115	115	122	156	176	202	222	228

* Concentration of glycol at half reaction.

[a] This run was stopped in acid potassium iodide with consequent loss of accuracy. [b] At this, and higher, glycol concentrations the curvature was insufficient for the evaluation of ϕ_1, as can be seen by examination of the plots of log titre against time (Fig. 1).

These are shown in Fig. 2, and the values so calculated are:

$$k_f = 2\cdot1 \text{ (sec.}^{-1}\text{ mole}^{-1}\text{ l.)},\ 10^4k_b = 140 \text{ (sec.}^{-1}),\ 10^4k = 300 \text{ (sec.}^{-1}).$$

This method of calculation has certain limitations. The accuracy of ϕ_1 is low, particularly for runs which are complete in less than 4 min., and the concentration range of the glycol is limited to 10—20 mmole l.$^{-1}$. It is assumed that the stoicheiometric concentration of periodate is determined by titration, *i.e.*, that the value determined equals the sum of [Per] + [C]. Any error in this assumption will affect the curved part of Fig. 1, and hence the value of ϕ_1 (but not of ϕ_2, provided that the error is proportional). In an attempt to show that the method of stopping the run had no effect, one experiment {that with $10^3[\text{G}] = 10\cdot47$ (mole^{-1} l.), Table 1} was made in which the aliquot portions were added to acid potassium iodide, instead of to the usual stopping solution of sodium hydrogen carbonate.[1b] In this acid solution both iodate and periodate ions react with iodide ions, liberating iodine, and the accuracy is therefore limited because the titrations represent small differences in a large quantity. However, with this experimental limitation we find that the method of stopping the reaction had no effect on the results, and our assumptions on the stoicheiometry of the titrations are probably correct.

FIG. 3. *Variation of root ϕ_2 with glycol concentration. (Slope of broken line = $1/k_s$.)*

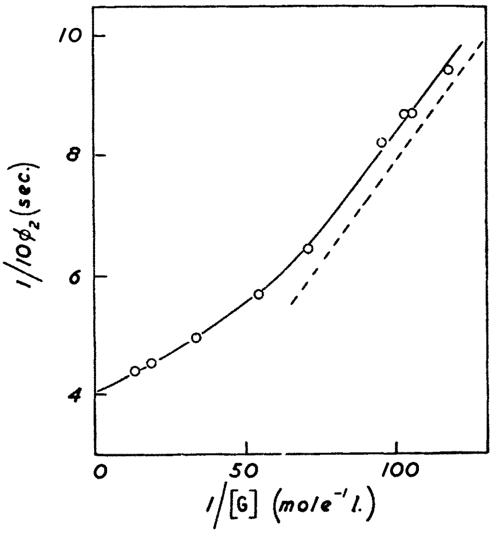
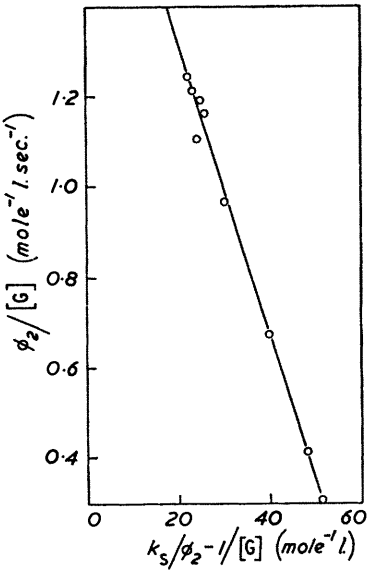


FIG. 4. *Method* 2. *Use of eqn.* 8.



Method 2. The variation of ϕ_2 with varying concentration of 2-methylbutane-2 : 3-diol, at pH 4·5 (Table 1), is shown in Fig. 3. This is analogous to the plots of $1/k'$ against $1/[\text{G}]$,[1a,b] and the marked curvature would be expected for a reaction in which the reactants and the cyclic intermediate are not in equilibrium. From equation (4) the negative root ϕ_2 fits the quadratic:

$$\phi_2^2 - \phi_2(k_f[\text{G}] + k_b + k) + kk_f[\text{G}] = 0 \quad . \quad . \quad . \quad . \quad (7)$$

and from the definition of the limiting second-order rate constant, $k_s = kk_f/(k_b + k)$ (derived from the stationary state hypothesis), equation (7) reduces to:

$$\phi_2/[G] = k_f - \{(k_b + k)(k_s/\phi_2 - 1/[G])\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

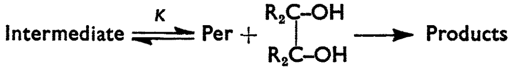
Thus a plot of $\phi_2/[G]$ against $(k_s/\phi_2 - 1/[G])$ (Fig. 4) should be linear, the slope being $-(k_b + k)$ and the intercept on the ordinate k_f, and on the abscissa $k_f(k_b + k)$. The limiting second-order rate constant k_s, and the root ϕ_2, can both be determined accurately in this system (cf. Experimental section) (and their values will not depend upon the method of stopping the reaction). We calculate the following values: $k_f = 1{\cdot}95$ (sec.$^{-1}$ mole^{-1} l.); $10^4k_b = 77$ (sec.$^{-1}$); $10^4k = 244$ (sec.$^{-1}$); and $K = k_f/k_b = 253$ (mole^{-1} l.).

These values are in fair agreement with those obtained by the simpler and less precise method 1, which depends upon analysis of the induction period of the reaction. Extrapolation of Fig. 3 to infinite glycol concentration gives a value of k, the rate constant for breakdown of the intermediate, of 247×10^{-4} (sec.$^{-1}$), in good agreement with the value obtained from the more rigorous treatment outlined above. (Such an extrapolation should give a reasonably accurate value for k even when the reactants and intermediate are not in equilibrium, although the apparent value of K will have no precise meaning.)

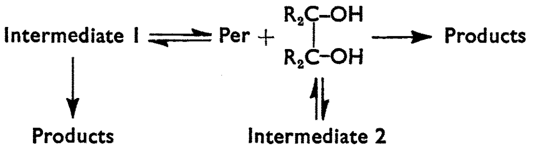
These methods for the determination of the rate constants for the formation and decomposition of the cyclic intermediate can only be used in certain special cases such as that described here. They supplement the spectrophotometric method (Part III), which itself can only be applied to systems in which the formation of the intermediate is not too fast to measure, but is much faster than its breakdown.

This analysis of the kinetic form enables us to distinguish between various possible mechanisms for periodate oxidations. For the oxidation of ethanediol, with glycol in large excess, Duke *et al.*[1a] observed that the reciprocal of the first-order rate constant varied linearly with the reciprocal of glycol concentration, and suggested that this proved postulated reaction through an intermediate where k_f and $k_b \gg k$, and $k_f/k_b = K$.

It was later pointed out that other mechanisms would satisfy this simple kinetic form,[2] *e.g.*:



or



Here the complex between glycol and periodate need not necessarily be an intermediate in the formation of the products. However, our analysis of the kinetics of oxidation of 2-methylbutane-2 : 3-diol, at pH 4·5, proves that the complex is a necessary intermediate, and that the original suggestion by Duke *et al.*[1a] is at least in some, and probably in all cases, correct.

APPENDIX

By using the general solution (eqns. 1, 2), we can analyse the conditions in which the kinetic form of the reaction can be used to show that the reactants and intermediate are, or are not, in equilibrium. The tests which can be used are summarised briefly as: (*a*) curvature of the plots of log [Per] *versus* time (Fig. 1), (*b*) curvature of the " reciprocal " plots,[1] and (*c*) a difference between the slope of the " reciprocal " plot and $1/k_s$. The conditions in which these tests can be used can be stated briefly as: (*a*) curvature will be observed only if ϕ_1 is not too large compared with ϕ_2; (*b*) and (*c*) if $k_f/k_b \gtrsim 20$ the " reciprocal " plot will be linear (except for a small part near to the intercept), with a slope $\approx 1/k_s$, even when reactants and the intermediate are not in equilibrium. If $k_f/k_b > 100$, non-attainment of equilibrium will be shown by test (*c*), although if k_f/k_b is large it may be difficult to follow the reaction in glycol concentrations low enough for the evaluation of k_s.[1a, b]

In general, lack of curvature of the plots of log [Per] *versus* time, or $1/k'$ *versus* $1/[G]$, cannot be taken as proof of attainment of equilibrium between reactants and the cyclic intermediate. Agreement between the slope of the " reciprocal " plot and $1/k_s$ (test *c*) is a much more useful criterion, but this can fail in certain cases, and the only rigorous and general methods are those physical methods (*e.g.*, spectral or pH changes) which give direct evidence about the rate of formation of the cyclic intermediate.

EXPERIMENTAL

The materials were prepared, and the reactions followed, by the procedures outlined in earlier papers. All reactions were followed in water, at 0°, at pH 4·5 and ionic strength = 0·021 mole^{-1} l.

The data on which the limiting second-order rate constant, k_s is evaluated are as in Table 2.

TABLE 2.

Initial concns. (10^{-4}M) [Per]	[G]	Second-order rate constant k'' (sec.$^{-1}$ mole^{-1} l.)
13·33	23·37	1·48
10·25	6·38	1·46
6·17	3·94	1·50
3·00	3·28	1·46

i.e., k_s = 1·48 (sec.$^{-1}$ mole^{-1} l.).

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