Part **919**. The Mechanism of Oxidation of α -Glycols by Periodic Acid. Spectroscopic Evidence for the Formation of an Intermediate. $III.^1$

By G. J. BUIST, C. A. BUNTON, and J. H. MILES.

The reversible formation of an intermediate between periodic acid and and α -glycol is, for most glycols, faster than the irreversible decomposition of this intermediate to the products. For suitable systems this formation can be followed spectrophotometrically. For a series of open-chain α -glycols in the pH range 8.5-11.5 the relative rates of formation are: ethane- > propane-1: 2-> 2-methylpropane- $1: 2- \approx$ meso-butane-2: 3-> (-)-butane-2: 3->2-methylbutane-2: 3-diol.

FROM a study of the kinetic form of the oxidation of some open-chain α -glycols it is possible to calculate both the equilibrium constant, K, for the formation of a cyclic intermediate and the first-order rate constant, k, for its breakdown to products. ^{1, 2a, b} This evidence can give no information on the mechanism by which the intermediate is formed from, and breaks down to, the glycol and periodic acid, because this simple kinetic treatment can be applied only if the intermediate is in equilibrium with the reactants. I.e., for the sequence:

$$\begin{array}{c} R_2C\text{-}OH + \text{Periodate} \xrightarrow{k_f} \text{Intermediate} \xrightarrow{k} \text{Products} \\ | & [Per] \\ R_2C\text{-}OH \\ [G] \end{array}$$

the rate of decomposition to products, k[C], must be much less than $k_{\rm f}[{\rm Per}][G]$ and $k_{\rm b}[C]$, and then $k_t/k_b = K$ (Part II). These conditions are not always fulfilled, and it is then sometimes possible to obtain values for $k_{\rm f}$ and $k_{\rm b}$ from the overall chemical kinetics. (This special case is discussed for the oxidation of 2-methylbutane-2: 3-diol at pH 4-5, in the succeeding paper.)

It was noticed that the pH change on mixing of periodic acid and an α -glycol was faster than the oxidation, but was not instantaneous.^{2b} This suggests that the formation of the intermediate is not instantaneous. It therefore seemed possible to follow this rapid formation of an intermediate by physical methods.

Addition of ethanediol to a periodate solution in the pH range 9-11, at 0°, gave a change in optical density, slow enough to be followed but much faster than the overall reaction. It was assumed that this initial change was due to the formation of the intermediate.

For a reaction with the glycol in excess the first-order rate constant for the interconversion of periodate into intermediate is:

$$k' = k_{\rm f}[{\rm G}] + k_{\rm b}$$

Kinetic runs on the formation of the intermediate were carried out with several glycols, at various pH values, examples being shown in Fig. 1. The plots of the logarithms of $(E_{\infty} - E_t)$ versus time t (where E_t and E_{∞} are the optical densities at times t and infinity) are straight lines. The slope of these straight lines give the values of k', and these when plotted against the glycol concentration give a straight line (Fig. 2). From such results we calculate values of k_t and k_b . It is necessary to show that these values have the significance which we attach to them. The intermediate and reactants are in equilibrium in all the conditions and with all the compounds studied by this spectrophotometric method. Therefore the ratio k_t/k_b , determined spectrophotometrically, should equal the equilibrium constant, K, determined by chemical kinetics (Part II). The agreement (Table 1) is reasonably good, within the rather large uncertainties of the observations.

Part II, preceding paper.
(a) Duke et al., J. Amer. Chem. Soc., 1947, 69, 3054; 1956, 76, 3803; (b) Buist, Bunton, and Shiner, Research, 1953, 6, 45; Buist and Bunton, J., 1954, 1406.

4576

TABLE 1. Comparison between k_t/k_b and the chemically determined equilibrium constant.

Diol	pН	k_t (sec. ⁻¹ mole ⁻¹ l.)	$10^{3}k_{b}$ (sec. ⁻¹)	k_t/k_b (mole ⁻¹ l.)	K * (mole ⁻¹ l.)
Ethane-1 : 2	10.6	14·7	930	1580	1800
2-Methylpropane-1 : 2	10.6	1·82	700	260	360
meso-Butane-2 : 3	9·25	28·9	91·2	317	373
2-Methylbutane-2 : 3	0·95	5·33	89·0	60	67

The spectrophotometrically determined values of k_b differ slightly from the calculated values given in Table 2. * Part II.

The intercepts of plots such as that shown in Fig. 2 give the values of k_b ; it is not easy to determine these accurately, partly because an extrapolation to zero glycol concentration is required, but also because in many cases $k_t[G] \gg k_b$, and so the intercepts are near the origin. The slopes of the lines can be determined much more accurately, and it

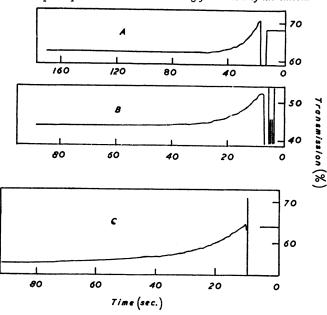


FIG. 1. Spectrophotometric traces showing formation of the intermediate.

A, Propane-1: 2-diol, pH 9·12, $[G] = 1.01 \times 10^{-8}M$. B, 2-Methylpropane-1: 2-diol, pH 10·62, $[G] = 5.11 \times 10^{-2}M$. C, Ethane-1: 2-diol, pH 10·62, $[G] = 3.72 \times 10^{-8}M$.

is therefore convenient, in most cases, to determine k_b indirectly from the known values of k_f and K'', where K'' is the equilibrium constant for formation of the doubly negatively charged intermediate from the doubly negatively charged periodate and the glycol. This is the appropriate equilibrium constant for the region pH > 9.0 where these doubly negatively charged species predominate (Parts I and II). The calculation does of course require that the reactants and intermediate be in equilibrium (Part II).

There are considerable limitations to the spectrophotometric method for obtaining the rates of formation of the intermediate. First, at many pH values the formation of the intermediate is too fast for the recording equipment of the spectrophotometer. Secondly, if the rate of decomposition of the intermediate to the products is comparable with its rate of formation, a steady infinity value will not be reached. Under these conditions k_t and k_b cannot be calculated without knowledge of the extinction coefficients of all the chemical species involved, and it was not possible to determine these. Thirdly, at certain

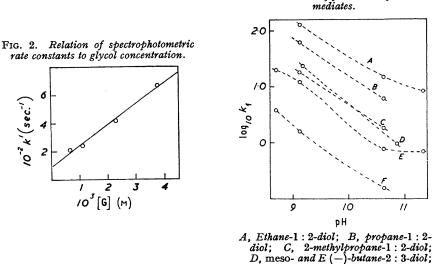
pH values and wavelengths, the extinction coefficients of the intermediate and periodate are such that the change in optical density on mixing the reagents is too small for useful measurement.

However, within these experimental limitations the method gives positive information on the formation of an intermediate, and shows the effects of pH and structural changes on the rates of formation of the intermediates, mostly in the pH range 9—11.

Increasing methyl-substitution decreases the rates of formation of the intermediate (Fig. 3 and Table 2). This effect is probably steric, because the inductive effect of the methyl groups should increase the electron-density on the oxygen atoms of the glycol, and hence their ability to attack the iodine atom. Tracer evidence on the periodate oxidation of pinacol shows that the oxygen atoms of the product come from the pinacol itself.^{2b}

FIG. 3.

Rates of formation of inter-



F. 2-methylbutane-2: 3-diol.

If, as seems probable, this is so for other glycols, the formation of the cyclic intermediate will be akin to esterification, in which the hydroxyl-oxygen atom will attack the iodine atom.

The rates of formation of the intermediates from *meso-* and (-)-butane-2: 3-diol are very similar (Fig. 3 and Table 2), although the equilibrium constants for the formation of these intermediates are very different, that for the *meso*-isomer being the lower (Part II). This difference in stability is presumably due to the steric hindrance in the fully formed

TABLE 2. Spectrophotometrically determined values of k_{t} , and calculated values of k_{b}

$(\lambda = ca. 2220 \text{ A}).$											
Diol		Eth	ane		Propan	e-1:2-	2	2-Methy	lpropa	ne-1 : 2	2-
рН	9.	1 10	0.6 1	1.3	9.1	10.6		9.	1 1	0.6	
\bar{k}_1 (sec. ⁻¹ mole ⁻¹ l.)	130			8.4	62	6.2		18.	-	1.82	
$10^{4}k_{\rm b} \; ({\rm sec.}^{-1})$	720	8	2 4	6	220	22		510	E	51	
K"		180	0	-	280	0			360		
Diol	(—)-Buta	ane-2:	3-	meso-But	ane-2:3-		2-Meth	ylbutaı	ne-2:3	-
pH				11.3	9.25	10.9	0.11	0.95	8.7	9.1	10· 6
\bar{k}_t (sec. ⁻¹ mole ⁻¹ l.)	20.5	12.0	0.78	0.69	28.9	0.91	4 ·8	$5 \cdot 3$	3 ·8	1.6	0.12
$10^{4}k_{\rm b}~({\rm sec.}^{-1})$	39	15	1.0	0.9	78	2.4			40	17	1.6
<i>K</i> "	\	80	ò0		3	73				940	

TABLE 3. Sequences of values of $k_{\rm b}$ and K'' with methyl-substitution.

Substitution with no hindering methyl groups:

Inc. K", dec. k_b : ethane- < propane-1: 2- < (-)-butane-2: 3-diol

Effect of hindering methyl groups:

Dec. K", inc. k_b : (-)-butane-2: 3- > meso-butane-2: 3- > 2-methylpropane-1: 2-diol

cyclic intermediate, but as there is no kinetic steric effect on the formation of the intermediate we must assume that the slow step of this formation is the attack of the first oxygen atom of the glycol on the iodine atom of the periodate. In partial confirmation of this, examination of molecular models suggests that there will be no difference between the steric effects of the methyl groups, for the two isomers, on this attack of the first oxygen atom. We therefore assume that in the formation of the cyclic intermediate the slow step is the formation of a monochelated intermediate (a), and that this ring closes rapidly to form the cyclic intermediate (b). It is probable that the dipoles between the carbon atoms and hydroxyl groups of the glycol will keep these groups in the anti-configuration, and we may therefore represent the formation of the cyclic intermediate as:

$$\begin{array}{c} \mathsf{HO}\text{-}\mathsf{CR}_2 \\ \mathsf{R}_2\mathsf{C}\text{-}\mathsf{OH} \end{array} + \operatorname{Per} \underbrace{\overset{\mathsf{Slow}}{\longleftarrow}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \begin{array}{c} \mathsf{HO}\text{-}\mathsf{CR}_2 \\ | \\ \mathsf{R}_2\mathsf{C}\text{-}\mathsf{O} \end{array} + \underbrace{\mathsf{Per}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \begin{array}{c} \mathsf{Rer} \\ \mathsf{R}_2\mathsf{C}\text{-}\mathsf{O} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \begin{array}{c} \mathsf{Rer} \\ \mathsf{R}_2\mathsf{C}\text{-}\mathsf{O} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \begin{array}{c} \mathsf{Rer} \\ \mathsf{R}_2\mathsf{C}\text{-}\mathsf{O} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \begin{array}{c} \mathsf{Rer} \\ \mathsf{Rer} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} \end{array} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{C}\text{-}\mathsf{O}} + \underbrace{\mathsf{Rer}}_{\mathsf{R}_2\mathsf{-}\mathsf{O}} + \underbrace{\mathsf{Rer}}_{$$

(As we have no knowledge as to the form of the periodic acid in this reaction we represent it by the symbol Per.)

If we accept this model for the structure of the intermediate (preceding paper), it follows that its decomposition can be subject to steric acceleration, and we find that the values of $k_{\rm b}$ for 2-methylpropane-1: 2- and meso-butane-2: 3-diol are much greater than for (-)butane-2: 3-diol (Table 2). There is steric pressure between the oxygen atoms attached to the iodine atom, and the methyl groups, in these cyclic intermediates of the two former glycols, but not for the latter (Part II). In confirmation of this, the sequence of values of k_b , for the various glycols, is similar to that of K'', the equilibrium constant relating the concentrations of the doubly negatively charged periodate ions, and the doubly negatively charged intermediate. It can be seen that this reaction sequence will give a very low concentration of the monochelated intermediate (a). This agrees with the observation that intermediates between periodic acid and monohydric alcohols have never been detected.³

In the pH range 8.5—11 an increase of pH decreases the rate of formation of the cyclic intermediate. This variation of $k_{\rm f}$ (and of $k_{\rm b}$) with pH is almost independent of the glycol (Fig. 3). The values for the rates of formation of the cyclic intermediate of 2-methylbut an e-2: 3-diol have been estimated spectrophotometrically in solutions of pH < l and > 8.5, and by chemical methods at pH 4.48, where $k_t = 1.9$ (sec.⁻¹ mole⁻¹ l.) (succeeding paper). There must therefore be a rate maximum in the range of pH 4.5-8.5, and possibly in the range of pH 1-4.5. Such maxima are observed in the oxidation of pinacol,³ and this makes it reasonable to accept the view that the rate of oxidation of pinacol is the rate of formation of an intermediate which rapidly breaks down to the products.

EXPERIMENTAL

A Cary recording spectrophotometer was used in all the experiments. Three different types of cell were used. One was of brass with windows of fused silica, and an evacuated jacket; it had an inner jacket which could be filled with crushed ice.⁵ This construction had

- ³ Crouthamel et al., J. Amer. Chem. Soc., 1949, **71**, 3031; 1951, **73**, 82. ⁴ Price et al., ibid., 1938, **60**, 2726; 1942, **64**, 552, unpublished results, Buist and Miles.
- ⁵ Passerini and Ross, J. Sci. Instr., 1953, 30, 274.

the grave disadvantage that the reaction mixture was in contact with brass, the usable pH range being thereby restricted. Therefore an all-quartz, vacuum-jacketed cell was obtained; in this design misting of the windows was avoided by a vacuum-jacket, and water at 0° was circulated in an inner jacket enclosing the cell. This cell was intended for general use at temperatures down to that of liquid air, but it succumbed to thermal strain at this temperature. A simpler version of this cell was therefore constructed with an outer brass water-jacket surrounding a fused-silica Cary cell; misting of the windows was avoided by an outer air space through which dry air was passed. The apparatus was lagged with asbestos. Temperature control was in the range $0-0.5^{\circ}$. The least reliable results are those with compounds whose equilibrium constant is low (because here the change in optical density is least) or in which the rate of formation of the intermediate is low.

The procedure for following the reaction was to fill the cell with a solution (10 c.c.) of periodate in the appropriate phosphate buffer at 0°. A small volume (0.02—0.20 c.c.) of a concentrated aqueous solution of the glycol was then added, and the solutions were mixed by bubbling air or nitrogen, or by hand. The measured reaction rate was independent of the method of mixing. The absorption-time curve was automatically recorded, at $\lambda = ca$. 2220 Å, and was followed for a few minutes, by which time a steady "infinity" value for the absorption had been reached. An aliquot part was then removed, and its glycol concentration determined by periodate titration. Graphical methods were used for calculation of the first-order rate constants.

Although most of the work described here was on the rates of formation of the cyclic intermediates, the overall rate of oxidation was followed spectrophotometrically in a few cases. This method gave fair agreement with the chemical method (Table 4), least satisfactory with

	[Diol]	First-order rate consta	ant $(10^{-4} \text{ sec.}^{-1})$
Diol	(M)	Spectrophotometric	Chemical
Ethane	0.0464	44.9	39.5
	0.0132	39.3	31.4
	0.00572	$25 \cdot 9$	$22 \cdot 6$
Propane-1 : 2	0.045	120	107
(-)-Butane 2:3	0.012	298	287
	0·0 3 0	296	295

TABLE 4. Spectrophotometric determination of the overall rate of reaction; pH 5.44; I = 0.104 (mole $l.^{-1}$).

the slower runs where effects due to ultraviolet light ⁶ or to the brass of the cell would be most serious. The agreement between the ratio k_f/k_b and the chemically determined equilibrium constant shows that uncertainties of this nature are not affecting the experiments on the rates of formation of the intermediates.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1. [Received, May 6th, 1957.]

⁶ Head and Standing, J., 1952, 1457.