



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

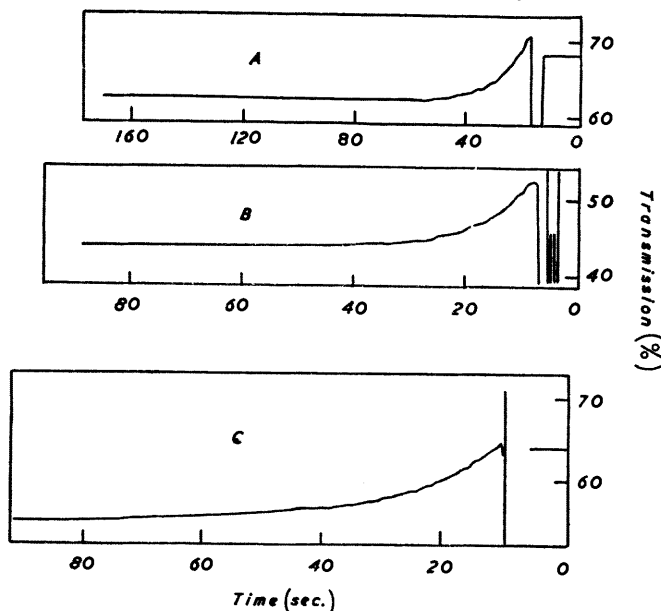
Diol	pH	$k_t$ (sec. <sup>-1</sup> mole <sup>-1</sup> l.)	$10^3 k_b$ (sec. <sup>-1</sup> )	$k_t/k_b$ (mole <sup>-1</sup> l.)	$K^*$ (mole <sup>-1</sup> l.)
Ethane-1 : 2- .....	10.6	14.7	930	1580	1800
2-Methylpropane-1 : 2- .....	10.6	1.82	700	260	360
meso-Butane-2 : 3- .....	9.25	28.9	91.2	317	373
2-Methylbutane-2 : 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,  $[G] = 1.01 \times 10^{-3}M$ .  
 B, 2-Methylpropane-1 : 2-diol, pH 10.62,  $[G] = 5.11 \times 10^{-3}M$ .  
 C, Ethane-1 : 2-diol, pH 10.62,  $[G] = 3.72 \times 10^{-3}M$ .

is therefore convenient, in most cases, to determine  $k_b$  indirectly from the known values of  $k_t$  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.<sup>2b</sup>

FIG. 2. Relation of spectrophotometric rate constants to glycol concentration.

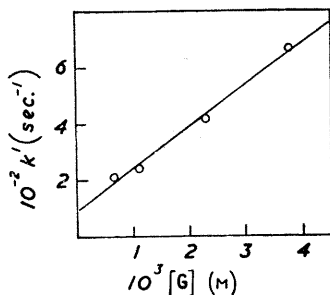
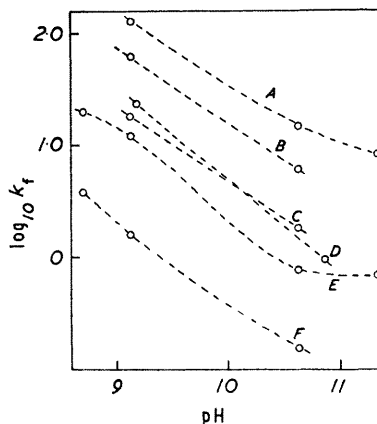


FIG. 3. Rates of formation of intermediates.



A, Ethane-1 : 2-diol; B, propane-1 : 2-diol; C, 2-methylpropane-1 : 2-diol; D, meso- and E (–)-butane-2 : 3-diol; 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  $k_b$  ( $\lambda = ca. 2220 \text{ \AA}$ ).

Diol	Ethane			Propane-1 : 2-		2-Methylpropane-1 : 2-					
pH .....	9.1	10.6	11.3	9.1	10.6	9.1	10.6				
$k_t$ (sec. <sup>-1</sup> mole <sup>-1</sup> l.) ...	130	14.7	8.4	62	6.2	18.1	1.82				
$10^4 k_b$ (sec. <sup>-1</sup> ) .....	720	82	46	220	22	510	51				
$K''$ .....	1800			2800		360					
Diol	(–)-Butane-2 : 3-				<i>meso</i> -Butane-2 : 3-		2-Methylbutane-2 : 3-				
pH .....	8.7	9.1	10.6	11.3	9.25	10.9	0.11	0.95	8.7	9.1	10.6
$k_t$ (sec. <sup>-1</sup> mole <sup>-1</sup> l.) ...	20.5	12.0	0.78	0.69	28.9	0.91	4.8	5.3	3.8	1.6	0.15
$10^4 k_b$ (sec. <sup>-1</sup> ) .....	39	15	1.0	0.9	78	2.4			40	17	1.6
$K''$ .....	8000				373		940				



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°. 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  $\lambda = ca. 2220 \text{ \AA}$ , 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

TABLE 4. *Spectrophotometric determination of the overall rate of reaction ; pH 5.44 ; I = 0.104 (mole l.<sup>-1</sup>).*

Diol	[Diol] (M)	First-order rate constant (10 <sup>-4</sup> sec. <sup>-1</sup> )	
		Spectrophotometric	Chemical
Ethane- .....	0.0464	44.9	39.5
	0.0132	39.3	31.4
	0.00572	25.9	22.6
Propane-1 : 2- .....	0.045	120	107
(—)-Butane 2 : 3- .....	0.012	298	287
	0.030	296	295

the slower runs where effects due to ultraviolet light <sup>6</sup> 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.

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<sup>6</sup> Head and Standing, *J.*, 1952, 1457.