The Mechanism of Oxidation of α-Glycols by Periodic Acid. Part I. Ethylene Glycol.

By G. J. Buist and C. A. Bunton.

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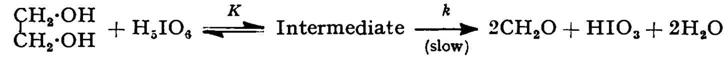
The kinetics of oxidation of ethylene glycol by periodic acid have been studied in aqueous solution, at 0°, over a wide range of pH. The kinetic form shows that an intermediate complex is formed in high concentration, in equilibrium with the glycol and periodic acid, and allows the determination of equilibrium and rate-coefficients for the formation of the complex, and its decomposition. The effect of pH on these coefficients shows that the decomposing entity is $(CH_2{\cdot}O)_2IO_4H_2^-$ or its dehydrated species $(CH_2{\cdot}O)_2IO_3^-$.

The kinetics of the oxidation of α-glycols by periodic acid in aqueous solution have been studied by Price and his co-workers (*J. Amer. Chem. Soc.*, 1938, **60**, 2726; 1942, **64**, 552) for several compounds over a range of pH; they observed the marked effect of acidity on reaction rate. A careful study of the effect of reactant concentration on rate was made by Duke (*ibid.*, 1947, **69**, 3054), in the oxidation of ethylene glycol; this system has been further investigated by Taylor (*ibid.*, 1953, **75**, 3912). Duke's results were found to obey the equation

$$k' \propto [\mathrm{G}]/(1 + K[\mathrm{G}])$$

where k' is the first-order rate coefficient with respect to periodic acid, [G] is the concentration of ethylene glycol, and K is a constant. This relation was explained in terms of a rapid reversible formation of an intermediate between the glycol and periodic acid, followed by slow decomposition of the intermediate :



$$\left.\begin{matrix}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\end{matrix}\right. + \mathrm{H_5IO_6} \overset{K}{\rightleftharpoons} \text{Intermediate} \xrightarrow[\text{(slow)}]{k} 2\mathrm{CH_2O} + \mathrm{HIO_3} + 2\mathrm{H_2O}$$

This reaction sequence requires the kinetic law

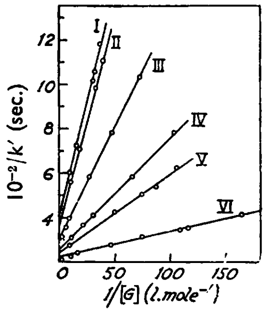
$$k' = kK[\mathrm{G}]/(1 + K[\mathrm{G}]),\ \textit{i.e.},\ 1/k' = 1/kK[\mathrm{G}] + 1/k \qquad . \ . \ . \ (a)$$

The results gave values for the equilibrium constant K and the rate coefficient k, for the formation and decomposition, respectively, of the intermediate, and showed that the equilibrium was heavily in favour of the intermediate.

However, since under his conditions ([periodic acid] in aqueous solution = 0·008M) Duke observed no effect of acidity on rate, it appeared that a systematic study of the effects of both acidity and reactant concentration might give evidence for the nature of the intermediate and its mode of decomposition.

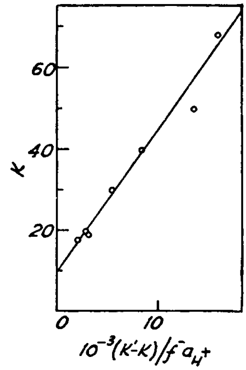
The oxidation of ethylene glycol, in aqueous periodic acid at 0°, was studied over a pH range 1—9, with wide variations of reactant concentrations and ionic strength (Buist, Bunton, and Shiner, *Research*, 1953, **6**, 45). The relation deduced by Duke (*loc. cit.*) was confirmed over this range of acidity. Furthermore, it was found that both the equilibrium constant K and the rate coefficient k were dependent upon acidity and upon ionic strength I. Examples of the values obtained are given in Table 1, and the data from which they are obtained are illustrated in Fig. 1.

FIG. 1. *Examples of dependence of first-order rate constant on concentration of ethylene glycol.*



I, pH = 1·14; $I = 0·08$
I , pH = 1·14; $I = 0·13$
III, pH = 1·45; $I = 0·03$
IV, pH = 1·94; $I = 0·01$
V, pH = 1·98; $I = 0·13$
VI, pH = 4·34; $I = 0·13$

FIG. 2. *Dependence of equilibrium constant on acidity.*



Observations on the change of pH during the reaction suggest the cause of this dependence. When an excess of the glycol is added to a periodic acid solution at pH 2 an immediate drop in pH occurs, followed by a slow decrease, due to the decomposition of the intermediate, with formation of the relatively strong iodic acid. This initial drop in pH shows that the intermediate is a stronger acid than periodic acid. A similar experiment at pH 5 gives a similar initial drop in pH, followed by a slow *increase.* This increase, during the decomposition of the intermediate, must be due to the replacement of doubly-negatively charged ions by singly-negatively charged iodate ions. Since kinetic data show that *ca.* 95% of the periodic acid is combined under these conditions, these doubly-negatively charged ions must be derived from the glycol–periodate complex, and not simply from the periodic acid. Examples of the change of pH with time are given in Table 2.

TABLE 1. *Effect of* pH *and ionic strength on* k *and* K.

pH	0·96	1·13	1·15	1·45	1·61	1·94	1·98	3·05	4·34	4·34
I (mole l.$^{-1}$) ...	0·134	0·084	0·134	0·03	0·134	0·01	0·134	0·134	0·134	0·021
10^4k (sec.$^{-1}$) ...	20·3	24·8	27·9	33·0	36·8	39·5	41·7	45·1	45·5	45·9
K (l. mole^{-1}) ...	17·7	19·5	18·7	30·1	40	50	68	141	189	196

pH	5·25	6·23	6·76	7·01	7·01	7·30	7·68	9·19	9·58
I (mole l.$^{-1}$) ...	0·05	0·065	0·09	0·030	0·129	0·123	0·12	0·130	0·130
10^4k (sec.$^{-1}$) ...	44·0	32·8	18·5	16·5	11·6	6·94	2·73	0·070	0·030
K (l. mole^{-1}) ...	188	237	345	476	540	—	~1000	—	~2500

TABLE 2.

Aqueous solution, 0°. Glycol = 0·05M. Periodate = 0·01M.

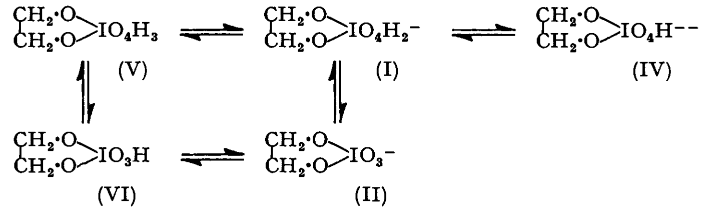
(*a*) Time (sec.)	0	20	80	200	420	800	1080	1260
pH	2·36	2·23	2·17	2·15	2·13	2·11	2·11	2·11

(*b*) Time (sec.)	0	30	125	215	320	550	840	1150	1380	1680
pH	5·11	4·55	4·62	4·72	4·83	5·10	5·40	5·62	5·70	5·75

In considering an interpretation of the rate data, we must consider not only the equilibria between the various species of periodic acid, *viz.*,

$$\begin{tikzcd}
H_5IO_6 \arrow[r, shift left] & H^+ + H_4IO_6^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & IO_4^- + 2H_2O \arrow[l, shift left] \\
& H^+ + H_3IO_6^{--} \arrow[u, shift left] &
\end{tikzcd}$$

and the effect of acidity on these equilibria (Crouthamel *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 82), but also the related equilibria between the various intermediate species, which are formed by the co-ordination of a glycol molecule with periodic acid or its ions :

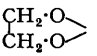


In so far as the dehydrated species have the same charge as their precursors, they must show a similar pH dependence, and our rate data do not differentiate between intermediate species of the same charge formed between one molecule of a glycol and one of a periodic acid.

The effect of pH on the equilibrium constant between ethylene glycol and periodic acid, all species of periodic acid and the intermediate complex being considered, can be predicted qualitatively from the fact that the co-ordinated glycol complex is a stronger acid than periodic acid, and therefore the equilibrium constant increases with increasing pH (cf. Table 1). A prediction of the effect of pH on the rate of decomposition of the intermediate cannot be made on such a simple basis, and requires detailed consideration of all the possible reactions involved. In principle, any of the intermediates may decompose to give the products of reaction, but, as will be shown, the only decomposing entity is the singly-charged ion (I) or its dehydrated species (II).

Nature of Reacting Species, and Dependence on Acidity.—The possible reactions involved in the formation and decomposition of the intermediates are

$$\begin{tikzcd}
H_5IO_6 \arrow[r, shift left, "\bar{K}_1"] & \underset{+\,G}{\mathrm{Per}^-} \arrow[l, shift left] \arrow[r, shift left, "\bar{K}_2"] \arrow[d, shift left, "K'"] & \mathrm{Per}^{--} \arrow[l, shift left] \\
\underset{(\text{or } HGIO_4)}{H_3GIO_4} \arrow[r, shift left, "K_1'"] \arrow[d, "k_0"] & \underset{(\text{or } GIO_3^-)}{H_2GIO_4^-} \arrow[l, shift left] \arrow[u, shift left] \arrow[r, shift left, "K_2'"] \arrow[d, "k_1"] & HGIO_4^{--} \arrow[l, shift left] \arrow[d, "k_2"] \\
{} & {} & {}
\end{tikzcd}$$



(III)

where G represents the residue (III) and Per⁻ and Per⁻⁻ represent the totality of singly- and doubly-negatively charged periodate ions respectively. In so far as the periodate and intermediate complex species are in equilibrium, we have no evidence for the actual route of formation of the intermediates, and use the above formulation for convenience in calculation. Taylor (*loc. cit.*) has put forward thermodynamic arguments to show that IO_4^- is the reactive species in the formation of the intermediate. The reasoning is erroneous since thermodynamic data alone can give no evidence for the mechanism of a kinetic process.

The apparent first and second ionisation constants of periodic acid, $\bar{K}_1$ and $\bar{K}_2$, are given by

$$\bar{K}_1 = \frac{f^-\{[H_4IO_6^-] + [IO_4^-]\}a_{H^+}}{[H_5IO_6]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\bar{K}_2 = \frac{f^{=}a_{H^+}[Per^{--}]}{f^-\{[H_4IO_6^-] + [IO_4^-]\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where f^z is the activity coefficient of the *z*-charged periodate ions and f^z_i used below is that of the *z*-charged intermediate complex ions.

The experimentally observed equilibrium constant, K, and rate coefficient, k, are calculated from the kinetic data by equation (*a*) (p. 1406).

Now
$$K = [\text{Total intermediate}]/[\text{Glycol}][\text{Total periodate}] \quad . \quad . \quad . \quad (3)$$

i.e.,
$$K = \frac{[H_3GIO_4] + [H_2GIO_4^-] + [HGIO_4^{--}]}{[\text{Glycol}]\{[H_5IO_6] + [Per^-] + [Per^{=}]\}} \quad . \quad . \quad . \quad . \quad (3a)$$

Similarly, we can consider the equilibria between the intermediates :

$$[H_3GIO_4] = a_{H^+}[H_2GIO_4^-]f_i^-/K_1' \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and
$$[HGIO_4^{=}] = K_2'[H_2GIO_4^-]f_i^-/a_{H^+}f_i^{=} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We do not in these equations differentiate between the hydrated and dehydrated intermediate species, and the activity coefficients for all neutral species are assumed equal to unity.

These expressions give

$$K = \frac{[H_2GIO_4^-]\left\{1 + \dfrac{f_i^-a_{H^+}}{K_1'} + \dfrac{f_i^-K_2'}{f_i^{=}a_{H^+}}\right\}}{[\text{Glycol}]\left\{1 + \dfrac{f^-a_{H^+}}{\bar{K}_1} + \dfrac{f^-\bar{K}_2}{f^{=}a_{H^+}}\right\}[Per^-]} = K'\left\{\frac{1 + \dfrac{f_i^-a_{H^+}}{K_1'} + \dfrac{f_i^-K_2'}{f_i^{=}a_{H^+}}}{1 + \dfrac{f^-a_{H^+}}{\bar{K}_1} + \dfrac{f^-\bar{K}_2}{f^{=}a_{H^+}}}\right\} \quad . \quad (6), (7)$$

since $K' = [H_2GIO_4^-]/[\text{Glycol}][Per^-]$

The total rate of decomposition of the intermediate is given by

$$k[C] = k_0[H_3GIO_4] + k_1[H_2GIO_4^-] + k_2[HGIO_4^{=}] \quad . \quad . \quad . \quad . \quad (8)$$

where k_0, k_1, and k_2 are the respective first-order rate coefficients for the decomposition of the various species, and [C] is the total concentration of the intermediates. Therefore

$$k[C] = [H_2GIO_4^-]\left\{\frac{k_0a_{H^+}}{K_1'}f_i^- + k_1 + \frac{k_2K_2'}{a_{H^+}}\frac{f_i^-}{f_i^{=}}\right\} \quad . \quad . \quad . \quad . \quad (8a)$$

but $[C] = [H_3GIO_4] + [H_2GIO_4^-] + [HGIO_4^{--}]$

$$= [H_2GIO_4^-]\left\{\frac{a_{H^+}}{K_1'}f_i^- + 1 + \frac{K_2'}{a_{H^+}}\cdot\frac{f_i^-}{f_i^{=}}\right\}$$

$$\therefore \quad k = \frac{k_1 + \dfrac{k_0a_{H^+}}{K_1'}f_i^- + \dfrac{k_2K_2'}{a_{H^+}}\dfrac{f_i^-}{f_i^{=}}}{1 + \dfrac{a_{H^+}}{K_1'}f_i^- + \dfrac{K_2'f_i^-}{a_{H^+}f_i^{=}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Reactions in Solutions of pH > 5.—Preliminary measurements of the change of pH in aqueous solutions of periodic acid and ethylene glycol show that the first ionisation constant, K_1', for the intermediate is not less than 2×10^{-2}, and so $a_{H^+}/K_1' \ll 1$; also as the apparent first ionisation constant of periodic acid, $\bar{K}_1$, is $\sim 4 \times 10^{-3}$, $a_{H^+}/\bar{K}_1 \ll 1$.

We assume that k_0, k_1, and k_2 are independent of pH and ionic strength, and we can therefore express the rate coefficient k in terms of k_1 and k_2 (at this high pH we neglect the undissociated intermediate species):

$$k = \left\{k_1 + \frac{k_2K_2'}{a_{H^+}} \cdot \frac{f_i^-}{f_i^=}\right\} \Big/ \left\{1 + \frac{K_2'}{a_{H^+}} \cdot \frac{f_i^-}{f_i^=}\right\} \quad . \quad . \quad .. \quad . \quad . \quad (10)$$

If we assume that $k_2 \sim 0$, (10) reduces to

$$k = \{k_1 a_{H^+} f_i^= / f_i^-\}/\{K_2' + a_{H^+} f_i^= / f_i^-\} \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

Equation (10*a*) allows a test of the validity of these assumptions to be made by plotting $1/k$ against $f_i^-/a_{H^+} f_i^=$. To allow an assignment of numerical values to a_{H^+}, f_i^-, and $f_i^=$, we assume that a glass electrode gives a measure of the hydrogen-ion activity, *i.e.*, that pH $= -\log_{10} a_{H^+}$, and that the activity coefficients f_i^- and $f_i^=$, for the singly- and doubly-negatively charged intermediate ions, can be calculated from the expression $-\log f^z = 0{\cdot}486z^2\sqrt{I}/(1 + \sqrt{I})$. The first assumption, in effect, requires the liquid-junction potential to be constant in the range of pH considered.

The very large change of hydrogen-ion activity in the pH range 5—9 renders this test somewhat insensitive in its present form over this whole range. The test, however, indicates that $k_2 \sim 0$, *i.e.*, that the doubly-negatively charged intermediate species does not decompose, and gives the following values for the rate coefficient, k_1, of the singly-negatively charged intermediate, and its ionisation constant, K_2':

$$k_1 = 45{\cdot}7 \times 10^{-4} \text{ sec.}^{-1}; \quad K_2' = 1{\cdot}16 \times 10^{-7} \text{ mole l.}^{-1}$$

More precise values for these quantities are derived later.

Reactions in Solutions of pH <5.—The approximate value obtained above for K_2' allows us to neglect the presence of the doubly-negatively charged intermediate in solutions of pH <5. With this simplification, equation (9) reduces to

$$k = \left\{k_1 + f_i^- \cdot \frac{a_{H^+}}{K_1'} \cdot k_0\right\} \Big/ \left\{1 + \frac{a_{H^+}}{K_1'} \cdot f_i^-\right\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$i.e., \quad 1/k = 1/k_1 + f_i^- a_{H^+}/K_1'k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

if the term including k_0 is negligible compared with k_1 in the pH range studied. Again we make the approximations which allow numerical values to be assigned to a_{H^+} and f_i^-.

In Table 3 are given values of $f_i^- a_{H^+}$ and of the corresponding calculated and observed values of $1/k$; the agreement shows that equation (11*a*) is obeyed, *i.e.*, that k_0 is small or zero, and allows a value of $7{\cdot}4 \times 10^{-2}$ mole l.$^{-1}$ to be assigned to K_1'. The estimated value of k_1 is $45{\cdot}7 \times 10^{-4}$ sec.$^{-1}$.

TABLE 3. *Dependence of rate constant on hydrogen-ion activity.*

pH	I	$10^3 f_i^- a_{H^+}$	$1/k$ (calc.) (sec.)	$1/k$ (obs.) (sec.)	pH	I	$10^3 f_i^- a_{H^+}$	$1/k$ (calc.) (sec.)	$1/k$ (obs.) (sec.)
4·33	0·134	0·034	219	218	1·45	0·03	30·2	308	303
3·05	0·134	0·67	221	222	1·15	0·134	53·3	377	358
1·98	0·134	7·8	242	240	1·13	0·084	57·6	389	403
1·94	0·01	10·4	250	253	0·95	0·134	84·5	469	492
1·61	0·134	18·2	273	272					

By similar considerations we can use the experimental data obtained in solutions of pH <5 to obtain numerical values for the constants of the equilibria involved. In this acidity range we can neglect K_2' and $\bar{K}_2$, and equation (7) reduces to

$$K = K'\left\{1 + f_i^- \frac{a_{H^+}}{K_1'}\right\} \Big/ \left\{1 + f^- \cdot \frac{a_{H^+}}{\bar{K}_1}\right\} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Using the experimentally determined values in equation (7), we find that $K = K'$ at pH $= 4\cdot3$; this allows us to assign a numerical value to K'. We further assume that the activity coefficients f^- and f_i^- for the singly-negatively charged periodate and intermediate ions are equal. Then equation (12) rearranges to

$$K = \frac{\bar{K}_1(K' - K)}{f^- a_{\mathrm{H}^+}} + \frac{K'\bar{K}_1}{\bar{K}_1'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12a)$$

and we can plot K against $(K' - K)/f^- a_{\mathrm{H}^+}$. Again we make the previously mentioned approximations to the values of a_{H^+} and f^-. This graphical plot is shown in Fig. 2.

The values estimated from Fig. 2 are: (*a*) $\bar{K}_1 = 3\cdot6 \times 10^{-3}$, which can be compared with the values obtained by Crouthamel *et al.* (*loc. cit.*) by ultra-violet absorption spectrophotometry, of 4×10^{-3}, and that from buffer measurements of $4\cdot0 \times 10^{-3}$; and (*b*) $\bar{K}_1' = 6\cdot8 \times 10^{-2}$, comparing well with the value $7\cdot4 \times 10^{-2}$ obtained by consideration of the effect of acidity on the rate of decomposition of the intermediate complex.

For results in alkaline solution we have the approximate value $45\cdot7 \times 10^{-4}$ sec.$^{-1}$ for k_1, and $1\cdot16 \times 10^{-7}$ for the second dissociation constant of the intermediate complex.

We know also that the singly-negatively charged intermediate is the only decomposing entity under our experimental conditions, and with these simplifications it is possible to use the data in the range of pH >5 to obtain a more precise value of K_2'.

The rate of decomposition of the intermediate in solutions of pH >5 is given by equation (10), but as $k_2 = 0$, this simplifies to:

$$k = k_1/(1 + K_2'f_i^-/a_{\mathrm{H}^+}f_i^=) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10b)$$

i.e., $\log K_2' - \log a_{\mathrm{H}^+} + \log f_i^-/f_i^= = \log(k_1/k - 1)$. Plotting pH $+ \log f_i^-/f_i^=$ against $\log(k_1/k - 1)$ gives a straight line, as shown by data in Table 4, and a value for the second ionisation constant of the intermediate $K_2' = 1\cdot12 \times 10^{-7}$ mole l.$^{-1}$. The straight line obeys the equation

$$\log(k_1/k - 1) = 1\cdot06\{\mathrm{pH} + \log(f^-/f^=) - 6\cdot95\}$$

The experimentally observed slope is 1·06, whereas equation 10(*b*) predicts that it should be unity. This discrepancy is presumably due to the approximations made in assigning numerical values to the hydrogen-ion activity and the activity coefficients.

TABLE 4.

pH	I	pH + log $(f^-/f^=)$	log $(k_1/k - 1)$ Obs.	Calc.	pH	I	pH + log $(f^-/f^=)$	log $(k_1/k - 1)$ Obs.	Calc.
6·23	0·065	6·53	−0·41	−0·46	7·30	0·123	7·68	0·75	0·77
6·76	0·090	7·11	0·17	0·16	7·68	0·120	8·06	1·20	1·19
7·01	0·030	7·23	0·25	0·30	9·19	0·130	9·57	2·82	2·78
7·01	0·129	7·40	0·47	0·49	9·58	0·130	9·96	3·18	3·19

The values of K, observed in the pH range 5—9, are compared in Table 5 with those calculated from equation (7), both the potentiometrically determined value for $\bar{K}_2$ (Crouthamel *et al.*, *loc. cit.*) and that determined in this work by pH measurements in periodic acid buffer being used.

TABLE 5.

pH	I	K (l. mole^{-1}) Obs.	Calc.[1]	Calc.[2]	pH	I	K (l. mole^{-1}) Obs.	Calc.[1]	Calc.[2]
5·25	0·050	188	196	194	7·01	0·129	540	556	359
6·23	0·065	237	250	229	7·68	0·120	1000	1130	469
6·76	0·090	345	400	305	9·58	0·130	~2500	1820	529
7·01	0·030	476	455	325					

[1] Taking $\bar{K}_2 = 1\cdot16 \times 10^{-8}$ (this work). [2] Taking $\bar{K}_2 = 4\cdot0 \times 10^{-8}$ (Crouthamel *et al.*, *loc. cit.*).

The values obtained in this work for the various equilibrium and rate coefficients are given in Table 6, together with the values of earlier workers.

TABLE 6. *Rate and equilibrium coefficients.*

Coeff.	Value	Method of determination
K_1	$3 \cdot 6 \times 10^{-3}$	From plot of K (pH ~2)
	4×10^{-3}	Spectrophotometric (Crouthamel *et al., loc. cit.*)
	$4 \cdot 0 \times 10^{-3}$	Buffer measurements
K_2	$4 \cdot 0 \times 10^{-8}$	Potentiometric (as above)
	$1 \cdot 16 \times 10^{-8}$	Buffer measurements
K_1'	$7 \cdot 4 \times 10^{-2}$	From $1/k$ plot (pH 1—4)
	$6 \cdot 8 \times 10^{-2}$	From K plot (pH ~2)
K_2'	$1 \cdot 12 \times 10^{-7}$	From log $[k_1/k - 1]$ plot (pH 6—9)
	$1 \cdot 16 \times 10^{-7}$	From $1/k$ plot (pH 4—7)
k_1	$45 \cdot 7 \times 10^{-4}$	From $1/k$ plot (pH 1—4)
	$45 \cdot 7 \times 10^{-4}$	From $1/k$ plot (pH 5—7)
K'	189	From results at pH 4·3

DISCUSSION OF RESULTS

All the experimental results on the kinetics of oxidation of ethylene glycol by periodic acid can be explained in terms of the singly-negatively charged intermediate as the sole decomposing species.

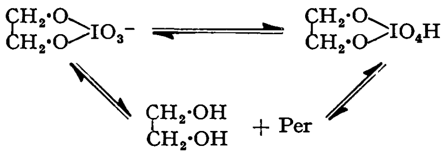
In the quantitative consideration of the effect of acidity on reaction rate we consider salt effects simply as the effect of ionic strength on the equilibria involved, and the results obtained suggest that salt effects on the rate coefficient, k_1, can be neglected.

It is relevant to speculate on the reason for the singly-negatively charged intermediate's being the sole decomposing entity. As was pointed out, the effects of acidity and ionic strength give no differentiation between the hydrated and the dehydrated intermediate species. We suggest that the decomposing entities must be the dehydrated species, and such dehydration cannot occur with the doubly negatively charged intermediate (IV), which is therefore not a decomposing entity.

The decomposition of the dehydrated uncharged intermediate formed by the change (V) $\rightleftharpoons$ (VI) + H_2O may be considered a possibility, but the molecule (VI) would be a strong acid, and would be fully ionised under all our experimental conditions. We have been unable, for ethylene glycol, to extend our measurements to solutions of acidity high enough to observe the existence of this neutral intermediate species.

We therefore consider the decomposition of the singly negatively charged intermediate formed by

(II)



The decomposition of (II) would be a reaction involving no formation or destruction of charge, and so would not be subject to a large salt effect, and it would show the general characteristics of an internal rearrangement :

It would therefore be idle to speculate on the nature of the carbon–carbon bond fission for this decomposition (Hughes and Ingold, *Quart. Reviews*, 1952, **6**, 34).

EXPERIMENTAL

Materials.—Ethylene glycol (B.D.H.) was distilled before use. Sodium metaperiodate was prepared from the paraperiodate (Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 2679) and recrystallised from water. Potassium dimesoperiodate ($K_4I_2O_9,9H_2O$) was prepared from potassium metaperiodate and potassium hydroxide and recrystallised from water.

The following buffer solutions were used : pH 3—5, sodium acetate–perchloric acid;

pH 5—7·5, sodium dihydrogen phosphate–sodium hydroxide; pH 8·5—10, ammonia—perchloric acid.

Below pH 3 a buffer is unnecessary, as the pH change in the course of the reaction has a negligible effect on rate, and here the pH was adjusted by the addition of perchloric acid.

Sodium perchlorate (recrystallised) was used to adjust the ionic strength where necessary.

Kinetic Measurements.—All kinetic measurements were carried out in aqueous solution at 0°, with 0·001M-periodate solutions. Measurements at a given pH and ionic strength were independent of the buffer and the source of the periodate.

At arbitrary times aliquot parts of the reaction mixture were quenched in potassium iodide. As the reaction between potassium iodide and periodate is slow in neutral solution, the usual method for the determination of periodate (Jackson, "Organic Reactions," Vol. II, p. 361, Wiley, 1944) was slightly modified. A mixture of 2 c.c. of 4M-potassium iodide and 5 c.c. of 1M-sodium hydrogen carbonate solution was added to 10-c.c. portions of the reaction mixture. The samples, after standing, at 0° to prevent loss of iodine, were titrated with 0·0005M-sodium arsenite, with a starch indicator. Total glycol concentration was determined by addition of excess of periodate.

pH *Measurements.*—pH's were measured with a Cambridge pH meter, a glass electrode being used. A silver–silver chloride reference electrode was used with a conventional ground-glass cap liquid junction. The meter was standardized with a 0·05M-phthalate buffer, pH 4·00 at 0°.

Examples of two kinetic runs are given below:

Run No. 93. pH = 0·95, I = 0·134, $[\text{Glycol}]_\infty$ = 0·093M, $[\text{Periodate}]_0$ = 0·00087M.

Time (sec.)	0	120	240	360	480	600	720	840	960
Titre (obs.), c.c.	7·99	6·88	5·91	5·14	4·39	3·74	3·21	2·83	2·35
Titre (calc.), c.c.	7·99	6·88	5·90	5·08	4·36	3·74	3·22	2·77	2·38

Calculated titre = $7{\cdot}99e^{-k't}$; $k' = 12{\cdot}62 \times 10^{-4}$ sec.$^{-1}$.

Run No. 103. pH = 4·34, I = 0·134, $[\text{Glycol}]_\infty$ = 0·0214M, $[\text{Periodate}]_0$ = 0·00091M.

Time (sec.)	0	55	106	160	215	275	325	375	420
Titre (obs.), c.c.	9·09	7·48	6·20	5·10	4·20	3·31	2·78	2·31	1·91
Titre (calc.), c.c.	9·09	7·45	6·17	5·07	4·14	3·33	2·77	2·31	1·95

Calculated titre = $9{\cdot}09e^{-k't}$; $k' = 36{\cdot}6 \times 10^{-4}$ sec.$^{-1}$.

Runs with periodate in excess gave results identical with those with glycol in excess.

In all cases the values of k and K, the rate and equilibrium coefficients for the formation and decomposition of the intermediate, were obtained by plotting $1/k'$ against 1/[Glycol] (Fig. 1). Slight deviations from a straight line are noticed at high glycol concentrations. Such deviations were noticed previously by Duke and Bremer (*Iowa State Coll. J. Sci.*, 1951, **25**, 527; *Chem. Abs.*, 1951, **45**, 8390); they may be due to the formation of diglycol intermediate species, as pointed out by the above workers, but in general the deviations become marked only when the glycol is in sufficiently high concentration to change the solvent properties of the medium.

Apparent Ionisation Constants of Periodic Acid.—The first and the second apparent ionisation constants of periodic acid were determined by measuring the pH of periodate buffers in aqueous solution at 0°. For the determination of $\bar{K}_1$, a 0·08M-solution of sodium metaperiodate was mixed with the half-equivalent amount of perchloric acid. For $\bar{K}_2$, the buffer was made up similarly with 0·005M-potassium dimesoperiodate, and a half-equivalent of sulphuric acid added. Carbonate-free solutions were used.

Activity coefficients were calculated as previously described.

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William Ramsay & Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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