have slopes of k_2'' as a function of Cl^-, and intercepts with values of k_1'' at various Cl^-. A plot is then made of k_1'' *vs.* Cl^- and k_2'' *vs.* Cl^-. These plots yield straight lines which have slopes of k_1 and k_2 and intercepts of k_2K_1 and k_4K_1, respectively. The rate constants were calculated and the average values are shown in Table II.

TABLE II

RATE AND EQUILIBRIUM CONSTANTS 40°

$[Ti^{+3}] = 0.015\ M$, $[ClO_4^-] = 0.5\ M$

$k_1 \times 10^2$	$k_2 \times 10^2$	$k_3 \times 10^3$	$k_4 \times 10^2$	K_1
8.89 ± 0.9	3.59 ± 0.4	3.40 ± 0.3	1.36 ± 0.2	2.18 ± 0.2

The rate constants were determined at both 40 and 50°. The energies of activation and the entropies of activation for the various steps in the reaction were then calculated. The results are shown in Table III.

TABLE III

ACTIVITY ENERGIES AND ENTROPIES 40°

$k_1 \times 10^2$	8.89	± 0.9	$k_4 \times 10^2$	1.36	± 0.2
$\Delta F^{\ddagger}_{313}$, kcal.	19.9	± 0.1	$\Delta F^{\ddagger}_{313}$, kcal.	21.0	± 0.1
$\Delta H^{\ddagger}$, kcal.	26	± 15%	$\Delta H^{\ddagger}$, kcal.	10	± 50%
$\Delta S^{\ddagger}$, e.u.	20	± 50%	$\Delta S^{\ddagger}$, e.u.	−36	± 50%
$k_2 \times 10^2$	3.5	± 0.4	K_1	2.18	± 0.2
$\Delta F^{\ddagger}_{313}$, kcal.	20.4	± 0.1	ΔF_{313}, kcal.	17.8	± 0.1
$\Delta H^{\ddagger}$, kcal.	25	± 14%	ΔH, cal.	2500	± 50%
$\Delta S^{\ddagger}$, e.u.	17	± 50%	ΔS, e.u.	−50	± 100%
$k_3 \times 10^3$	3.40	± 0.3			
$\Delta F^{\ddagger}_{313}$, kcal.	20.4	± 0.1			
$\Delta H^{\ddagger}$, kcal.	6	± 50%			
$\Delta S^{\ddagger}$, e.u.	−46	± 50%			

The reaction is thought to proceed through the formation of an activated complex, the disproportionation of which is the rate-determining step. The following four equations have been proposed to explain the kinetics of the reaction

$$Ti^{+3} + ClO_4^- \rightleftarrows [\text{complex}] \longrightarrow TiO^{++} + ClO_3$$

$$Ti^{+3} + ClO_4^- + H^+ \rightleftarrows [\text{complex}] \longrightarrow Ti(OH)^{+3} + ClO_3$$

$$TiCl^{++} + ClO_4^- \rightleftarrows [\text{complex}] \longrightarrow TiO^{++} + ClO_3 + Cl^- \ [\text{or } TiOCl^+]$$

$$TiCl^{++} + ClO_4^- + H^+ \rightleftarrows [\text{complex}] \longrightarrow Ti(OH)^{+3} + ClO_3 + Cl^- \ [\text{or } TiOHCl^{+2}]$$

From the standpoint of the free energies involved and the probability of reaction most likely to occur, the first and third equations above would seem to be the most important. The radical ClO_3 is rapidly reduced further to the final product Cl^-. It may well be true that the affinity of the Ti(IV) for OH^- and $O^=$ accounts for the low activation energy of this reaction as compared with reductions of perchlorate with Fe(II), Sn(II), Cr(II) and others.

AMES, IOWA

[CONTRIBUTION NO. 321 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

The Kinetics of the Periodate Oxidation of Ethylene Glycol and a Series of Methylated Ethylene Glycols

BY FREDERICK R. DUKE AND VERNON C. BULGRIN

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The specific periodate oxidation of the homologous series of glycols, ethylene glycol through pinacol, shows a discontinuity in mechanism between trimethylethylene glycol and pinacol. The latter is very slowly oxidized in an acid-catalyzed bimolecular step, while the former, as with the other glycols studied, proceeds rapidly in a non-catalyzed unimolecular step. The effect of stepwise methyl group substitution in ethylene glycol is determined, both in the free energy of complex formation with periodate and on the unimolecular rate constant.

The mechanism of the periodic acid cleavage of ethylene glycol may involve an intermediate coördination compound of the oxidant and reductant, the rate-determining step being the disproportionation of the intermediate.[2] The rate of the reaction has been demonstrated to be nearly independent of hydrogen ion concentration in the *p*H range three to seven.[2,3] Waters[4] attributed the constancy of the rate in this region to the fact that hydrogen ion catalysis is balanced by decreasing ionization of H_5IO_6 to the reactive $H_4IO_6^-$. Crouthamel, Martin and co-workers, in a spectrophotometric study of periodate species in solution,[5,6] showed that the concentration of negative ion, predominantly IO_4^-, is nearly constant in the *p*H range three to seven.

Price[3] found the rate of oxidation of pinacol to be a peculiar function of hydrogen ion concentration, having a sharp maximum at *p*H 2 and a minimum for the range four to six.

A kinetic study of the oxidation of the series ethylene glycol through pinacol was undertaken, in an effort to observe the effect of methyl substitution on the rate and equilibrium constants and to determine at which point in the series the change in reactivity exhibited by pinacol begins to show up.

Experimental

Ethylene and propylene glycols obtained from the Matheson Co. were twice distilled before using. *meso*-2,3-Butanediol, which had been prepared by the fermentation of corn using *Aerobacter aerogenes*,[7] was purified by recrystallization from dry isopropyl ether.[8] *levo*-2,3-Butanediol was pre-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] F. R. Duke, THIS JOURNAL, **69**, 3054 (1947).

[3] C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942).

[4] W. A. Waters in H. Gilman, "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 12.

[5] C. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, THIS JOURNAL, **71**, 3031 (1949).

[6] C. Crouthamel, A. Hayes and D. S. Martin, *ibid.*, **73**, 82 (1951).

[7] E. R. Kooi, E. I. Fulmer and L. A. Underkofler, *Ind. Eng. Chem.*, **40**, 1440 (1948).

[8] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

pared by the *Aerobacillus polymyxa* fermentation of corn,[7] and was purified by fractional distillation. Trimethylethylene glycol was prepared by oxidation of the unsaturated hydrocarbon with performic acid.[9] It was purified by fractional distillation using a Todd Scientific Co. 40-plate column. Pinacol hydrate was prepared through the condensation of acetone,[10] and was purified by recrystallization from water.

Physical properties such as melting and boiling points, refractive indices and optical rotation, and analysis by periodate oxidation showed the purity of all the glycols to be better than 99%. Stoichiometric cleavage of pinacol in 0.1 *M* acid solution indicated that the pinacol rearrangement is insignificant at the acidities in the investigation.

The water used for all reactant solutions and for all dilutions was redistilled from alkaline permanganate. All inorganic chemicals were the best available reagent grade. Solutions of G. Frederick Smith Co. paraperiodic acid stored in a brown bottle were found to be stable over a period of several months. Variation of *p*H in the reacting solutions was achieved by addition of the required amount of sodium hydroxide or perchloric acid. Ionic strength was maintained constant at 0.2 by addition of sodium nitrate solution.

Melting ice and melting benzene to obtain temperatures of 0.00 ± 0.05° and 5.25 ± 0.05°, respectively, were used as constant temperature baths, a mixture of the solid and liquid phases being stirred in 2-liter wide-mouth Dewar flasks. The benzene was saturated with water to obtain a reproducible temperature. In some of the runs a mercury thermoregulator and water-bath were used to give a temperature of 25.25 ± 0.05°.

For *levo*-butylene glycol at −4° (supercooled solutions), an ice–water–HCl-bath was used. By occasionally adding a few drops of concentrated HCl, the temperature could be kept constant at −4.12 ± 0.02°.

The reaction vessels consisted of 50-ml. volumetric flasks with additional 48 or 49 ml. marks. The required amount of 1.00 *M* glycol, plus sodium hydroxide or perchloric acid to give the desired *p*H, and 5.0 ml. of 2.0 *M* sodium nitrate were placed in the flask and the contents diluted to 48 (or 49) ml. After at least 30 minutes in the bath, 2.00 (or 1.00) ml. of 0.200 *M* periodic acid at the bath temperature were added and the timer, an Air Force surplus stopwatch, started. At known time intervals, 5.0-ml. aliquots were discharged into the quenching mixture. For reaction mixtures of *p*H greater than 2, the quenching mixture consisted of 5 ml. of 10% potassium iodide solution saturated with sodium bicarbonate to which a measured excess, usually 0.500 ml., of 0.1000 *N* sodium arsenite had been added. The excess arsenite was titrated with 0.01 *N* I_2 solution. For reaction mixtures of *p*H less than 2, local excesses of acid introduced by the reaction aliquot caused erratic results, some of the periodate being reduced past the iodate stage. For these reaction mixtures, the quenching solutions consisted of 5 ml. of acidified 10% potassium iodide. The liberated I_2 was titrated with 0.01 *N* thiosulfate. In view of the large blank, the latter procedure was inherently less accurate than was the arsenite procedure. *p*H measurements were taken at room temperature after the reaction was substantially over. The *p*H had been shown to vary not more than 0.1 unit during a reaction.

Discussion and Results

Ethylene, propylene, *meso*- and *levo*-butylene and trimethylethylene glycols were found to react according to the scheme

$$IO_4^- + G \underset{\text{rapid}}{\overset{K}{\rightleftharpoons}} C \underset{\text{slow}}{\overset{k}{\longrightarrow}} \text{products}$$

similar to that proposed by Duke[2] for the ethylene glycol cleavage. The choice of IO_4^- over $H_4IO_6^-$ as the reactive periodate species is arbitrary; since these species are in rapid equilibrium with one another and with the glycol and complex, it is not possible to demonstrate which is actually doing the reacting. However, it is easy to picture coördination of the tetrahedral IO_4^- with a glycol molecule in much the same manner as with two water molecules to give an octahedral ion. The kinetics are expressed by the equation

$$-\frac{d[P]T}{dt} = k[C] = k^1[P]_T$$

where

$$\frac{1}{k^1} = \frac{1}{k} + \frac{1}{kK[G]}\left\{1 + \frac{1}{K_D} + \frac{A_{H^+}\ IO_4^-}{K_1K_D\ H_5IO_6}\right\} \quad (1)$$

A_{H^+} = activity of hydrogen ion

IO_4^- and H_5IO_6 are the activity coefficients, 0.75 and 1.0, respectively

K_1 and K_D are defined by the equilibrium

$$H_5IO_6 \overset{K_1}{\rightleftharpoons} H^+ + H_4IO_6^-$$

$$H_4IO_6^- \overset{K_D}{\rightleftharpoons} 2H_2O + IO_4^-$$

[C] = concn. of intermediate
[G] = concn. of uncoördinated glycol
$[P]_T$ = concn. of total periodate

Equation 1 is derivable directly from the relations

$$[C] = [IO_4^-][G]K$$

$$[P]_T = [H_5IO_6] + [H_4IO_6^-] + [IO_4^-] + [C]$$

and the expressions for the dissociation equilibrium of periodic acid.

Equation 1 predicts that the rate should be independent of *p*H for the *p*H range three to seven. Experimental values of the pseudo first-order rate constants in acid solution are in excellent agreement with those calculated from equation 1, using values of *k* and *K* obtained as described in a later section. Agreement of the observed points with the calculated curves substantiates the postulate that a negative ion, IO_4^- or $H_4IO_6^-$, is the reactive periodate species, the observed lowering of rate in acid solution (below *p*H three) being due to decreasing ionization of H_5IO_6.

It can be calculated that, provided the glycol is present in sufficient excess, [G], the concentration of uncoördinated glycol, is nearly constant during a reaction. For the *p*H range three to seven, where the third term in the brackets of equation 1 becomes negligible, a plot of $1/k^1$ *vs.* $1/[G]$ should give a straight line with intercept $1/k$ and slope $[1 + K_D]/kKK_D$. The observed variations of k^1 with [G] are given in Table I.

In addition, at very dilute and equal concentrations of periodate and glycol (0.00160 *M* was used) the reaction appears to be second order. Plots of $1/[P]_T$ *vs.* time gave straight lines with slopes equal to *kK* times a factor *f*, where

$$f = \frac{[G]/[P]_T}{1 + \frac{1}{K_D} + K[G]}$$

In practice, a combination of the $1/k^1$ *vs.* $1/[G]$ and the second-order plots were used to determine the best values of *k* and *K*. A preliminary plot of $1/k^1$ *vs.* $1/[G]$ total gave a respectable value of *k* from the intercept and a rough value of *K* from the limiting slope at high glycol concentrations. These were used to calculate *f* and subsequently *K* from the slope of the second-order plot. From this value of

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(9) A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

(10) R. Adams and E. W. Adams, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 459.

TABLE I

VARIATION OF PSEUDO FIRST-ORDER RATE CONSTANTS WITH GLYCOL CONCENTRATION

pH 4–7; $[P]_0 = 0.0080\ M$

	$[G]_0$	$k^1 \times 10^3$, sec.$^{-1}$ 0.00°	$k^1 \times 10^3$, sec.$^{-1}$ 5.25°
Ethylene	0.0196	3.16	6.03
	.0235	3.40	6.62
	.0294	3.59	7.13
	.098	4.32	9.25
	.196	4.48	9.84
Propylene	0.0200	10.7	21.9
	.0240	11.4	23.9
	.0300	11.9	25.5
	.100	13.1	28.3
	.200	13.5	29.0
			29.9
meso-Butylene	0.0206	10.4	16.6
			17.0
	.0247	11.4	20.7
	.0309	12.8	24.4
	.0412	14.6	27.4
			27.8
	.103	17.7	36.6
		18.5	37.0
Trimethylethylene	0.0200	12.7	18.1
			17.9
	.0240	15.0	21.8
	.0300	17.1	27.8
	.0400	20.4	35.4
		20.3	35.9
	.0800	26.0	54.7
		0.00	−4.12
levo-Butylene	0.0100	18.4	
	.0120	22.3	
	.0140	27.4	14.5
			15.1
	.0160	28.5	15.6
	.0180	30.8	
	.0200	33.6	17.1
			17.8
	.0240	34.2	
	.0300	33.8	
	.0400		19.2
	.100		19.9
			20.9

K, values of [G] were calculated and $1/k^1$ *vs.* $1/[G]$ plotted. The entire process was repeated, the second set of calculations usually resulting in self-consistency and in agreement between the two methods for obtaining K.

TABLE II

RATE AND EQUILIBRIUM CONSTANTS

Glycol	K	$k \times 10^3$, sec.$^{-1}$
0.00 ± 0.05°		
Ethylene	193 ± 10	4.60 ± 0.10
Propylene	350 ± 20	13.7 ± 0.5
meso-Butylene	73 ± 5	20.8 ± 0.5
levo-Butylene	180 ± 20	47 ± 2
Trimethylethylene	43 ± 5	34 ± 1.5
5.25 ± 0.05°		
Ethylene	124 ± 10	10.2 ± 0.2
Propylene	215 ± 15	30.8 ± 2.0
meso-Butylene	38 ± 4	48 ± 2
levo-Butylene[a]	395 ± 20	21.3 ± 1.0
Trimethylethylene	13.7 ± 1.3	119 ± 10

[a] *levo*-Butylene glycol at −4.12°.

Values of the rate and equilibrium constants determined in this manner are given in Table II.

Errors given are estimated maximum errors, based upon reproducibility of the rate constants and agreement between the two methods for calculating K.

The thermodynamic functions for complex formation, and the activation energies for the disproportionation reaction are given in Tables III and IV.

TABLE III

THERMODYNAMIC FUNCTIONS FOR COMPLEX FORMATION AT 0°

Glycol	ΔH, kcal.	ΔF, kcal.	ΔS, e.u.
Ethylene	−12.8 ± 10%	−2.86 ± 0.02	− 36 ± 30%
Propylene	−14.0	−3.18	− 40
meso-Butylene	−18.7	−2.33	− 60
levo-Butylene	−27.8	−2.82	− 92
Trimethylethylene	−32.8	−2.04	−113

TABLE IV

ACTIVATION ENERGIES AND ENTROPIES FOR THE DISPROPORTIONATION REACTION

Glycol	$\Delta H^\ddagger$, kcal.	$\Delta F^\ddagger$, kcal.	$\Delta S^\ddagger$, e.u.
Ethylene	+22.4 ± 5%	+18.9 ± 0.0	+13 ± 20%
Propylene	+23.5	+18.3	+19
meso-Butylene	+23.5	+18.1	+20
levo-Butylene	+27.6	+17.6	+37
Trimethylethylene	+35.6	+17.8	+65

Errors given are estimated maximum errors, based upon estimated maximum errors in the rate and equilibrium constants.

With the substitution of the fourth methyl group, an abrupt change in reactivity resulted. Not only was pinacol oxidized at a much lower rate than were the other glycols studied, but the reaction became second order, first order in periodate and first order in glycol. In addition, the rate was a decided function of hydrogen ion concentration. Second-order rate constants, taken from the slopes of plots of

$$\log \frac{[P]_T}{[P]_T + [G]_0 - [P]_0}$$

versus time, were obtained over the range of pH 0.3 to 7.

Assuming IO_4^- as the reactive species, the following scheme is proposed

$$IO_4^- + G \xrightarrow{k} \text{products}$$

$$-\frac{d[P]_T}{dt} = k[IO_4^-][G] = k^1[P]_T[G]$$

where k' is a function of hydrogen ion concentration. Letting k_0 be the rate constant for the uncatalyzed reaction at pH 4–7 and k_H the rate constant for a first-order hydrogen ion catalyzed reaction, the rate expression becomes

$$-\frac{d[P]_T}{dt} = \frac{k_0 + k_H[H^+]}{f}[P]_T[G]$$

The factor f is given by

$$f = 1 + \frac{1}{K_D} + \frac{A_{H^+}\,IO_4^-}{K_1K_D\,H_5IO_6}$$

the symbols having their previous significance. A plot of log $(fk^1 - k_0)$ *vs.* log $[H^+]$ should give a

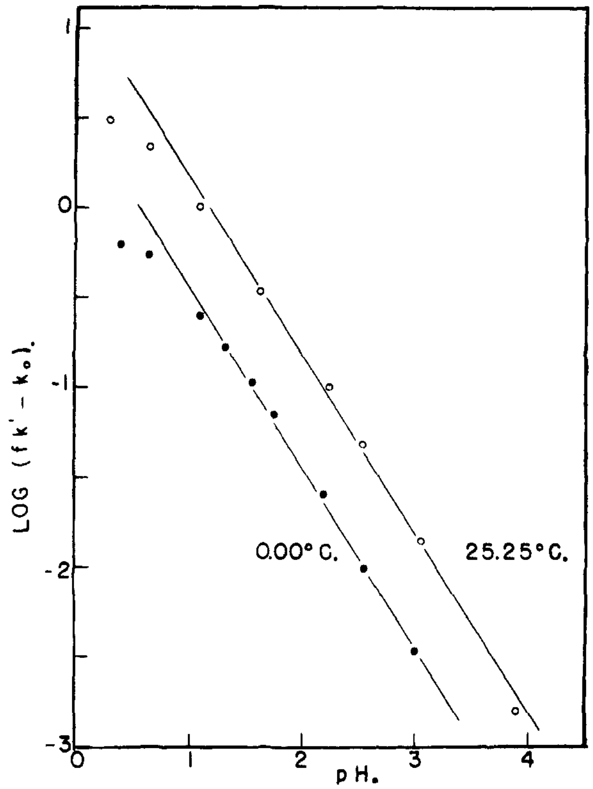

Fig. 1.—Pinacol plot showing first-order hydrogen ion dependency. Slope of each line is -1.0; intercept is log k_H/γ_{H^+}.

straight line with slope of unity and intercept equal to log k_H. If log $(fk^1 - k_0)$ is plotted against pH, the slope should be -1.00 and the intercept log k_H/H^+. Such plots are given in Fig. 1. The straight lines are drawn with slopes of -1.00. Rate constants k_0 and k_H and estimated activation energies are given in Table V.

TABLE V

RATE CONSTANTS FOR THE PINACOL OXIDATION

$$-\frac{d[P]_T}{dt} = k_0 + k_H[H^+][IO_4^-][G]$$

	0.00°	25.25°	$\Delta H^{\ddagger}$, kcal.
k_0	0.0014	0.0044	+7.2
k_H	4.0	13.2	+7.6

The pinacol reaction might still proceed through an intermediate complex. It is estimated that if the equilibrium constant for the formation of an intermediate complex were of the order of magnitude of unity, it would be difficult to detect the presence of the intermediate complex by means of rate data.

An equilibrium constant for the formation of an intermediate coördination compound with pinacol would be expected to be small, in view of the steric requirements of the four methyl groups, forcing the hydroxyls out of a *cis*-configuration. Such a consideration presumably accounts for the fact that the equilibrium constant for *levo*-butylene glycol is roughly three times as large as that for the *meso*-glycol. The observed hydrogen ion catalysis for the pinacol oxidation might be explained on the basis of the conjugate acid of the glycol being the reactive species; it seems more probable, however, that the preliminary acid-catalyzed complex formation has become the slow step with the subsequent disproportionation of the complex being a fast following step.

In conclusion, it should be pointed out that the mechanism assigned to the oxidation of the first five members of the series is indistinguishable kinetically from the following[11]

$$IO_4^- + G \overset{K}{\rightleftharpoons} C$$

$$IO_4^- + G \xrightarrow{k} \text{products}$$

In this case, the complex serves merely as a storehouse for the reactants. Since all intermediates including the activated complex are included in species C, the question is whether or not the substance C undergoes substantial rearrangement on going from the average energy to the energy of the activated complex. Thus far, this question has not been answered.

AMES, IOWA

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[11] J. E. Taylor, THIS JOURNAL, **75**, 3912 (1953), presents arguments in favor of the periodate–glycol complex being inert.