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The Periodate-Glycol Reaction. 5. Complex Formation and Kinetic Analyses of 1,2-Propanediol and 1,2-Butanediol

Jay E. Taylor* and Hitoshi Masui*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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The reactions of periodate with 1,2-propanediol and 1,2-butanediol were investigated in detail. These reactions are similar to that of ethanediol in that there are extensive formations of a periodate−glycol complex, and the IO_4^- form of periodate appears to be the primary reactant. However, they differ at pH 5.4 in that a small induction period was noted and rate equations previously used with ethanediol were inapplicable. At pH 1.08, the reactions proceeded similarly to ethanediol without a noticeable induction period. All data were fitted using a finite difference simulation (FDS) technique, and rates of the complex's formation, dissociation, and conversion to products have been evaluated at three temperatures. When feasible, the FDS rate constants were found to compare favorably to those obtained from an analytical integration procedure. The activation energies for product formation and the enthalpies of complex formation are similar to those of ethanediol.

Introduction

The formation of reaction complexes has been observed in a variety of chemical reactions. Reaction complexes may serve as intermediates or may inactivate the reactants. Previous studies have demonstrated that a complex forms in the periodate ion or periodic acid oxidations of ethanediol. This complex was assumed to be an intermediate to product formation,[1] but it was later shown that the rate data could also be explained by assuming the complex to be an inactive entity in equilibrium with the reactants.[2] Additional data from other glycols have supported the former assumption.[3]

New rate data from the oxidation of 1,2-propanediol and 1,2-butanediol have been evaluated, and it is the purpose of this paper to present these data and emphasize their significance in the light of previous observations. The emphasis centers on the roles of complexes and equilibria as they affect the oxidation reactions. Buist and Bunton[4] previously studied 1,2-propanediol and concluded that the complex acts as an intermediate.

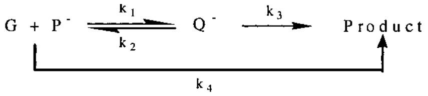
Prior Conclusions (PC). To provide a comparison of earlier works with the present data, a summary of the previous investigations follows.

PC 1: The periodate oxidations of ethanediol[5,6] and pinacol[7] were found to have maximum rates at a pH 4−6 plateau and pH ∼1.5, respectively, and pinacol[7] had a minimum rate at pH 6−7. The primary oxidant for ethanediol was determined to be IO_4^-, whereas for pinacol, it was H_5IO_6. The pH effect is solely a function of the periodic acid equilibria shown below.

$$H_5IO_6 \rightleftarrows H_4IO_6^- + H^+ \tag{1}$$

$$H_4IO_6^- \rightleftarrows IO_4^- + 2H_2O \tag{2}$$

PC 2: The oxidation of ethanediol (G) by periodate (P^-), was found to be coupled to a rapid equilibrium with a complex (Q^-), according to the scheme[2] as seen in equation (3). The maintenance of a rapid equilibrium during the reaction permitted the analytical integration of the rate data, as previously detailed.[2] The resulting first or second order rate constants were independent of glycol concentrations.



(3)

PC 3: The oxidation of pinacol[7] appeared to be second order, with no indication of or need to correct for complex formation.

PC 4: The validity of the following principle was demonstrated.[5]

Any condition that alters the ground-state energy of a reactant or reactants by an equilibrium process must in turn alter the observed second-order[8] *activation energy by an equal amount.*

PC4 is a result of the similarity of the van't Hoff and Arrhenius equations. A rigorous broad application of PC4 is appropriate under conditions whereby the rates of formation and dissociation of the complex are significantly greater than the rate of product formation. For many reactions, the impact of acid, base, or hydration equilibria fulfill these conditions. Since complex formation for the ethanediol−periodate reaction also satisfies these conditions, it has been possible to determine the heat of formation of the complex and other corresponding thermodynamic values.[2,5] These calculations are possible under the conditions indicated above, i.e., rapid equilibrium of Q^- and second order rate data as determined from a previously derived integral.[2] If however the rate of establishment of the equilibrium is slow compared to product formation and the complex is an essential intermediate, the reaction would also be second order with no kinetic evidence of complex formation. In contrast, if the rate of formation of the complex is similar to that of product formation, the two reactions would be competitive, and would deviate from simple order kinetics.

Data and Discussion

The oxidations of 1,2-propanediol and 1,2-butanediol show both similarity and contrast to the oxidation of ethanediol. Changes in acidity alter the rates in a manner similar to ethanediol; i.e., the rate maximizes over the range of pH 3−6 and decreases upon adding more acid or base. In contrast, the data at pH 5.4 cannot be integrated as was done with ethanediol.

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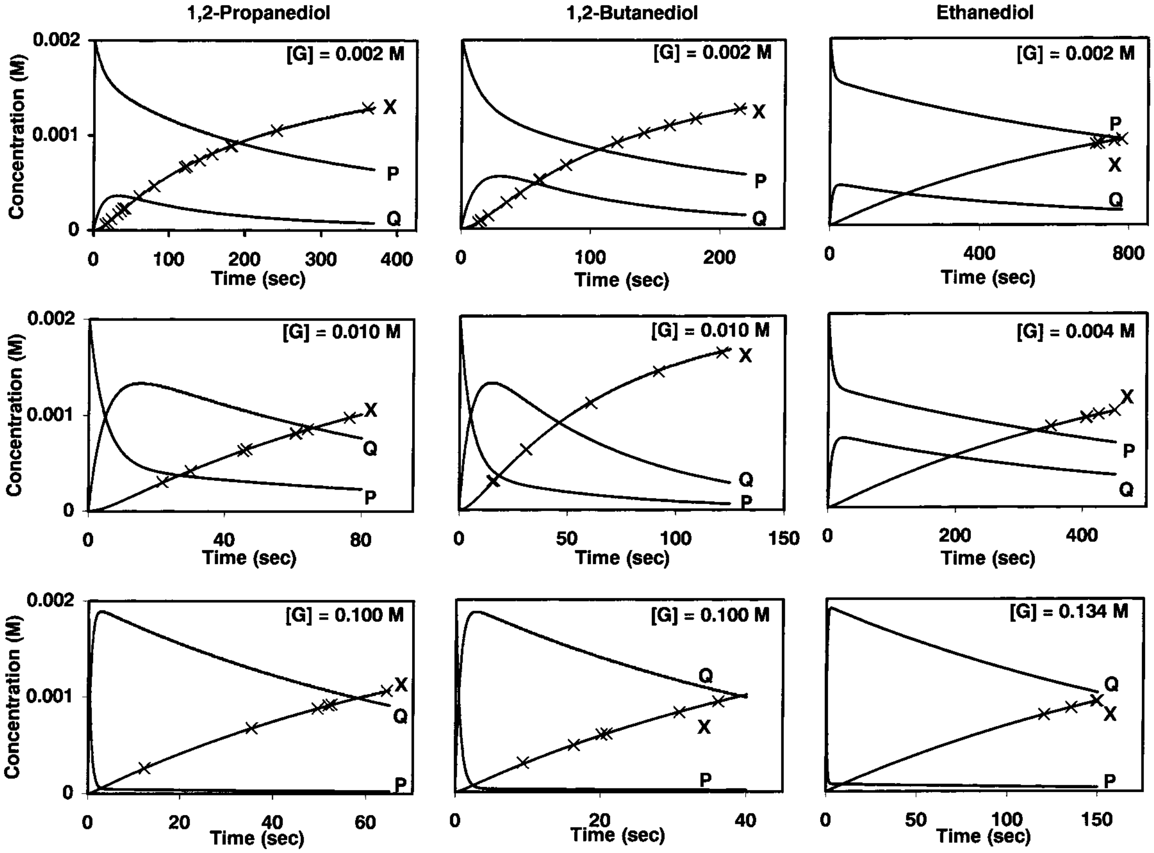


Figure 1. Experimental data fitted by the FDS procedure for the periodate oxidation of propanediol, butanediol, and ethanediol in a pH 5.4, 0.002 M aqueous periodate solution at 0 °C. P, Q, and X denote the calculated concentrations of periodate, intermediate, and product, respectively. The crosses are the experimental data for the product.

The Data at pH 5.4. The rate data at pH 5.4 (representing a plateau of rates as previously noted), 0 °C, and a glycol:periodate (G:P$^-$) ratio of 1:1 do not follow first or second order kinetics. The apparent second order rate constants increase with time, whereas the apparent first order rate constants exhibit a maximum. Also note that the observed rate data are characterized by an initial period of induction (see Figure 1). At higher temperatures and higher G:P$^-$ ratios, these effects become less evident. At G:P$^-$ ratios of 25:1, reasonably well stabilized constants were obtained based on either first or second order calculations. Under these conditions, the data may be interpreted as either first or second order kinetics regardless of the actual mechanism. As has been, and will be, demonstrated, second order assumptions have a greater utility for energy evaluations.

Periodate oxidations of glycols can be characterized by a set of individual reaction steps:

$$\mathrm{P}^- + \mathrm{G} \rightarrow \mathrm{Q}^- \qquad \mathrm{rate}_1 = k_1 P^- G \tag{4}$$

$$\mathrm{Q}^- \rightarrow \mathrm{P}^- + \mathrm{G} \qquad \mathrm{rate}_2 = k_2 Q^- \tag{5}$$

$$\mathrm{Q}^- \rightarrow \mathrm{product} \qquad \mathrm{rate}_3 = k_3 Q^- \tag{6}$$

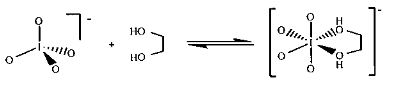
$$\mathrm{P}^- + \mathrm{G} \rightarrow \mathrm{product} \qquad \mathrm{rate}_4 = k_4 P^- G \tag{7}$$

$$K_\mathrm{F} = 1/K_\mathrm{D} = k_1/k_2 \tag{8}$$

where K_F and K_D are equilibrium constants for formation and decomposition of the complex Q$^-$. In a previous publication,[5] k_3 and k_4 were denoted k_S and k_A, respectively.

The impact of these reactions depends on rates$_{1-4}$ of eqs 4–7. If rate$_1$ and rate$_2$ are significantly faster than rate$_3$ or rate$_4$, then the conditions previously described under PC2 and PC4 apply, and the data from such a reaction can be quantitatively evaluated by integration as per PC2. The integration technique allows the evaluation of K_F or K_D and k_3 or k_4 when applicable.[2,5] If however rate$_1$ and rate$_2$ are competitive or overlapping with rate$_3$ or rate$_4$, the integration technique is no longer valid.

The Complex. Replacement or removal of OH groups from H_5IO_6 or $H_4IO_6^-$ occurs with much greater facility at neutral pH than a corresponding dehydration of a glycol. Thus, it may be assumed that in forming the complex the oxygens of the glycol displace the H_5IO_6 oxygens to form a complex similar to that shown in eq 9, and that the aldehyde or ketone oxygens of the product originate from the glycol. This mechanism is supported by the oxygen-18 labeling work of Bunton and Shiner.[9] For the complex to form products the glycol hydrogens must migrate, and this may occur through a tautomerization as shown below.



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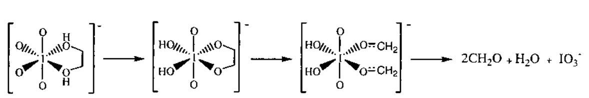

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Computer Simulation. Since there appears to be no rigorous mathematical solution for eqs 5–7 when overlapping of rates occurs, a finite difference simulation (FDS) technique has been developed and applied. Although somewhat less precise than

TABLE 1: Rate Constants

		FDS procedure				integration method		
°C	pH	k_1	k_2	k_3	K_F	k_3	k_4	K_F
1,2-Propanediol								
0.00	5.4	18.0	0.041 7	0.012 2	432		(5.27)^a	
15.00	5.4	20.2	0.203	0.118	100		(11.8)^a	
25.00	5.4	20.8	0.533	0.470	39		(18.3)^a	
0.00	1.08	10.9	0.201	0.005 08	54	0.005 02	0.267	53.2
15.00	1.08	11.2	0.261	0.045 7	43	0.043 2	1.66	38.5
25.00	1.08	14.8	0.420	0.188	35	0.162	4.63	28.6
1,2-Butanediol								
0.00	5.4	16.5	0.026 4	0.018 1	625		(11.3)^a	
15.00	5.4	19.9	0.136	0.172	146		(25)^a	
25.00	5.4	23.2	0.465^b	0.642^b	49.9^b		(32)^a	
0.00	1.08	10.4	0.123	0.007 03	85	0.006 94	0.560	80.6
15.00	1.08	22.5	0.339	0.0606	66	0.059 5	3.38	56.8
25.00	1.08	35.5	0.662	0.238	54	0.221	9.63	43.5
Ethanediol								
0.00	5.4	18.7	0.097 3	0.004 39	192	0.004 38	0.81	185
0.00	1.08					0.002 35	0.042	19.7

[a] From eq 12 using FDS data. [b] These data were attained with very short reaction times (~2 s).

integration, all of the rate constants can be evaluated, and K_F can be calculated from eq 11 or 12 under all conditions.

$$k_1/k_2 = K_F \tag{11}$$

$$K_F k_3 = k_4 \tag{12}$$

The validity of eq 12 was previously demonstrated.[5] Although k_4 appears not to be a critical entity, its determination is significant in the evaluation of the constants related to complex formation, as will be demonstrated.

Typical concentration versus time data from the FDS computations are shown in Figure 1. Note that, at 1:1 ratios of G:P$^-$, Q$^-$ is formed at a detectable rate, and its initial upsurge is concurrent with its decomposition to product. At higher ratios of G:P$^-$, larger concentrations of Q$^-$ form more rapidly and the decomposition occurs at a greater rate. These effects are dramatically portrayed by the graphs of Figure 1 at various glycol concentrations for both propanediol and butanediol at 0 °C. Also, increases in temperature increase the rate of decomposition (eq 6) and correspondingly decrease complex concentrations (not shown).

The observations of Buist and Bunton on 1,2-propanediol[4] were made under conditions of excess glycol, and a rate equation applicable to these pseudounimolecular conditions was used. The FDS procedure now allows data to be analyzed at all concentrations.

The FDS procedure gives a complete reproduction of the experimental data based on eqs 4−6. If eq 6 is replaced by eq 7, the induction periods are not duplicated; therefore, eq 6 is deemed the dominant pathway. This obviously supports the proposal by earlier workers on the intermediacy of the complex, but does not eliminate the possibility that k_4 may be a secondary reaction.

The possibility that $Q^- + P^- \rightarrow$ product was also considered, but the kinetic data at two or more glycol concentrations could not be reproduced by one set of rate constants; thus, this proposal was rejected.

To test further the validity of the computer simulation, earlier data on ethanediol was subjected to the FDS procedure. The results were compared to those obtained from the integration method, with good agreement (Table 1). These comparisons are possible through eqs 11 and 12.[2,5] The FDS procedure also shows that Q$^-$ is formed very rapidly compared to product formation for ethanediol, as had been previously assumed.[2,5] See Figure 1 where the graphs of the three glycols are compared.

Activation Energies at pH 5.4. From eqs 11 and 12, it is obvious that

$$\Delta H_F = E_1 - E_2 = E_3 - E_4 \tag{13}$$

where ΔH_F is the enthalpy of formation of the complex intermediate, and $E_1 - E_4$ are the activation energies for the reaction steps in eqs 4−7, respectively. See footnote *a*, Table 2. Calculations of activation energies for the ranges 0−15, 0−25, and 15−25 °C, using both first and second order rate data, show some interesting trends and variations (see Table 2). The first order activation energies for the decomposition of Q$^-$ (eq 6) are essentially constant at 23 ± 1 kcal/mol over the entire ranges of temperatures and pH. This value of 23 ± 1 kcal/mol was also noted for ethanediol, suggesting a general consistency among a variety of glycols. Since ΔH_F and E_4 (second order activation energy) are influenced by pH and other reaction conditions in the same way, it is clear from eq 13 that the variations in ΔH_F and E_4 cancel, and E_3 remains a constant. Duke and Bulgrin[10] also observed a constancy of E_3 among certain glycols, but with no further explanation.

Values of E_4 at 12.5 °C are in the range of 7 kcal/mol, indicating that ΔH_F is about 15.5 cal/mol for both glycols according to eq 13. These values are similar to those from ethanediol, but are less precise.

The Data at pH 1.08. As previously noted, the oxidation rates of these substituted glycols decrease upon adding acid or base. In basic solutions, significant buffer effects have been observed. To avoid this additional complexity, only acid media have been evaluated.

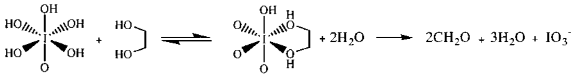
The rates at pH 1.08 have been determined both by computer simulation and by integration. The results are consistent and are shown in Table 1. The decreased rates at the lower pH for the oxidations of 1,2-propanediol and 1,2-butanediol are similar to that of ethanediol, but opposite that of pinacol, which has an increased rate at low pH. For the ethanediol and the present glycols, IO_4^- or $H_4IO_6^-$ acts as the main oxidant, whereas for pinacol H_5IO_6 acts as the main oxidant.

Activation Energies at pH 1.08. The same general considerations apply at pH 1.08 as were indicated at pH 5.4. Again, E_3 is unchanging at 23 kcal/mol, but E_4 is much larger at pH 1.08 than at pH 5.4, and there is a corresponding decrease of ΔH_F in keeping with eq 13. See Table 2. The reactions at pH 5.4 and pH 1.08 are represented by eqs 9 and 14, respectively.

TABLE 2: Activation Energies Computed by the Arrhenius Equation[a,b]

		FDS procedure				integration method		
°C	pH	E_1	E_2	E_3	ΔH_F	E_3	E_4	ΔH_F
				1,2-Propanediol				
7.5[c]	5.4	1.2	16.5	23.7	−15.3		(8.4)[g]	
12.5[d]	5.4	0.9	16.5	23.6	−15.6		(8.0)[g]	
20.0[e]	5.4	0.5	16.5	23.5	−16.1		(7.4)[g]	
7.5[c]	1.08	1.0	2.7	22.8	−2.4	22.4	19.0	−3.4
12.5[d]	1.08	2.0	4.8	23.4	−2.8	22.5	18.3	−4.0
20.0[e]	1.08	4.8	8.1	24.1	−3.5	22.6	17.5	−5.1
				1,2-Butanediol				
7.5[c]	5.4	2.0	17.0	23.5	−15.1		(8.4)[g]	
12.5[d]	5.4	3.0	17.9	23.1	−14.8		(8.3)[g]	
20.0[e]	5.4	4.8	19.7[f]	22.5[f]	−13.6[f]		(8.9)[f,g]	
7.5[c]	1.08	8.0	10.6	22.4	−2.6	22.4	18.7	−3.7
12.5[d]	1.08	7.9	10.9	22.8	−2.9	22.4	18.4	−4.0
20.0[e]	1.08	7.8	11.4	23.3	−3.4	22.4	17.8	−4.6

[a] In previous papers[2,5] the activation energies were tabulated as $\Delta H^{\ddagger}$ from $\Delta H^{\ddagger} = E - RT$. Either $\Delta H^{\ddagger}$ or E fits equally well with PC 4 or eq 13 since this correction is not applied to ΔH_F. [b] E values from FDS data have an uncertainty of ±0.5 or greater. [c] 0.00−15.00 °C. [d] 0.00−25.00 °C. [e] 15.00−25.00 °C. [f] See footnote *b* in Table 1. [g] From eq 13 using FDS data.


(14)

Under acidic conditions water is released to form the complex. Additional energy is required to remove these water molecules, and it is this energy that must be added to E_4 at pH 5.4 to give E_4 at pH 1.08. If other factors were equal, ΔH for the reaction $IO_4^- \rightarrow H_5IO_6$ could be evaluated. Unfortunately, $H_6IO_6^+$ forms in strongly acidic solutions with a significant heat of formation, as previously observed.[7]

$$H_5IO_6 + H^+ \rightarrow H_6IO_6^+ \qquad (15)$$

Reaction 15 overlaps and distorts the equilibria, eqs 1and 9, to the extent that a large decrease in rate occurs as the pH is decreased from 1.5 to 0.6. Correction for eq 15 is not feasible at this time since the equilibrium constant has not been evaluated. There is also a possible change in mechanism from pH 5.4 to 1.08.

Conclusion

Although the possibility exists that different glycols may proceed by differing mechanisms, the similarity of activation energies, as seen in this paper, suggests that this is not the case for these glycols. However, there are at least modest differences in mechanisms at pH 5.4 and 1.08.

Experimental Section

FDS Procedure. The kinetic data were simulated using the finite difference method. The differential equations were based on eqs 4−6 with time increments of 1/6400 the overall duration of the experimental kinetic run. The rate constants were determined using a least-squares, nonlinear, grid-search algorithm.[11] Low concentration (0.002 M) and high concentration (0.10 or 0.134 M) data were simultaneously fitted for each glycol, minimizing the product, π_{SD}, of the standard deviations between experimental and simulated data from the two sets of concentration data. The dependence of the fit on each rate constant was estimated by fixing the rate constant, 10% above and below the optimized value, and reoptimizing the fit with the remaining two rate constants. The change in π_{SD} was used to estimate the variance of each rate constant according to a published procedure.[11]

Titration. The acid iodide stop reaction and thiosulfate titration have been employed for periodate analyses with excellent accuracy.[2,7] To improve efficiency, a new titration technique has been developed. Two burets are employed. The first buret features a 9.809 mL bulb on top of a 60 cm long, 2 mm i.d. capillary tube with 10 evenly spaced 0.3 mL volume bulbs and calibrations between bulbs. The buret contains 0.0237 M $Na_2S_2O_3$. The titration is carried to a near end point using the top bulb and an appropriate number of small bulbs.

The second buret is 56 cm long precision bore tube with 500 divisions and a capacity of 4 mL. It is filled with the above $Na_2S_2O_3$ diluted 1:5. Thyodene indicator is added. The solution is transferred to a Nessler type tube for the final addition.

Of most importance, both burets are coated with silicone,[12] which allows total drainage under rapid flow conditions. Each buret is filled from a reservoir and has an autofill top and a straight bore stopcock containing a PFTE plug with metering valve (Kimble). The overall titration is done rapidly with a reproducibility of ±0.02.%.

Both 1,2-propanediol and 1,2-butanediol (99%, Aldrich) were redistilled, taking only the center portion. The periodate (99.99%, Aldrich) was used as obtained, but one purchase was found to be impure and was recrystallized three times before use.

Acknowledgment. The authors are greatly indebted to Larry Maurer for his construction of the burets and reaction flasks.

References and Notes

(1) An intermediate cyclic ester or coordination complex, as suggested by F. R. Duke (*J. Am. Chem. Soc.* **1947**, *69*, 3054) was based on earlier proposals. This idea was further promoted by C. J. Buist and C. A. Bunton (*J. Chem. Soc.* **1954**, 1406).

(2) Taylor, J. E. *J. Am. Chem. Soc.* **1953**, *75*, 3912.

(3) For example: Bulgrin, V. C.; Dahlgren, G., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 3883.

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(6) Taylor, J. E.; Soldano, B.; Hall, G. A. *J. Am. Chem. Soc.* **1955**, *77*, 2656.

(7) Taylor, J. E. *J. Phys. Chem.* **1995**, *99*, 59.

(8) Since the initial concept was established from second order data, the statement has been clarified to include this restriction.

(9) Bunton, C. A.; Shiner, V. J. *J. Chem. Soc.* **1960**, 1593.

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