The Periodate−Glycol Reaction. 4. Activation Energies, Equilibria, and a Mechanism

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The reaction of ethanediol with periodate ion has been investigated in detail at six temperatures, seven pH's, and multiple glycol concentrations. From these data, a quantitative determination of rate constants and activation energies as well as equilibrium constants and enthalpies for complex formation has been made as they vary with the applied conditions. The data have been interpreted as either first order with the complex serving as an intermediate or as second order with the complex serving as an inert entity. Additional equilibria that impact the reaction are hydration of IO_4^- in neutral conditions and the protonation of H_5IO_6 in acid solutions. In evaluating the data, the following generalization has been applied: *Any condition that alters the ground-state energy of a reactant or reactants by an equilibrium process must in turn alter the activation energy by an equal amount.* The conclusions that have been made are as follows: (1) IO_4^- is the primary reactant with ethanediol; H_5IO_6 is a secondary reactant. (2) Characteristics of the previously identified complex are further defined. (3) There are complementary deviations in second-order activation energies versus enthalpies of complex decomposition as temperatures and pH are changed. The second-order activation energy plus corresponding enthalpy of complex decomposition equals the first-order activation energy which is invariant under all conditions. (4) There is no correlation between rate constants and complex formation. (5) Pinacol does not form an identifiable complex and reacts primarily with H_5IO_6, yet the variations in activation energies with pH are essentially the same for pinacol and second-order ethanediol. (6) With the evidence of similarity of second-order ethanediol rate data to pinacol data and the constancy of first-order ethanediol rate constants, it is concluded that the complex under consideration is not an intermediate, but instead deactivates the reactants. A second presumed complex or deviate from the observed complex is the true intermediate.

Introduction

The system under primary consideration is the quantitative reaction of ethanediol with periodate ion or periodic acid to form formaldehyde and iodate ion. Prior publications have been previously reviewed.[1,2] This work is a continuation of an earlier study.[1] The corresponding reaction of pinacol has been evaluated in detail.[2] Although pinacol does not form a detectable complex,[2,3] ethanediol does.[1,4] The intermediacy of the complex has been generally assumed[4,5] for the reaction of ethanediol. However, this assumption has been questioned.[1]

The complex is defined as

$$K_D = P^-G/Q^- = 1/K_F \tag{1}$$

where K_D and K_F are the dissociation and formation constants, and P^-, G, and Q^- are the effective concentrations (or activities) of periodate ion, glycol, and complex, respectively, under equilibrium and/or reaction conditions. For the periodate−ethanediol reaction, the complex forms and decomposes at a very rapid rate (compared to product formation) such that true equilibrium conditions are maintained during the bulk of the reaction.

With the assumption of intermediacy of Q^- the rate is

$$dx/dt = k_S[Q^-] \tag{2}$$

where k_S is the "first-order" rate constant.

Upon assuming *nonintermediacy* of Q^-, the rate is

$$dx/dt = k_A[P^-][G] \tag{3}$$

and k_A is the "second-order" rate constant.

Since $k_S[Q^-] = k_A[P^-][G]$ and with eq 1

$$k_S = k_AK_D = k_A/K_F \tag{4}$$

Because of the equilibrium, eq 1, the terms "first" and "second order" are of no real significance, but will be used primarily for convenience.

Due to the interdependence of P^-, G, and Q^-, i.e., $a - x = G + Q^-$ and $b - x = P^- + Q^-$, where a and b are the initial glycol and periodate ion concentrations, respectively, and x is the amount reacted at any time, t, it was necessary to incorporate a quadradic equation to derive precise rate equations. These equations have been integrated to give eqs 5 and 7 in an earlier publication[1] and are used herein for the computation of rate and equilibrium constants for ethanediol. This, of course, was unnecessary for pinacol.[2]

Later, Buist and Bunton[4] used the equation

$$k' = kKG/(1 + KG) \tag{5}$$

as first suggested by Duke.[5] Equation 5 is imprecise because the relationships among P^-, G, and Q^- are approximated. These investigators did work on ethanediol only at 0 °C, and no calculations of activation energies could be made. Essentially, all their work has been done with excess glycol concentrations, i.e., pseudo-first-order rate conditions, and from this they concluded that the periodate−glycol reaction is truly first order. Further, Buist and Bunton did not identify the "second order" rate constant as I had previously described it[1] or even considered it as a possibility. In so doing, they missed some highly critical functional and mechanistic aspects of this reaction.

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TABLE 1: Rate and Equilibrium Constants[a]

		pH							
	T (°C)	5.60	4.10	3.62	3.15	2.02	1.58	1.08	0.61
1. $k_A{}^{b,c}$	45.06	5.39	5.46	5.58	5.76		5.12	4.07	2.962
2. $K_F{}^{c,f}$	45.06	2.58	2.58	2.67	2.79		5.35	6.59	7.18
3. $\Delta H_A{}^{\ddagger\,g}$	35^d	5.90	6.03	6.21	6.63		11.50	14.76	17.46
4. $k_A{}^{b,e}$	35.04	3.898	3.911	3.938	3.989	3.544	2.878	1.939	1.221
5. $K_F{}^{c,f}$	35.04	6.12	6.12	6.23	6.36	7.37	7.72	8.35	8.51
6. $\Delta H_A{}^{\ddagger\,g}$	30^d	6.11	6.18	6.26	6.73	9.84	12.36	15.66	18.26
7. $k_A{}^e$	25.02	2.697	2.695	2.702	2.667	1.998	1.413	0.794	0.4337
8. $K_F{}^f$	25.02	15.4	15.4	15.4	15.3	13.7	12.35	10.75	10.1
9. $\Delta H_A{}^{\ddagger\,g}$	14.5^d	6.98	7.02	7.34	8.12	13.13	16.16	18.30	19.37
10. $\Delta H_D{}^h$	14.5^d	16.4	16.3	16.1	15.3	9.9	6.7	4.1	2.7
11. $k_A{}^e$	15.03	1.749	1.755	1.723	1.650	0.956	0.565	0.2703	0.1365
12. $K_F{}^f$	15.03	41.15	41.15	40.3	38.9	26.5	19.6	14.1	12.1
13. $\Delta H_A{}^{\ddagger\,g}$	9.5^d	7.12	7.25	7.53	8.54	14.07	17.07	18.70	19.54
14. $\Delta H_D{}^h$	9.5^d	16.2	16.0	15.7	14.8	8.7	5.6	3.7	2.3
15. $k_A{}^e$	3.99	1.025	1.019	0.981	0.876	0.3455	0.1657	0.0708	0.03371
16. $K_F{}^f$	3.99	126.6	125.6	120.5	108.7	48.5	28.9	18.2	14.2
17. $\Delta H_A{}^{\ddagger\,g}$	7.5^d	7.47	7.56	7.88	8.87	14.67	17.34	18.78	19.53
18. $\Delta H_D{}^h$	7.5^d	15.6	15.5	15.1	14.3	8.0	5.3	3.5	2.0
19. $k_A{}^e$	0.00	0.810	0.804	0.765	0.667	0.2212	0.1012	0.04214	0.01980
20. $K_F{}^f$	0.00	185	182	172	154	57	32.6	19.7	14.7
21. $\Delta H_A{}^{\ddagger\,g}$	2^d	8.32	8.38	8.83	9.73	16.26	18.04	19.01	19.51
22. $\Delta H_D{}^h$	2^d	14.3	14.2	13.4	13.1	6.1	4.5	3.0	1.3

[a] "First-order" rate constant $k_S = k_A/K_F$. "First-order" activation energies: $\Delta H_S{}^\ddagger = 22.7 \pm 0.5$ kcal/mol under all conditions 0−25 °C from eq 11. [b] Corrected using extrapolated K_F data. [c] Extrapolated from data at 25 °C and below; ΔH_D at 35 and 45 °C are not included due to their uncertainty. [d] Estimated temperatures, i.e., averages of 45/25 (35), 35/25 (30), 25/4 (14.5), 15/4 (9.5), 15/0 (7.5), 4/0 (2) °C. [e] Units, L/(mol s); k_A = "second-order" rate constant. [f] Units, L/mol; $K_D = 1/K_F$; K_F and K_D are formation and decomposition constants for Q. [g] Units kcal/mol; $E_A - RT = \Delta H_A{}^\ddagger$, the "second-order" activation energy. [h] Units, kcal/mol; $\Delta H_F = -\Delta H_D$; enthalpies of formation and decomposition.

Experimental Section

The rapid, high-precision experimental procedures used in obtaining the present data have been described in detail.[2] Although the experimental procedure has been previously described,[2] some further details will follow.

To start the reaction, 9.7821 ± 0.0006 mL each of 0.002 000 M KIO_4 and a selected glycol, using a silicone-coated autopipet, were placed in dual-compartment flasks.[1,2] Upon attaining temperature in the water bath, the reaction was started abruptly and stopped instantaneously by the described procedure.[2] The stop solution was 2 mL of 1 M KI mixed with 10 mL of 0.1 M H_3PO_4. The resulting I_2 was then mainly reduced with 9.7260 ± 0.0006 mL of 0.076 M $Na_2S_2O_3$, and the titration was completed with 0.0152 M $Na_2S_2O_3$ from a microburet using Thyodene indicator and a Nessler type tube to detect the end point.

Glycol reduces IO_4^- to IO_3^- but acid KI reduces IO_4^- to I_2, thereby giving a very large blank for the titration. Although neutral KI reduces IO_4^- to IO_3^-, this reaction is not instantaneous and can serve as a competing instead of a stopping reaction. Also, with neutral KI careful pH adjustment prior to adding the stop is essential; otherwise, highly erratic data are obtained.

Despite the large blank with acid KI, it has been possible to attain reproducibilities of ±0.2% in the observed rate constants as with pinacol,[2] when the reaction is carried roughly to 50% completion. At 35 and 45 °C, the deviation is somewhat larger. The $Na_2S_2O_3$ is standardized with 0.002 000 M KIO_4. Three-fourths of this titer is subtracted from each reactant titer; this value divided by one-fourth of the standardization titer times 0.002 M KIO_4 gives $b - x$ for the rate equation.

All experiments used 0.002 000 M KIO_4 at eight pH values. The ethanediol concentrations included 0.002 000, 0.008 000, 0.032 00 and 0.1280 M at 3.99, 14.98, and 25.02 °C, 0.002 000, 0.004 00, and 0.1368 M at 0 °C, and 0.002 000 and 0.004 00 M at 35.04 and 45.06 °C.

TABLE 2: Sample of Original Data at pH 2.0 and 15.03 °C Using 0.002 000M KIO_4

glycol	time (s)	$b - x^a$ ($M/\times 10^2$)	k(obs)	k_A	$k_A(\mathrm{ave})^b$	K_D or $1/K_F$
0.002 000	378.7	0.1198	0.883	0.954	0.953	0.0377
	465.7	0.1097	0.884	0.951		
	413.1	0.1157	0.882	0.951		
0.008 000	93.45	0.1162	0.771	0.952		
	105.2	0.1086	0.776	0.955		
	86.21	0.1208	0.774	0.956		
0.032 00	29.77	0.1238	0.510	0.950		
	31.80	0.1197	0.511	0.951		
	34.31	0.1143	0.517	0.961		
0.128 0	20.72	0.1132	0.2155	0.946		
	19.70	0.1159	0.2172	0.955		
	22.36	0.1074	0.2182	0.958		

[a] $b - x = [IO_4^-]$ at time t. [b] Best value of K_D was determined, and k_A was evaluated. Minor corrections are then applied to k_A.

From these data, computations of the rate constants k_A and equilibrium constants K_D were made at each pH and temperature combination using eqs 5 and 7 of an earlier paper.[1] Excellent consistency for k_A and K_D was obtained over each range of glycols. The results are tabulated in Table 1. Examples of the original data that were used in the computation of Table 1 are given in Table 2. Note that 12 or more rate determinations were made for each k_A−K_D pair at 4−25 °C.

Data in basic solutions are not included because of the necessity of using buffers that affect the reaction kinetics.

All molar solutions were made at 20 °C, and corrections for volume changes were applied at the temperatures noted above. pH was measured or estimated by interpolation or from related data at each temperature. If appropriate, each rate was altered proportionally to the rate of change with pH so that the rates at different temperatures could be compared at the same pH, as was done with pinacol.[2] Activation energies were calculated between the indicated two temperatures and are assigned midpoint temperatures. Graphing procedures give a much lower sensitivity.

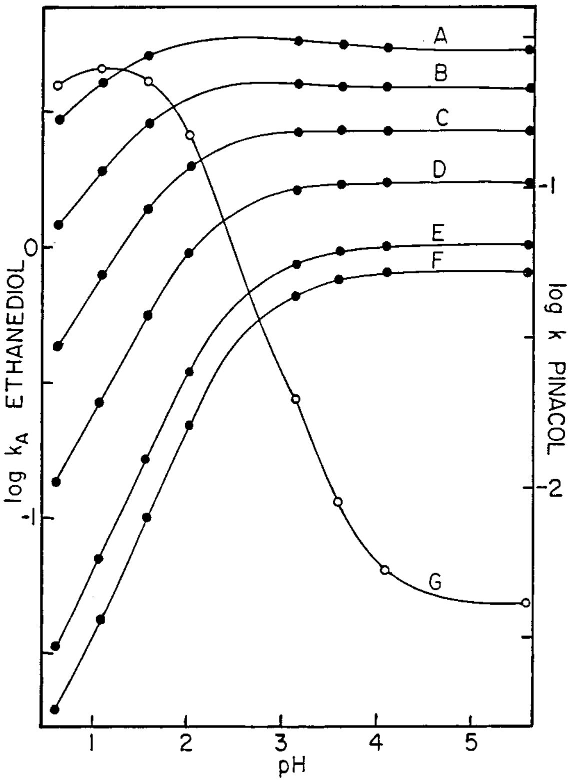

Figure 1. Plots of log k_A ("second-order" rate constants) vs pH for ethanediol and pinacol. Units for k, L/(mol s). A, 45.06; B, 35.04; C, 25.02; D, 14.98; E, 3.99; F, 0.00 °C. G represents pinacol at 25 °C.

Ethanediol, 99.5% pure, was redistilled taking only the middle fraction. Potassium periodate, 99.99% pure, was used for the periodate solutions which were stored in a dark area to avoid decomposition by light. These chemicals were supplied by Aldrich Chemical Co.

Data and Discussion

Rate Data. The computed rate data are listed along with corresponding activation energies in Table 1. The equilibrium complex with enthalpies of formation are also included. Each set of rate data with constants is identified by a single subscript.

In Figure 1, the "second order" rate constants k_A are graphed to show the variation with pH. For contrast, these data are compared with pinacol at 25 °C which is also second order, but without the complication of complex formation.

Correlation with pH. The rates of oxidation of ethanediol by KIO_4 are in keeping with the following equation, but with modest deviations at low pH.

$$k_A = kK_i/(K_i + H^+) \qquad (6)$$

where K_i is the ionization constant for periodic acid[6] and k is the corrected rate constant. Assuming the ionization constant K_i for H_5IO_6 is 0.023 at 25 °C[6] and the rate constant k_A is 2.697 at pH 5.6 at 25 °C, the calculated k at pH 0.6 is ~0.18. The observed k_A at 25 °C and pH 0.6 is 0.434, which is more than double the calculated k.

The rate of oxidation of pinacol with pH, like ethanediol, was also previously shown to correlate well, but not precisely, with eq 7 showing a small excess rate in neutral solutions and a maximum peak at pH 1−1.5.

$$k' = k[H^+]/(K_i + [H^+]) \qquad (7)$$

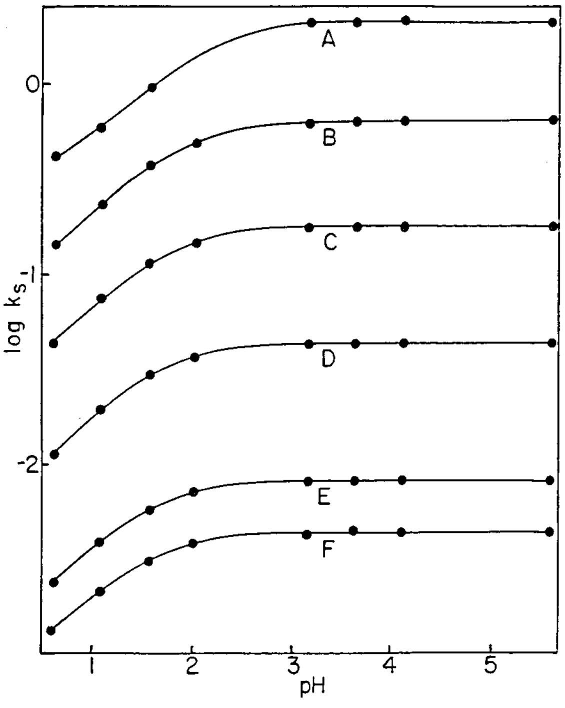

Figure 2. Plots of log k_S ("first-order" rate constants) versus pH for ethanediol. Units for k_s, s^{-1}. A, 45.06; B, 35.04; C, 25.02; D, 14.98; E, 3.99; F, 0.00 °C.

Thus, both glycols exhibit dual reactivity with both H_5IO_6 and IO_4^- as will be further demonstrated in the Comparisons with Pinacol section.

Another equilibrium has been shown to affect the rate of pinacol oxidation[2] and should also be of significance for ethanediol.

$$H^+ + H_5IO_6 \rightleftarrows H_6IO_6^+ \qquad (8)$$

The effect on ethanediol is to reduce the rate in acid solutions, thereby accounting in part for the previously described differences in predicted and observed rates. In Figure 1, a small maximum is seen at pH 2 at 45 °C followed by a modest decrease in rate constants with decreasing pH. It is thereby indicated that at 45 °C a sizable portion of the reaction of ethanediol is with H_5IO_6. The large activation energies at pH 0.6−1.5, compared to those at pH 5.6, indicate a larger proportional increase in rate at higher temperatures for the reaction with H_5IO_6 as compared to the reaction with IO_4^-. For example, compare pH 5.6 and 0.61, line 21, Table 1.

The much smaller "first order" rate constants, k_S, also vary with pH but do not correlate with eq 6 at 25 °C. See Figure 2. The reason is from eq 4; k_S is a product of k_A and K_D or $1/K_F$. Since K_D or K_F does not follow eq 6, as seen in the following section, neither can k_S follow eq 6 with any degree of precision. The rigidity of the graphs of k_S at various temperatures is seen by comparing Figures 1 and 2. Since K_i, the ionization constant, varies with temperature, there should be a corresponding variation in k_S similar to k_A in Figure 1. This is not the case, thereby indicating its lack of sensitivity to change with the ionization constant.

It is interesting to note that Buist and Bunton found excellent correlations in their "first-order" pH−rate constant comparisons.[4] It appears, therefore, that they were in error due either to inadequate data and/or a misinterpretation of the data (eq 5, etc.).

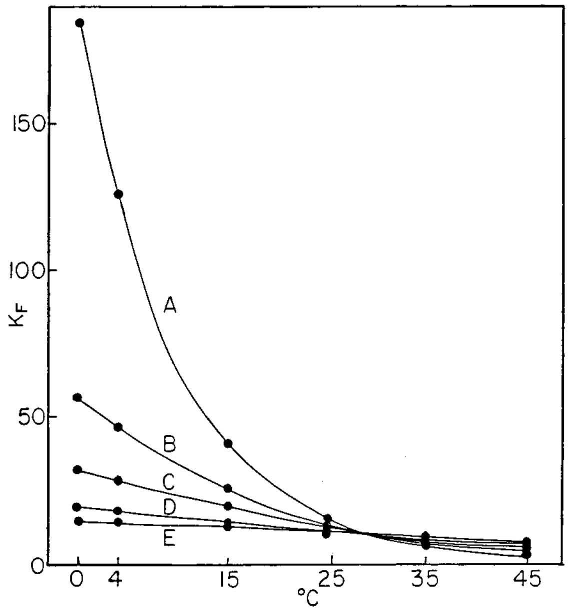

Figure 3. K_F, complex Q^- formation constants vs temperature at pH: A, 5.60; B, 2.02; C, 1.58; D, 1.08; E, 0.61.

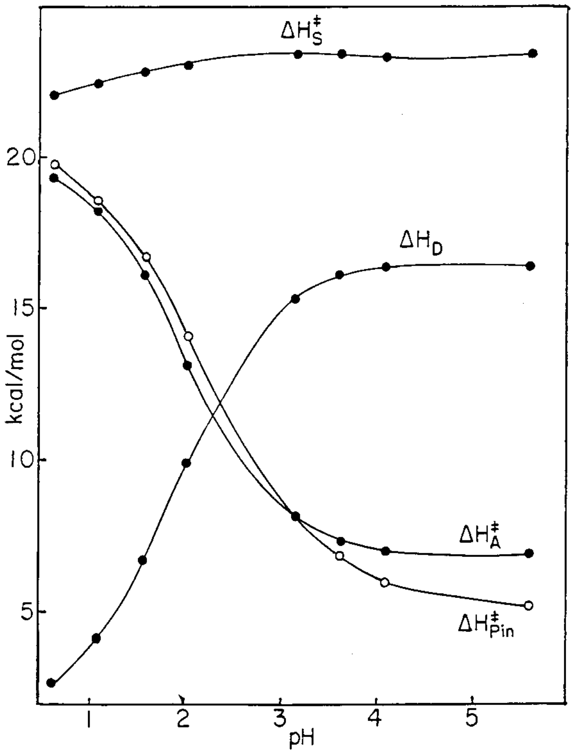

Figure 4. Comparison of ΔH values. $\Delta H_S^\ddagger$ and $\Delta H_A^\ddagger$ are "first"- and "second"-order activation energies, respectively, for ethanediol at 14.5 °C; $\Delta H_{Pin}^\ddagger$ is the second-order activation energy for pinacol at 20 °C. ΔH_D is the enthalpy for complex Q^- decomposition.

The Complex. Equilibrium constants for complex formation, K_F, as they vary with pH are graphed in Figure 3. At 0−25 °C, K_F increases with increasing pH, e.g., line 20, Table 1, but due to the corresponding decrease in enthalpy, ΔH_F (increase in ΔH_D), with increasing pH (Figure 4) there is a reversal of K_F, and the overall much smaller values of K_F at 35 and 45 °C decrease with increasing pH, e.g., line 2, Table 1. Obviously there is no correlation of K_F with eq 6. At 35 and 45 °C, the K_F are sufficiently small that they could not be experimentally determined with good accuracy so the numbers listed in Table 1 at 35 and 45 °C (lines 2 and 5) for K_F were determined by extrapolation using the Arrhenius equation. These small values of K_F were used to correct the experimental second-order rate constants to give the numbers listed with k_A at 35 and 45 °C. It may be concluded that, with further increases in temperature, experimental evidence for the presence of Q^- would become nonexistent.

Interdependence of Enthalpies and Activation Energies. Since ΔH is computed from a ratio of equilibrium constants by the van't Hoff equation and activation energies from a ratio of rate constants by the Arrhenius equation, any change in ΔH that results from a change of active concentration of reactant or reactants must be reflected in the change in observed activation energy. More precisely stated, the principle is as follows:

Any condition which alters the ground-state energy of
a reactant or reactants by an equilibrium process must
in turn alter the observed activation energy by
an equal amount (9)

The above principle is supported by previous data. See Tables I, II, III, and IV of ref 1. Corrections were made for two equilibria: one for complex formation using eq 1 and the other for hydration equilibria,

$$IO_4^- + 2H_2O \rightleftharpoons H_4IO_6^- \qquad \Delta H = -10.9\ \text{kcal/mol}^6 \tag{10}$$

Constant values for the "second order" activation energy and for the equilibrium constant were thereby attained.[1]

Enthalpy and Activation Energy Drifts with Temperature. In keeping with the above, it is seen in Table 1 that $\Delta H_A^\ddagger$ increases, ΔH_F increases, and ΔH_D decreases each by the same amount at a given pH as temperature is decreased. $\Delta H^\ddagger_A$ is the "second order" activation energy, and ΔH_F and ΔH_D are the enthalpies of formation and decomposition of the complex Q. Equation 10 applies at higher pH as previously described but does not apply at the acidic lower pH due to the greater stability of H_5IO_6 as compared to $H_4IO_6^-$; instead, eq 8 applies. Accordingly, these variations with pH are the result of two impinging equilibria, eqs 8 and 10. Corrections similar to those of Table IV, ref 1, have not been made due to uncertainty in evaluating eq 8.

The Phenomenon of $\Delta H_S^\ddagger$ Constancy. The "first order" activation energy, $\Delta H_S^\ddagger$, is graphed in Figure 4 which may be calculated from Table 1 using eq 4 and the Arrhenius equation or by applying eq 11. Equation 11 follows from eq 4.

$$\Delta H_A^\ddagger + \Delta H_D = \Delta H_S^\ddagger \tag{11}$$

The result is $\Delta H_S^\ddagger = 22.7 \pm 0.5$ kcal/mol, which is essentially constant over the entire range of pH and temperature. A slight downward trend with decreasing pH does exist, but it is within the bounds of experimental error. Activation energies from rate data at 35 and 45 °C are not included, since $\Delta H_A^\ddagger$ values above 25 °C were obtained by extrapolation. However, $\Delta H_S^\ddagger$ calculated from the extrapolated data is also closely in the range of 23 kcal/mol.

The constancy of $\Delta H_S^\ddagger$ is again due to an equilibrium phenomenon in which the following equation applies.

$$Q^- \overset{K_D}{\rightleftharpoons} P^- + G \xrightarrow{k_A} \text{products} \tag{12}$$

Equation 12 is essential for the validation of eq 11 since both k_A and K_D (or K_F) are determined by the existing active concentrations of P^- and G. Under no circumstances can eq 11 be valid without the enforced equilibrium of eq 12.

In addition, principle 9 applies. Upon comparing ΔH_F ($-\Delta H_D$) with $\Delta H_A^\ddagger$, it is obvious that as ΔH_F increases algebraically there is an equal increase in $\Delta H_A^\ddagger$ within experimental error. See Table 1. These energy changes are the result of alterations from the original ground-state energies of P^- and G. Then from eq 12, both $\Delta H_A^\ddagger$ and ΔH_F must be equally altered. In contrast, $\Delta H_A^\ddagger$ and ΔH_D ($-\Delta H_F$) are equally altered, but in opposite directions. Thus with eq 11, the increases in $\Delta H_A^\ddagger$ are matched by decreases in ΔH_D, and the original basic energy state is maintained for $\Delta H_S^\ddagger$; therefore, it is constant under all presently imposed conditions.

The constancy of $\Delta H_S^\ddagger$ implies that it is a number with little meaning and is merely the sum of two significant constants. This occurs only as a result of a three-way impact: that of the applied equilibria (eqs 6 and 8), the equilibrium of eq 12, and principle 9.

Comparisons with Pinacol. In Figure 1, the rate characteristics of pinacol and ethanediol are in sharp contrast, indicating different mechanisms; yet in Figure 4, there is a close correlation of the activation energies.

Dual mechanisms, i.e., reactions with both H_5IO_6 and IO_4^-, were indicated with pinacol[2] and are presently noted with ethanediol. These conclusions are further supported by Figure 4. Since, as previously emphasized, activation energies are a function of ratios of rates at two temperatures, it is indicated that the rate ratios for pinacol and "second order" ethanediol, k_A, are similar. Accordingly, the major reactant for ethanediol is IO_4^- and the minor reactant is H_5IO_6; pinacol is reversed with the major reactant being H_5IO_6 and the minor reactant IO_4^-. Thus, the two glycols share the same mechanisms but with different intensities as demonstrated by the differing rates and similar activation energies.

Pinacol also exhibits the same phenomenon, as described above, of activation energy drifts with temperature. Of course, no compensating effects with ΔH_D were observed since pinacol does not form a detectable complex.

The large changes in activation energies with pH for ethanediol and pinacol, as seen in Figure 4, may be explained at least in part as follows.

In neutral solution

$$IO_4^- \rightarrow IO_3^- + [O] \tag{13}$$

where [O] represents oxidation capacity. In acid solutions

$$H_5IO_6 \rightarrow HIO_3 + [O] + 2H_2O \tag{14}$$

The primary difference between eqs 13 and 14 is the release of water of hydration in the latter equation. This represents an absorption of energy which must be compensated by an increase in activation energy. The protonic equilibrium, eq 8, also provides a major contribution in the acidic region. The possibility of two different mechanisms, at low and higher pH, may also have an impact.

The Mechanism. The intermediacy of Q^- as herein defined has been widely acclaimed and generally accepted. In view of the conclusions from this paper, this appears not to be the case. The evidence is summarized.

1. The rate of product formation does not correlate proportionally with Q, complex concentration, under varying conditions; therefore, they appear to be noninterdependent. For validation in Table 1, compare the rate constants k_A or k_S (i.e., $k_A K_D$) with the equilibrium constants K_F or K_D under the conditions of changing pH at a given temperature or changing temperature at a given pH.
2. Pinacol which is clearly second order and "second-order" ethanediol exhibit similar deviations in $\Delta H^\ddagger$ due to eqs 8 and 10. There is no equivalent effect with "first-order" ethanediol rate data since $\Delta H_S^\ddagger$ is constant. See Figure 4.
3. There is close correlation of k_A, the "second-order" rate constant with eq 6, but the correlation of k_S, the first-order rate constant, with eq 6 is poor.
4. Evidence for the complex Q is evident only in appreciable reactant concentrations and at lower temperatures. Upon diluting the reactants greatly or upon raising the temperature sufficiently, evidence for the complex decreases or disappears.
5. The "first-order" activation energy $\Delta H_S^\ddagger$ appears to have no mechanistic significance since it exhibits no changes with pH whereas the "second-order" activation energy $\Delta H_A^\ddagger$ does show appropriate trends.

In contrast to the above conclusions, there is indisputable evidence that *cis*-glycols react more rapidly than *trans*-glycols.[7,8] Also, *trans*-1,2-dimethyl-1,2-cyclopentanediol has been shown to be unreactive, but the cis isomer does react with periodate.[9] Spacing of the hydroxyl groups is indicated to be an important consideration for determining relative reactivity of glycols. This strongly supports the concept of a cyclic intermediate.

In view of the conclusions of this paper, as they contrast with the above evidence, it is proposed that there are two complexes: the Q^- of this paper which is unreactive and another unidentified reactive complex which is the true intermediate and has a very low activation energy. There is also the possibility that the observed Q^- may exist in two forms, active and inactive.

Conclusion. The effects of active equilibria on reaction kinetics have not been extensively studied. This paper demonstrates the unique results that may occur from such investigations.

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