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Hydration, entropy, and energy relationships for periodate oxidations

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ABSTRACT: Periodate oxidations of ethanediol and pinacol each occur in two phases; these are (1) formation and (2) decomposition of the intermediate complex. In phase (1), an increase in acidity gives $IO_4^- \rightarrow H_5IO_6 \rightarrow H_6IO_6^+$. The rate of oxidation of ethanediol decreases with increasing acidity, whereas the rate of oxidation of pinacol maximizes with H_5IO_6. For both glycols, the activation energy increases and ΔS_{act} decreases with increasing acidity. In phase (2), the energy of activation is essentially constant with pH, whereas the rate decreases, and the entropy of activation decreases modestly as pH decreases. The latter correlates with the nonhomogeniuty of product formation. Rates for 3-chloro-1,2-propanediol are also listed. Pentaerythritol forms an inactive complex with IO_4^- or H_5IO_6 indicating the importance of chelation in the formation of the intermediate complex. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: rates; oxidations; energy

INTRODUCTION

Initially, the study of the periodate glycol reaction was undertaken as a traditional mechanistic survey.[1–4] In this paper, evaluations include absolute rate relationships with emphasis on entropies of activation for pinacol and ethanediol. It is the purpose of this paper to present data applicable to these two compounds. There may of course be certain other potential applications. Additional supporting data for 3-chloro-1,2-propanediol are also included. At pH 5.6, the reaction[5] is

$$IO_4^- (P) + CH_2OHCH_2OH\,(G) = Q \rightarrow IO_3^- + 2CH_2O + H_2O \text{ and } Q = [O_4I^{O-CH_2}_{O-CH_2}] \quad (1)$$

where IO_4^- is periodate ion and the intermediate Q is formed by a direct combination of reactants. A similar reaction occurs at pH 0.6 with H_5IO_6 substituted for IO_4^-.

The periodate glycol reaction is of particular interest since a clearly identifiable intermediate is in evidence.[5–7] Although this intermediate cannot be isolated, one of the primary purposes of this paper is to describe and evaluate additional chemical characteristics of this ubiquitous (for this reaction) substance.

Upon designating active IO_4^- as P, active glycol as G and Q the intermediate as in Eqn (1), then $P = p_o - x -$ Q, $G = g_o - x - Q$ where p_o and g_o are the initial concentrations and x is the extent of reaction. The rate constants k are defined by Eqns (2–4).

$$P + G \rightarrow Q, \quad \text{Rate} = k_A\,PG \quad (2)$$

$$Q \rightarrow P + G, \quad \text{Rate} = k_D Q \quad (3)$$

$$Q \rightarrow \text{Products}, \quad \text{Rate} = k_S Q \quad (4)$$

Since Eqns (2) and (3) represent forward and reverse reactions, a potential equilibrium may then be established providing the existence of k_A is allowed. Thus,

$$K_D = PG/Q = k_A/k_D \quad (5)$$

and K_D is the dissociation constant.

The intrinsic rate is presently defined as the rate attained by a mixture of $P + G$ which is allowed to equilibrate as in Eqn (5). However, if P, G, or Q (Eqn (3)) are then altered by exterior additions or eliminations, the intrinsic value will no longer be valid. To avoid this difficulty in the present proposal, it is essential to establish a basic mechanism which is maintained for the duration of the reaction. This condition has been observed only for a limited number of glycols and can occur only if the rate constant k_S is significantly less than k_A and as follows.

Under extreme conditions, the equilibrium concentration of Q is very small and is not kinetically detectable.

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Accordingly, the rate of Q formation becomes the limiting rate and equals the rate of Q decomposition. Since Q is very small, the rate of product formation becomes very slow and, as a reasonable approximation, Q may be omitted in the rate expression, and Eqn (1) becomes rate controlling. Examples include pinacol[2] (2,3-dimethyl-2,3-butanediol) and other structurally crowded glycols.

Under other conditions, there are, however, two unique glycols for which Q is intrinsically at equilibrium during the course of the reaction; yet Q is kinetically detectable and cannot be neglected. These are ethanediol and 3-chloro-1,2-propanediol. Again k_S must be significantly smaller than k_A, and K_D must maintain equilibrium conditions as with Eqn (5). Proof of this condition with ethanediol follows.

When p_o and g_o (the initial concentrations of periodate and glycol) are mixed, an equilibrium mixture of Q, P, G is formed, as in Eqns (2), (3), (5). If k_S is small enough such that the equilibrium can be effectively maintained by regeneration of Q from Eqn (1). A steady state condition may then be established such that Q's lost by decomposition via k_S (Eqn (3)) are replaced by Q's generated via k_A (Eqn (1)) during the major part of the reaction.

From Eqn (5)

$$K_D\mathrm{Q} = \mathrm{PG} \tag{6}$$

and with steady state conditions

$$k_A\mathrm{PG} = k_S\mathrm{Q} = k_A K_D \mathrm{Q} \tag{7}$$

and

$$k_S = k_A K_D \tag{8}$$

Based on these concepts, a precise rate equation was derived from Eqns (1) and (4) with p_o and g_o representing the initial values.

$$\mathrm{d}x/\mathrm{d}t = k_A\mathrm{PG} = k_A(p_o - x - \mathrm{Q})(g_o - x - \mathrm{Q}) \tag{9}$$

and

$$K_D = \mathrm{PG}/\mathrm{Q} = (p_o - x - \mathrm{Q})(g_o - x - \mathrm{Q})/\mathrm{Q} \tag{10}$$

Upon solving for Q as a quadratic equation (These equations were initially presented as a general solution for equilibrium reactions. Later it was demonstrated that the appropriate applications were very limited. The following notations changes have been made k_A was k'; k_S was k'', K_D was K.) and substituting in Eqn (10), two rate equations were obtained,[1] integrated,[1] and computerized;[3] one for $g_o > p_o$ and one for $p_o = g_o$. The Integrated equations are given in Reference [1].

In order to apply these equations, rate data from three or more concentrations of one reactant are essential. For the PG reaction 0.002 M periodate is reacted with 0.002, 0.01, and 0.05 M glycol. In practice, rate data at 0.01 and 0.05 M glycols first provide values for k_A and Q. This same value of Q is then substituted using 0.002 M data. If k_A is duplicated, K_D can be evaluated as an established constant and Eqns (1–10) are verified. Then k_A and k_S become unique constants subject to individual characteristics within the limitations of Eqn (8). Again Eqns (9) and 10 and the integrands can be applied only if K_D is independent of k_A and k_S. Proof that this can occur has been demonstrated with ethanediol in keeping with the above restrictions. Other glycols with hydrocarbon substituents do not apply.

CHELATION ENERGY

Pentaerythritol PE with its closely aligned dual pairs of hydroxyls $C(CH_2OH)_4$ does form an inactive complex has shown that PE is oxidized only to the extent of 0.069% in 6 hrs at 22 °C with IO_4^- or H_5IO_6. This has been demonstrated as follows. Three concentrations each of 1,2-butanediol and 3,3-dimethylbutanediol at pH 5.6 were reacted with 0.002 M KIO_4 at 0 °C, both neat and with 0.1 M PE. The rate decreases by PE, similar for both glycols at 0 °C, were as follows: 0.002 M, −13.5%; 0.01 M, −7%; 0.050 M, −4%. Ethanediol, 0.002 M and pH 5.6, and pinacol, 0.00925 M at pH 1.0 (H_5IO_6) each showed −13% rate reduction at 0 °C. However, upon replacing the weight of PE by an equal weight of (1) methanol or (2) acetone in no case was the change in rate of oxidation greater than 1%. Ethanol in similar amounts at 0 °C is also inactive.[3]

Thus, it is shown that PE forms a complex with IO_4^- and with H_5IO_6, and that the complex is of sufficient stability to compete with Q. Since alcohols show little evidence of complex formation, it is concluded that an initial contact of glycol OH's with periodate is followed immediately by cyclic chelation: a five-member ring with glycols and six-member ring with PE. Chelation thereby provides the initial energy for complex formation in Y, and the complex is further activated for decomposition by H transfers to form Q (Eqn (11)).

Activation energies have been previously evaluated for the initial and final sections of Eqn (8). These are 7.1 kcal/mol for the initial contact, k_A, and 16.8 kcal/mol for decomposition of Q. Thus, the two-part mechanism is further emphasized and gives a total 23.9 kcal/mol (23.3 kcal/mol was calculated if certain additional corrections are applied, as described in reference [1].) for the overall activation energy.

In further detail, Q formation via k_A includes the loss of a single H_2O. Since ΔH for $2H_2O + IO_4^-$ is 10.9 kcal/mol,[8] the loss of one H_2O, presumably 5.5 kcal, can account for most of the 7.1 kcal activation energy. The second part, 16.8 kcal includes fissure of a labile C—C bond.

Please note that in the initial paper[1] of this series the calculations of rates and thermodynamic values at pH 5.6 were adjusted for partial hydration, etc., and that E_{act} numbers were converted to ΔH_{act}, etc. Due to the uncertainties of the extent of $H_6IO_6^+$ at the various pH, it seems pointless to make corrections at one end of the pH scale and not the other. So E_{act} values are presented without further correction but with notations of special conditions as was also done in a preceding paper.[3]

pH EFFECTS

A reassessment of data from previous papers[2,3] has provided additional information concerning pH effects on reaction rates. Although k_S, k_A, and K_D are related by Eqn (8), k_A and K_D are individually altered by pH changes but k_S is a composite of k_A and K_D. Thus any calculated values, of rate, E_{act} and ΔS_{act} reflect this background, as described in Tables 1 and 2.

pH effects on k_A

pH effects on k_A will be evaluated first. Pinacol is ethanediol with four added methyl groups. These methyls restrict the rate of contact of $P+G$ and greatly decrease the overall rate of reaction. The result is that k_A is the only evident reaction rate constant for pinacol; since $k_A = k_S$: whereas both k_A and k_S are individually evident for ethanediol.

As previously noted,[3] changing pH in the range of pH 5.6–0.61 has a pronounced effect on the active forms of periodate.

$$\begin{array}{ccccc} \text{pH } 5.6\ H_4IO_6^- & f & H_5IO_6\, f & H_6IO_6^+\ \text{pH } 0.61 \\ & & \downarrow\uparrow & \\ & & IO_4^- & \end{array} \qquad (12)$$

Three factors must be evaluated.

$$\text{Partial hydration of } IO_4^- \text{ to } H_4IO_6^- \qquad (13)$$

$$\text{Ionization of } H_5IO_6 \text{ to } H_4IO_6^- \qquad (14)$$

$$\text{Protonation of } H_5IO_6 \text{ to } H_6IO_6^+ \qquad (15)$$

The most prominent factor is Eqn (14). Equation (15) is also very evident at low pH as was demonstrated during the oxidation of pinacol.[2]

Table 1. k_A rate data for pinacol

pH	15 °C	25 °C	35 °C	E_{act}	ΔS_{act}
5.60	0.00308	0.00417	0.00532	4.8	−52
4.10	0.00378	0.00535	0.00715	5.6	−50
3.62	0.00604	0.00907	0.01284	6.7	−46
3.15	0.01224	0.01983	0.02954	7.8	−40
2.78	0.02304	0.0396	0.0619	8.7	−37
2.02	0.0696	0.1500	0.2635	11.7	−23
1.58	0.0884	0.2261	0.4539	14.4	−13
1.08	0.0862	0.2504	0.593	17.0	−4
0.61	0.0688	0.2196	0.602	19.1	+3

Table 2. k_A rate data for ethanediol

pH	15 °C	25 °C	35 °C	E_{act}	ΔS_{act}
5.60	1.749	2.697	3.898	7.1	−33
4.10	1.755	2.695	3.911	7.1	−33
3.62	1.723	2.702	3.938	7.3	−32
3.15	1.650	2.667	3.989	7.8	−31
2.02	0.956	1.998	3.433	11.6	−18
1.58	0.565	1.413	2.878	14.4	−10
1.08	0.2703	0.794	1.939	17.4	−1
0.62	0.1365	0.4337	1.221	19.3	+5

ETHANEDIOL *VERSUS* PINACOL

As the pH is varied from 5.6 to 0.61, pinacol[2] exhibits a peak rate at pH 1–1.5 which contrasts sharply with ethanediol[3] whose peak rate is at pH 4–7, as described in Tables 1 and 2. These data are in marked contrast with the E_{act} values. Both ethanediol and pinacol have E_{act}–pH curves which are essentially identical from pH 0.61 to 3.15. Above pH 3.15, a small digression is observed and presumably continues beyond pH 7. Both curves show a high of 19+ at pH 0.61 which decreases to 7.8 at pH 3.15, as described in Tables 1 and 4.

The overall increases in E_{act} with decreasing pH are 12 kcal for ethanediol and 14 kcal for pinacol. These numbers may be compared with the heat of hydration of IO_4^- (to H_5IO_6) which has been given as 10.9 kcal/mol.[9] For ethanediol the E_{act} at pH 5.6 is 7.07 kcal and 19.32 kcal at pH 0.61. Therefore,

$$10.9 + 7.1 + x = 19.3 \qquad (16)$$

and x can be attributed to the additional heat of formation of $H_6IO_6^+$ from H_5IO_6, since $H_6IO_6^+$ is largely unreactive. The evidence arises from both spectral and rate data, and an equation has been derived.[2] Based on this equation at pH 0.61 and 25 °C, the theoretical rate constant has been estimated in Reference [2] as $k_A = 0.33$, whereas the observed rate constant was 0.220, as described in Table 1. In view of the lower observed reactivity, it is concluded that roughly one-third of the periodate exists as $H_6IO_6^+$ at pH 0.61. The discrepancy narrows rapidly with increasing pH so that at pH 3 the $H_6IO_6^+$ concentration is nearly zero. At pH 5.6, and 25 °C 0.002 M periodate is 97.5% IO_4^-. These data show the extent of the effects of hydration and protonation on the overall rates of reaction.

Although ethanediol and pinacol follow the same mechanism (as first noted by Buist *et al.*[9]) there is mobility due to temperature. Upon greatly increasing temperature, the ethanediol rate of oxidation would maximize[3] at a low pH similar to pinacol. Evidence of this has been observed at 45 °C. Also any evidence of $H_6IO_6^+$ would eventually disappear at higher temperatures, since the equilibrium constant,[2]

$$K = [H^+][H_5IO_6]/[H_6IO_6^+] \qquad (17)$$

increases with temperature.

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In contrast, if the temperature were greatly decreased, the pinacol peak at pH 1 (25 °C) would disappear and the rate would become less than at pH 5. Both the differences in activation energies and the increase in $H_6IO_6^+$ would enhance this change. At very low temperatures, the latter impact in reverse could be so overwhelming that the observed pH effect would be largely disguised.

ΔS_A: ENTROPY AND k_A

Since entropy of activation is related to the frequency factor and since k_A represents the initial contact of P + G, changes in the entropy as it varies with pH can be evaluated. k_A for both pinacol and ethanediol are discussed since the basic mechanisms are similar as previously indicated.

Note that with decreasing pH, IO_4^- becomes increasingly hydrated, as shown in Eqn (12). Since k_A represents the rate of formation of the complex, the presence of the hydrate represents an additional barrier, both physical and chemical, to Q formation. The chemical interaction is hydration, thus an increased hydration provides increased heat which increases E_{act} as previously discussed.[3]

Increased hydration also provides increases in the mass of the periodate ion. As IO_4^- changes to H_5IO_6, the mass changes from 190.9 to 208.9 and again to 209.9 as $H_6IO_6^+$ is formed. Since entropy represents a change in disorder, an increase in mass should have a more profound effect. This may be observed in Tables 1 and 2. In turn, the frequency factor is altered as made evident by the changes in ΔS_{act}, as described in Tables 1 and 2.

Thus, the change in k_A encompasses both entropy and energy relationships with hydration as the common factor. Lesser hidden effects also apply as will be discussed.

A comment on the mechanism by which the glycol attacks the hydrated periodic acid seems appropriate. A direct addition would lead to an octadentate and an overcrowded iodine nucleus. It is proposed that as the glycol contacts H_5IO_6, hydrogen bonding occurs, and the complex is stabilized by H_2O elimination. It is this energy which necessitates the increased activation energy at the lower pH, as described in Table 2.

Table 3. Equilibria data for K_D (ethanediol)

pH	15 °C	25 °C	35 °C	E_{act}	ΔS_{act}
5.6	0.0243	0.0649	0.1634	16.8	51
4.10	0.0243	0.0649	0.1534	16.8	51
3.62	0.0248	0.0649	0.1605	16.5	50
3.15	0.0257	0.0654	0.1533	16.0	48
2.02	0.0377	0.0730	0.1357	11.3	33
1.58	0.0510	0.0810	0.1295	8.2	23
1.08	0.0535	0.0930	0.1198	4.6	11
0.61	0.0481	0.0990	0.1175	3.1	6

ΔS_D: ENTROPY AND K_D

Since K_D represents an equilibrium constant and k_A, a rate constant, corresponding calculations of ΔH_D and ΔS_D have been made. (The Eyring equation defined ΔG for rate data, and $\Delta G = RT\ln K$ was applied for K_D data.) From Eqn (8), complementary energy changes and entropy can be derived.

$$E_A + \Delta H_D = E_S \qquad (18)$$

where E_S is a constant. The corresponding relationship with entropies is also valid, as described in Tables 2, 3, 4.

$$\Delta S_A + \Delta S_D = \Delta S_S \qquad (19)$$

but ΔS_S is not constant as will be discussed.

The changes in ΔS for K_D are large and similar in scope to those for k_A, as described in Table 3. K_D represents a reverse equilibrium with dehydration corresponding to a pH increase. Again, the overall factor of hydration is the primary, though not exclusive, factor, and the change in entropy again is a mass effect which alters the rate as the reverse equilibrium occurs.

$$Q + 2H_2O\, f \quad H_5IO_6 + G + P \qquad (20)$$

ΔS_S: ENTROPY AND K_S

Both ΔS_A and ΔS_D of Eqn (20) vary greatly with hydration. The difference between these two large values is relatively small, as described in Table 4. With the elimination of hydration as causative, the large mass effect is eliminated, and another lesser effect upon k_S becomes evident.

The k_S values as previously determined[3] show a decrease with decreasing pH. This same pattern was repeated at seven temperatures, yet the activation energies are essentially constant over these same temperatures. Obviously activation entropy, and not activation energy, is the major factor in this pH–rate relationship. Compare k_S,

Table 4. k_S rate data for ethanediol

pH	15 °C	25 °C	35 °C	E_{act}	ΔS_{act}
5.60	0.0425	0.1753	0.637	23.9	18
4.10	0.0426	0.1752	0.639	23.9	18
3.62	0.0427	0.1756	0.632	23.8	18
3.15	0.0424	0.1748	0.627	23.8	18
2.02	0.0359	0.1459	0.481	22.9	14
1.58	0.02882	0.1137	0.373	22.6	13
1.08	0.01932	0.0738	0.232	21.9	9
0.62	0.01139	0.0428	0.1435	22.3	10

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(Q decomposition) equations taken from Table 4 at the pH extremes:

$$\text{at pH } 5.6, \quad Q \rightarrow IO_3^- + 2\,CH_2O, \qquad \Delta S_{act} = 18 \quad (21)$$

$$\text{at pH } 0.61, \quad HQ \rightarrow HIO_3 + 2\,CH_2O, \quad \Delta S_{act} = 10 \quad (22)$$

An ion and a neutral molecule are the products at higher pH, whereas only neutral molecules represent both reactants and products at the lower pH. The degree of disorder is obviously small and concurs with the small change in ΔS with pH. The attraction of ionic IO_3^- for water molecules compared with the lesser attraction by the neutral products may represent the overt effect on ΔS.

3-CHLORO-1,2-PROPANEDIOL, CP

As previously noted, CP is a very sensitive chemical. The rate data are included primarily to support the equilibrium concept as described for ethanediol. Note that good values were obtained under a variety of conditions. CP reacts at rates intermediate between ethanediol and pinacol, and the equilibrium concept can be appropriately applied. The data are tabulated in Table 5.

Table 5. 3-Chloro-1,2-propanediol

°C	pH	K_D	k_A[a]	k_S
25.02	5.4	0.091	1.48 ± 0.01	0.135
	1.06	0.21	0.408 ± 0.002	0.086
15.02	5.4	0.0385	0.895 ± 0.001	0.076
	1.06	0.022	0.135 ± 0.002	0.00279
0.00	5.4	0.010	0.355 ± 0.01	0.0036
	1.06	0.129	0.0189 ± 0.001	0.00244

[a] The ± numbers represent average deviations. The data points totalled 26 at 25 °C, fewer at the lower temperatures.

CONCLUSIONS

The rate constants k_A and k_S are both very real and can be mathematically defined. Entropies as well as enthalpies of activation are shown to be altered by changes in hydration of periodate with pH, but for different reasons.

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