

Hydride Abstraction from 1,2-Diols by the Pentaqua(oxo)chromium(IV) Ion

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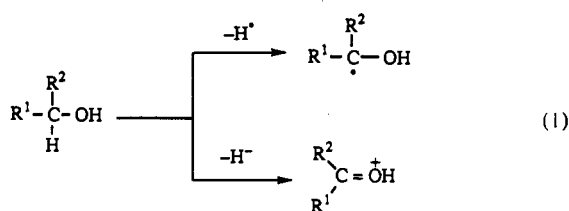
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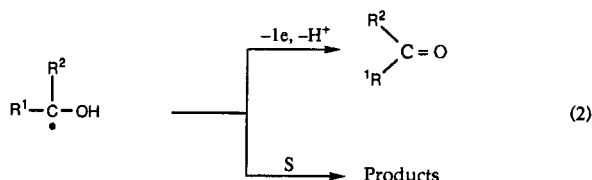
Kinetic studies of the oxidation of 1,2-diols by the pentaqua(oxo)chromium(IV) ion, $(\text{H}_2\text{O})_5\text{Cr}^{\text{IV}}=\text{O}^{2+}$, were carried out in dilute aqueous solutions of perchloric acid. These reactions yield the superoxochromium(III) ion CrOO^{2+} , providing evidence that the two-electron reduction of $\text{Cr}^{\text{IV}}\text{O}^{2+}$ to Cr^{2+} occurred in a single step. The rate constants for the primary and secondary diols are comparable to each other and approximately 10 times larger than that for pinacol ($k = 3.7 \text{ L mol}^{-1} \text{ s}^{-1}$). The kinetic isotope effect of the O–H hydrogens is negligible, $k_{\text{H}}/k_{\text{D}} = 0.95\text{--}1.3$, whereas that for the C–H hydrogens is substantial, $k_{\text{H}}/k_{\text{D}} = 3.7\text{--}4.8$. A 2-equiv mechanism is proposed, in which CrO^{2+} abstracts a hydride ion from an α -position in the primary and secondary diols and from a β -position in pinacol.

Introduction

The oxidation of alcohols by high-valent chromium, and by O_2 or peroxides activated by low-valent chromium, might take place by either a one-electron (H atom) or a two-electron transfer (H^-) as shown in eq 1.^{1–5}

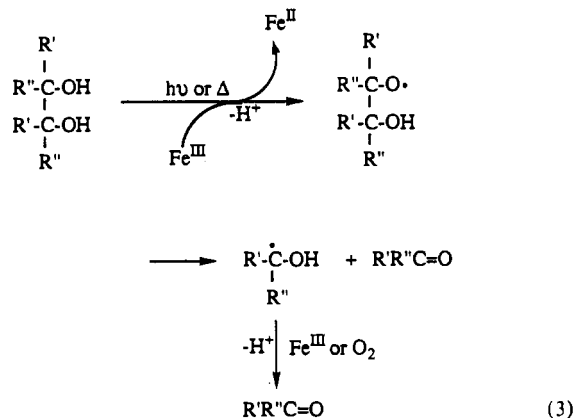


The radical formed by the H atom pathway in eq 1 would then react further with the oxidant or other substrates (S) present in solution (eq 2).⁶



The limited data on the oxidation of diols^{7–10} include the observation of oxidative cleavage of the C–C bond by Ce^{IV} and Pb^{IV} . The formation of a bidentate intermediate was reported with lead but not with cerium.⁷ It was recently shown that photochemical oxidation of tertiary diols by an Fe(III) porphyrin

yields the corresponding alkoxy radicals, which then decompose to alkyl radicals and ketones. The alkyl radicals are then further oxidized by Fe(III) or O_2 to the corresponding ketone (eq 3).¹¹



The pentaqua(oxo)chromium(IV) ion, $(\text{H}_2\text{O})_5\text{CrO}^{2+}$ (hereafter CrO^{2+}), is a powerful and reactive oxidant.⁵ It is sufficiently long-lived ($t_{1/2} = 30 \text{ s}$ in 1.0 M HClO_4 at $25 \text{ }^\circ\text{C}$) to be used as a reagent in mechanistic studies. A 2-equiv (hydride transfer) mechanism has been identified for the oxidation of primary and secondary alcohols⁵ and for the reaction of H_2O_2 ^{12a} with CrO^{2+} . The oxidation of phenols, however, involves a one-electron path, which leads to the formation of the corresponding phenoxyl radical in the rate determining step.^{12b} As such, the phenols are distinct from all the others.

Here we report the results of the study of the oxidation of diols by CrO^{2+} in aqueous acidic solution. The reaction involves cleavage of the C–C bond and yields the corresponding ketones or aldehydes.

Experimental Section

Reagents. Water was purified by passing the laboratory distilled and deionized water through a Millipore water system. Ethylene glycol, *cis*- and *trans*-1,2-cyclohexanediol (Aldrich), deuterium oxide (99.9 atom % D), and ethylene-*d*₄ glycol were used without purification. Pinacol was purified by sublimation under vacuum. The kinetic isotope effect (kie) of the O–H bond was determined by conducting experiments in D_2O and H_2O . Deuterated pinacol (pinacol-*d*₁₂) was prepared from

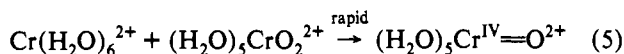
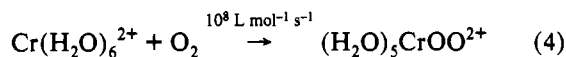
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acetone- d_6 by a modification of a literature method.¹³ The temperature was controlled in all the kinetic experiments by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature.

The UV-visible absorption spectra and kinetic measurements were recorded with a Shimadzu UV-3101PC scanning spectrophotometer. The organic products were identified by using a Hewlett-Packard Model 5790 gas chromatograph and a 3390A integrator. The products were chromatographed on an OV-101 column at 30 °C by injection of liquid-phase samples. The concentration of acetone was determined from the GC peak areas by using an external standard. Formaldehyde was determined by chromotropic acid analysis.¹⁴

Reactions. All the reactions were carried out in O_2 -saturated solutions. The perchloric acid concentration and the ionic strength ($HClO_4 + LiClO_4$) were both 0.10 M except in experiments designed to study the effects of these variables. Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of Cr^{3+} with Zn/Hg. Injection of Cr^{2+} into an acidic aqueous solution saturated with O_2 gives rise to CrO^{2+} . Some $CrOO^{2+}$ was also formed (eqs 4 and 5),¹⁵ but it did



not interfere. The saturated solutions of O_2 were prepared by bubbling O_2 through the solution for about 10 min. In a typical kinetic experiment, CrO^{2+} was formed *in situ* by injecting 100 μ L of 0.01 M Cr^{2+} ($[Cr^{2+}]_{\text{final}} = 0.2 \text{ mM}$) into a 2-cm spectrophotometric cell filled with 5.0 mL of an O_2 -saturated solution (1.26 mM at 25 °C) of 1.0–3.0 mM diol. Under these conditions, the reaction between Cr^{2+} and O_2 rapidly produced $\sim 0.04 \text{ mM } CrO^{2+}$ ($\sim 20\%$ based on total Cr^{2+}), which then reacted with the diol.

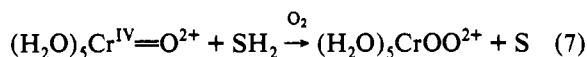
Kinetic Measurements. The kinetic data for the oxidation of diols by CrO^{2+} were collected by following the formation of the product, $CrOO^{2+}$, at 290 nm ($\epsilon = 3100 \text{ L mol}^{-1} \text{ cm}^{-1}$).¹⁶ The rate constant k_{ψ} of eq 6 was obtained by fitting the absorbance-time data to the first-order kinetic expression $Abs_t = Abs_{\infty} + (Abs_0 - Abs_{\infty})\exp(-k_{\psi}t)$, where $Abs =$ absorbance.

$$\frac{d[CrO_2^{2+}]}{dt} = k_{\psi}[CrO^{2+}] \quad (6)$$

Results

Diols. The diols studied were ethylene glycol, *cis*- and *trans*-1,2-cyclohexanediol, and pinacol. All the reactions were carried out in O_2 -saturated solutions. Under these conditions, Cr^{2+} reacts rapidly with O_2 to yield $CrOO^{2+}$ and CrO^{2+} (eqs 4 and 5).

The superoxochromium(III) ion does not react with diols under these conditions. The oxochromium(IV) ion, a strong oxidant,^{12a} reacts with diols in the presence of O_2 to yield $CrOO^{2+}$ (eq 7)



As shown in Figure 1, the pseudo-first-order rate constants k_{ψ} (eq 8) varied linearly with the diol concentration at constant ionic strength and acidity, yielding the second-order rate constants (k_{diol}). The values of the rate constants (k_{diol}) are summarized in Table 1.

$$k_{\psi} = k_{\text{dec}} + k_{\text{diol}}[\text{diol}] \quad (8)$$

The small intercepts in Figure 1 represent the rate constant for the decomposition of CrO^{2+} in the absence of the diol. The range of values is $k_{\text{dec}} = 0.01\text{--}0.02 \text{ s}^{-1}$ at 25 °C in 0.1 M $HClO_4$. At this point, the decomposition of CrO^{2+} is not completely

Table 1. Second-Order Rate Constants and Kinetic Isotope Effects for the Oxidation of 1,2-Diols and Alcohols by CrO^{2+} in 0.1 M Perchloric Acid at 25 °C

diol/alcohol	k ($\text{L mol}^{-1} \text{ s}^{-1}$)	k_H/k_D	ref
$CH_2(OH)CH_2(OH)^a$	33 ± 2		this work
$CH_2(OD)CH_2(OD)^a$	28 ± 3^b	1.2	this work
$CD_2(OH)CD_2(OH)^a$	8.9 ± 0.5^c	3.7	this work
<i>cis</i> -1,2-(OH) $_2$ C $_6$ H $_{10}$	30 ± 1		this work
<i>cis</i> -1,2-(OD) $_2$ C $_6$ H $_{10}$	26 ± 3^b	1.2	this work
<i>trans</i> -1,2-(OH) $_2$ C $_6$ H $_{10}$	57 ± 1		this work
$[(CH_3)_2C(OH)]_2$	3.7 ± 0.2		this work
$[(CH_3)_2C(OD)]_2$	3.9 ± 0.7^b	0.95	this work
$[(CD_3)_2C(OH)]_2$	0.77 ± 0.10^c	4.8	this work
CH_3OH	52.2 ± 1.4		5
CD_3OH	15.1 ± 1.7^c	3.5	5
CH_3CH_2OH	88.4 ± 4.4		5
$C_6H_5CH_2OH$	56.0 ± 3.5		5
$(CH_3)_2CHOH$	12.0 ± 0.4		5

^a The rate constants were not corrected for the further oxidation of the product, HCHO (eq 9). ^b In D_2O . ^c In H_2O .

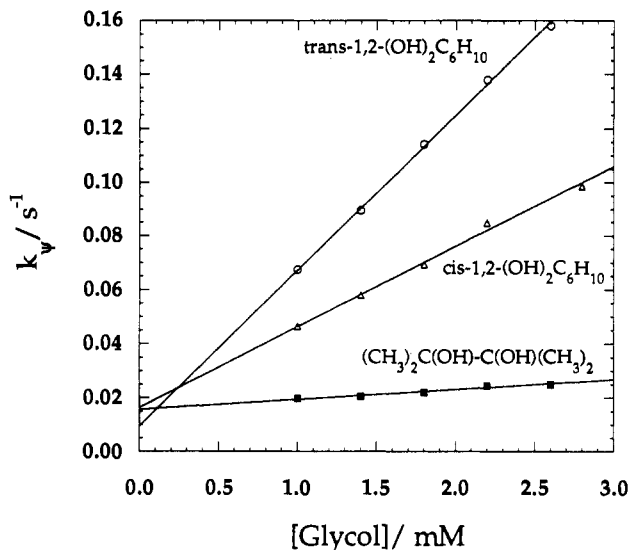


Figure 1. Dependence of the pseudo-first-order rate constants (k_{ψ}) for the oxidation of 1,2-diols by CrO^{2+} on the concentration of diols in 0.1 M perchloric acid at 25 °C.

understood, but there is some indication that the order of the self-decomposition reaction with respect to $[CrO^{2+}]$ is higher than unity.¹² This unspecified kinetic order may be one reason that k_{dec} shows some scatter; others are the fact that in most situations decomposition is a very small part of the observed process and that secondary reactions (such as those to be described shortly, in which a product undergoes further reaction) cause a rate enhancement that is taken up in the intercept, since that part is independent of [diol].

It was observed that the pseudo-first-order rate constant increased with an increase in the ionic strength of the solution. This was shown to be caused by the enhancement of k_{dec} (representing the rate of decomposition of CrO^{2+} , but not necessarily the correct reaction order) with ionic strength, and not to a variation of k_{diol} .^{12a,c} The pseudo-first-order rate constant, however, was independent of the solution acidity in the range 0.1–1.0 M $HClO_4$. The kinetic isotope effects (k_H/k_D) on the O–H groups were negligible. The oxidation of ethylene- d_4 glycol, however, showed a significant $k_H/k_D = 3.7$. The activation parameters for the reactions of 1,2-cyclohexanediols with CrO^{2+} were obtained from the variation of the rate constants with temperature (Table 2). The isokinetic relationship plot, Figure 2, shows that ΔH^\ddagger is a linear function of ΔS^\ddagger for the reactions of primary and secondary alcohols and 1,2-cyclohexanediols with CrO^{2+} . The slope, the *isokinetic temperature*, is $264 \pm 37 \text{ K}$.

According to the expected stoichiometry, $[HCHO]_{\infty}/[CrO^{2+}]_0 = 2/1$ (eq 9). The reaction of 40 μ M CrO^{2+} with 1 mM ethylene

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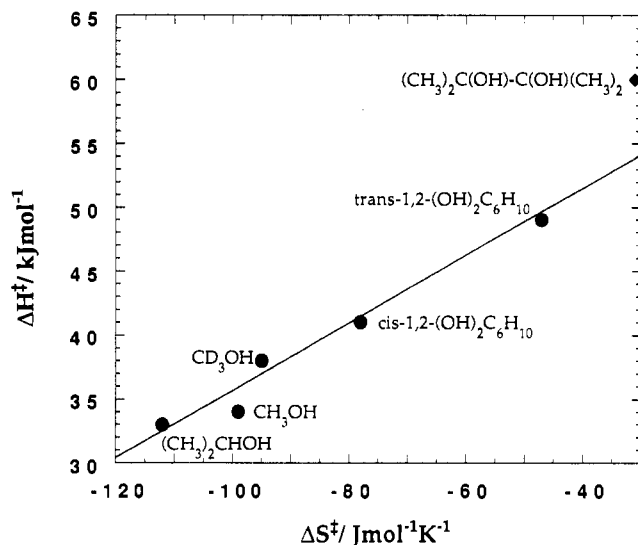
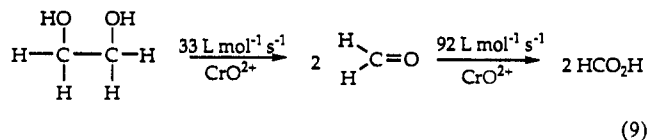
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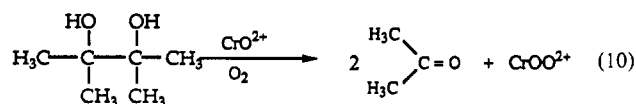
Table 2. Activation Parameters for the Oxidation of Diols, Methanol, and 2-Propanol by CrO²⁺ in 0.1 M HClO₄ Solutions

substrate	activation parameters	
	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)
CH ₃ OH	34 ± 6 ^a	-99 ± 20 ^a
CD ₃ OH	38 ± 7 ^a	-95 ± 21 ^a
<i>cis</i> -1,2-(OH) ₂ C ₆ H ₁₀	41 ± 3	-78 ± 9
<i>trans</i> -1,2-(OH) ₂ C ₆ H ₁₀	49 ± 4	-47 ± 15
(CH ₃) ₂ CHOH	33 ± 3 ^a	-112 ± 14 ^a
[(CH ₃) ₂ C(OH)] ₂	60 ± 5	-31 ± 18

^a Reference 5.**Figure 2.** Plot of ΔH^\ddagger vs ΔS^\ddagger for the reactions of alcohols and 1,2-diols with CrO²⁺ in 0.1 M HClO₄.

glycol yielded 66 μM formaldehyde. This actually represents a 95% yield, since the calculation must also take into account the losses of HCHO and CrO²⁺ in the secondary reaction⁵ also shown in eq 9. A theoretical yield of 70 μM HCHO was calculated for this experiment by use of the program KINSIM.¹⁷

Pinacol. The oxidation of pinacol by CrO²⁺ in 0.1 M HClO₄ in the presence of O₂ yielded CrOO²⁺. Acetone was also formed in almost quantitative yield (eq 10). The pseudo-first-order rate

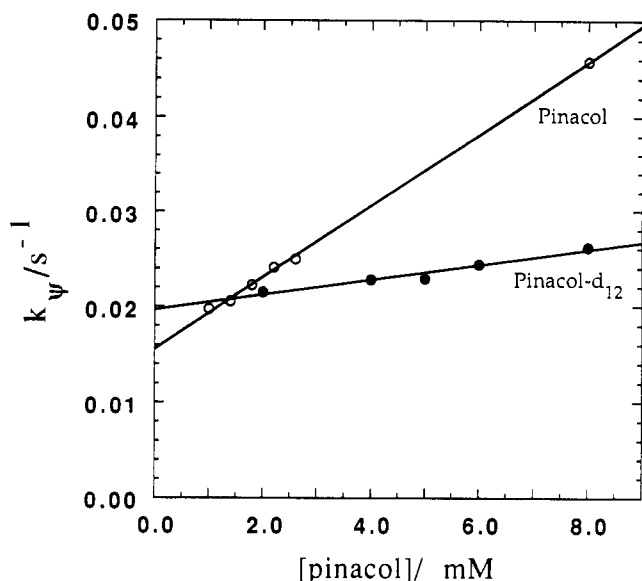


constants are linearly dependent on the concentration of pinacol, with an intercept of 0.016 s⁻¹ and a slope of 3.7 ± 0.2 L mol⁻¹ s⁻¹ at 25 °C (Figure 3).

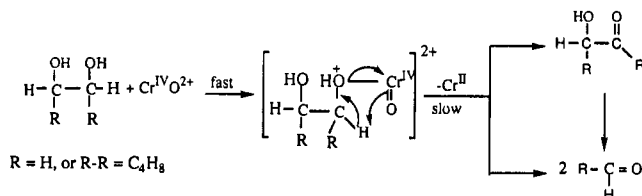
The second-order rate constant is acid-independent in the range 0.1–1.0 M H⁺. The kie on deuteration of OH groups of pinacol (experiments in D₂O) was again negligible, $k_{\text{H}}/k_{\text{D}} = 0.95$. On the other hand, the kie of the C–H (β) hydrogens, when pinacol-*d*₁₂ was oxidized, is significant, $k_{\text{H}}/k_{\text{D}} = 4.8$, as given in Table 1 and Figure 3.

Discussion

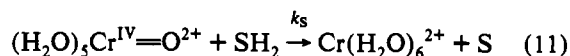
The 1-equiv reduction of CrO²⁺ yields Cr(III), which does not undergo any further oxidation–reduction reactions under the

**Figure 3.** Dependence of k_ψ on the concentration of pinacol and pinacol-*d*₁₂ for the oxidation of pinacol with CrO²⁺ in 0.1 M perchloric acid at 25 °C.

Scheme 1



experimental conditions. A 2-equiv reduction, on the other hand, produces Cr²⁺ as a reactive intermediate (eq 11).



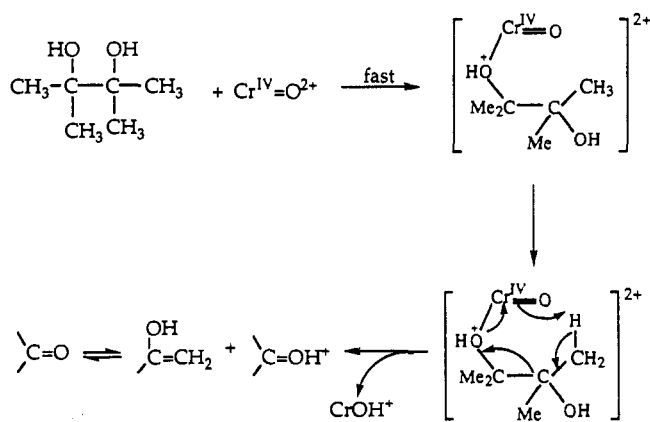
In this work the intermediate Cr²⁺ was trapped by O₂ to yield CrOO²⁺ (eq 4). Therefore the formation of CrOO²⁺ from reduction of CrO²⁺ in the presence of O₂ can be taken as sound evidence for a two-electron mechanism.

Reactions of Ethylene Glycol and 1,2-Cyclohexanediols with CrO²⁺. In our previous study⁵ of the oxidation of numerous alcohols by the chromyl ion, CrO²⁺, a 2-equiv mechanism was identified. It was proposed that CrO²⁺ abstracts a hydride ion from the α -C of the alcohol. The Cr²⁺ produced reacts rapidly with O₂, yielding CrOO²⁺. The reactions of 1,2-diols with CrO²⁺ also yield the superoxochromium(III) ion, indicating that Cr²⁺ was again produced in a single-step, 2-equiv process.¹⁵ This result and the significant primary kie found for the C–H bond of the glycol, together with the absence of a kie upon deuteration of the O–H bond, suggest a hydride abstraction mechanism for the oxidation of primary and secondary diols by CrO²⁺.

It should be noted that this is exactly opposite to the findings for phenols, where there is no kie for C–H bonds but a marked kie for O–H bonds. From this and other evidence, we inferred that phenols react by a 1-equiv mechanism.^{12b} Thus we propose for the diols a mechanism that is similar to the hydride abstractions from primary and secondary alcohols.⁵ This is shown for ethylene glycol and 1,2-cyclohexanediols in Scheme 1.

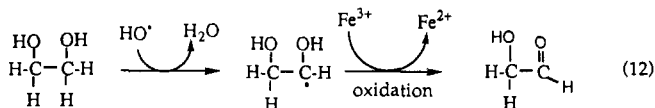
The hydride abstraction and the C–C bond cleavage in the oxidation of ethylene glycol may take place concertedly. On the other hand, it is possible that the reaction yields hydroxyacetaldehyde (Scheme 1), which then rearranges to formaldehyde in an acid-catalyzed process prior to or during the analysis of formaldehyde by the chromotropic acid method.¹⁴ The intermediacy of hydroxyacetaldehyde would seem plausible, given

Scheme 2



that the reaction of ethylene glycol with goethite, α -FeOOH, yields both formaldehyde and hydroxyacetaldehyde in the relative yields that depend on the solution acidity.^{11a} Also, in the oxidation of ethylene glycol to formaldehyde and formic acid at a platinum electrode in aqueous medium, hydroxyacetaldehyde has been reported as an intermediate.¹⁸

The oxidation of ethylene glycol by Fenton's reagent involves hydrogen atom abstraction by HO \cdot to yield a carbon-centered radical.¹⁹ This is then followed by the oxidation of the radical to hydroxyacetaldehyde (eq 12) or by rearrangement and reduction to acetaldehyde.



In the present work the one-electron process can be clearly ruled out on the basis of the nature of the chromium product, CrOO^{2+} , which can result only from a 2-equiv process.

The enthalpy of activation, ΔH^\ddagger , for the oxidation of 1,2-cyclohexanediols is somewhat higher than that obtained for secondary alcohols. This difference may be attributed to the increased steric demands of the cyclohexane ring, relative to the acyclic alcohols, in the transition state for hydride abstraction. Furthermore, the intramolecular H-bonding in 1,2-diols may reduce the efficiency of the binding of the diol to Cr(IV), leading to a higher energy transition state.

The rate constant for the oxidation of *trans*-1,2-cyclohexanediol is about twice as large as that for the *cis* isomer. The similarity in the rate constants between cyclopentanol ($30.6 \text{ L mol}^{-1} \text{ s}^{-1}$)⁵ and the two 1,2-cyclohexanediols strongly argues against the chelation in the reaction of the diols. This is different from the oxidation of diols by Pb(IV),⁷ where a chelated intermediate has been proposed.

Reaction of Pinacol with CrO^{2+} . The quantitative formation of acetone and CrOO^{2+} from the oxidative cleavage of pinacol by CrO^{2+} (eq 10) and the failure of all attempts to trap alkyl radicals using acrylonitrile or Co(III) provide clear evidence for the 2-equiv oxidation path. Furthermore the *k*_H/*k*_D = 4.8) was significant. All these data are consistent with the mechanism shown in Scheme 2. The rate-controlling step is the abstraction of a hydride ion from the β -position of pinacol. This is followed by the cleavage of the C–C bond and the formation of acetone and an enol, which tautomerizes to the more stable acetone.

The slower reaction of pinacol, compared to other diols in this work, is probably a result of several factors. As shown in Scheme 2, the reaction with pinacol proceeds through a six-membered cyclic transition state. In case of primary and secondary diols,

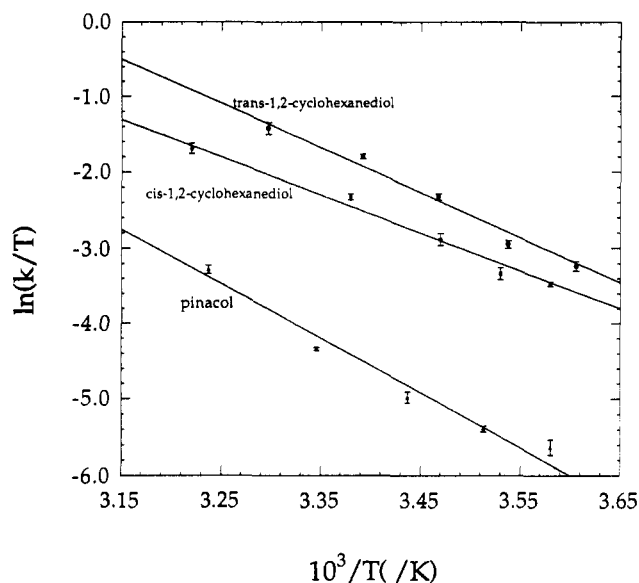


Figure 4. Plot of $\ln(k/T)$ against $1/T$ for the reaction of various diols with CrO^{2+} in 0.1 M HClO_4 .

the reactions involve the more favorable five-membered cyclic transition states (Scheme 1). The steric effect of the methyl groups may contribute to a slower reaction. Also, the heterolytic C–H bond strength may be greater in the case of pinacol, where a methyl group is involved. This effect may be minor, however, since it has been shown that alcohols with very different homolytic C–H bond strengths have similar rate constants for the reactions with CrO^{2+} .⁵

The activation parameters (Table 2) were calculated from the plot of $\ln(k/T)$ vs $1/T$, Figure 4. The enthalpy of activation of pinacol is higher than those for *cis*-1,2-cyclohexanediol and 2-propanol (Table 2) and is in part responsible for the rate constant of pinacol being small relative to those of the 1,2-cyclohexanediols and 2-propanol. The enthalpy of activation, $\Delta H^\ddagger = 60 \pm 6 \text{ kJ mol}^{-1}$, lies between the values for the oxidation of pinacol by Cr(VI), $\Delta H^\ddagger = 40.5 \text{ kJ mol}^{-1}$,⁸ and Os(VIII), $\Delta H^\ddagger = 78 \text{ kJ mol}^{-1}$.¹⁰ Oxidative cleavage of pinacol has been proposed as the rate-controlling step for both oxidants, although the nature of the proposed intermediate is different. In the case of Cr(VI), a chromate ester is believed to be involved, whereas Os(VIII)–glycol complexes have been invoked in the case of OsO_4 .

There is a possibility of β -hydride abstraction from primary and secondary diols (or alcohols) by CrO^{2+} in these reactions. However, many alcohols, such as CH_3OH and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, as shown in Table 1, have no β -hydrogen and the rates of the hydride abstraction from these alcohols by CrO^{2+} are all comparable, and at least 10 times greater than for pinacol. The rate constants for oxidation of these alcohols by CrO^{2+} are also close to the rate constants for other alcohols, such as $\text{CH}_3\text{CH}_2\text{OH}$ and 1,2-diols which have both α - and β -hydrogens (Table 1). Finally the isokinetic plot of the activation parameters, (ΔH^\ddagger vs ΔS^\ddagger), Figure 2, suggests similar mechanisms for oxidations of primary and secondary alcohols and 1,2-diols. The point for pinacol lies away from the line; it evidently adopts a different mechanism, as put forth in Scheme 2.

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