

KINETICS AND MECHANISM OF THE OXIDATION OF SOME
DIOLS BY CHROMIUM(VI) IN PERCHLORIC ACID MEDIUM

KALYAN KALI SEN GUPTA,* TAPASHI SAMANTA and SAMARENDRA NATH BASU†

Department of Chemistry, Jadavpur University
Calcutta 700 032, India.

(Received in UK 13 August 1986)

Abstract - Chromic acid oxidations of some diols have been studied in perchloric acid medium. The reactions are first-order with respect to the diols and acid chromate ion. The rate increases with the increase in acidity but the orders with respect to perchloric acid are different (1.25-2.0). The rate of the oxidation reactions at $[\text{HClO}_4] = 1.0 \text{ M}$ and temperature = 35°C , follow the order pinacol > 2,3-butane diol > ethylene glycol. The activation parameters of the oxidation reactions have been calculated. Plausible reaction mechanisms have been suggested.

The chromic acid oxidations of a number of alcohols have been studied¹⁻⁹. Most of the investigations were carried out either in mineral acid or acetic acid medium. It has been established¹⁰⁻¹⁴ that HCrO_4^- , reacts with different anions like chloride, sulphate, phosphate and acetate to give complexes of different stabilities. Consequently, the rates and mechanisms of the oxidations of alcohols by chromic acid in different acids and ligand environments would be different.

Recently, the chromic acid oxidations of some alkanols have been studied^{15,16} in perchloric acid medium. These reactions have been shown to occur through intermediate ester formation between protonated alcohol and the reactive Cr(VI) species, and subsequent C-H bond rupture of the alkanols. We, therefore, felt that a reinvestigation of the reactions involving chromic acid and diols in perchloric acid medium was necessary in view of the interesting results obtained in the oxidations of monools by the same oxidant under comparable conditions of the experiments.

EXPERIMENTAL

Reagents Potassium dichromate (G.R., E.Merck), perchloric acid (BDH) and sodium perchlorate (Riedel, Germany) were used. All the organic materials were of the highest purity available. Ethylene glycol (BDH), 2,3-butane diol (Fluka A.G.) and pinacol (BDH) were used. These compounds were purified either by distillation or by recrystallisation from benzene. Solutions were made in doubly distilled water. All other reagents were chemically pure.

Kinetic Measurements The details of kinetic measurements have been mentioned in earlier papers^{15,16}. Most of the experiments were carried out at $[\text{Cr(VI)}]_0$, $[\text{H}^+]_0$ and temperature of $3.34 \times 10^{-3} \text{ M}$, 1.0 M and 35°C respectively and at [ethylene glycol]₀, [2,3-butane diol]₀ and [pinacol]₀ of 2×10^{-2} , 5×10^{-3} & $5 \times 10^{-3} \text{ M}$ respectively,

* To whom all correspondence should be sent

† Department of Chemistry, Asutosh College, Calcutta 700 026.

unless otherwise mentioned. The ionic strength (μ) of the reaction mixtures were maintained constant by the addition of the requisite amount of NaClO_4 , whenever necessary. Again, since the oxidation rates of the diols are much faster than those of the monools at $[\text{H}^+]_0 = 1.0 \text{ M}$ and temperature of 35°C , the present reactions were studied at lower $[\text{substrate}]_0 : [\text{oxidant}]_0$ ratios.

Product Analysis The reaction products of the oxidation of the diols by chromic acid (maintaining kinetic conditions) were identified by the preparation of 2:4 DNP derivatives. Immediate precipitation occurred in all these cases. The precipitates thus obtained were filtered, washed and dried in vacuum.

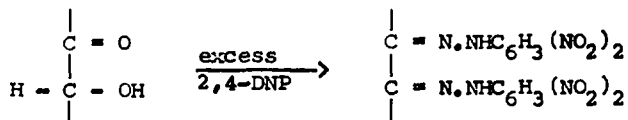
From ethylene glycol : DNP derivative of formaldehyde;
m.p. = $165\text{--}166^\circ\text{C}$ (lit m.p.^{17a} = 166°C)

From 2,3-butane diol : DNP derivative of acetaldehyde;
m.p. = $167\text{--}168^\circ\text{C}$ (lit m.p.^{17a} = 168°C)

From pinacol : DNP derivative of acetone;
m.p. = 127°C (lit m.p.^{17a} = 128°C)

The m.m.p remained undepressed on admixture with authentic DNP derivatives of the respective aldehydes and ketone.

The filtrate, containing excess 2,4-DNP was allowed to stand overnight, in each case. It is interesting that voluminous precipitates appeared in the filtrates of the reaction mixtures containing ethylene glycol and 2,3-butane diol, whereas no such precipitation occurred in the filtrate of the other reaction mixture. The precipitates obtained under this condition were filtered, washed and dried as before. These 2,4-DNP derivatives were characterised by very high melting points, $325\text{--}327^\circ\text{C}$ & $313\text{--}315^\circ\text{C}$ respectively. The values correspond to the 2,4-DNP derivatives of glyoxal^{17b} (328°C) and biacetyl^{17b} (315°C). These observations are to be expected if the initial oxidation products, namely glycolaldehyde and acetoin, in the oxidations of ethylene glycol and 2,3-butane diol respectively react with excess 2,4-DNP to give their corresponding osazone¹⁸ as shown below



The infrared spectra of the osazones obtained from the products and that of the glyoxal and biacetyl were found to be identical in all respects.

The results of the product analyses indicate the absence of organic acids. This is believed to be due to the fast hemiacetal and hemiketal formation of the initial product with excess of diols in presence of acid catalyst.

RESULTS

Effect of Variation of Reactant Concentrations: The reactions were carried out at different $[\text{Cr(VI)}]_0$ but at constant $[\text{diol}]_0$, $[\text{H}^+]_0$ and temperature (conditions were the same as those mentioned above). The concentrations of $[\text{Cr(VI)}]_t$ were varied between the limits $(0.667\text{--}6.67) \times 10^{-3} \text{ M}$. The values of k_{cor} ,

$$\left\{ k_{\text{cor}} = \frac{k_{\text{obs}} [\text{Cr(VI)}]_t}{[\text{HCrO}_4^-]} \right\} \text{ were calculated as mentioned}$$

earlier¹⁶ and were found to be $(3.7 + 0.01) \times 10^4$, $(5.5 + 0.02) \times 10^4$ and $(1.0 + 0.03) \times 10^3 \text{ (sec}^{-1}\text{)}$ for the respective reactions. The results indicate that HCrO_4^- is the reactive oxidising species and the order with respect to the oxidant is one.

The reactions were also studied at different substrate concentrations but at constant $[\text{Cr(VI)}]_0$, $[\text{H}^+]_0$ and temperature. The results, plotted in Figure 1 show that the reactions are first-order with respect to each organic substrate.

Effect of Variation of Perchloric Acid Concentration The effect of variation of $[\text{H}^+]_0$ at constant ionic strength (1.0 M) was studied at different $[\text{HClO}_4]_0$ but at constant reactant concentrations and temperature. These oxidations were found to be acid catalysed. The slopes of $\log k_{\text{obs}}$ against $-\log [\text{HClO}_4]_0$ plots (Figure 2) for the oxidations of different alcohols are 1.8, 2.0 and 1.25 for the respective reactions. The plots of $\log k_{\text{obs}}$ against $-\text{H}_0$ however, failed to give linear relationship. The values of Hammett acidity function were taken from Roczek and Aylward¹⁹.

Table 1. Effect of Salt Concentrations on Reaction Rates

(a) [ethylene glycol]₀ = 2 × 10⁻²M
 (b) [2,3-butane diol]₀ = 5 × 10⁻³M [H⁺]₀ = 1.0 M
 (c) [pinacol]₀ = 5 × 10⁻³M [Cr(VI)]_t = 3.34 × 10⁻³M

[NaClO ₄] ₀ × 10 ¹ M	(a) k _{obs} × 10 ⁴ (sec ⁻¹)	(b) k _{obs} × 10 ⁴ (sec ⁻¹)	(c) k _{obs} × 10 ³ (sec ⁻¹)
0	4.57	6.74	1.24
0.8	4.80	6.85	1.54
1.6	5.33	7.68	1.60
2.4	5.82	8.34	1.83
3.2	6.40	8.93	2.02
4.0	6.62	9.60	2.26

Table 2. Effect of Manganese (II) ion on Reaction Rates

[Cr(VI)]₀ = 3.34 × 10⁻³M (a) [ethylene glycol]₀ = 2 × 10⁻²M
 [H⁺]₀ = 1.0 M (b) [2,3-butane diol]₀ = 5 × 10⁻³M
 (c) [pinacol]₀ = 5 × 10⁻³M

[Mn ²⁺] ₀ × 10 ³ M	(a) k _{obs} × 10 ⁴ (sec ⁻¹)	(b) k _{obs} × 10 ⁴ (sec ⁻¹)	(c) k _{obs} × 10 ³ (sec ⁻¹)
0	4.57	6.74	1.24
0.4	3.15	5.99	1.13
0.8	2.99	5.56	1.03
1.2	2.93	5.4	0.95
1.6	2.93	5.4	0.95

Table 3. Activation Parameters for the Oxidations of Different Diols

Diol	ΔH [#] (kJ mole ⁻¹)	-ΔS [#] (J.deg ⁻¹ mole ⁻¹)
Ethylene glycol	60.7	79.2
2,3-butane diol	48.3	104.2
Pinacol	40.6	125.0

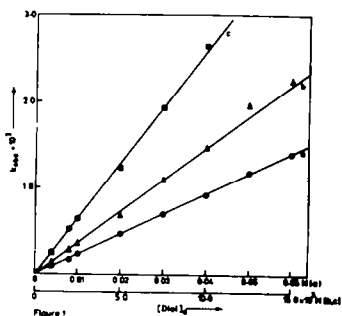


Figure 1. Variation of first-order rate constants with substrate concentrations. Plots of k_{obs} against $[\text{Diol}]_0$

● → ethylene glycol
 ▲ → 2,3-butane diol ■ → pinacol.

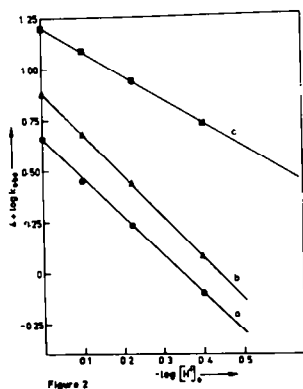


Figure 2. Dependence of first-order rate constants on $[\text{H}^+]$. Plots of $\log k_{\text{obs}}$ against $-\log [\text{H}^+]_0$

● → ethylene glycol
 ▲ → 2,3-butane diol ■ → pinacol.

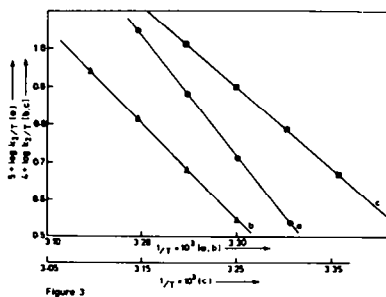


Figure 3. Influence of temperature on second-order rate constants. Plots of $\log (k_2/T)$ against $1/T$.

● → ethylene glycol
 ▲ → 2,3-butane diol ■ → pinacol.

Effect of Variation of Sodium Perchlorate Concentration The effect of variation of $[\text{NaClO}_4]$ on the rate of oxidation was measured at constant $[\text{Cr(VI)}]_0$, $[\text{diol}]_0$, $[\text{HClO}_4]_0$ and temperature. The rates were found to increase in $[\text{NaClO}_4]_0$ from $(0.8-4.0) \times 10^{-1}$ M. The results are recorded in Table 1. This indicates that the reaction may involve ions of similar type or ion and dipolar species²⁰.

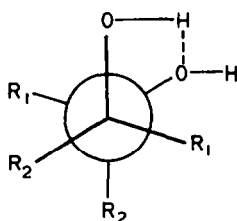
Effect of Variation of Manganous ion Concentration The rate of oxidation of diols by Cr(VI) was studied under various concentrations of Mn^{2+} ions, but at constant $[\text{Cr(VI)}]_0$, $[\text{diol}]_0$, $[\text{HClO}_4]_0$ and temperature. The pseudo-first-order rate constants decreased by 36, 20 and 23 % at $[\text{Mn}^{2+}] = 1.2 \times 10^{-3}$ M for the respective reactions. The addition of NaClO_4 of the same strength as that of Mn^{2+} ions did not influence the rate of oxidation. The results indicate that Mn^{2+} ion catalyses the disproportionation of the intermediate valence states of chromium²¹. The results have been recorded in Table 2.

Effect of Variation of Temperature and Activation Parameters The second-order rate constants (k_2) for the oxidations of diols at different temperatures were calculated from the relation, $k_2 = k_{\text{obs}}/[\text{diol}]_0$. The least square plot of $\log(k_2/T)$ against $1/T$ (Figure 3) was used to calculate the enthalpy of activation (ΔH^\ddagger) followed by the calculation of entropy of activation (ΔS^\ddagger) as mentioned in earlier communication. The results are detailed in Table 3.

DISCUSSION

The kinetics of oxidation of ethylene glycol, 2,3-butane diol and pinacol by chromium (VI) in perchloric acid medium are first-order with respect to $[\text{HCrO}_4^-]$ as well as $[\text{diol}]_0$ but the order with respect to $[\text{HClO}_4]$ are different (1.25-2.0). Moreover, the products are formaldehyde, acetaldehyde and acetone respectively. Since all these oxidations were carried out with the same oxidant but with different diols under same conditions of acidity, the difference in order with respect to $[\text{acid}]$ is believed to be due to the difference in protonation of organic substrate and not due to protonation of H_2CrO_4 .

Ethylene glycol exists in two distinct conformations²², the anti and the gauche. But in the latter, the hydroxyl groups are close enough to form intramolecular hydrogen bonds. So most of the molecules are in the gauche form, despite the steric and dipolar repulsion of the hydroxyl groups. 2,3-butane diol exists in both the meso and the dl-conformations in which the hydroxyl groups are gauche to each other. But the difference in absorption frequency^{23, 24a} of the bonded and unbonded hydroxyl groups indicate that the intramolecular H-bonding is stronger in the dl-form. Moreover, steric repulsion amongst Me-groups is less in the dl-form. So dl-conformation of 2,3-butane diol is regarded as the preponderant form. Similarly, pinacol is also considered to exist mainly as intramolecular hydrogen bonded gauche conformation.



$R_1 = R_2 = \text{H}$ for ethylene glycol

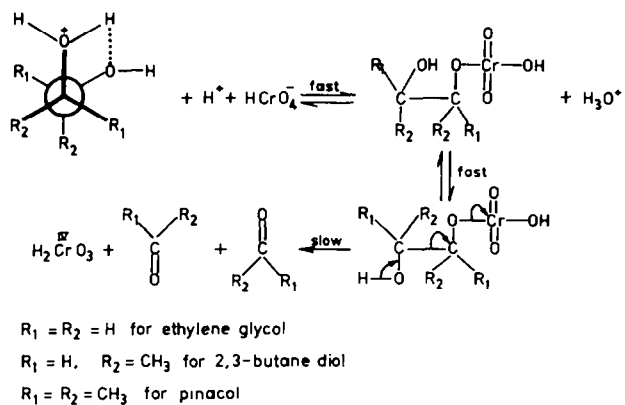
$R_1 = \text{H}$; $R_2 = \text{CH}_3$ for 2,3-butane diol

$R_1 = R_2 = \text{CH}_3$ for pinacol

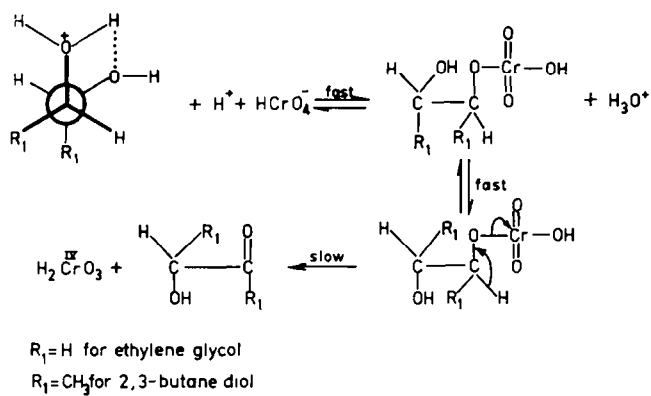
Like monools, the oxidations of diols were also studied at the acidity (1.0 M). So it is likely that the diols (like monools) behave as base and exist in equilibrium with protonated species. Moreover protonation facilitates intramolecular hydrogen bonding and thereby stabilises the gauche form more. Hence the protonated diols and not the molecular or anionic forms of diol, are considered to be the effective reductant. The variation of order with respect to $[\text{acid}]$ from 1.25 to 2.0 corroborates this. This variation is also in conformity with the order of basicity of the diols. 2,3-butane diol, being a 2° ol, is more basic than ethylene glycol (1° ol) due to +I effect. But pinacol, a 3° ol, behaves as the weakest Lewis base, since the corresponding conjugated acid becomes less stable due to lesser degree of solvation which is caused by its greater size and consequently smaller ionic potential. The order of the basicity is thus



Diols are oxidised under the same conditions as those of the monools, so the effective oxidant is believed to be the same, namely protonated HCrO_4 . Thus, the reactions occur between protonated diols and protonated HCrO_4 . The positive primary kinetic salt effect is in keeping with the ion-dipole interaction²⁰.



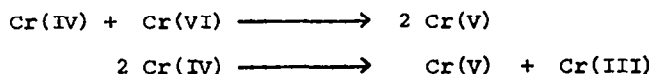
Scheme 1



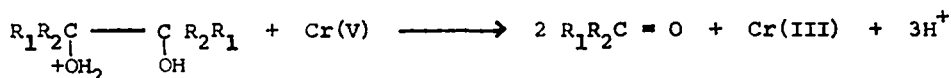
Scheme 2

These reactions are believed to proceed via the fast formation of intermediate chromate ester. Subsequently, slow disproportionation of the ester occurs. There is no direct kinetic evidence of such an ester, hence the equilibrium for the esterification step is considered to be very low. The presence of the bulkier HCrO_4^- group in the intermediate chromate ester introduces higher steric strain. This overrides the stabilisation energy due to intramolecular hydrogen bonding. So the esters may undergo fast rearrangement to the more stable anti conformation. The formation of formaldehyde, acetaldehyde and acetone in the respective reactions indicates that the products are obtained by C-C bond ruptures as shown in Scheme 1 to give the products and Cr(IV).

Cr(IV), generated in the rate-determining step, rapidly reacts with Cr(VI) or/and disproportionates^{24b} to yield Cr(V).



Cr(V), a stronger oxidant, reacts rapidly with the reactive reductants as



The rates of oxidation of the respective diols are 2.35×10^{-2} , 1.46×10^{-1} and 2.44×10^{-1} (lit. mole⁻¹ sec⁻¹) at 35°C. These indicate that the rates of the reactions follow the order

pinacol > 2,3-butane diol > ethylene glycol

This is also in conformity with the enthalpy of activation data. This difference in the rate of the reaction is supposed to be due to more stability of the carbonium ion by inductive (+I) and hyperconjugative effects in the cases of pinacol and 2,3-butane diol; these effects being absent in the case of ethylene glycol. Again, the stability of the tertiary carbonium ion is expected to be more than the secondary carbonium ion due to more inductive and hyperconjugative effect.

The effect of methyl substitution on the degree of cleavage was confirmed and it was found that pinacol readily gave C-C cleavage to acetone. However, earlier reports³ suggested that a cyclic ester is formed between the reactants prior to electron transfer, which finally decomposes in a fashion similar to that suggested for oxidation by lead tetraacetate²⁵ and periodic acid²⁶. But it is not essential that the reaction should occur exclusively via cyclic ester formation in the present reaction. Since, if that be the case, then the products viz. hydroxy-aldehyde and hydroxyketone in the oxidations of ethylene glycol and 2,3-butane diol are unlikely to be formed. Thus it is apparent that the proposed acyclic mechanism in the oxidation of diols by chromic acid cannot be ruled out.

REFERENCES

1. K.B.Wiberg : 'Oxidations in Organic Chemistry', Academic Press, (New York), Part A. p. 69 (1965).
2. F.H.Westheimer : Chem. Rev., 45, 419 (1949).
3. F.H.Westheimer and A.Novick : J. Chem. Phys., 11, 506 (1943).
4. K.B.Wiberg and H.Schäfer : J. Am. Chem. Soc., 91, 927 (1969).
5. K.B.Wiberg and H.Schäfer : ibid., 91, 933 (1969).
6. F.Hasan and J.Rocek : ibid., 94, 8946 (1972).
7. A.C.Chatterjee and S.K.Mukherjee : Z. Phys. Chem. (N.F.), 207, 372 (1957).
8. A.C.Chatterjee and S.K.Mukherjee : Z. Phys. Chem. (N.F.), 208, 281 (1958).
9. J.Rocek : Collection Czech. Chem. Comm., 22, 1509 (1957).
10. M.C.R.Symons : J. Chem. Soc., 4331 (1963).
11. F.Holloway : J. Am. Chem. Soc., 74, 224 (1952).
12. M.Cohen and F.H.Westheimer : ibid., 74, 4387 (1952).
13. D.C.Lee and R.Stewart : ibid., 86, 3051 (1964).
14. K.K.Sen Gupta and J.K.Chakladar : J. Chem. Soc., (Perkin II), 929 (1973).
15. K.K.Sen Gupta, T.Samanta and S.N.Basu : Tetrahedron, 41, 205 (1985).
16. K.K.Sen Gupta, T.Samanta and S.N.Basu : Tetrahedron, (in press).

17. (a) R.C.Weast : 'Hand Book of Chemistry and Physics', The Chemical Rubber Co., Ohio, U.S.A., 52nd edition, C-303 (1971-72).
(b) A.I.Vogel : 'A Text Book of Practical Organic Chemistry' English Language Book Society and Longman Group. Ltd., 4th. edition, p. 1190 ; 1194.
18. J.March : 'Advanced Organic Chemistry', McGraw-Hill (New York), 2nd edition, p. 826 (1977).
19. J.Roczek and D.E.Aylward : *J. Am. Chem. Soc.*, 97, 5452 (1975).
20. K.J.Laidler : 'Chemical Kinetics', Tata McGraw-Hill Publishing Company Ltd. (New Delhi), 2nd edition, p.229.
21. W.Watanabe and F.H.Westheimer : *J. Chem. Phys.*, 17, 61 (1949).
22. E.L.Eliel : 'Steriochemistry of Carbon Compounds', Tata McGraw-Hill, (New Delhi), p. 131, (1979).
23. S.Mizushima, T.Shimanouchi, T.Miyazawa, K.Abe and M.Yasumi : *J. Chem. Phys.*, 19, 1477 (1951).
24. (a) L.P.Kuhn : *J. Am. Chem. Soc.*, 74, 2492 (1952).
(b) K.K.Sen Gupta and J.K.Chakladar : *J. Chem. Soc.*, (Dalton), 222 (1974).
25. R.Criegee : 'Oxidations in Organic Chemistry', edited by K.B.Wiberg., Academic Press (New York), Part A, p. 278 (1965).
26. C.A.Bunton : 'Oxidations in Organic Chemistry', edited by K.B.Wiberg, Academic Press (New York) Part A, p. 367 (1965).