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Kinetics of Oxidation of Some Dihydroxy Ethers by Permanganate in Perchloric Acid Medium

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Reactivities of some dihydroxy ethers, *viz.*, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol (200, 400, 600 LR) by permanganate have been studied in presence of perchloric acid. The reaction rate increases with increase in $[H^+]$ and the order with repect to $[H^+]$ is 0.4 ± 0.1 at $[H^+] \leq 0.4$ mol dm^{-3} but 1.3 ± 0.1 at $[H^+] > 0.4$ mol dm^{-3}. The reaction occurs through the protonation of ether group of the substrate in a fast preequilibrium followed by a slow rate-determining oxidation step. The substrates are oxidised to give formaldehyde. The reactions have been shown to occur by one-step two-electron transfer process.

INTRODUCTION

Diols are known to react with chromium(VI)[1], manganese(VII)[2], bromate[3], iridium(IV)[4], vanadium(V)[5], periodate[5], lead tetra-acetate[5], persulphate[6] in acid medium and by copper(III)[7], silver(III)[7], cupric tartarate[8] and ruthenium tetroxide[8] in alkaline medium. There is no literature data involving the oxidations of dihydroxy ethers by different oxidants. The present report deals with the reactivities of diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol (200, 400, 600 LR) by permanganate in acid medium.

EXPERIMENTAL

Reagents: Perchloric acid, potassium permanganate, potassium iodide, sodium thiosulphate were all of A.R. grade. The organic compounds (Fluka) were of the highest purity available and the solutions were made in double distilled water.

Kinetic Measurements: The reactions were studied under the condition in which the substrate concentrations were in large excess compared to that of permanganate. Solutions of MnO_4^- and the mixture containing substrate and $HClO_4$ were separately thermostated (± 0.1°C) for nearly 1 h. The reaction rates were followed by removing an aliquot from the reaction mixture at known intervals of time and quenching the reaction by adding an excess of potassium iodide solution to it. The liberated iodine was then estimated against a standard thiosulphate solution. Generally 8–10 experimental readings were taken in each run. The pseudo-first-order rate constants (k_{obs}) were reproducible to within ±5%.

Product analyss: The product analyses of the oxidations of dihydroxy ethers by permanganate were carried out with the reaction mixture: [dihydroxy ether] $= 5 \times 10^{-2}$ mol dm^{-3}, $[MnO_4^-] = 1 \times 10^{-3}$ mol dm^{-3} and $[HClO_4] = 0.5$ mol dm^{-3}. The reaction mixture (30 mL) for each substrate was kept at 30°C for 2 h. It was then filtered to remove suspended particles. The filtrate was divided into two parts. First part of the filtrate was treated with 2 mL 12 N sulphuric acid in a test tube and a little solid chromotropic acid and the tube was heated for 10 min in a water bath at 60°C. The pinkish violet colour indicated the presence of formaldehyde[9]. The second part of the filtrate was then treated with an excess of 2,4-dinitrophenyl hydrazine hydrochloride solution and left overnight. The precipitate was filtered, washed thoroughly with water and recrystallised from alcohol-water mixture. The melting points of the dried products were determined and analysed (Table-1).

TABLE-1
MELTING POINTS AND THE C, H, N ANALYSIS OF THE 2,4-DNP DERIVATIVES OF THE OXIDATION PRODUCTS

Substrate	m.p. (°C) of 2,4-DNP derivative	% Analysis, Found		
		C	H	N
Diethylene glycol	165–166	40.53	2.63	25.50
Triethylene glycol	166–168	40.20	2.72	26.02
Tetraethylene glycol	167–169	40.09	3.01	25.91
Polyethylene glycol, 200 LR	164–165	40.36	2.69	25.80
Polyethylene glycol, 400 LR	168–169	40.21	2.85	25.32
Polyethylene glycol, 600 LR	167–168	40.07	2.78	25.94

Polymerisation Test: A solution of $KMnO_4$ (2 mL, 1×10^{-3} mol dm^{-3}) was added to a solution containing respective dihydroxy ether compounds (2 mL, 5×10^{-2} mol dm^{-3}) and acrylamide [4 mL, 40% (w/v)]. The acidity was adjusted to 0.6 mol dm^{-3} and total volume to 10 mL. The dihydroxy ethers failed to give any polymer. The result is in conformity with a one-step two-electron transfer process with no free radical intermediate.

RESULTS AND DISCUSSION

Effect of reactant concentrations: The pseudo-first-order rate constants (k_{obs}) were determined at different $[MnO_4^-]$ but at constant [dihydroxy ether], $[H^+]$ and temperature. The k_{obs} values (Table-2) are independent of $[MnO_4^-]$ in the range $(0.5–1.5) \times 10^{-3}$ mol dm^{-3}. The effect of changing [dihydroxy ether] was studied at constant $[MnO_4^-]$ and $[H^+]$. Plots of k_{obs} *vs.* [dihydroxy ether] at each temperature give straight lines passing through the origin. The results as recorded in Table-3 indicate that each reaction is first order with respect to [dihydroxy ether].

TABLE-2

EFFECT OF [MnO_4^-] ON THE RATE OF OXIDATION AT 303 K [MnO_4^-] = (0.5–1.5) × 10^{-3} mol dm^{-3}; [Dihydroxy ether] = 5.0 × 10^{-2} mol dm^{-3}; [H^+] = 0.5 mol dm^{-3}; μ = 0.6 mol dm^{-3}

Substrate	$k_{obs} \times 10^4$ (s^{-1})
Diethylene glycol	4.11 ± .13
Triethylene glycol	4.48 ± .09
Tetraethylene glycol	5.39 ± .08
Polyethylene glycol, 200 LR	6.40 ± .06
Polyethylene glycol, 400 LR	7.65 ± .11
Polyethylene glycol, 600 LR	8.71 ± .10

TABLE-3

VARIATION OF PSEUDO-FIRST-ORDER RATE CONSTANTS FOR [MnO_4^-] WITH SUBSTRATE(S) CONCENTRATIONS AT DIFFERENT TEMPERATURES

MnO_4^-] = 1 × 10^{-3} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3}

Temp. (K)	[S] × 10^2 (mol dm^{-3})	$k^a_{obs} \times 10^3$ (s^{-1})	$k^b_{obs} \times 10^3$ (s^{-1})	$k^c_{obs} \times 10^3$ (s^{-1})	$k^d_{obs} \times 10^3$ (s^{-1})	$k^e_{obs} \times 10^3$ (s^{-1})	$k^f_{obs} \times 10^3$ (s^{-1})
298	2.5	0.356 (.0142)	0.490 (.0196)	0.504 (.0202)	0.560 (.0224)	0.711 (.0284)	0.766 (.0306)
	5	0.716 (.0143)	0.985 (.0197)	1.020 (.0204)	1.080 (.0216)	1.440 (.0288)	1.560 (.0312)
	10	1.410 (.0141)	1.930 (.0193)	2.110 (.0211)	2.210 (.0221)	2.850 (0.0285)	3.060 (.0306)
	15	2.160 (.0144)	2.930 (0.195)	3.010 (.0200)	3.310 (.0220)	4.270 (.0284)	4.600 (.0306)
	20	2.830 (.0141)	3.900 (.0195)	4.160 (.0208)	4.400 (.0220)	5.690 (.0284)	6.140 (.0307)
	25	3.520 (.0141)	4.950 (.0198)	5.210 (.0208)	5.530 (.0221)	7.230 (.0289)	7.640 (.0305)
303	2.5	0.524 (.0209)	0.707 (.0283)	0.783 (.0317)	0.870 (.0348)	1.070 (.0428)	1.170 (.0468)
	5	1.150 (.0230)	1.430 (.0286)	1.590 (.0318)	1.710 (.0342)	2.160 (.0343)	2.300 (.0460)
	10	2.240 (.0224)	2.830 (.0283)	3.160 (.0316)	3.470 (.0347)	4.280 (.0428)	4.690 (.0469)
	15	3.140 (.0209)	4.240 (.0282)	4.740 (.0316)	5.210 (.0347)	6.410 (.0427)	7.030 (.0468)
	20	4.190 (0.209)	5.710 (.0283)	6.440 (.0322)	6.930 (.0346)	8.500 (.0425)	9.400 (.0470)
	25	5.270 (.0211)	7.160 (.0286)	7.880 (.0.315)	8.680 (.0347)	10.700 (.0427)	11.700 (.0466)

Temp. (K)	$[S] \times 10^2$ (mol dm^{-3})	$k^a_{obs} \times 10^3$ (s^{-1})	$k^b_{obs} \times 10^3$ (s^{-1})	$k^c_{obs} \times 10^3$ (s^{-1})	$k^d_{obs} \times 10^3$ (s^{-1})	$k^e_{obs} \times 10^3$ (s^{-1})	$k^f_{obs} \times 10^3$ (s^{-1})
308	2.5	0.735 (.0294)	1.010 (.0404)	1.25 (.05)	1.40 (.056)	1.64 (.0656)	1.73 (.0692)
	5	1.450 (.029)	2.150 (.043)	2.47 (.0494)	2.83 (.0566)	3.26 (.0652)	3.51 (.0702)
	10	2.920 (.0292)	4.210 (.0421)	4.90 (.0499)	5.60 (.056)	6.55 (.0656)	6.95 (.0695)
	15	4.410 (.0294)	6.130 (.0423)	7.51 (.0501)	8.40 (.056)	9.87 (.0658)	10.40 (.0694)
	20	5.900 (.0295)	8.320 (.0416)	9.96 (.0498)	11.20 (.0561)	13.20 (.0658)	13.90 (.0669)
	25	7.380 (.0295)	10.200 (.0409)	12.40 (.0498)	14.20 (.0568)	16.40 (.0658)	17.40 (.0696)
313	2.5	1.050 (.042)	1.420 (.0568)	1.87 (.0748)	2.20 (.0880)	2.46 (.0984)	2.90 (.116)
	5	2.130 (.0426)	2.860 (.0572)	3.77 (.0754)	4.43 (.0886)	4.95 (.0990)	5.84 (.1168)
	10	4.210 (.0421)	5.690 (.0569)	7.500 (.075)	8.83 (.0883)	9.80 (.0985)	11.60 (.1165)
	15	6.340 (.0423)	8.540 (.0569)	11.30 (.0751)	13.20 (.0882)	14.80 (.0989)	17.50 (.1166)
	20	8.440 (.0422)	11.700 (.0560)	15.00 (.0750)	17.60 (.0881)	19.80 (.0990)	23.40 (.1169)
	25	10.500 (.0422)	14.300 (.0572)	18.80 (.0752)	22.20 (.0888)	24.70 (.0989)	29.20 (.1168)

Figures in parentheses represent the values of second order rate constants for the respective substrates. a = diethylene glycol; b = triethylene glycol; c = tetraethylene glycol; d = polyethylene glycol, 200 LR; e = polyethylene glycol, 400 LR; f = polyethylene glycol, 600 LR.

Effect of ionic strength: The reaction was studied at different ionic strengths maintained by the addition of $NaClO_4$ but at constant $[MnO_4^-]$, [dihydroxy ether], $[H^+]$ and temperature. The pseudo-first-order rate constant decreases with increase in $NaClO_4$ concentrations at $[H^+] \leq 0.4$ mol dm^{-3} but is independent of $[NaClO_4]$ at $[H^+] > 0.4$ mol dm^{-3} (Table-4).

TABLE-4

INFLUENCE OF IONIC STRENGTH ON THE PSEUDO-FIRST-ORDER RATE CONSTANT

$[MnO_4^-] = 1 \times 10^{-3}$ mol dm^{-3}; [Diethylene glycol] $= 5 \times 10^{-2}$ mol dm^{-3};
Temp. = 303 K.

μ^a (mol dm^{-3})	0.635	0.735	0.835	0.935	1.035	1.135
$k_{obs} \times 10^4$ (s^{-1})	1.570	1.390	1.27	0.928	0.723	0.517
μ^b (mol dm^{-3})	0.635	0.835	-.935	1.035	1.135	1.235
$k_{obs} \times 10^4$ (s^{-1})	5.250	5.130	5.170	4.980	5.150	5.080

a, $[H^+] = 0.1$ mol dm^{-3}; b, $[H^+] = 0.6$ mol dm^{-3}

Effect of hydrogen ion concentration: The effect of varying $[H^+]$ on the pseudo-first-order rate constant was also studied over a wide range [(0.1–1.0) mol dm^{-3}] of $[H^+]$ keeping $[MnO_4^-]$, [dihydroxy ether], ionic strength and temperature constant. The rate increases with increase in $[H^+]$. However the increase in rate is small at $[H^+] \leq 0.4$ mol dm^{-3} but above that concentration of $[H^+]$, the rate increases abruptly (Fig. 1). The order with respect to $[H^+]$ is less than unity 0.4 ± 0.1) at $[H^+] \leq 0.4$ mol dm^{-3} but 1.3 ± 0.1 at $[H^+] > 0.4$ mol dm^{-3}.

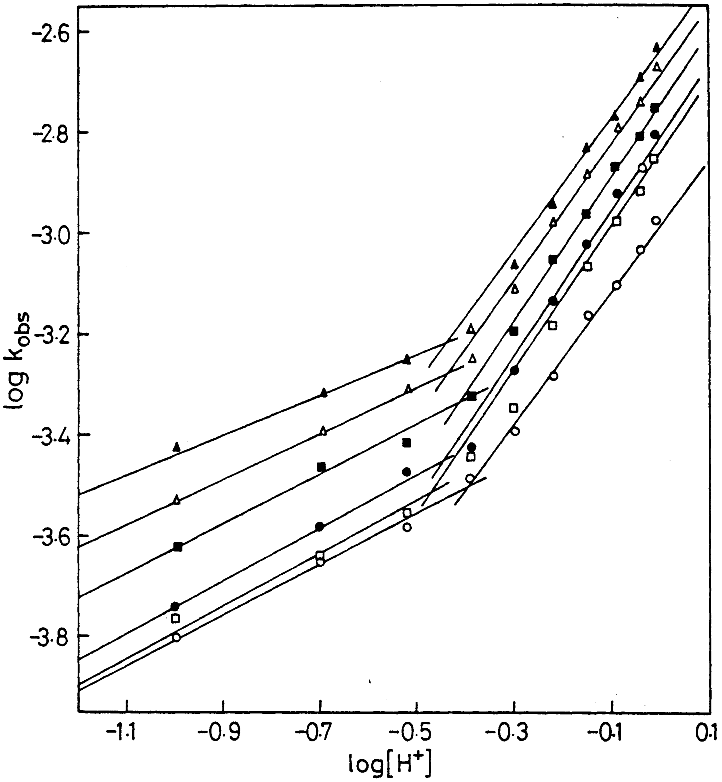


Fig. 1. Dependence of the reaction rate on $[H^+]$. Plots of log k_{obs} *vs.* log $[H^+]$ at [substrate] $= 5 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.64$ mol dm^{-3}, $[MnO_4^-] = 1 \times 10^{-3}$ mol dm^{-3} and temperature = 303 K. (○) Diethylene glycol; (□) Triethylene glycol; (●) Tetraethylene glycol; (■) Polyethylene glycol, 200 LR; (Δ) Polyethylene glycol, 400 LR; (▲) Polyethylene glycol, 600 LR.

Activation parameters: The second order rate constant ($k_2 = k_{obs}$/ [substrate]) were determined at different temperatures (298–313 K). The activation enthalpies ($\Delta H^{\neq}$) were calculated from the plots of log (k_2/T) *vs* 1/T (Fig. 2). Moreover entropies of activation ($\Delta S^{\neq}$) were calculated.

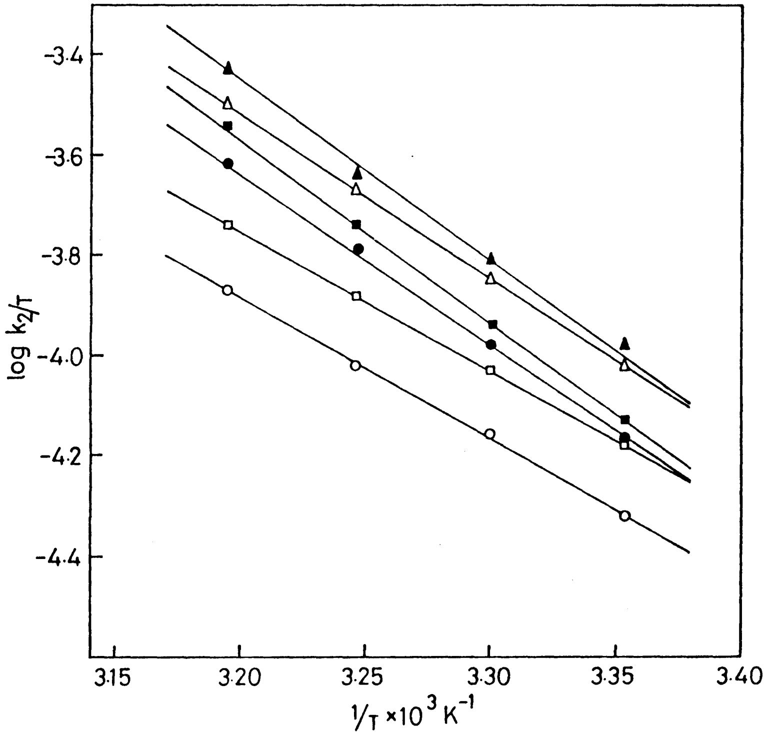


Fig. 2. Influence of temperature on second order rate constants of the oxidation of dihydroxy ether compounds by MnO_4^-. Plots of log k_2/T against $1/T$. (○) Diethylene glycol; (□) Triethylene glycol; (●) Tetraethylene glycol; (■) Polyethylene glycol, 200 LR; (Δ) Polyethylene glycol, 400 LR; (▲) Polyethylene glycol, 600 LR.

The activation parameters are recorded in Table-5. The enthalpy of activation is linearly related to the entropy of activation ($\gamma = 0.9905$). The isokinetic temperature has been calculated to be 275 K. The isokinetic behaviour is also supported by the linear plot of log k_2' *vs.* log k_2 ($\gamma = 0.9898$) where k_2' and k_2 are the second order rate constant at the temperatures 303 K (T_1) and 308 K (T_2), respectively. All these indicate that a similar mechanism may be operative in all these reactions. The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1 - f)/(T_1 - T_2f)$, where f is the slope of the Exner plot[10]. The value of β was found to be 268 K which is lower than T, (mid point of the experimentally used range of temperature) and is in conformity with a large number of reactions[11] for which $\beta - T$ is negative. The reactions are believed to be entropy controlled.

TABLE-5
VALUES OF ACTIVATION PARAMETERS FOR THE OXIDATION OF DIHYDROXY ETHERS BY MnO_4^-

Substrate	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
Diethylene glycol	27 ± 2	−187 ± 7
Triethylene glycol	26 ± 2	−188 ± 7
Tetraethylene glycol	33 ± 4	−164 ± 13
Polyethylene glycol, 200 LR	35 ± 2	−156 ± 7
Polyethylene glycol, 400 LR	31 ± 4	−168 ± 13
Polyethylene glycol, 600 LR	33 ± 4	−160 ± 13

Ethers are not attacked by nucleophiles and by bases. This lack of reactivity, coupled with their ability to solvate make ethers good solvents for many processes. Highly volatile ethers being hazardous, high boiling dihydroxy ethers like diethylene glycol[12] (b.p. 245°C), triethylene glycol[12] (b.p. 278.3°C), tetraethylene glycol[12] (b.p. 328°C) etc. are preferred. The presence of hydroxyl group in the substrate makes them reactive. Moreover, ethers are weakly basic and are converted to reactive dialkyl oxonium salts under strongly acidic condition since ethereal oxygen is more reactive[13] towards protonation than alcoholic oxygen. In low acidity, substrates(s) undergoe (s) protonation to yield protonated substrate which reacts with MnO_4^- to form ester (Scheme-1).

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+$$

$$SH^+ + MnO_4^- \xrightarrow{k_2} \text{Complex}$$

$$\text{Complex} \xrightarrow{\text{fast}} \text{Products}$$

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_1k_2[S]_t[H^+][MnO_4]}{k_{-1} + k_1[H^+]}$$

$$k_{obs} = \frac{k_1k_2[S]_t[H^+]}{k_{-1} + k_1[H^+]}$$

Scheme-1

The experimentally obtained order with respect to each reagent and identified product is in keeping with the Scheme 1. Moreover, the reaction between two oppositely charged ions (in rds) is disfavoured with increasing ionic strength[14] of the medium. This was corroborated in practice justifying the suggested mechanism.

In higher acidity, order with respect to [H$^+$] becomes higher. Hence, it is suggested that in higher acidity, protonation of permanganate anion [MnO_4^-] yields permanganic acid ($HMnO_4$).

$$MnO_4^- + H^+ \overset{k}{\rightleftharpoons} HMnO_4$$

This reacts with the protonated substrate to form an unstable intermediate which subsequently undergoes slow decomposition to the products.

$$SH^+ + HMnO_4 \xrightarrow{k_3} \text{Complex}$$

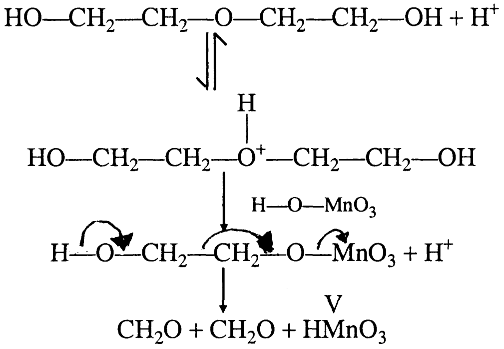
$$\text{Complex} \xrightarrow{\text{fast}} \text{Products}$$

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_1 k_3 K[S]_t[MnO_4^-]\,[H^+]^2}{k_{-1} + k_1[H^+]}$$

$$k_{obs} = \frac{k_1 k_3 K[S]_t[H^+]^2}{k_{-1} + k_1[H^+]}$$

Scheme-2

This Scheme-2 is in keeping with the order with respect to each reagent. Moreover, the finding that ionic strength has no effect on the rate of reaction corroborates the suggested mechanism. The reaction between diethylene glycol and MnO_4^- in acid medium leading to the formation of formaldehyde is shown below.



In case of higher dihydroxy ethers, rate of reaction increases with increase in chain length. This may be due to the fact that increase in chain length facilitates the generation of the protonated substrate and hence the formation of the complex with protonated substrate and permanganic acid. During reaction Mn(VII) is reduced to Mn(V). The existence of Mn(V) during MnO_4^- oxidation has already been reported$^{15-19}$. The experimental solution after reaction gives a black residue which is due to the production of MnO_2. Then Mn(V) is believed to undergo fast disproportionation to Mn(IV) and Mn(VIII) as

$$3HMnO_3 \xrightarrow{\text{fast}} 2MnO_2 + MnO_4^- + H^+ + H_2O \qquad (1)$$

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