Kinetics of Cooxidation of 1,2-Glycols & Esters by Periodate in Basic Medium

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The rates of periodate oxidation of 1,2-glycolsin the presence of esters in basic medium are more than the rates of oxidation of 1,2-glycols or esters alone under identical conditions. The orders in both [ester] and [I,2-glycol] have been found to be fractional. An inverse dependence of rate on [base] has been observed. The reactivities of different glycols are in the order ethylene glycol <propane-1,2-diol
>butane-1,2-diol. A probable mechanism involving glycol-periodate complex as one of the reactive species is proposed to explain the kinetic data.

Recently Rocek *et al.!* -3 have reported a direct threeelectron transfer in the Cr(VI) oxidation of several substrates either alone or in combination with other substrates. Since periodate (IO_4) is structurally closely related to CrO₄, it was considered of interest to study the periodate oxidation of binary mixtures of organic substrates. Preliminary investigations revealed that methyl acetate (MA) which is unreactive towards periodate in basic medium gets oxidised in the presence ;f 1,2-glycols and the rate of oxidation of the latter is also found to be more. In view of this a detailed kinetic study of the oxidation of various l,2-glycols in the presence of several esters has been undertaken to see whether cooxidation is taking place in this reaction and if so to arrive at a satisfactory mechanism for the reaction.

Materials and Methods

Ethylene glycol and propane-I,2-diol (BDH, AR) were distilled just before use. Butane-I,2-diol (Fluka, AG) and potassium periodate (BDH) were used as such. Methyl, ethyl, *n*-propyl and *n*-butyl acetates, ethyl formate, ethyl propionate and ethyl butyrate (all AR samples) were distilled before use. Stock solution of periodate was standardised using iodometric procedure.

Kinetic method

Solutions of periodate, methyl acetate and solutions containing requisite amounts of glycol and base were thermally equilibrated separately for 30 min. Appropriate quantities of methyl acetate followed by periodate were added to the glycol-base mixture, noting the time during the addition of periodate. The unreacted periodate was estimated at regular time intervals by quenching the reaction with a solution of potassium iodide and phosphate buffer. The pseudofirst order rate constants, k_{obs} , were obtained from the slopes of linear log $[1O_4]$ versus time plots.

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Product analysis

Formaldehyde and acetic acid were identified as the reaction products by their characteristic tests⁴ in the oxidation of ethylene glycol in the presence of methyl acetate. In the case of other glycols, viz. propane-1,2diol and butane-I,2-diol, acetaldehyde and propanaldehyde were respectively obtained apart from formaldehyde and acetic acid.

Stoichiometry

Formaldehyde, was estimated colorimetrically by measuring the absorbance of the coloured complex formed by the addition of chromotropic acid at $\lambda = 560$ nm and comparing it with the standard Beer's law plot. The results indicated that three mol of formaldehyde were formed for every two mol of periodate consumed, in accordance with Eq. (I)

$$
2IO4 + CH2OH - CH2OH + CH3COOCH3 \rightarrow
$$

3HCHO + 2IO₃ + CH₃COOH + H₂O ... (1)

Similar stoichiometric run in the case of oxidation of 1,2-glycol alone revealed the formation of 2 mol of formaldehyde.

Results and Discussion

Under the conditions [substrate] \geq [IO₄] a plot of $log [IO₄]$ versus time was linear (Fig. 1A) indicating a first order dependence of the rate on [periodate]. The orders in both [I,2-glycoIJ and [ester] were found to be fractional each as revealed by the slopes of the linear plots of log k_{obs} versus log [1,2-glycol] or log [methyl acetate] (Fig. I, B and C). The rate of the reaction decreased with increase in [base]. For example, under the conditions [ethylene glycol] = $[$ methyl acetate] $= 1.0 \times 10^{-2}$ mol dm⁻³, $[IO₄]=1.0 \times 10^{-3}$ mol dm⁻³ and temp. = 323 K, $k_{obs} \times 10^2$ decreased from 6.23 to 0.96 min⁻¹ when 10^3 [OH⁻] was increase from 5 to 25 mol dm $^{-3}$.

The oxidation kinetics of 1,2-glycols by periodate are well documented⁵⁻⁷. Methyl acetate in the present

Fig. 1- (A) Plot of log $(a-x)$ versus time {[ethylene glycol] $=[$ methyl acetate] = 0.01 mol dm⁻³; [IO₄] = 0.001 mol dm⁻³; $[KOH] = 0.01$ mol dm⁻³; temp. 323 K}, (B) Plot of log [ethylene $glycol$ + 3 versus $log k_{obs}$ + 2, conditions same as in Fig. (1A) except [ethylene glycol]. (C) Plot of log [methyl acetate] + 3 versus $\log k_{obs}$ + 2, conditions same as in Fig. IA except [methyl acetate].

study was found to be totally inactive towards periodate. Also there was no perceptible reaction between methyl acetate and glycol since the absorption band around 230 nm of the ester remained unaffected in the presence of glycol. However, methyl acetate in the presence of glycoi reacted with periodate to give the oxidised products in accordance with Eq. (I). The rate of oxidation of 1,2-glycol was also considerably enhanced in the presence of ester. These observations are similar to those observed with Cr(VI) as the oxidant¹⁻³. Hence, occurrence of a cooxidation reaction of methyl acetate in the presence of glycol is assumed here also.

In the oxidation of 1,2-glycol by periodate the formation of glycol periodate diester (C_1) is well established⁸ (Scheme 1).

The orders of the reaction in both [methyl acetate] and [1,2-glycol] are fractional indicating that both methyl acetate and 1,2-glycol are involved in the formation of some complex. Since there is(i) no interaction between 1,2-glycol and methyl acetate, (ii) methyl acetate by itself is inert towards periodate and (iii) the rate of

oxidation of glycol is enhanced in the presence of methyl acetate, it appears reasonable to assume that the intermediate complex (C_1) , which is formed in the glycol oxidation by periodate, is the species which oxidises the ester.

Methyl acetate in the presence of base exists in two different forms according to the equilibrium (2).

$$
CH3-C(=0)-OCH3+OH- $\underset{\leftarrow}{\overset{K}{\rightleftarrows}}$
CH₃-C(OH)(O⁻)-OCH₃ ... (2)
$$

The decrease in rate with increase in [OH^{-1} indicates that probably the neutral ester molecule is the reactive species. The possibility of hydrolysis of ester, followed by cooxidation is precluded because the reaction rate in the presence of the added acetate ion or methanol (the possible products of hydrolysis) remains unaffected.

The various glycols studied, viz. ethylene glycol, propane-I ,2-diol and butane-l ,2-diol behave similarly in the presence of methyl acetate as far as the kinetic results, corresponding products of oxidation and stoichiometry are concerned. Hence, it is presumed that all the glycols in the presence of ester undergo oxidation by a similar mechanism. The probable mechanism is shown in Scheme 2.

The formation of a cyclic intermediate (C_1) is envisaged as the first step in Scheme 2. This periodategycol complex (C_1) is presumed to attack the ester in the second step at the carbonyl group or at the

alcoholic carbon of the ester. In oxidation of esters by other oxidants, the attack by the oxidants is generally shown at the alcoholic carbon of the ester⁹. Experiments with different substituents in the acid moiety of the ester reveal that increasing the electronreleasing ability of the substituent decreases the rate of the reaction in the order: ethyl formate> ethyl acetate $>$ ethyl propionate $>$ ethyl butyrate. The corresponding rate constants (10² k_{obs}) are 13.5, 1.5, 1.2 and 1.0 \min ⁻¹ under the conditions [ethylene glycol][ester] $= 1.50 \times 10^{-2}$ mol dm⁻³, [KOH] = 1.0×10^{-2} mol dm⁻³, $[IO_4] = 1.0 \times 10^{-3}$ mol dm⁻³ and temp. = 323 K. A plot of $log (k/k_0)$ _{obs} versus σ^* is linear with a ρ^* of + 2.0 (Fig. *2A).* All these clearly indicate that the carbonyl group of the ester is the site of attack in the reaction. Positive ρ^* -value suggests an electrondeficient reaction centre and hence the carbonium ion of the carbonyl carbon of the ester is shown to be the reactive centre. On the other hand variation of substituents in 1,2-glycol results in an increase in the rate with increase in electron-releasing ability of the substituents. The different glycols react in the order: ethylene glycol < propane-I ,2-diol < butane-I ,2-diol. Their corresponding rate constants $(k_{obs} \times 10^2)$ min⁻¹ are 1.15, 3.90 and 6.20 under the conditions [glycol] $=[$ methyl acetate] = [KOH] = 1.0 × 10⁻² mol dm⁻³, $[1O_4^-] = 1 \times 10^{-3}$ mol dm⁻³ and temp. = 323 K. A ρ^* value of -1.2 obtained from the plots of log $(k/k_o)_{obs}$

Fig. 2-(A) Plot of log $(k/k_o)_{obs}$ versus σ^* for substituents in acid moiety of ester. (B) Plot of log $(k/k_o)_{obs}$ versus σ^* for substituents in glycol. (C) Plot of $1/k_{obs}$ versus $1/[$ ethylene glycol] (conditions same as in Fig. 1B). (D) Plot of $(1/k_{obs})$ versus $1/[$ methyl acetate] (conditions same as in Fig. IC).

versus σ^* (Fig. 2B) points to the formation of an electron-rich reactive centre. This indicates that the attack: by the periodate-glycol complex is nucleophilic in nature. Hence, a nucleophilic attack by complex (C_1) is shown on the carbonyl carbon of the ester in the second step to form another complex (C_2) . The complex (C_2) thus formed in step-2 is assumed to breakdown in a rate-determining step-3 to give rise to products (see Scheme 2). This step is shown to involve a proton elimination from the alcoholic carbon of the ester based on the fact that the reaction rate decreases with increase in electron-donating capacity of the substituent at alcoholic carbon of the ester. The order of reactivity is thus seen to be: methyl acetate> ethyl α acetate > *n*-propyl acetate > *n*-butyl acetate under similar conditions of concentration and temperature. The corresponding rate constants ($k_{obs} \times 10^2$) are 1.82, 1.55, 1.35 and 1.01 min^{-1} respectively. Absence of polymerisation of acrylonitrile monomer indicates that the oxidation does not involve free radicals. This is in keeping with the proposed ionic mechanism involving elimination of $H⁺$ ion through heterolytic cleavage of $C-H$ bond. Step-4 in the mechanism (Scheme 2) envisages a second mol of periodate to interact with $H_2IO_3^-$ in a fast step to give two mol of $10₃$. This accounts for the stoichiometry of two mol of periodate (Eq. I) even though the order with respect to periodate is one.

The rate law obtained from the above mechanism is given by Eq. (3)

$$
\frac{-d[\text{IO}_4^-]}{dt} =
$$
\n
$$
\frac{k K_1 K_2 [\text{IO}_4^-] [\text{glycol}] [\text{ester}]}{\{1 + K_1 [\text{glycol}]\} {\{1 + (K + K_2)[\text{ester}] + K[\text{OH}^-] \}}}
$$
\n... (3)

This rate law implies a first order dependence in [10*i]* and fractional order dependence in both [methyl acetate] and [1,2-glycol] in keeping with the observed results. It also explains the decrease in rate with increase in $[OH^-]$.

The reciprocal of Eq. (3) after simplification gives

$$
\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2} \left[\frac{1}{\text{[glycol]}} + K_1 \right]
$$

$$
\times \left[\frac{1 + K[\text{OH}^-]}{\text{[ester]}} + K + K_2 \right] \qquad \qquad \dots \text{ (4)}
$$

Equation (4) predicts linear plots with different intercepts for (i) $1/k_{\text{obs}}$ against 1/[glycol] at constant [ester] and [OH $^{-}$] and (ii) $1/k_{obs}$ against 1/[ester] at constant [glycol] and [OH ⁻]. Such plots have been realised in the present study (Fig. 2, C and D), indicating the validity of the rate law and hence, the proposed mechanism.

The effect of temperature on the rates of oxidations of different 1,2-glycols in the presence of methyl acetate has been studied and the E_{exp} values are 84.3, 95.7 and 114.9 kJ mol⁻¹ respectively for ethylene glycol, propane-I,2-diol and butane-I,2-diol.

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References

1 Hasan F & Rocek J, *J Am chem Sac,* 94 (1972) 9073.

- 2 Hasan F & Rocek J, *J Arn chem Sac,* 97 (1975) 1444.
- 3 Ip D & Rocek J, *J Arn chem Sac,* 101 (1979) 6311.
- 4 Feigel, *Spot tests* in *organic analysis* (Elsevier Publishing Company, New York) 1966,454.
- 5 Buist G J & Bunton C A, *J chem Soc,* (1954) 1406.
- 6 Duke F R & Bulgarin V C, *J Arn chem Sac,* 76 (1954) 3803.
- 7 Bose J C, Foster A B & Stephens R W, *J chem Sac* (1959) 3314.
- 8 Malaprade L, *Compt Rend Acad Sci,* 186 (1928) 382; Griegee R, Kraft L & Rank B, *Ann,* 507(1933) 159;Angyal S J & Young R J, *J Arn chem Soc,* 81 (1959) 5251, 5467.
- 9 Uma V, Sethuram B & Navaneeth Rao T, *Indian J Chern,* 22A (1983) 65; Vedavrath R, Sethuram B & Navaneeth Rao T, *Indian J Chem,* 17A (1979) 410; Surender Rao V, Sethuram B & Navaneeth Rao T, *Indian J Chern,* 18A (1979) 37.