

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

N SWARNALAKSHMI, V UMA, B SETHURAM & T NAVANEETH RAO\*

Department of Chemistry, Osmania University, Hyderabad 500 007

Received 5 December 1983; revised and accepted 4 April 1984

The rates of periodate oxidation of 1,2-glycols in 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 [1,2-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.*<sup>1-3</sup> have reported a direct three-electron transfer in the Cr(VI) oxidation of several substrates either alone or in combination with other substrates. Since periodate ( $\text{IO}_4^-$ ) is structurally closely related to  $\text{CrO}_4^{2-}$ , 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 of 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 1,2-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-1,2-diol (BDH, AR) were distilled just before use. Butane-1,2-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

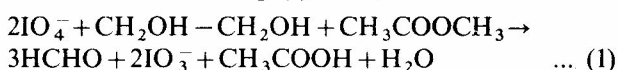
Solutions of periodate, methyl acetate and solutions containing requisite amounts of glycol and base were thermally equilibrated separately for 30 min. Appropriate quantities of methyl acetate followed by periodate were added to the glycol-base mixture, noting the time during the addition of periodate. The unreacted periodate was estimated at regular time intervals by quenching the reaction with a solution of potassium iodide and phosphate buffer. The pseudo-first order rate constants,  $k_{\text{obs}}$ , were obtained from the slopes of linear  $\log [\text{IO}_4^-]$  versus time plots.

### Product analysis

Formaldehyde and acetic acid were identified as the reaction products by their characteristic tests<sup>4</sup> in the oxidation of ethylene glycol in the presence of methyl acetate. In the case of other glycols, viz. propane-1,2-diol and butane-1,2-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. (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]  $\gg$   $[\text{IO}_4^-]$  a plot of  $\log [\text{IO}_4^-]$  versus time was linear (Fig. 1A) indicating a first order dependence of the rate on [periodate]. The orders in both [1,2-glycol] and [ester] were found to be fractional each as revealed by the slopes of the linear plots of  $\log k_{\text{obs}}$  versus  $\log [1,2\text{-glycol}]$  or  $\log [\text{methyl acetate}]$  (Fig. 1, 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<sup>-3</sup>,  $[\text{IO}_4^-] = 1.0 \times 10^{-3}$  mol dm<sup>-3</sup> and temp. = 323 K,  $k_{\text{obs}} \times 10^2$  decreased from 6.23 to 0.96 min<sup>-1</sup> when  $10^3 [\text{OH}^-]$  was increased from 5 to 25 mol dm<sup>-3</sup>.

The oxidation kinetics of 1,2-glycols by periodate are well documented<sup>5-7</sup>. Methyl acetate in the present



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 ester<sup>9</sup>. Experiments with different substituents in the acid moiety of the ester reveal that increasing the electron-releasing 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 ( $10^2 k_{\text{obs}}$ ) are 13.5, 1.5, 1.2 and 1.0  $\text{min}^{-1}$  under the conditions [ethylene glycol][ester] =  $1.50 \times 10^{-2} \text{ mol dm}^{-3}$ , [KOH] =  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{IO}_4^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and temp. = 323 K. A plot of  $\log(k/k_0)_{\text{obs}}$  versus  $\sigma^*$  is linear with a  $\rho^*$  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  $\rho^*$ -value suggests an electron-deficient 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-1,2-diol < butane-1,2-diol. Their corresponding rate constants ( $k_{\text{obs}} \times 10^2$ )  $\text{min}^{-1}$  are 1.15, 3.90 and 6.20 under the conditions [glycol] = [methyl acetate] = [KOH] =  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{IO}_4^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and temp. = 323 K. A  $\rho^*$ -value of -1.2 obtained from the plots of  $\log(k/k_0)_{\text{obs}}$

versus  $\sigma^*$  (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 acetate > *n*-propyl acetate > *n*-butyl acetate under similar conditions of concentration and temperature. The corresponding rate constants ( $k_{\text{obs}} \times 10^2$ ) are 1.82, 1.55, 1.35 and 1.01  $\text{min}^{-1}$  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  $\text{H}^+$  ion through heterolytic cleavage of C-H bond. Step-4 in the mechanism (Scheme 2) envisages a second mol of periodate to interact with  $\text{H}_2\text{IO}_3^-$  in a fast step to give two mol of  $\text{IO}_3^-$ . This accounts for the stoichiometry of two mol of periodate (Eq. 1) even though the order with respect to periodate is one.

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

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

This rate law implies a first order dependence in  $[\text{IO}_4^-]$  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  $[\text{OH}^-]$ .

The reciprocal of Eq. (3) after simplification gives

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2} \left[ \frac{1}{[\text{glycol}]} + K_1 \right] \times \left[ \frac{1 + K [\text{OH}^-]}{[\text{ester}]} + K + K_2 \right] \quad \dots (4)$$

Equation (4) predicts linear plots with different intercepts for (i)  $1/k_{\text{obs}}$  against  $1/[\text{glycol}]$  at constant [ester] and  $[\text{OH}^-]$  and (ii)  $1/k_{\text{obs}}$  against  $1/[\text{ester}]$  at constant [glycol] and  $[\text{OH}^-]$ . 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.

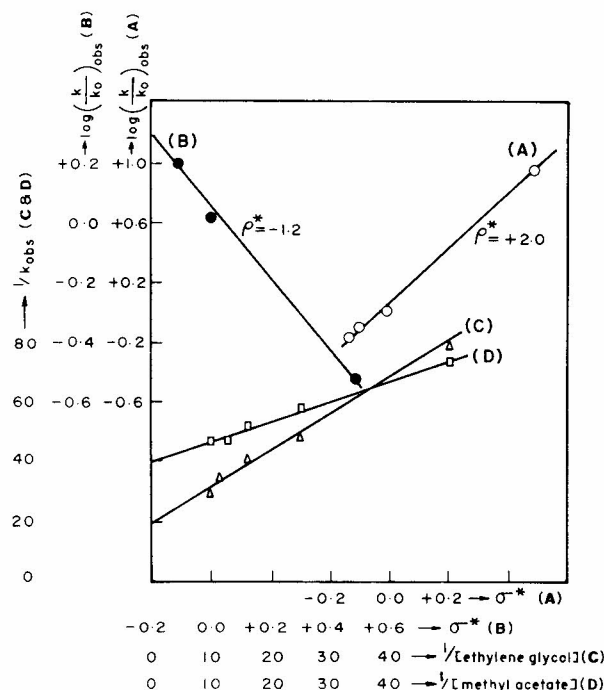


Fig. 2—(A) Plot of  $\log(k/k_0)_{\text{obs}}$  versus  $\sigma^*$  for substituents in acid moiety of ester. (B) Plot of  $\log(k/k_0)_{\text{obs}}$  versus  $\sigma^*$  for substituents in glycol. (C) Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{ethylene glycol}]$  (conditions same as in Fig. 1B). (D) Plot of  $(1/k_{\text{obs}})$  versus  $1/[\text{methyl acetate}]$  (conditions same as in Fig. 1C).

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<sup>-1</sup> respectively for ethylene glycol, propane-1,2-diol and butane-1,2-diol.

#### Acknowledgement

One of the authors (NSL) is grateful to the UGC, New Delhi for the award of a teacher fellowship.

#### References

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

- 2 Hasan F & Rocek J, *J Am chem Soc*, **97** (1975) 1444.
- 3 Ip D & Rocek J, *J Am chem Soc*, **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 Am chem Soc*, **76** (1954) 3803.
- 7 Bose J C, Foster A B & Stephens R W, *J chem Soc* (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 Am chem Soc*, **81** (1959) 5251, 5467.
- 9 Uma V, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **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 Chem*, **18A** (1979) 37.