

Kinetics of Co-oxidation of Ethylene Glycol & Propan-2-ol by Acid Bromate

P NARASIMHA CHAR, S SONDU, B SETHURAM & T NAVANEETH RAO*

Department of Chemistry, Osmania University, Hyderabad 500 007

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Acid bromate oxidation of a mixture of ethylene glycol and propan-2-ol proceeds much faster than that of either of the two substrates taken alone. The products of oxidation are acetone and formic acid. The order in $[\text{BrO}_3^-]$ is unity and in $[\text{ethylene glycol}]$ and $[\text{propan-2-ol}]$ it is fractional. The rate increases with increase in $[\text{H}^+]$ and percentage of acetic acid in the reaction medium. The amount of acetone formed from propan-2-ol during a particular time period in the presence of ethylene glycol is nearly twice that formed in its absence. A mechanism involving formation of a termolecular complex involving ethylene glycol, propan-2-ol and bromate and decomposition of this complex in the rate-determining step is proposed. The nature of the complex formed has not been ascertained.

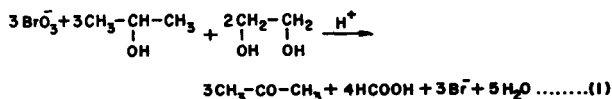
Recently we have reported the co-oxidation of 1,2-glycols and aliphatic esters by periodate in basic medium¹. Preliminary studies in the present investigation have shown that the rate constant of acid bromate oxidation of a mixture of ethylene-glycol (EG) and propan-2-ol is almost twice that of the sum of the rate constants of the individual substrates under identical conditions. This indicates that co-oxidation is taking place. Detailed kinetic investigation of acid bromate coordination of EG + propan-2-ol is therefore called for in order to arrive at a suitable mechanism.

Materials and Methods

Potassium bromate, sulphuric acid and mercuric acetate were of AR grade (BDH) and were used as such. Acetic acid (AR, BDH), ethyleneglycol (EG) and propan-2-ol (AR) samples were purified before use.

All the experiments were carried out in aqueous medium under pseudo-first order conditions using ten-fold excess of substrates over the oxidant and the kinetics were followed iodometrically. Mercuric acetate was used as a scavenger for Br^- formed as one of the products. The rate constants were calculated by the least squares method.

Acetone and formic acid were identified as the reaction products by their characteristic tests. One of the oxidation products, viz. acetone was estimated colorimetrically by measuring the absorbance of the coloured complex formed by the addition of salicylaldehyde and KOH solution and comparing it with the standard Beer's law plot. The results indicated that 1 mol of acetone was formed for every mol of bromate consumed in the presence of EG in accordance with Eq. (1).



Results and Discussion

The kinetic results are summarised below:

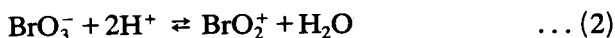
(i) Under the conditions $[\text{substrate}] \ll [\text{BrO}_3^-]$ the order in $[\text{BrO}_3^-]$ was unity (Fig. 1A).

(ii) The orders in $[\text{EG}]$ and $[\text{propan-2-ol}]$ were both fractional (Figs 1B and 1C).

(iii) The rate increased with increase in $[\text{H}^+]$ and the order in $[\text{H}^+]$ was two, indicating the involvement of two protons in this process (Table 1).

(iv) The rate increased with increase in percentage of acetic acid in the reaction medium and the plot of $\log k_{\text{obs}}$ versus $1/D$ was linear with a positive slope (Fig. 1D) indicating that probably a positive ion and a dipole are involved in the rate-determining step.

Second order dependence of rate on $[\text{H}^+]$ indicates that two protons are involved in the reaction and the probability is the protonation of BrO_3^- (see Eq. 2).



This shows that BrO_2^+ is the reactive species. Such a reactive species has also been proposed by earlier workers² in the bromate oxidation.

(v) Linear plots of $1/k_{\text{obs}}$ versus $1/[\text{EG}]$ and $1/[\text{propan-2-ol}]$ with definite intercepts on Y-axes indicates the involvement of the substrates in complex with Br (V).

(vi) The first order rate constant ($k_{\text{obs}} \times 10^4 \text{ s}^{-1}$) under the conditions $[\text{BrO}_3^-] = 5.00 \times 10^{-3}$

Scheme 1 leads to rate law (3)

$$\frac{-2.303 \frac{d \log [\text{BrO}_3^-]}{dt}}{k_{\text{obs}}} = \frac{k_1 k_2 k_3 [\text{EG}] [\text{ProPan-2-ol}] [\text{H}^+]^2}{\{1+k_1 [\text{H}^+]^2\} \{1+k_2 [\text{EG}] + k_3 [\text{ProPan-2-ol}] + k_1 k_2 [\text{ProPan-2-ol}] [\text{EG}]\}} \quad \dots(3)$$

Rate law (3) envisages first order dependence in [Br(V)] and fractional order dependence in both [EG] and [propan-2-ol] in keeping with the observed results. It also explains the increase in rate with increase in [H⁺]. The reciprocal of the Eq. (3) after simplification leads to Eq. (4) which

$$\frac{1}{k_{\text{obs}}} = \left[\frac{1+k_1 [\text{H}^+]^2}{k_1 k_2 [\text{H}^+]^2} \right] \left[\frac{1}{k_2 [\text{EG}]} + 1 \right] \left[\frac{1}{k_3 [\text{ProPan-2-ol}]} + 1 \right] \quad \dots\dots\dots(4)$$

predicts linear plots with same intercepts for (i) 1/*k*_{obs} versus 1/[EG] at fixed [propan-2-ol] and [H⁺]

and (ii) 1/*k*_{obs} versus 1/[propan-2-ol] at fixed [EG] and [H⁺]. Such plots have been realised in the present work.

The *K*₁ and *K*₂ values calculated from the oxidation of EG alone with Br(V) were found to be 0.24 and 22.9 respectively. The *K*₂ values calculated from the slope and intercept of the plot of 1/*k*_{obs} versus 1/[EG] at higher [propan-2-ol] (Eq. 4) is found to be 22.6 which is in excellent agreement with the value (22.9) obtained for the individual oxidation of EG indicating the validity of the rate law and hence the proposed mechanism. The *K*₃ value calculated in a similar fashion was 5.00. Substitution of these values in Eq. (3) gives the *k* value as 3.29 × 10⁻² mol dm⁻³s⁻¹.

References

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