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

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Acid bromate oxidation of a mixture of ethylene glycol and propan-2-ol proceeds much faster than that of the either of the two substrates taken alone. The products of oxidation are aceton and formic acid. The order in $[BrO_3^-]$ is unity and in [ethylene glycol] and [propan-2-ol] it is fractional. The rate increases with increase in $[H^+]$ 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 accetate 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).

3CH_-CO-CH_+ 4HCOOH + 3Br + 5H20(1)

Results and Discussion

The kinetic results are summarised below:

(i) Under the conditions [substrate] \leq [BrO₃⁻] the order in [BrO₃⁻] was unity (Fig. 1A).

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

(iii) The rate increased with increase in $[H^+]$ and the order in $[H^+]$ 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 $\log k_{obs}$ 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 $[H^+]$ indicates that two protons are involved in the reaction and the probability is the protonation of BrO_3^- (see Eq. 2).

$$BrO_3^- + 2H^+ \neq BrO_2^+ + H_2O \qquad \dots (2)$$

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 $1/k_{obs}$ versus 1/[EG] and 1/[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 $(k_{obs} \times 10^4 \text{ s}^{-1})$ under the conditions $[\text{BrO}_3^- = 5.00 \times 10^{-3}]$



Fig. 1--(A) Plot of $\log(a/a - x)$ versus time ([BrO₃] = 5.00 × 10⁻³;mol dm⁻³; [propan-2-ol] = 2.50 × 10⁻² mol dm⁻³; [ethylene glycol] = 2.50 10⁻² mol dm⁻³; [H₂SO₄] = 1.00 mol dm⁻³ [mercuric acetate] = 0.100 mol dm⁻³; temp = 313K)

(B) Plot of log k_{obs} versus log[ethylene glycol]([EG] = 2.00 × 10⁻² to 5.00×10^{-2} mol dm⁻³; [propan-2-ol] = 5.00× 10⁻² mol dm⁻³; other conditions same as in (A)).

(C) Plot of $\log k_{obs}$ versus $\log[\text{propan-2-ol}]$ ([Propan-2-ol] = 2.00 × 10⁻² to 3.00×10^{-2} mol dm⁻³; [EG] = 5.00×10^{-2} mol dm⁻³). (D) Plot of $\log k_{obs}$ versus 1/D

mol dm⁺³, [propan-2-ol] = 2.50×10^{-2} mol dm⁻³, [EG] = 2.50×10^{-2} mol dm⁻³, [H₂SO₄] = 1.00 mol dm⁻³, [mercuric acetate] = 0.100 mol dm⁻³ are 7.29, 7.31, 7.25 and 7.33 at [NaClO₄] = 0.05, 0.10, 0.15 and 0.20 mol dm⁻³ respectively indicating that NaClO₄ has no effect on the reaction rate.

In the oxidation of 1,2-glycols by acid bromate the formation of a complex between the substrate and oxidant is well established. However, no such complex has been observed between bromate and propan-2-ol³. The fact that there is no interaction between propan-2-ol and EG as such and the fractional order dependence of rate on [EG] and [propan-2-ol] indicate that both the substrates are involved in the formation of some sort of complex with the oxidant. The kinetic evidence for such a complex comes from the plot of $1/k_{obs}$ versus 1/[substrate] which gives clear intercept on $1/k_{obs}$ axis. The exact nature of the complex is difficult

Table 1–Effect of Varying $[H^+]$ on Rate Constants of
Br(V) Oxidation of Ethylene Glycol + Propan-2-ol

 $[BrO_3^-] = 5.500 \times 10^3 \text{ mol } dm^{-3}; [ethylene glycol] = 2.50 \times 10^{-2} mol dm^{-3} [propan-2-ol] = 2.50 \times 10^{-2} mol dm^{-3}; [Hg(OAc)_2]$

	$\approx 0.100 \text{ mol am}$	$^{\circ}$; temp = 318K	
$[H^+]$	$k_{ m obs}(10^{-4})$	$[H^+]$	$k_{\rm obs}(10^{-4})$
mol dm ⁻³	s ^{- 1}	mol dm ⁻³	S ⁻¹
0.594	1.79	1.94	16.6
0.788	4.19	2.15	28.3
1.11	7.67	3.35	66.5

to decide at this stage. No induced polymerisation of acrylonitrile was observed when it was added to the reaction systems. The experimental observation that the rate constant of acid bromate oxidation of a mixture of two substrates is twice that of the individual substrates under identical conditions suggests that co-oxidation is taking place. In order to see whether the rate enhancement due to cooxidation results in the formation of more of the reaction products for a certain time interval, we have estimated one of the products, i.e. acetone colorimetrically. The results indicate that under the conditions $[BrO_3^-] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$, [H₂SO₄] — 1.00 mol dm^{-3} , $[Hg(OAc)_2]$ 0.10 mol dm^{-3} , temp = 313K. [EG] 0.25 mol dm^{-3} [propan-2-ol] and 0.24 mol dm^{-3} the amounts of acetone formed in presence and absence of EG is 0.414 mmol and 0.218 mmol (for 20 ml of reaction mixture in 30 min) respectively, thus providing additional support for the occurrence of co-oxidation of the two substrates. Based on the above experimental observations the probable mechanism is shown in Scheme 1.



Scheme 1 leads to rate law (3)

$$\frac{-2 \cdot 303 \underline{d} \log[BrO_{3}]}{\underline{d} 1} = \underline{k} \operatorname{obs} = \frac{\underline{k} \underline{K}_{1} \underline{K}_{2} \underline{K}_{3} [EG] [Pro Pan - 2 - oi] [H^{+}]^{2}}{\{1 + \underline{K}_{2} [EG] + \underline{K}_{3} [Pro Pan - 2 - oi] + \underline{K}_{1} \underline{K}_{2} [Pro Pan - 2 - oi] [EG]\}} \dots (3)$$

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

$$\frac{1}{\underline{k}_{obs}} = \left[\frac{1+\underline{K}_{i} [\underline{H}^{+}]^{2}}{\underline{k}\underline{K}_{1} [\underline{H}^{+}]^{2}}\right] \left[\frac{1}{\underline{K}_{2} [EG]} + 1\right] \left[\frac{1}{\underline{K}_{3} [ProPan-2-o1]} + 1\right]$$
.....(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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