

## Kinetics and mechanism of oxidation of some aliphatic esters by bromate in acid medium

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The kinetics of oxidation of methyl, ethyl and *n*-butyl acetates by bromate in aq.  $\text{H}_2\text{SO}_4$  is first order in both  $[\text{Br(V)}]$  and  $[\text{ester}]$  and second order in  $[\text{H}^+]$ . The rate increases with decrease in the dielectric constant of the medium. From the effect of  $[\text{H}^+]$  and  $[\text{HOAc}]$  on rate,  $\text{BrO}_2^+$  is established as the reactive species. Electron releasing groups in ester moiety increase the rate and vice versa with a  $\rho^*$ -value = -2.1. A mechanism involving direct oxidation of ester before hydrolysis by bromate has been proposed and verified.

Potassium bromate, a powerful oxidant (redox potential of 1.44 V in acid media) has been widely used in the oxidation of several organic functional groups<sup>1-5</sup>. It is known that aliphatic esters are oxidised by oxidants like  $\text{Ce(IV)}$ <sup>6</sup>,  $\text{Co(III)}$ <sup>7</sup>,  $\text{Mn(VII)}$ <sup>8</sup>,  $\text{Mn(III)}$ <sup>9</sup> and  $\text{Ti(III)}$ <sup>10</sup> etc. by two distinct mechanisms: (i) Direct oxidation of ester and (ii) hydrolysis followed by the oxidation of the hydrolytic products. It appears that kinetics of oxidation of esters by bromate has not been investigated so far, and hence the title investigation. Further it will be interesting to know which one of these two mechanisms is operative in this case.

### Materials and Methods

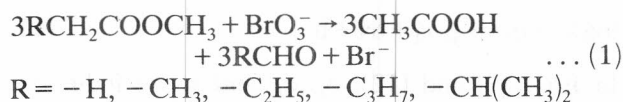
Potassium bromate (BDH, AR) was used as such. All the esters used were of AR grade Methyl acetate (BDH), ethyl acetate (BDH) and *n*-propyl acetate (Reidel) were of the highest purity. The reactions were carried out under pseudo-first order conditions using ten-fold excess of  $[\text{ester}]$  over  $[\text{BrO}_3^-]$  in amber coloured bottles and followed iodometrically for over 70% of the reaction. The rate constants were computed from the linear plots of  $\log [\text{oxidant}]$  versus time.

### Stoichiometry and products analysis

The products of oxidation were identified as acetic acid<sup>11</sup> and the corresponding aldehyde/ketone. The aldehydes/ketones were characterised by co-TLC of their 2,4-dinitrophenylhydrazone derivatives with those of the authentic ones using benzene and methyl acetate as the solvent systems.

The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of bromate over ester (in differ-

ent ratios) at 45°C for 24 hr, and estimating the residual bromate in different sets. The reactions followed the overall stoichiometric equation (1)



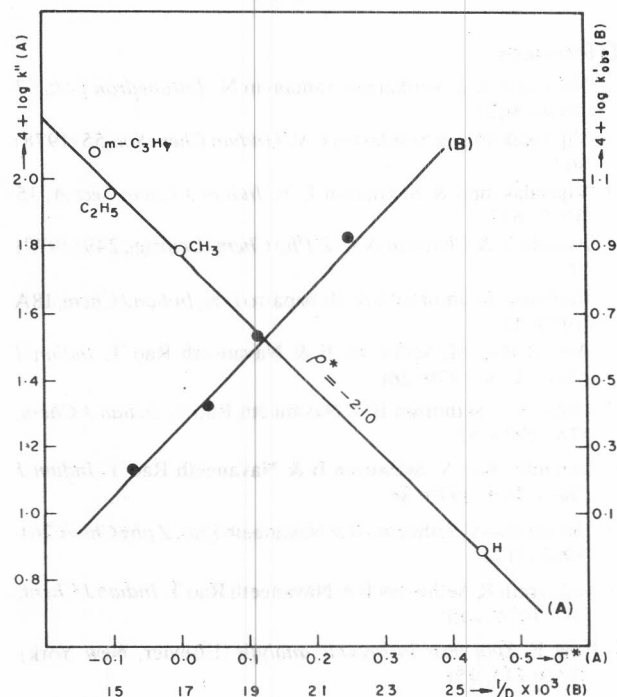
### Results and Discussion

The experiments were conducted in 0.50 mol  $\text{dm}^{-3}$  sulphuric acid under pseudo-first order conditions,  $[\text{substrate}] \gg [\text{oxidant}]$ . Mercuric acetate was added to the reaction mixture in order to prevent the *in situ* formation of  $\text{Br}_2$ . The kinetic results are summarised below.

Under the conditions  $[\text{ester}] \gg [\text{BrO}_3^-]$  the order in  $[\text{BrO}_3^-]$  was unity. This was also verified by the initial rate method. The rate increased with increase in  $[\text{ester}]$ , and the order in  $[\text{ester}]$  was also unity as revealed by the linear plot of  $\log k_{\text{obs}}$  versus  $\log [\text{ester}]$ . This was found to be true for all the esters studied. The rate increased with increase in  $[\text{H}^+]$  at fixed  $[\text{ester}]$  and  $[\text{Br(V)}]$  and the order in  $[\text{H}^+]$  was two, indicating the involvement of two protons in the reaction (Table 1). For the calculation of  $[\text{H}^+]$  the second dissociation constant of  $\text{H}_2\text{SO}_4$  was also taken into account. The increase in  $k_{\text{obs}}$  with increase in  $[\text{H}^+]$  did not follow Hammett's acidity function ( $H_0$ ). A change in the ionic strength of the medium had no effect but increase in acetic acid content of the medium enhanced the reaction rate. Further, plots of  $\log k_{\text{obs}}$  against  $1/D$  were linear with positive slopes (Fig. 1B) indicating involvement of a positive ion and a dipole in the rate-determining step. That the oxidation reaction did not involve free radicals was

Table 1—Effect of  $[H^+]$  on  $k_{\text{obs}}$  in  $\text{BrO}_3^-$ -methyl acetate reaction ( $[\text{BrO}_3^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ ; [methyl acetate] =  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{Hg}(\text{OAc})_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ ; temp = 318 K)

| $[H^+]$<br>( $\text{mol dm}^{-3}$ ) | $1 + \log [H^+]$ | $k_{\text{obs}} \times 10^4$ | $4 + \log k_{\text{obs}}$ |
|-------------------------------------|------------------|------------------------------|---------------------------|
| 0.506                               | 0.704            | 1.41                         | 0.150                     |
| 0.758                               | 0.879            | 3.07                         | 0.487                     |
| 1.01                                | 1.00             | 5.37                         | 0.730                     |
| 1.21                                | 1.08             | 7.59                         | 0.880                     |
| 1.51                                | 1.17             | 11.2                         | 1.05                      |


 Fig. 1A—(A) Plot of  $4 + \log k''$  versus  $\sigma^*$  ( $[\text{BrO}_3^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ ; [ester] =  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$ ; temp = 318 K). (B) Plot of  $\log k_{\text{obs}}$  versus  $1/D$ 

indicated by the absence of polymerisation of monomers like acrylonitrile or acrylamide.

Since two protons are involved in the rate-determining step (see Eq. 2), the species



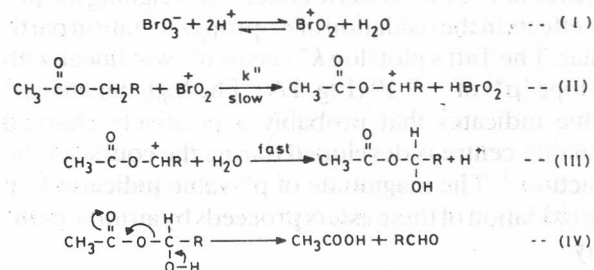
$\text{BrO}_2$  is assumed to be the reactive species in the present reaction. Such a reactive species was also proposed by several other workers during the oxidation of organic compounds by acid bromate<sup>12</sup>. This was further confirmed by the results of study on the effect of dielectric constant on rate. As the reactions are conducted in  $0.5 \text{ mol dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ , it is most likely that esters get hydrolysed before oxidation. Therefore, it is important to know whether the oxidation is taking place before or after hydrolysis. Hydrolysis followed by oxida-

 Table 2—Comparison of bimolecular rate constants ( $k''$ ) of hydrolysis and oxidation of esters

( $[\text{BrO}_3^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ ; [ester] =  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$ ; temp = 318 K)

| Acetate          | $k''_{\text{O}} \times 10^3$<br>( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )<br>(oxidation) | $k''_{\text{H}} \times 10^4$<br>( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )<br>(hydrolysis) |
|------------------|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| Methyl           | 1.80                                                                                             | 3.06                                                                                              |
| Ethyl            | 10.5                                                                                             | 2.95                                                                                              |
| <i>n</i> -Propyl | 12.5                                                                                             | 2.62                                                                                              |
| Isopropyl        | 1.27                                                                                             | 2.10                                                                                              |
| <i>n</i> -Butyl  | 21.2                                                                                             | 2.30                                                                                              |

tion is ruled out on following considerations: (i) the rates of oxidation were several times greater than the rates of hydrolysis under similar conditions (Table 2). The rates of hydrolysis were measured in the absence of  $\text{BrO}_3^-$ ; and (ii) the order of reactivities of acid-catalysed hydrolysis of acetates follow the order: methyl > ethyl > *n*-propyl > *n*-butyl > isopropyl, while a reverse trend has been observed in the oxidation suggesting that the hydrolysis followed by oxidation may not be the likely path (Table 2). Based on the above experimental observations as probable mechanism, shown in Scheme 1 as proposed.



Scheme 1

$\text{HBrO}_2$  produced in step (ii) gets further reduced by a number of ester molecules giving finally  $\text{Br}^-$  ions. Taking step (ii) as the rate-determining, the rate of disappearance of bromate is given by Eqs (3) and (4)

$$-\frac{d[\text{BrO}_3^-]}{dt} = k''[\text{BrO}_3^-][\text{ester}] \quad \dots (3)$$

However,

$$\begin{aligned} [\text{BrO}_2] &= K[\text{BrO}_3^-][\text{H}^+]^2/[\text{H}_2\text{O}] \\ &= K'[\text{BrO}_3^-][\text{H}^+]^2 \end{aligned}$$

Therefore,

$$-\frac{d[\text{BrO}_3^-]}{dt} = k''K'[\text{BrO}_3^-][\text{H}^+]^2[\text{ester}] \quad \dots (4)$$

Table 3—Activation parameters for the oxidation of esters by  $\text{BrO}_3^-$ 

[ester] =  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$   
 $[\text{H}_2\text{SO}_4] = 5.00 \times 10^{-1} \text{ mol dm}^{-3}$ ;  $[\text{Hg}(\text{OAc})_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$  temp = 318 K

|                  | $E_{\text{exp}}$ | $\Delta H^\ddagger$<br>( $\text{kJ mol}^{-1}$ ) | $\Delta G^\ddagger$ | $\Delta S^\ddagger$<br>( $\text{JK}^{-1} \text{mol}^{-1}$ ) |
|------------------|------------------|-------------------------------------------------|---------------------|-------------------------------------------------------------|
| Acetate          |                  |                                                 |                     |                                                             |
| Methyl           | 88.9             | 86.0                                            | 94.8                | -27.7                                                       |
| Ethyl            | 99.9             | 97.1                                            | 90.1                | 22.0                                                        |
| Isopropyl        | 111              | 108                                             | 95.7                | 38.0                                                        |
| <i>n</i> -Propyl | 77.8             | 74.9                                            | 89.6                | -46.2                                                       |
| <i>n</i> -Butyl  | 66.7             | 63.8                                            | 88.2                | -76.7                                                       |

Equation (4) provides satisfactory explanation for all the experimental results. From Table 2 it is clear that the order of reactivities of the esters is: *n*-butyl > *n*-propyl > ethyl > methyl > isopropyl. This could be due to the polar effects of alkyl groups as we go from methyl to *n*-butyl acetates. The increase in the polar effects may facilitate the hydride ion transfer to the oxidant, thus increasing the rate of oxidation. If only polar effects are responsible for the order of reactivities of these esters, then the rate of oxidation of isopropyl acetate must be greater than those of *n*-propyl, ethyl and methyl acetate. However, the reversal in rates could be due to steric effects outweighing the polar effects in the oxidation of isopropyl acetate in particular. The Taft's plot ( $\log k^*$  versus  $\sigma^*$ ) was linear with a slope ( $\rho^*$ ) of -2.10 (Fig. 1A). The high negative  $\rho^*$  value indicates that probably a positively charged reaction centre is developed during the course of the reaction<sup>13</sup>. The magnitude of  $\rho^*$ -value indicates that the oxidation of these esters proceeds by an ionic pathway.

Activation parameters have been determined using standard equations and the values are presented in Table 3. It is clear that oxidation of these esters is enthalpy-controlled, the reaction having the highest rate has the lowest activation energy and vice versa. The isokinetic temperature ( $\beta$ ) determined from the slope of linear plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  was 400 K, well above the experimental temperature range used (318-328 K) supporting the conclusion that oxidation of these esters by bromate is enthalpy-controlled. Constancy of  $\Delta G^\ddagger$  values indicates that all the esters are oxidised by an identical mechanism.

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