Kinetics of Acid Bromate Oxidation of Tertiary Alcohols: Dimerisation of Bromate

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The oxidation of trimethylcarbinol, dimethylethylcarbinol, triethylcarbinol, dimethylphenylcarbinol, dimethylbenzylcarbinol, 2,3-dimethylbutane-2,3-diol (pinacol), 2-methyl-3-phenylbutane-2,3-diol, 2,3-diphenylbutane-2,3-diol by bromate in acid medium is first order in \([\text{Br(V)}]\). However, the first order rate constants decrease with increase in \([\text{bromate}]\) and the inverse first order rate constants are linearly related with \([\text{Br(V)}]\). Increase in \([\text{substrate}]\) increases the rate and the reaction exhibits Michaelis-Menten's type of kinetic behaviour. Ionic strength effect is marginal, but increase in the acidity of the medium enhances the rate. The oxidation rate is also susceptible to changes in dielectric constant of the medium. The results are suggestive of a mechanism which involves fast pre-equilibrium complexation between \(\text{Br(V)}\) and the substrate yielding two complexes which differ only by a proton, followed by rate-determining carbonyl compound formation and an intermediate which is subsequently oxidised to give products. The retardation effect of bromate may be due to the formation of a bromate dimer, which is inactive towards reduction.

Natarajan and Venkatasubramanian observed, during the oxidation of secondary alcohols by bromate, the formation of alcohol-bromate ester occurring in the rate-determining step with no \(\alpha-C-H\) bond cleavage. This is in contrast to the behaviour of primary alcohols where the decomposition of the bromate ester was found to be the rate-determining step and \(\alpha-C-H\) bond cleavage was also observed. Tertiary alcohols undergo facile oxidation by acid bromate. However, literature does not record, to the best of our knowledge, any kinetic investigation on the oxidation of tertiary alcohols by acid bromate. We have presently studied the kinetics of acid bromate oxidation of trimethylcarbinol, dimethylethylcarbinol, triethylcarbinol, dimethylphenylcarbinol, dimethylbenzylcarbinol, 2,3-dimethylbutane-2,3-diol (pinacol), 2-methyl-3-phenylbutane-2,3-diol and 2,3-diphenylbutane-2,3-diol.

Materials and Methods
The source of \(\text{Br(V)}\) was \(\text{KBrO}_3\) (BDH, AR). The tertiary alcohols mentioned above (Fluka or BDH, AR) were used after purification. Acidity of all solutions was adjusted using sulphuric or perchloric acid (BDH, AR). Purified acetic acid and conductivity water were used as solvents. Solutions of the substrates were prepared either in conductivity water or in aq acetic acid.

Product analysis and stoichiometry
In a typical experiment, a mixture of trimethylcarbinol (0.74 g; 0.1 mol), \(\text{KBrO}_3\) (8.35 g; 0.5 mol) and perchloric acid (15.6 g; 2.0 mol) was made up to 100 ml with water. The mixture was kept for about 20 hr in the dark, and treated overnight with an excess of a saturated solution (200 ml) of 2,4-dinitrophenylhydrazine in 2 \(M\) HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, recrystallized from ethanol, dried and weighed. The product was identical (m.p. and m.m.p.) with an authentic sample of the 2,4-DNP of acetone. Similar experiments with other alcohols yielded the corresponding ketones (40-60%).

The formation of formic acid was confirmed by \(\text{HgCl}_2\) test and it was estimated with chromotropic acid after reducing with Mg powder.

Oxidation products of pinacol and 2,3-diphenylpinacol were acetone and acetophenone respectively and were estimated as their 2,4-DNP derivatives.

Stoichiometric runs indicated that 1 mol of oxidant consumed 1 mol of the substrate to give the corresponding ketones.

Kinetic measurements
The reactions were carried out under pseudo-first order conditions using 100-fold excess of alcohol over \(\text{Br(V)}\). All the reactions were carried out in a dark room where only yellow incandescent bulb was used. The reactions were followed iodometrically for over 70% of the reaction. Rate constants were computed from the linear plots of \(\log[\text{oxidant}]\) against time. The reproducibility of \(k_1\) was within \(\pm 3\)% and the mean values are reported.

Results
Under the conditions \([\text{BrO}_3^-]\) (2.0 to 25.0 \(\times 10^{-4}\) mol dm\(^{-3}\)) \(< \ (< [\alpha-\text{alcohol}])_0\) (0.01 mol dm\(^{-3}\)) \(<
Table 1 — Rate Dependence on \([\text{Oxidant}]_0\) in \(\text{Br(V)}\) Tertiary Alcohol System at 40 ± 0.1°C

<table>
<thead>
<tr>
<th>[H(^+)] (\text{mol dm}^{-3})</th>
<th>2.0</th>
<th>4.0</th>
<th>8.0</th>
<th>10.0</th>
<th>12.5</th>
<th>16.0</th>
<th>20.0</th>
<th>25.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylcarbinol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>6.55</td>
<td>5.87</td>
<td>4.68</td>
<td>4.23</td>
<td>3.92</td>
<td>3.44</td>
<td>2.92</td>
<td>2.56</td>
</tr>
<tr>
<td>2.0</td>
<td>58.83</td>
<td>42.23</td>
<td>26.86</td>
<td>24.21</td>
<td>20.82</td>
<td>16.35</td>
<td>13.71</td>
<td>11.23</td>
</tr>
<tr>
<td>3.0</td>
<td>56.82</td>
<td>41.66</td>
<td>25.16</td>
<td>22.21</td>
<td>19.51</td>
<td>16.13</td>
<td>12.73</td>
<td>10.83</td>
</tr>
<tr>
<td>Dimethylphenylcarbinol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>35.71</td>
<td>28.57</td>
<td>21.28</td>
<td>18.37</td>
<td>16.40</td>
<td>13.89</td>
<td>11.90</td>
<td>10.41</td>
</tr>
<tr>
<td>3.0</td>
<td>311.0</td>
<td>168.1</td>
<td>148.7</td>
<td>112.01</td>
<td>86.13</td>
<td>68.19</td>
<td>55.17</td>
<td>39.78</td>
</tr>
<tr>
<td>2,3-Diphenylbutane-2,3-diol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>22.23</td>
<td>17.00</td>
<td>13.43</td>
<td>10.01</td>
<td>8.85</td>
<td>7.32</td>
<td>6.37</td>
<td>5.11</td>
</tr>
<tr>
<td>3.0</td>
<td>283.2</td>
<td>160.7</td>
<td>142.8</td>
<td>91.12</td>
<td>74.14</td>
<td>58.38</td>
<td>47.17</td>
<td>32.11</td>
</tr>
</tbody>
</table>

\(s\) and \((p)\) are the rate constants obtained in sulphuric acid and perchloric acid medium respectively. Values in parentheses are obtained in the presence of \(\text{Hg(II)} \times 10^{-4} \text{ mol dm}^{-3}\) ions.

\([\text{H}_2\text{SO}_4]/[\text{HClO}_4] \times 2.0 \text{ mol dm}^{-3}\), \(\text{HOAc-H}_2\text{O} (1:1 \text{ v/v})\) while determining the order with respect to \([\text{Br(V)}]\) certain peculiarities were observed. The reaction data fitted well into a first order plot. But, the pseudo-first order rate constant \((k_1)\) as obtained from the \(\log [\text{BrO}_3^-]\) against time plot, decreased with increase in \([\text{bromate}]_0\). The same decreasing trend in \(k_1\) was also obtained at various acidities (Table 1) and also at various \([\text{substrate}]\).

At fixed \([\text{H}^+]\) and \([\text{Br(V)}]\) and varying \([\text{substrate}]\), the plots of \(k_\text{obs}\) against \([\text{substrate}]\) were reminiscent of Michaelis-Menten kinetics (Fig. 1). The non-linear increase in \(k_\text{obs}\) towards limiting value at higher \([\text{substrate}]\) was indicative of complex formation prior to the rate-determining step.

At fixed \([\text{t-alcohol}]\) and \([\text{Br(V)}]\) and varying \([\text{H}^+]\), a direct dependence of \(k_\text{obs}\) on \([\text{H}^+]\) was observed (Table 2). The increase in \(k_1\), with increase in \([\text{H}^+]\), followed Hammett's \(H_0\) acidity function.

A change in the ionic strength of the medium had no effect, but an increase in acetic acid content of the medium enhanced the reaction rate. Further, plots of \(\log k_1\) against \(1/D\) and against \(D = 1/2D + 1\) were linear. That the oxidation reaction did not involve free radii...
cals was indicated by the absence of polymerisation of monomer like acrylonitrile or acrylamide.

The oxidation of all t-alcohols was studied at different temperatures and the activation parameters were evaluated (Table 3). The average error in the values of \(\Delta H^\circ\), \(\Delta S^\circ\) and \(\Delta G^\circ\) (at 313 K) are: ± 2 kJ mol\(^{-1}\), ± 5 J mol\(^{-1}\) K\(^{-1}\) and ± 3 kJ mol\(^{-1}\) respectively.

**Discussion**

The dependance of rate on [acid] indicates that the protonation of either bromate ion or t-alcohol may take place.

The rates of oxidation of n-butanol \((k_1 = 41.12 \times 10^{-4} \text{s}^{-1})\), s-butanol \((k_1 = 18.64 \times 10^{-4} \text{s}^{-1})\) and t-butanol \((k_1 = 0.42 \times 10^{-4} \text{s}^{-1})\) under similar conditions follow the order: n-butanol > s-butanol > t-butanol. The rate constants of oxidation of benzyl alcohol, methylphenylcarbinol and dimethylphenylcarbinol are found to be \(3.49 \times 10^{-4}\), \(1.06 \times 10^{-4}\) and \(2.47 \times 10^{-6} \text{s}^{-1}\) respectively under identical conditions. The order of reactivities is: benzyl alcohol > methylphenylcarbinol > dimethylphenylcarbinol. If the protonated alcohol was the reactive species, then the order should have been reversed. Hence, the reaction between protonated alcohol and bromate is ruled out. This shows that the reacting species are neutral molecules of t-alcohol and protonated bromate, obtained by the protonation of \(\text{BrO}_3^–\).

The equilibria (1 and 2) are invoked to explain the acid dependence (slopes obtained from the plots of log \(k_1\) against \(H_0\) are 1.3 to 1.6) and the effect of dielectric constant on the oxidation of t-alcohol by acid bromate:

\[
\text{H}^+ + \text{BrO}_3^– \rightleftharpoons \text{HBrO}_3 \quad \text{(1)}
\]

\[
\text{H}^+ + \text{HBrO}_3 \rightleftharpoons \text{H}_2\text{BrO}_3 \quad \text{(2)}
\]

(Equilibrium 2 finds support from the literature\(^4,5\)).

Both HBrO\(_3\) and H\(_2\)BrO\(_3\) are the probable active oxidant species with protonation constants 0.50 dm\(^3\)/mol and 0.21 dm\(^6\)/mol\(^2\) respectively\(^6\). An increase in [acid] favours H\(_1\)BrO\(_3\) and H\(_2\)BrO\(_3\) formation and leads to an increase in rate. Therefore, the oxidation is assumed to be brought about by Br(V) in the form of HBrO\(_3\) and H\(_2\)BrO\(_3\).

A distinct decrease in \(k_1\) with increase in [bromate], an observation uncommon in oxidation studies in bromate oxidations, suggests that there is some initial disturbance or simultaneous reaction present along with the main one. The possibility of bromine formation and its subsequent oxidation is ruled out because (i) tertiary alcohols do not undergo oxidation by bromine and (ii) identical results were obtained both in the presence and absence of mercuric acetate (Table 1) which complexes the product bromide ion as HgBr\(_2\)/HgBr\(_4^2–\) (ref.\(^7\)). The other possibility for the decrease in \(k_1\) with increase in [oxidant] may be due to the dimerisation of bromate\(^8\) (See Eq.\(^3\)).

\[
\text{Br}_2\text{O}_3 \text{ is inactive towards reduction}^8. \text{ Increase in [bromate] favours the formation of the above species resulting in decrease in } k_1 \text{ values. The formation of Br}_2\text{O}_3 \text{ is also favoured with increase in [acid] which re-}
\]

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**Table 2 — Effect of Varying [H\(_2\)SO\(_4\)] on Reaction Rate at 40 ± 1°C**

<table>
<thead>
<tr>
<th>[H(_2)SO(_4)] mol dm(^{-3})</th>
<th>(k_1 \times 10^4) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.43</td>
</tr>
<tr>
<td>1.5</td>
<td>1.11</td>
</tr>
<tr>
<td>2.0</td>
<td>2.42</td>
</tr>
<tr>
<td>2.5</td>
<td>5.86</td>
</tr>
<tr>
<td>3.0</td>
<td>13.43</td>
</tr>
<tr>
<td>3.5</td>
<td>31.61</td>
</tr>
<tr>
<td>4.0</td>
<td>63.14</td>
</tr>
</tbody>
</table>

*Significant values obtained.

* Sloppe of log \(k_1\) against \(-H_0\) Plots

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**Table 3 — Thermodynamic Parameters for Acid Bromate Oxidation of Tertiary Alcohols**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(k_1 \times 10^4) s(^{-1})</th>
<th>(\Delta H^#) (kJ mol(^{-1}))</th>
<th>(\Delta S^#) (J K(^{-1}) mol(^{-1}))</th>
<th>(\Delta G^#) (kJ mol(^{-1}))</th>
<th>PZ (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylcarbinol</td>
<td>24.21</td>
<td>79.96</td>
<td>78.3</td>
<td>98.50</td>
<td>5.3 \times 10^8</td>
</tr>
<tr>
<td>Dimethylthelycarbinol</td>
<td>23.90</td>
<td>79.01</td>
<td>78.2</td>
<td>98.49</td>
<td>6.4 \times 10^8</td>
</tr>
<tr>
<td>Triethylcarbinol</td>
<td>21.42</td>
<td>74.68</td>
<td>77.7</td>
<td>98.78</td>
<td>6.2 \times 10^8</td>
</tr>
<tr>
<td>Dimethylphenylcarbinol</td>
<td>18.37</td>
<td>75.17</td>
<td>76.6</td>
<td>99.16</td>
<td>6.5 \times 10^8</td>
</tr>
<tr>
<td>Dimethylbenzylicarbinol</td>
<td>19.89</td>
<td>74.96</td>
<td>76.7</td>
<td>98.97</td>
<td>6.4 \times 10^8</td>
</tr>
<tr>
<td>2,3-Dimethylbutane-2,3-diol</td>
<td>13.51</td>
<td>77.31</td>
<td>72.5</td>
<td>100.00</td>
<td>10.0 \times 10^8</td>
</tr>
<tr>
<td>2-Methyl-3-phenylbutane-2,3-diol</td>
<td>12.69</td>
<td>78.12</td>
<td>71.3</td>
<td>100.15</td>
<td>55.0 \times 10^8</td>
</tr>
<tr>
<td>2,3-Diphenylbutane-2,3-diol</td>
<td>10.11</td>
<td>78.50</td>
<td>70.8</td>
<td>100.76</td>
<td>12.0 \times 10^8</td>
</tr>
</tbody>
</table>
results in a decrease in $k_1$ values. The magnitude of decrease in $k_1$ will be more at higher [acid] which is in accord with the results presented in Table 1. A similar tendency was also observed in the acid bromate oxidation of unsaturated dicarboxylic acids. At low [acid] $k_1$ remained practically constant but, at higher [acid] $k_1$ values decreased with increase in [oxidant].

Since all these bromine oxides are polymeric in nature (it is not possible at present to decide about the extent of their presence as mixtures or single compounds), the active bromine oxide concentration decreases and hence a decrease in the pseudo-first order rate constants as in Ce(IV) oxidations.

Sagar studied the oxidation of triethylcarbinol by chromic acid in acidified aq acetic acid and has suggested three alternatives (Eqs 4-6) for the oxidation of tertiary alcohols.

$$R_2COCHOCH_3 + \text{H}_2\text{O} \rightarrow R_2C = \text{O} + \text{R}^+ + \text{CrO}_3\text{H}^- \ldots (5)$$

According to Sagar reaction (4) is the most probable; the olefin formation by the dehydration in chromic acid solution is followed by rapid oxidation to epoxide which is then further degraded. But, no olefin was detected by him.

Since in most cases acid bromate resembles acid chromate in its oxidation reaction, in the present study also one can assume the same three alternatives, viz. (i) formation of the olefin in the slow step followed by a fast bromate oxidation; (ii) formation of a tertiary alcohol-bromate ester in the fast step which decomposes into products in the slow step; and (iii) slow formation of a carbonium ion and its rapid oxidation by bromate to form products.

The third alternative, which involves some kind of rapid oxidation of a carbonium ion, is ruled out on the basis of the following two observations: (i) triethylcarbinol is the first product of oxidation of the triethylmethane. This shows that hydration of the carbonium ion is faster than its oxidation, provided, the evidence for a carbonium ion intermediate in the hydrocarbon oxidation is valid. (ii) The rapid oxidation of carbonium ion demands zero order in [oxidant], which is not the case.

A decision between the first and second processes may be made from a determination of the rate dependence on [oxidant], intermediates and final products obtained.

The first alternative of Sagar that the intermediate should be oxidised rapidly or at a rate proportional to that of the dehydrogenation step and should be independent of [oxidant] is not operative in the present case because (i) no olefinic compound (intermediate) has been identified and (ii) the rate is directly proportional to the first power of the [oxidant]. This is supported by the following facts: (i) the oxidation of unsaturated acids by acid bromate is first order each in olefin and bromate, and the rate constants correlate well with the $H_0$ function; and (ii) unsaturated compounds undergo fast bromine oxidation/addition. For example in bromate-olefin system, addition of KBr (0.01 mol dm$^{-3}$) increased (27 times) the rate (due to Br$_2$ production as: BrO$_3^-$ + Br$^-$ + 6 H$^+$ = 3 Br$_2$ + 3 H$_2$O; $K = 10^{13}$) and only brominated products have been identified. However, in r-alcohol-bromate system, no change in rate has been observed even after adding KBr and identical products are obtained both in the presence and absence of KBr. This clearly indicates that the mechanism is not routed through first alternative suggested by Sagar.

The non-linear increase in $k_{obs}$ towards limiting value at high [substrate] in r-alcohol-bromate system is indicative of complex formation prior to the rate-determining step, though, independent spectroscopic evidence could not be obtained. However, the plot of $1/k_{obs}$ against $1/[\text{substrate}]$ (Fig.1) is linear with an intercept thereby providing kinetic evidence for the formation of an intermediate complex. Therefore, we have assumed that ester mechanism (Eqs 7-9) is the most probable. The formation of corresponding ketones supports this mechanism.

$$\text{C}_6\text{H}_5\text{CH} = \text{C} - \text{C} - \text{OH} + \text{H}O - \text{Br}_3\text{O}_3\text{H} \xrightarrow{\text{K}_d} \text{complex } \left[ \text{C}_1 \right] + \text{H}_2\text{O} \ldots (7)$$

$$\text{C}_6\text{H}_5\text{CH} = \text{C} - \text{CH} - \text{CH}_3 + \text{H}O - \text{Br}_3\text{O}_3\text{H} \xrightarrow{\text{K}_d} \text{complex } \left[ \text{C}_1 \right] + \text{H}_2\text{O} \ldots (8)$$

$$\text{complex } \left[ \text{C}_1 \right] \xrightarrow{\text{K}_d} \text{products} \ldots (9)$$

The oxidation of benzyl alcohol and methylphenylcarbinol occurs via $-\text{C} - \text{CH} \rightarrow \text{C} = \text{O}$ path which suggests that the mechanism of oxidation in these aromatic alcohols is the same as in aliphatic monohydric primary and secondary alcohols, i.e. formation of alcohol-bromate ester and cleavage $\propto$-C-H bond. The case of dimethylphenylcarbinol, which is r-alcohol, is different and takes place through the formation of an ester, no doubt, but, the ester after the formation of transition state is cleaved in such a manner that direct oxidation to ketone occurs and some cleavage oxidative product is formed (see Eqs 10-13). Since the amount of acetophenone and formic acid formed is
found to be 54% and 57% respectively, it is reasonable to assume that the ester of dimethylphenylcarbinol undergoes C-C bond cleavage in accord with Eqs. 10-13. In the case of tertiary butanol, acetone (58%) and formic acid (67%) are the products.

\[
\text{CH}_3\text{COCH}_3 + \text{H}^+ + \text{Br}^+ \rightarrow \text{C} = \text{O} + \text{H}_2\text{CBrO}_2 + \text{H}_2\text{O} \quad \ldots (10)
\]

Similarly the complex [C\text{3}] may break-down as:

\[
\text{CH}_3\text{COCH}_3 + \text{H}^+ + \text{Br}^+ \rightarrow \text{C} = \text{O} + \text{H}_2\text{CBrO}_2 + \text{H}_2\text{O} \quad \ldots (11)
\]

Acetone (62%) and acetonone (60%) are the products of oxidation of pinacol and 2,3-diphenylpinacol respectively. It is not out of context to mention that Wender and coworkers and Mayer and Stiles studied the pinacol-pinacolone rearrangement in concentrated acid solutions and the \( k_1 \) was of the order of 10\(^{-6}\) s\(^{-1}\) at 165°C. Therefore, under the present experimental conditions (2.0 mol dm\(^{-3}\) acid, 40°C) the pinacol-pinacolone rearrangement is negligible, and the same is confirmed by testing the keto compound after keeping the pinacol in 2.0 mol dm\(^{-3}\) H\(_2\)SO\(_4\) for 48 hr. Hence it is concluded that the neutral pinacol molecule is participating in the bromate oxidation. The same was also substantiated by earlier workers in Cr(VI) and Ce(IV) oxidations. The oxidative scheme, therefore, may be assumed as given in Eqs. 14-21.

\[
\text{C}_6\text{H}_5\text{COCH}_3 + \text{H}^+ + \text{Br}^+ \rightarrow \text{C} = \text{O} + \text{H}_2\text{CBrO}_2 + \text{H}_2\text{O} \quad \ldots (14)
\]

\[
\left[ \begin{array}{c}
\text{C}_6\text{H}_5\text{COCH}_3 + \text{H}^+ + \text{Br}^+ \\
\text{H}^+ + \text{Br}^+ \end{array} \right] \xrightarrow{k_{1,2,3}} \left[ \begin{array}{c}
\text{C}_6\text{H}_5\text{COCH}_3 + \text{H}^+ + \text{Br}^+ \\
\text{H}^+ + \text{Br}^+
\end{array} \right] \quad \ldots (15)
\]

\[
\text{HO} + \text{H}_2\text{CBrO}_2 \xrightarrow{k_{\text{slow}}} 2 \text{H}^+ + \text{Br}^+ + \text{H}_2\text{O} \quad \ldots (16)
\]

Bromide was identified with AgNO\(_3\). The stoichiometry 3:1 (pinacol/2,3-diphenylpinacol:bromate) was also in accord with the results. No cyclic mechanism has been assumed because, there is no change in the rate of oxidation of malic acid\(^21\) and of dextro- and meso-tartaric acids\(^22\). For butane-1,2-, 1,3-, 1,4- and 2,3-diols the oxidation rates are approximately the same\(^23\).

The rate law for the proposed mechanism may be derived as follows:

\[
\text{Rate} = \frac{-d[\text{Br(V)}]}{dt} = \left[ \frac{-d[C_1]}{dt} \right] + \left[ \frac{-d[C_2]}{dt} \right]
\]

\[
= k_d[\text{complex}_1] + k_d[\text{complex}_2] \quad \ldots (22)
\]

\[
= k_d K_1 K_4[\text{sub}][\text{H}^+][\text{BrO}_3^-]
\]

\[
+ k_d K_1 K_2 K_3[\text{sub}][\text{H}^+]^2[\text{BrO}_3^-] \quad \ldots (23)
\]

But the bromate is present in complexed, uncomplexed and inactive form. Hence, the total bromate ion concentration can be given as:

\[
[\text{Br}^{\text{V}}] = [\text{BrO}_3^-] + [\text{complex}_1] + [\text{complex}_2] + [\text{Br}_2\text{O}_3^-] \quad \ldots (24)
\]

\[
= [\text{BrO}_3^-] + k_x_k_y[\text{H}^+]^x[\text{Br}^{\text{V}}]^y + k_x_k_y[\text{H}^+]^x[\text{Br}_2\text{O}_3^-] \quad \ldots (25)
\]

\[
= \sum_{x,y} \left( k_x_k_y[\text{H}^+]^x[\text{Br}^{\text{V}}]^y + k_x_k_y[\text{H}^+]^x[\text{Br}_2\text{O}_3^-] \right)
\]

But the bromate ion concentration can be given as:

\[
[\text{Br}^{\text{V}}]_{\text{Total}} = \frac{[\text{Br}^{\text{V}}]}{[\text{Br}_2\text{O}_3^-]} \quad \ldots (26)
\]

Substituting \([\text{Br}_2\text{O}_3^-]\) value in Eq. (22)

\[
\frac{-d[\text{Br}^{\text{V}}]}{dt} = \frac{\sum_{x,y} \left( k_x_k_y[\text{H}^+]^x[\text{Br}^{\text{V}}]^y + k_x_k_y[\text{H}^+]^x[\text{Br}_2\text{O}_3^-] \right)}{[\text{Br}_2\text{O}_3^-]}
\]

\[
= \frac{k_x_k_y[\text{H}^+]^x[\text{Br}^{\text{V}}]^y + k_x_k_y[\text{H}^+]^x[\text{Br}_2\text{O}_3^-]}{[\text{Br}_2\text{O}_3^-] + \sum_{x,y} \left( k_x_k_y[\text{H}^+]^x[\text{Br}^{\text{V}}]^y + k_x_k_y[\text{H}^+]^x[\text{Br}_2\text{O}_3^-] \right)}
\]
The mechanism is supported by the observed rate law, fractional order dependence in [substrate], and variable order in [H+] . This is further corroborated by the solvent influence on the reaction rate. The intermediate ester(s) is less polar than the reactants due to dispersal of charge, hence decreasing polarity of the solvent is expected to stabilize the bromate ester(s) in preference to the reactants thereby enhancing the rate. Such a solvent influence has actually been observed.

Dividing the rate with [Br(V)]1 , taking reciprocal and rearranging Eq.29 we get:

\[
\frac{1}{k_1} = \left[ \frac{1}{k_d K_k} \right] + \left[ \frac{1}{k_0 + k_l K_k} \right] \left[ \frac{1}{k_i [H^+]} + k_2 [H^+] + k_4 [S] + k_6 [S]^2 \right] + k_1 [S] [BrO_3] \\
\]

According to Eq.30 at fixed [substrate] and [acid], \(1/k_1\) against [BrO_3] should be linear with a definite intercept. Such a realisation supports the proposed mechanism and the bromate dimer formation. It is also evident from Eq.30 that the slope of the \(1/k_1\) versus [BrO_3] plot should be inversely proportional to [substrate], which is also compatible with the results.

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