Oxidative mechanism of glycolic acid and formaldehyde by acid bromate: A critical study

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Kinetics and mechanism of oxidation of glycolic acid (GA) by acid bromate (free from the autoca-talytically generated molecular bromine oxidation) is studied in detail. The reaction exhibits first order each in [GA] and [oxidant] and second order in [acid]. Reaction rates are very much susceptible to change in dielectric constant (ε) of the medium. The reaction exhibits solvent isotope effect (1.8 ± 0.01 at 303 K) but primary isotope effect is absent. The rate determining step is the esterification of glycolic acid with acid bromate, followed by a fast disproportionation of the ester through a C–C bond cleavage to yield formaldehyde. This product undergoes oxidation with a faster rate than glycolic acid ending up with formic acid, inert towards further oxidation. An independent study of oxidation of formic acid is also made and results are correlated with the observations of the later part of the reaction. Related activation parameters are evaluated and discussed. An attempt is also made to compare the similar oxidations of other substrates and oxidants.

Glycolic acid (GA) being a bifunctional compound, its oxidation can proceed by many possible routes. Rocek and co-workers in the GA oxidation by chromic acid, demonstrated that Cr(VI) acted as a three electron oxidant. In a similar study with permanganate, Sengupta et al. noticed that the oxidation involves the rupture of C–C bond without proceeding through usual steps viz., alcohol → carbonyl compound → carboxylic acid, in which Mn(IV) was the active species rather than Mn(VII). A kinetic isotope effect of 5.8 was observed by Banerji in the pyridinium chlorochromate-GA reaction. The reaction rate increased by substituting alkyl group in HOCH₂–COOH and hydride ion transfer was assumed in the rate determining step. In the study of oxidation by manganese(II) sulphate, Khamrui et al. summarised that the mechanism involved rapid and reversible formation of Mn(III)-GA complex followed by its decomposition to yield a transient free radical. Similar mechanism was also forwarded by Mehta and coworkers with aquo-manganese(III). On the otherhand, a transient 1:1 cyclic complexation between GA and Mn(III) pyrophosphat, with the stability constant of 44.0 mol dm⁻³, which was followed by a C–C bond cleavage in the rate determining step to yield products was proposed by Rao and Gandhi. The oxidative kinetics of the same substrate by Ce(IV) was studied by a number of workers. Grover and Gupta, made a comparative kinetic study of substituted glycolic acids by ceric ions in sulphuric acid medium. Catalytic activity by manganese(II) was also noticed in these investigations. In a similar study with Ce(IV) as an oxidant, Dayal et al. and later Prasad and Choudary postulated C–C bond cleavage as the rate determining step. Amzad et al. and Calvaruso et al. studied the oxidation of α-hydroxy acids including GA by Ce(IV) in perchloric acid medium and established an innbersphere mechanism involving a thermodynamically more stable and kinetically more reactive complex. In the Cu(II)-catalysed oxidation of GA by vanadium(V) in sulphuric acid medium, Rao et al. suggested prior formation of a complex between copper(II) and GA, which got oxidised by V(V) to give an aldehyde as an end product. A similar study was also undertaken by Choudhari and Prasad. Cobalt(III) perchlorate and cobalt(III) sulphate were extensively used for the oxidation of different types of organic substrates including GA. A general pattern in all these oxidations included the formation of a short lived intermediate complex which subsequently disproportionated in the rate determining electron transfer step.

Similar studies using acid bromate as an oxidant are lacking and hence the present work.
this study it is observed that the product is also getting oxidised by acid bromate, hence two distinct reactions, a slow reaction followed by a faster one. An attempt is also made to explain the complex and/or competitive reactions.

Materials and Methods

All the reagents employed were of AnalR grade or high purity. All standard solutions were made in conductivity water and/or in glacial acetic acid following the standard procedures. Glycolic acid was standardised by cerimetry. Under subdued light and nitrogen atmosphere, the solutions were thermostated for an hour at the desired temperature. The reactions were initiated by the addition of bromate to the temperature equilibrated solutions of substrate and other reagents. The progress of the reaction was monitored by estimating unreacted bromate iodometrically to a starch end-point. The plots of log[bromate], versus time exhibited bi-variancy with respect to depletion of [bromate]. All reactions proceeded in two distinct steps, with an identical characteristic of an initial slow reaction followed by a faster one. The plots of log[bromate], against time, comprised of two distinct straight lines, (with corr. coeff. 0.995 in each case) having two different slopes corresponding to slow and faster stages of the reaction. Hence the pseudo-first order rate constants \( k_G \) and \( k_f \) corresponding to slow and fast stages of the reaction, with respect to bromate, were computed from the slopes of two linear parts of the plots of log[bromate], versus time. Second order rate constants \( k_2 \), \( \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \) were calculated by dividing \( k_1 \) \( \text{s}^{-1} \) with [substrate]. Triplicate kinetic runs showed that kinetic data was reproducible within \( \pm 5\% \) and mean values were reported.

A Schimadzu multipurpose recording double beam spectrophotometer model MPS-5000 equipped with a temperature controller was used for absorption studies.

Stoichiometry

In the presence of adequate acid, mercuric acetate, and excess of bromate over the [substrate], the stoichiometry established is 3:2, amounting to four electron oxidation of the substrate.

The reaction mixture was allowed to stand for 60 h at the same conditions as in the kinetic determination to enable the completion of the reaction. At the end, reaction mixture was separated with diethyl ether, washed with water and concentrated. Formic acid was the product of oxidation as identified by its qualitative tests and quantitatively estimated with chromotropic acid after reducing it with Mg powder. The optical density was measured at 570 nm and the concentration of formic acid was calculated using \( e' = 0.57 \text{ dm}^3 \text{ ug}^{-1} \) (ref. 20).

Results

The molecular bromine is expected to be generated by an autocatalytic bromate-bromide (reduction product of bromate) reaction. As \( \text{Br}_2 \) is also a powerful oxidising agent, its interference with the reaction under study was eliminated by the addition of a bromo-complexing agent like mercury(II) acetate, which forms unionisable bromocomplexes. Multi-fold mercuric acetate concentrations did not affect the rate constants, revealed that it acted as only a bromide ion scavenger without perturbing the kinetic data of the Br(V)-GA reaction.

Preliminary investigations in which [bromate] was monitored, taking excess of mineral acid and substrate revealed that the depletion of bromate occurred in two distinct steps; a slow step followed by a rapid one, indicating that the reaction followed a complicated kinetics, possibly involving competitive and consecutive reactions.

Dependence of rate on the initial bromate concentration

Kinetic data were collected for initial [bromate] in the range 2.0 to 20.0 \( \times 10^{-4} \) mol dm\(^{-3}\). All the experiments exhibited an identical characteristic, an initial slow reaction followed by a faster one. The transition to rapid stage was almost independent of the [bromate]\(_1\). The plots of log[bromate], versus time, for different initial concentrations, had two distinct straight lines for the slow and faster steps of the reaction with correlation coefficients of 0.996 and 0.994 respectively. The fairly constant, \( k_G(\text{s}^{-1}) \) values for slow step and \( k_f(\text{s}^{-1}) \) values for fast step confirms that slow and fast depletions of bromate followed first order kinetics (Fig. 1). The oxidation of formaldehyde studied independently revealed that the rate was independent of initial [bromate]. The slow depletion of bromate was solely attributed to the oxidation of glycolic acid and rapid one may be due to interference of more reactive intermediate/product (to be visualised in due course to be formaldehyde) or both.

Dependence of rate on [glycolic acid]

\( k_G \) values increased linearly with increase in initial [GA], indicating first order in [GA] (Table 1),
Table 1—Effect of varying [reactants] and solvent composition on the rate of acid bromate oxidation of glycolic acid at 313 K

<table>
<thead>
<tr>
<th>$10^4 \times [\text{Br}(V)]$ (mol dm$^{-3}$)</th>
<th>$10^2 \times [\text{GA}]$ (mol dm$^{-3}$)</th>
<th>$[\text{H}_2\text{SO}_4]$ (mol dm$^{-3}$)</th>
<th>$\text{HOAc} - \text{H}_2\text{O}$</th>
<th>$10^4 \times$ rate constant (s$^{-1}$)</th>
<th>$k_G$</th>
<th>$k_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>1.0</td>
<td>30-70</td>
<td>1.44</td>
<td>2.90</td>
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<tr>
<td>8.0</td>
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<tr>
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<td>3.28</td>
<td></td>
</tr>
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<tr>
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<td>1.0</td>
<td>40-60</td>
<td>2.94</td>
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</tr>
<tr>
<td>10.0</td>
<td>1.0</td>
<td>1.0</td>
<td>50-50</td>
<td>11.20</td>
<td>6.60</td>
<td></td>
</tr>
</tbody>
</table>

$[\text{Hg(OAc)}_2] = 0.01 \text{ mol dm}^{-3}$

whereas $k_I$ values increased slightly and reached a maximum. The oxidation of formaldehyde (independent study) also exhibited a fractional order dependence on initial $[\text{HCHO}]$.

Effect of [acid] on the rate of reaction

The effect of sulphuric acid on the rate of reaction was studied at constant ionic strength. From the plots of log $k_G$ versus log[acid], it was observed a second order dependence on [acid] in the range of 0.5 to 2.00 mol dm$^{-3}$. $k_G$ and $k_I$ values increased with increase in [acid] and the difference in their values was narrowed on increasing [acid] due to less acceleration of the later part of the reaction involving the oxidation of the product. The same is in agreement with the observation of the oxidation of formaldehyde wherein, acid dependence is less than unity in the range (0.1 to 1.0 mol dm$^{-3}$) studied, as its rates of oxidation are very high at higher [acid] and cannot be measured in the present setup.

Effect of dielectric constant of the medium

The increase in dielectric constant ($\varepsilon$) of the medium by varying the composition of acetic acid and water, decreased the rate constant (Table 1).
and the plot of log \( k \) (\( k_G \) or \( k_f \)) versus \( 1/\varepsilon \) was linear with a positive slope.

Added salts like \( \text{Na}_2\text{SO}_4 \) and \( \text{NaHSO}_4 \) had no effect on the rate of reaction.

The rate of reaction was neither accelerated in the presence of benzoyl peroxide nor retarded in the presence of acrylonitrile, ruling out the possibility of free radicals in the reaction.

**Effect of temperature**

GA-Br(V) and HCHO-Br(V) reactions were studied at different temperatures ranging from 308 to 328 K in sulphuric acid and evaluated activation parameters are recorded in Table 2.

**Discussion**

In acid solutions bromate exists in the protonated and unprotonated forms. Amis et al.\(^22\) proposed \( \text{BrO}_3^- \) as the oxidising species in bromate oxidations of iodide. Ambar and Guttmann\(^23\) as well Wright and Barton\(^24\) suggested that in moderately strong acid solutions \( \text{H}_2\text{XO}_3^- \) is the existing form of halate; in the case of bromate it is \( \text{H}_2\text{BrO}_3^- \). However, Reddy et al. observed that both, \( \text{HBrO}_3^- \) and \( \text{H}_2\text{BrO}_3^- \), are the species existing in acid medium with protonation constants of \( K_{p1} = 0.529 \text{ dm}^3 \text{ mol}^{-1} \) and \( K_{p2} = 0.21 \text{ dm}^6 \text{ mol}^{-2} \) respectively\(^25,26\).

The rate acceleration with an increase in [acid] and the study of dielectric constant effect on the rate of the reaction, mitigate the chances of participation of \( \text{BrO}_3^- \) as the reactive species. The second order dependence of rate on [acid] in the range studied also confirms that \( \text{H}_2\text{BrO}_3^- \) is the reactive species.

In an aqueous solutions of GA, 12.16% of it is present in the dissociated form when \( [\text{GA}] = 0.01 \text{ mol dm}^{-3} \) as its \( P_{ka} = 3.85 \). In the presence of molar sulphuric acid the GA dissociation is completely suppressed and only \( 1.48 \times 10^{-6} \text{ mol dm}^{-3} \) is present in the dissociated form, hence negligible. Therefore, it is more appropriate to assume undissociated glycolic acid as the reactive species.

Inspite of considerable variations in the structure, glycolic and lactic acids are oxidised at the same rate \( (1.43 \times 10^{-2} \text{ and } 1.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \). The structural insensitivity observed in the hydroxy acids oxidation by Br(V) rules out the possibility of bromate ester decomposition being the rate determining step. This step involves the cleavage of stronger \( C - H \) bond and is bound to be influenced by structural changes in hydroxy acids, as was seen in chromic acid oxidation\(^27\) or in the oxidation with bromine\(^28\). The absence of kinetic isotope effect \( (k_H/k_D = 1) \) also confirms that \( C - H \) bond is not cleaved in the rate determining step. The relative ease of oxidation of glycolic acid shows that, the oxidative decarboxylation is energetically more favourable and \( \alpha \)-hydrogen is not involved in oxidation at all. The assumption of bromate ester formation being the slow step could only explain the observed insensitivity to structural influences. Inorganic esterification reactions of this type are known to be not influenced by structural variations in alcohol moiety\(^29,30\).

Acid catalysed reactions are expected to be faster in D\(_2\)O as D\(_2\)O is a stronger acid than H\(_2\)O. However, labile hydrogens like those present in

<table>
<thead>
<tr>
<th>Table 2—Activation parameters of acid bromate oxidation of glycolic acid and formaldehyde*</th>
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</thead>
<tbody>
<tr>
<td>[Br(V)] = 0.001 mol dm(^{-3}); [substrate] = 0.01 mol dm(^{-3}); [H(_2)SO(_4)] = 1.0 (0.1)* mol dm(^{-3}); [Hg(OAc)(_2)] = 0.01 mol dm(^{-3}); Dielectric constant = 55.59</td>
</tr>
<tr>
<td>Reaction</td>
</tr>
<tr>
<td>Slow step of GA-oxidation</td>
</tr>
<tr>
<td>Fast step of GA-oxidation</td>
</tr>
<tr>
<td>Oxidation of formaldehyde</td>
</tr>
</tbody>
</table>

*The average error in the values of \( \Delta H^\ddagger \), \( \Delta S^\ddagger \) and \( \Delta G^\ddagger \) (at 313 K) are: \( \pm 2 \text{ kJ mol}^{-1} \), \( \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} \) and \( \pm 3 \text{ kJ mol}^{-1} \) respectively.

*Value in the parenthesis corresponds to the oxidation of formaldehyde.
hydroxyl or carboxyl groups undergo rapid exchange in D$_2$O. If O–H bond is cleaved either in rate determining step or prior to it, O–H/O–D isotope effect comes into play. This cancels the rate enhancing effect of D$_2$O and may result in an inverse isotope effect. In the present reaction, an inverse solvent isotope effect ($k_{H_2O}/k_{D_2O} = 1.8 \pm 0.01$ at 303 K) observed indicating that −OH group and/or −COOH group is/are involved in the rate determining step.

Based on the aforesaid reasons, the possible mechanism for the reaction is outlined as in (Eqs 1 and 2)

$$\begin{align*}
    H\text{-}\text{COOH} + \text{HBrO}_2^+ &\xrightarrow{\text{slow}} H\text{-}\text{COOH} + \text{H}_2\text{BrO}_3^- + \text{H}_2\text{O} \quad (1) \\
    H\text{-}\text{COOH} + \text{HBrO}_2^+ &\xrightarrow{\text{fast}} \text{HCHO} + \text{CO}_2 + \text{HBrO}_2^- + \text{H}^+ \quad (2)
\end{align*}$$

The bromate ester formed in Eq. (1) may also react with proximate carboxylic acid group to form a cyclic ester (Eq. 3), which may subsequently decompose to products.

$$\begin{align*}
    \text{HCHO} + \text{CO}_2 + \text{HBrO}_2^- + \text{H}^+ &\xrightarrow{\text{slow}} \text{H}_2\text{BrO}_3^- + \text{H}_2\text{O} \quad (3)
\end{align*}$$

An analogy for the above cyclic ester could be the cyclic chromic ester or a Pb(IV) ester, which vicinol diols are capable of forming ester with chromic acid and Pb(IV) acetate respectively. In these cases the formation of monoester is more likely to be the slow step, followed by its rapid decomposition.

In the above mechanistic picture (Eq. 1), the formation of bromate ester is due to the nucleophilic attack by the alcoholic hydroxyl at the bromine atom of H$_2$BrO$_3$. But an alternate mode of attack (Eqs 4 and 5) by carboxyl group cannot be ruled out.

$$\begin{align*}
    H\text{-}\text{COOH} + \text{HBrO}_2^+ &\xrightarrow{\text{slow}} H\text{-}\text{COOH} + \text{H}_2\text{BrO}_3^- + \text{H}_2\text{O} \quad (4) \\
    H\text{-}\text{COOH} + \text{HBrO}_2^+ &\xrightarrow{\text{fast}} \text{HCHO} + \text{CO}_2 + \text{HBrO}_2^- + \text{H}^+ \quad (5)
\end{align*}$$

Such an ester has been conceived in the reaction between bromine and oxalic acid$^{32}$ Eqs (6 and 7) and acid bromate oxidation of oxalic acid$^{33}$.

$$\begin{align*}
    \text{O}_2\text{C}^-\text{O}^- + \text{Br}_2 \xrightarrow{\text{slow}} \text{O}_2\text{C}^-\text{O}^- + \text{HBr} \quad (6) \\
    \text{O}_2\text{C}^-\text{O}^- + \text{H}^+ &\xrightarrow{\text{fast}} 2\text{CO}_2 + \text{HBr} \quad (7)
\end{align*}$$

The other alternative mechanism (Eqs 8, 9) that can also satisfy the kinetic results is the formation of glyoxylic acid as the intermediate.

$$\begin{align*}
    \text{CHO} + \text{COOH} &\xrightarrow{\text{slow}} \text{CHO} + \text{COOH} \quad (8) \\
    \text{CHO} + \text{COOH} &\xrightarrow{\text{fast}} 2\text{CO}_2 + \text{H}_2\text{O} \quad (9)
\end{align*}$$

Glyoxylic acid (OHC−COOH) and oxalic acid (HOOC−COOH), which have the same degree of oxidation are oxidised all the way to carbon dioxide and water and could not be any intermediates.

Formaldehyde is oxidised to formic acid which is inert towards further oxidation. Under the conditions [Br(V)] ≫ [GA], the formation of HCHO and HCOOH are identified and estimated quantitatively. Hence the formation of glyoxylic acid as intermediate and its further oxidation to carbon dioxide is ruled out under the present experimental conditions, ([Br(V)] ≪ [GA]).

Hence it is confirmed that the glycolic acid is oxidised to HCHO (further to formic acid) through Eqs (1) to (5).

The rate equation in consonance with Eqs (1) to (5) is given by Eq. (10).

$$k_\text{c} = \frac{d[\text{Br(V)}]/dt}{[\text{Br(V)}]} = k_\times K_p [\text{H}^+]^2 [\text{GA}] \quad \ldots (10)$$

The esterification constant $k_\times$ is evaluated as $1.43 \times 10^{-1}$ from the slopes of the plots of $k_\times$ versus [H$^+$]$^2$ or $k_\times$ versus [GA] which are in good agreement with each other.

The mechanism proposed here is further supported by the study of energy of activation ($E_a$). If $E_a$ value is about 50 kJ mol$^{-1}$ the oxidation of hydroxy acids/alkohols to carbonyl compounds takes place in normal way in which H of C−H
bond is attacked, as per the observations of Chaterji and Antony in the oxidation of alcohol to aldehydes by chromic acid. Whereas Price and Knell observed $E_a$ values to be 92.94 and 93.37 kJ mol$^{-1}$ in glycol cleavage by chromic acid and periodic acid respectively, in which oxidation is taking place when $H$ of $O-H$ is attacked resulting the rupture of C-C bond. The energy of activation, of about 90 kJ mol$^{-1}$, suggests C-C bond fission via reversible complex formation between hydroxy acid and Br(V) species. In the present study of acid bromate oxidation of glycolic acid, energy of activation (76.63 kJ mol$^{-1}$) is in between 50 and 90 kJ mol$^{-1}$ suggesting that the oxidation to carbonyl compounds is taking place mostly by the cleavage as shown in Eqs (1) to (5) and also in the normal way to some extent. But the product analysis confirms that the oxidation is taking place only by fission of C-C bond as the oxidative product is only HCOOH obtained by further oxidation of HCHO.

There is a formal analogy between the mechanism proposed herein, and chromate ester mechanism for the oxidation of alcohols by Cr(VI) oxide. Chromic acid oxidations are known to exhibit a pronounced kinetic isotopic effect, ($k_p/k_D = 7$) for the oxidation of isopropyl alcohol, and a negative $\rho$ has consistently been obtained for the oxidations of several substituted alcohols. These observations establish unequivocally that decomposition of the chromic ester constitutes the slow step. But, the oxidation of alcohols by Br(V) is characterised by the absence of substituent effect and kinetic isotopic effect.

Other way of demonstrating that in the present system the decomposition of the ester is a fast one is to study the oxidation of other hydroxy acids like benzilic acid. According to the proposed mechanism, it is predicted that the rates of oxidation of benzilic and mandelic acids should be the same. The same is realised from their oxidations.

**Fast stage of the reaction**

It is observed that in most of the reactions, the product is also oxidised along with the substrate, when the product has tendency to undergo the oxidation. However, its contribution to the total rate is not appreciable as [product] is in negligible proportion than [substrate].

On the other hand when product(s) has greater tendency to react with oxidant, through its high complexing activity, its contribution to the rate will be appreciable. Some times it supercedes the oxidation of substrate, ultimately the preferential oxidation of product alone takes place leaving back the substrate unreacted, consuming available oxidant, though its concentration is also very low in comparison with the substrate.

In the present study, the later part of the kinetic data pertains to the oxidation of product, formaldehyde.

To establish this fact, the oxidation of formaldehyde is also studied independently. From the kinetic data available (Table 3), the mechanism of oxidation of formaldehyde is shown as below.

\[
K_y \frac{k_d [\text{complex}]}{k_{slow}} \rightarrow \text{products}
\]

... (11)

In consistance with Eq. (11) the rate law is manifested by the following equation at low concentration of acid (0.1 mol dm$^{-3}$), treating HBrO$_3$ as the reactive species.

\[
k_F = -\frac{d[\text{Br(V)}]/dt}{[\text{Br(V)}]^r}
\]

\[
k_F = \frac{k_y K_p [H^+][\text{HCHO}]}{1 + K_p [H^+] + K_y K_p [H^+][\text{HCHO}]}
\]

... (12)

\[
1 = \frac{1}{k_f} + \frac{1}{k_d K_y K_p [H^+] [\text{HCHO}] + 1}
\]

... (13)

<table>
<thead>
<tr>
<th>Table 3—Effect of varying [reactants] and solvent composition on the rate of acid bromate oxidation of formaldehyde at 313 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2 \times [\text{Br(V)}]$ (mol dm$^{-3}$)</td>
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<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>8.0</td>
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</table>

[Hg(OAc)$_2$] = 0.01 mol dm$^{-3}$
From the plot of $1/k_F$ versus $1/[\text{HCHO}]$, which is linear the values of $k_d$ and $K_y$ are evaluated from the intercept and slope as $5 \times 10^{-4}$ (s$^{-1}$) and $8.75 \times 10^3$ (dm$^3$ mol$^{-1}$) respectively. Similarly it can be shown that the complexation constant of $\text{H}_2\text{BrO}_3$ and HCHO as the reactive species at higher acid concentration is also of the same order. Though formaldehyde involves in rapid complexation with HBrO$_3$ as and when formed, its contribution to the rate is not appreciable in the beginning as decomposition of its complex is a slow step ($k_d = 5 \times 10^{-4}$ s$^{-1}$). But it will be accountable when HCHO reaches an optimum concentration where its rate of oxidation is greater than glycolic acid.

The transition from slow stage to a fast stage occurs after completion of 40% of the reaction as visualised from the plots of log($a - x$) versus time (Fig. 1). At inflection point the [HCHO] can be estimated as equivalent to the [bromate] consumed is $4 \times 10^{-4}$ mol dm$^{-3}$.

From the knowledge of $K_y$ and $k_d$ values, and the rate constant ($k_F$) of the later part of the reaction, the [HCHO] can be evaluated theoretically from Eq. (12). The [HCHO] evaluated as $4.5 \times 10^{-4}$ mol dm$^{-3}$, is in good agreement with the observed data. Hence the later part of the oxidation is attributed to be the preferential oxidation of formaldehyde over glycolic acid on account of its high complexing ability, ($K_y > k_d$) with Br(V)$_3$, though, its concentration is very low.

Further evidence is also obtained from the study of oxidation of formaldehyde, with low concentration of Br(V)$_3$ i.e., of the order of $5 \times 10^{-4}$ mol dm$^{-3}$, which is the concentration expected to be in the reaction mixture under the kinetic conditions of present study in the presence and absence of glycolic acid. Both reactions have proceeded with the same rate till the completion of formaldehyde. In the presence of glycolic acid, the oxidation of glycolic acid is observed only after the complete oxidation of formaldehyde and a plot completely inverted to the oxidation of glycolic acid alone is obtained i.e., fast depletion followed by the slow depletion of bromate (Fig. 2). The rate constant $k_F = 2.8 \times 10^{-4}$ s$^{-1}$ and $k_F = 1.43 \times 10^{-4}$ s$^{-1}$ obtained from this plot are also in good agreement with the present study of oxidation of GA alone.

The substrate effect reveals the first order dependence on [GA], from the slow stage of the reaction and zero order dependence from the later part of the reaction. In the fast stage of the reaction, the rate is manifested by the unreacted [Br(V)] in the reaction mixture and [HCHO] obtained in the present study of oxidation of GA.

At inflection point unreacted [Br(V)] is $6 \times 10^{-4}$ mol dm$^{-3}$. The theoretical rate constant can be calculated with maximum possible concentration of Br(V) - HCHO complex is $6 \times 10^{-4}$ mol dm$^{-3}$ obtained by 1:1 complexation of Br(V) with formaldehyde and from the knowledge of $k_d$ and $K_y$ as $3.2 \times 10^{-4}$ s$^{-1}$. It is in good agreement with the rate constants ($k_F$) observed at higher [S]. This also supports the assumption that the first (slow) stage of the reaction pertains to the oxidation of GA alone and second (fast) stage of the reaction is attributed solely to the preferential oxidation of formaldehyde.

Moreover the activation parameters related to the later part of the glycolic acid oxidation are also in good agreement with the oxidation of formaldehyde with in experimental errors supports the assumption (Table 2).

References