Oxidation of Some Organic Compounds by Aqueous Bromine Solutions

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1 Introduction

Oxidations and reductions of organic compounds involving hydride transfer have been identified in chemical and biochemical systems. Our interest in the aqueous bromine oxidations arises from the use of bromine as an external electrophile in intermolecular hydride transfers.[1] The review deals with oxidations of some common functional groups by bromine in aqueous media, and covers the literature from 1967 to 1992. Prior to this, the state of the field was summarized by Barker[2] in 1964. The review does not deal with additions to alkenes,[3] allylic substitutions, or electrophilic aromatic or aliphatic substitutions.[4] These areas have all been reviewed within the recent past. Some generalities about the chemistry of bromine besides the kinetics and mechanism of oxidation of several organic substrates with aqueous bromine are presented in this review.

2 Aqueous Solution Equilibria of Br_2 and Reactivity with Organic Compounds

Bromine is used as an oxidant in both acidic and alkaline solutions. A considerable degree of order can be found in the reactions of chlorine, bromine, and iodine in aqueous solution if full and proper use is made of the standard oxidation potentials appropriate to the elements and their ions. Direct measurements of standard potentials have been carried out for the couple $\frac{1}{2}Br_2/Br^-$ with the result given in equation 1.[5]

$$\tfrac{1}{2}Br_2 + e \rightleftharpoons Br^-(aq)\ E^{\ominus}_{(V)} = 1.065 \qquad (1)$$

From the standard potential diagrams originally given by Latimer[6] for the halogens at unit hydronium ion activity we have equation 2.

$$BrO_4^- \xrightarrow{+1.76} BrO_3^- \xrightarrow{+1.49} HOBr \xrightarrow{+1.59} Br_2 \xrightarrow{+1.07} Br^- \qquad (2)$$
$$\text{(with } BrO_3^- \xrightarrow{+1.51} Br_2 \text{ as a direct path)}$$

These diagrams give us what are believed to be the most reliable guides to the aqueous chemistry of the elements at present available.

It is possible to compare the bromine reduction potential with the standard potentials of other common oxidants used in organic chemistry (equations 5 and 6).[7]

$$MnO_4^- + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O \qquad E^{\ominus}_{(V)} = 1.679 \qquad (5)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O \qquad E^{\ominus}_{(V)} = 1.33 \qquad (6)$$

We can see that bromine is a less powerful oxidant and therefore more selective.

Molecular bromine, Br_2, like all the halogens is to some extent soluble in water (3.58 g/100ml at 20 °C).

In acid, neutral, or alkaline solution the standard potential of the couple $\frac{1}{2}O_2, 2H^+/H_2O$ is + 1.23, 0.81, or 0.40V respectively. Depending on the precise conditions of pH, bromine should therefore be capable of oxidizing water. In contrast with the behaviour of fluorine, the reaction tends to be slow, however, and disproportionation is the initial result (equation 7)

$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^- \qquad (7)$$

The weak hypobromous acid so produced then undergoes slow decomposition (equation 8).

$$2HOBr \rightarrow Br_2 + H_2O + \tfrac{1}{2}O_2 \qquad (8)$$

so that oxidation of water is the overall result. However, in the case of bromine, creation of HOBr and HBr by disproportionation raises the acidity and eventually stops the reaction for, as the potentials show, the oxidation of water by bromine does not proceed at unit activity of hydrogen ions.

It was of interest to know the composition of bromine solutions as a function of pH and of added bromide since bromide is produced in the course of an oxidation.[8] It is necessary to have an excess of added bromide in the solution to suppress formation of hypobromous acid and maintain a constant Br_2/Br_3^- ratio throughout the course of the bromine oxidation. The use of an initial excess of chloride concentration also applies to oxidation by chlorine.[9]

Quantitative data should contribute to mechanistic studies of the participation of bromine species in phenomena such as spectral absorption, complex formation, and oxidation reactions, and they may be used in defining the experimental conditions that ensure a maximal concentration of the species known to be active in a particular process.

Disregarding the insignificant contribution of Br^+ and $HOBr^+$ and the questionable existence of Br_5^-, the composition of aqueous bromine solutions is governed by three equilibria (equation 9).

$$\frac{[H^+][BrO^-]}{[HOBr]} = K_1$$
$$\frac{[H^+][Br^-][HOBr]}{[Br_2]} = K_2 \qquad (9)$$
$$\frac{[Br^-][Br_2]}{[Br_3^-]} = K_3$$

A cubic equation was derived that permits calculation of the composition of aqueous bromine solution in terms of HOBr, Br_2, Br_3^-, and Br^- as a continuous function of the pH, the total bromine concentration, and the mole fraction of oxidant consumed.

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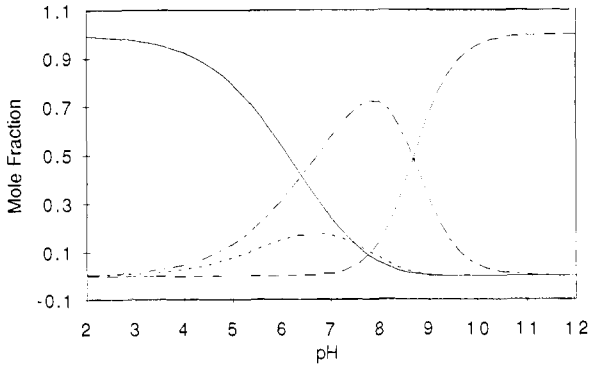


Figure 1 Composition of aqueous bromine as a function of pH with initial $[Br_2] = 0.1$ M — $[Br_2]$; ---- $[Br^{3-}]$; - - - [HOBr]; --- $[BrO^-]$.

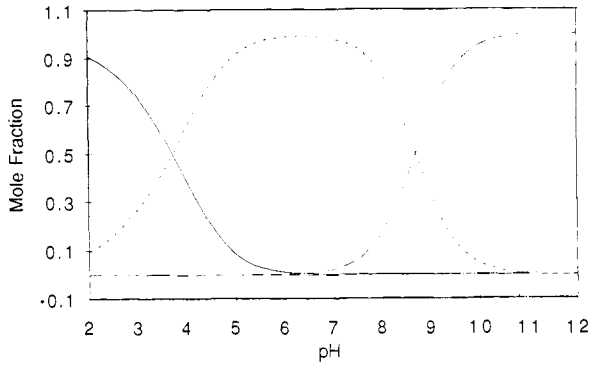


Figure 2 Composition of aqueous bromine as a function of pH with initial $[Br_2] = 0.0001$ M. — $[Br_2]$; --- $[BrO^-]$; ---- [HOBr].

Figures 1 and 2 show the composition of aqueous bromine solution as a function of pH with different initial concentrations of bromine. The high concentration 0.1 M (Figure 1) is what might be used preparatively. The low concentration 10^{-4} M (Figure 2) is what might be used in kinetic studies. Notice that depending on the pH, three possible different oxidants can be observed.

The elemental bromine is not the only source of electrophilic bromine and for some oxidizing purposes other 'positive bromine' compounds may be useful sources of the necessary electrophile. For example, we can use *N*-bromosuccinimide or related compounds as selective oxidizing agents. These compounds often oxidize OH groups without disturbing other oxidizable groups.[10]

Bromine is considered a strong oxidizing agent. Aqueous bromine is used in oxidation of several organic substrates, including alcohols, aldehydes, carboxylic acids, and α-hydroxy-acids. In aqueous media, electrochemical oxidations of aliphatic alcohols (and amines) to corresponding aldehydes take place at anode potentials not exceeding + 0.8 V *vs.* Standard Hydrogen Electrode (SHE) (equations 10—12).[11]

$$R{-}CH_2OH \longrightarrow R{-}C(=O){-}H + 2H^+ + 2e^- \quad (10)$$

$$R{-}CH_2NH_2 \longrightarrow R{-}C(=NH){-}H + 2H^+ + 2e^- \quad (11)$$

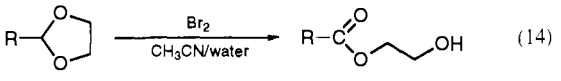
$$R{-}C(=NH){-}H + H_2O \longrightarrow R{-}C(=O){-}H + NH_3 \quad (12)$$

Alcohols, aldehydes, and hemiacetals are oxidized by bromine in aqueous solution by what appear to be very similar mechanisms. The kinetic studies of Kaplan,[12] Perlmutter-Hayman,[13] and others[14] show that the reaction is indeed an oxidation not a bromination, and that bromine is the oxidant, not hypobromous acid; the latter's oxidations are decidedly slower. Furthermore, the reaction does not involve formation of a hypobromite ester, RCH_2OBr.

Recent work illustrates the utility of bromine as an oxidant. Williams *et al.*[15] have found that bromine oxidation of aldehydes in alcohol solutions in the presence of $NaHCO_3$ buffer is a preparatively useful way of converting aldehydes directly into esters (equation 13). Under the same conditions, secondary alcohols are not oxidized.

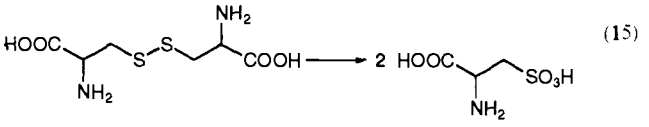
$$R{-}C(=O){-}H \xrightarrow[NaHCO_3]{Br_2/R'OH} R{-}C(=O){-}OR' \quad (13)$$

Han, Linert, Schmid, and Jameson[16] have studied the oxidation of formic acid by aqueous bromine in the presence of cyclodextrin. Bromine forms a stable 1:1 complex with cyclodextrin and the bound bromine is less reactive than the free solution species. On the other hand, Mingotaud[17] and colleagues have shown that cyclic acetals can be oxidized by bromine in aqueous acetonitrile to give esters of ethane-1,2-diol (equation 14). The reaction is preparatively useful.



(14)

In addition, oxidation of disulfide bonds by bromine is a well-known process in amino-acid chemistry. Most recently, Sanchez-Cano, Montiel, and Aldaz[18] have oxidized L-cystine to L-cysteic acid using bromine generated electrochemically from HBr solution (equation 15).



(15)

L - cystine L - cysteic acid

The deuterium kinetic isotope effect that has been found for the oxidation of CH_3CD_2OH ($k_H/k_D \sim 4$ in acid at 25 °C) shows that the rate-controlling step requires scission of the C–H bond. The variation of oxidation rate with pH is particularly illuminating. It shows that the anions of alcohols, aldehyde hydrates, and the cyclic hemiacetal D-glucose are oxidized very much faster than are the neutral molecules.

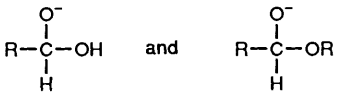
In acid solution (pH 1 to 4), the rates of oxidation of both ethanol and of acetaldehyde are about constant, the aldehyde being oxidized several hundred times faster than the alcohol. As the pH is increased beyond 5, the rate of oxidation of both substrates rises, and it can be shown that the rate becomes proportional to the anion concentration. If an estimate is made of the (very small) degree of ionization of aldehydes, hydrates, and alcohols in neutral solution, one concludes that the anions are oxidized about 10^{10} times faster than the neutral molecules.

The removal of a hydride ion from the anions by molecular bromine appears to be the most satisfactory mechanism for this reaction (Scheme 1).

$$CH_3CH_2OH + OH^- \rightleftharpoons H_2O + CH_3CH_2O^-$$
$$CH_3CH_2O^- + Br_2 \rightarrow CH_3CHO + HBr + Br^-$$
$$HBr + OH^- \rightarrow H_2O + Br^-$$

Scheme 1

Aldehyde hydrates and their close analogues, hemiacetals, presumably react similarly *via* the ions (structures 1 and 2)



(1) (2)

The action of bromine and permanganate on alcohols and aldehyde hydrates are, thus, very similar [19] Both involve the organic anion, and the facile oxidations are due principally to low energies of activation in each case

It is interesting to note the effect of the oxidant's charge on the activation entropies The permanganate oxidations have large negative entropies of activation, whereas the bromine oxidations appear to have entropies of activation near zero The negative charge on both reactants in the permanganate–organic anion reactions is clearly reflected in the unfavourable entropy term

3 Kinetic Studies

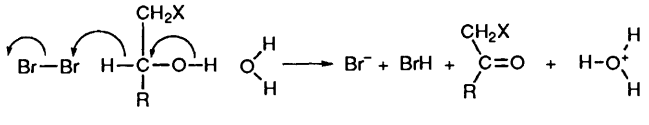
3.1 Alcohols

Studies with different primary and secondary alcohols have been carried out in order to establish the correct mechanism for the oxidation of alcohols by bromine

The rate constants of bromine oxidation of 11 primary alcohols in aqueous acetic acid[20] give a good correlation in a Taft plot, the value of ρ^* being $-2\,84 \pm 0\,06$ at 25 °C The rate constant for benzyl alcohol deviates a little from the best line for the other ten compounds, and the phenyl group seems to be less deactivating than expected by the Taft equation However, the phenyl group is known to behave differently in many reactions and it may well be due to its ability to interact by resonance The oxidation reactions are first order with respect to both bromine and to the different alcohols The results reported in this study are discussed in terms of a mechanism involving an initial slow hydride ion transfer from the alcohol to bromine, followed by the rapid loss of the hydroxylic proton The reaction constant of $-2\,84$ clearly shows that synchronous removal of the hydroxylic proton is not likely As the polar requirement upon the carbinol carbon of hydride release from C(1)–H and proton release from O–H are opposite, a fully concerted process might be expected to have a reaction constant nearer zero

On the other hand, a detailed study of the kinetics of the oxidation of substituted benzyl alcohols[21] by bromine in aqueous acetic acid as solvent was performed In solvents of composition 1 1, 1 3, and 3 1 (v/v) acetic acid–water, bromine exclusively oxidized benzyl alcohol to benzaldehyde It was found that electron-withdrawing groups decrease the rates of oxidation of *meta*- and *para*-substituted benzyl alcohols The results for ten compounds give a good correlation in the Hammett plot with a reaction constant of $\rho = -2\,29$ at 25 °C In fact the results obtained give direct evidence of a hydride-transfer mechanism in the oxidation of benzyl alcohol by bromine A study of the effect upon rate constants of acidity and buffer ions in a fully aqueous solvent was not possible in that case because of the preference for substitutions at low acidities

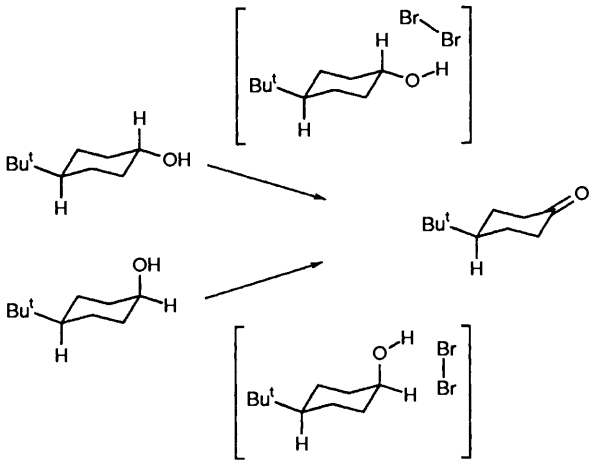
In the group of secondary alcohols, the kinetics of the bromine oxidation of aliphatic, aromatic, and cyclic alcohols have been investigated Mechanism (a) was originally proposed by Swain *et al* [22] for the oxidation of secondary alcohols by bromine This mechanism implies a rate-determining step



Mechanism (a)

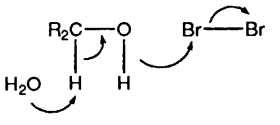
involving a hydride transfer from carbon followed by a fast proton removal from oxygen, or a partly concerted process in which the proton removal is not completely separated from the hydride abstraction

Cyclic mechanism (b) was proposed[23] to account for the insensivity of these oxidations to the stereochemical configurations of the alcohol moiety The results on the oxidation of *cis*- and *trans*-4-(t-butyl)-cyclohexanols[24] correspond closely with those of Barker *et al* mentioned earlier In the oxidation with bromine, the rate ratio for *cis*- and *trans*-4-(t-butyl)-cyclohexanols is only 1 2 and might be compared with the corresponding ratio of 3 23 in oxidations by Cr^{6+} [25]



Mechanism (b)

Deno and Potter[26] have questioned the validity of both mechanisms These authors have studied the pH rate profile for these oxidations and have also compared the alcohol oxidations with the oxidative cleavage of ethers The proposal of Deno and Potter, mechanism (c), involves a direct attack of bromine on the



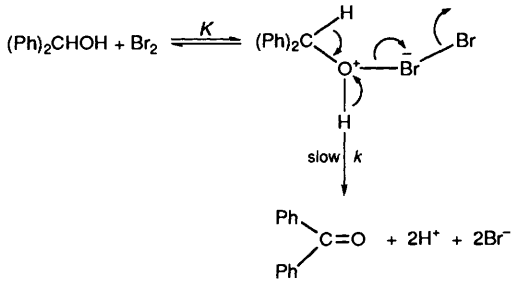
Mechanism (c)

hydroxylic oxygen followed by an abstraction of a proton (from the secondary carbon) by water The authors claim that the ether-cleavage and alcohol oxidations have a unifying feature

In order to clarify this aspect, the kinetics of the oxidation of several substituted secondary alcohols in aqueous acetic medium were investigated [21 27] Electron-withdrawing substituents retard the reaction and electron-releasing substituents increase the rate of oxidation The results point to a rate-determining abstraction of the α-hydrogen as a hydride anion

Later, a kinetic study of oxidation of benzhydrol by aqueous bromine was carried out in an exhaustive way [28] The reaction with respect to both the bromine and the substrate benzhydrol is first-order and the authors proposed tentatively on the basis of experimental data, which included determination of the primary isotope effect, solvent isotope effect, and an absence of buffer dependence, the following scheme (Scheme 2)

The observed negative value of activation entropy also suggests an ordered transition state as proposed But the same authors consider[29] from results obtained for the oxidation of substituted benzhydrols by aqueous bromine that it is not correct to think of a single mechanism in Br_2 oxidations of organic compounds The mechanism may change in response to the nature of the substituents



Scheme 2

3.2 Aldehydes

As mentioned above, kinetic studies show that the probable mechanism of the oxidation of alcohols to carbonyl compounds by aqueous solutions of bromine involves loss of hydrogen from C(1)—H as hydride ion rather than as a proton On the other hand, this pathway of hydride removal may not be general for all oxidations of oxygenated compounds by bromine and it is claimed that the mechanism of oxidation of ethers involves a transition state in which the direction of electron flow is similar to that of oxidations with chromic acid in which proton loss occurs [18]

$$RCHO + H_2O \rightleftharpoons RCH(OH)_2$$
$$RCH(OH)_2 + Br_2 + B \rightarrow RCOOH + HBr_2 + BH^+$$
$$HBr_2 \rightleftharpoons H^+ + 2Br$$

Scheme 3

Kudesia[30 31 32] carried out the study of the kinetics of buffered aqueous bromine oxidation of some aliphatic aldehydes He suggested the mechanism shown in Scheme 3 for the oxidation of the isobutyraldehyde, where RCHO represents isobutyraldehyde and B represents base In the papers there is no evidence for the species HBr_2 and it is not necessary to suggest that it is an intermediate

The order of reaction was found to be one with respect to the aldehyde concerned and to molecular bromine The increase of rate with increase of buffer acetate concentration shows that the reaction is subject to general base catalysis A large solvent isotope effect ($k_{H\,O}/k_{D\,O} = 3\,6$) was also found, providing evidence of transfer of proton from aldehyde hydrate oxygen in the rate-determining step The same mechanism was already described previously in the literature for several aliphatic aldehydes

In order to establish the mechanism for the aqueous bromine oxidation of aromatic aldehydes, a detailed study of the oxidation of benzaldehyde and ten substituted benzaldehydes was carried out [33] The results confirm the reasonable expectation that the kinetics of the oxidation of aromatic aldehydes to carboxylic acids with bromine should be similar to those of aliphatic aldehydes Thus, for example, the reaction is first order with respect to concentration in both bromine and benzaldehyde, and tribromide ion is not a significant oxidant

The observed lack of dependence of rate upon nature of substituent is considered the consequence of a mechanism in which two consecutive stages of opposite polar requirement together determine the overall rate of reaction The first stage is hydration which may be rate-limiting either through a rate process (equation 16) or a rapidly achieved equilibrium (equation 17) with small equilibrium constant followed by removal of hydride ion from the hydrate by bromine (Scheme 4)

This scheme is analogous to other consecutive reactions of carbonyl compounds in which addition followed by elimination leads to a low overall polar effect It is reasonable that benzaldehyde is hydrated to a lesser extent than aliphatic aldehydes in aqueous solution, although there is no knowledge of the equilibrium constant

$$PhCHO + H_2O \longrightarrow \left.\begin{matrix} \\ \end{matrix}\right\} PhCH(OH)_2 \quad (16)$$
$$PhCHO + H_2O \overset{fast}{\rightleftharpoons} \quad (17)$$

$$PhCH(OH)_2 + Br \longrightarrow PhC^{\cdot}(OH)_2 + HBr + Br$$
$$PhC^{\cdot}(OH)_2 \overset{fast}{\longrightarrow} PhCO_2H + H^+$$

Scheme 4

The oxidation of benzaldehyde with a 50-fold excess of bromine was still insufficient to depress the order of unity with respect to bromine and suggested that equation 17 may operate An unusual observation is that the rate constant for oxidation of benzaldehyde increases with diminishing concentration of bromine in the presence of a relatively large concentration of benzaldehyde One explanation is that the lower concentrations of bromine involved may approach that of benzaldehyde hydrate, thus diminishing the kinetic importance of hydration

3.3 Polyfunctional Molecules

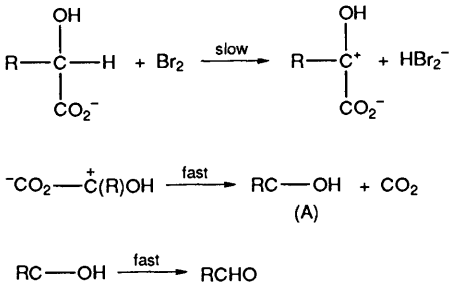
3 3 1 α-Hydroxy Carboxylic Acids

The principal mechanistic conclusions from the kinetic investigations were [34 35] (i) the anions of the hydroxy acids are more reactive than the acids, (ii) in neutral and alkaline media the oxidizing species is HOBr whereas in the pH range 2—5, molecular bromine is the active species, and (iii) a hypobromite ester is formed as an intermediate All the previous detailed investigations had been performed in the pH range 2—11 Banerji[36] carried out studies on the kinetics of oxidation of substituted mandelic acids by bromine in strongly acidic solutions The oxidation was first order with respect to each of the hydroxy-acid and bromine

However the results presented by Banerji differ considerably from those of Pink and Stewart[34] obtained in weakly acid solution, but are in agreement with those obtained in the case of chromic acid and permanganate oxidations of mandelic acid Moreover the rate of oxidation of the nine substituted mandelic acids correlates well ($r = 0\,995$) with σ^+ values, with a reaction constant $\rho^+ = -2\,65 \pm 0\,05$ at 25 °C The negative reaction constant points to an electron-deficient carbon centre in the transition state The formation of a hypobromite ester is unlikely in view of the almost equal ease of the oxidation of mandelic acid and its methyl ether The correlation with σ^+ values together with the substantial kinetic isotope effect, $k_H/k_D = 5\,14$, suggests a considerable carbonium ion character in the transition state Based on the results reported by Banerji, a credible mechanism would be transfer of a hydride ion from the hydroxy acid to the oxidant Absence of any appreciable solvent isotope effect suggests that the removal of hydroxylic proton is not synchronous with the hydride ion transfer This is more so in view of the magnitude of the reaction constant The polar requirement, on the carbinol carbon, of the hydride ion release from the C—H bond is opposite to that of proton release from the O—H group, and in a fully concerted process the reaction constant is likely to be nearly zero

It is interesting to point out the results obtained on the oxidation of glycollic, lactic, α-hydroxybutyric, and 2-phenyllactic acids by aqueous bromine [37] The reaction is of first order with respect to both the oxidant and the anion of the hydroxy acid The active oxidizing species is molecular bromine The oxidation of α-hydroxy acids is similar to that of alcohols As mentioned before, the oxidation of alcohols by bromine involves removal of the hydride ion from the carbinol carbon However, the oxidation of α-hydroxy acid involves decarboxylation and this may also be either simultaneous with the hydride ion removal or a fast reaction afterwards No α-keto acid was detected as product and hence its formation as a discrete intermediate is unlikely The following mechanism may then be proposed The decarboxylation is shown as a rapid reaction following the rate-determining step but it may well be synchronous The intermediate (A) is likely to be highly unstable and

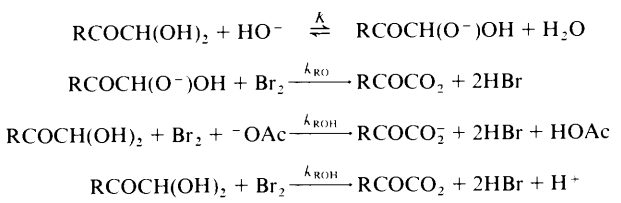
should rearrange almost instantaneously to an aldehyde (Scheme 5)



Scheme 5

3 3 2 Glyoxaldehydes

Bromine oxidation of phenylglyoxal hydrate in aqueous acetate buffer has been studied [1] The reaction is first order in bromine and in phenylglyoxal hydrate, and shows specific base and buffer catalysis, with a kinetic isotope effect at zero buffer concentration and in the buffer-catalysed reaction The data are interpreted in terms of hydride abstraction by molecular bromine, both from phenylglyoxal hydrate with concerted deprotonation and from the anion of phenylglyoxal hydrate The mechanism shown in Scheme 6 has been proposed

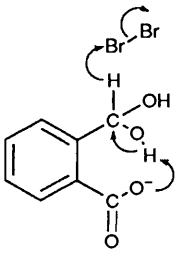


Scheme 6

3 3 3 2-Carboxybenzaldehyde

Bromine oxidation of 2-carboxybenzaldehyde was studied and its rate of oxidation compared with benzaldehyde [38 24]

The relatively rapid rate of oxidation of 2-carboxybenzaldehyde indicates a very significant contribution to the rate from intramolecular catalysis by the neighbouring carboxylate group Barker and Dahm[33] have shown that for a wide variety of substituents, the maximum variation in rate from that of the parent benzaldehyde is a factor of *ca* 3, whereas the presence of the *o*-carboxylate group causes a 73-fold rate increase The large rate increase caused by the 2-carboxylate group would be a result of proton removal by the carboxylate in the rate-determining step as shown below in (3)



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