The Kinetics and Mechanism of the Oxidation of Mandelic Acid and Related Compounds with Bromine and with Hypobromous Acid

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Hypobromous acid is much more effective than bromine in oxidising mandelic acid in weakly acidic solution to benzaldehyde and carbon dioxide. The carboxylate ion is oxidised *ca.* 9·5 times faster than the undissociated acid and the Hammett reaction constant obtained from rate measurements of six mandelic acids in the carboxylate ion form is −0·43. The reaction is catalysed by silver acetate but does not appear to be general base catalysed. For the oxidation of ethyl *p*-chloromandelate and β-hydroxy-β-*p*-chlorophenylpivalic acid, bromine is more effective than hypobromous acid; whereas the latter reagent is more effective in oxidising benzilic acid. Benzoylformic acid is oxidised by hypobromous acid in concurrent first- and second-order processes. The mechanisms of these reactions are discussed.

BROMINE WATER appears to oxidise by way of hydride transfer from C(1) many simple organic functional groups, *e.g.* alcohols, aldehydes, and ethers (see *e.g.*, refs. 1—6). Hypobromous acid is less effective than molecular bromine as an oxidant for these classes. On the other hand, oxalic acid which lacks an α-hydrogen atom is oxidised readily to carbon dioxide by hypobromous acid and not by molecular bromine. The mechanism of this oxidation has been described in terms of an intermediate acyl hypobromite.[1]

The rates of the thermal reaction of bromine with lactic, phenyl-lactic, and mandelic acids in unbuffered aqueous solutions are reported to be kinetically of the second order in bromine.[7] Rates of reaction increase with the addition of alkali and it was suggested as a consequence that the reaction takes place between molecular bromine and the anion of the acid. Tribromide ion is not an oxidant and the organic products were not identified. Most recently, Pink and Stewart [8,9] have reported on the kinetics of the oxidation of hydroxy-acids and related compounds with bromine. Although they did not use pure hypobromous acid as an oxidant basic features of the reaction were observed.

Quantitative studies of the oxidations of alcohols [10] and aldehydes [11] with chlorine water indicate that both hypochlorous acid and molecular chlorine are effective oxidants. Mechanisms involving either hydride transfer or alkyl hypochlorites have been proposed. The kinetics of the oxidation with chlorine water of pyruvic, D-gluconic, and lactic acids in the range pH 1—11 have been reported.[12] Pyruvic acid is chlorinated to 2-chloropyruvic acid in a process whose rate is controlled by enolisation. The rates of the reactions of chlorine with the α-hydroxy-acids increase rapidly with increasing pH reaching a maximum at pH *ca.* 7 and thereafter decrease. At the higher pH values the oxidant is considered to be hypochlorous acid. The mechanism suggested for the oxidation of the α-hydroxy-acids to the products, which are stated to be the α-keto-acids, involves an intermediate alkyl hypochlorite which decomposes by a reaction path which may be catalysed by hydroxide ion.

This paper reports a detailed study of the kinetics of the reaction of bromine and of hypobromous acid with mandelic acid. Other compounds were investigated in a more preliminary manner, a particular aim being to identify the oxidant.

RESULTS

Oxidation of Mandelic Acid.—In water at 25° the reaction of mandelic acid with bromine after several weeks asymptotically approaches the mole ratio 1 : 1·8, respectively. Simple tests showed the presence of bromine substituted compound(s) in the product, though no pure compounds were isolated. With similar concentrations (*ca.* 0·05M) of reactants the rate of loss of bromine measured titrimetrically in water at 25° is about twice the rate of oxidation of L-mandelic acid measured polarimetrically. Bromine continued to be consumed after the optical rotations indicated that no L-mandelic acid remained. In further preliminary experiments, the reaction of bromine (0·044M) with mandelic acid (0·0102M) in water at 25° was followed by titrimetric analysis of bromine, and by measurement of the increase in optical absorption at 252 nm due to the formation of a product containing a conjugated carbonyl group. Plots of the analyses against time showed that the oxidation stage occurred during an initial rapid consumption of bromine. Later in the reaction, whereas bromine continued to be consumed, the optical density at 252 nm slowly decreased. The results indicated that in water, bromine is consumed in both an oxidation and a substitution reaction. The acidity of the solution increases during the reaction due to hydrobromic acid, the rate of oxidation decreases and the reaction becomes increasingly one of substitution.

In an aqueous buffer of pH 5, mandelic acid and bromine react in the mole ratio 1 : 2, respectively and an 86% yield of benzoic acid was isolated. A similar experiment with *p*-chloromandelic acid produced *p*-chlorobenzoic acid in 85% yield. It had been observed in these experiments that soon after mixing the reactants an oil formed which

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[3] R. M. Barter and J. S. Littler, *J. Chem. Soc.* (*B*), 1967, 205.

[4] P. T. McTigue and G. M. Sime, *J. Chem. Soc.*, 1963, 1303.

[5] B. Perlmutter-Hayman and Y. Weissman, *J. Amer. Chem. Soc.*, 1969, **91**, 668.

[6] B. G. Cox and P. T. McTigue, *Austral. J. Chem.*, 1964, **17**, 1210.

[7] R. M. Purkayastha and R. C. Ghosh, *Z. Phys. Chem.* 1930, **7**, 285.

[8] J. M. Pink and R. Stewart, *Canad. J. Chem.*, 1971, **49**, 649.

[9] J. M. Pink and R. Stewart, *Canad. J. Chem.*, 1971, **49**, 654.

[10] I. K. Kozinenko and E. A. Shilov, *J. Chim. Ukraine*, 1960, **26**, 206.

[11] I. K. Kozinenko and E. A. Shilov, *J. Chim. Ukraine*, 1959, **25**, 606.

[12] E. A. Shilov and A. A. Yasnikov, *J. Chim. Ukraine*, 1952, **18**, 611.

subsequently disappeared. The oil was isolated and identified as benzaldehyde from its i.r. spectrum and m.p. of the 2,4-dinitrophenylhydrazone derivative.

The second-order rate constant for the oxidation of mandelic acid (0·00523M) with bromine (0·00209M) in aqueous acetate buffer of pH 4·78 at 0° is $10^{4}k_{2} = 4{\cdot}37$ l mol^{-1} s^{-1}. That for the oxidation of mandelic acid (0·00389M) with hypobromous acid (0·00245M) in aqueous acetate buffer of pH 4·78 at 0° is $10^{2}k_{2} = 5{\cdot}54$ l mol^{-1} s^{-1}, *i.e.*, the reaction with hypobromous acid is faster by a factor of *ca.* 12. In both cases the reactions were followed by titrimetric analysis of the oxidant. During oxidations by hypobromous acid the formation of bromine was observed in the reaction mixtures. The oxidation of mandelic acid proceeded rapidly until no more hypobromous acid remained; oxidation of unreacted mandelic acid with the generated bromine was very much slower. That bromine was much less efficient in oxidising mandelic acid is also illustrated by the need to set the reactivity of bromine at zero to obtain constant rate coefficients when employing a second-order, integrated rate equation based upon the reaction stoicheiometry (1).

$$\mathrm{PhCHOHCO_2H + 2\ HOBr \longrightarrow PhCHO + 2\ H_2O + CO_2 + Br_2} \quad (1)$$

The extent of bromination by hypobromous acid of *p*-chloromandelic acid was determined in buffers of different acidity in order to select those for the kinetic study of the oxidation reaction. In suitable reaction mixtures, the rate of consumption of hypobromous acid (inclusive of generated bromine) measured titrimetrically was compared with the rate of formation of *p*-chlorobenzaldehyde measured spectrophotometrically at 262 nm. At pH 1 and 2, hypobromous acid (and/or bromine) is consumed in a reaction which does not effect oxidation, whereas in the range pH 3—6 the reaction is exclusively oxidation.

Table 1 records the rate constants for the oxidation of *p*-chloromandelic acid by hypobromous acid in various buffers over the range pH 2·86—5·54. These rate constants may be expressed as a function of the concentration of the carboxylate ion form of *p*-chloromandelic acid. The correlation of the data to the line of best fit has a coefficient (r) of 0·99293. The anion reacts with a rate constant *ca.* 9·5 times greater than a value for the undissociated acid ($10^{2}k_{2} = 0{\cdot}60$ l mol^{-1} s^{-1}) obtained by extrapolation. For the calculation, the value of $\mathrm{p}K_{\mathrm{a}} = 3{\cdot}3$ used for *p*-chloromandelic acid was obtained by interpolation of a Hammett plot of the pK_{a} values of four substituted mandelic acids.[13,14]

TABLE 1

Second-order rate constants for the oxidation of *p*-chloromandelic acid (*ca.* 0·004M) with hypobromous acid (*ca.* 0·0025M) in aqueous buffers at 0°

pH of solvent	Buffer composition	$10^{2}k_{2}$ l mol^{-1} s^{-1}
5·54	0·3M-NaOAc + HOAc	5·40
4·78	0·3M-NaOAc + HOAc	5·22
4·41	0·3M-NaOAc + HOAc	5·38
4·22	0·3M-NaOAc + HOAc	5·32
4·24	0·2M-NaOAc + HOAc + 0·1M-NaClO$_4$	5·30
4·10	0·1M-NaOAc + HOAc + 0·2M-NaClO$_4$	5·25
3·82	0·3M-NaOAc + HOAc	4·68
3·34	0·3M-HK$_2$PO$_4$ + H$_3$PO$_4$	3·20
3·06	0·3M-KH$_2$PO$_4$ + H$_3$PO$_4$	2·72
3·02	0·3M-KH$_2$PO$_4$ + H$_3$PO$_4$	2·30
2·86	0·3M-NaOAc + H$_2$SO$_4$	1·90
2·89	0·2M-NaOAc + H$_2$SO$_4$ + 0·1M-NaClO$_4$	2·01
2·86	0·1M-NaOAc + H$_2$SO$_4$ + 0·2M-NaClO$_4$	1·80

The rates of oxidation by hypobromous acid of mandelic acid and five *m*- or *p*-substituted derivatives were measured in aqueous buffer of pH 4·78 at 0°. The results are summarised in Table 2. The line of best fit drawn to correlate these rate constants with Hammett normal substituent constants gives a value for the reaction constant (ρ) of −0·43 ($r = 0{\cdot}97899$). In the case of *p*-methylmandelic acid the rate of loss of hypobromous acid was greater than the rate of appearance of *p*-methylbenzaldehyde. Consequently, the reaction was arranged to be pseudo-first order by using a large excess of the oxidant and analysing the benzaldehyde spectrophotometrically.

TABLE 2

Second-order rate constants for the oxidation of mandelic acids (*ca.* 0·004M, except *p*-Me which was 0·00012M) with hypobromous acid (*ca.* 0·0025M) in aqueous buffer of 4·78 at 0°

Substituent	H	*p*-Cl	*m*-F
$10^{2}k_{2}$/l mol^{-1} s^{-1}	5·49	5·22	4·26
	m-Cl	*m*-NO$_2$	*p*-Me
$10^{2}k_{2}$/l mol^{-1} s^{-1}	4·00	2·74	6·75

The addition of silver acetate to reaction mixtures of hypobromous and *p*-chloromandelic acids prevented the generation of bromine. By analysing the rate of consumption of hypobromous acid (titrimetrically) independently of the rate of formation of *p*-chlorobenzaldehyde (spectrophotometrically) in a given run it was shown that silver acetate does not oxidise *p*-chloromandelic acid but catalysed the oxidation by hypobromous acid. A quantitative measure of this catalysis is shown by the rate constants in Table 3. Rate constants in this series were calculated from a second-order, integrated rate equation based upon the reaction stoicheiometry (2). The results may also be

$$\mathrm{PhCHOHCO_2H + HOBr + AgOAc \longrightarrow PhCHO + CO_2 + H_2O + AgBr + HOAc} \quad (2)$$

expressed as a plot of rate constants for oxidation *versus* concentration of silver acetate. Extrapolation of the line of best fit ($r = 0{\cdot}98899$) to zero concentration of silver acetate, *i.e.* the uncatalysed reaction, predicts a rate constant of $10^{2}k = 1{\cdot}76$ l mol^{-1} s^{-1}; the value obtained experimentally was $10^{2}k = 1{\cdot}81$ l mol^{-1} s^{-1}.

TABLE 3

Second-order rate constants for the oxidation of *p*-chloromandelic acid (*ca.* 0·015M) with hypobromous acid (*ca.* 0·005M) at 0° in aqueous acetate buffer of pH 3 containing silver acetate

10^{3}[AgOAc]/M	8·57	10·10	10·81	12·94	13·90
$10^{2}k_{2}$/l mol^{-1} s^{-1}	3·19	3·59	3·78	4·37	4·15
10^{3}[AgOAc]/M	15·17	16·02	20·02	21·28	
$10^{2}k_{2}$/l mol^{-1} s^{-1}	4·84	5·06	5·45	5·72	

Oxidation of Ethyl p-*Chloromandelate, β-Hydroxy-β-*p-*chlorophenylpivalic Acid, and Benzilic Acid.*—Reactions between the above named compounds with bromine and

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[13] E. Grimsell, *Svensk. kem. Tidskr.*, 1942, **54**, 2.

[14] W. H. Banks and C. W. Davies, *J. Chem. Soc.*, 1938, 73.

with hypobromous acid were carried out with a particular aim of identifying the more effective oxidant. The low solubility of two of the organic substrates in water necessitated a mixed solvent and limited the concentrations of reactants used.

Typical results for the rates of consumption, measured titrimetrically, of bromine and of hypobromous acid by ethyl *p*-chloromandelate are shown in Table 4. The solvent consisted of acetic acid (5 ml), water (10 ml), and aqueous acetate buffer of pH 5 (85 ml of 0·3M-buffer). Corrections have been made for the loss of oxidant to the solvent. The consumption of bromine by the organic substrate was accompanied by the formation of an absorption peak at 253 nm, characteristic of a conjugated carbonyl group.

TABLE 4

Second-order rate coefficients for the reaction of ethyl *p*-chloromandelate (0·0052M) with bromine and with hypobromous acid at 35°

t/h	0	1	5·25	7·5	22·0
$10^3[Br_2]$/M	2·61	2·47	2·01	1·92	1·50
10^2k_2/l mol^{-1} s^{-1}		8·26	2·77	2·39	1·52
t/h	0	2·25	5·25	8·5	22·5
10^3[HOBr]/M	2·50	2·39	2·29	2·24	2·02
10^3k_2/l mol^{-1} s^{-1}		1·07	0·91	0·71	0·54

A typical result of the rate of consumption of bromine by β-hydroxy-β-*p*-chlorophenylpivalic acid in a similar solvent is shown in Table 5. The consumption of bromine was accompanied by the formation of an absorption peak at 258 nm. The rate of loss of hypobromous acid to this substrate under similar conditions was so slow that it could not be detected.

TABLE 5

Second-order rate coefficients for the reaction of β-hydroxy-β-*p*-chlorophenylpivalic acid (0·004M) with bromine at 35°

t/h	0	1	2	3·5	5·25	21·5
$10^3[Br_2]$/M	1·35	1·25	1·18	1·04	0·91	0·15
10^3k_2/l mol^{-1} s^{-1}		5·51	4·66	5·21	5·46	8·77

Benzilic acid on reacting with bromine in aqueous acetate buffer of pH 4·8 at 25° for two days gave benzophenone, isolated in 92% yield. The oxidation of benzilic acid (0·00367M) with bromine (0·00307M) in aqueous acetate buffer of pH 4·78 at 0° has a second-order rate constant of $10^2k_2 = 3·55$ l mol^{-1} s^{-1}. The reaction of benzilic acid (0·00398M) with hypobromous acid (0·00287M) under similar conditions had a half-life of *ca.* 1 min and consequently the rate was too fast to measure with the methods available.

The Oxidation of Benzoylformic Acid.—The consumption of bromine (initially 0·034M) by benzoylformic acid (initially 0·00984M) measured titrimetrically in aqueous buffer of pH 5 at 25°, asymptotically approaches the mole ratio 1 : 1. Benzoic acid was isolated as the product in 83% yield. The electronic absorption spectrum of a solution of benzoylformic acid in the buffer at 25° was unchanged over a period of 1 h, which demonstrates its thermal stability.

The kinetic order of bromine with respect to concentration was shown to be zero by measuring the first-order rate constants for the consumption of benzoylformic acid (0·00102M) spectrophotometrically at 252 nm in the presence of three different initial concentrations of bromine. The rate constants obtained at 0° for the concentrations of bromine $10^2[Br_2] = 1·01$, 2·02, and 4·04, were $10^4k_1 =$ 1·42 1·45, and 1·56 s^{-1} respectively.

Similarly, the kinetic order of hypobromous acid with respect to concentration was determined and the results are summarised in Table 6. Expressed graphically, the results approximate a straight line which on extrapolation to zero concentration of hypobromous acid does not go through the origin but intersects the rate constant axis at $10^4k_1 = 0·9$ s^{-1}. The slope of the line is the second-order rate constant, $10^2k_2 = 1·95$ l mol^{-1} s^{-1}. An interesting comparison is the first-order rate constant of $10^4k_1 =$ 1·42 s^{-1} for the oxidation of benzoylformic acid (0·00102M) with bromine (0·010M), with that of $10^4k_1 =$ *ca.* 1·5 s^{-1} for the oxidation of benzoylformic acid (0·0003M) with hypobromous acid (0·003M), under similar reaction conditions.

TABLE 6

First-order rate constants for the oxidation of benzoylformic acid (0·003M) with hypobromous acid in aqueous acetate buffer of pH 4·90 at 0°

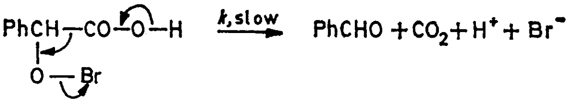
10^3[HOBr]/M	10^4k_1/s^{-1}	10^3[HOBr]/M	10^4k_1/s^{-1}
0·47	0·95	5·26	1·97
0·86	1·21	6·53	2·38
0·94	1·03	9·32	2·92
1·64	1·26	10·5	3·15
2·15	1·21	13·0	3·45
2·34	1·34	15·8	3·73
4·30	1·96	17·2	4·22
4·66	2·04		

DISCUSSION

In unbuffered aqueous solution, bromine is consumed by mandelic acid in both an oxidation and a substitution reaction. In aqueous buffer of pH 5 bromine exclusively oxidised mandelic acid. The effective oxidant for *p*-chloromandelic acid is hypobromous acid which oxidises with a rate *ca.* 13 times faster than a solution of bromine at 0°, under similar conditions. However, this is not a true measure of the relative reactivities of the oxidants as the solution of bromine at pH 4·8 is hydrolysed[15] to hypobromous acid to the extent of *ca.* 14%. Consequently, there can be very little oxidation by molecular bromine.

The mechanism of hydride transfer from C(1) is excluded as the product retains this hydrogen. This contrasts with the oxidations by chlorine water where the products are reported[12] to be the keto-acids. We regard the kinetic and other data presented here to be accommodated by the mechanism (3) and (4).

$$\mathrm{PhCHOHCO_2H + HOBr \underset{}{\overset{K,\,fast}{\rightleftharpoons}} PhCHOBrCO_2H + H_2O} \quad (3)$$



$$\mathrm{PhCH(OBr)\!-\!CO\!-\!O\!-\!H \xrightarrow{k,\,slow} PhCHO + CO_2 + H^+ + Br^-} \quad (4)$$

Other examples of oxidative decarboxylation effected by hypohalous acids or salts are known, these include

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[15] H. A. Liebhafsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1508.

oxalic acid,[16,17] aldonic acids,[18] and primary, secondary, and tertiary amino-acids.[19] Reactions of the type shown in equation (3) have been identified for alcohols in aqueous solutions of hypochlorous acid. The kinetics of the forward (k_1) and reverse (k_{-1}) reactions have been studied for t-butanol[20] and both are general acid and base catalysed. The pH profile in the range pH 2·90—5·85 shows a minimum at pH 4·4. The equilibrium constant with t-butanol ($K = k_1/k_{-1}$) is *ca.* 38 and for the uncatalysed forward reaction, $10^4k_1 =$ *ca.* 1·7—17 s^{-1} at 25°.

The oxidation of mandelic acid does not appear to be general base catalysed under the conditions studied suggesting the possibility that equation (3) is rate controlling through an equilibrium constant rather than a rate process. The oxidation is catalysed by silver acetate and this could be ascribed to its activity in assisting the removal of bromide ion in equation (4).

The reaction constant was measured at an acidity such that the substituted mandelic acids were completely ionised. The relatively small magnitude of ρ found for this polar reaction suggests that the mechanism is unlikely to consist of a single rate-determining stage. The mechanism suggested would require that ρ for the forward reaction of equation (3) is somewhat larger than that for the reverse reaction. Both of these reactions could be expected to have a negative ρ value because the oxygen atom acts as the nucleophile in either direction. Further, the suggestion requires that the bond breaking and making processes of equation (4) are concerted so that the polar nature of the aromatic ring is of little importance. The greater reactivity of hypobromous acid than bromine specifically for this reaction of oxidative decarboxylation may be rationalised. The polar requirement for decarboxylation is that electron-withdrawing substituents in the organic residue increase reactivity. The replacement of hydroxy by hypobromite is favourable to decarboxylation for reasons of polarity and also because the attached bromine atom is a better anionic leaving group than hydrogen. Bromine does not react significantly with alcohols to produce hypobromite. The carboxylate ion form is commonly more reactive than the undissociated acid in decarboxylations.

Hypobromous acid is much more effective than bromine in the oxidative decarboxylation of benzilic acid to give benzophenone and carbon dioxide. We assume that this reaction proceeds by a similar mechanism to that for mandelic acid. The mechanism could not operate for a β-hydroxy-acid nor for an ester of mandelic acid. We confirm that for β-hydroxy-β-*p*-chlorophenylpivalic acid and ethyl *p*-chloromandelate that molecular bromine is the effective oxidant and the products appear to be those of the usual oxidation of a secondary alcohol.

Benzoylformic acid is oxidised by bromine water to benzoic acid and carbon dioxide by a process which is kinetically zero order in bromine; consequently it was not possible to identify the oxidant. Benzoylformic acid is oxidised by hypobromous acid to similar products in two concurrent processes one of which is zero order and the other first order in hypobromous acid. The first-order rate constant for the oxidation of benzoylformic acid by either oxidant present in a 10-fold excess is $10^4k_1 =$ *ca.* 1·5 s^{-1}. The first-order rate constant for the hypobromous acid oxidation extrapolated to zero concentration of the oxidant gives $10^4k_1 = 0{\cdot}9$ s^{-1}. For the oxidations which are zero order in oxidant, the probable first and rate-determining stage is that of hydration of the benzoylformic acid. Oxidation of the hydrate by hypobromous acid would then proceed *via* a hypobromite as in the case of mandelic acid.

There is no direct evidence for the existence of benzoylformic acid hydrate. The species has been invoked to account for the rapid oxidative cleavage of benzoylformic acid by lead tetra-acetate in acetic acid containing a little water.[21] Equilibrium constants for the hydration of glyoxylic acid and its anion are reported as 6×10^{-4} and $1{\cdot}6 \times 10^{-2}$, respectively.[22] The mechanism proposed implies that the rate constant for the hydration of benzoylformic acid is $10^4k_1 =$ *ca.* 1·5 s^{-1}, at 0° in the acetate buffer at pH 4·9. The literature does not appear to contain a value but comparison may be made with the hydration of acetaldehyde[23] which has a rate constant of $10^3k_1 =$ *ca.* 1 s^{-1} at 0° in acetate buffer of pH 5.

The mechanism of the oxidation of benzoylformic acid by hypobromous acid which is first order in each component, and consequently bimolecular, must proceed differently. It is suggested for this reaction that the hypobromite intermediate is formed in the rate determining step by nucleophilic addition of hypobromous acid to the carbonyl group of benzoylformic acid.

EXPERIMENTAL

For general details see ref. 24.

Materials.—Hypobromous acid to a maximum concentration of 0·04M was prepared by the method described by Branch and Jones.[25] Analytical reagent grade bromine was used without further purification.

Pure DL- and L-mandelic acid, benzilic acid, and benzoylformic acid, were obtained from commercial materials by recrystallisation. The five substituted mandelic acids used were prepared by the method described by Jenkins.[26] The ethyl ester of *p*-chloromandelic acid was prepared

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[16] Y. Knoller and B. Perlmutter-Hayman, *J. Amer. Chem. Soc.*, 1955, **77**, 3212.

[17] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, 1932, **28**, 518.

[18] R. L. Whistler and K. Yagi, *J. Org. Chem.*, 1961, **26**, 1050.

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[22] J. Kuta and P. Valenta, *Coll. Czech. Chem. Comm.*, 1963, **28**, 1593.

[23] R. P. Bell and B. de B. Darwent, *Trans. Faraday Soc.*, 1950, **46**, 34.

[24] P. Aukett, Ph.D. Thesis, Brighton Polytechnic, 1970.

[25] S. J. Branch and B. Jones, *J. Chem. Soc.*, 1954, 2317.

[26] S. S. Jenkins, *J. Amer. Chem. Soc.*, 1931, **53**, 2341.

by esterification of the acid.[27] β-Hydroxy-β-*p*-chlorophenylpivalic acid was prepared by the condensation of *p*-chlorobenzaldehyde, isobutyric anhydride, and sodium isobutyrate.[28] All m.p.s were in good agreement with literature values.[13, 26, 29, 30]

Kinetic Procedures and Calculation of Results.—Bromine and hypobromous acid were analysed by titrimetric analysis with solutions of sodium arsenite and iodine. This method estimates the sum of the concentrations of bromine, hypobromous acid, and tribromide ion. Polarimetric measurements were used in the case of L-mandelic acid. Other substrates were estimated spectrophotometrically in the usual manner. Aliquot portions of reaction mixtures were quenched in solutions of sodium arsenite. Neither arsenite nor arsenate absorbed in the spectral region used. Stoicheiometric measurements were carried out semi-kinetically and in those which required lengthy reaction times sealed ampoules were used. Reaction flasks were covered with aluminium foil to exclude light in all experiments.

Rate constants were calculated from the appropriate integrated rate equations, their exact form depended upon the reaction under measurement. All kinetic runs were carried out at least in duplicate with reproducibility within 5%. Reactions were studied in extent mainly to at least two half-lives. Calculation of rate constants in reactions using hypobromous acid were complicated because of an assumption implicit in the second-order rate equation based on the reactions (5) and (6). The assumption that

$$\mathrm{PhCHOHCO_2H + HOBr \longrightarrow PhCHO + CO_2 + H_2O + HBr} \quad (5)$$

$$\mathrm{HBr + HOBr \xrightarrow{fast} Br_2 + H_2O} \quad (6)$$

when all the hypobromous acid is consumed only bromine is present is incorrect because of the reversibility of equation (6). The effect is small during the first 50% reaction (with respect to hypobromous acid) and rate coefficients for this period were constant.

Where a linear relationship was considered a possibility between rate constants and some other property of the reaction system, the line of best fit was obtained by the method of least squares. The correlation of the data is expressed by the correlation coefficient which was calculated for each regression line.

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