51. *Kinetics and Mechanism of Aromatic Halogenation by Hypohalous Acids. Part III.** *Chlorination of* p-*Anisic Acid by Hypochlorous Acid in 75% Acetic Acid.*†

By G. Stanley and J. Shorter.

Measurements of initial rate of reaction at 20° have been made for the chlorination by hypochlorous acid of *p*-anisic (*p*-methoxybenzoic) acid in aqueous acetic acid containing 75% (w/w) of acetic acid. The dependence of rate on the concentrations of hypochlorous acid c_1 and anisic acid c_2 is given by $r_0 = Ac_1c_2/(1 + Bc_1)$, where A and B are constants. The initial rate is virtually independent of the hydrogen-ion concentration, for the influence of acids on r_0 is comparable with that of their sodium salts.

These results are interpreted in terms of reaction between a non-ionic chlorinating species and an active form of the anisic acid, produced at a finite rate from the bulk form of the ether. The natures of the chlorinating species and active form are discussed. Molecular chlorine is unimportant as a chlorinating species in the absence of added chloride, the effective halogenating species probably being acetyl hypochlorite. It is suggested that there is considerable formation of unreactive complexes of aromatic ether with acetic acid, and that the active form is a hydrated anisic acid molecule.

The reaction mechanism thus differs from that of the chlorination of aromatic compounds by hypochlorous acid in water,[1,2] and from that of bromination by hypobromous acid in 75% acetic acid,[3,4] where halogen cations constitute the halogenating species.

Bradfield and Brynmor Jones and their colleagues have often studied the kinetics and mechanism of the halogenation of aromatic ethers and anilides in acetic acid. Most of this work has been concerned with chlorination by molecular chlorine in acetic acid containing 1% of water,[5] but recently Branch and Brynmor Jones[3,4] studied the bromination of aromatic ethers by hypobromous acid in aqueous acetic acid containing 75% (w/w) of acetic acid. They concluded that hypobromous acid was itself rather unreactive, and that the effective brominating species was either the solvated cation $\overset{+}{\mathrm{Br}}\mathrm{OH_2}$ or the free cation $\overset{+}{\mathrm{Br}}$, present in amount controlled by the hydrogen-ion concentration through the equilibria

$$\mathrm{HOBr} + \mathrm{H_3\overset{+}{O}} \rightleftharpoons \overset{+}{\mathrm{Br}}\mathrm{OH_2} + \mathrm{H_2O} \ ; \ \overset{+}{\mathrm{Br}}\mathrm{OH_2} \rightleftharpoons \overset{+}{\mathrm{Br}} + \mathrm{H_2O}$$

This is in agreement with the results of Derbyshire and Waters[6] and of Wilson and Soper[7] on the reactions of hypobromous acid with aromatic compounds in aqueous solution. Our present work on the reaction of aromatic ethers with hypochlorous acid in 75% acetic acid arose as an extension of that of Branch and Brynmor Jones. It comprises the investigation of the chlorination of nine *p*-alkoxybenzoic acids and several *para*-substituted anisoles. The arrangement of electron-attracting and -releasing groups in the molecules ensured that chlorination would occur only in one of the positions *ortho* to the alkoxyl group. Preliminary experiments showed that the kinetics were more complicated than those of bromination by hypobromous acid in 75% acetic acid, and it was decided that initial-rate

---

* Part II, *J.*, 1955, 2921.

† Presented in outline at the XVIth International Congress of Pure and Applied Chemistry, Paris, 1957.

[1] Derbyshire and Waters, *J.*, 1951, 73.

[2] de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

[3] Branch and Brynmor Jones, *J.*, 1954, 2317.

[4] *Idem*, *J.*, 1955, 2921.

[5] Part XVII, Brynmor Jones and Richardson, *J.*, 1955, 2772.

[6] Derbyshire and Waters, *J.*, 1950, 564.

[7] Wilson and Soper, *J.*, 1949, 3376.

measurements provided the best means of investigation. This paper describes a detailed study of anisic (*p*-methoxybenzoic) acid, and Part IV (following paper) describes a less detailed survey of the other ethers.

Nuclear halogenation of aromatic compounds by hypochlorous acid has previously been studied. Derbyshire and Waters[1] showed that the reaction of hypochlorous acid with sodium toluene-ω-sulphonate in aqueous solution was catalysed by mineral acid and concluded that chlorine cations were the effective species. de la Mare, Ketley, and Vernon[2] studied the reactions of hypochlorous acid with aromatic compounds in water and in aqueous dioxan, in the presence of silver perchlorate to suppress the chloride-ion concentration and thus eliminate the intervention of molecular chlorine. The kinetics were complicated, but the authors showed that the mechanism involved chlorine cations. They could distinguish between the action of solvated $\overset{+}{\mathrm{Cl}}\mathrm{OH}_2$ and free $\overset{+}{\mathrm{Cl}}$ cations, the part played by each depending on the reactivity of the aromatic compound. At hypochlorous acid concentrations above 0·001M, chlorine monoxide, derived from the reversible dehydration of hypochlorous acid, was found to play a part. de la Mare, Ketley, and Vernon[8] have also shown that in solutions of hypochlorous acid in 98% acetic acid, acetyl hypochlorite is an important chlorinating species. Studies of side-chain substitution in anilides have been made by Soper and his colleagues.[9, 10] Here the hypochlorite ion appears to be effective.

Addition reactions involving hypochlorous acid and unsaturated compounds such as allyl alcohol were studied by Israel[11] and by Shilov[12] and their colleagues; molecular hypochlorous acid and chlorine monoxide are important chlorinating species. Experiments carried out in the presence of sodium acetate and acetic acid buffers suggested that acetyl hypochlorite was then an important intermediate. (The participation of acyl hypohalites in the reactions of hypohalous acids with organic compounds in buffer solutions has also been suggested in connection with the iodination of phenol[13] and the bromination of aromatic compounds.[7])

Hypochlorous acid thus functions in a variety of ways in its reactions with organic compounds.

EXPERIMENTAL

Purification of Acetic Acid.—Acetic acid containing 2% of chromium trioxide (" AnalaR ") was distilled, then redistilled from 0·2% of naphthalene-2-sulphonic acid in the theoretical amount of " AnalaR " acetic anhydride.[14] Head and tail fractions were rejected and the final distillate had m. p. 16·5°, corresponding to 99·95% purity. The reaction medium containing 75% (w/w) of acetic acid ($n_D^{20} = 1·3756$) was prepared by adding the calculated volume of acetic acid (after allowance for the slight water content of the purified acid) to a known volume of distilled water.

Anisic Acid.—The preparation of very pure anisic acid required for kinetic studies is difficult. The product obtained from *p*-hydroxybenzoic acid and methyl iodide by Brynmor Jones's method[15] proved unsatisfactory. Measurements of the rate of chlorination by hypochlorous acid clearly showed the presence of the more reactive *p*-hydroxybenzoic acid. Presumably loss of methyl iodide by volatilisation prevented quantitative conversion into anisic acid, and repeated crystallisation failed to remove all traces of *p*-hydroxybenzoic acid. An alternative method of preparation was therefore adopted. Anisaldehyde was prepared by treating

---

[8] de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12s,

[9] Mauger and Soper, *J.*, 1946, 71.

[10] Pryde and Soper, *J.*, 1931, 1510.

[11] Israel, Martin, and Soper, *J.*, 1950, 1282; Israel, *J.*, 1950, 1286; Craw and Israel, *J.*, 1952, 550; Reeve and Israel, *J.*, 1952, 2327.

[12] Shilov and Kupinskaya, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 621; Shilov, *ibid.*, 1952, **84**, 1001.

[13] Painter and Soper, *J.*, 1947, 342.

[14] Orton and Bradfield, *J.*, 1927, 983.

[15] Brynmor Jones, *J.*, 1935, 1874.

p-hydroxybenzaldehyde with methyl iodide and potassium carbonate in *cyclo*hexanone,[16] and was then oxidised to anisic acid by neutral potassium permanganate. The anisic acid was recrystallised several times from acetic acid and from benzene; it had m. p. 184°, in agreement with that given by Gray and Brynmor Jones.[17] The advantage of this method is that any unmethylated hydroxy-compound remains with the insoluble inorganic matter and is removed by filtration before the *cyclo*hexanone is distilled off.

Hypochlorous Acid.—Water was saturated with chlorine from a cylinder and then shaken with silver sulphate for about ½ hr. After filtration, the aqueous solution of hypochlorous acid was distilled at *ca.* 15 mm. and 20°. The vapour of a water-bath was sufficient to heat the flask, thus preventing superheating and minimising decomposition of hypochlorous acid. Silver chloride was deposited during distillation, so it was advisable for the capillary " leak " not to extend to the base of the flask. The distillation was carried out in diffused light, but it was not found necessary to blacken the apparatus. The hypochlorous acid solutions thus obtained were about 0·05M (by iodometry) and had pH 4·2—4·4 (measured by glass electrode and Cambridge Instrument Company pH meter). From the dissociation constant of hypochlorous acid (*ca.* $3{\cdot}2 \times 10^{-8}$ at 20°; see Sidgwick [18]), the pH of 0·05M-hypochlorous acid containing no other free acid should be 4·4. The product thus appeared to be of good quality. The acid was prepared daily as required.

Kinetic Measurements.—All measurements were made at 20°. Solutions of hypochlorous acid and aromatic ether in 75% acetic acid were mixed and the progress of the reaction followed by removal of samples and analysis for residual hypochlorous acid. Reaction rates were generally high and it was necessary to use an H-shaped vessel to permit rapid mixing of the reactants [3] and a special 5 c.c. pipette for sampling. The latter was of the automatic type, the filling and emptying being controlled by a tap and rubber bulb attached to the overflow bulb. The pipette was calibrated by weighing samples of 75% acetic acid.

In the kinetic experiments, aqueous hypochlorous acid was diluted with glacial acetic acid to give a solution in 75% acetic acid of concentration 1·25 times that desired in the ultimate reaction mixture. 50 c.c. of this solution were placed in one limb of the reaction vessel and 10 c.c. of ether solution (of concentration five times that desired in the reaction mixture) in the other. In most experiments the concentrations of hypochlorous acid and ether were in the range 0·004—0·01M. Two 5 c.c. samples of hypochlorous acid solution were taken from the reaction vessel and analysed by iodometry so that the initial concentration in the reaction mixture was accurately known. The remaining 40 c.c. of hypochlorous acid were rapidly mixed with the ether solution. Samples were withdrawn at intervals appropriate to the speed of the reaction and were run into excess of potassium iodide solution, previously freed from dissolved oxygen by a stream of nitrogen. This procedure stopped the halogenation of the aromatic ether, and the iodine liberated was titrated with 0·003N-sodium thiosulphate. Measurements were usually made to the stage at which 20—25% of the hypochlorous acid had reacted with the ether, about five samples being taken.

Initial rate was obtained by plotting the thiosulphate titres against the time, drawing the tangent at zero time, and measuring the slope. Rates were expressed as moles of HOCl used per litre per second. Accurate drawing of the tangent was difficult when the graph had a pronounced curvature. In such cases r_0 was also obtained by estimating the rate at fixed intervals along the graph, and extrapolating to zero time.

The Absence of Any Effect of Chloride Ion present in the Hypochlorous Acid.—de la Mare and his colleagues,[2] in their studies of the reactions between hypochlorous acid and aromatic compounds in aqueous solution, have generally added silver perchlorate to reduce the chloride-ion concentration and thereby eliminate the participation of molecular chlorine produced through the reaction $HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$. Derbyshire and Waters [1] showed that the addition of chloride ion accelerates the chlorination of sodium toluene-ω-sulphonate by aqueous hypochlorous acid. They were satisfied, however, that chlorine produced from chloride-ion normally present as impurity was not significant. We have now shown as follows that there is no important effect of chloride impurity on the chlorination in 75% acetic acid.

The approximate concentrations of chloride ion and chlorine in 0·005M-hypochlorous acid in 75% acetic acid can easily be calculated. Freshly distilled aqueous hypochlorous

---

[16] Gray and Brynmor Jones, *J.*, 1954, 1467.
[17] *Idem, J.*, 1953, 4179.
[18] Sidgwick, " The Chemical Elements and their Compounds," Oxford, 1950, p. 1214.

acid may be taken to have a molarity of 0·05 and a pH of 4·2; the dissociation constant of hypochlorous acid is taken to be $3{\cdot}2 \times 10^{-8}$ at 20° and the hydrolysis constant of chlorine, $K_h = [HOCl][H^+][Cl^-]/[Cl_2]$, to be 3×10^{-4} (Jakowkin [19]). It is necessary to assume that this value for K_h in water may be applied to 75% acetic acid; it should not be seriously different. The hydrogen-ion concentration of 75% acetic acid enters into the calculation, and, as shown later, this may be taken as 10^{-2}. From these data the concentrations of chloride ion and chlorine in an 0·005M-hypochlorous acid in 75% acetic acid can be calculated as *ca.* 3×10^{-6} and 4×10^{-7} respectively. (The actual concentrations may well be much lower than these values, for there is probably extensive combination between the acetic acid and hypochlorous acid.) If molecular chlorine is an important chlorinating species under the ordinary conditions of the kinetic experiments, raising the chloride-ion concentration to 10^{-4} by adding sodium chloride should increase r_0 greatly. It was found, however, that 10^{-4}M-sodium chloride had no effect (Table 1), irrespective of whether the salt was dissolved in the anisic acid solution or the hypochlorous acid solution before mixing. Further, the concentration of chlorine should depend greatly on the hydrogen-ion concentration, and the absence of any great effect of hydrogen-ion concentration on the rate (see later) confirms that molecular chlorine is not normally an important chlorinating species. At concentrations of sodium chloride rather above 10^{-4}, r_0 rises steeply with chloride concentration (Table 1), presumably owing to the participation of molecular chlorine, which is evidently extremely reactive in 75% acetic acid.*

Implicit in the above considerations is the assumption that significant decomposition of hypochlorous acid does not occur between carrying out the distillation and starting the kinetic experiment, an interval of about 30 min. Hypochlorous acid may decompose according to the equations [20] $2HOCl \longrightarrow 2HCl + O_2$; $3HOCl \longrightarrow 2HCl + HClO_3$. The pH of distilled hypochlorous acid falls by only 0·01 unit in 30 minutes' standing in diffused light. Iodometric measurement of the stability of the solution in 75% acetic acid showed that a 0·007M-solution was decomposed only to the extent of about 0·2% in 30 minutes' standing in the reaction vessel. The decomposition is thus very slow and while it may well increase considerably the amount of chloride ion present, the amount produced during the time in question would not invalidate the argument.

TABLE 1. *The effect of sodium chloride.*

10^3[HOCl] (M) ...	4·81	4·81 [a]	4·81	7·26	7·26	5·25	5·25	5·25
10^4[NaCl] (M)	0	1	1	0	1	0	5	10
$10^6 r_0$	5·06	5·13	5·06	6·42	6·49	5·28	9·53	17·45

[Anisic acid] = 0·01M. *a* denotes that the sodium chloride was dissolved initially in the hypochlorous acid solution. In the other experiments the salt was dissolved in the anisic acid solution.

Further, if molecular chlorine was normally an important halogenating species, erratic results would have been obtained. The quality of the distilled hypochlorous acid as measured by pH varied; presumably this corresponded to variations in the content of hydrochloric acid. The time taken to prepare for the kinetic experiments also varied and this would have led to variations in the amount of chloride ion produced by the decomposition of hypochlorous acid. Nevertheless the results were highly reproducible and this would hardly have been so if the mechanism involved a species produced from an impurity present in varying amount.

DISCUSSION

Dependence of r_0 on Concentrations of Anisic Acid and Hypochlorous Acid, and the Effects of Sodium Salts and of Acids in 75% Acetic Acid at 20°.—Initial rate is directly proportional to the concentration of anisic acid in the range 0—0·01M (Figure). At very low concentrations the rate is proportional to the concentration of hypochlorous acid, but

---

* Branch and Brynmor Jones [3] found that molecular bromine and bromine monochloride were very unreactive towards aromatic ethers in 75% acetic acid. This low reactivity was confirmed here; the addition of an excess of bromide ion to convert the hypochlorous acid completely into bromine monochloride and bromine virtually stopped the halogenation of anisic acid.

[19] Jakowkin, *Z. phys. Chem.*, 1899, **29**, 613.

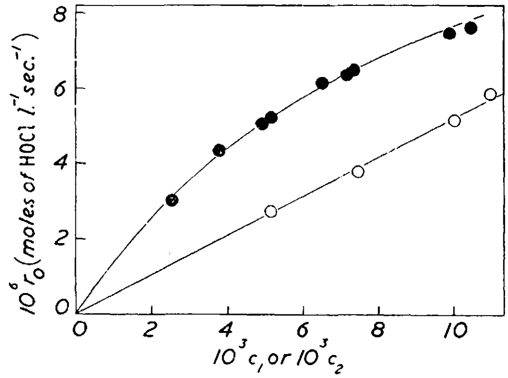
[20] Sidgwick, ref. 18, p. 1215.

at higher concentrations the order of reaction falls. A possible relation to express this behaviour is:

$$r_0 = Ac_1c_2/(1 + Bc_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c_1 is the concentration of hypochlorous acid, c_2 that of anisic acid, and A and B are constants. If this relation is valid the graph of $1/r_0$ against $1/c_1$ (c_2 being constant) should be linear. This is found to be so, and, from the slope and intercept, A and B are 0·155 and 102 respectively. The dependence of r_0 on c_1, when $c_2 = 0{\cdot}01$, given by expression (1) with these values of A and B, is shown by the curve in the Figure. The agreement with experiment is satisfactory.

Similar behaviour was found with reaction solutions that were 0·1M in sodium acetate or nitrate, and was also found for other *p*-alkoxybenzoic acids and for methyl anisate and *p*-chloroanisole (Part IV, following paper).



The dependence of initial rate r_0 on anisic acid concentration c_2 and hypochlorous acid concentration c_1.

○ $c_1 = 0{\cdot}00505$M (range 0·00504—0·00506). c_2 varying.
● $c_2 = 0{\cdot}01$M. c_1 varying.

The simplest interpretation of these results is that the mechanism involves a chlorinating species reacting with an active form of anisic acid, produced from unreactive bulk form at a finite rate, as in the following scheme:

$$\underset{c_2}{\mathrm{E_b}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{c_3}{\mathrm{E_a}} \qquad\qquad \underset{c_3}{\mathrm{E_a}} + \underset{fc_1}{\mathrm{D}} \xrightarrow{k_3} \text{product}$$

$\mathrm{E_b}$ represents the bulk form and $\mathrm{E_a}$ the active form of anisic acid. D is the chlorinating species, assumed present in concentration proportional to that of hypochlorous acid as determined by iodometry, f being the proportionality constant.

If the concentration of $\mathrm{E_a}$ be assumed to reach a small stationary value at the start of the kinetic experiment, then

$$r_0 = (k_1k_3f/k_2)c_1c_2/[1 + (k_3f/k_2)c_1] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is expression (1) with $A = k_1k_3f/k_2$ and $B = k_3f/k_2$.

The effects of various salts and of acids on r_0 are shown in Tables 2—5. The effects of sodium salts are complex, and specific to the anion. 0·025M-Sodium nitrate raises r_0 by about 20% (Table 2), but the addition of salt up to 0·1M has little further effect. Very low concentrations of sodium perchlorate and sodium hydrogen sulphate (Tables 3 and 4)

TABLE 2. *The effect of sodium nitrate and nitric acid.*

10^2[NaNO$_3$] (M) ...	0	2·5	5 ^{b}	5	10	4	2·5	0
10^2[HNO$_3$] (M) ...	0	0	0	0	0	1	2·5	5
$10^6 r_0$	5·05	6·17	6·30	6·24	5·80	6·30	5·96	6·05

[Anisic acid] = 0·01M; mean [HOCl] = 0·00487M (range 0·00477—0·00492). *b* denotes that the sodium nitrate was dissolved initially in the anisic acid solution. In the other experiments the strong electrolyte was dissolved in the hypochlorous acid solution.

TABLE 3. *The effect of sodium perchlorate and perchloric acid.*

$10^2[NaClO_4]$ (M)	0	2·5	5	10	0
$10^2[HClO_4]$ (M)	0	0	0	0	5
10^6r_0	5·05	4·76	5·60	6·56	6·08

[Anisic acid] = 0·01M; mean [HOCl] = 0·00490M (range 0·00487—0·00495).

TABLE 4. *The effect of sodium hydrogen sulphate and sulphuric acid.*

$10^2[NaHSO_4]$ (M)	0	2·5	5	10	0
$10^2[H_2SO_4]$ (M)	0	0	0	0	5
10^6r_0	5·15	5·20	5·40	5·95	6·18

[Anisic acid] = 0·01M; mean [HOCl] = 0·00507M (range 0·00505—0·00515).

TABLE 5. *The effect of sodium acetate.*

$10^2[NaOAc]$ (M)	0	5	10
10^6r_0	5·00	4·91	5·15

[Anisic acid] = 0·01M. [HOCl] = 0·00485M.

have little catalytic effect (there are slight signs of inhibition) but higher concentrations increase r_0, the effect of perchlorate being the greater. Sodium acetate has little effect on r_0 (Table 5). The sodium salts thus exert small effects which are generally catalytic and which appear to be roughly in the order of the strengths of the corresponding acids, which is $HClO_4 > HNO_3 > H_2SO_4 \gg AcOH$. Tables 2 to 4 also show that in the presence of nitric, perchloric, and sulphuric acids r_0 does not differ very greatly from the value with the same concentration of sodium salt. With nitric acid there is no important difference; the effect of 0·05M-perchloric and -sulphuric acids is slightly greater than that of the sodium salts. Now the hydrogen-ion concentration in 75% acetic acid is about 10^{-2}.* Therefore the reaction mixture's being made 0·05M in strong acid will increase the hydrogen-ion concentration approximately five-fold. It thus appears that in 75% acetic acid there is little catalysis by hydrogen ion of the chlorination of anisic acid by hypochlorous acid. Similar results were found in the case of other *p*-alkoxybenzoic acids, and of methyl anisate and *p*-chloroanisole (Part IV). These results are in contrast to those of Branch and Brynmor Jones[3] on the bromination of aromatic ethers by hypobromous acid in 75% acetic acid, and to those on the chlorination of various aromatic compounds by hypochlorous acid in aqueous solution.[1, 2] The results in Table 5 on the effect of acetate ions confirm the absence of hydrogen-ion catalysis. Branch and Brynmor Jones found that the bromination was much retarded by sodium acetate's repressing the ionisation of acetic acid.

The Kinetics of the Reaction in 40% *Acetic Acid Solution.*—Table 6 shows that in 40% acetic acid the reaction is of first order in hypochlorous acid up to at least 0·01M. In the notation used for 75% acetic acid, $A = 0{\cdot}095$ and B is certainly less than 5.

Table 7 shows that in 40% acetic acid the catalytic effect of 0·05M-sodium perchlorate is comparable with that found in 75% acetic acid, but there as a much larger effect of perchloric acid. The rate is increased linearly with the concentration of perchloric acid when the perchlorate-ion concentration is maintained constant by addition of sodium perchlorate. The reaction in 40% acetic acid is evidently subject to a considerable catalysis by hydrogen ion. The hydrogen-ion concentration of 40% acetic acid is 0·009; that of 0·05M-perchloric acid in 40% acetic acid will be about 0·052. It can now be seen from

---

* Values for the hydrogen-ion concentration of concentrated aqueous solutions of acetic acid can be derived from $K_a = 1{\cdot}75 \times 10^{-5}$ at 20° and Kipling's[21] calculations of the amounts of the various molecular species present. The dissociation constant, derived from measurements on dilute solutions, is assumed to refer to the equilibrium between monomeric acetic acid hydrate and the ions, and thus $[H^+] = (K_a[\text{hydrate}])^{\frac{1}{2}}$. The hydrate concentration for aqueous acetic acid of any composition may be calculated from Kipling's graphs.

[21] Kipling, *J.*, 1952, 2858.

TABLE 6. *The effect of hypochlorous acid concentration in* 40% *acetic acid.*

10^3[HOCl] (M)	4·27	4·48	5·58	6·70	9·83
$10^6 r_0$	1·18	1·22	1·60	1·92	2·80
$10^4 r_0$/[HOCl]	2·76	2·73	2·87	2·87	2·85

[Anisic acid] = 0·003M.

TABLE 7. *The effect of sodium perchlorate and perchloric acid in* 40% *acetic acid.*

10^2[HClO$_4$] (M)	10^2[NaClO$_4$] (M)	$10^6 r_0$	$10^6 r_0$ (calc.)
0	0	1·50	—
0	5	1·67	1·67
1·75	3·25	2·60	2·63
3·25	1·75	3·48	3·44
5	0	4·40	4·40

[Anisic acid] = 0·003M; mean [HOCl] = 0·00530M (range 0·00526—0·00533). $10^6 r_0$ (calc.) = 1·67 + 54·5[HClO$_4$].

Table 7 that raising the hydrogen-ion concentration by about 0·043 increases the rate (at the given concentrations of hypochlorous acid, anisic acid, and perchlorate ion) by 2·73 units. Hence when no perchloric acid is added about 0·57 unit of r_0 is due to a hydrogen-ion catalysed reaction and 1·10 units to an uncatalysed reaction. Comparable figures for 75% acetic acid (estimated from the Figure and Table 3) are about 0·03 and 1·73 respectively.

The Reaction Mechanism.—The virtual absence of any effect of hydrogen ion in 75% acetic acid suggests that it plays no part in the mechanism by controlling the concentration of the chlorinating species. The mechanism involving chlorine cations, found for aqueous solutions by Derbyshire and Waters [1] and by de la Mare, Ketley, and Vernon [2] is thus of little importance in 75% acetic acid. The hypochlorite ion is likewise excluded. For the reasons given earlier, molecular chlorine may also be rejected. Chlorine monoxide, produced by the reversible dehydration of hypochlorous acid, would lead to second-order kinetics in hypochlorous acid.[2] The chlorinating species might be molecular hypochlorous acid in a hydrated state as in aqueous solution but this has generally been found rather unreactive in aromatic substitution,[1, 2] although it is effective in addition reactions.[11, 12] The remaining possibility is that the observed behaviour of hypochlorous acid is directly connected with the high concentration of acetic acid. There are several observations which are best explained by supposing that there is considerable combination between acetic and hypochlorous acids in 75% acetic acid, and that the chlorinating species arises from this.

When the solvent is changed from 75% to 40% acetic acid there is a great increase in the rate of a hydrogen-ion catalysed reaction. It seems likely that this hydrogen-ion catalysed reaction involves the generation of chlorine cations from molecular hypochlorous acid as in aqueous solution. The suppression of this reaction when the solvent is changed from 40% to 75% acetic acid suggests that the concentration of free molecular hypochlorous acid has been reduced to a very low level in 75% acetic acid. Correspondingly the degree of combination of acetic acid with the hypochlorous acid must rise from a relatively low level in 40% acetic acid to a high value in 75% acetic acid. It is reasonable to attribute the reactivity of hypochlorous acid in 75% acetic acid to this combination of acetic and hypochlorous acids, rather than to residual molecular hypochlorous acid, particularly since the velocity of the reaction that is not catalysed by hydrogen ion rises when the medium is changed from 40% to 75% acetic acid (see above). If a combination of hypochlorous and acetic acids constitutes the chlorinating species in 75% acetic acid, then the factor f of expression (2) should rise greatly when the solvent is changed from 40% to 75% acetic acid. The observed rise in the quantity $B = k_3f/k_2$ of expressions (1) and (2) is in accord with this, although changes in k_3 and k_2 may also be involved.

Two other observations are in accord with a high degree of combination between acetic acid and hypochlorous acid in 75% acetic acid. First, only a small effect of chloride ion was observed compared with that found for a reaction in aqueous solution by Derbyshire and Waters,[1] where 10^{-4}M-added chloride increased the rate by 30% (cf. Table 1). This suggests that the formation of chlorine is inhibited. Secondly, the absence from the rate expression of terms of the second order in hypochlorous acid, at concentrations ten times greater than those at which other authors [2,11] have found them to be appreciable, could mean that hypochlorous acid is in a state very different from that in its aqueous solutions.

It seems likely that acetic and hypochlorous acids are mainly combined in the form of a hydrogen-bonded complex, analogous to the acetic acid dimer. There is, however, no obvious reason why such a complex should be any more reactive than hydrated molecular hypochlorous acid, and it is therefore suggested that there is present a small concentration of acetyl hypochlorite which constitutes the chlorinating species: $\mathrm{AcOH} + \mathrm{HOCl} \rightleftharpoons \mathrm{AcOH,HOCl} \rightleftharpoons \mathrm{AcOCl} + \mathrm{H_2O}$. The presence of acetyl hypochlorite in considerable concentration in solutions containing much water seems unlikely. Acetyl hypochlorite has been prepared in various non-aqueous solvents but has never been isolated.[22] According to Bockemüller and Hoffmann [23] it is readily hydrolysed by water.

The suggestion that acetyl hypochlorite is the chlorinating species brings the present work into agreement with the previous work on hypochlorous acid in sodium acetate–acetic acid buffers. Molecular acetic acid acts as a catalyst for substitution [9] and addition [11,12] reactions of hypochlorous acid in aqueous solutions. The rates of such reactions in buffer solutions rise with increase in acetic acid concentration, while change in the sodium acetate concentration has little effect. This has been taken to mean that acetic acid reacts with hypochlorous acid to give highly reactive acetyl hypochlorite and that the formation and subsequent reaction of the acetyl hypochlorite are not catalysed by hydrogen ion. It should be mentioned, however, that there is disagreement between the properties of the supposed acetyl hypochlorite as observed in the present work and in that with buffer solutions on the one hand, and in the work of de la Mare, Ketley, and Vernon [8] on the other. The latter authors prepared acetyl hypochlorite in glacial acetic acid and found its reactions to be greatly catalysed by hydrogen ion. Further they consider that hypochlorous acid in 98% acetic acid attacks aromatic compounds through intermediate formation of acetyl hypochlorite, the reactions again being catalysed by hydrogen ion. It is possible that the properties of acetyl hypochlorite in this respect vary with the medium and the nature of the organic substrate. It should, however, be borne in mind that the reactive entity in buffer solutions and in 75% acetic acid, which has been presumed to be acetyl hypochlorite, might be merely the hydrogen-bonded complex of acetic and hypochlorous acids postulated above but considered unreactive.

With regard to the nature of the active form of anisic acid there are various possibilities but it is suggested that the most likely are those which connect reaction as an active form with the presence of a high concentration of acetic acid. It may be envisaged that in solution in 75% acetic acid, anisic acid will be combined as complexes both with acetic acid and with water molecules. It is possible that the bulk of the anisic acid is present as hydrated anisic acid and that this is unreactive; the active form would then be a complex of anisic and acetic acids. On the other hand it seems more likely that the bulk of the anisic acid is present as unreactive complex with the acetic acid, while the active form is the hydrated anisic acid molecule.

It is thus suggested that acetic acid is playing a dual rôle in the reaction. On the one hand it serves to produce reactive acetyl hypochlorite from hypochlorous acid; on the other it keeps the bulk of the anisic acid in the form of unreactive complex.

As to the nature of the complexes it seems likely that anisic acid will form hydrogen-bonded complexes with acetic acid and with water analogous to the dimeric form and hydrate of acetic acid itself. This cannot, however, be the only mode of complex

[22] Anbar and Ginsburg, *Chem. Rev.*, 1954, **54**, 925.

[23] Bockemüller and Hoffmann, *Annalen*, 1935, **519**, 174.

formation, for the active and unreactive forms are not restricted to phenolic ethers containing a carboxyl group. Methyl anisate and *p*-chloroanisole show the same kinetic behaviour as anisic acid (Part IV). Hydrogen bonding involving the ether oxygen atom could provide another means of complex formation. There is also the possibility that the complexes are electrostatic in character, since the dipole moments of the aromatic ethers are high. A study of a wide range of compounds at several temperatures in a variety of solvents will be necessary before a final decision can be made as to the nature of the complexes, and indeed before it is certain that the interpretation in terms of complexes is correct.

Salt Effects.—It was shown above that the effects of sodium salts on the initial rate are generally catalytic and in the same order as the strengths of the corresponding acids, *i.e.*, $HClO_4 > HNO_3 > H_2SO_4 \gg AcOH$. de la Mare, Ketley, and Vernon[2] found that the reaction between hypochlorous acid and aromatic compounds in aqueous solution is greatly catalysed by sulphate ions; toluene-*p*-sulphonate ions are rather less effective, and perchlorate ions have scarcely any effect. These observations are explained in terms of the idea that any anion X^-, provided its nucleophilic power is appreciable, will combine with chlorine cations to form a chlorinating species ClX. The large effect of sulphate and the small effect of perchlorate is the opposite of what was found here, and is another indication of the profound difference of mechanism.

The present results resemble more closely those found by Robertson[24] for the halogenation of aromatic compounds by solutions of molecular halogens in acetic acid. In these reactions lithium perchlorate exerts a small catalytic effect, which is roughly the same as that of perchloric acid, while sodium acetate has practically no effect. The effect of chlorides and sulphuric acid is intermediate, and Robertson states that the effects of salts are " in the order of their conductivities ". This is considered to show that the salts exert an activity effect which promotes the anionisation of a halogen atom Ha from the intermediate ArH,Ha_2.

It seems likely that the influence of salts in the present work is explicable along similar lines. Acetyl hypochlorite will probably form a transition complex with the aromatic ether, which will lose first an acetate ion and then a proton to give the chloro-ether. An increase in electrolyte concentration should favour the reaction by promoting the separation of the acetate ion.

Comparison of Reactions of Hypobromous and Hypochlorous Acids in 75% *Acetic Acid.*—It is interesting that the effective halogenating species for hypochlorous acid should not be analogous to that for hypobromous acid[3] and a tentative explanation can be put forward which may lie in the relative reactivities of the acetyl hypohalites. Acetyl hypochlorite is possibly a much more reactive halogenating species than acetyl hypobromite, just as molecular chlorine is much more reactive than molecular bromine. On the other hand the very reactive halogen cations may well be produced by the reaction with hydrogen ion much more readily for hypobromous acid in 75% acetic acid than for hypochlorous acid in the same medium (Derbyshire and Waters[1] found that in the bromination of sodium toluene-ω-sulphonate in water a second-order velocity constant of 10^{-2} mole $l.^{-1}$ $sec.^{-1}$ could be obtained with $6{\cdot}3 \times 10^{-4}$M-perchloric acid, while a similar velocity in the chlorination required 3·9M-perchloric acid.) Hence it is perhaps not surprising that an acetyl hypohalite mechanism is preferred for hypochlorous acid, while a halogen-cation mechanism predominates for hypobromous acid.

It is further interesting that Branch and Brynmor Jones[3] found no results which suggested the intervention of an active form of ether in the reaction with hypobromous acid in 75% acetic acid. Probably the bromine cations are sufficiently reactive to attack the bulk form of the ether.

The Course of the Reaction.—Although the principal measurements here were of initial

---

[24] Robertson, *J.*, 1949, 295; 1954, 1267.

rate, some study of the course of the reaction was made. Measurements were carried out up to the point at which about 80% of the hypochlorous acid had reacted. The results are summarised in Table 8. The calculation of $(a - x)$ depends on the assumption that the reaction is not complicated by polysubstitution. On grounds of electronic theory this would not be expected to occur, but the point was checked by measuring the stoicheiometry. When reaction had effectively ceased, 1·03 mol. of hypochlorous acid had reacted with each mol. of anisic acid. The 3% departure from unity is doubtless due to slight autodecomposition of hypochlorous acid.

TABLE 8. *The course of the reaction in* 75% *acetic acid.*

t (sec.)	$10^3(b - x)$	10^3x	$10^3(a - x)$	t (calc.)
0	6·00	0	10·0	0
89	5·51	0·49	9·51	90
174	5·08	0·92	9·08	176
269	4·63	1·37	8·63	276
537	3·64	2·36	7·64	549
1020	2·45	3·55	6·45	1027
1457	1·75	4·25	5·75	1459
1815	1·34	4·66	5·34	1820

b = initial molar concentration of hypochlorous acid, a = initial molar concentration of anisic acid, x = amount of hypochlorous or anisic acid reacting per litre.

If the reaction steps over the whole course of the reaction remain as in the mechanism postulated on the basis of initial rate measurements, then

$$\mathrm{d}x/\mathrm{d}t = A(a - x)(b - x)/[1 + B(b - x)] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which gives on integration

$$t = \frac{2{\cdot}303}{(a - b)A} \log_{10} \frac{b(a - x)}{a(b - x)} - \frac{2{\cdot}303\,B}{A} \log_{10} \frac{a - x}{a} \quad . \quad . \quad . \quad (4)$$

The validity of expression (4) can be tested by using the values of A and B (0·155 and 102 respectively) derived from initial rate studies to calculate times t(calc.) corresponding to the experimental values of x. The values of t(calc.) are in Table 8, and there is good agreement with the experimental values of t. The expression based on initial-rate measurements appears to be valid over at least 80% of the course of the reaction.

In the presence of salts and acids, however, complications may develop during the reaction, for it was found that these influenced the way in which the rate fell. With 0·025M-sodium nitrate the rate falls away rapidly, but at higher concentrations the fall is progressively less marked. Similarly, as sodium nitrate is replaced by nitric acid the fall is less marked. In the case of perchloric and sulphuric acids and their salts such effects seem only slight. Sodium acetate appeared to hold the rate constant over a long period. No explanation of these observations can as yet be offered.

The authors thank Dr. Brynmor Jones for suggesting this work and that of the following paper, and for encouragement during its course. One of us (G. S.) is indebted to the Northumberland Education Committee for the extension of a Major Award.

UNIVERSITY OF HULL.

[*Received, August* 26*th*, 1957.]