# *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part I. Acid-catalysed Chlorination by Aqueous Solutions of Hypochlorous Acid.*

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[Reprint Order No. 4836.]

In the presence of perchloric acid and silver perchlorate, the chlorination of anisole by *ca.* 0·001M-hypochlorous acid in aqueous solution appears to be a reaction of the kinetic form $-d[ClOH]/dt = k[ClOH] + k'[ClOH][H^+]$, the rate being almost independent of the concentration of aromatic compound over the range 0·004—0·01M. To achieve this kinetic form, the concentrations of chloride and of hypochlorite ions require to be reduced, by the presence of silver ions and of acid respectively, to insignificant levels. In aqueous dioxan, the rate is virtually the same as in water. By using, in the mixed solvent, higher concentrations of anisole, it can be shown that a term $k''[ClOH][H^+][ArH]$ enters into the kinetic expression. It is considered that the velocity coefficients $k$ and $k'$ give measures of the rates of heterolytic fission, to yield $Cl^+$, of ClOH and $ClOH_2^+$ respectively. The coefficient $k''$ gives a measure of the rate of attack of $ClOH_2^+$ on the aromatic compound. These conclusions are confirmed and amplified by investigation under similar conditions of the reactions of phenol, mesitylene, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. Disturbances of the kinetics in the presence of anions $X^-$ are discussed. The spontaneous decomposition of hypochlorous acid was negligibly slow under all the conditions investigated.

THE kinetics of reactions in aqueous solution between hypochlorous acid and aromatic substances have not been studied extensively. For phenol in neutral and alkaline conditions Soper and Smith (*J.*, 1926, 1588) found kinetics consistent with a rate-determining reaction between un-ionised hypochlorous acid and the phenoxide ion. More recently, for the chlorination of sodium toluene-ω-sulphonate by hypochlorous acid in the presence of mineral acid Derbyshire and Waters (*J.*, 1951, 73) found the kinetic form $-d[ClOH]/dt = k[ArH][ClOH][H^+]$, involving either the chlorinium ion, $Cl^+$, or the hypochlorous acidium ion, $ClOH_2^+$.

Extensive investigations in these laboratories (cf. Hughes, Ingold, and Reed, *J.*, 1950, 2400) have shown that the nitronium ion, $NO_2^+$, rather than its hydrated form, the nitracidium ion ($H_2NO_3^+$), is frequently the electrophilic reagent involved in nitration. It is of interest to extend knowledge of aromatic substitutions by consideration of halogenation processes. The work of Bradfield and Jones and their co-workers (cf. Bradfield and Jones, *Trans. Faraday Soc.*, 1941, **37**, 726; Bradfield, Davies, and Long, *J.*, 1949, 1389) and of P. W. Robertson and his co-workers (cf. de la Mare and Robertson, *J.*, 1943, 279; Robertson, Dixon, Goodwin, McDonald, and Scaife, *J.*, 1949, 294), as also of Wilson and Soper (*J.*, 1949, 3376), demonstrates that molecular, rather than ionic, electrophilic reagents are of considerable importance when solutions of the halogens are allowed to react with aromatic substances. Our attention has been turned, therfore, to the reactions of hypochlorous acid; and an account of our preliminary investigations was given by de la Mare, Hughes, and Vernon (*Research*, 1950, **3**, 192). Neutral or alkaline conditions were avoided, since studies of the analogous electrophilic addition reactions have revealed extremely complicated kinetic forms (cf. Israel, *J.*, 1950, 1286). The intervention of chlorine, through the reaction $ClOH + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$, was prevented by the addition of sufficient silver perchlorate to reduce the significance of this equilibrium to negligible proportions. In order to increase the range of concentration of aromatic compound available for investigation, aqueous dioxan was in some cases used as solvent.

## EXPERIMENTAL

(a) *Materials and Methods.*—To purify commercial mercuric oxide, it was dissolved in perchloric acid and precipitated by the addition of sodium hydroxide. After repetition of this process, the product was washed with much hot distilled water. Hypochlorous acid was prepared by shaking a solution of chlorine in water with excess of purified mercuric oxide. The product was distilled *in vacuo* at about 35° in the dark, and stored over purified mercuric oxide for not more than 5 days, during which time the rate of reaction with anisole under standard conditions remained unaltered. Bulk samples of hypochlorous acid prepared in this way were usually about 0·05M.

The following organic substances were purified by fractional distillation of good commercial specimens: anisole, b. p., 153·8°/763 mm., $n_D^{25}$ 1·5149; mesitylene, b. p., 162°/760 mm., $n_D^{25}$ 1·4958; methyl *m*-tolyl ether, b. p. 174°/763 mm., $n_D^{25}$ 1·5070; methyl *p*-tolyl ether (reactive impurities first removed by partial bromination), b. p. 176°/758 mm., $n_D^{25}$ 1·5094. *p*-Dimethoxybenzene on recrystallisation had m. p. 57·5°; toluene-*p*-sulphonic acid had m. p. 104°; and phenol, after distillation, had m. p. 40°.

Solutions of these substances were made up by weight, in water or in mixtures of water and dioxan. The latter solvent was first refluxed with hydrochloric acid in a current of nitrogen for 6 hr., and was then partially dried with solid sodium hydroxide. Peroxide impurities were then removed by shaking with ferrous sulphate, and the product was distilled from solid sodium hydroxide in an atmosphere of nitrogen and was stored under nitrogen in the dark. Such material was completely inert to hypochlorous acid under the conditions of the rate measurements.

Solutions of silver perchlorate were prepared by shaking excess of freshly precipitated silver oxide with perchloric acid. The product was filtered, and its silver content was estimated in conventional manner. It was neutral in reaction. Other reagents were of analytical grade.

For rate measurements, the reagents (usually *ca.* 250 ml.), except the hypochlorous acid, were brought to the temperature of the thermostat in a darkened bottle. Hypochlorous acid (usually *ca.* 3 ml.), previously warmed to the temperature of the thermostat, was added, the mixture was shaken, and at appropriate intervals, portions (usually 10 or 25 ml.) were pipetted into flasks containing excess of ice-cold aqueous potassium iodide solution (500 g./l., sufficient to dissolve the precipitate of silver iodide), this solution and the titration vessel having previously been flushed with nitrogen. The liberated iodine was then titrated with *ca.* 0·003N-sodium thiosulphate solution, sodium starch glycollate or starch being used as indicator.

In early experiments, erratic results were obtained when the hypochlorous acid was prepared from unpurified mercuric oxide. It is believed that the lack of reproducibility was caused by the presence of nitrite ions, which were detected colorimetrically in water which had been kept over unpurified mercuric oxide (cf. Winkler, *Report Pharm.*, 1829, **31**, 475). Added mercuric perchlorate ($10^{-6}$—$10^{-3}$M) had no effect on the rate of reaction between anisole and acidified hypochlorous acid. Carefully redistilled hypochlorous acid reacted with anisole, in the presence of added mineral acid and silver perchlorate, at the same rate as similar samples which had been kept either over mercuric oxide (our usual practice) or over bismuth hydroxide (cf. Israel, Martin, and Soper, *J.*, 1950, 1282). Spontaneous decomposition of the hypochlorous acid was shown by blank experiments to be negligibly slow, even in the presence of silver ions, added mineral acid, and dioxan.

(b) *Rate Measurements for the Chlorination of Anisole in Aqueous Solution* (*at* 25° *except where otherwise specified*).—The following are details of a typical experiment, with 0·0099M-anisole, 0·0006M-hypochlorous acid, 0·012M-perchloric acid, and 0·013M-silver perchlorate; 10-ml. portions were titrated with 0·0033N-sodium thiosulphate.

| Time (min.) | 0·00 | 10·25 | 19·00 | 26·75 | 38·75 | 47·50 | 68·00 |
|---|---|---|---|---|---|---|---|
| Titre (ml.) | 4·52 | 4·14 | 3·82 | 3·60 | 3·25 | 2·99 | 2·55 |
| $10^2k_1$ (min.$^{-1}$) * | — | 0·86 | 0·86 | 0·85 | 0·85 | 0·87 | 0·84 |

* All values of $k_1$ quoted in this paper are in these units, and have been calculated by the formula $k_1 = 2{\cdot}303\,[\log_{10}(a_0/a_t)]/t$, where $a_t$ is the titre at time $t$ minutes.

The following results show the variation in rate coefficient with the concentration of added silver perchlorate, for the reaction between 0·0066M-anisole and 0·0005M-hypochlorous acid, catalysed by 0·0090M-perchloric acid.

| [Ag$^+$] (M) | 0·0064 | 0·013 | 0·033 | 0·13 |
|---|---|---|---|---|
| $10^2k_1$ (min.$^{-1}$) | 0·71 | 0·66 | 0·65 | 0·67 |

Similar results were obtained at other concentrations of acid. It appears to require, at this concentration of anisole, somewhat more than 0·006M-silver ion to reduce the concentration of chloride ion to insignificance; at concentrations of silver ion greater than this, the rate coefficient for the chlorination is substantially constant.

The following are results obtained when the initial concentration of hypochlorous acid was varied; they refer to the chlorination of 0·0066M-anisole in the presence of 0·013M-silver perchlorate, catalysed by 0·60M-perchloric acid.

| | | | |
|---|---|---|---|
| [HOCl] (M) | 0·0010 | 0·0005 | 0·0002 |
| $10^2k_1$ (min.$^{-1}$) | 8·5 | 7·6 | 7·8 |

Similar results were obtained at lower concentrations of acid; hence, the dependence of the rate on the acidity and on the concentration of the aromatic compound being temporarily neglected, the kinetic form for the reaction, over the concentration range given, is $-d[\text{ClOH}]/dt \propto [\text{ClOH}]$.

The following are results for the chlorination of anisole by 0·0005M-hypochlorous acid, in the presence of 0·013M-silver perchlorate, catalysed by 0·012M-perchloric acid, showing the very small dependence of the rate on the concentration of anisole:

| | | | | | |
|---|---|---|---|---|---|
| Anisole (M) | 0·0099 | 0·0088 | 0·0066 | 0·0055 | 0·0033 |
| $10^2k_1$ (min.$^{-1}$) | 0·85 | 0·88 | 0·89 | 0·83 | 0·87 |

In aqueous dioxan, the rate of reaction, other conditions being the same, was found to be almost identical with that in water, and the former solvent was therefore used to extend the range of concentration of anisole available for investigation. The following are results for the chlorination of anisole by hypochlorous acid in the presence of 0·065M-silver perchlorate, with 0·050N-perchloric acid as catalyst:

| | | | | |
|---|---|---|---|---|
| Anisole (M) | 0·008 | 0·015 | 0·019 | 0·028 |
| $10^2k_1$ (min.$^{-1}$) | 1·41 | 1·59 | 1·78 | 1·95 |

Other results * are plotted in Figs. 1 and 2, and show that the dependence of the rate on the concentration of anisole, though small, is quite definite under these conditions.

The following results show the temperature-dependence of the rate of chlorination of 0·0066M-anisole by 0·0007M-hypochlorous acid, in the presence of 0·16M-silver perchlorate, with 0·012M-perchloric acid as catalyst:

| | | | |
|---|---|---|---|
| Temp. | 0·0° | 24·7° | 35·0° |
| $10^2k_1$ (min.$^{-1}$) | 0·30 | 0·93 | 1·65 |

(c) *Product of Chlorination of Anisole.*—To an aqueous solution (25 l., containing 0·0055M-anisole, 0·05M-silver perchlorate, and 0·12M-perchloric acid), there were added, at intervals of 3 hr. or more, twelve portions, each 200 ml., of 0·07M-hypochlorous acid. The product was then extracted with ether, and the ethereal extract was dried ($CaCl_2$) and fractionated, giving 16·0 g. (82%), $n_D^{25}$ 1·5377, b. p. 198—201°, m. p. *ca.* −50° (Found: C, 58·4; H, 4·8; Cl, 25·2. Calc. for $C_7H_7OCl$: C, 59·0; H, 4·9; Cl, 24·9%). These properties are those of a mixture of *o*-chloroanisole, $n_D^{25}$ 1·5433, f. p. −26·5°, and *p*-chloroanisole, $n_D^{25}$ 1·5338, f. p. −18·0°.

Since Dr. Lars Melander (personal communication) had kindly informed us that some *p*-benzoquinone can be isolated from the reaction of *p*-dimethoxybenzene with acidified hypochlorous acid,† the following experiment was carried out. Anisole (0·0049M) was allowed to react to completion with 0·0006M-hypochlorous acid in the presence of 0·013M-perchloric acid and 0·016M-silver perchlorate. The resulting solution was filtered, and the optical density was compared with that of water at various wave-lengths, in 0·2-cm. silica cells, with a Unicam model S.P. 500 spectrophotometer. The absorption curve for anisole passes through a maximum at 2750 Å, and through a minimum at 2450 Å. That for *p*-benzoquinone passes through a maximum ($\varepsilon$ = 17,700) at 2420 Å (Braude, *J.*, 1945, 490). The solutions both of anisole and of chlorinated anisole had similar absorption curves, passing through minima in the neighbourhood of 2450 Å, at which wave-length the optical densities were respectively 0·28 and 0·22. *p*-Benzoquinone is therefore not formed in the reaction of hypochlorous acid with anisole. In a separate experiment, it was found that a negligible amount of demethylation occurs during the chlorination, since very little phenolic material can be extracted by alkali from the crude product of the reaction.

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* At high concentrations of aromatic compounds, a larger concentration of silver ion was found necessary in order to reach a region in which the rate was independent of the silver-, and therefore of the chloride-ion concentration. This may be the result of complex-formation between the aromatic compound and silver ion (cf. Andrews and Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 3313). The results in the Figures all refer to conditions under which further addition of silver ion did not significantly affect the rate.

† For this reason, the reaction of *p*-dimethoxybenzene with hypochlorous acid has not been further investigated, though we have confirmed that the initial rate of disappearance of hypochlorous acid is nearly the same as for anisole.

(d) *Kinetics of Chlorination of Other Aromatic Substances.*—Results similar to those obtained for anisole were obtained for phenol; for the reaction of 0·0037M-phenol with 0·0003M-hypochlorous acid, in the presence of 0·0204N-silver perchlorate and 0·012M-perchloric acid, $10^2k_1$ was very consistently 0·86.

Similarly, for the chlorination of 0·0027M-phenol by 0·0005M-hypochlorous acid, in the presence of 0·06M-silver perchlorate and 0·60M-perchloric acid, consistent values for $10^2k_1$ (average 9·2; range 8·7—9·8) show that the reaction at high concentrations of acid is still of first order with respect to hypochlorous acid.

The dependence of the rate on the concentration of silver ions, and of acid, was in every way similar to that obtained with anisole. Thus the following are data for the chlorination of 0·0092M-phenol by 0·0005M-hypochlorous acid in the presence of 0·012M-perchloric acid:

*Chlorination by hypochlorous acid* ($<$ 0·001M) *in 50% aqueous dioxan at 25° in the presence of* 0·065M-*silver perchlorate.*

FIG. 1. $HClO_4$, 0·012M.

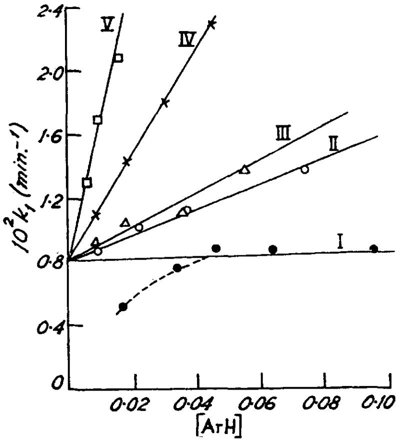
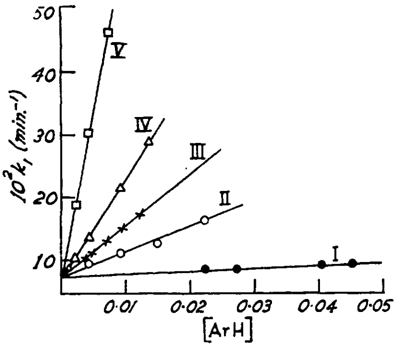


FIG. 2. $HClO_4$, 0·60M.



I = methyl *p*-tolyl ether; II = anisole; III = mesitylene; IV = phenol (in water: $Ag^+$ = 0·15M); V = methyl *m*-tolyl ether.

| | | | | | |
|---|---|---|---|---|---|
| [$Ag^+$] (M) | 0·008 | 0·016 | 0·040 | 0·080 | 0·16 |
| $10^2k_1$ (min.$^{-1}$) | 1·36 | 1·14 | 1·16 | 1·09 | 1·09 |

The dependence of the rate on the concentration of aromatic compound, and of acid, is shown for mesitylene, methyl *p*-tolyl ether, and phenol by the following data for chlorinations catalysed by 0·050N-perchloric acid: *

| | | | | |
|---|---|---|---|---|
| Methyl *p*-tolyl ether (M) | 0·052 | 0·065 | 0·078 | — |
| $10^2k_1$ (min.$^{-1}$; $Ag^+$ = 0·027M) | 1·17 | 1·12 | 1·20 | — |
| Phenol * (M) | 0·002 | 0·006 | 0·0098 | 0·018 |
| $10^2k_1$ (min.$^{-1}$; $Ag^+$ = 0·027M) | 1·37 | 2·20 | 2·65 | 4·01 |
| Mesitylene (M) | 0·013 | 0·025 | 0·035 | — |
| $10^2k_1$ (min.$^{-1}$; $Ag^+$ = 0·065M) | 1·92 | 2·59 | 3·22 | — |

For all these compounds, the individual kinetic runs showed that the reactions were of the first order with respect to hypochlorous acid. The Figures show similar results at other acidities, including data for methyl *m*-tolyl ether.

(e) *Product of Chlorination of Phenol.*—To an aqueous solution (22 l., containing 0·106M-phenol, 0·05M-silver perchlorate, and 0·12M-perchloric acid) there were added, at intervals of 3 hr. or more, 25 batches, each containing 200 ml. of *ca.* 0·06M-hypochlorous acid. The product was extracted with ether, and, after removal of most of the ether, the mixed chlorophenols were methylated with methyl sulphate and alkali. The product was made acid and extracted with ether; the ethereal extract was dried and fractionated, giving 25·3 g. of mixed chloroanisoles (76%), b. p. 198—201°, $n_D^{25}$ 1·5370, m. p. *ca.* −49° (Found: C, 59·6; H, 5·0; Cl, 25·4. Calc. for $C_7H_7OCl$: C, 59·0; H, 4·9; Cl, 24·9%).

(f) *Kinetics of Chlorination of Anisole in the Presence of Added Anions.*—The following

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* Here, and also in Figs. 1 and 2, the values for phenol are for aqueous solution, and those for other compounds are for 50% dioxan–water.

results are for the chlorination of 0·0077—0·0099M-anisole by *ca.* 0·0005M-hypochlorous acid in the presence of 0·013M-silver perchlorate and 0·012M-perchloric acid :

| Catalyst | None | $ClO_4^-$ | $p$-$C_6H_4Me{\cdot}SO_3^-$ | | $SO_4^{--}$ | | |
|---|---|---|---|---|---|---|---|
| | | 2·2M | 0·012M | 1·0M | 0·0002M | 0·006M | 0·03M |
| $10^2k_1$ (min.$^{-1}$) | 0·85 | 1·33 | 0·72 | 2·2 | 1·14 | 1·33 | 1·69 |

The following results for the chlorination of 0·0077M-anisole by high concentrations of hypochlorous acid, in the presence of 0·013M-silver perchlorate and 0·012M-perchloric acid, illustrate that, at concentrations of hypochlorous acid greater than about 0·001M, the rate of reaction becomes partly proportional to the square of the concentration of hypochlorous acid; a similar result is found if mineral acid is omitted from the chlorinating mixture, so that the pure kinetic form, $v \propto$ [HOCl], is no longer obtained.

| [HOCl] (M) | 0·0005 | 0·0010 | 0·0020 | 0·0030 | 0·0060 | 0·012 |
|---|---|---|---|---|---|---|
| $10^2k_1$ | 0·86 | 0·98 | 1·61 | 2·52 | 4·21 | 6·37 |

## DISCUSSION

In our preliminary communication (de la Mare, Hughes, and Vernon, *loc. cit.*), it was recorded that the reaction between hypochlorous acid and anisole, in the presence of silver perchlorate, was of the kinetic form $-d[ClOH]/dt \propto [ClOH]$, and that the velocity coefficient was dependent on the acidity, and was independent of the concentration of aromatic compound, being the same for anisole (0·003—0·01M), phenol (0·003—0·008M), and $p$-dimethoxybenzene. It was concluded that the measured rate was that of the heterolytic fission of ClOH and $ClOH_2^+$, the reactions involved being shown in the scheme below :

$$ClOH \underset{b}{\overset{a}{\rightleftharpoons}} Cl^+ + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$ClOH + H^+ \underset{d}{\overset{c}{\rightleftharpoons}} ClOH_2^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$Cl\overset{+}{O}H_2 \underset{f}{\overset{e}{\rightleftharpoons}} Cl^+ + OH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$Cl^+ + ArH \underset{g}{\longrightarrow} ArCl + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The conditions of reaction used in this preliminary study were such that the kinetics were not quite of pure form, being generally of an order slightly greater than unity with respect to hypochlorous acid. In the present investigation, this complication was eliminated by the use of concentrations of hypochlorous acid less than 0·001M.

The results illustrated in Figs. 1 and 2 accord in every detail with the requirements of equations (1)—(4). For the less reactive substances, such as methyl $p$-tolyl ether and anisole, the rate of reaction is only slightly dependent on the concentration of aromatic compound, this dependence being only detectable with certainty when the concentration of aromatic compound attainable in solution is increased by the addition of dioxan to the aqueous solvent. For all the compounds, at a given concentration of acid, the plot of first-order velocity coefficient, calculated with respect to the disappearance of hypochlorous acid, extrapolates back, within experimental error, to the same point. This extrapolated value, which is independent of the nature of the compound, and therefore must refer to some characteristic of the hypochlorous acid, depends on the concentration of hydrogen ion, as is illustrated by the following values :

| $[H^+]$ (M) | 0·000 | 0·012 | 0·050 | 0·60 |
|---|---|---|---|---|
| $10^2k_1$ (min.$^{-1}$, found) | — | 0·82 | 1·10 | 5·0 |
| $10^2k_1$ [min.$^{-1}$, calc. from eqn. (5)] | (0·75) | 0·84 | 1·10 | 5·0 |

The rate of reaction approximates, therefore, at small concentrations of aromatic compound, to the expression :

$$-d[ClOH]/dt = k[ClOH] + k'[ClOH][H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $10^2k = 0{\cdot}75$ min.$^{-1}$, $10^2k' = 7{\cdot}1$ l. mole$^{-1}$ min.$^{-1}$. It is considered that these terms are best interpreted as representing the rates of heterolytic fission respectively of ClOH and $ClOH_2^+$.

A consequence of the proposed mechanism is that, if the concentration of aromatic compound is sufficiently reduced, a point should eventually be reached at which the aromatic compound is unable successfully to compete with the reassociation of $Cl^+$ and $OH^-$, or of $Cl^+$ and $H_2O$. Just as in the analogous case of nitration, therefore, the rate of reaction should begin to decrease with decreasing concentration of aromatic compound, and this decrease should have its onset at lower values of the concentration of aromatic compound the more reactive this compound. In full agreement with these expectations, a falling-off in rate is observed, for phenol, at *ca.* 0·0015M; for anisole, at *ca.* 0·005M; and for methyl *p*-tolyl ether, at *ca.* 0·05M, as is shown for the last compound by the broken line in Fig. 1. No extensive investigation of this behaviour has been made, since Derbyshire and Waters (*loc. cit.*) examined carefully the chlorination of the toluene-ω-sulphonate ion, which is considerably less reactive than methyl *p*-tolyl ether, and observed the limiting kinetic form $-d[ClOH]/dt \propto [ArH][ClOH][H^+]$.

An alternative trial explanation of the observation that the reaction, although dependent on the concentration of aromatic compound, provided this is sufficiently low, becomes independent of it above a critical concentration of aromatic compound, is that the reaction rate, above the critical concentration, is determined by the slow transfer of a proton to the hypochlorous acid.* Such a hypothesis would mean, however, that there could be operative under these conditions only one chlorinating agent (namely, $H_2OCl^+$), which could give a range of concentration of aromatic compound over which the kinetic form, $-d[ClOH]/dt = k[ArH][ClOH][H^+]$, could be observed. The scheme of equations (1)—(4), however, allows the presence in the solution of two chlorinating species, $Cl^+$ and $ClOH_2{}^+$; and the possibility then exists that a sufficiently reactive aromatic compound may react with the latter cation directly, without waiting for the formation of the chlorinium ion, $Cl^+$. Our proposed mechanism (in contrast with the above slow-proton-transfer hypothesis) allows, therefore, that the kinetic equation for the reaction may contain a term proportional to $[ClOH][H^+][ArH]$, even above the critical concentration of aromatic compound, so that the kinetic equation in these circumstances becomes:

$$-d[ClOH]/dt = k[ClOH] + k'[ClOH][H^+] + k''[ClOH][H^+][ArH] \quad . \quad . \quad . \quad . \quad (6)$$

Figs. 1 and 2, in which the full lines refer to concentrations greater than the critical value, show that the results require the inclusion of all these terms.† Thus the plots of velocity coefficient against the concentration of aromatic compound are linear, with positive slopes dependent on the nature of the compound. The following table shows that these slopes are dependent on the acidity.

*Dependence of first-order velocity coefficients on the concentration of aromatic compound.*

| | Slope ($s$, l. mole$^{-1}$ min.$^{-1}$) of graph of $10^2k_1$–[ArH] | | | $10^{-2}s/[H^+] = k''$, l.$^2$ mole$^{-2}$ min.$^{-1}$ | | |
|---|---|---|---|---|---|---|
| Compound | $[H^+] =$ 0·012 | $[H^+] =$ 0·050 | $[H^+] =$ 0·60 | $[H^+] =$ 0·012 | $[H^+] =$ 0·050 | $[H^+] =$ 0·60 |
| Methyl *p*-tolyl ether ……… | 0·5 | 1·25 | 40 | 0·4 | 0·5 | 0·7 |
| Anisole …………………… | 7·8 | 33 | 394 | 6·5 | 6·5 | 6·6 |
| Mesitylene ………………… | 10·3 | 63 | 800 | 8·6 | 12·6 | 13·3 |
| Phenol ……………………… | 32·5 | 163 | 1530 | 27·1 | 32·6 | 25·5 |
| Methyl *m*-tolyl ether ……… | 89 | — | 5000 | 74 | — | 83 |

For methyl *p*-tolyl ether, the dependence of the rate of reaction on the concentration of aromatic compound is so small that it cannot accurately be determined from the graphs.

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* Such a hypothesis does not allow for the inclusion in the kinetic expression of a term dependent only on the concentration of hypochlorous acid; this term can only be explained on the basis of a slow change in the latter substance, as is most reasonably ascribed to the breaking of the Cl–O bond (cf. de la Mare, Hughes, and Vernon, *loc. cit.*).

† At concentrations below the critical concentration, the rate is limited, not by the rate of fission of ClOH and $ClOH_2{}^+$, but by the reactivity of the aromatic compound. Hence the rate expression, $-d[ClOH]/dt \propto [ClOH][H^+][ArH]$ is observed; the proportionality factor includes a small contribution from $k''$. In principle, there should still be a contribution also from a term in the rate expression, $-d[ClOH]dt \propto [ClOH][ArH]$; but this would be very difficult to observe experimentally, since at concentrations sufficiently below the critical value for the observations of a pure kinetic form, that fraction of the rate dependent on this term would be very small, and would probably even be obscured by the spontaneous decomposition of hypochlorous acid. To obtain a measurable rate with the toluene-ω-sulphonate ion, for example, Derbyshire and Waters (*loc. cit.*) worked at concentrations of aromatic compound *ca.* 0·03M, and of perchloric acid in the range 2—4M.

In the case of the other four compounds, the near constancy in the values of $k''$ shown in the last three columns of the Table show that the increase in reaction velocity with concentration of aromatic compound is directly dependent on the acidity. Hence, above the critical concentration of aromatic compound, the kinetic equation (6) satisfactorily represents the results, and we may conclude that the rate is not, under our conditions, controlled by the rate of a proton-transfer to the oxygen of the hypochlorous acid molecule.

The reactions of cations with anions are usually rather rapid. Hence such reactions as are shown by equations (7) and (8) might readily be expected to compete with those of the aromatic compound with the hypochlorous acidium and chlorinium ions:

$$ClOH_2^+ + Cl^- \longrightarrow Cl_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$ClOH_2^+ + OCl^- \longrightarrow Cl{\cdot}OCl + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The importance of $Cl_2$ and of $Cl_2O$ as chlorinating agents has often been stressed (cf. Shilov, Kupinskaya, and Yasnikow, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 435; Shilov and Kupinskaya, *ibid.*, p. 621; Israel, Martin, and Soper, *J.*, 1950, 1282; Reeve and Israel, *J.*, 1952, 2327). Hence it is not at all surprising that chlorination of anisole by hypochlorous acid is more rapid in the absence of silver ions. It appears to be necessary to reduce the concentration of $Cl^-$ to below about $10^{-9}$M in order to suppress completely any reaction through molecular chlorine.

In a similar way, it may be calculated from the acidic dissociation constant of HOCl ($K = 3 \times 10^{-8}$ at 20°; Shilov, *J. Amer. Chem. Soc.*, 1938, **60**, 490) that the concentration of hypochlorite ion must be reduced, by the presence of acid, to below about $10^{-6}$N to eliminate completely the reaction route through $Cl_2O$. If mineral acid is not added at all to the reaction medium, or if the concentration of hypochlorous acid is allowed to exceed about 0·001M, the reaction begins to depend on the square of the concentration of hypochlorous acid, as was shown on p. 1294.

It may, in fact, be stated as a general rule that any anion $X^-$, provided its nucleophilic power is appreciable, will combine with the hypochlorous acidium ion or the chlorinium ion to form a chlorinating entity ClX:

$$ClOH_2^+ + X^- \longrightarrow ClX + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

There are many reports in the literature concerning the existence of such chlorinating agents (cf., *e.g.*, Shilov and his co-workers, *locc. cit.*; Soper, Israel, and their co-workers, *locc. cit.*; Derbyshire and Waters, *loc. cit.*). In the present work, it has been recorded that the ions $Cl^-$, $OCl^-$, $HSO_4^-$, $p$-$C_6H_4Me{\cdot}SO_3^-$, and $ClO_4^-$ fall in decreasing order of effectiveness in catalysing the reaction in this way, the perchlorate ion in particular having very little effect, even at high concentrations.

Since the formation of ClX by such a route may or may not be rate-determining, and seeing also that ClX may be formed directly from ClOH, it can be seen that the presence of such an anion in a solution in which ClOH is acting as a chlorinating agent may introduce kinetic terms proportional to $[ClOH][X^-]$, $[ClOH][X^-][H^+]$, $[ClOH][X^-][ArH]$, and $[ClOH][X^-][H^+][ArH]$. Shilov (*Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 1001; cf. *Chem. Abs.*, 1952, **46**, 9958) has stated that the conclusions proposed as result of our preliminary investigation (de la Mare, Hughes, and Vernon, *loc. cit.*) are inconsistent with his work. His conclusions apply, however, to conditions of low acidity and of high concentration of hypochlorous acid, and often also to experiments in which other anions were present. Our conclusions are in no way inconsistent with his, seeing that in our work we have gone to considerable trouble to eliminate the disturbances of this sort. The specific criticism that our results are vitiated by the addition of silver salts because these accelerate the decomposition of hypochlorous acid has been shown repeatedly in the course of this investigation to be inapplicable; blank determinations have shown that such a decomposition is of negligible rate in comparison with the reactions under investigation.

In nitration, it has been found possible to distinguish kinetically between nitration by the nitronium ion, $NO_2^+$, and by the nitracidium ion $H_2NO_3^+$. The present results show that a similar kinetic distinction can be drawn between the chlorinium ion, $Cl^+$, and the hypochlorous acidium ion, $ClOH_2^+$. Ingold ("Structure and Mechanism in Organic

Chemistry," Bell and Sons, London, 1953, p. 293) has recently discussed, and made plausible theoretically on the basis of a suggestion due to D. J. Millen, that there should be an energy barrier between these ions in aqueous solution, despite the fact that one is merely the hydrate of the other. The observation of a slow rate-determining reaction of $ClOH$ and of $ClOH_2^+$, in each case giving an electrophilic reagent more powerful than its precursor, is in our opinion best interpreted as in equations (1)—(4), though other possibilities are consistent with the observed kinetics. Thus Professor R. S. Mulliken (personal communication) has put forward the view that these slow reactions might be the isomerisations :

$$\mathrm{Cl{-}O{-}H} \longrightarrow \mathrm{H{-}Cl{=}O}\ (\longleftrightarrow \mathrm{H{-}Cl^{+}{-}O^{-}}) \qquad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\mathrm{Cl{-}OH_2^{+}} \longrightarrow \mathrm{H{-}Cl{=}\overset{+}{O}{-}H}\ (\longleftrightarrow \mathrm{H{-}Cl^{+}{-}O{-}H}) \qquad . \quad . \quad . \quad . \quad . \quad (11)$$

We prefer our formulation, on the grounds that such entities as $\mathrm{H{-}Cl{=}\overset{+}{O}{-}H}$ would not be expected to be particularly good chlorinating agents. Thus attack by the latter ion on an aromatic compound requires in the transition state that a proton and a hydroxide ion be lost from the electrophilic chlorine in a single process, whereas the hypochlorous acidium ion can attack and chlorinate by the splitting of a single bond, releasing a water molecule to the solvent.

We are greatly indebted to Professor E. D. Hughes, F.R.S., for the suggestion which led to the inception of this investigation, as also to him and to Professor C. K. Ingold, F.R.S., for many valuable discussions. We are happy to acknowledge technical assistance from Mr. E. Grayson. Analyses are partly by Mr. A. V. Winter of this Department.

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[*Received, November 26th,* 1953.]