798. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part IX.*[1] *Mixtures of Acetic Acid and Aqueous Hypochlorous Acid.*

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The kinetics of chlorination of various aromatic substances by mixtures of aqueous hypochlorous acid and acetic acid (especially 51% and 76% acetic acid) have been examined. The reactions are generally of the kinetic form: $-d[\text{" ClOH "}]/dt = k[\text{ArH}][\text{" ClOH "}]$. The dependence of rate on acidity indicates that both a neutral and a cationic species can contribute to these reactions. Arguments are adduced to make probable that these species are chlorine acetate and its protonated form, $ClOAcH^+$

IN 1953 was given [2] a preliminary report of the kinetics of chlorination of certain aromatic compounds by hypochlorous acid in aqueous acetic acid. In particular, it was reported that these reactions are in general subject to catalysis by added mineral acids. In this respect, they resembled the corresponding reactions in water [3,4,5] and in anhydrous and slightly aqueous acetic acid.[1,2] The detailed interpretation of these results is, however, complicated by the fact that there are a number of chlorinating species, *viz.*, ClOH, $ClOH_2^+$, Cl_2O, Cl_2OH^+, ClOAc, $ClOAcH^+$, and Cl^+, all of which might contribute to the chlorination (the symbolism " ClOH " acknowledges this diversity). Since we have now established [1] that the bulk source of active chlorine in these solutions is hypochlorous acid, it is possible to amplify and extend our earlier conclusions.

EXPERIMENTAL

Most of the materials and general methods have been described in previous papers.[1,4,5] Solvents are specified as percentages by weight; rate coefficients have been calculated by the standard formulæ, and the minute has been taken as the unit of time. The xylenes were obtained by careful fractional distillation of commercial specimens: *o*-, b. p. 142°/760 mm., n_D^{25} 1·5028; *m*-, b. p. 139°/760 mm., n_D^{25} 1·4946; *p*-, b. p. 138°/760 mm., n_D^{25} 1·4931. Mesitylene, b. p. 164°/756 mm., *p*-chloroanisole, b. p. 70·5—71°/7 mm., and chlorobenzene, b. p. 131·5°/756 mm., were obtained similarly. Benzoic acid, m. p. 122°, and *p*-anisic acid, m. p. 183° (prepared essentially as recommended by Stanley and Shorter [6]) were carefully recrystallised before use. Hexadeuterobenzene was kindly supplied by Dr. T. M. Dunn. Solutions of

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[1] de la Mare, Hilton, and Vernon, preceding paper.
[2] de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12S.
[3] Derbyshire and Waters, *J.*, 1951, 73.
[4] de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.
[5] de la Mare, Harvey, Hassan, and Varma, *J.*, 1958, 2756.
[6] Stanley and Shorter, *J.*, 1958, 246, 256.

sodium perchlorate were prepared by neutralisation of "AnalaR" perchloric acid with "AnalaR" sodium hydroxide; they were free from halide.

The following is an example of a typical kinetic run, for 0·0468M-toluene and 0·004M-hypochlorous acid in 76% acetic acid at 25°:

Time (min.)	0	0·50	2·00	3·00	4·00	4·70	6·00	7·00
Titre (ml.)	3·85	3·65	3·15	2·85	2·55	2·30	2·10	1·81
k_2 (l. mole^{-1} min.$^{-1}$)	—	2·3	2·2	2·2	2·2	2·4	2·1	2·4

For toluene in this solvent and in those containing less water, it has been our experience that the rate coefficients, calculated through the course of a run, and followed generally to more than 50% reaction, show no systematic trend. Decomposition of control solutions, from which the aromatic compound had been omitted, was negligible; the rate was only slightly greater in the presence of added lithium chloride, and was unaffected by the presence or concentration of silver perchlorate when this was added to ensure the absence of free chlorine. Thus with 0·00255M-ClOH and 0·010M-$AgClO_4$, the following results were obtained:

Toluene (M)	0·0468	0·0702	0·0936
k_2 (l. mole^{-1} min.$^{-1}$)	2·3	2·3	2·4

Acids catalyse the reaction, and the general kinetic behaviour is similar. For toluene and 0·002—0·005M-ClOH with 0·010M-$AgClO_4$ in 76% acetic acid at 25°, the following results were obtained.

$HClO_4$ (M)	0·00	0·06	0·25	0·49	0·98
k_2 (l. mole^{-1} min.$^{-1}$)	2·4	3·2	6·1	12·0	53

The following results show, in more detail, effects of added electrolytes. They refer to 0·07M-toluene and 0·004—0·007M-ClOH in 77% acetic acid at 25°.

$HClO_4$ (M)	0	0·121	0·243	0·611	1·23
k_2 (l. mole^{-1} min.$^{-1}$)	2·84	4·32	6·59	19·0	>108
NaOAc (M)	0	0·077	0·155	0·385	0·670
k_2 (l. mole^{-1} min.$^{-1}$)	2·84	2·77	2·69	2·56	2·20
$NaClO_4$ (M)	0	0·149	0·298	0·595	
k_2 (l. mole^{-1} min.$^{-1}$)	2·84	3·80	4·63	7·16	

These results are plotted in Fig. 1; results for other relatively reactive compounds are in Table 1.

TABLE 1. *Chlorination in* 76% *acetic acid at* 25°.

ArH (M)		$AgClO_4$ (M)	ClOH (M)	$HClO_4$ (M)	k_2 (l. mole^{-1} min.$^{-1}$)
t-Butylbenzene	0·016	0·010	0·0025	0·0	1·0
o-Xylene	0·0406	0·010	0·0025	0·0	9·3
p-Xylene	0·0406	0·010	0·0025	0·0	11·1
m-Xylene	0·0160	0·012	0·0020	0·0	200
	0·0160	0·012	0·0020	0·123	280
Mesitylene	0·0306	0·012	0·0059	0·0	V. fast
p-Chloroanisole	0·041	0·012	0·0038	0·0	9·0
	0·041	0·012	0·0083	0·123	15·7
p-Anisic acid	0·010	0·000	0·0065	0·0	7·9
	0·010	0·000	0·0065	0·244	14·0
	0·010	0·0236	0·0065	0·00	8·4
	0·010	0·0236	0·0065	0·244	14·7

For benzene and other relatively unreactive compounds, decomposition of control solutions was relatively large, but was considerably reduced by the addition of perchloric acid. The following is an example of a typical kinetic run, with 0·0449M-benzene, 0·00441M-hypochlorous acid, 0·0118M-silver perchlorate, and 0·492M-$HClO_4$ at 25°:

Time (min.)	0·0	3·0	5·8	9·3	14·3	31·1	42·3	69·3
Titre (ml.)	8·80	8·60	8·50	8·35	8·10	7·35	6·70	6·05
10^3k_1	—	(7·7)	6·0	5·6	5·8	5·8	6·4	6·3

The initial rate of decomposition in a control run was $0{\cdot}1 \times 10^{-3}$ min.$^{-1}$, whence $k_2 = (6{\cdot}0 - 0{\cdot}1) \times 10^{-3}/0{\cdot}0449 = 0{\cdot}131$ l. mole^{-1} min.$^{-1}$. With 0·246M-$HClO_4$, $k_2 = 0{\cdot}068$.

Table 2 records further results similarly calculated.

Chlorobenzene and benzoic acid reacted too slowly for the rate to be substantially larger than the control decomposition except when the concentration of perchloric acid was very high.

TABLE 2. *Chlorination of* 0·0449M-*benzene in* 76% *acetic acid containing* 0·0118M-$AgClO_4$ *at* 25°.

(*a*) 0·492M-$HClO_4$ and $[ClOH]_{init.}$ (M)		0·0044	0·0069	0·0077	0·0109
k_2		0·123	0·157	0·127	0·150
(*b*) $HClO_4$ (M)	0	0·123	0·246	0·488	0·492
k_2	0·016 *	0·042	0·068 †	0·155 ‡	0·153

* Without $AgClO_4$; in the presence of $AgClO_4$, the control decomposition of hypochlorous acid was so large that satisfactory measurements could not be made. † Hexadeuterobenzene, k_2 = 0·079. ‡ Without $AgClO_4$, k_2 = 0·155.

In these circumstances, however, the kinetic form was the same as for the morereactive compounds. Results are given in Table 3.

Chlorination in 51% acetic acid was essentially similar (see Table 4).

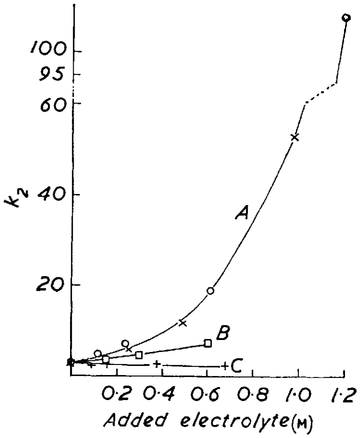

FIG. 1. *Chlorination of toluene by " hypochlorous acid " in aq. acetic acid; effects of added electrolytes.*

A, $HClO_4$: ○ 7% acetic acid;
76% acetic acid +0·01M-$AgClO_4$.
B, $NaClO_4$: □ 77% acetic acid.
C, NaOAc: + 77% acetic acid.

TABLE 3. *Rates of chlorination* (k_2 *in l. mole*$^{-1}$ *min.*$^{-1}$) *with* 0·006M-ClOH *and* 0·0118M-$AgClO_4$ *in* 76% *acetic acid at* 25°.

$HClO_4$ (M)	0·98	1·47	1·96	2·45	2·93
k_2(PhCl)	0·070	0·242	1·14	6·0	—
k_2($Ph{\cdot}CO_2H$)	0·025	0·027	0·065	0·24 *	1·6

* The same rate was obtained in the absence of silver perchlorate.

TABLE 4. *Chlorination by hypochlorous acid in* 51% *acetic acid.*

(*a*) ClOH, 0·0052M; $AgClO_4$, 0·01M

Toluene (M)	0·0234	0·0468	0·069	0·092
k_2	2·3	2·4	2·4	2·4

(*b*) Toluene, 0·0468M

$AgClO_4$ (M)	0·01	0·01	0·01	0·01	0·005	0·002	0·000
ClOH (M)	0·002	0·006	0·009	0·004	0·004	0·004	0·004
k_2	2·4	2·4	2·4	2·4	2·4	2·5	4·6 *

(*c*) Toluene, 0·0468M; $AgClO_4$, 0·01M; ClOH, *ca.* 0·005M

$HClO_4$ (M)	0·00	0·07	0·10	0·20	0·00	0·00
NaOAc (M)	0·00	0·00	0·00	0·00	0·005	0·010
k_2	2·4	3·1	4·5	9·1	2·43	2·45

* This reaction, in which silver perchlorate was omitted from the solution, showed second-order rate coefficients which rose steadily over the course of the reaction; at 45% reaction, the integrated second-order rate coefficient had risen from 4·6 to 5·9. A similar rise was noted when the reaction was carried out in the presence of added 0·01M-lithium chloride; the initial rate coefficient was then 6·4 l. mole^{-1} min.$^{-1}$.

In 86% acetic acid, the following results were obtained for 0·0936M-toluene with 0·0026M-ClOH.

$HClO_4$ (M)	0·00	0·15	0·25	0·30
k_2 (l. mole^{-1} min.$^{-1}$)	1·9 *	2·8	4·7	5·5

*Identical in 95% acetic acid.

Addition of lithium chloride (0·05M) had no significant effect on the rate of chlorination.

For representative cases, it has been established preparatively that the reactions studied involve substitution in the aromatic nucleus. Thus by the isotopic-dilution procedure described in Part VII, for the chlorination of toluene by hypochlorous acid in 75% acetic acid, the following isomeric proportions were estimated as percentages of hypochlorous acid used up: *p*, 27·3; *o*, 70·3.

In a preparative experiment, 0·84M-hypochlorous acid (400 ml.) was added to a solution of toluene (40 g.) in acetic acid (1 l.) to which had been added perchloric acid (100 g.) and water (250 ml.). The medium was therefore *ca.* 66% acetic acid containing *ca.* 6M-perchloric acid. The aromatic material was recovered and fractionally distilled; the main chlorotoluene fraction (32 g.), b. p. 157—159°/760 mm., n_D^{25} 1·5238, had f. p. $-37°$, raised 6° by addition of 2 g. of *p*-chlorotoluene to 30 g. of material. So, from the f. p. diagram given by Wahl, Normand, and Vermuylen,[7] the reaction mixture contained 64% of *o*-chlorotoluene. Chlorination of toluene by chlorine in aqueous acetic acid was also examined briefly. To a solution of toluene in acetic acid was added a solution of chlorine. Water in appropriate amount was then added, and samples were removed at intervals for titration. Results were: for *ca.* 0·15M-toluene and *ca.* 0·01M-chlorine, in 95·1% acetic acid, $k_2 = 0·43$; in 90·2% acetic acid, $k_2 = 1·43$; in 85·0% acetic acid, $k_2 = 5·0$; in 75·5% acetic acid, $k_2 = 16·5$ l. mole^{-1} min.$^{-1}$ at 25°.

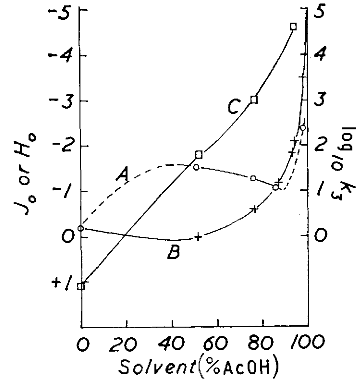

FIG. 2. *Solvent effects on acidity, and on rates of acid-catalysed chlorination, in mixtures of acetic acid and water.*

A, $\log_{10} k_3$. *B*, H_0. *C*, J_0.

NOTE: Graph B includes values extrapolated (see text) from results given in ref. 9.

Some measurements have also been made of the trends in the degree of ionisation of indicators in mixtures of acetic acid and water. Aliquot parts of a solution of *o*-nitroaniline (m. p. 71°) in 7·9M-perchloric acid were added to known volumes of acetic acid and the mixtures were then made up to known volumes with water. The optical densities of the resulting solutions were measured in 1 cm. cells against appropriate control solutions with a Unicam S.P. 500 spectrophotometer, in the region of maximum absorption, 4100 Å. The results were as follows:

Solvent (wt. % H_2O)	100	100	48·0	23·4	13·0	6·7
Perchloric acid (M)	0·00	0·87	0·87	0·87	0·87	0·87
Optical density (4100Å)	0·815	0·456	0·525	0·278	0·098	0·022
H_0	—	$-0·18$	$-0·03$	$-0·58$	$-1·15$	$-1·85$

In the neutralised solution (optical density, 0·815), it has been assumed that none of the base is protonated. From this value and the measured optical densities in the presence of acid, the extents of protonation in the various solvent mixtures have been calculated. For comparison with data from the literature, values of H_0 have been calculated by using the formula:[8] $H_0 = \mathrm{p}K_{\mathrm{BH}^+} - \log\{[\mathrm{BH}^+]/[\mathrm{B}]\}$; the value of $\mathrm{p}K_{\mathrm{BH}^+}$ for *o*-nitroaniline was taken as $-0·29$. The value ($-0·18$) determined thus for 0·869M-perchloric acid agrees tolerably with that ($-0·12$)

[7] Wahl, Normand, and Vermuylen, *Bull. Soc. chim. France*, 1922, **31**, 570.

[8] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

interpolated from the data given by Paul and Long,[8] and the present data fit satisfactorily (cf. Fig. 2) with those determined by Ludwig and Adams [9] for acetic acid containing up to 5% of water, from which, by linear extrapolation to our concentration of perchloric acid by the formula suggested,[9] the values of H_0 for acetic acid containing 0·87M-perchloric acid and 5%, 1%, and 0% of water by weight are respectively −2·10, −3·50, and −5·02. The most notable feature of the present results is that, for this indicator, 0·87M-perchloric acid has slightly more protonating power in water than in 50% acetic acid; further increase in the percentage of acetic acid, however, increases the extent of protonation by this concentration of perchloric acid.

Similar measurements were made with 4-methoxytriphenylmethanol (m. p. 58—62°; prepared by Baeyer and Villiger's method [10]). Measurements of the optical density were made at the absorption maximum,[11] 4750 Å, with the following results:

Solvent (wt. % H_2O)	100	100	48	23·4	6·7
Indicator concn. (arbitrary units)	0·05	1·0	4·0	1·0	1·0
Perchloric acid (M)	6·30	0·79	0·79	0·79	0·79
Cell length (cm.)	2·00	2·00	2·00	1·00	0·50
Optical density (4750 Å)	0·149	0·00	0·263	0·415	0·702
J_0	−6·87	+1·09	−1·75	−2·99	−4·59

In order to compare the tendency of perchloric acid in these different solvents to promote heterolysis of the type: $R_3C{\cdot}OH + H^+ \rightleftharpoons R_3C^+ + H_2O$, values of J_0 have been calculated by the formula: $J_o = \mathrm{p}K_{ROH} - \log\{[R^+]/[ROH]\}$. It has been assumed that the indicator was completely ionised in 6·3M-perchloric acid; that the Beer–Lambert law is obeyed; and that $\mathrm{p}K_{ROH}$ for this indicator [11] is −3·40. The values tabulated for aqueous solutions are interpolated from the table given by Deno and his co-workers.[12] The Table shows that the extent of carbonium ion formation from this indicator in solvents containing 0·87M-perchloric acid increases steadily as the percentage of acetic acid in the solvent is increased. Under our conditions this indicator is not appreciably converted into its acetate.[13] We do not claim, however, to have established, by the present results, acidity scales of general validity for these mixed solvents.

DISCUSSION

(a) *Acid-catalysed Chlorination in Aqueous Acetic Acid.*—All the reactions which fell into this class had rates which were, within experimental error, proportional to the first power of the concentration of hypochlorous acid, as judged either by the constancy of rate coefficients through the course of a single kinetic run or by varying the initial concentration of hypochlorous acid. The kinetics can be represented by the partial equation:

$$-\mathrm{d}[\text{“ ClOH ”}]/\mathrm{d}t = k[\mathrm{ArH}][\text{“ ClOH ”}]$$

The dependence of rate on acidity has the form shown in Fig. 1. Addition of small amounts of perchloric acid has only a small effect on the rate of reaction; the rate rises linearly with the molar concentration of acid up to *ca.* 0·4M, and more rapidly thereafter. In the region of high acidity, therefore, the full kinetic form is:

$$-\mathrm{d}(\text{“ ClOH ”}]/\mathrm{d}t = k_2[\mathrm{ArH}][\text{“ ClOH ”}] + k_3[\mathrm{ArH}][\text{“ ClOH ”}]\mathrm{f}([H^+])$$

The rate is increased much more by added perchloric acid than by the addition of an equal amount of sodium perchlorate. We conclude that the bulk of the reactivity observed in the presence of perchloric acid in excess of that found in the presence of an equivalent amount of sodium perchlorate represents reaction through a protonated species. The following are the values of the rate coefficients for the acid-catalysed reactions of

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[9] Ludwig and Adams, *J. Amer. Chem. Soc.*, 1954, **76**, 3853.

[10] Baeyer and Villiger, *Ber.*, 1902, **35**, 3027.

[11] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[12] Deno, Berkheimer, Evans, and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344 (correction, p. 6535).

[13] Bethell and Gold, *J.*, 1958, 1905.

toluene in various solvents; the rate without added acid has been deducted, and (since the results refer to acidities below 0·4M-$HClO_4$), f([H^+]) has been taken as identical with [H^+].

Solvent (% AcOH)	0[5]	51	76	86	98 ‡	100
k_3 (l.^{2} mole^{-2} min.$^{-1}$)	1·5	33	19 *	12	240	V. fast (*ca.* 3000) †

* 14, after correction also for salt effect.
† de la Mare and Vernon, unpublished results. ‡ Ref. 1.

The results for these chlorinations to some extent resemble those recorded by Branch and Jones[14] for bromination by hypobromous acid in 75% acetic acid. In the latter reaction, however, the catalysis by added mineral acid is much more marked. The variation in rate with composition of the solvent was considered by these authors to be consistent with bromination by $BrOH_2^+$ or Br^+, but they were unable to exclude the possibility that in concentrated acetic acid the reagent is $BrOAcH^+$.

A similar ambiguity is present in our results. The reaction in pure water is regarded[4,5] as a reaction through Cl^+. It might be thought that, were this the reagent throughout the range of solvent composition, the rate of reaction would follow either the degree of carbonium ion formation from a triarylmethanol or the extent of protonation of a simple base. The absence of any such correlation is shown in Fig. 2. Carbonium ion formation rises steadily as the percentage of acetic acid in the solvent is increased; protonation of *o*-nitroaniline passes through a very shallow minimum in the region 50% acetic acid. The rate of chlorination, however, passes through a maximum in the region 50% acetic acid, and then through a minimum in the region 90% acetic acid; and this behaviour is general, for Stanley and Shorter[6] found that acid-catalysis of chlorination of anisic acid is much more pronounced in 40% than in 75% acetic acid.

It seems likely to us, therefore, that the faster chlorination in 50% acetic acid than in water represents chlorination by the protonated species $ClOAcH^+$. This reaction must be subject to a solvent effect in the direction that increase in the concentration of acetic acid decreases the rate of reaction; for in the region 50—85% acetic acid the rate decreases, whereas the concentration of chlorine acetate must increase. A kinetic solvent effect in this direction implies that the transition state for chlorination is more strongly solvated than the initial state, provided that water is regarded as more solvating than acetic acid. The very marked increase in rate in pure acetic acid may perhaps result from the fact that the bulk source of active chlorine is now chlorine acetate instead of hypochlorous acid.

From the rates determined at acidity 0·49M or greater, the following relative rates of chlorination under conditions of acid-catalysis can be deduced:

Compound	PhMe	PhH	PhCl	Ph·CO_2H	Ph·CO_2Et
Rel. rate of chlorination ($ClOHAc^+$) *	69	1	0·097	0·004	—
Rel. rate of nitration[15] (NO_2^+)	23	1	0·035	—	0·0037

* These values have been corrected for the rate in the absence of mineral acid, but not for the salt effect. This should not much affect the comparison of toluene and benzene, since both would have to be corrected similarly; nor should it influence the other comparisons, since they are derived from reactions carried out at still higher acidities, where the rate increases rapidly with increase at concentration of perchloric acid.

ortho,para-Directing groups seem to give higher reactivities with this reagent than with the nitronium ion. The value for toluene is in good accordance with that (60) obtained for toluene and Cl^+ in water.[5]

(b) *Uncatalysed Chlorination in Aqueous Acetic Acid: Chlorine Acetate as an Electrophile.*—The uncatalysed chlorination of toluene and the other aromatic compounds studied in aqueous acetic acid has a rate which depends on the first power of the concentrations of aromatic compound and of hypochlorous acid. It is independent of the concentration of silver ions, provided that these are present in amount greater than about 0·002M. It

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[14] Branch and Jones, *J.*, 1954, 2317.

[15] Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959; Ingold and Smith, *J.*, 1938, 905; Bird and Ingold, *J.*, 1938, 918.

is unaffected by the addition of base to the medium. As can be seen from Fig. 1, it is far too rapid to be explained as an acid-catalysed chlorination; 75% acetic acid, for example, can be considered [6] to contain only *ca.* 0·01M-hydrogen ions.

The kinetic form is thus:

$$-\mathrm{d}[\text{“ ClOH ”}]/\mathrm{d}t = k_2[\mathrm{ArH}][\text{“ ClOH ”}]$$

Since hypochlorous acid is a very ineffective chlorinating agent,[16] and therefore could not possibly react with toluene under these conditions, it is concluded that the effective reacting species is molecular chlorine acetate, as Stanley and Shorter [6] proposed for *p*-anisic acid and *p*-chloroanisole.

From the results given in Part VIII,[1] and those of the present work, can be obtained the following values, which describe the effect of solvent on the apparent second-order rate coefficient for the reaction of chlorine acetate with toluene.

Solvent (% AcOH)	100	98	95	86	76	51
k_2 (l. mole^{-1} min.$^{-1}$)	*ca.* 17	1·1	1·9	1·9	2·3	2·4

Two factors are concerned with this change in rate. First, the concentration of chlorine acetate decreases as the concentration of water is increased. Secondly, the intrinsic rate of its reaction with an aromatic compound must increase, just as the rate of molecular chlorination of toluene and of naphthalene increases, with increase in the water content of the solution.[17] These two factors affect in opposite directions the observed rate of chlorination, so the latter decreases at first, and then passes through a shallow minimum; it is in fact not far from constant over quite a wide range of solvent composition.

It is possible to make approximate allowance for the change in concentration of chlorine acetate, if it is assumed that the equilibrium constant for this reaction is independent of the medium and is given [1] by the value $K = [\mathrm{ClOAc}][\mathrm{H_2O}]/[\mathrm{ClOH}][\mathrm{HOAc}] = ca.\ 0{\cdot}0025$. The true second-order rate coefficients for the reaction of chlorine acetate with toluene are on this basis:

Solvent (% AcOH)	100	98	95	86	76	51
k_2^{ClOAc} (l. mole^{-1} min.$^{-1}$, corr.)	*ca.* 17	34	160	500	1300	3650

Although these values are only approximate, they show that the corrected rate increases with increase in the water content of the solvent. A similar trend has been observed in chlorinations and brominations involving molecular halogens,[17,18] and has been attributed [19] to development of charge in the transition state formed from initially neutral reactants. For toluene and molecular chlorine in acetic acid the effect of added water has not been studied systematically, but the following values are available [17,20,21] for reaction at 25°:

Solvent (% AcOH)	99·87	98·7	95	90	85	76
$k_2^{\mathrm{Cl_2}}$ (l. mole^{-1} min.$^{-1}$)	0·032	0·059 *	0·43	1·43	5·0	16·5

* Calc. from data [17] at 34·7° and $E = 13$ kcal. mole^{-1}.

Relative Reactivities of Reagents.—The most striking feature of the present results is the conclusion that chlorination of toluene in acetic acid, or in aqueous acetic acid, is considerably faster with molecular chlorine acetate than with molecular chlorine. This result implies the reactivity sequence, $\mathrm{Cl{-}OAc} > \mathrm{Cl{-}Cl} \gg \mathrm{Cl{-}OH}$.

If the main factor determining the reactivity of a reagent ClX with an aromatic compound were the electron affinity of X, as measured by the strength of HX as an acid, a different order, namely $\mathrm{Cl{-}Cl} > \mathrm{Cl{-}OAc} > \mathrm{Cl{-}OH}$ would be expected; this prediction

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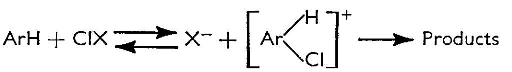
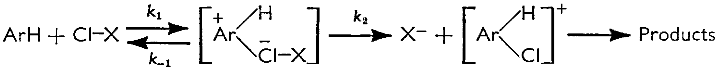
[16] Soper and Smith, *J.*, 1926, 1582.
[17] de la Mare and Robertson, *J.*, 1943, 279.
[18] Walker and Robertson, *J.*, 1939, 1515.
[19] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 763.
[20] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.
[21] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1959, **81**, 1063.

has been thought appropriate[22] for aromatic substitutions in which the stages essential to the rate process are:

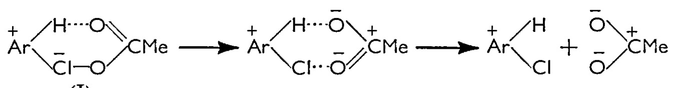

. . . . . . (1)

It seems clear, therefore, that other factors can be involved in determining the reactivity in the example now under observation. It does not seem possible to provide a satisfactory explanation in terms of either the homolytic or the heterolytic energies of bond-fission of ClX; for the Cl–O bond appears to be stronger than the Cl–Cl bond;[23] and organic chlorides, RCl, undergo heterolysis much more readily than the corresponding acetates, ROAc.[24] We have consequently been led to seek an interpretation in terms of special structural features of the transition states involved in the reaction.

Arguments have been presented (cf. refs. 17, 25, 26) based on kinetic forms, environmental effects, and structural comparisons, suggesting that molecular halogenation by chlorine and by bromine should be described in terms of the more elaborate scheme of equation (2), rather than by the simplified scheme of equation (1). It is unlikely, in the examples here considered, that the second stage is reversible, and the still later stage involving proton-loss is not rate-determining: hexadeuterobenzene is chlorinated at substantially the same rate as benzene.

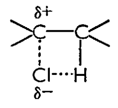

. . (2)

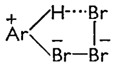
It would be consistent with the present results if the second stage involved a cyclic process, thus:

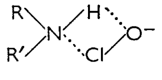

(I)

An analogous transition state has been proposed tentatively for nitration by dinitrogen pentoxide.[27] The fission of the Cl–O bond in the complex ArH,ClOAc (I) could be facilitated by hydrogen-bonding through a six-membered ring, but that in ArH,ClOH could not; and the Cl–Cl bond in the corresponding complex involving molecular chlorine is geometrically not so suitably placed for participitating in interaction with the adjacent hydrogen atom.

On this basis, therefore, we can rationalise the order of reactivity, ClOAc $>$ Cl_2 $\gg$ ClOH, in chlorination by neutral reagents. No doubt cases could be envisaged in which the interaction between X in the electrophile Cl–X and the displaced proton was so great in the transition state that a primary isotope effect would be observed. In the present case, the absence of a primary isotope effect indicates that the Ar–H bond is not much stretched in the transition state; it may be noted by way of analogy that Maccoll and


II)


(III)


(IV)

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[22] Cf. Benford and Ingold, *J.*, 1938, 929.

[23] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954.

[24] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 588.

[25] Robertson, *J.*, 1954, 1267.

[26] de la Mare and Ridd, " Aromatic Substitution: Nitration and Halogenation," Butterworths, London, 1959.

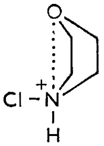
[27] Gold, Hughes, Ingold, and Williams, *J.*, 1950, 2452.

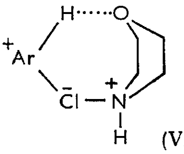
Thomas [28] envisage the gas-phase dehydrochlorination of aliphatic halides as proceeding through a transition state (II) in which the hydrogen assists in removing the chlorine heterolytically, but the C–H bond is not much stretched in the transition state.

Consideration of special circumstances which affect the ease of breaking of the Cl–X bond in the complex formed between the electrophile and the substrate undergoing reaction is helpful in rationalising features of some other reactions. Experimental evidence has been produced [29] which suggests that the tribromide ion, though negatively charged, can act as an electrophile. Structure (III) provides a possible representation of the transition state. An extreme example of essentially the same kind is perhaps that for *N*-chlorination by the hypochlorite ion, a very specific reagent for effecting this process, which has been represented [30] as shown in structure (IV). It would be interesting to know whether this reaction is subject to a primary isotope effect.

Carr and England have recently found that the *N*-chloromorpholinium cation can effect direct chlorination of the phenol molecule.[31] Since the boat form of the *N*-chloromorpholinium cation might well be stabilised by electrostatic interaction as indicated in structure (V),[32] it is possible that the transition state for chlorination by this species may be represented as in structure (VI).

(V)





(VI)

If complexes such as ArH,ClX are important intermediates leading towards aromatic substitution through a scheme such as is indicated in equation (2), the possibility must be envisaged that the reaction could be diverted before the second stage had proceeded. One possible such diversion would involve capture of the halide ion by the aromatic molecule, and this might result in *cis*-addition to the unsaturated system. There are several indications in the literature that this is a reaction path sometimes adopted. For instance, Cristol, Stermitz, and Ramey,[33] somewhat to their surprise, obtained *cis*-1,2-dichloroacenaphthene from acenaphthylene and chlorine in a number of aprotic solvents of differing ionising power; they called attention to this feature of the reaction, as well as to other stereochemically related situations. Recently Dr. N. V. Klassen, working in these laboratories, has obtained evidence for the formation of *cis*-9,10-dichloro-9,10-dihydrophenanthrene from phenanthrene and chlorine in acetic acid and in other solvents under conditions which suggest that the reaction is heterolytic in character.

Addition of chlorine to butadiene does not seem to involve a cyclic intermediate, [34] but Young, Hall, and Winstein [35] have shown that an important direct product of reaction of bromine with cyclopentadiene involves *cis*-1,4-addition. It seems likely that many such cases involve cyclic (*e.g.*, four- or six-centred) transition states, for which a rigid structure favours the intramolecular trapping of the potentially nucleophilic fragment as it attempts to dissociate. The relevant transition states (*e.g.*, VII) may have considerable polar character. By way of analogy it may be pointed out that some intramolecular rearrangements of allylic halides have considerable polarity in the transition state (*e.g.*, VIII).[36,37]

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[28] Maccoll and Thomas, *Nature*, 1955, **176**, 392.

[29] Berliner and Beckett, *J. Amer. Chem. Soc.*, 1957, **79**, 1425; Bell and Ramsden, *J.*, 1958, 161.

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

[31] Carr and England, *Proc. Chem. Soc.*, 1958, 350.

[32] Cf. Lyle, *J. Org. Chem.*, 1957, **22**, 1280.

[33] Cristol, Stermitz, and Ramey, *J. Amer. Chem. Soc.*, 1956, **78**, 4939.

[34] Mislow and Hellman, *J. Amer. Chem. Soc.*, 1951, **73**, 244.

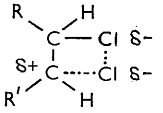
[35] Young, Hall, and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 4338.

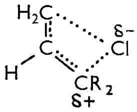
[36] Young, Winstein, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958.

[37] de la Mare and Vernon, *J.*, 1954, 2504.

In both cases the schemes are capable of elaboration, if the facts demand, to include consideration of one,[36] two,[38,39] or more further intermediates. In our present representation of the intermediates concerned in chlorination we have focused attention only on those structural features which seem to us important in interpreting the known chemistry.

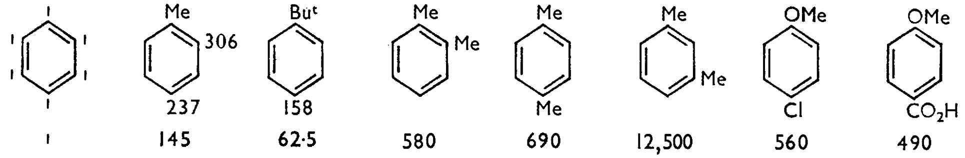
(VII)





(VIII)

Structural Effects in Chlorination by Chlorine Acetate.—The results given above allow calculation of the relative rates and partial rate factors for chlorination by chlorine acetate as shown. The spread of reactivity is rather greater, as judged by the reactivity of toluene relative to that of benzene, than for the positively charged reagent $ClOAcH^+$, but it is not as great as is found for molecular chlorine.[17,26] The partial rate factors given for toluene and t-butylbenzene [5] have been calculated from the observed orientations. The rates for *o*- and *p*-xylene are reasonably in accordance with those predicted for the additivity principle,[20,26] provided it is assumed that the partial rate factor for *meta*-substitution in toluene is 3; but *m*-xylene is not quite as reactive as would be expected from application of this principle. The values for *p*-chloroanisole and *p*-anisic acid were determined only incidentally; they suggest that, in the *meta*-position, chlorine and carboxyl substituents are approximately equally deactivating, as in the acid-catalysed chlorinations; and that the *o*-methoxyl group is still more powerfully activating.



Relative rates of chlorination (ClOAc).

Comparison with Stanley and Shorter's Investigation.[6]—Stanley and Shorter [6] recently examined the chlorination of a number of aromatic compounds, including *p*-chloroanisole and *p*-anisic acid, in 75% acetic acid and in 40% acetic acid. Our rates agree quite well with theirs, the difference in temperature being borne in mind. They also noticed that acid-catalysis was more marked in the more aqueous solvent, and concluded, from the relative insensitivity of rate to concentration of mineral acid, that chlorine acetate was an electrophilic reagent effective for these compounds. They used concentrations of perchloric acid up to 0·05M only, and considered that perchloric acid increased the rate of chlorination in 75% acetic acid only by a salt effect; we differ from them in that we believe that there is a real contribution from a positive chlorinating species produced by protonation of chlorine acetate, though it is true that this mode of reaction is of minor importance at low concentrations of added acid and becomes dominant only at quite high acidity.

The main point of difference between their discussion and ours arises because they observed orders of reaction less than one with respect to hypochlorous acid. They concluded on this basis that the reaction involved the partly rate-determining formation, from anisic acid, of an active form, which they thought might be the hydrated form, produced in a relatively slow step from a complex between anisic acid and acetic acid.

In our investigation, we have not observed orders of reaction less than one with respect to hypochlorous acid except occasionally for relatively less reactive compounds in the absence of silver ions. Typical kinetic runs quoted in the experimental section illustrate this point; rate coefficients showed no consistent trend with progress of the reaction, and

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[38] Winstein, Clippinger, Fainberg, and Robinson, *J. Amer. Chem. Soc.*, 1954, **76**, 2597.
[39] Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1265.

furthermore were substantially constant, or if anything rose slightly (indicating an order slightly greater than one), with increasing initial concentration of hypochlorous acid. In our experience, therefore, the kinetic behaviour reported by Stanley and Shorter is not general.

We are indebted to Professor E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for their interest and for valuable criticism. We thank Mr. C. Bilby and Miss E. Williams for technical assistance. Personal correspondence with Dr. J. Shorter is gratefully acknowledged.

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