797. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part VIII.*[1] *Chlorine Acetate in Slightly Aqueous Acetic Acid.*

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The absorption spectra of solutions of chlorine acetate and of hypochlorous acid in mixtures of acetic acid and water have been measured. The results indicate that chlorine acetate is nearly completely converted into hypochlorous acid by hydrolysis in 99·5% acetic acid; the equilibrium constant for the formation of chlorine acetate by the reaction: $\mathrm{ClOH} + \mathrm{HOAc} \rightleftharpoons \mathrm{ClOAc} + \mathrm{H_2O}$ is about 0·0025. The kinetics of chlorination of toluene and of anisole have been measured in slightly aqueous acetic acid containing hypochlorous acid. Evidence has thereby been obtained for chlorination by molecular chlorine acetate, and by its protonated derivative; the rate of formation of the former can be rate-determining for anisole, and for other sufficiently reactive aromatic compounds.

IN water, in the absence of nucleophilic ions other than the perchlorate ion, aromatic chlorination by hypochlorous acid follows kinetic forms [2-5] which have been interpreted as indicating chlorination through $\mathrm{ClOH_2^+}$, the hypochlorous acidium ion,[2,3,5] and $\mathrm{Cl^+}$, the chlorinium ion [2-4] (reactions 1, 2):

$$\mathrm{ClOH} \longrightarrow \mathrm{Cl^+} + \mathrm{OH^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{ClOH} + \mathrm{H^+} \rightleftharpoons \mathrm{ClOH_2^+};\ \mathrm{ClOH_2^+} \longrightarrow \mathrm{Cl^+} + \mathrm{H_2O} \quad . \; . \; . \; . \; . \; . \quad (2)$$

Added anions, X^-, of appropriate nucleophilic power, can divert the reaction through other chlorinating species, as shown in eqn. (3). In mixtures of water and hydroxylic

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[1] Part VII, de la Mare, Harvey, Hassan, and Varma, *J.*, 1958, 2756.

[2] de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 192.

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

[4] Swain and Ketley, *J. Amer. Chem. Soc.*, 1955, **77**, 3410.

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

solvents, such species must always be considered as possible carriers of electrophilic chlorine, as must their protonated forms, since they can be formed by equilibria of the types shown in eqn. (4). Such equilibria sometimes introduce ambiguity into the kinetic interpretation of chlorination in such mixed solvents, whether the chlorine is supplied as molecular chlorine or as hypochlorous acid.

$$\mathrm{ClOH_2^+ + X^- \rightleftharpoons ClX + H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{ClOH + HOAc \rightleftharpoons ClOAc + H_2O;\ ClOAc + H^+ \rightleftharpoons ClOAcH^+} \quad . \; . \; . \; . \; . \quad (4)$$

This investigation provides some new spectrophotometric and kinetic evidence concerning the existence and mode of action of chlorine acetate and its protonated form in acetic acid containing small amounts of water.

EXPERIMENTAL

Some of the materials and the general methods have been described elsewhere.[3,6] Solvents specified as $x\%$ acetic acid contained $(100 - x)$ ml. of water per 100 ml. of solution; these were prepared by addition of water, or of an aqueous solution, to acetic acid, or to chlorine acetate solutions, of known water content, this being determined from the f. p. as measured by use of a thermometer calibrated by the N.P.L. It was assumed that the f. p. of pure acetic acid is 16·65°,[7] and appropriate correction was made, where necessary, for the presence of other solutes, by using the molal f. p. depression constant of acetic acid,[8] *viz.*, 3·90.

An expression such as " hypochlorous acid " specifies all species in mobile equilibrium and analysable as hypochlorous acid by the usual method. All reactions were at 25° except where otherwise stated, and rate coefficients are means of values substantially constant over at least 50% of the reaction; they have been calculated by conventional formulæ. The compounds used had the following properties: toluene, b. p. 110°, n_D^{25} 1·4940; *m*-xylene, b. p. 139°, n_D^{25} 1·4946; anisole, b. p. 153°/760 mm.; they had been carefully fractionally distilled before use.

Solutions of chlorine acetate were prepared as has been described elsewhere.[9, cf. 10] Chlorine was bubbled into a solution of mercuric acetate in acetic acid; the mixture was shaken, and then distilled under reduced pressure, care being taken to exclude moisture. The first fractions were colourless, and contained reactive chlorine, as determined by titration with sodium thiosulphate. The solution was stable for considerable periods. It was very reactive; the initial second-order rate-coefficient for the reaction with toluene for one such solution was 17 l. mole^{-1} min.$^{-1}$, but the kinetic forms were not followed in detail under these conditions because the reactions were very sensitive to the presence of traces of water.

Spectra of Solutions of Chlorine Acetate and of Hypochlorous Acid in Acetic Acid.—The spectra of solutions of chlorine acetate (prepared as described above), of mixtures of this with water, and of mixtures of hypochlorous acid and acetic acid, were determined in 1-cm. cells by the use of a Unicam S.P. 500 spectrophotometer. A blank, which contained only the solvent, was used in all the measurements. The solvent was not transparent enough for measurements to be made below about 2500 Å.

Fig. 1 shows the results obtained when small amounts of water were added to a solution of chlorine acetate in nearly anhydrous acetic acid. It was noted that, in the solutions to which water had been added, the extinction coefficient at 2500 Å gradually fell to a constant value, and the graphs refer to spectra determined after this change was complete. These results show clearly that two absorbing species are in equilibrium, since the final spectra pass through an isosbestic point at 3040 Å. The equilibrium is not established instantaneously under these conditions.

Proof that hypochlorous acid is the main chlorine-containing species when more than about 0·5% of water is present in the solvent comes from comparison of Fig. 1 with Fig. 2. The latter shows the spectra of hypochlorous acid in water (graph *E*) and in aqueous acetic acid (composite graph *F*), prepared by diluting aqueous hypochlorous acid with acetic acid. All

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[6] de la Mare and Robertson, *J.*, 1943, 276, 279.

[7] Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239.

[8] Eichelberger, *ibid.*, 1934, **56**, 799.

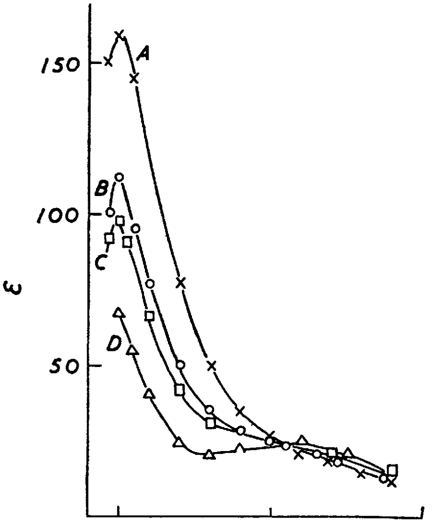
[9] de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12s.

[10] Anbar and Dostrovsky, *J.*, 1954, 1094, 1105.

these spectra have two rather broad absorption bands of low intensity, though the maximum of the band at *ca.* 2370 Å, observed in water, cannot be reached in acetic acid because the solvent is not sufficiently transparent. Change in the solvent from water towards acetic acid has some effect on the detailed form of the curve, but the spectra in 74%, 96%, and 98% acetic acid are almost identical, and are identical also with that (curve *D*, Fig. 1) of a solution of chlorine acetate to which water had been added in sufficient amount to ensure complete hydrolysis.

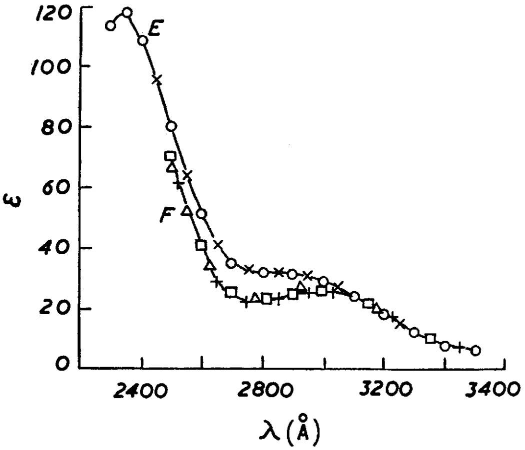
Solutions containing less than about 0·5% of water clearly contain some other chlorine-containing species. This is identified as chlorine acetate from its method of formation and from its spectrum, which accords with that observed by Anbar and Dostrovsky [10] for chlorine acetate in carbon tetrachloride. The extinction coefficient (ε) at the maximum (2500 Å) for a solution in 99·9% acetic acid (Fig. 1) could be increased by adding a little acetic anhydride to the medium, and values of 229 and 245 were recorded in this way on different specimens; in the latter case, the attainment of equilibrium was catalysed by the presence of a trace of sulphuric acid. Anbar and Dostrovsky [10] recorded a value of $\varepsilon_{2500} = 240$ for chlorine acetate in carbon tetrachloride.

FIG. 1. *Absorption spectra of solutions of chlorine acetate in aqueous acetic acid.*



(*A*) 0·07%, (*B*) 0·16%, (*C*) 0·31%, (*D*) 1·0% water.

FIG. 2. *Absorption spectra of hypochlorous acid in water and in aqueous acetic acid.*



Curve (*E*): ○, ClOH in water; ×, ClOH in 0·01N-H_2SO_4.
Curve (*F*): △, ClOH in 74% HOAc; □, ClOH in 96% HOAc; +, ClOH in 98% HOAc.

Using this value for chlorine acetate, and $\varepsilon_{2500} = 70$ for hypochlorous acid, we can calculate the ratio of chlorine acetate to hypochlorous acid for the solutions for which absorption spectra are plotted in Fig. 1. The f. p.s of these solutions were determined, and these allow estimates to be made also of the amounts of water in these solutions; so data are available for estimating the equilibrium constant for the reaction: $ClOH + HOAc \rightleftharpoons ClOAc + H_2O$. The Table summarizes the data, and compares the observed values of the extinction coefficients with those calculated for the relation:

$$K = [ClOAc][H_2O]/[ClOH][HOAc] = 0{\cdot}0025$$

The agreement is fair, consideration being given to assumptions which have been made in the treatment, and the difficulties of the experimental measurements. It is clear that chlorine acetate is half-converted into hypochlorous acid by the addition of *ca.* 0·044M (0·08%) water, and that the equilibrium constant for the above equilibrium is of the order indicated. Better accordance between observed and experimental values would be obtained if the maximum extinction coefficient of chlorine acetate in acetic acid were 230, as compared with 240 in carbon tetrachloride. Since there seems little doubt that water is considerably associated in acetic acid, and since acetic acid itself exists to some extent as dimer,[11] a full investigation of this system would require consideration of the activities of acetic acid and of water in these solvents, and this would go beyond the scope of this study.

Freezing points and extinction coefficients of solutions of chlorine acetate in aqueous acetic acid.

F. p. of solvent	H_2O (%) in solvent *	[ClOAc]/[ClOH] (calc. from ε_{2500})	ε_{2500} obs.	ε_{2500} calc.
16·63°	0·00	(∞) †	240 ‡	(240) †
16·47	0·07	1·4	169	160
16·29	0·16	0·33	112	125
16·00	0·31	0·20	98	104
14·80	1·00	0	70	(70)

* From f. p., allowance being made for the presence of 0·005M-ClOAc.
† Values in parentheses are assumed. ‡ In CCl_4; ref. 10.

Kinetic Measurements.—The kinetics were followed by conventional methods. Preliminary measurements were made with solutions in acetic acid, to which were added the appropriate quantities of aqueous solutions of hypochlorous acid and other materials. Silver ions were always present in sufficient amount to prevent reaction through free chlorine. It was found more convenient, for the measurements recorded here, to use solutions of chlorine acetate in acetic acid, to which were added the appropriate aqueous solutions. These mixtures were allowed to attain equilibrium in the thermostat; the reaction was then started by addition of the aromatic compound. The following is a typical kinetic run, for anisole (0·033M) with " hypochlorous " acid (0·004M) and silver perchlorate (0·01M) in 96·7% acetic acid.

Time (min.)	0·42	0·84	1·30	1·77	2·28
Titre (ml. of 0·005N-$Na_2S_2O_3$)	7·40	5·18	3·48	2·43	1·58
k_1 (min.$^{-1}$)	—	0·85	0·84	0·82	0·83

The following results show the effect of varying the composition of the solvent, for 0·03—0·04M-anisole with 0·003—0·007M-chlorine acetate and 0·006—0·01M-silver perchlorate:

Solvent (% HOAc)	99·5	99·2	98·7	97·7	96·7	95·0
k_1 (min.$^{-1}$)	1·1	0·59	0·45	0·64	0·85	1·8

The reaction went to completion within 0·3 min. when silver perchlorate was absent; addition of more than 0·006M-silver perchlorate had little effect on the rate. The following are the results of varying the concentration of anisole and of added electrolytes, for chlorine acetate, 0·002—0·007M; and silver perchlorate, 0·006M in 98% acetic acid. Concentrations are in terms of 0·01M.

ArH	$HClO_4$	NaOAc	$LiClO_4$	k_1 (min.$^{-1}$)	ArH	$HClO_4$	NaOAc	$LiClO_4$	k_1 (min.$^{-1}$)
4·60	0	0	0	0·45	9·2	0	0·50	0	1·76
9·21	0	0	0	0·46	4·6	0	1·00	0	2·82
18·4	0	0	0	0·45	9·2	0	1·00	0	2·79
4·6	0	0	0·99	0·49	4·6	1·23	0	0	6·52
4·6	0	0·50	0	1·26	9·2	1·23	0	0	6·68

For 0·163M-*m*-xylene with 0·006M-chlorine acetate and 0·006M-silver perchlorate in 98% acetic acid, k_1 was found to be 0·47 min.$^{-1}$.

For toluene, the rate is dependent, at least in part, on the concentration of organic compound, as is shown by the following results for 0·006M-silver perchlorate in 98% acetic acid. (Concentrations are in 0·01M.)

ArH	$HClO_4$	NaOAc	$LiClO_4$	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)	ArH	$HClO_4$	NaOAc	$LiClO_4$	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
9·41	0	0	0	0·158	1·65	9·41	0	0·50	0·00	0·179	1·91
18·82	0	0	0	0·198	1·06	18·82	0	0·50	0·00	0·340	1·81
9·41	0	0	0·99	0·174	1·79	9·71	1·23	0·00	0·00	0·395	4·18
18·82	0	0	0·99	0·254	1·35	18·82	1·23	0·00	0·00	0·86	4·56

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

DISCUSSION

From the absorption spectra of slightly aqueous solutions of chlorine acetate, it is clear that hypochlorous acid is the major component of the potential chlorinating species in acetic acid containing 1% or more of water.

The rate of reaction of anisole or of *m*-xylene with such solutions, whether they are obtained from aqueous hypochlorous acid and acetic acid or from chlorine acetate in acetic acid and water, is independent of the concentration of aromatic compound and is catalysed by acids. Since it is also catalysed by sodium acetate, this measurably slow reaction cannot be the rate of formation of Cl^+ from ClOAc or $ClOAcH^+$; it is suggested, therefore, that it represents the rate of formation of chlorine acetate from hypochlorous acid and acetic acid:

$$\mathrm{ClOH + HOAc \rightleftharpoons ClOAc + H_2O}$$

This reaction would be expected to be catalysed by acids, through the route:

$$\mathrm{ClOH + H^+ \rightleftharpoons ClOH_2^+;\ ClOH_2^+ + HOAc \longrightarrow ClOAcH^+ + H_2O}$$

The upper limit for the rate of formation of chlorine acetate by nucleophilic attack of acetic acid on hypochlorous acid in 98% acetic acid is given by $k_2 = k_1/[\mathrm{HOAc}] = 0{\cdot}026$ l. mole^{-1} min.$^{-1}$. Anbar and Dostrovsky [10] have estimated by a similar indirect method that this reaction in water has a rate coefficient $k_2 = 5{\cdot}7$ l. mole^{-1} min.$^{-1}$. The change with solvent is in the direction expected for a nucleophilic displacement involving neutral molecules and a more polar transition state,[cf. 12] and provides a reasonable interpretation of the increase in the rate of this reaction as the water content of the solvent is increased from 1·3 to 5%.

Base-catalysis presumably involves a nucleophilic displacement on hypochlorous acid by acetate ions:

$$\mathrm{AcO^- + ClOH \longrightarrow ClOAc + OH^-}$$

The catalytic coefficient for this reaction in 98% acetic acid is from our data 2·3 l. mole^{-1} min.$^{-1}$. The value, 0·31 l. mole^{-1} min.$^{-1}$, which Anbar and Dostrovsky [10] interpret similarly, refers to water as solvent. This difference also is in the direction expected theoretically,[12] for we are now concerned with nucleophilic displacement by a negative ion on a neutral molecule, and charge initially present is dispersed in the transition state. Our results do not throw any light on the part which may be played in these reactions by intermediates in which the octet of chlorine is expanded,[13] but they seem to accord generally with the interpretation of exchange reactions of hypohalites developed by other workers.[10,13]

The kinetic form, with anisole as substrate, does not establish whether chlorine acetate, when it is formed, reacts as such or in some derived form. Some evidence on this point comes, however, from the kinetic form observed in the similar chlorinations of the less reactive compound, toluene. In this case, the rate is slower, and dependent on the concentration of aromatic compound:

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

It is apparent, therefore, that the equilibrium concentration of the chlorinating species is maintained throughout the course of the reaction, which is catalysed by acids but not by bases. The equilibrium concentration of chlorine acetate must be essentially independent (since environmental effects will be only of secondary importance) of the presence of mineral acid and of base. So the chlorinating species is probably molecular chlorine acetate when no acid is added; and either Cl^+ or $ClOAcH^+$ when mineral acid is added.

There is, of course, no proof supplied by the kinetic form that these reactions of the less reactive compounds do not proceed by attack by hypochlorous acid when no mineral acid

[12] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[13] Anbar and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 1073; Anbar, Guttmann, and Rein, *ibid.*, 1959, **81**, 1816.

is added. Hypochlorous acid itself is, however, a very ineffective chlorinating species;[14] and it is considered very unlikely that this could be the reagent under the present conditions, when the substrate is the rather unreactive compound, toluene. The hypochlorous acidium ion, $ClOH_2^+$, is present, it is considered, in its equilibrium concentration by rapid proton transfer, and cannot itself be responsible for the main part of the acid-catalysed chlorination; for if it were, there is no reason why a rate independent of the concentration of aromatic compound should be reached under conditions involving added mineral acid. It could, however, be contributing to the rate-determining formation of Cl^+ under these, but not under basic conditions.

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[14] Soper and Smith, *J.*, 1926, 1582.