718. *Studies of* N-*Halogeno-compounds. Part V.* The Interaction of Dialkylchloramines with Phenols.*

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Solutions of diethylchloramine and phenols interact in the main by a direct mechanism and not by preliminary hydrolysis of the chloramine to hypochlorous acid. The kinetics can be interpreted in terms of interaction of phenoxide ions and diethylchlorammonium cations. Such active species are in harmony with an observed constant rate of interaction over a wide range of pH, decreasing both in more strongly acid and in more strongly alkaline solution. From the kinetic data, the acid ionisation constant of the diethylchlorammonium cation is 0·09. Its reactivity towards phenols is approximately 10^3 times that of hypochlorous acid, whilst hypochlorous acid is some 10^3 times as reactive as a chlorinating agent towards phenol (Hurst and Soper, *J.*, 1949, 107) as is *N*-chloroacetanilide. Unlike *N*-chloroacetanilide, which hydrolyses to hypochlorous acid at a rate proportional to the hydroxyl-ion concentration, diethylchloramine hydrolyses at a rate apparently independent of the alkalinity.

The interaction of *N*-chloroacetanilide with phenols was shown by Hurst and Soper (*loc. cit.*) to be due to two concurrent reactions: (*a*) a rate of hydrolysis of the chloramine to hypochlorous acid dependent on the hydroxyl-ion concentration and independent of the phenol concentration, and (*b*) a direct chlorination of the phenoxide ion by the chloramine molecule acting as an electrophilic substituting reagent. It may be expected that the reactivity of a chloramine as an electrophilic chlorinating agent will be related to the ease of separation of positive chlorine from it, and this in turn should parallel the ease of proton release from the parent amine or amide. Hence the more acidic the amine or amide the more reactive should be its chloramine as an electrophilic chlorinating agent in direct chlorinations and, in comparison with *N*-chloroacetanilide, the dialkylchloramines should be much less effective as direct chlorinating agents. Contrary to expectation, however, their kinetic behaviour towards phenol indicated a high mutual reactivity which was constant over a wide range of pH. Decreased activity was observed in alkaline solutions and, for some phenols, also in more strongly acid solutions.

The solutions of dialkylchloramines were prepared by addition of hypochlorous acid to a slightly alkaline solution of the dialkylammonium chloride. Absorption spectra showed that no detectable free hypochlorous acid was present, and that no alkyldichloramine was formed by dealkylation. There was no loss of oxidising titre of the hypochlorous acid in the formation of the chloramine. Examination of the stability of diethyldichloramine solutions was made by observation of the ultra-violet spectrum of the chloramine (Metcalf, *J.*, 1942, 148), which was unchanged over the pH range 2—13 and quite distinct from that or hypochlorite (Corbett, Metcalf, and Soper, *J.*, 1953, 1927). There was no appreciable formation of hypochlorite by the reaction $Et_2NCl + NaOH = NaOCl + Et_2NH$ even in 0·5N-sodium hydroxide, although under similar conditions chloramine is appreciably converted into hypochlorite. In these alkaline solutions the ultra-violet spectrum of dialkylchloramine was unchanged. The diethylchloramine was also stable in sulphuric acid solution at pH 2 for at least 3 hr.

The rate of reaction between the dialkylchloramine and phenol was examined in a series of buffered aqueous solutions at 25·0°, the phenol solution being added last to initiate the reaction. The rate of chlorination of the phenol or disappearance of the chloramine was measured by addition of aliquots to acidified potassium iodide solution and titration of the liberated iodine with thiosulphate. In the presence of excess of phenol the rate followed a first-order equation, and was not appreciably affected by the concentration of the boric acid buffer. Typical results are given in Table 1, k_1 being in min.$^{-1}$; they indicate that k_1, given by $v = k_1[R_2NCl]$, is, to a first approximation, proportional to the total phenol present and apparently is unaffected by the proportion of phenol in

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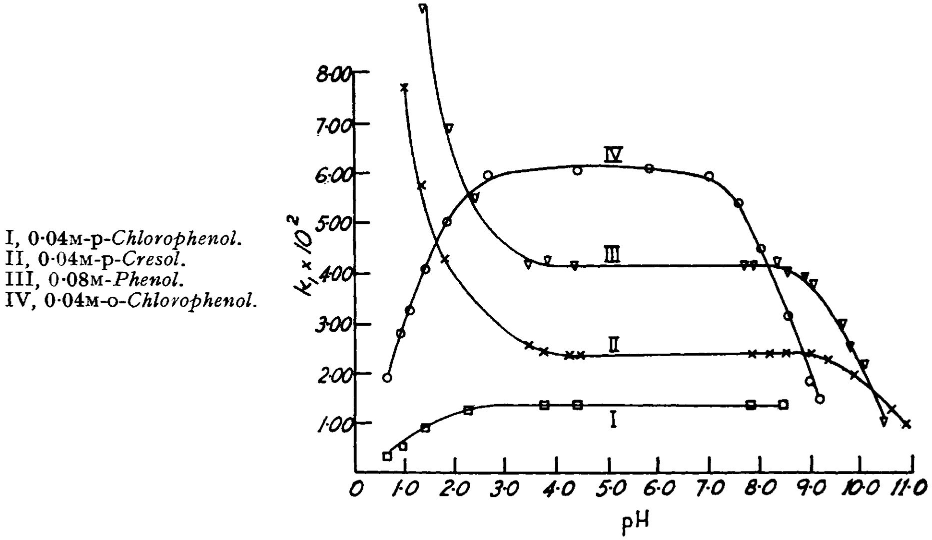
* Part IV, *J.*, 1953, 1927.

the form of the more reactive phenoxide ion. In contrast to this behaviour of diethylchloramine, *N*-chloroacetanilide was found by Hurst and Soper (*loc. cit.*) to become increasingly reactive with increasing alkalinity owing to (1) increased rate of hydrolysis to hypochlorous acid and (2) increased direct reaction with the increased fraction of phenol in the form of phenoxide ion. In further contrast diethylchloramine becomes less reactive to phenol in the more alkaline solutions, as is shown in Table 2, in which k_2 is given by $v = k_2[PhOH][R_2NCl]$ and is related to k_1 by the equation $k_2 = k_1/[PhOH]$. Here [PhOH] represents the un-ionised phenol present in the solution, K_a', the ionisation constant of phenol, being taken as $1{\cdot}1 \times 10^{-10}$. Similar results were obtained in alkaline solutions with *o*- and *p*-chlorophenol and *p*-cresol (see Figure). In all cases the specific rate, k_1, diminished in more alkaline solutions as though the chloramine were capable of reacting with the phenol and incapable of reacting with the more reactive phenoxide ion, into which the phenol is converted in alkaline solution. Such an explanation would be contrary to experience, when the attacking chlorinating reagent is electrophilic.



An alternative explanation of the kinetic behaviour is that the reaction occurs between protonated dialkylchlorammonium ion and the phenoxide ion, *i.e.*, $v = k_3[R_2NHCl^+][PhO^-]$. Comparison with k_2 shows that

TABLE 1.

$[Et_2NCl] = 0{\cdot}0075$M. Boric acid buffer = 0·05M (calc. on H_3BO_3).

pH	8·79	8·98	9·24
[Phenol], M	$100k_1$	$100k_1$	$100k_1$
0·02	1·05	1·02	0·98
0·04	1·87	1·88	1·80
0·08	3·61	3·66	3·44
0·20	8·77	8·52	8·04
$100[PhO^-]/[PhO^- + PhOH]$	5·3	9·5	16·0

TABLE 2.

Phenol = 0·08M.

pH	8·04	8·98	9·24	9·53	9·76	9·99	10·22	10·51
$100\,k_1$, min.$^{-1}$	4·01	3·66	3·44	2·83	2·38	2·00	1·43	0·92
$100\,[PhOH]/[PhOH + PhO^-]$	98·8	90·5	84·0	72·9	61·4	48·3	35·5	21·9
k_2, min.$^{-1}$ moles l.$^{-1}$	0·508	0·505	0·513	0·487	0·486	0·519	0·507	0·523

$$k_3 = k_2[PhOH][R_2NCl]/[R_2NHCl^+][PhO^-] = k_2K_a''/K_a'$$

where $K_a'' = [H^+][R_2NCl]/[R_2NHCl^+]$. Hence, constant values of velocity coefficients k_2, based on the unlikely assumption of a reaction between un-ionised phenol and chloramine, must result in constant values of k_3 based on an interaction of phenoxide ions with the dialkylchlorammonium ions. Such molecular species will be highly reactive towards each other.

Behaviour in acid solution. Since $[PhO^-] = K_a'[PhOH + PhO^-]/(K_a' + [H^+])$ and $[R_2NHCl^+] = [H^+][R_2NHCl^+ + R_2NCl]/(K_a'' + [H^+])$, we have

$$\begin{aligned} v &= k_3[PhO^-][R_2NHCl^+] \\ &= k_3[PhOH + PhO^-][R_2NHCl^+ + R_2NCl] \,.\, K_a'[H^+]/\{(K_a' + [H^+])(K_a'' + [H^+])\} \end{aligned}$$

Further, since k_1 is evaluated in the presence of excess of phenol by the equation

$$v = k_1[R_2NHCl^+ + R_2NCl],$$
$$k_1 = k_3[PhOH + PhO^-] \,.\, K_a'[H^+]/\{(K_a' + [H^+])(K_a'' + [H^+])\}$$

It folows that in solutions of medium acidity, where $K_a'' \gg [H^+] \gg K_a'$,

$$k_1 = k_3[PhOH] \,.\, K_a'/K_a'' = \text{constant}$$

In highly acid solutions, where $[H^+] \gg K_a'$, $k_1 = k_3[PhOH] \,.\, K_a'/(K_a'' + [H^+])$ and when $[H^+]$ becomes commensurate with K_a'', k_1 diminishes. Finally, in alkaline solutions, where K_a'' and $K_a' > [H^+]$,

$$k_1 = [PhO^- + PhOH][H^+]/k_3K_a'' = \text{constant} \times [H^+] = \text{constant}/[OH^-]$$

Hence, for a constant concentration of a particular phenol, k_1 should be constant over a range of pH, diminishing in more strongly alkaline and also in more strongly acid solutions. Values for *o*-chlorophenol are shown in Table 3. For work in acid solutions, the diethylchloramine was prepared from diethylamine and hypochlorous acid free from chloride. Such preparations of diethylchloramine duplicated the behaviour in neutral and alkaline solution of diethylchloramine prepared from diethylamine hydrochloride and hypochlorous acid.

TABLE 3.

o-Chlorophenol = 0·04M.

pH	1·08	1·80	2·22	4·41	6·03	7·06	8·03	8·53	9·10
$k_1 \times 10^2$	3·14	4·96	5·44	5·93	5·94	5·94	4·31	2·98	1·30

A similar decrease in speed is observed in the case of *p*-chlorophenol with increasing acidity, as shown in the Figure. For the more easily chlorinated phenol and *p*-cresol, the rate increases with increasing acidity. This may possibly be due to the development of chlorine in the solution, or alternatively to the fact that, with these phenols, the dialkylchlorammonium ion can substitute both the phenoxide ion and the un-ionised phenol, the latter reaction becoming the more important and dominating in the more acid solutions. If the enhanced reactivity were due to the development of chloride and the formation of chlorine by the reaction, $H^+ + Cl^- + Et_2NCl = Cl_2 + Et_2NH$, the observed rates would be due to the chance impurity of chloride ion and would not be reproducible whereas duplicate experiments carried out at different times gave concordant results. Hence it is considered that the dialkylchlorammonium ion can chlorinate both the phenoxide ion and the un-ionised phenol in the more reactive phenols.

The observed higher reactivity of *o*-chlorophenol than of phenol in the plateau region of the graph is additional confirmation of a mechanism involving phenoxide ions, the higher ionisation constant of the chlorophenol providing a higher concentration of the reactive ion.

Ionisation constant of the dialkylchlorammonium ion. The decrease in reactivity in more acid solutions of the chlorophenols, if these phenols react with diethylchloramine by the mechanism involving the phenoxide ion only, can be related to the ionisation constant K_a''' of the equilibrium, $Et_2NHCl^+ \rightleftharpoons H^+ + Et_2NCl$. Since in acid solutions

$$k_1 = k_3[PhOH]K_a'/(K_a'' + [H^+])$$

and since the condition for the plateau part of the reactivity curve is that $K_a'' \gg [H^+]$, the specific rate, k_1, is reduced to half the plateau value when $[H^+] = K_a''$. This reduction of k_1 to half the plateau value occurs at approximately pH 1 for both *o*- and *p*-chlorophenol, indicating that K_a'' is approximately 0·1 (actual values 0·098 and 0·080).

Rate of hydrolysis of diethylchloramine. In the interaction of *N*-chloroacetamide with phenol (Hurst and Soper, *loc. cit.*) it was found that, whilst the chloramine could react directly with the phenoxide ion, there occurred a simultaneous reaction of zero order with regard to phenol concentration. This was due to the hydrolysis $PhAcNCl + OH^- = PhAcNH + OCl^-$. Similar hydrolysis might be expected of the dialkylchloramines and may be expressed as a phenol-independent term in the rate equation $k_1 = k_0 + k_2$[total phenol]. A plot of the values of k_1 given in Table 1 against [total phenol] at the pH's of 8·79, 8·98, and 9·24 gave intercepts for $100k_0$ of 0·19, 0·24, and 0·22 min.$^{-1}$, respectively, indicating that for diethylchloramine the hydrolysis rate appears to be independent of pH. To examine this conclusion further, the rates of a series of reactions at pH 4·4 were measured, various *p*-cresol concentrations being used. The results, shown herewith, gave a similar value for the hydrolysis rate k_0, *viz.*, 0·25 × 10^{-2} min.$^{-1}$. The mean rate k_0 is 0·225 × 10^{-2} min.$^{-1}$.

[*p*-Cresol]	0·016	0·024	0·040	0·080
$k_1 \times 10^2$, min.$^{-1}$	1·04	1·45	2·28	4·26
$k_1 \times 10^2$, min.$^{-1}$ = 0·25 + 50·0[total phenol]	1·05	1·45	2·25	4·25

Two hydrolysis mechanisms conform to a rate of production of hypochlorous acid which is independent of pH. The alternative mechanisms are (*a*) an interaction of diethylchloramine and water (cf. Sidgwick, "Chemical Elements and Compounds," Oxford University Press, 1950, p. 704, on the hydrolysis of nitrogen trichloride) or (*b*) an interaction of diethylchlorammonium ion and hydroxyl ion. Such alternatives cannot be differentiated by rate measurements.

The hydrolysis constant of diethylchloramine. The hydrolysis constant of chloramine (Corbett, Metcalf, and Soper, *J.*, 1953, 1927) is 2·8 × 10^{-10} at 15°. Diethylamine being a stronger base than ammonia, *i.e.*, the amine cation being a weaker acid than NH_4^+, one would expect the hydrolysis of diethylchloramine to be less than that of chloramine.

Since both the rate of formation of diethylchloramine from diethylamine and hypochlorous acid (Edmond and Soper, *loc. cit.*) and now the rate of hydrolysis of diethylchloramine are known, an estimate can be made of the hydrolysis constant of the reaction :

$$Et_2NCl + H_2O \underset{k_2}{\overset{k_0}{\rightleftharpoons}} Et_2NH + HOCl$$

This hydrolysis constant, $K_h = [Et_2NH][HOCl]/[Et_2NCl] = k_0/k_2$. The rate of formation of diethylchloramine is given by $v = k_{2(obs.)}$ [total HOCl][total amine], and at pH 2·3—3·5, $v = k_{2(obs.)}[HOCl][Et_2NH_2^+]$, as practically all the hypochlorous acid is un-ionised and the amine is present as cations. The relation of $k_{2(obs.)}$ to k_2, defined by $v = k_2[HOCl][Et_2NH]$, is that $k_2 = k_{2(obs.)}[Et_2NH_2^+]/[Et_2NH] = k_{2(obs.)}K_b''/[OH^-]$. The ratio $k_{2(obs.)}/[OH^-]$ over the pH range 2·31—3·51 was found to be constant and equal to $9{\cdot}53 \times 10^{11}$ min.$^{-1}$ moles^{-2} l.^{2}, whence $k_2 = 9{\cdot}53 \times 10^{11} \times 1{\cdot}26 \times 10^{-3}$ and $K_h = k_0/k_2 = 0{\cdot}225 \times 10^{-2}/9{\cdot}53 \times 10^{11} \times 1{\cdot}26 \times 10^{-3} = 2{\cdot}0 \times 10^{-12}$. This value of K_h is of the right order of magnitude, and some confirmation of it is given by work of L. C. Baker (University of New Zealand, Thesis, 1941) on the equilibrium $Et_2NCl + NH_3 \rightleftharpoons NH_2Cl + Et_2NH$, spectrophotometric studies of which gave an equilibrium constant at room temperature of 3·5 × 10^{-2}. This constant is the ratio of the hydrolysis equilibrium constants of (*a*) $Et_2NCl + H_2O \rightleftarrows HOCl + Et_2NH$ and (*b*) $NH_2Cl + H_2O \rightleftarrows HOCl + NH_3$, and the value of the latter (Corbett, Metcalfe, and Soper, *loc. cit.*) is 2·8 × 10^{-10} at 15°. This gives a value for the diethylchloramine hydrolysis constant of 9·8 × 10^{-12}. The comparison with the ratio of the two specific rate constants is not unsatisfactory when it is borne in mind that the rate constant of formation was determined at pH 2·3—3·5 and that of the hydrolysis at pH 4·4 and 8·8—9·2.

Relative reactivities of the phenoxide ions with the dialkylchloramine ion. From the foregoing evidence, the rate of interaction of diethylchloramine and phenol can be represented as a sum of two rates :

$$\begin{aligned} v = k_1[\text{chloramine}] &= k_0[\text{chloramine}] + k_2[\text{chloramine}][\text{phenol}] \\ &= k_0[\text{chloramine}] + k_3[PhO^-][R_2NHCl^+] \end{aligned}$$

i.e.,

$$k_1 - k_0 = k_3[PhOH + PhO^-] \,.\, K_a'[H^+]/\{(K_a' + [H^+])(K_3'' + [H^+])\}$$

and at the flat portion of the curve $k_1 - k_0 = k_3[\text{PhOH}]K_a'/K_a''$, whence k_3 can be calculated. The value of K_a'' being taken as 0·09, the reactivities k_3 of the various phenoxide ions towards the dialkylchlorammonium ion are given below. In this Table the phenols fall into an order of reactivity given by the values of k_3 similar to that observed in the substitution of phenols by hypochlorous acid. This rate constant k_3 interprets the kinetics in terms of interaction between dialkylchlorammonium ions and phenoxide ions and explains the anomaly that over a wide range of pH (see Figure) the apparent reactivity of *o*-chlorophenol towards a chloramine is greater than that of *p*-cresol. The effectiveness of the diethylchlorammonium cation as a chlorinating agent is approximately 1000 times greater than that of hypochlorous acid, whilst *N*-chloroacetanilide (Hurst and Soper, *loc. cit.*) chlorinates phenol some 1000 times less rapidly than the hypochlorous acid.

Phenol	Concn., M	$(k_1 - k_0) \times 10^2$	$K_a{}^1 \times 10^{10}$	$k_3 \times 10^{-8}$	$k \times 10^{-5}$ *
p-Cresol	0·04	2·06	0·67	7·7	9·0
Phenol	0·08	3·84	1·3	3·93	3·3
o-Chlorophenol	0·04	5·72	7·7	1·67	0·59
p-Chlorophenol	0·04	1·02	4·1	0·56	0·49

* Chlorination of phenols by hypochlorous acid, Soper and Smith, *J.*, 1926, 1589.

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