CCVI.—*The Halogenation of Phenols.*

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THE iodination of phenols has been investigated by Cofman (J., 1919, **115**, 1040), who concluded that the active iodinating agent was hypoiodous acid, free iodine having apparently no direct iodinating effect. Similar views were held on the mechanism of bromination (Baines, J., 1922, **121**, 2810), but recently Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340) has shown that bromine is a more active brominating agent than hypobromous acid. Both Cofman and Francis are of the opinion that probably the only active halogenating agent is the positive halogen ion. This conclusion can be tested using halogens and hypohalous acids, since, although the actual degrees of ionisation of these substances into positive halogen ions (Stieglitz, *J. Amer. Chem. Soc.*, 1901, **23**, 796) are not known—except in the case of hypoiodous acid (Murray, J., 1925, **127**, 882)—their relative ionisations may be calculated from other data. For, assuming the existence of such equilibria as

$$\mathrm{HOCl} \rightleftharpoons \mathrm{OH}' + \mathrm{Cl}^{\bullet}$$
$$\mathrm{Cl_2} \rightleftharpoons \mathrm{Cl}' + \mathrm{Cl}^{\bullet}$$

then

$$\frac{K_{\mathrm{HOCl}}}{K_{\mathrm{Cl_2}}} = \frac{[\mathrm{OH}'][\mathrm{Cl}^{\bullet}]}{[\mathrm{HOCl}]} \Big/ \frac{[\mathrm{Cl}'][\mathrm{Cl}^{\bullet}]}{[\mathrm{Cl_2}]} = \frac{[\mathrm{Cl_2}][\mathrm{OH}'][\mathrm{H}^{\bullet}]}{[\mathrm{Cl}'][\mathrm{HOCl}][\mathrm{H}^{\bullet}]} = \frac{K_W}{K_J},$$

where K_J is the hydrolysis constant of chlorine (Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613) and equals $4{\cdot}84 \times 10^{-4}$. Similar expressions hold for bromine and for iodine, the hydrolysis constants being $5{\cdot}2 \times 10^{-9}$ and 3×10^{-13} respectively (Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485; Bray, *ibid.*, 1910, **32**, 932). On substituting these values in the above expression, the ionisation constants of chlorine and hypochlorous acid will be in the ratio $4{\cdot}5 \times 10^{10}$ to 1; and one would expect that their chlorinating efficiencies would be in the same ratio. The corresponding values for bromine and iodine and their hypohalous acids are 5×10^5 and 30 respectively. Thus, whilst hypochlorous acid would have little chlorinating effect in comparison with free chlorine, we should expect the effects of iodine and hypoiodous acid to be of the same order of magnitude.

In order to test this theory of halogenation by positive halogen ion, the chlorination of phenols has been studied, using hypochlorous acid and chlorine as chlorinating agents. The much greater stability of hypochlorous acid (as compared with hypobromous and hypoiodous acids) has allowed of a sharp differentiation between the mechanisms of substitution of phenols by these two chlorinating agents.

The mechanism of the interaction with hypochlorous acid was investigated by the isolation method. The reaction speed is approximately proportional to the phenol and hypochlorous acid concentrations, and is greatly affected by the alkalinity or acidity of the mixture. In acid and in dilute alkaline solutions (hydroxyl-ion concentration in the neighbourhood of 10^{-7}) the reaction speed increases in direct proportion to the hydroxyl-ion concentration until it becomes too rapid for measurement. In more strongly alkaline solution (hydroxyl-ion concentration about 10^{-2}), the speed decreases to measurable dimensions, and is now inversely proportional to the hydroxyl-ion concentration.

These facts can be interpreted in two ways. Interaction may take place either between the phenol molecule and the hypochlorite ion or between hypochlorous acid and the phenoxide ion, the reaction speed being given by the alternative equations

$$v = k_2'[\mathrm{OCl}'][\mathrm{PhOH}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$v = k_2[\mathrm{HOCl}][\mathrm{PhO}'] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

On both hypotheses addition of alkali, by causing increased ionisation, would first increase and then decrease the speed as was observed. The alternative hypotheses cannot, however, be differentiated by studying the reaction between a simple phenol and hypochlorous acid, since it follows from the ionic equilibria of hypochlorous acid and a phenol that

$$[\mathrm{OCl}'][\mathrm{PhOH}]/[\mathrm{HOCl}][\mathrm{PhO}'] = K_a'/K_a'' = \text{constant},$$

where K_a' and K_a'' are the respective ionisation constants. It is obvious that any test of the first explanation will be equally satisfactory when applied to the second explanation, if it is based on the constancy of k_2 or k_2'.

It is shown later from other evidence that the mechanism involves the phenoxide ion and hypochlorous acid. The constant k_2, rather than k_2', is therefore calculated in the following preliminary proof of the correctness of the suggested mechanism of the reaction.

The calculation of the velocity coefficient in the presence of excess of alkali involves the hydrolysis constant of sodium hypochlorite (Soper, J., 1924, **125**, 2227), since the hypochlorous acid and the phenol are present almost entirely as ions, sodium hypochlorite and phenoxide in the presence of $N/10$-hydroxyl-ion being hydrolysed only to the extent of 0·1 and 0·001% respectively.

$$dx/dt = k_2[\mathrm{HOCl}][\mathrm{PhO}'] = k_2K_h'/[\mathrm{OH}'] . [\mathrm{OCl}'][\mathrm{PhO}']$$
$$= k_2K_h'/[\mathrm{OH}'] . (b - x)(a - x)$$

or

$$\frac{k_2K_h'}{[\mathrm{OH}']} = \frac{1}{t(a - b)}\ln\frac{b(a - x)}{a(b - x)}$$

where K_h' represents the hydrolysis constant of the hypochlorite.

The terms $a - x$ and $b - x$ in this equation represent the activities of the hypochlorite and phenoxide ions which are some fraction of the concentrations of sodium hypochlorite and phenoxide, respectively, dependent on the ionic strength (Lewis and Randall, " Thermodynamics," 1924) of the mixture. In the absence of data on the activities of these ions, we have taken them as equal to the concentrations of their respective salts. The effective concentration of the hydroxyl ion was taken as the product of the concentration of free base and its appropriate activity coefficient. The results obtained at 25·0° with *p*-cresol and alkaline hypochlorite are in Table I, where time is shown in minutes.

TABLE I.

[HOCl] $= 10^{-3}$; [*p*-cresol] $= 2 \times 10^{-3}$; [NaOH] $= 0{\cdot}019$; γ[OH′] $= 0{\cdot}01424$.

Time.	[OCl′] $\times 10^4$.	$k_2 \times 10^{-5}$.
0	8·28	—
4·03	5·51	8·59
6·78	4·26	8·75
9·67	3·19	9·26
13·08	2·13	10·3
17·15	1·48	10·5

[HOCl] $= 10^{-3}$; [*p*-cresol] $= 2 \times 10^{-3}$; [NaOH] $= 0{\cdot}038$; γ[OH′] $= 0{\cdot}02904$.

Time.	[OCl′] $\times 10^4$.	$k_2 \times 10^{-5}$.
0	8·90	—
3·40	7·44	8·39
7·88	5·95	8·59
11·65	4·93	8·82
15·75	4·03	9·10
21·03	3·07	9·60
27·23	2·24	10·1

Another experiment, in which [HOCl] $= 10^{-3}$; [*p*-cresol] $= 10^{-2}$; [NaOH] $= 10^{-1}$; γ[OH′] $= 0{\cdot}0712$, gave values of $k_2 \times 10^{-5}$ which gradually decreased from 9·37 to 8·70.

The velocity coefficient can also be calculated from measurements of the reaction speed in water. The ionisation constants of hypochlorous acid (Soper, *loc. cit.*) and of *p*-cresol (Boyd, J., 1915, **107**, 1538) are $1{\cdot}0 \times 10^{-8}$ and $0{\cdot}67 \times 10^{-10}$, respectively. The hydrogen-ion concentration will therefore be governed by the hypochlorous acid, and in *M*/1000-solution will be $3{\cdot}1 \times 10^{-6}$, but will increase slightly in concentrated solutions of *p*-cresol. During the reaction, hypochlorous acid disappears, and it might be anticipated that the acidity of the mixture would diminish. Actually indicators show that at the conclusion of the reaction the acidity has slightly increased. This is probably due to a very slight reduction of the hypochlorous acid, for even traces of hydrochloric acid would materially affect the hydrogen-ion concentration. In the calculations which follow, the hydrogen-ion concentration has been regarded as constant.

In aqueous solution both hypochlorous acid and *p*-cresol are mainly un-ionised. The concentration of the phenoxide-ion will be determined by the acidity of the solution and the ionisation constant of the cresol, thus

$$[\mathrm{R{\cdot}O'}] = K_a''[\mathrm{R{\cdot}OH}]/[\mathrm{H}^{\cdot}].$$

The velocity is given by

$$dx/dt = k_2[\mathrm{R{\cdot}O'}][\mathrm{HOCl}] = k_2[\mathrm{HOCl}]{\cdot}K_a''[\mathrm{R{\cdot}OH}]/[\mathrm{H}^{\cdot}] = k_2K_a''(b - x)(a - x)/[\mathrm{H}^{\cdot}]$$

or

$$\frac{k_2K_a''}{[\mathrm{H}^{\cdot}]} = k = \frac{1}{t(a - b)}\ln\frac{b(a - x)}{a(b - x)}.$$

Mixtures were used in which the hypochlorous acid was $M/1000$, and the *p*-cresol concentration varied from 10^{-3} M to 4×10^{-2} M. Table II shows one experiment in detail, and Table III summarises all the experiments.

Table II.

$[\mathrm{R{\cdot}OH}] = 10^{-2}$; $[\mathrm{HOCl}] = 10^{-3}$.

Time.	[HOCl] $\times 10^3$.	$k_2K_a''/[\mathrm{H}^{\cdot}]$.
0	0·821	—
3·60	0·583	9·81
6·85	0·449	9·16
7·97	0·402	9·39
9·57	0·362	8·96

TABLE III.

[R·OH] $\times 10^3$.	k.	$[\mathrm{H}^{\cdot}]$ $\times 10^6$.	$k_2 \times 10^{-5}$.
1	19·5	3·17	9·23
2	13	3·19	6·19
5	10	3·22	4·81
10	9·3	3·26	4·53
20	8·8	3·37	4·43
40	8·0	3·55	4·24

The higher value for the velocity coefficient when equimolar quantities of hypochlorous acid and cresol interact is due to the chlorination of the chlorocresol formed. The average value for the velocity coefficient in aqueous solution when excess of the cresol is present may be taken as 5×10^5, as compared with the value 10×10^5 in alkaline solution. The lower value obtained in water is probably to be attributed partly to the fact that activities are not accurately represented by concentrations, partly to some uncertainty in the ionisation constants concerned, and partly to the effect of the presence of other substances on the degrees of ionisation.

The addition of acids, with the exception of hydrochloric acid, decreased the observed speed. The effect of hydrochloric acid doubtless depends on the formation of chlorine, and is dealt with in Section 2.

The comparison of velocity coefficients calculated from the observed speeds in aqueous and in strongly alkaline solution is a stringent test of the mechanism, as it involves concentrations of the reacting species which differ by several thousand times in the two cases. This test has been repeated for other phenols. The results are summarised in Table IV.

TABLE IV.

[R·OH].	[HOCl].	[H·] × 10⁶.	[NaOH].	γ[OH'].	k_2.
Phenol ($K_a'' = 1·1 \times 10^{-10}$).					
0·005	0·0010	3·24	—	—	$3·24 \pm 0·27 \times 10^5$
0·010	0·0010	—	0·10	0·0712	$3·34 \pm 0·07 \times 10^5$
0·010	0·0010	—	0·04	0·0249	$3·21 \pm 0·08 \times 10^5$
o-*Chlorophenol* ($K_a'' = 7·7 \times 10^{-10}$).					
0·004	0·0010	3·61	—	—	$10·6 \pm 0·7 \times 10^4$
0·010	0·0010	—	0·10	0·0712	$5·9 \pm 0·1 \times 10^4$
m-*Cresol* ($K_a'' = 0·98 \times 10^{-10}$).					
0·002	0·0010	3·19	—	—	$3·50 \pm 0·18 \times 10^6$
0·002	0·0005	—	0·50	0·373	$4·38 \pm 0·03 \times 10^6$
o-*Nitrophenol* ($K_a'' = 7·5 \times 10^{-8}$).					
0·004	0·0010	18·3	—	—	$1·65 \pm 0·13 \times 10^3$
0·010	0·0010	—	0·015	0·004	$1·01 \pm 0·02 \times 10^3$
p-*Nitrophenol* ($K_a'' = 9·6 \times 10^{-8}$).					
0·010	0·0010	31·0	—	—	$1·40 \pm 0·10 \times 10^3$
0·010	0·0010	—	0·015	0·004	$0·68 \pm 0·03 \times 10^3$

The agreement between the velocity coefficients calculated over such exceptionally wide ranges of concentration is satisfactory and shows that the mechanism proposed is of general character; moreover, it eliminates the possibility of concurrent interaction of the hypochlorite ion with the phenoxide ion.

In order to differentiate between the two possible mechanisms of chlorination of a phenol by hypochlorous acid, the chlorination of salicylic acid has been studied. Here the alternative mechanisms become

$$v = k_2'[HO·C_6H_4·CO_2H][OCl'] \quad . \quad . \quad . \quad . \quad (3)$$

$$v = k_2['O·C_6H_4·CO_2'][HOCl] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this case, unlike that of a simple phenol, the expression representing k_2/k_2' is not constant, but is inversely proportional to the hydroxyl-ion concentration. It is therefore possible, by examination of the speed of reaction in media of different hydroxyl-ion concentrations, to differentiate between the two theories, for on one mechanism only will velocity coefficients be obtained which are independent of the alkalinity of the medium.

The second ionisation constant of salicylic acid (Senter and Bulle, J., 1912, **101**, 2532) is approximately 1×10^{-13}. In *N*/10-hydroxyl ion the disodium salt is 50% hydrolysed, and in *N*-hydroxyl ion 9% hydrolysed. If the interaction involves the hypochlorite ion, then the speed, on change of the alkalinity from *N*/10 to *N*, will be decreased 55 times,* whilst if the phenoxide ion is involved the

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* The ratio of undissociated acid to monosodium salt is decreased 10 times and the monosodium salt concentration is decreased 5·5 times, giving a total decrease in the concentration of the undissociated acid of 55 times. The hypochlorite-ion concentration remains unaltered. The calculation is approximate, as the activities are not known.

corresponding decrease will be certainly less than 10 times (due to a 10-fold decrease in the un-ionised hypochlorous acid) since the concentration of the phenoxide ion has been increased 1·8 times, giving a net decrease of 5·5 times. Actually the observed decrease is 2·7 times, which is in favour of the phenoxide-ion theory.

TABLE V.

[Salicylic acid] = 10^{-2}; [HOCl] = 10^{-3}; $v = d[\mathrm{OCl}']/dt$ (in mols./min.).

	[NaOH] = 0·10.		[NaOH] = 0·20.		[NaOH] = 1·00.	
$[\mathrm{OCl}'] \times 10^3$.	t.	$v \times 10^5$.	t.	$v \times 10^5$	t.	$v \times 10^5$.
0·9	2·00	1·53	2·00	1·24	7·75	0·59
0·8	8·90	1·39	10·25	1·18	25·60	0·51
0·7	16·75	1·18	19·00	1·05	46·00	0·44
0·6	26·00	1·06	29·85	0·90	100·00	0·37

Further confirmation of the theory that the reaction involves the phenoxide ion is obtained from the behaviour in the initial stages of the reaction. The phenomenon is particularly clearly defined with *p*-nitrophenol, but is of general occurrence. If sodium hypochlorite is mixed with the phenol, the reaction proceeds smoothly without initial disturbance. If, however, sodium phenoxide be mixed with hypochlorous acid, as much as 35% of the hypochlorous acid may disappear before a portion of the solution can be removed for titration. The reaction after the initial disturbance is normal. The initial fall of titre in the one case is obviously due to the high concentrations of hypochlorous acid and phenoxide ion. An example of this effect is given in Table VI.

TABLE VI.

HOCl (10^{-3}) added to *p*-nitrophenol (10^{-2}) and NaOH ($1·5 \times 10^{-2}$).		*p*-Nitrophenol (10^{-2}) added to HOCl (10^{-3}) and NaOH ($1·5 \times 10^{-2}$).	
Time.	$[\mathrm{OCl}'] \times 10^4$.	Time.	$[\mathrm{OCl}'] \times 10^4$.
0	10	0	10
0·93	6·44	0·93	9·74
4·97	6·29	4·63	9·60
12·00	6·17	27·97	9·11

2. *Chlorination of Phenols and Phenolic Ethers by Chlorine.*

The presence of small traces of hydrochloric acid has a great effect on the speed of interaction of hypochlorous acid and a phenol. The speed is independent of the concentration and nature of the phenol, and is dependent on the hypochlorous acid concentration and the square of the hydrochloric acid concentration, thus :

$$v = k_1[\mathrm{H}^{\cdot}][\mathrm{Cl}'][\mathrm{HOCl}] = k_1[\mathrm{HCl}]^2[\mathrm{HOCl}] \quad . \quad . \quad . \quad (5)$$

It is obvious that the speed measured is that of the formation of chlorine from hydrochloric and hypochlorous acids,* the chlorine immediately reacting with the phenolic substance present. Using *p*-nitrophenol, a slower speed is observed, but on increasing its concentration the same limiting speed is obtained. Chlorine, therefore, chlorinates a phenol more rapidly than does hypochlorous acid. Some of the observed results obtained at 25·0° are in Table VII.

TABLE VII.

$[HCl] = 2 \times 10^{-4}$; $[HOCl] = 10^{-3}$.

Substance.	*p*-Cresol.	Phenol.	Phenetole.	Anisole.	*p*-Nitrophenol.
Conc. to give limiting speed	$<2 \times 10^{-3}$	$<2 \times 10^{-3}$	4×10^{-3}	10^{-2}	10^{-2}
$k \times 10^{-6}$	2·17	2·14	2·16	2·14	2·06

The velocity coefficient is unimolecular, since the concentration of the hydrochloric acid is constant, each molecule of chlorine which reacts with the phenol giving one molecule of hydrochloric acid, which in turn forms chlorine.

3. *The Action of Hypochlorous Acid on Phenolic Ethers.*

In dilute alkali, in which the existence of chlorine is excluded, no fall in titre of the mixture of ether and hypochlorous acid is observed. In water, however, a slow reaction occurs, the rate of which is only slightly dependent on the concentration of the ether present, and is thus probably due to chlorine. It is concluded that there is no detectable interaction between hypochlorous acid and the ether. By purification of the hypochlorous acid, as described in the experimental section, it was found that only a 2% loss of titre in 4 hours was experienced in a mixture of aqueous anisic acid and hypochlorous acid at 25°. This behaviour supports the theory that hypochlorous acid reacts with the phenoxide ion. Anisole, phenetole, and anisic acid cannot form the phenoxide ion, and therefore do not react.

The behaviour of chlorine is significant. It can chlorinate the ether as well as the phenol, so that the chlorination of phenolic

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* This velocity of formation of chlorine allows of the calculation of the speed of hydrolysis of chlorine, which is generally regarded as extremely rapid. The hydrolysis constant $[HOCl][H^{\cdot}][Cl']/[Cl_2]$ is $4{\cdot}84 \times 10^{-4}$ (Jakowkin, *loc. cit.*), and equals the ratio of the velocity coefficient of hydrolysis (k') to that of formation of chlorine by the reversible reaction (k)

$$HCl + HOCl \underset{k'}{\overset{k}{\rightleftharpoons}} Cl_2 + H_2O.$$

Thus $k'/k = 4{\cdot}84 \times 10^{-4}$, whence $k' = 1{\cdot}06 \times 10^{3}$. The speed of hydrolysis of chlorine is therefore relatively slow.

substances does not necessarily involve the phenoxide ion. This does not exclude the possibility of reaction between chlorine and the phenoxide ion in a solution of a phenol.

4. *Reactivity and Constitution.*

The velocity coefficients of chlorination by hypochlorite of a number of phenols have been measured at 25·0°, chiefly in alkaline solution because control of the hydroxyl-ion concentration is facilitated. The results are in Table VIII.

TABLE VIII.

	k_2.	K_a''.	$k_2\,K_a''$.
Phenol	$3{\cdot}3 \times 10^{5}$	$1{\cdot}1 \times 10^{-10}$	$3{\cdot}63 \times 10^{5}$
o-Cresol	$1{\cdot}25 \times 10^{6}$	$0{\cdot}63 \times 10^{-10}$	$7{\cdot}88 \times 10^{-5}$
m-Cresol	$4{\cdot}4 \times 10^{6}$	$0{\cdot}98 \times 10^{-10}$	$42{\cdot}00 \times 10^{-5}$
p-Cresol..........................	$9{\cdot}0 \times 10^{5}$	$0{\cdot}67 \times 10^{-10}$	$6{\cdot}0 \times 10^{-5}$
o-Chlorophenol..................	$5{\cdot}9 \times 10^{4}$	$7{\cdot}7 \times 10^{-10}$	$4{\cdot}55 \times 10^{-5}$
p-Chlorophenol	$4{\cdot}90 \times 10^{4}$	$4{\cdot}1 \times 10^{-10}$	$2{\cdot}0 \times 10^{-5}$
3-Chloro-*p*-cresol	$1{\cdot}67 \times 10^{5}$		
o-Nitrophenol	$1{\cdot}01 \times 10^{3}$	$7{\cdot}5 \times 10^{-8}$	$7{\cdot}58 \times 10^{-5}$
m-Nitrophenol	$5{\cdot}89 \times 10^{3}$	$1{\cdot}0 \times 10^{-8}$	$5{\cdot}89 \times 10^{-5}$
p-Nitrophenol	$6{\cdot}84 \times 10^{2}$	$9{\cdot}6 \times 10^{-8}$	$6{\cdot}57 \times 10^{-5}$
1 : 3 : 4-Xylenol	$2{\cdot}02 \times 10^{6}$		

The velocity coefficients differ considerably from one another, but the products of the velocity coefficient and the ionisation constant of the phenols are grouped in a noteworthy manner about the value 7×10^{-5}. It appears that the reactivity of the phenoxide ion is proportional to its affinity for hydrogen ion. Those ions derived from phenols of high ionisation constant are least reactive. These results may be compared with those of Boyd and Thomas (J., 1919, **115**, 1239), who found a similar relation between the rates of interaction of phenoxide ions with olefine oxides.

5. *Discussion.*

1. Since the speed of interaction of a phenol and hypochlorous acid is proportional to the product of the concentrations of the un-ionised acid and the phenoxide ion, the halogenating agent cannot be the positive halogen ion, for its concentration is proportional to the hypohalous acid concentration divided by that of the hydroxyl ion, *i.e.*, $[Cl^{\bullet}] = K[HOCl]/[OH']$. The idea must also be abandoned in the case of chlorine, as its speed of chlorinating acetanilide, for example (Orton and King, J., 1911, **109**, 1369), is independent of the excess of chlorine ions present. It appears that the molecules of chlorine or of hypochlorous acid react as whole molecules, and that therefore an intermediate complex must exist as a transient stage of the reaction.

2. It is probable that the theory of the reactivity of the phenoxide ion which has been proved for the interaction of hypochlorous acid and phenols also applies to the similar reactions involving hypobromous and hypoiodous acids. The conclusion of Vortmann (*Ber.*, 1923, **56**, 234) that the alkali hypoiodite is the effective iodinating agent is based on evidence which also supports the mechanism involving the phenoxide ion. We find that the speed of iodination is decreased in strong alkaline solution, which can be explained by the great decrease in the concentration of the un-ionised hypoiodous acid.

3. Hypochlorous acid does not react with phenolic ethers, since they do not form the phenoxide ion, but chlorine interacts easily with both phenols and ethers. It is probable, however, that the interaction of chlorine with the phenol involves both the highly reactive phenoxide ion and the un-ionised phenol. Any alteration in the degree of ionisation of the phenol might be expected to alter the proportions of the isomeric products formed. Thus Arnall (J., 1924, **125**, 811) found that the proportions of *o*-, *m*-, and *p*-nitrophenols formed on nitration varied with the concentration of nitric acid present. This observation is consistent with the present theory of the reactivity of the phenoxide ion, the concentration of which varies with the acidity of the medium. The slower speed of bromination by bromine water in strong acid solution attributed by Francis (*loc. cit.*) to a decrease in the concentration of " nascent " bromine is also naturally explained on the present theory by the decrease in concentration of the phenoxide ion, the bromination of which is probably faster than that of the un-ionised molecule.

EXPERIMENTAL.

Method of Titration.—The course of a reaction was followed by estimation of the iodine liberated by the hypochlorous acid from acidified potassium iodide. The titration of iodine in the presence of a phenol must be carried out in acid solution in order to prevent interaction of the iodine and phenol. The consequent presence of free hydriodic acid, which is easily oxidised, is a source of error in the titration. The difficulty was overcome by using oxygen-free solutions and carrying out the titration in an atmosphere of nitrogen (compare Soper, J., 1924, **125**, 1899). Perfectly sharp end-points, with $N/500$-thiosulphate, were obtained in this way, even in the presence of $3N$-sulphuric acid.

Preparation and Purification of Hypochlorous Acid.—The hypochlorous acid was prepared by passing chlorine into water containing yellow mercuric oxide in suspension, or by distillation of a bleaching powder solution through which carbon dioxide was passed. Both specimens of hypochlorous acid behaved in the same way after purification. Two methods of purification were used : (*a*) repeated distillation of the hypochlorous acid from yellow mercuric oxide under reduced pressure ; (*b*) simply shaking the hypochlorous acid with yellow mercuric oxide and after some time filtering off the oxychloride. The latter method was the one finally adopted, since the distillation method gave a hypochlorous acid which, on addition of sulphuric acid, formed traces of chlorine, the presence of which was manifested by the greater rate of reaction with phenol.

Purity of Phenols.—Kahlbaum specimens were purified either by several crystallisations from suitable solvents or by distillation, preferably under reduced pressure. Two distillations were usually found sufficient to give a pure phenol, the reactivity of which was unaltered by further distillation.

Water.—A high grade of conductivity water was used throughout. In such water a sample of hypochlorous acid showed no fall of titre in 60 hours.

Summary.

1. The interaction of phenols with hypochlorous acid in aqueous and in alkaline solution has been shown to involve the phenoxide ion and the un-ionised hypochlorous acid.

2. The reactivity of the ion with hypochlorous acid is least when the phenol from which it is derived is most strongly acidic. The reactivity of the ions of the simple phenols is roughly proportional to their affinity for hydrogen ions.

3. The chlorination of phenols and phenolic ethers by chlorine is a much faster reaction than the rate of formation of chlorine from a mixture of hydrochloric and hypochlorous acids, the velocity coefficient of which is $2{\cdot}2 \times 10^6$ at 25°. The calculated velocity coefficient of the hydrolysis of chlorine at this temperature is $1{\cdot}06 \times 10^3$.

4. The mechanism of halogenation of phenols is discussed.

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