A Kinetic Study of the Formation and Hydrolysis of tert.*-Butyl Hypochlorite.*

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The formation of *tert.*-butyl hypochlorite from the alcohol and hypochlorous acid and its hydrolysis have been investigated in a series of buffer solutions ranging in pH from 6·3 to 2·7. By the use of ^{18}O as tracer it has been shown that in both reactions the bond between the *tert.*-butyl group and the oxygen atom remains intact. Kinetic investigations showed the reaction to be subject to general acid–base catalysis. The rate coefficients for a number of catalysts have been determined. A mechanism of these reactions is postulated involving various active intermediates such as H_2OCl^+, acetyl hypochlorite, and other related compounds of the type ACl, where A is the anion of any general acid. The relationship between the reactions of *tert.*-butyl hypochlorite and those of hypochlorous acid is discussed.

As part of a broader investigation we have examined the formation and hydrolysis of *tert.*-butyl hypochlorite. This ester was chosen because it is one of the most stable of alkyl hypochlorites and because of the interest in its reactions with various organic compounds.

Alkyl hypochlorites are formed readily when chlorine is passed into a solution of an alcohol in aqueous alkali, and also when an alcohol is treated with sodium hypochlorite solution (Sandmeyer, *Ber.*, 1885, **18**, 1767; 1886, **19**, 859; Chattaway and Backeberg, *J.*, 1923, **123**, 2999). *tert.*-Butyl hypochlorite is also formed easily by the action of the alcohol on free hypochlorous acid in aqueous solution or on chlorine monoxide in carbon tetrachloride solution. On the other hand, it undergoes rapid hydrolysis when shaken with dilute alkali, but remains unchanged after prolonged shaking with aqueous acid. These apparently conflicting results are now to be explained.

As a first stage in the elucidation of the mechanisms of the hydrolysis and formation reactions of *tert.*-butyl hypochlorite, we have determined the mode of fission of the hypochlorite linkage. The alternative modes of bond breaking are shown in the reaction schemes below, where the dotted line represents the linkage which is broken :

$$\mathrm{Bu^tO\cdots Cl} + \mathrm{H_2O} \rightleftharpoons \mathrm{H{-}O\cdots Cl} + \mathrm{Bu^tO\cdots H} \qquad (1)$$

$$\mathrm{Bu^t\cdots O{-}Cl} + \mathrm{H_2O} \rightleftharpoons \mathrm{H\cdots O{-}Cl} + \mathrm{Bu^t\cdots O{-}H} \qquad (2)$$

By the use of compounds labelled with ^{18}O it is possible to distinguish between the two paths. Formation reactions were carried out by starting with alcohol of normal isotopic composition and water enriched in ^{18}O and also with alcohol enriched in ^{18}O and normal water. The results of the isotopic experiments are summarised in Table 1.

TABLE 1. *Isotopic changes in the formation of* tert.*-butyl hypochlorite.*

	Atom % excess of ^{18}O in aqueous medium	Atom % excess of ^{18}O in *tert.*-butanol	Atom % excess of ^{18}O in *tert.*-butyl hypochlorite	Atom % excess of ^{18}O in water recovered
N-NaOH...	0·85	0·00	0·00	0·84
	0·00	0·86	0·79	0·00
N-$HClO_4$...	0·00	0·86	0·76	0·00

A similar study was made of the hydrolysis of *tert.*-butyl hypochlorite, starting with ^{18}O-labelled compound and normal water, and also in one case starting with enriched water and normal hypochlorite. The results are presented in Table 2.

TABLE 2. *Isotopic changes in the hydrolysis of* tert.*-butyl hypochlorite.*

	Atom % excess of ^{18}O in aqueous medium	Atom % excess of ^{18}O in *tert.*-butyl hypochlorite	Atom % excess of ^{18}O in *tert.*-butanol
5N-NaOH	0·00	0·86	0·85
	0·00	0·79	0·78
	0·87	0·00	0·00
1N-$HClO_4$	0·00	0·79	0·77

The isotopic data show unambiguously that the formation and hydrolysis reactions proceed under all conditions according to scheme (1), the bond between the alkyl group and the oxygen atom remaining intact throughout. Isotopic results alone, however, are not sufficient to indicate details of mechanism although they limit considerably the number of possible reaction schemes. Further information regarding these reactions was sought by a kinetic investigation.

No chemical method is available for following the rate of interconversion of hypochlorous acid and an alkyl hypochlorite, since the two materials undergo identical reactions with most reagents. However, it was shown by the authors (*J.*, 1954, 1105) that differences exist in the ultra-violet absorption spectra of the two compounds. Use was made of these differences for following the progress of hydrolysis or formation reactions, the change of ultra-violet light absorption with time representing the rate of reaction. Rate constants were calculated from the formula

$$k_{\text{obs.}} = (1/2{\cdot}3t) \log (D_\infty - D_0)/(D_\infty - D_t) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $k_{\text{obs.}}$ is the rate constant of the reaction, and D_0, D_t, and D_∞ are the optical densities at times 0, t, and ∞. Since these reactions are reversible, and of first order either way, the observed rate constant $k_{\text{obs.}}$ is composed of the sum of the rate constants of the forward and the reverse reaction, $k_{\text{obs.}} = k_f + k_h$. Whenever possible the rate constants were observed both for the formation and for the hydrolysis reaction and the means of these results used. The observed rate constant may be resolved into its components with the aid of the equilibrium constant for the reaction. It can be readily shown that

$$K \frac{[H_2O]}{[Bu^tOH]} = \frac{C(\varepsilon_2 - \varepsilon_1)}{C\varepsilon_2 - D_\infty} - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is the equilibrium constant for the hydrolysis reaction, C the initial concentration of *tert.*-butyl hypochlorite, and ε_1 and ε_2 the extinction coefficient of *tert.*-butyl hypochlorite and hypochlorous acid in l. mole^{-1} cm.$^{-1}$. From over 200 experiments the value of K at

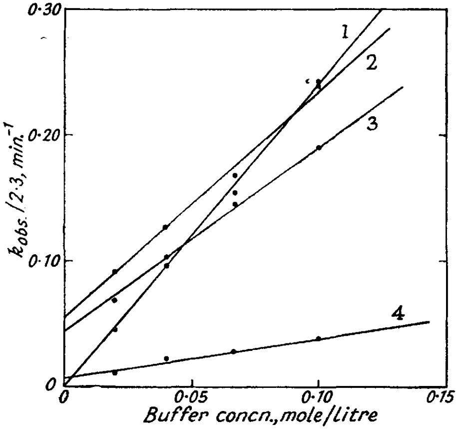
25° has been obtained as 0·024 ± 0·003. Most of the rate constants presented in this paper have not been resolved into their components.

The reactions were carried out in aqueous solutions containing some *tert.*-butanol (usually 1·55 mole/l.) and maintained at the appropriate pH value by means of buffers. The presence of *tert.*-butanol is necessary in order to ensure complete solubility of the *tert.*-butyl hypochlorite. The rates were found to depend both upon the pH of the solution and upon the buffer concentration. For runs at constant pH and ionic strength the rates were found to be a linear function of the buffer concentration :

$$k_{\text{obs.}} = k' + k_{\text{buffer}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

For each value of pH a set of such linear equations was obtained, and after solving them by the method of least squares, the constants k' and k_{buffer} were obtained. A few of the results are tabulated in Table 3, and as an illustration plots of $k_{\text{obs.}}$ against buffer concentration for various pH values are shown in Fig. 1.

Fig. 1. *Effect of buffer concentration on rate of hydrolysis of* tert.*-butyl hypochlorite.*



1, Acetate buffer, pH 4·5.
2, Phosphate buffer, pH 5·85.
3, Acetate buffer, pH 5·4.
4, Phosphate buffer, pH 3·9.

Fig. 2. *Effect of* pH *on rate of hydrolysis and formation of* tert.*-butyl hypochlorite.*

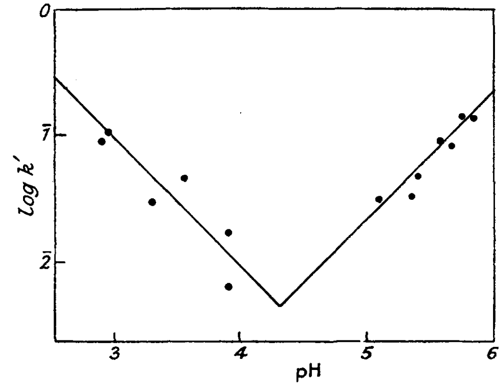


Table 3. *Values of k' and k_{buffer} for the hydrolysis and formation of* tert.*-butyl hypochlorite at various* pH *values at 25°.*

		k_{buffer}, l./mole/min.				k_{buffer}, l./mole/min.	
pH	k', min.$^{-1}$ × 10^2	acetate	phosphate	pH	k', min.$^{-1}$ × 10^2	acetate	phosphate
2·90	9·0	8·2	—	5·43	4·2	2·2	—
2·95	10·3	—	3·3	5·58	8·6	—	3·18
3·57	7·2	4·65	—	5·75	13	1·8	—
3·9	1·7	—	0·72	5·85	13	—	4·0

The constants k' and k_{buffer} obtained in this way are composite and require further resolution. In Fig. 2 the values of log k' are plotted against pH and, as will be noticed, a pronounced minimum in the rate occurs at a pH value of about 4·4. For the purpose of this paper we shall refer to media with pH values lower than 4·4 as acid, and those with pH higher than 4·5 will be called basic. It is apparent that the reaction is catalysed both by hydrogen and by hydroxyl ions and therefore k' should be of the form

$$k' = k_w + k_{\text{H}}[\text{H}^+] + k_{\text{OH}}[\text{OH}^+] \quad . \; . \; . \; . \; . \; . \quad (4)$$

where k_w is the rate coefficient of the uncatalysed reaction, and k_{H} and k_{OH} are the catalytic rate coefficients for the hydrogen and the hydroxyl ion, respectively. Again applying the method of least squares to the set of these equations, we obtain the following values for the three constants: $k_w = 1{\cdot}6 \times 10^{-4}$ min.$^{-1}$; $k_{\mathrm{H}} = 1{\cdot}3 \times 10^{2}$ l. mole^{-1} min.$^{-1}$; $k_{\mathrm{OH}} = 2{\cdot}7 \times 10^{7}$ l. mole^{-1} min.$^{-1}$ at 25°. Equation (4) can be rewritten in the form:

$$k' = k_w + k_{\mathrm{H}}[\mathrm{H}^+] + k_{\mathrm{OH}} \times 10^{-14}/[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

and from this the pH value for which a minimum in the rate should occur can be calculated to be

$$[\mathrm{H}^+] = 10^{-7}\sqrt{k_{\mathrm{OH}}/k_{\mathrm{H}}}$$

Substituting the values obtained above in this equation, we obtain for $\mathrm{pH}_{\mathrm{min.}}$ the value 4·4, and for the minimum rate the value $\sim 10^{-2}$ min.$^{-1}$.

The total buffer catalytic coefficient, k_{buffer}, can be written as

$$k_{\mathrm{buffer}} = k_{\mathrm{HA}}[\mathrm{HA}] + k_{\mathrm{A}^-}[\mathrm{A}^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where k_{KA} and k_{A^-} are the catalytic rate coefficients for the buffer acid and its anion respectively. Using a technique identical with that used for obtaining the other catalytic coefficients, we obtained the values for k_{HA} and k_{A^-}. The general expression for the observed rate constant is therefore given by:

$$k_{\mathrm{obs.}} = k_w + k_{\mathrm{H}}[\mathrm{H}^+] + k_{[\mathrm{OH}]}[\mathrm{OH}^-] + \Sigma k_{\mathrm{HA}}[\mathrm{HA}] + \Sigma k_{\mathrm{A}^-}[\mathrm{A}^-] \quad . \quad . \quad (6)$$

which is the classical expression for a case of general acid–base catalysis. In Table 4 are presented the catalytic rate coefficients for a number of acid anions derived from an analysis of the observed rates by the methods outlined above. It should be noted that each of the constants presented in Table 4 is derived from some 300 separate kinetic runs.

TABLE 4. *Catalytic constants of acids and their conjugate bases for the formation and hydrolysis reactions of* tert.*-butyl hypochlorite at* 25·2° *and aqueous* 1·55M-tert.*-butanol solution.*

Acid	k_{HA}	k_{A^-}	Acid	k_{HA}	k_{A^-}	Acid	k_{HA}	k_{A^-}
H_3O^+ ...	$1{\cdot}1 \times 10^{2}$	$<10^{-4}$	$CH_3{\cdot}CO_2H$	5·7	$3{\cdot}1 \times 10^{-1}$	HClO ...	$2{\cdot}4 \times 10$	$9{\cdot}1 \times 10^{3}$
H_3PO_4 ...	$8{\cdot}2 \times 10$	$1{\cdot}1 \times 10^{-2}$	$H_2PO_4^-$ ...	3·6	$4{\cdot}5 \times 10$	H_2O	$<10^{-4}$	$2{\cdot}3 \times 10^{7}$

Hypochlorous acid and the hypochlorite ion are both catalysts for the hydrolysis and the formation reaction. This fact causes a certain amount of trouble in interpreting the kinetic measurements, for the concentration of these materials changes in the course of the reaction. This effect can be seen from the results of Table 5, where the observed rates are tabulated for various initial concentrations of hypochlorous acid.

TABLE 5. *The effect of initial concentration of hypochlorous acid on the rate of formation of* tert.*-butyl hypochlorite in* M/50*-acetate buffer solution and at* pH 4·7.

$10^3 \times$ Initial concn. (M) of HOCl	17·7	15·3	12·0	9·45	6·45
$10^3\ k_{\mathrm{obs.}}$, min.$^{-1}$	262	249	235	226	205

Fortunately, the catalytic coefficients of hypochlorous acid and its ion are sufficiently small to be neglected, except in the region of the rate minimum and low buffer concentrations. From experiments in this range the value of the catalytic coefficients for hypochlorous acid (and ion) and other weak acids can be determined. The resolution of the kinetic data to yield various coefficients in this range is complicated by the presence of the square term in the rate equations. We may write for experiments with constant buffer composition and concentration:

$$\mathrm{d}[\mathrm{HOCl}]/\mathrm{d}t = -[\mathrm{HOCl}]\{k_1[\mathrm{HOCl}] + k'\} + [\mathrm{BuOCl}]\{k_2[\mathrm{HOCl}] + k''\} \quad . \quad . \quad (7)$$

where k_1 and k_2 are the catalytic coefficients of HOCl for the formation and the reverse reaction, and k' and k'' are of the form $\Sigma k_i C_i$, where k_i is the catalytic coefficient of the catalyst i present in the concentration C_i.

Setting $[\mathrm{Bu^tOCl}] + [\mathrm{HOCl}] = C$, and $[\mathrm{HOCl}] = x$, we have

$$\mathrm{d}x/\mathrm{d}t = -(k_1 + k_2)x^2 - [(k' + k'') - k_2C]x + k''C$$

This equation may be rewritten in the form

$$\mathrm{d}x/\mathrm{d}t = px^2 + qx + r = p(x - x_\infty)(x - x'_\infty)$$

where $p = -(k_1 + k_2)$, $q = -[(k' + k'') - k_2C]$, $r = k''C$, and x_∞ and x'_∞ are the roots of the quadratic equation $px^2 + qx + t = 0$. The differential equation may be integrated to give

$$1 + \Delta/(x - x_\infty) = R\mathrm{e}^{-p\delta t}$$

where $\Delta = x_\infty - x'_\infty$ and R is the integrating factor. Observing x at constant intervals of time, *e.g.*, at t_i, $t_i + \delta$, $t_i + 2\delta$, we may write $(1 + \Delta y_{i+1})/(1 + \Delta y_i) = \mathrm{e}^{-p\delta t}$, which can be rearranged to $1 + \Delta y_{i+1} = E(y_{i+1} - y_i)$, where $y_i = 1/(x_i - x_\infty)$ and $E = \Delta/(\mathrm{e}^{-p\delta t} - 1)$. Solution of the last equation by the method of least squares gives values of Δ and E, and thence the values of $p = -(k_1 + k_2)$; k'' can then be easily obtained if it is remembered that $k''C = r - px_\infty x'_\infty$ and that $x'_\infty = x_\infty - \Delta$.

The order of this reaction with respect to *tert.*-butanol is of some interest. In the runs described so far this reagent was present in great and constant excess, and no information as to the order of the reaction with respect to it could be derived. A number of reactions were carried out using varying concentrations of *tert.*-butanol; the results are tabulated in Table 6. From Expts. 58, 59, 60 and 216, 217, it is clear that the rate of reaction is independent of alcohol concentration. Interpretation of the results at higher concentrations of alcohol is complicated by the operation of a complex solvent effect. Variation of the proportion of alcohol or dioxan in the medium affects simultaneously several of the reaction parameters. In addition to the direct effect of the change of medium on the rate-controlling process, the dissociation constant of the buffer acid and the activity of hydrogen or hydroxyl ions will also be affected. The direction and magnitude of the latter effects are known (cf. Conway, "Electrochemical Data," Elsevier, Amsterdam, 1952, p. 196). The presence of increasing quantities of dioxan or *tert.*-butanol will cause a decrease in the concentration and activity of the hydrogen ion as compared with identical buffer solution in pure water. The effect of this on the reactions under study will be analogous to an apparent shift of pH to a higher value, and will be different on either side of the minimum in the rate. On the acid side, the addition of alcohol or dioxan will cause a reduction in the rate (cf. Expts. 225—227), whilst on the alkaline side a similar addition will cause an increase in the rate (cf. Expts. 58, 59). This effect is superimposed on that of solvent variation on the reaction rate, and the result will depend on the relative magnitude and direction of the two effects. It is therefore impossible to derive unambiguous results from the effect of solvent on the rate-determining process, and to use this safely in considerations of the mechanisms of these reactions. Somewhat similar considerations

TABLE 6. *Rates of formation and hydrolysis of* tert.*-butyl hypochlorite in presence of varying concentrations of* tert.*-butanol and dioxan.*

Expt. No.	Buffer acid concn.	Ratio of buffer acid to buffer anion	Molarity of *tert.*-butanol	Vol. % of dioxan	10^3 $k_{\text{obs.}}$, min.$^{-1}$
34	M/50-Phosphate	196 : 4	3·6	0	60
35	($H_2PO_4^-$; $HPO_4^=$)	,,	2·7	0	54
30	,,	,,	1·55	0	38
36	,,	,,	0·68	0	35
39	,,	,,	0·35	0	29
58	,,	3 : 1	0·68	0	200
59	,,	,,	0·35	0	190
60	,,	,,	0·18	0	180
214	M/25-Acetate	1 : 1	1	0	420
215	,,	,,	1	9·0	1000
216	,,	,,	1	28·6	1140
217	,,	,,	0·125	28·6	1160
225	M/50-Acetate	4 : 1	1·55	0	260
226	,,	,,	0·48	0	440
227	,,	,,	0·125	0	830

apply to the effect of changing ionic strength of the media on the reaction rates (see Table 7).

TABLE 7. *Effect of ionic strength of the buffer solution on the rate of formation and hydrolysis of* tert.*-butyl hypochlorite.*

Buffer solution, M/50		$k_{\text{obs.}}$, min.$^{-1}$ × 10^3 At $\mu = 0{\cdot}05$	$k_{\text{obs.}}$, min.$^{-1}$ × 10^3 At $\mu = 0{\cdot}45$	Buffer solution, M/50		$k_{\text{obs.}}$, min.$^{-1}$ × 10^3 At $\mu = 0{\cdot}05$	$k_{\text{obs.}}$, min.$^{-1}$ × 10^3 At $\mu = 0{\cdot}45$
Phosphate buffer	pH 5·5	250	1850	Acetate buffer	pH 5·7	420	560
	,, 5·3	330	1700		,, 5·4	1060	1210
	,, 4·8	160	1240		,, 3·8	440	530
	,, 4·6	160	900		,, 3·6	580	650
	,, 3·3	330	1090				

DISCUSSION

The kinetic and isotopic data presented in the preceding pages may be interpreted by the following general mechanism;

$$\left.\begin{aligned} \mathrm{HOCl} + \mathrm{HA} &\overset{k_1}{\rightleftharpoons} \mathrm{ACl} + \mathrm{H_2O} \\ \mathrm{ACl} + \mathrm{BuOH} &\underset{k_{-2}}{\rightleftharpoons} \mathrm{BuOCl} + \mathrm{HA} \end{aligned}\right\}\ \text{acid region}$$

$$\left.\begin{aligned} \mathrm{HOCl} + \mathrm{A^-} &\overset{k_1}{\rightleftharpoons} \mathrm{ACl} + \mathrm{OH^-} \\ \mathrm{ACl} + \mathrm{BuO^-} &\underset{k_{-2}}{\rightleftharpoons} \mathrm{BuOCl} + \mathrm{A^-} \end{aligned}\right\}\ \text{alkaline region}$$

This mechanism leads to first-order kinetics, the rate constants being given, assuming that [ACl] remains very small throughout, by expressions of the type

$$k' = k_{\mathrm{HA}}[\mathrm{HA}](k_1k_2[\mathrm{H_2O}] + k_1k_2[\mathrm{ROH}])/(k_1(\mathrm{H_2O}] + k_2[\mathrm{ROH}])$$

An essential feature of this mechanism is the participation of the intermediate ACl, derived from the catalyst HA, by a process which may be regarded either as a nucleophilic substitution on the halogen of hypochlorous acid or alkyl hypochlorite, or as a chlorination of the active hydrogen of the catalysts. For a substance HA to be an effective catalyst for the formation and hydrolysis reactions of alkyl hypochlorites, it must react with hypochlorous acid or the alkyl hypochlorite to form an intermediate compound, more reactive with respect to chlorination and hydrolysis than the parent compounds. The catalyst need not necessarily be an acid, although most of the common examples belong to this class, and in the general case the rate-determining step is not the transfer of a proton to HOCl or $\mathrm{Bu^tOCl}$.

The effectiveness of the intermediate ACl as a chlorination agent can be correlated with the electronegative character of the group A, since the more positive the chlorine atom is in these compounds, the readier will be its attack on a nucleophilic centre. Increasing the electronegativity of the group A will make the intermediate more reactive, and as a consequence a parallelism should exist between the activity of the intermediate and the strength of the acid from which it is derived. Using these considerations, we may arrange the following compounds in the order of their activity as halogenating agents:

$$\mathrm{Bu^tOCl} < (\mathrm{Bu^tOHCl})^+;\ \mathrm{Bu^tOCl} < \mathrm{HOCl} < \mathrm{CH_3{\cdot}COCl};\ \mathrm{HOCl} < (\mathrm{H_2OCl})^+;\ \mathrm{HOCl} < \mathrm{Cl_2O} < \mathrm{Cl_2}$$

Some of the catalysts encountered in our work, and the active intermediates derived from them, are listed in Table 8.

TABLE 8. *Catalysts and active intermediates in the formation and hydrolysis of alkyl hypochlorites.*

Catalysts ...	$\mathrm{H_2O}$	$\mathrm{H_3O^+}$	$\mathrm{CH_3{\cdot}CO_2H}$	$\mathrm{H_3PO_4}$	$\mathrm{H_2PO_4^-}$	$\mathrm{HPO_4^{2-}}$	HOCl	HCl	$\mathrm{H_2SO_4}$	ROH
Intermediates	HOCl	$\mathrm{H_2OCl^+}$	$\mathrm{CH_3{\cdot}CO{\cdot}OCl}$	$\mathrm{H_2PO_4Cl}$	$\mathrm{HPO_4Cl^-}$	$\mathrm{PO_4Cl^{2-}}$	$\mathrm{Cl_2O}$	$\mathrm{Cl_2}$	$\mathrm{HSO_4Cl}$	ROCl

A more detailed consideration of these catalysts will be presented below.

A special case of the general mechanism presented above occurs when the catalyst is the hydroxonium ion, H_3O^+:

$$\begin{aligned} HOCl + H_3O^+ &\overset{k_1}{\rightleftharpoons} H_2OCl^+ + H_2O \\ H_2OCl^+ + BuOH &\rightleftharpoons HOCl + BuOHCl^+ \\ BuOHCl^+ + H_2O &\underset{k_{-3}}{\rightleftharpoons} BuOCl + H_3O^+ \end{aligned}$$

with k_1 and k_{-3} rate the controlling. The intermediates in this case are the conjugate acids of hypochlorous acid and the alkyl hypochlorite. The mechanism has been expressed as proceeding in three stages in order to maintain the symmetry between the formation and the hydrolysis reactions; since, if in the formation reaction an intermediate of the type H_2OCl^+ is assumed, there seems to be no reason for excluding the intermediate $BuOHCl^+$ in the hydrolysis reaction. The rate-determining step in this special case is actually the proton transfer to the HOCl and BuOCl molecules.

For the acid region only, it is possible to formulate a general reaction scheme involving only proton transfers as rate-determining steps:

$$HOCl + HA \rightleftharpoons H_2OCl^+ + A^-$$

However, according to this formulation only one active intermediate is possible, H_2OCl^+, a limitation which appears to be unnecessarily severe, particularly as in the reactions in the alkaline region, where no generalisation based on rate-determining proton transfers is possible, we assume the existence of intermediates ACl, and we have already seen that such compounds are at least as reactive as is H_2OCl^+. We therefore prefer the more general formulation presented above.

Combining the expression for the catalytic rate coefficients (p. 1099) of the hydrolysis and formation reactions with that of the equilibrium constant, and substituting its value ($K = k_{-1}k_{-2}/k_1k_2 = 0{\cdot}024$, cf. p. 1095), we can show that, provided k_1 is not much smaller than k_{-2} and excepting solvent effects, the observed rate constant will not be particularly sensitive to changes in alcohol concentration. On general considerations (p. 1099) we should expect k_1 to be always somewhat greater than k_{-2}, and our observation of the relative independence of the rate on alcohol concentration is in complete accord with the mechanism postulated above (cf. Table VI). It follows from the same considerations that the observed rate constants will have a value between k_1 and k_{-2}, and since these rate coefficients probably do not differ very greatly from one another, we may take the observed rate constant as representing approximately the rate of formation of the active intermediate ACl. The observed catalytic coefficients discussed below have been interpreted in this way.

Another special case of our general mechanism arises in the alkaline region, if unbuffered solutions are used and the sole reagent is the hydroxyl ion. The reaction scheme then reduces to:

$$HOCl + BuO^- \rightleftharpoons BuOCl + OH^-$$

In these circumstances the rate of reaction should be of first order with respect to alcohol. However, we have not succeeded in measuring rates of reaction in unbuffered alkaline solution, and even in the most favourable case, the contribution of the buffer ions to the total rate outweighed that of the hydroxyl ion, and made the rate independent of alcohol concentration.

It is important to note, that even under the alkaline conditions used in this work, the reaction is between un-ionised hypochlorous acid and the catalyst or butoxide ion. The catalytic effect of the hydroxide ion on the formation reaction is accordingly due to its effect on the concentration of the butoxide ion. The rate equation for the formation reaction can be written as

$$v_f = k[HOCl][BuO^-] + k'[HOCl][A^-]$$

and since $[BuO^-] = K[BuOH][OH^-]$, the equation may be rewritten in the form

$$v_f = [HOCl](k''[BuOH][OH^-] + k'[A^-])$$

Soper and Smith (*J.*, 1926, 1582) have also demonstrated that the chlorination of phenol occurs by reaction between un-ionised hypochlorous acid and the phenoxide ion and not between phenol and hypochlorite ion. A great increase in the hydroxyl-ion concentration to the point where ionisation of hypochlorous acid becomes appreciable would be expected to cause a decrease in the rate commensurable with the decreased concentration of free acid. We have not succeeded in obtaining rate constants at such high pH values, but the effect may be illustrated adequately by examples taken from the preparative chemistry of alkyl hypochlorites. No *tert.*-butyl hypochlorite is formed when *tert.*-butanol is added to a strongly alkaline solution of sodium hypochlorite. It is only when the pH of the solution is reduced to below 10 that rapid separation of the hypochlorite takes place. Similarly, when chlorine is passed through an alkaline solution of *tert.*-butanol, no hypochlorite is formed until most of the alkali has been destroyed by the chlorine, whereupon a sudden separation of *tert.*-butyl hypochlorite occurs. These facts are interpreted as due to the small concentration of free hypochlorous acid in strongly alkaline solution, and the consequent suppression of the formation reaction. As the pH of the solution is reduced below 10, the concentration of un-ionised hypochlorous acid increases rapidly, and reaction with *tert.*-butoxide ions ensues.

We turn now to a more detailed discussion of the various reaction intermediates. The ion H_2OCl^+ has been assumed by Derbyshire and Waters (*J.*, 1951, 73) to be the intermediate in the acid-catalysed chlorination of sodium toluene-*p*-sulphonate by hypochlorous acid, this being analogous to the intermediate $(H_2OBr)^+$ suggested for the acid bromination of the same compound (Derbyshire and Waters, *J.*, 1950, 564; Derbyshire, *Research*, 1952, 5, 240). Derbyshire and Waters (*loc. cit.*) used rather high concentrations of acid (0·3—4M) to obtain reasonable rates of chlorination, and the kinetics were of first order in the toluenesulphonate. Using the more reactive materials, phenol and anisole, and lower concentrations (0·01—0·1M) of strong acids as catalysts, de la Mare, Hughes, and Vernon (*Research*, 1950, **3**, 192, 242) obtained rates of chlorination which were of zero order with respect to the compound substituted, and concluded that the observed rate was that of production of the positive chloronium ion Cl^+ from HOCl and a strong acid. This conclusion was criticised by Shilov (*Doklady Akad. Nauk U.S.S.R.*, 1952, **84**, 1001), who interpreted these results in terms of rate-controlling production of free chlorine from HOCl and traces of chloride ion. However, it appears from the note of de la Mare, Hughes, and Vernon (*loc. cit.*) that this possibility is excluded by the experimental precautions. In any case, the rate-controlling reaction in the chlorinations described by them cannot be the same as that found in our work. For the rate constant reported by these authors, $3{\cdot}1 \times 10^{-4}$ sec.$^{-1}$, is some 10^4 times slower than the rate-controlling step found by us under similar conditions (cf. Table 4). We interpret this difference as due to the fact that, whereas the rate observed in our case is that of the formation of H_2OCl^+, *i.e.*, the rate of proton transfer to HOCl, the rate observed by de la Mare, Hughes, and Vernon (*loc. cit.*) is that of subsequent decomposition of the H_2OCl^+ ion into Cl^+ and water. H_2OCl^+ is a less effective chlorinating agent than Cl^+ and cannot effect the chlorination of an aromatic compound, yet it is sufficiently active to effect the conversion of alcohols into hypohalites. We may illustrate our point by considering the sequence of events which will take place upon the chlorination by acidified hypochlorous acid of a series of compounds of increasing reactivity. With the least reactive compound a first-order rate with respect to substrate will be observed, changing to a zero-order rate with more reactive compounds, the rate then representing the rate of formation of Cl^+. With still more reactive compounds a first-order rate will again be observed corresponding to the reaction between H_2OCl^+ and the substance examined. With the most reactive compounds a second zero-order reaction with respect to substrate will be observed, the rate then representing the rate of formation of H_2OCl^+.

It should be noted that the rate of proton transfer to hypochlorous acid observed in the present work is probably the first measurement of such a transfer to a simple inorganic molecule (cf. Bell, " Advances in Catalysis," Vol. IV, Acad. Press, 1952, p. 135).

The chlorination of phenols may also be explained in these terms. The phenolic hydrogen is probably chlorinated rapidly to give the hypochlorite which is in equilibrium with hypochlorous acid and $(H_2OCl)^+$, the chlorination of the aromatic ring occurring by Cl^+, which is produced by the decomposition of the protonated hypochlorous acid (cf. Arkhangelskaya and Likhosherstov, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 1914).

In Table 8, Cl_2 appears as a possible intermediate if chloride ions are present. In such circumstances there will be an additional term in the general catalytic equation (6) (p. 1097). According to our method of analysis, and the concentration of Cl^- being assumed to be constant and due to traces of chloride in the reagents and solvent, this term will be included in the spontaneous " water reaction," k_w. We have already demonstrated that this term is negligibly small, and thus the contribution of Cl_2 in our reactions is not significant. It may well be that the accuracy of our results is somewhat reduced by chance variation in the amounts of traces of chloride present.

Acetyl hypochlorite or chlorine acetate, $CH_3{\cdot}CO{\cdot}OCl$, has been shown to be easily formed under conditions similar to those prevailing in this study (Anbar and Dostrovsky, *J.*, 1954, 1105), and the assumption that this substance is an active intermediate is quite reasonable. A similar assumption has been made by de la Mare, Ketley, and Vernon (*Research*, 1953, **6**, 125) in their study of chlorinations in media containing acetic acid. For very active substances a zero-order rate with respect to the substrate has been observed by them, and the observed rate taken to be the rate of formation of acetyl hypochlorite. In view of the difference in the media used, their rate (0·05 l. mole^{-1} min.$^{-1}$) is in good agreement with our catalytic coefficient for acetic acid (cf. Table 4) which represents the rate of formation of acetyl hypochlorite. Acetyl hypochlorite has also been shown to be an active intermediate in the chlorohydrin formation reaction of allyl alcohol (Israel, *J.*, 1950, 1286), and the catalytic constant for its formation from acetic acid (14·5 l. mole^{-1} min.$^{-1}$) is in better agreement with our value (5·7 l. mole.$^{-1}$ min.$^{-1}$). Mauger and Soper (*J.*, 1946, 41) and Painter and Soper (*J.*, 1947, 342) have shown that acyl hypohalites are active intermediates in *N*-chlorination reactions and in the iodination of phenol.

The action of hypochlorous acid as a catalyst had already been mentioned in connection with the complication it introduces into the kinetics. The active intermediate derived from hypochlorous acid is chlorine monoxide. Its rate of formation from hypochlorous acid and from *tert.*-butyl hypochlorite is governed by the catalytic coefficient of HOCl. The value for this coefficient (Table 4) is somewhat higher than that reported by Israel, Martin, and Soper (*J.*, 1950, 1282), *viz.*, 8·2 l. mole^{-1} min.$^{-1}$, and much higher than Shilov's value (*loc. cit.*), *viz.*, 1·6 l. mole^{-1} min.$^{-1}$. Chlorine monoxide is also an active intermediate in the addition reactions of hypochlorous acid to unsaturated linkages (cf. Shilov, *loc. cit.*; Israel, *J.*, 1950, 1286).

Some of the other catalysts of Table 8 have been assumed also by others. Thus Derbyshire and Waters (*J.*, 1951, 73) mention the probable participation of chlorine sulphate in chlorination reaction, and chlorine phosphate is probably an intermediate in the addition reactions studied by Shilov (*Doklady Akad. Nauk U.S.S.R.*, 1951, **81**, 435, 1621).

EXPERIMENTAL

(A) *Experiments with Compounds labelled with* ^{18}O.—*Preparation of materials.* *tert.*-Butyl alcohol labelled with ^{18}O was prepared by two methods.

(*a*) Acetone (58 g.) was dissolved in water enriched in ^{18}O (180 c.c. of 0·82 atom % excess of ^{18}O), concentrated sulphuric acid (2 ml.) was added, and the mixture refluxed for 1 hr. After neutralisation with metallic calcium, the mixture was filtered, and the acetone recovered quantitatively by fractional distillation. Labelled acetone (0·5 mol., 29 g.) thus obtained was added to a solution of Grignard reagent prepared from magnesium (12 g.) and excess of methyl bromide. When the addition of acetone had been completed, the mixture was decomposed by addition of water (250 ml.). After separation of the solids, the aqueous layer was fractionally distilled, and the *tert.*-butanol fraction dried (K_2CO_3). The alcohol obtained contained 0·78 atom % excess of ^{18}O. The yield of alcohol was only 30% based on acetone taken. The following method of preparation proved to be more convenient and efficient and was used in all subsequent preparations.

(*b*) *tert.*-Butyl acetate (116 g., 1 mole) (*Org. Synth.*, 1944, **24**, 18) was added to water enriched in ^{18}O (180 g.; 0·88 atom % excess of ^{18}O). After addition of concentrated sulphuric acid enriched in ^{18}O (10 ml.; 0·81 atom % excess of ^{18}O) the mixture was refluxed until a clear solution was obtained (about 1 hr.). On cooling, metallic calcium equivalent to the sulphuric acid was added, and the solution was filtered and fractionated. The alcohol was dried by azeotropic distillation with benzene; the yield was 70% based on ester. The alcohol contained 0·86 atom % excess of ^{18}O. From the residual solution acetic acid enriched with ^{18}O was isolated by distillation.

The enriched sulphuric acid used in this preparation was made in the following manner. To analytical-grade sulphur (32 g.) in a 3-necked flask, fitted with reflux condenser and dropping funnel, was added water enriched in ^{18}O (80 ml.; 0·81 atom % excess of ^{18}O), and the mixture stirred. Through a dropping funnel, bromine (300 g.) was added as fast as its colour disappeared. Towards the end of the reaction it was necessary to heat the mixture. When all the sulphur had dissolved, the mixture was distilled until the temperature of the residue reached 130°. After addition of a few drops of nitric acid to oxidise impurities, the pressure was reduced and the distillation continued until the temperature reached 220° (at 100 mm. Hg). The residue consisted of pure sulphuric acid of 99% concentration.

Reactions with Labelled Compounds.—(a) *Formation of* tert.*-butyl hypochlorite in alkaline medium.* *tert.*-Butyl hypochlorite was prepared by passing chlorine through a solution of labelled *tert.*-butanol (20 g.; 0·86 atom % excess of ^{18}O) in 10% sodium hydroxide solution (200 ml.) of normal isotopic composition. When a layer of *tert.*-butyl hypochlorite had formed, the flow of chlorine was stopped, and the hypochlorite layer separated, washed with 10% sodium hydrogen carbonate solution, and dried (K_2CO_3). The *tert.*-butyl hypochlorite so obtained was analysed for the isotopic proportion of the oxygen atoms as follows. *tert.*-Butyl hypochlorite (1 ml.) was added to toluene (1 ml.) in a small flask fitted with a small reflux condenser. The flask was exposed to sunlight until the yellow colour of the hypochlorite was destroyed (3—5 min.), and the *tert.*-butanol which formed was separated by fractionation from the benzyl chloride and excess of toluene. The alcohol was analysed for its isotopic composition by the method of Anbar, Dostrovsky, Klein, and Samuel (to be published), and found to contain 0·79 atom % excess of ^{18}O.

This reaction was repeated with *tert.*-butanol of normal isotopic content and water enriched with ^{18}O (200 ml. of 10% sodium hydroxide solution, 0·85 atom % excess of ^{18}O). The hypochlorite was isolated and analysed as described above. The alcohol obtained finally had normal isotopic composition.

(b) *Formation of* tert.*-butyl hypochlorite in acid medium.* ^{18}O-Labelled *tert.*-butanol (4 g., 0·86 atom % of ^{18}O) was dissolved in 200 ml. of an aqueous solution 0·4N with respect to hypochlorous acid and 1N to perchloric acid, all of normal isotopic composition. Carbon tetrachloride (15 ml.) was added, and the mixture shaken for 15 min. at room temperature. The carbon tetrachloride layer was separated, dried (K_2CO_3), and shaken with N-sodium hydroxide solution (100 ml.) of normal isotopic composition until the yellow colour disappeared. The carbon tetrachloride layer was separated, and the aqueous layer fractionated to obtain *tert.*-butanol. The alcohol was dried and analysed for its isotopic composition, and found to contain 0·76 atom % excess of ^{18}O.

(c) *Hydrolysis of* tert.*-butyl hypochlorite in alkaline media.* *tert.*-Butyl hypochlorite of normal isotopic composition (2 ml.) was added to 5N-sodium hydroxide (7 ml.; 0·87 atom % excess of ^{18}O) and shaken in a separating funnel for a few minutes. The alcohol was isolated by salting out, dried twice (K_2CO_3), and analysed, and found to have a normal isotopic composition. The labelled sodium hydroxide used in this experiment was prepared by decomposing 3% sodium amalgam with the appropriate amount of enriched water. The hydrolysis experiment was repeated with use of normal water and labelled *tert.*-butyl hypochlorite [obtained as under (*a*) above]. Starting with hypochlorite of isotopic composition 0·86 atom % of ^{18}O, an alcohol was obtained containing 0·85 atom % of ^{18}O. In a duplicate experiment a hypochlorite of 0·79 atom % of ^{18}O yielded an alcohol containing 0·78 atom % of ^{18}O.

(d) *Hydrolysis of* tert.*-butyl hypochlorite in acid media.* ^{18}O-Labelled *tert.*-butyl hypochlorite (2 ml., 0·79 atom % excess) was dissolved in N-perchloric acid of normal isotopic composition (200 ml. were necessary for homogeneous solution). After ½ hr., the mixture was made alkaline with sodium hydroxide pellets and distilled. The first 10 ml. of the distillate were collected and fractionated. The *tert.*-butanol azeotrope was dried twice (K_2CO_3) and analysed; it contained 0·77 atom % excess of ^{18}O.

Kinetic Measurements.—*Materials.* *tert.*-Butyl hypochlorite was prepared by Chattaway and Backeberg's method (*J.*, 1923, **123**, 2999), and hypochlorous acid by that of Shilov and

Gladtchikova (*J. Amer. Chem. Soc.*, 1938, **60**, 490). *tert.*-Butyl alcohol was purified by careful fractionation through a 40-plate column. Reaction media for the hydrolysis reaction were prepared by diluting the required proportions of stock solutions of the buffer components to the appropriate total concentration with distilled water and adding the calculated amount of pure sodium perchlorate to bring the ionic strength up to that of the most concentrated buffered medium.

Reaction media for the formation reactions were prepared by dilution of the required proportions of the stock buffer solution with aqueous hypochlorous acid. Sodium perchlorate was added to bring the ionic strength to the required level.

The procedure for a kinetic run was as follows: For a hydrolysis reaction the appropriate quantity of the hypochlorite was measured into a stoppered silica absorption cell, 10-mm. optical path, containing the correct amount of *tert.*-butanol. The cell, together with a matched twin containing the reaction medium and *tert.*-butanol but no hypochlorite, is placed in the "thermospacer" compartment of a Beckman Model DU Spectrophotometer and kept at a constant temperature by circulating water from a thermostat at 25·2° through this compartment. After addition of the hypochlorite, a standard volume of the reaction medium at the thermostat temperature is pipetted in. The cell contents are mixed by vigorous shaking, and readings of optical density at 2900 Å carried out as often as possible (15-sec. intervals) for fast runs, or at regular longer intervals for the slower runs. For the formation reaction the procedure is only slightly different. The reaction cell is filled with the reaction medium prepared as described above, while the reference matched cell contains the diluted buffer solution, identical with the reaction media but for the absence of hypochlorous acid. The required amount of alcohol is pipetted into each cell and, after shaking, measurements of optical density are begun. At the end of every kinetic run, the whole of the ultra-violet absorption curve between 2100 and 3500 Å was determined in order to check the absence of contamination. The spectrophotometer used in this work was modified slightly to increase its sensitivity. The modifications consisted in replacing the 2000-megohm photocell load resistor by one of 10,000 megohm and using a more sensitive galvanometer arranged potentiometrically to read small differences in current. The pH of the reaction mixtures were then determined by means of a Beckman model H pH meter and the total hypochlorite content measured by iodometric procedure using either the visual end point or the "dead-stop" end point (cf. Stone and Scholten, *Anal. Chem.*, 1952, **24**, 671). Examples of two kinetic runs, taken at random, are presented below.

Formation of tert.*-butyl hypochlorite from hypochlorous acid in aqueous* 1·55M-tert.-*butanolic phosphate buffer solution* [Expt. No. 68(1)].

Buffer concentration = 0·05M; pH = 3·0; μ = 0·10; initial [HOCl] = 9·3 × 10^{-3}M; temp. = 25·2°.

Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$
1	237	234	1¾	222	243	2½	212·5	247	3¼	206	257
1¼	230	250	2	219	238	2¾	211	238	4	203	238
1½	225	253	2¼	215	250	3	208	248	∞	195	—

$k = 5\cdot64 \pm 0\cdot16 \times 10^{-1}$ min.$^{-1}$; $K' = C(\varepsilon_2 - \varepsilon_1)/(C\varepsilon_2 - D_\infty) - 1 = 0\cdot72$.

Hydrolysis of tert.*-butyl hypochlorite in* 1·55M-tert.*-butanolic phosphate buffer solution* [Expt. No. 86(2)].

μ = 0·10; buffer concn. = 0·40M; pH = 5·0; initial Bu^{t}OCl = 100 × 10^{-2}M; temp. = 25·2°.

Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$	Time, min.	10^3D	$10^3k/2\cdot3$, min.$^{-1}$
¾	142	26·6	1¾	146	28·0	3½	152·5	27·8	8½	166	26·0
1	143	27·0	2¼	148	27·5	4¼	155	27·4	10	170	26·5
1¼	144	27·2	2¾	150	28·0	6	160	26·8	11	173·5	27·9
1½	145	27·2	3¼	151·5	27·4	7¼	163·5	26·8	∞	207	—

$k = 6\cdot23 \pm 0\cdot13 \times 10^{-2}$ min.$^{-1}$; $K' = C(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 C - D_\infty) - 1 = 0\cdot64$.

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