812. *Kinetics of the Reaction between Phosphine and Sodium Hypochlorite in Alkaline Solution.*

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The reaction between phosphine and sodium hypochlorite, both in aqueous solution at pH's in the range 12—13, has been investigated. The reaction is $PH_3 + 2NaOCl \longrightarrow H_3PO_2 + 2NaCl$ and obeys the kinetic expression $-d[NaOCl]/dt = k[PH_3][NaOCl]/[OH^-]$, where $k = 3{\cdot}47 \times 10^{10} \exp(-12{,}200/\boldsymbol{RT})$. A reaction scheme involving the following stages is proposed: $OCl^- + H_3O^+ \rightleftharpoons HOCl + H_2O$ (fast); $PH_3 + HOCl \longrightarrow [PH_3O] + H^+ + Cl^-$ (rate-determining); $[PH_3O] + OCl^- \longrightarrow H_3PO_2 + Cl^-$ (very fast).

REACTION between phosphine in solution and alkaline hypochlorite is very fast.[1] For this reason alkaline hypochlorite solutions are used for scrubbing traces of phosphine from gaseous effluents. This investigation of the kinetics of reaction in aqueous solution was undertaken as part of a series of studies designed to determine the limiting factors in the efficiency of phosphine-scrubbing systems.

A modification of the technique devised by Hartridge and Roughton [2] was chosen because it was found possible to estimate hypochlorite concentrations during the reaction by means of the absorption peak at 2900 Å. No physical method could be found for estimating phosphine concentration either during the reaction or in stationary concentration.[3] Attempts to stop the reaction at predetermined time intervals by means of a faster reaction [4] were also unsuccessful: no suitable faster reaction was discovered.

Limitations in the flow-rates, hypochlorite and phosphine concentrations, and size of the apparatus restricted the investigation to the pH range 12—13 and to observed reaction times of 0·02—2·0 seconds.

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[1] Unpublished work.
[2] Hartridge and Roughton, *Proc. Roy. Soc.*, 1923, *A*, **104**, 376.
[3] Denbigh and Page, *Discuss. Faraday Soc.*, 1954, **17**, 145.
[4] Pinsent. *Discuss. Faraday Soc.*. 1954, **17**, 140.

EXPERIMENTAL

Solutions.—In the absence of automatic recording of hypochlorite concentration it was necessary to make up fresh reagent solutions for determination of each point on the kinetic curves, by appropriate dilution of stock solutions with de-aerated sodium hydroxide solutions. Sodium hydroxide was used to adjust the pH of the solutions because the use of buffers was impracticable in the presence of hypochlorite.

The stock phosphine solution was prepared by saturating a de-aerated sodium hydroxide solution with phosphine, generated by aqueous hydrolysis of magnesium aluminium phosphide in an autoclave. Withdrawals of stock solution were made by displacement with more phosphine.

The diluted solutions were analysed by estimating the total phosphorus present in all forms and residual phosphorus after extraction of dissolved phosphine with a mixture of carbon disulphide and carbon tetrachloride. The phosphorus compounds in solution were oxidised to phosphate with bromine, first in alkaline, then in acid solution and, after removal of the excess of bromine, the phosphate was determined colorimetrically in a Unicam S.P. 500 spectrophotometer by the molybdovanadophosphoric acid method.[5] Phosphine accounted for 95—99% of all forms of phosphorus present in solution. Errors in reproducibility of dilution, sampling, and estimation were less than ±1·5%. In a typical series of runs at the same nominal phosphine concentration, solutions were used with phosphine concentrations in the range 1·39 ± 0·02 mmoles/l.

Diffusion of phosphine from solution during a run was minimised by a thin layer of silicone oil (Midland Silicones M.S. 200) on the surface of the solution; throughout a run the phosphine concentration remained constant to within ±1% (typically 3·14 ± 0·03 mmoles/l.).

The hypochlorite stock solution was prepared by absorbing chlorine gas in a de-aerated sodium hydroxide solution. Its pH was adjusted by addition of sodium hydroxide, and dilution was effected as for the phosphine solutions. The stock solution was kept away from direct light. Periodic estimations were made with potassium iodide and standard sodium thiosulphate solution.

It was found that oxidation of the phosphine led to the formation of hypophosphorous acid. This resulted in a progressive lowering of the pH of the reactant mixture. At the concentrations used, the maximum resulting diminution in sodium hydroxide concentration was 15% at 100% reaction: this was considered tolerable, especially as only the first 60—70% of the reaction was followed.

Procedure.—A block diagram of the apparatus is shown in Fig. 1. Details of the mixer and spectrophotometer cell compartment are shown in Figs. 2 and 3, respectively.

Reactant solutions were stored in 2½-l. Mariotte bottles. After adjustment of the temperature of the solutions by immersion in thermostat baths the bottles were placed in an insulated container, partly to maintain the temperatures and partly for safety. Nitrogen under constant pressure (40—100 cm.) was used to drive the solutions into a mixer through a double gate-clip, which released and stopped the two flows simultaneously. Relative rates of feed of the two solutions were determined by weighing the storage bottles before and after runs, and the values so obtained were checked periodically by running standard hypochlorite and sodium hydroxide solutions through the mixing system and measuring the hypochlorite concentration of the mixture. Relative rates remained constant during an experiment within ±0·3% and calculations of initial concentrations agreed with measurement within ±1%. Total flow-rates were determined from the time required to fill a calibrated 2-l. flask.

The mixer was made from ebonite. Four tangential jets imparted contrary swirls to each reactant solution. Tests of mixing efficiency were made with phenolphthalein and aqueous sodium hydroxide.[2] The results indicated that 98% mixing was achieved by the time the solutions emerged from the mixer. Further, three points were placed on an established rate curve by using lower total flow-rates than normal, indicating that mixing efficiency did not vary significantly with flow-rate. The average residence time in the mixer was ~0·01 sec. (volume of mixing compartment 0·510 ml.).

The mixture issuing from the mixer was passed through a length of glass tubing, of such geometry that Reynolds numbers $\geqslant$~4000 were achieved, and through the silica tube acting as the cell for the spectrophotometer. The geometry of the spectrophotometer was such that

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[5] Kitson and Mellon, *Analyt. Chem.*, 1944, **16**, 379.

it was necessary to vary the reaction length by using short lengths of glass tubing before the cell. These lengths were butt-jointed together, secured with rubber tubing, and clipped to a rigid frame. Cross-sectional areas of the individual tubes were within 3% of the average. Volumes were determined by filling the tubes with water from a burette.

The spectrophotometer cell-housing was specially constructed to replace a normal Unicam S.P. 500 cell compartment. Horizontal slits restricted the light path to the central axis of the silica-tube cell, and the position of the light path was determined photographically. Care was taken to eliminate stray light. The hypochlorite absorption peak at 2900 Å was used to estimate hypochlorite concentrations at predetermined reaction times. Standard calibration curves were made and checked periodically. The calibration curve did not vary with pH in the range 12—13. At the end of each reaction the residual hypochlorite was determined photometrically in the silica cell: this procedure also served to confirm that phosphine and hypophosphorous acid did not interfere with the estimations.

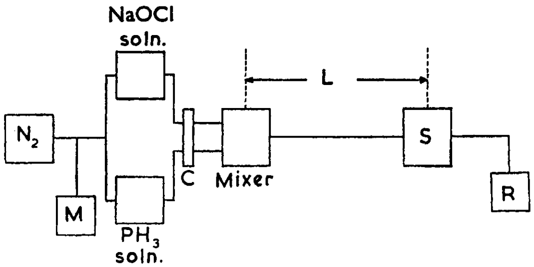

FIG. 1. Block diagram showing arrangement of apparatus.

M = Manometer; C = double gate-clip; L = reaction length; S = spectrophotometer cell; R = receiver.

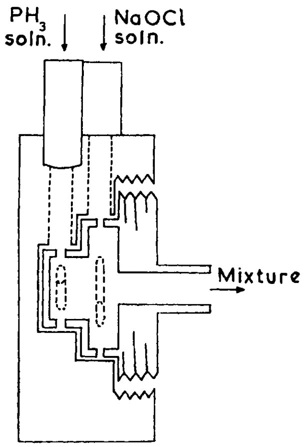

FIG. 2. The mixer (side view).

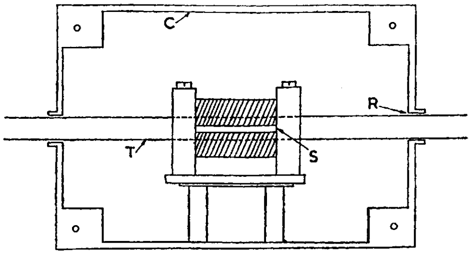

FIG. 3. Spectrophotometer cell compartment.

C = Brass case; R = light-tight rubber-seal; S = horizontal slit; T = silica observation tube; o = holes for securing studs.

The possibility of a photochemical reaction between phosphine and hypochlorite was considered. Varying the intensity of the spectrophotometer light beam had no effect on the estimates of hypochlorite concentration. Shielding the reaction tubes from direct light also had no effect.

RESULTS AND DISCUSSION

In the pH range 12—13, the overall reaction between phosphine and hypochlorite is $PH_3 + 2NaOCl \longrightarrow H_3PO_2 + 2NaCl$. The average number of moles of hypochlorite reacting in " infinite " time with 1 mole of phosphine in 57 experiments, in which an excess of hypochlorite was used, was $2{\cdot}01 \pm 0{\cdot}06$. This was confirmed by hypophosphite determinations [6] on products obtained from experiments in which an excess of phosphine

[6] Jones and Swift, *Analyt. Chem.*, **1953**, **25**, 1272.

was used: measurement agreed with theory to within ±3%. This finding is consistent with the fact that hypophosphite is oxidised by halogens only in acid solution.[7]

The rate of reaction was shown to be of the first order with respect to both phosphine concentration and hypochlorite concentration, by graphical estimation of initial rates of reaction and comparison of initial rates of reaction with initial concentrations of reactants, at a constant pH, *i.e.*, $-d[\mathrm{NaOCl}]/dt = k'[\mathrm{PH_3}][\mathrm{NaOCl}]$, where expressions in brackets relate to molar concentrations. At a constant pH the reaction obeyed the kinetic expression:

$$k't = \frac{1}{b - 2a} \log_e \left[\frac{a(b - 2x)}{b(a - x)}\right],$$

where a = initial molar concentration of phosphine, b = initial molar concentration of hypochlorite, and x = moles of phosphine reacted after time t. Graphs of t against $\log_e [a(b - 2x)]/[b(a - x)]$ gave straight lines, and values of k' obtained in replicate experiments at three different pH's are shown in Table 1. At each pH, individual values for k' were within ±5% of the average.

TABLE 1.

Approx. pH	Initial concentrations (mmoles/l.) Phosphine	Hypochlorite	Sodium hydroxide	Temp. °C.	$10^{-3}k'$ (l.mole.$^{-1}$ sec.$^{-1}$)
12	1·04	1·90	10	22	2·88
12	0·35	1·84	10	21	2·79
12	1·33	1·94	10	22	2·92
12	0·60	2·82	10	21	2·65
12	0·67	0·92	10	21	2·74
12·6	1·40	1·87	40	21	0·70
12·6	0·61	3·61	40	20—21	0·65
13	1·32	4·00	100	21—21·5	0·276
13	1·64	2·64	100	21—21·5	0·267

A first-order dependence of k' on hydrogen-ion concentration was shown by plotting $\log k'$ against pH (calculated from measured hydroxyl-ion concentration), so that the full rate expression is

$$-d[\mathrm{NaOCl}]/dt = k[\mathrm{PH_3}][\mathrm{NaOCl}]/[\mathrm{OH^-}] \quad \ldots\ldots \quad (1)$$

where $k = k'[\mathrm{OH^-}]$.

The temperature dependence of the rate constant k was investigated at four different temperatures in the range 1—35° C. Values obtained are summarised in Table 2.

TABLE 2.

Replicate reactions of phosphine and hypochlorite.

Temp.	Initial concns. (mmoles/l.) $\mathrm{PH_3}$	NaOCl	NaOH	k (sec.$^{-1}$)
1·6° ± 0·5°	1·01	3·16	40	6·9
10·3° ± 0·2°	1·30	3·17	40	13·2
25·0° ± 0·2°	0·87	2·12	40	37·5
34·8° ± 0·2°	1·05	2·99	40	78·2

The energy of activation was determined as 12·2 ± 0·5 kcal./mole, leading to the overall expression for the rate constant $k = 3{\cdot}47 \times 10^{10} \exp(-12{,}200/\boldsymbol{R}T)$.

Detailed consideration of possible errors in the measurements led to an estimate of ±10% maximum error in determination of values of k. Comparison of observed values with calculated values of k showed agreement within ±5%.

Discussion of a possible mechanism for the oxidation of phosphine by hypochlorite in alkaline solution is subject to the limitation that is has proved possible to follow only the decay in hypochlorite concentration throughout the reaction. Attempts to devise

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[7] Griffiths and McKeown, *Trans. Faraday Soc.*, 1934, **30**, 530.

methods for instantaneous estimation of phosphine or estimation of stationary concentrations of phosphine proved unsuccessful.

The effect of pH can be explained by postulating, as the rate-determining step, the reaction $PH_3 + HOCl \longrightarrow PH_3O + Cl^- + H^+$, in which the concentration of hypochlorous acid is regulated by the equilibrium $OCl^- + H_3O^+ \rightleftharpoons HOCl + H_2O$. The theoretical collision frequency between H_3O^+ and OCl^- is sufficiently large to permit this assumption provided electrostatic entropy corrections are made. Such an explanation has been postulated before in the hypochlorite oxidation of iodide to hypoiodite,[8] $d[IO^-]/dt = k[I^+][OCl^-]/[OH^-]$, where $k = 60$ sec.$^{-1}$ at 25° (cf. 37·5 sec.$^{-1}$ in present investigation), and in the corresponding oxidation of bromide ion.[9] It is also consistent with the relative oxidation potentials of the two oxidising species, *i.e.*, hypochlorite ion, $E_0 = 0{\cdot}89$ v, and hypochlorous acid, $E_0 = -2{\cdot}32$ v. Equilibria involving PH_4^+ ions are unlikely in alkaline solution,[10] K_a(for PH_4^+) $\gtrsim 10^{-29}$. Finally, an ionic rate-determining step does not fit the observation that the rate of reaction is only very slightly dependent on the ionic strength of the solution: a graph of $\log_{10} k$ against $\sqrt{I}$ gave a straight line of slope $-0{\cdot}1$.

The following overall reaction mechanism is postulated to explain the differences in rates between the two oxidation stages:

$OCl^- + H_3O^+ \rightleftharpoons HOCl + H_2O$	Very fast
$PH_3 + HOCl \longrightarrow [PH_3O] + Cl^- + [H^+]$	Rate-determining
$[PH_3O] + OCl^- \longrightarrow H_3PO_2 + Cl^-$	Very fast

The oxidation of $[PH_3O]$ must be at least ten times faster than the rate-determining step since no indication of a composite kinetic curve, such as was obtained in the kinetics of dealkylation of esters of phosphorus oxyacids by hydrogen bromide,[11] was observed up to at least 60% reaction.

Since the dissociation constant K_a of hypochlorous acid in water is $\sim 4 \times 10^{-8}$, the value of $[HOCl]/[OCl^-]$ in the pH region studied is in the range 2×10^{-5} to 2×10^{-6}. The rate-determining step in the reaction involves two neutral molecules and would be expected to have an A-factor of $\sim 10^{11}$ l. mole^{-1} sec.$^{-1}$. The effect of the preliminary equilibrium might therefore appear to reduce the A-factor to a value not greater than 10^5—10^6 l. mole^{-1} sec.$^{-1}$. However, the observed A-factor will depend both on the A-factor of the rate-determining step and on the entropy change in the preliminary equilibrium. The difference between the true rate constant, k_t, and the observed rate constant, k_{obs}, can be explained in terms of this entropy change and heat changes in the equilibrium.

The full rate equation (1) may be re-written:

$$-d[NaOCl]/dt = k_{obs}[PH_3][OCl^-][H^+]/K_w, \qquad (2)$$

where $K_w = [H^+][OH^-]$ and is temperature-dependent. The true rate constant for the rate-determining step is given in the expression,

$$-d[HOCl]/dt = k_t[PH_3][HOCl],$$

which, because hypochlorite ion is the only source of hypochlorous acid, is equivalent to

$$-d[OCl^-]/dt = k_t[PH_3][HOCl]. \qquad (3)$$

Comparison of expressions (2) and (3) and insertion of the acid dissociation constant, K_a, for hypochlorous acid gives:

$$k_{obs} = k_t K_w / K_a.$$

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[8] Yuan-Tsan Chia and Connick, *J. Phys. Chem.*, 1959, **63**, 1518.

[9] Farkas, Lewin, and Block, *J. Amer. Chem. Soc.*, 1949, **71**, 1988.

[10] Weston and Bigeleisen, *J. Amer. Chem. Soc.*, 1954, **76**, 3074.

[11] Cooke and Gerrard, *J.*, 1955, 1978.

Transition-state theory then gives:

$$\Delta S_{\text{obs}}^* = \Delta S_t^* + \Delta S_w^0 - \Delta S_a^0,$$

and

$$\Delta H_{\text{obs}}^* = \Delta H_t^* + \Delta H_w^0 - \Delta H_a^0,$$

where entropy and heat changes for the rate-determining step are denoted by subscript t, and standard entropy and heat changes for the dissociation of water and of hypochlorous acid in water are denoted by subscripts w and a, respectively.

The following values, at 25°, have been given by Pitzer:[12]

	ΔS^0 (cal. deg.$^{-1}$ mole^{-1})	ΔH^0 (cal.)
H_2O	−19·24	13,358
HOCl	−22·8	3,320

The correction terms then become:

$$(\Delta S_t^* - \Delta S_{\text{obs}}^*) = -22{\cdot}8 + 19{\cdot}24 = -3{\cdot}56 \text{ cal. deg.}^{-1}\text{ mole}^{-1} = \Delta S_c,$$

$$(\Delta H_t^* - \Delta H_{\text{obs}}^*) = 3320 - 13{,}358 = -10{,}038 \text{ cal.} \qquad = \Delta H_c,$$

so that $k_{\text{obs}}/k_t = \exp(\Delta S_c/\boldsymbol{R}) \exp(\Delta H_c/\boldsymbol{R}T) = e^{15{\cdot}06} \sim 10^{6{\cdot}5}$.

Thus the standard heat and entropy corrections for the preliminary equilibrium appear to offset the effect of the equilibrium on the molar concentration of the oxidising species in the rate-determining step.

We thank Mr. D. Severn for his collaboration in early experiments, Mr. P. B. Edwards who helped make some of the measurements, and Mr. N. L. Paddock and Dr. J. C. McCoubrey for helpful discussions.

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[*Received, March* 21*st*, 1962.]

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[12] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.