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Kinetics and Mechanism of Chlorination of Triethylphosphorothiolate in Dilute Aqueous Media at 25°

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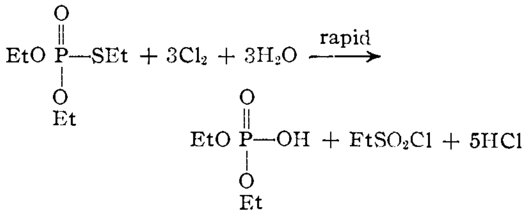
The kinetics and mechanism of chlorination of triethylphosphorothiolate (TEPT) in dilute aqueous solution were determined over a range of pH 4–10. In acid solutions (pH 4–5), the chlorination involves a reaction between molecular chlorine and TEPT, the rate being controlled by the formation of chlorine from hypochlorous acid, hydronium and chloride ions. In slightly acid and neutral solutions (pH 6–7), the kinetics indicate that, in addition to a reaction with molecular chlorine, TEPT is chlorinated by a concerted attack of both hypochlorous acid and hypochlorite ion. The latter reaction is minimized where chloride ion concentration is high. In alkaline solution (pH 8–10), the participating moiety in the reaction is the hypochlorite ion. Kinetic equations are derived for the reactions involved. A discussion of the mechanisms involved is given.

Introduction

The discovery that hypochlorite ion behaved as a catalyst in the hydrolysis of isopropyl methylphosphonofluoridate[1] (Sarin) prompted us to study the reactions of chlorine in dilute aqueous solution with other organophosphorous compounds. The present report is concerned with the interactions between chlorine and triethylphosphorothiolate (TEPT).

In contrast to the single reaction observed between chlorine and Sarin, *i.e.*, the hypochlorite ion catalyzed hydrolysis, the reaction between TEPT and chlorine is much more complex. At $p\mathrm{H} < 5$, a very rapid reaction occurs between TEPT and molecular chlorine in which three moles of Cl_2 is consumed and between four and five moles of acid is produced for each mole of reacting TEPT (Fig. 1). Of the total acid produced, three moles is formed rapidly, roughly paralleling the rate of decline in chlorine titer, the remainder of the acid forming at a considerably lower speed and only after the uptake of chlorine had ceased. Ethane sulfonyl chloride (as its sulfonamide) was isolated from reaction mixtures in which only three to four moles of acid had formed.

The reaction may be expressed as



$$\mathrm{EtO}\,\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\underset{\underset{\displaystyle\mathrm{Et}}{\underset{\displaystyle|}{\mathrm{O}}}}{\mathrm{P}}}\text{—SEt} + 3Cl_2 + 3H_2O \xrightarrow{\text{rapid}} \mathrm{EtO}\,\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\underset{\underset{\displaystyle\mathrm{Et}}{\underset{\displaystyle|}{\mathrm{O}}}}{\mathrm{P}}}\text{—OH} + EtSO_2Cl + 5HCl \quad \text{(a)}$$

$$EtSO_2Cl + H_2O \xrightarrow{\text{slow}} EtSO_3H + HCl \quad \text{(b)}$$

Although a total of eight moles of acid is produced in the reaction (both the sulfonic and phosphonic acids are strong acids), three moles is consumed in the formation of molecular chlorine from hypochlorous acid, leaving a maximum of five which can be measured.

In the pH range 5–8 two reactions appear to occur: one, an attack by molecular chlorine; the other, a concerted attack of both hypochlorous acid hypochlorite ion upon TEPT. At $p\mathrm{H} > 8$, the reactive species is hypochlorite ion, which apparently acts as a hydrolytic catalyst, similar to its action upon Sarin. However, the rate of the hypochlorite catalyzed hydrolysis of TEPT is much lower than the similar reaction with Sarin.[2]

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[1] J. Epstein, V. E. Bauer, M. Saxe and M. M. Demek, THIS JOURNAL, **78**, 4068 (1956).

[2] The bimolecular rate constant for the hypochlorite catalyzed hydrolysis of the phosphonofluoridate was found to be 600 l. mole^{-1} min.$^{-1}$ at 25°[1]; for TEPT, 2.4 l. mole^{-1} min.$^{-1}$.

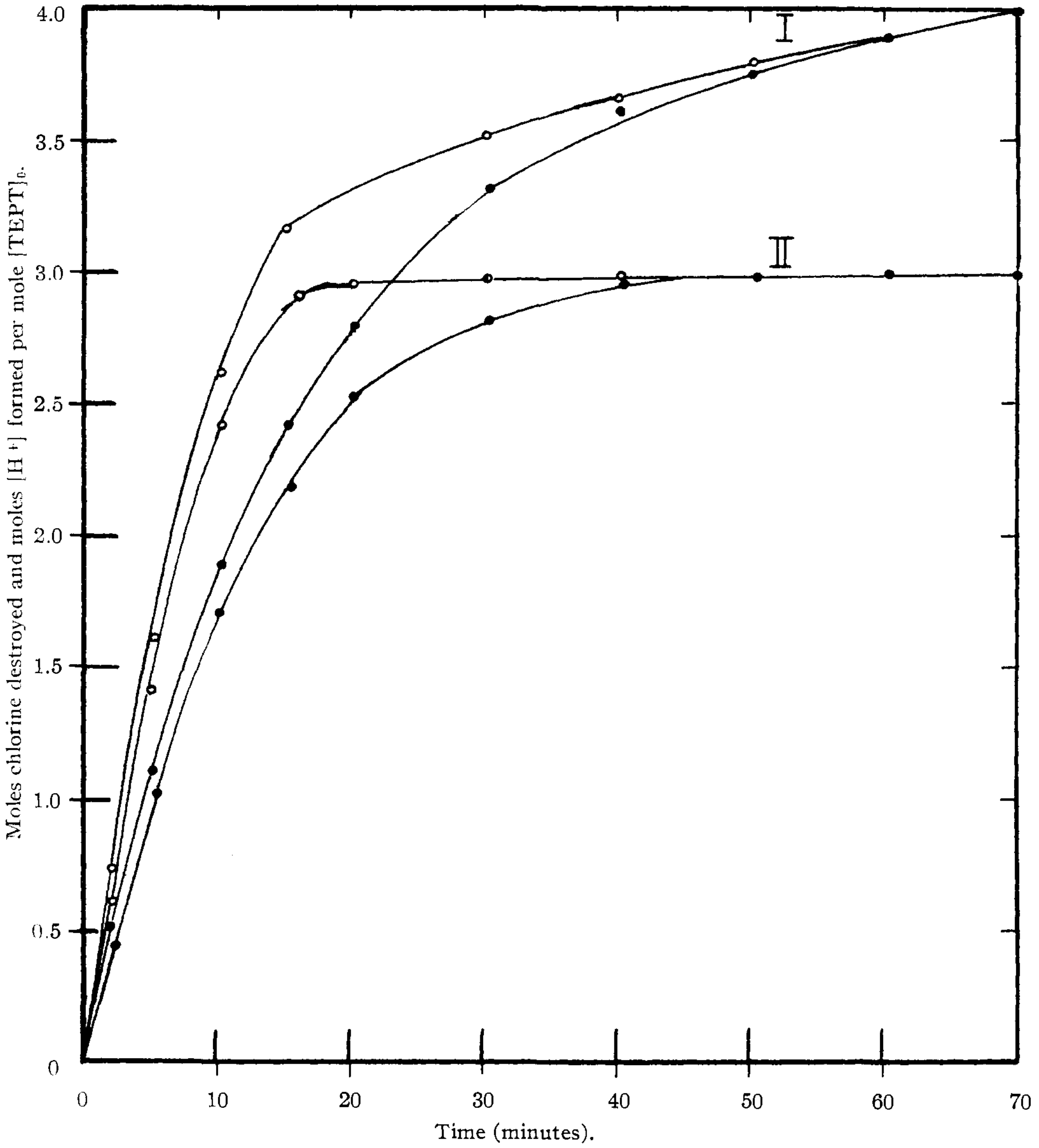
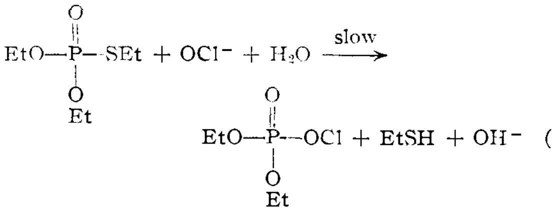
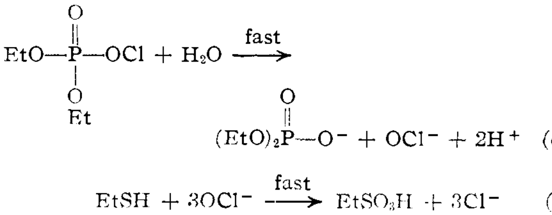


Fig. 1.—Rates of acid formation (I) and chlorine destruction (II) at *p*H 5, $\mu = 0.1$, $T = 25 \pm 0.5°$: ●, $[\mathrm{HOCl}]_0 = 2.38 \times 10^{-4}$ *M*, $[\mathrm{Cl}^-] = 1.16 \times 10^{-3}$ *M*; $[\mathrm{TEPT}] = 4.6 \times 10^{-5}$ *M*; O, $[\mathrm{HOCl}]_0 = 1.6 \times 10^{-4}$ *M*, $[\mathrm{Cl}^-] = 1.04 \times 10^{-3}$ *M*; $[\mathrm{TEPT}] = 4.6 \times 10^{-5}$ *M*.

The products of hydrolysis consume the hypochlorite, *i.e.*



$$\mathrm{EtO{-}\underset{\underset{\textstyle Et}{\textstyle O}}{\overset{\overset{\textstyle O}{\|}}{P}}{-}SEt} + \mathrm{OCl^-} + \mathrm{H_2O} \xrightarrow{\text{slow}} \mathrm{EtO{-}\underset{\underset{\textstyle Et}{\textstyle O}}{\overset{\overset{\textstyle O}{\|}}{P}}{-}OCl} + \mathrm{EtSH} + \mathrm{OH^-} \quad \text{(c)}$$



$$\mathrm{EtO{-}\underset{\underset{\textstyle Et}{\textstyle O}}{\overset{\overset{\textstyle O}{\|}}{P}}{-}OCl} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{(EtO)_2\overset{\overset{\textstyle O}{\|}}{P}{-}O^-} + \mathrm{OCl^-} + 2\mathrm{H^+} \quad \text{(d)}$$

$$\mathrm{EtSH} + 3\mathrm{OCl^-} \xrightarrow{\text{fast}} \mathrm{EtSO_3H} + 3\mathrm{Cl^-} \quad \text{(e)}$$

These conclusions were reached from a kinetic study of the chlorination reaction at constant *p*H over the range 4 to 10 and in the presence of varying amounts of chloride ion and TEPT. At any given *p*H (maintained constant by addition of alkali) and at fixed concentrations of chloride ion and TEPT, the rate of disappearance of active halogen (chlorine, hypochlorous acid and/or hypochlorite ion) was found to be first order with respect to the total active halogen concentration, enabling the calculation of a first-order constant (k_{obs}).[3] Deviations from first-order kinetics were observed only after 50% of the reaction had occurred. This could be explained by the fact that the rate of disappearance of active halogen was also

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(3) First-order rate constants based upon acid production rates when evaluated by Guggenheim's method (A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 1953, p. 48) were of the same order of magnitude as k_{obs}.

dependent in some measure upon the TEPT concentration (Fig. 2). At constant *p*H and TEPT concentration the k_{obs} was directly proportional to the chloride ion concentration (Fig. 3).

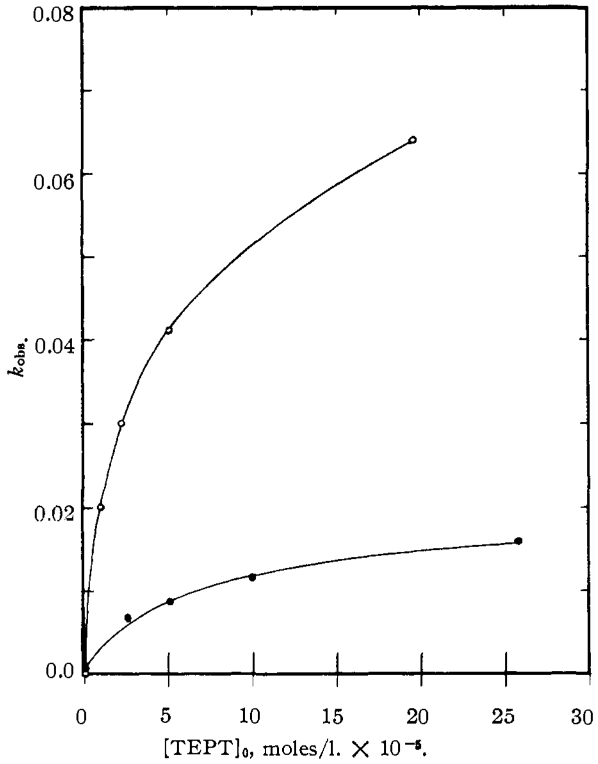

Fig. 2.—Dependence of the rate of chlorine destruction on the initial concentration of TEPT: ●, *p*H 7.0, [Cl^-] = 5×10^{-4} *M*, [HOCl] + [OCl^-] = 5.5×10^{-5} *M*, $\mu = 0.1$, $T = 25.0 \pm 0.5°$; ○, *p*H 4.0, [Cl^-] = 9×10^{-5} *M*, $[HOCl]_0 = 1.5 \times 10^{-4}$ *M*, $\mu = 0.1$, $T = 25 \pm 0.5°$.

At *p*H 5 (Fig. 3) the straight line relating k_{obs} to chloride ion concentration may be extrapolated to the origin, suggesting that no reaction ensues in the absence of chloride ion at this *p*H (this also implies that there is no reaction between TEPT and hypochlorous acid). Above *p*H 5, *e.g.*, *p*H 7, a second reaction independent of chloride ion and resulting in loss of halogen appears to be involved (intercept, Fig. 3, *p*H 7). The rate of halogen loss due to the chloride-independent reaction (which was much more rapid than the loss of chlorine in solutions without TEPT) was generally observed to occur in the *p*H range 5.5 to 8. Thus, the rate of disappearance of halogen could be arbitrarily divided into (a) a chloride ion concentration dependent reaction and (b) a chloride ion independent reaction. At *p*H < 5, the rate of halogen disappearance can be explained by assuming that only reaction (a) takes place; above *p*H 5, both reactions must be assumed to explain the observed rate. An analysis of the chloride ion concentration dependent reaction follows.

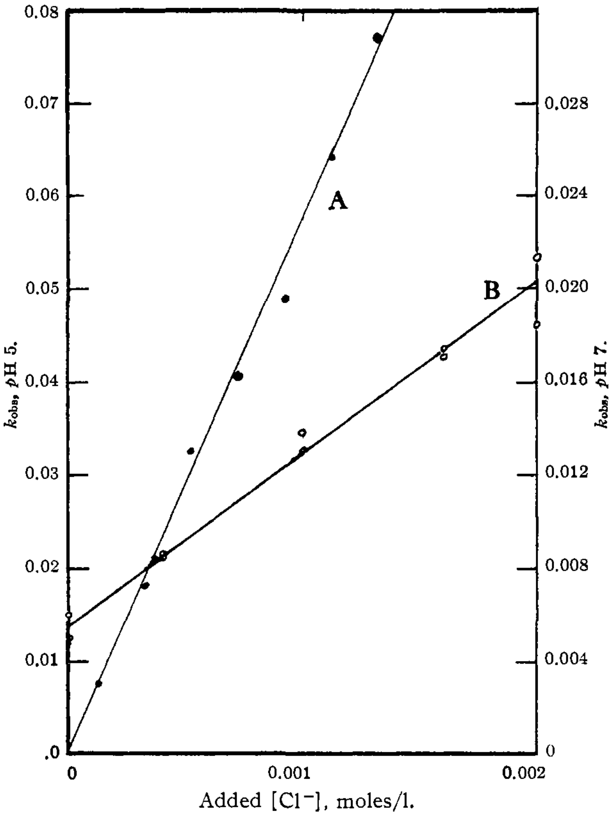

Fig. 3.—Dependence of the rate of chlorine destruction on chloride ion concentration: (A) ●, *p*H 5, [TEPT] = 4.5×10^{-5} *M*, $\mu = 0.1$, $T = 25 \pm 0.5°$; (B) ○, *p*H 7, [TEPT] = 4.5×10^{-5} *M*, $\mu = 0.1$, $T = 25 \pm 0.5°$.

The portion of the observed rate constant which is chloride ion concentration dependent ($k'_{obs} = k_{obs} - k^0_{obs}$, where k^0_{obs} is the rate constant at zero [Cl^-] concentration) divided by the [Cl^-] is related to *p*H as shown in Fig. 4; between *p*H 4 and 5, there appears to be a ten-fold increase in k'_{obs} for ten-fold increase in [H^+]; above this *p*H, the dependence of the rate on [H^+] is less than ten and variable. If, now, the rate is assumed to be dependent upon the hypochlorous acid concentration[4] rather than the total active halogen concentration, the resulting value for k'_{obs} is found to be independent of the [H^+] over the *p*H range of 6.5 to 8.0 (dotted line, Fig. 4).

The observation that, at constant initial concentration of TEPT, the rate of disappearance of hypochlorous acid in acid solution depended on the concentration of HOCl, chloride ion and hydronium ion raised to the first power, and that the dependence on TEPT was small, approaching a constant value as $[TEPT]_0$ was increased, suggested that the rate controlling step in the over-all reaction of TEPT with active halogen (equation g) was contained in the equilibrium involved in the formation of chlorine (equation f).

$$HOCl + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cl_2 + H_2O \qquad (f)$$

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[4] The hypochlorous acid concentration was calculated from the equation HOCl = ([H^+]/([H^+] + K_A)) $[HOCl]_t$, where $[HOCl]_t$ is the total active halogen concentration and K_A is the acid dissociation constant of hypochlorous acid under experimental conditions of ionic strength. The value of K_A used in this work, *viz.*, 8.45×10^{-8}, was calculated from the equation[5] $\log K_A = \log K + 2A\sqrt{C}$ where $K = 4 \times 10^{-8}$, $C = 0.1$ and $A = 0.51$ at 25°.

[5] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 970.

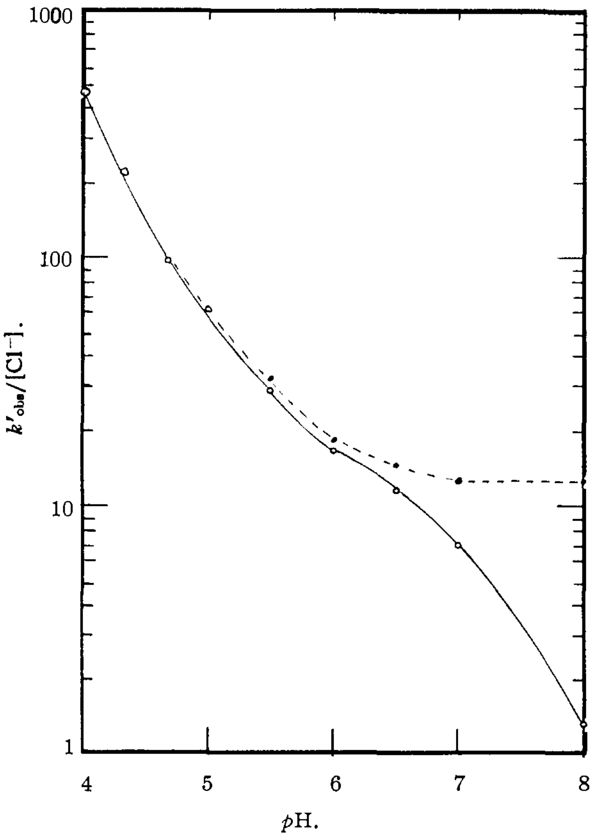
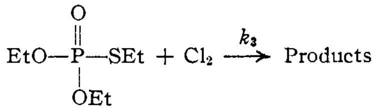


Fig. 4.—Dependence of rate of destruction of active chlorine by TEPT on $[H^+]$; $[TEPT] = 5 \times 10^{-5}\ M$, $T = 25 \pm 0.5°$, $\mu = 0.1$; —O—, observed values, ----●----, values corrected for ionization of hypochlorous acid.



$$\mathrm{EtO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OEt}{|}}{P}}{-}SEt} + Cl_2 \xrightarrow{k_3} \text{Products} \qquad (g)$$

where $k_3 >> k_1$ and k_{-1}.

At pH's between 6.5 and 8.0, where the rate appears to be independent of pH, the rate of chlorine formation may be controlled by a reaction of HOCl with Cl^- (equation e). This equilibrium has been suggested by Morris[6] as the mechanism involved in the hydrolysis of chlorine.

$$HOCl + Cl^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cl_2 + OH^- \qquad (e)$$

If the steady-state approximation is applied to the formation of chlorine, then

$$\frac{d[Cl_2]}{dt} = 0 = k_1[HOCl][H^+][Cl^-] + k_2[HOCl][Cl^-] - k_{-1}[Cl_2] - k_{-2}[Cl_2][OH^-] - k_3[Cl_2][TEPT] \qquad (1)$$

or

$$[Cl_2] = \frac{k_1[HOCl][Cl^-][H^+] + k_2[HOCl][Cl^-]}{k_{-1} + k_{-2}[OH^-] + k_3[TEPT]} = \frac{k_x[HOCl][Cl^-]}{k_y + k_3[TEPT]} \qquad (2)$$

where $k_x = k_1\ [H^+] + k_2$, and $k_y = k_{-1} + k_{-2}\ [OH^-]$. Also

$$-\frac{d[HOCl]}{dt} = k_1[HOCl][Cl^-][H^+] + k_2[HOCl][Cl^-] - k_{-1}[Cl_2] - k_2[Cl_2][OH^-] = k_x[HOCl][Cl^-] - k_y[Cl_2] \qquad (3)$$

Substituting the equivalence for Cl_2, equation 2 in equation 3, one obtains

$$-\frac{d[HOCl]}{dt} = \frac{k_xk_3[HOCl][Cl^-][TEPT]}{k_y + k_3[TEPT]} \qquad (4)$$

If total active halogen is experimentally measured,[4] then

$$[HOCl] = \frac{[H^+][HOCl]_t}{[H^+] + K_A}$$

Transposing

$$-\frac{d[HOCl]}{[HOCl]_t} = \frac{k_xk_3K'[Cl^-][TEPT]}{k_y + k_3[TEPT]}\,dt$$

where

$$K' = \frac{[H^+]}{[H^+] + K_A}$$

At constant pH, TEPT and Cl^- concentrations,[7] it was experimentally observed that

$$-\frac{dHOCl}{[HOCl]_t} = k_{obs}dt$$

Hence

$$k'_{obs} = \frac{k_xk_3K'[TEPT][Cl^-]}{k_y + k_3[TEPT]} \qquad (5)$$

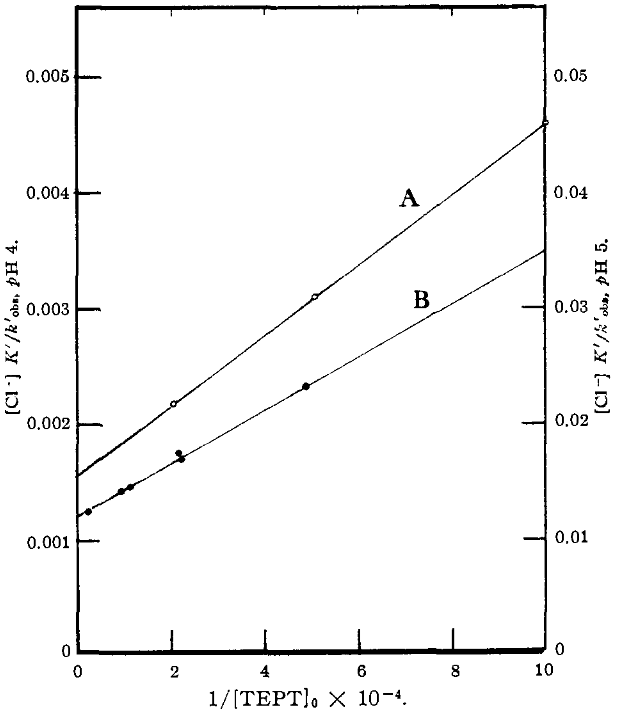


Fig. 5.—Relationship between the reciprocals of the first-order rate constant (at constant $[Cl^-]$) and [TEPT] concentration at pH 5 (A, ●) and pH 4 (B, O); $T = 25 \pm 0.5°$, $\mu = 0.1$.

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(6) J. C. Morris, THIS JOURNAL, **68**, 1692 (1946).

(7) With respect to Cl^-, this condition will prevail for all practica purposes where the added chloride is large as compared to the initial hypochlorous acid concentration, even though a mole of Cl^- is formed for each mole of hypochlorous acid decomposed. During the initial periods of the reaction, the concentration of TEPT may be considered approximately constant.

TABLE I

ANALYSIS OF CHLORIDE DEPENDENT RATE OF DESTRUCTION OF CHLORINE AS A FUNCTION OF pH AT $T = 25 \pm 0.5°$, $\mu = 0.1$

pH	$[TEPT]_0$ $\times 10^5$, M	$[HOCl]_0$, $\times 10^5$, M	$1/K'$	Av. $\frac{k'_{obs}}{[Cl^-]K'}$	k_y/k_3 $\times 10^5$	k_x exp.	k_x calcd.
4.0	0.98	14	1.0	216 ± 7	1.91	633	651
	1.96	15		325 ± 8			
	4.6	15		457			
	4.9	15		459 ± 11			
4.3	4.6	4.6	1.0	218	..	312	335
4.7	4.6	4.5	1.0	98	1.56	131	145
	51	5.8		127 ± 8			
5.6	4.5	3.5	1.008	57.6 ± 2.2	1.87	83.5	81.7
	4.6	8.4-23.8		60 ± 2.5			
	2.1	14.5		43.5			
	9.2	8.4		70.1			
	10.6	14.6		71.0			
	51.0	5.6		82.1			
5.5	4.8	4.8	1.026	30.2	1.19	37.6	38.4
	5.3	5.7		30.7 ± 0.8			
	8.5	7.7		30.0 ± 1.9			
	42.5	7.3		38.1 ± 0.6			
6.0	5.3	5.9	1.085	18.1 ± 1	1.97	25.8	24.7
	5.4	8.0		19.6 ± 0.1			
	20.0	13.3		22.5 ± 0.4			
	20.8	12.2		23.5 ± 3.7			
	27.0	7.5		23.6 ± 1.4			
	49.5	9.0		27.0 ± 3.3			
6.5	5.4	7.3	1.266	14.4 ± 1.2	1.78	19.2	20.4
	27	7.2		18.6 ± 1.2			
	49.5	6.7		18.2 ± 0.1			
7.0	4.8	4.5	1.845	12.5	2.18	18.4	19
	49.5	6.6		17.4 ± 1.6			

where [TEPT] and $[Cl^-]$ are assumed to be equal to their initial value, $[TEPT]_0$ and $[Cl^-]_0$. Equation 5 may be rewritten

$$\frac{[Cl^-]K'}{k'_{obs}} = \frac{k_y}{k_x k_3} \times \frac{1}{[TEPT]_0} + \frac{1}{k_x} \qquad (6)$$

A plot of $[Cl^-]K'/k'_{obs}$ *vs.* $1/[TEPT]_0$ should be linear at constant pH with a slope equal to $k_y/k_x k_3$ and intercept equal to $1/k_x$ from which k_x and k_y/k_3 can be evaluated. This was generally observed (*e.g.*, see Fig. 5). A compilation of the results is given in Table I.

The value of k_1 may be estimated from data at low pH levels, where $k_x = k_1[H^+]$ (since $k_1[H^+] >> k_2$). Similarly, at high pH levels where $k_2 >> k_1 [H^+]$, k_x can be set equal to k_2. From data at pH 4 and 7, k_1 was found to be 6.33×10^6 and k_2 to be 18.4 l. mole^{-1} min.$^{-1}$. The line of best fit (used for calculation of k_y/k_3 and k_x exp.) was constructed using the method of least squares. In some cases k_x exp. was determined by direct calculation from equation 5, assuming k_y/k_3 to be 2×10^{-5}. For purposes of comparison, k_x also was calculated from the above values of k_1, k_2 and the equation $k_x = k_1[H^+] + k_2$. These values are shown in Table I as k_x calcd.

TABLE II

CHLORIDE-INDEPENDENT REACTION AS A FUNCTION OF $[TEPT]_0$ AND pH AT $T = 25 \pm 0.5°$ AND $\mu = 0.1$

pH	$[TEPT]_0 \times 10^5$	Av. k^0_{obs} $(k_{obs} - k'_{obsd}) \times 10^3$
5.5	8.5	4.2 ± 0.9
	42.5	11.8 ± .2
6.0	5.4	7.3 ± .1
	27	11.9 ± .4
6.5	5.4	5.4 ± .6
	27	11.0 ± .000
7.0	2.6	3.5
	5.2	4.6
	10.4	6.8
	26	11.9
8.0	8	3.5
	40	11.0

Data relevant to the chloride independent reaction is shown in Table II. It is clear by comparing the values of k^0_{obs} for a given and low concentration of TEPT (*e.g.* 5×10^{-5}) at various pH levels that the relationship between k^0_{obs} and pH is bell-shaped in character, approaching a maximum around pH 6 and zero at pH 5 and 9. The data also reveal that the rate is fractionally dependent upon [TEPT], the dependence varying with pH. Other experiments at pH 7.0, in which the concentration of active halogen was varied while the [TEPT] was kept constant, indicated an order of dependence upon the total halogen concentration of greater than one. For example, it was found that a four-fold increase in active halogen content only doubled k^0_{obs}. The data appear to indicate that the chloride-independent reaction resulting in active halogen destruction does not occur unless significant concentrations of both hypochlorous acid and hypochlorite ion are present. At pH 9 and 10, the disappearance of active chlorine is first order with respect to both TEPT and hypochlorite ion and independent of both chloride and hydronium ions (Table III). As in the reaction under acid conditions, three moles of hypochlorite ion are consumed per mole of reacting TEPT (equations c, d and e).

TABLE III

HYPOCHLORITE CATALYZED HYDROLYSIS OF TEPT AT 25°, $\mu = 0.1$

pH[c]	$[OCl^-]_0 \times 10^4$	$[TEPT]_0 \times 10^4$	k[a]	$k^b_{OCl^-}$ l. mole^{-1} min.$^{-1}$
9.0	1.52	11.6	0.00274	2.36
9.0	1.34	5.8	.00148	2.55
10.0	1.06	11.4	.00253	2.22
10.0	1.24	5.25	.00126	2.40

[a] Pseudo first-order rate constant. [b] $k_{OCl^-} = k/[TEPT]_0$. [c] At these pH levels, the hydrolysis of TEPT by OH^- (bimolecular rate constant = 0.17 l. mole^{-1} min.$^{-1}$ at 25°) can be neglected.

Experimental

Apparatus.—A Precision Scientific Company constant temperature bath maintained a jacketed cylindrical reaction vessel at ±0.5°. The Beckman Model K Automatic Titrator was utilized to maintain constant pH and measure rate of acid production. pH measurements were made coincidentally with the Beckman Model G pH meter. Absorbance measurements were made on the Beckman DU spectrophotometer.

Materials.—The triethylphosphorothiolate employed in this study had the following characteristics: C, found 36.3 (calcd. 36.35); H, 7.5 (7.63); P, 15.8 (15.63); S, 16.2 (18.2); and molecular weight 226 (198). Its purity was >95%. Hypochlorous acid was prepared by the addition of nitric acid to an aqueous suspension of High Test Hypochlorite, a product of Mathieson Chemical Corporation, containing 70% calcium hypochlorite, and subsequent distillation. The distillate was treated with freshly precipitated HgO to remove hydrochloric acid and then redistilled. A 0.01 M solution of HOCl stored in a refrigerator was found to be relatively stable over a period of a month. The HOCl was standardized by titration according to established procedures.[8] Residual chloride was estimated by titration for free acidity. All other chemicals were of ACS reagent grade.

Procedure.—Approximately 250 ml. of 0.1 M KNO_3 containing known quantities of chloride ion were placed into a reaction vessel. A volume of hypochlorous acid solution, usually from 1 to 5 ml., so as to result in a final concentration of HOCl between 5×10^{-5} and 2×10^{-4} M was added. (The exact concentration was estimated spectrophotometrically as described below.) The pH was adjusted to the desired level by the addition of small increments of either NaOH or HNO_3 and maintained by the automatic addition of 0.01 N NaOH (Beckman Autotitrator). Then an accurately measured volume (1 to 2 ml.) of freshly prepared stock solution of TEPT was added. Zero time was taken as the time when one half of the TEPT solution had been added. The rate of acid formation was followed by noting the volume of 0.01 N NaOH needed to maintain constant pH per unit time. At regular intervals aliquots of the reaction mixture were withdrawn and analyzed for total active halogen content by the following method:

1 or 2 ml. aliquots of the reaction mixture were added to a solution of 2 ml. of 0.05 N nitric acid and 3 ml. of 2% potassium iodide solution. The optical density was measured at 353 mμ, using distilled water as the reference sample and correcting for the absorbance due to the presence of excess iodine ion. The first-order rate constants, k_{obs}, were calculated directly from the slopes of plots of the logarithm of corrected optical density as a function of time.[9]

Volume changes due to the addition of titrant and/or removal of aliquots during the course of the reaction were assumed to be negligible in all calculations, since they never amounted to more than 5% at the end of the reaction. Most measurements were made only during the early stages (first 30 minutes) where volume changes were never greater than 2%.

At pH <5, the hypochlorous acid was stable. At pH ~ 7, a spontaneous deterioration was noted. This was minimized when distilled water which had first been treated with chlorine was employed. The contribution to the slope of this spontaneous deterioration was only of the order of 0.001, a value which lay within the error involved in measuring the slope. Because of the various approximations involved and the fact that small errors in obtaining the slopes resulted in large deviations in the calculated constants, the precision in obtaining $k_{obs}/[Cl^-]$ was of the order of ±10%.

The hydroxyl ion catalyzed hydrolysis of TEPT was followed by titration of mixtures containing 0.0088 M NaOH and 0.0052 M TEPT or 0.005 M NaOH and 0.0116 M TEPT. Second-order rate constants were calculated directly from the data. The hypochlorite catalyzed reaction was measured by following the decline in hypochlorite concentration at pH's of 9 and 10, in mixtures containing from 0.0005 to 0.0015 M TEPT. First-order plots were obtained when $[OCl^-] \geq [OH^-]$ and $[TEPT]_0 \gg [OCl^-]$.

Isolation and Identification of Ethane Sulfonyl Chloride as Amide.—Two grams of TEPT was added to 200 ml. of cold saturated chlorine water. Chlorine gas was bubbled through the solution until a positive test for hypochlorite was obtained. After 5 minutes, sodium thiosulfate was added until all hypochlorite was removed. The solution was extracted with ether, the ether layer dried and concentrated. Ammonia gas was passed through the ether solution for 30 minutes. The precipitated ammonium chloride was separated, the ether extract further concentrated and separated from the tacky residue which formed. Cooling further gave the sulfonamide, m.p. 58°, in agreement with its reported value.

Calcd. for $C_2H_7NO_2S$: C, 22.0; H, 6.42; N, 12.85. Found: C, 22.3; H, 6.3; N, 12.60.

Discussion

Chloride-dependent Chlorination of TEPT.—The experimental results suggest some interesting speculations as to the rates and mechanism of hydrolysis of chlorine. This follows from the following considerations. The value obtained for k_1 of 6.33×10^6 (the specific rate constant for chlorine formation) is in fair agreement with the value obtained by Soper and Smith[10] who proposed that the rate of chlorine formation was rate controlling in the chlorination of phenols with hypochlorous acid. It is also sufficiently close to the values obtained by measurements of the hydrolysis rate of chlorine[11] to lend credence to the proposal that the formation of chlorine is rate controlling in the chlorination of TEPT in dilute acidic solutions. Using a value of 4.48×10^{-4} at 25° for the equilibrium constant[12] for the chlorine hydrolysis reaction, the reverse rate (k_{-1}), *i.e.*, rate of chlorine hydrolysis, is 3×10^3 min.$^{-1}$.

Referring to Table III, the value of k_y/k_3 appears to be constant over the pH range investigated and hence $k_y = k_{-1} + k_{-2}[OH^-]$ must also be con-

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[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 307.

[9] The data by A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1341, 1842 (1951), on the extinction coefficients indicate that the extinction coefficients of I_2 (19) and I_2Cl^- (550) were small compared to that of I_3^-(26,400) at 353 mμ. The measured optical density when corrected for the presence of I^- could be assumed to be due to only the presence of I_3^-. Under the conditions of the method described above' the total iodine released by the chlorine was equivalent to 1.03 $[I_3^-]$.

This method for determining total chlorine concentration is valid since (a) the reaction between chlorine and KI is much more rapid than that between TEPT and chlorine and (b) a reaction between iodine and TEPT does not occur under these conditions. While botb NaCl and NaBr served to accelerate the reaction, the addition of NaI only quenched it.

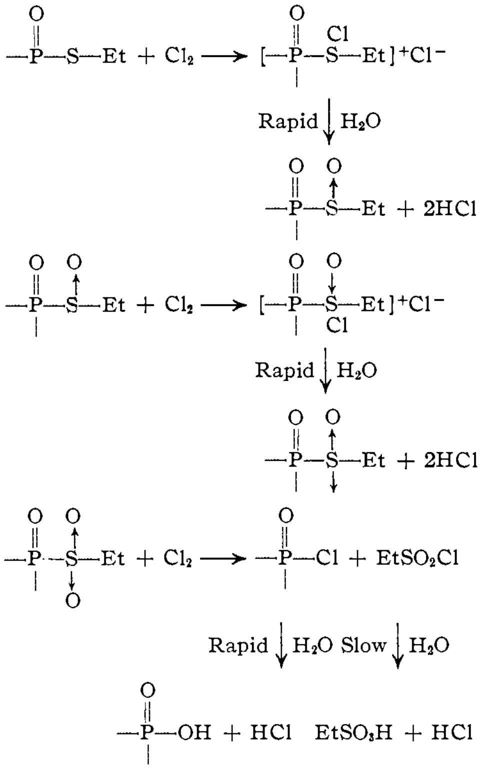
[10] F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 1582 (1926).

[11] E. A. Shilov and S. N. Solodushenkov, *Compt. rend. acad. sci. l'USSR*, **3**, No. 1, 17 (1936).

[12] A. A. Jakowkin, *Z. physik. Chem.*, **29**, 655 (1899).

stant. This can only be true if $k_{-1} >> k_{-2}$ [OH$^-$]. Hence k_{-2} cannot be much larger[13] than 10^9, since the constancy of k_y/k_3 is observed even at *p*H 7. Furthermore, it would appear that although chlorine is formed in neutral solution at a rate independent of hydrogen ion concentration, the hydrolysis of chlorine, even in neutral solution, takes place preferentially through a reaction with water molecules.

The specific rate constant for the chlorination of TEPT (k_3), calculated from $k_y/k_3 = 2 \times 10^{-5}$ where $k_y = 3 \times 10^3$, is 1.5×10^8 l. mole^{-1} min.$^{-1}$. It is believed that the chlorination of TEPT, as in the case of sulfides[14] occurs as



Chloride-independent Chlorination of TEPT.—Chlorine solutions are least stable at neutral and slightly alkaline *p*H levels. The rate of active halogen disappearance has been found to be proportional to the product of the hypochlorite ion and the square of the hypochlorous acid,[15] and it has been suggested that hypochlorous acid will oxidize hypochlorite ion. The instability of chlorine solutions, however, does not account for the destruction of active chlorine observed in the chloride ion independent reaction. Furthermore, the products of chlorination of TEPT[16] do not accelerate the destruction of chlorine, suggesting that there is no involvement of a catalytic impurity.

It is believed that although there is no appreciable reaction between TEPT and HOCl or TEPT and OCl$^-$ in neutral solution, there is a measurable rate when TEPT, HOCl and OCl$^-$ are present together in solution. This postulation is in accord with the termolecular concept of concerted displacement reactions suggested by Lowry[17] and extended by Swain.[17]

In any case, the relative magnitudes of the chloride-dependent as compared to the chloride-independent reaction will be dependent on chloride-ion concentration. For example, at *p*H 7 and a chloride of 10^{-3} *M*, the chloride ion independent reaction may constitute as much as 40% of the total rate; at 10^{-4} *M* chloride, 80%.

The Reaction of TEPT with OCl$^-$.—The kinetic data at *p*H's of 9 and 10 do not exclude the possibility of a direct attack on the sulfur atom of TEPT. A nucleophilic attack on phosphorus is postulated in this case since such an attack is known to occur with phosphorus compounds such as Sarin.[1] Assuming the attack is as postulated, it is interesting to compare the relative nucleophilicity of hypochlorite ion to Sarin and TEPT.

While, in the case of Sarin, k_{OH^-} was 4 to 5 times k_{OCl^-}, here k_{OCl^-} is observed to be on the order of 14 times k_{OH^-}. As in the case of the phosphonofluoridate, it is proposed that a bifunctional attack of the hypochlorite on the phosphorus atom and the phosphoryl oxygen is involved.

The increased reactivity of hypochlorite to TEPT is thought to be due to the increased polarizability of the phosphoryl group in TEPT because of a contribution by the adjacent sulfur atom. Spectral studies[18] on a number of phosphorus compounds suggest that the phosphoryl group is more subject to polarization when the phosphorus is attached to an alkylmercapto group than to a fluoride or alkoxy group.

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[13] J. C. Morris,[6] calculated a value of $k_{-2} = 5 \times 10^{14}$ from data of Shilov and Solodushenkov.[11] Dr. Takeru Higuchi has pointed out to us that, using data from "Oxidation Potentials," W. M. Latimer, 2nd Ed., Prentice–Hall, 1952, k_{-2}/k_2 is calculated to be approximately 2×10^9. From our value of 18.4 for k_2, k_{-2} is seen to be 3.7×10^{10}. Substitution of this value in the equation defining k_y, accounts for a two-fold change in the ratio k_y/k_3, a shift within experimental error.

[14] H. Gilman, "Organic Chemistry," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 858, 873.

[15] A. Skrabal, *Monatsh.*, **73**, 269 (1949); J. J. Weiss, *Z. Elektrochem.*, **37**, 20 (1931).

[16] This experiment was performed as follows: TEPT was allowed to react completely with a large excess (6 moles) of chlorine. The *p*H was then adjusted to 6.0. Measurements of available chlorine were constant over a period of 1 hr.

[17] Lowry, *J. Chem. Soc.*, 2254 (1927); C. G. Swain, THIS JOURNAL, **72**, 4578 (1950).

[18] J. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *ibid.*, **76**, 5185 (1954).