[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF NEW MEXICO]

The Exchange Reaction between Tin(IV) and Tin(II) in Absolute Ethyl Alcohol

BY E. GERALD MEYER[1] AND MILTON KAHN

A measurable exchange has been observed in absolute ethyl alcohol between the tin atoms in stannous and stannic chloride. Over a concentration range of 0.0438 to 0.2725 *M* total tin and a temperature range of 25.1 to 42.2° the exchange rate is well represented by $R = 5.02 \times 10^{16} e^{-23,700/RT}$ ($SnCl_2$)($SnCl_4$) where the units of R are moles liter^{-1} hr.$^{-1}$. A method has been developed for the separation of tin(II) from tin(IV) in absolute alcohol by means of precipitation of the tin(II) as stannous oxalate.

This paper deals with a study of the exchange reaction between tin(IV) and tin(II) chlorides in absolute ethyl alcohol. The reaction was found to be homogeneous and first order with respect to both the stannic chloride and stannous chloride concentrations.

Experimental

Radioactivity.—The 1.1-day Sn^{121} was used as tracer in all experiments. The Sn^{121} was produced by irradiating stannic chloride in the Los Alamos Fast Reactor for two hours. During a two-hour irradiation the activities of Sn^{113} and Sn^{123} produced are negligible compared to that of Sn^{121}. The 2.7-year Sb^{125} that is produced through decay of the 10-minute Sn^{125} is also negligible compared to the Sn^{121} activity.

Stock solutions of stannic chloride tracer were prepared by distilling the irradiated stannic chloride directly into alcohol.

The radiochemical purity of the tracer was checked by observing the decay of an active sample of tin. The tin sample decayed with a 27 ± 1-hour half-life over a period of five half-lives in satisfactory agreement with the previously reported value.[2] Also, the specific activity of an aliquot of an active stannic chloride solution was the same as that of an aliquot purified from arsenic carrier.

Chemicals.—Stannic chloride was prepared by the action of chlorine gas on Baker C.P. Analyzed tin. The crude product was distilled several times to eliminate the dissolved chlorine. The final product, a colorless liquid, was analyzed by precipitation of metastannic acid and found to be 99.5% pure.

Anhydrous stannous chloride was obtained from the Metal and Thermit Corp., New York City, under the trade name "Stannochlor." The stannous chloride was found to be 99.8% pure on the basis of a gravimetric tin analysis, 99.3% pure on the basis of a gravimetric chloride analysis, and 99.2% pure on the basis of an iodimetric titration.

U. S. Industrial Chemicals, Inc., absolute ethyl alcohol was stored over Drierite. Dried nitrogen was bubbled through the alcohol prior to use in order to remove dissolved oxygen.

Mallinckrodt Analytical Reagent Grade oxalic acid was ground to pass an eighty-mesh screen.

Phenylarsonic acid, obtained from Eastman Kodak Co., was used without further purification.

Procedure.—Reaction solutions were prepared on dissolving a known amount of stannous chloride in nitrogen-treated absolute alcohol, adding the necessary amount of active stannic chloride solution, and then diluting to a known volume with alcohol. All solutions were brought to equilibrium temperature before being mixed. The concentration of stannous chloride in each reaction solution was checked by an iodimetric titration. The concentration of stannic chloride was computed from the known composition of the active stannic chloride solution which had been analyzed by precipitation of metastannic acid.

Aliquots of a reaction solution were pipetted into small glass tubes. The air above the solution in each tube was displaced with nitrogen and then the tube was sealed and placed in a constant temperature (±0.1°) water-bath. Duplicate tubes were opened at known time intervals and the reactants were separated from a portion of each solution. Another portion was pipetted into a known quantity of standard iodine solution and the excess iodine titrated with thiosulfate to determine how much stannous chloride had been oxidized. If the stannous chloride titer did not check that obtained for the solution at the beginning of the experiment within 2%, the sample was discarded; about 3% of the samples were rejected. The timing of sample withdrawals was such that the fraction exchanged was measured over a range from about 20 to 80%. The reaction time was reckoned from the time of mixing of solutions.

Separation Procedure.—Oxalic acid was used to precipitate stannous oxalate. The completeness of the precipitation was dependent on the concentration of stannic chloride. However, recovery of at least 86% of the total tin(II) as stannous oxalate was possible for all reaction mixtures. The separation was effected by adding an appropriate amount of reaction solution to powdered oxalic acid. The suspension was stirred for approximately three minutes and then the undissolved oxalic acid and the stannous oxalate were removed by centrifugation. The precipitate was washed with two 5-ml. portions of 95% alcohol, dissolved in 0.5 ml. of 12 *f* hydrochloric acid, diluted with 5 ml. of water, and then a slight excess of 0.0315 *f* iodine solution was added to oxidize the tin(II) to tin(IV). The excess iodine was back-titrated with 0.0302 *f* thiosulfate, and the solution was diluted with water to 10 ml. The tin was then precipitated by the addition of 5 ml. of saturated aqueous phenylarsonic acid solution.[3] The suspension was heated in a steam-bath for ten minutes, cooled to room temperature, allowed to stand for 15 minutes, and centrifuged. The precipitate was washed with a 5-ml. portion of 95% alcohol and then mounted for the determination of the specific activity of the tin(II) fraction.

The supernatant liquid from the oxalate precipitate and the washings from the stannous oxalate were combined and treated with iodine solution and thiosulfate as mentioned above. The tin was precipitated with 6 *f* ammonium hydroxide and the hydrated tin oxide was washed with a 10-ml. portion of water, dissolved in 0.8 ml. of 12 *f* hydrochloric acid and diluted to 10 ml. with water. The tin was precipitated with phenylarsonic acid as described above and mounted for a check on the total tin and on the total activity.

The value for the equilibrium specific activity of the tin(II) fraction was obtained by completely oxidizing a portion of the reaction solution with iodine and then precipitating the tin with phenylarsonic acid from suitable aliquots of this solution. For each run the average value for the activity of three such samples was used as the equilibrium specific activity.

Measurement of Radioactivity.—Each precipitate was suspended in 5 ml. of 95% alcohol and then prepared for counting by filtration on a tared, 18-mm. diameter, Whatman #50 filter paper, dried for ten minutes at 110°, and weighed. The counting samples measured 14 mm. in diameter and were mounted on 2 × 2$^1/_2$ in. cardboard cards with scotch tape placed directly over the sample. These cards were placed in a holder which fixed the position of the sample relative to an Amperex #100C Geiger–Müller tube. All counting samples had activities within the range from 100 to 1000 counts per minute, and in this range the response of the counter was linear.

The samples mounted for counting varied somewhat in thickness, necessitating correctness for self-absorption of the beta particles. For example, the thicknesses of the Sn(II) samples for a particular run varied as much as 1.3 mg./sq. cm., and a similar variation was observed for the Sn(IV)

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[1] (a) This paper is a portion of the dissertation presented by E. Gerald Meyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, September, 1950; (b) University Fellow, University of New Mexico, 1948–1950; (c) present address, College of St. Joseph, Albuquerque, New Mexico.

[2] J. C. Lee and M. L. Pool, *Phys. Rev.*, **76**, 606 (1949).

[3] J. S. Knapper, K. A. Craig and G. C. Chandlee, THIS JOURNAL, **55**, 3945 (1933).

samples. In general, the Sn(II) samples obtained in a single run differed in thickness from the Sn(IV) samples, the difference running as high as 10 mg./sq. cm. The experimentally determined self-absorption correction amounted to a 1.15% increase in the total counting rate of a sample for each milligram increase in sample weight. The correction factor was constant over the range of thicknesses encountered (19–40 mg./sq. cm.).

Errors.—In all exchange experiments a material balance on the total tin and total activity was obtained within a probable error of ±3%. The error in the correction for radioactive decay was small because samples to be intercompared were counted within a few hours of one another. The main sources of experimental error were the uncertainty in the concentrations of the solutions (*ca.* ± 2%), uncertainty in the weight of the counting samples (*ca.* ± 1%), and the statistical fluctuations in the counting rate (*ca.* ± 1%). The probable error in the rates is thought not to be greater than 4%.

Results

The reaction investigated is $SnCl_2 + \overset{*}{Sn}Cl_4 = \overset{*}{Sn}Cl_2 + SnCl_4$, where the asterisks indicate radioactive atoms. The logarithmic form of the first order exchange law[4,5,6] for this particular reaction is

$$-\ln(1 - F) = \frac{R[(SnCl_2) + (SnCl_4)]t}{(SnCl_2)(SnCl_4)} \qquad (1)$$

where $(SnCl_2)$ = total concentration (active + inactive) of $SnCl_2$ in moles per liter. $(SnCl_4)$ = total concentration (active + inactive) of $SnCl_4$ in moles per liter. F = fraction exchange at time, t, = specific activity of stannous chloride at time, t, divided by the equilibrium specific activity of stannous chloride (specific activity of stannous chloride at time, $t = \infty$) where the specific activity of stannous chloride = 0 at time, $t = 0$. R = actual rate at which the exchange of tin atoms between $SnCl_2$ and $SnCl_4$ takes place. For any one experiment, R will be constant because $(SnCl_2)$ and $(SnCl_4)$ are constant.

According to equation (1), a plot of log $(1 - F)$ *vs.* time should give a straight line passing through 1.0 at zero time regardless of the mechanism. A typical set of data is plotted in Fig. 1.

Separation-induced exchange and coprecipitation effects[7] were absent within the experimental error. This is indicated by the fact that the curves in Fig. 1 extrapolate to zero fraction exchange at zero time as is required by the first order exchange law. Also, a number of zero-time measurements wherein the reactants were mixed and then immediately separated showed zero exchange at zero time.

When 50% exchange has taken place, $F_{1/2}$, $t = T_{1/2}$ by definition, substitution of $^1/_2$ for $(1 - F)$ and $T_{1/2}$ for t in equation (1) gives

$$R = \frac{(SnCl_2)(SnCl_4)\ln 2}{[(SnCl_2) + (SnCl_4)]T_{1/2}} \qquad (2)$$

Since in any one run $(SnCl_2)$ and $(SnCl_4)$ are known, it is possible to evaluate R, the rate of exchange, for this particular run, after having determined $T_{1/2}$, the half-time for exchange, from a plot of log $(1 - F)$ *vs.* t.

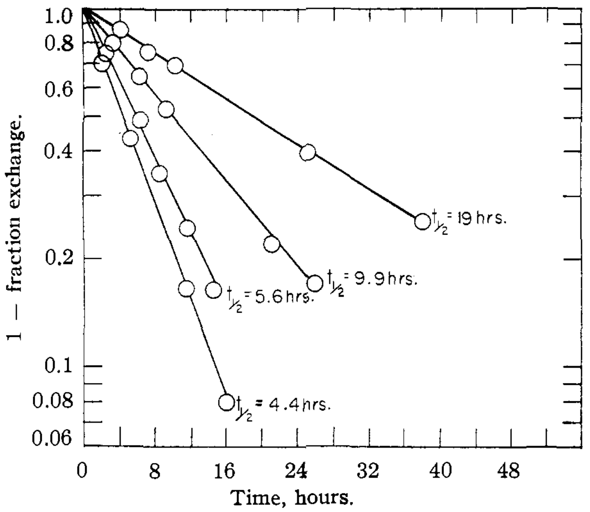

Fig. 1.—Semi-logarithmic plot of (1 − fraction exchange) against time for runs 7, 8, 9 and 10.

If the exchange reaction is first order with respect to both the stannous chloride and stannic chloride concentrations, $R = k(SnCl_4)(SnCl_2)$, substitution of $k(SnCl_4)(SnCl_2)$ for R in equation (2) gives

$$T_{1/2} = \frac{0.693}{[(SnCl_2) + (SnCl_4)]} \times \frac{1}{k} \qquad (3)$$

The data of Table I are plotted in Fig. 2. It is seen that the half-time of exchange varies inversely as the total tin concentration in accordance with equation (3).

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Expt.	Temp., °C.	Sn(II) concn., *f*	Sn(IV) concn., *f*	$t_{1/2}$, hr.	$R \times 10^4$, mole liter^{-1} hr.$^{-1}$	k, mole^{-1} liter· hr.$^{-1}$
1	25.1	0.0263	0.0283	57	1.66	0.222
2	25.1	.0430	.0460	37	4.17	.211
3	25.1	.0566	.0767	24	9.53	.217
4	29.4	.0213	.0225	42	1.80	.377
5	29.4	.0416	.0419	22	6.57	.377
6	29.4	.0630	.0629	15	14.6	.367
7	35.5	.0213	.0225	19	3.99	.833
8	35.5	.0416	.0419	9.9	14.4	.838
9	35.5	.0630	.0831	5.6	44.4	.847
10	35.5	.0975	.0936	4.4	75.3	.825
11	42.2	.0223	.0411	5.6	17.9	1.95
12	42.2	.0630	.0629	2.9	75.1	1.90
13	42.2	.0701	.0381	3.4	50.4	1.89
14	42.2[a]	.0701	.0381	3.4	50.4	1.89
15	42.2	.0812	.1913	1.3	30.3	1.95
16	42.2[b]	.0812	.1913	1.3	30.3	1.95

[a] Reaction vessel packed with glass wool. [b] Reaction vessel packed with glass helices.

Heterogeneous Catalysis.—Experiments 14 and 16, aside from having Pyrex glass wool or helices present in the reaction mixtures, were duplicates of experiments 13 and 15, respectively. In each case the half-times for exchange were the same within experimental error.

The Activation Energy.—The curve shown in Fig. 3 is a semi-logarithmic plot of the average

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[4] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[5] R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

[6] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 285 ff.

[7] R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949).

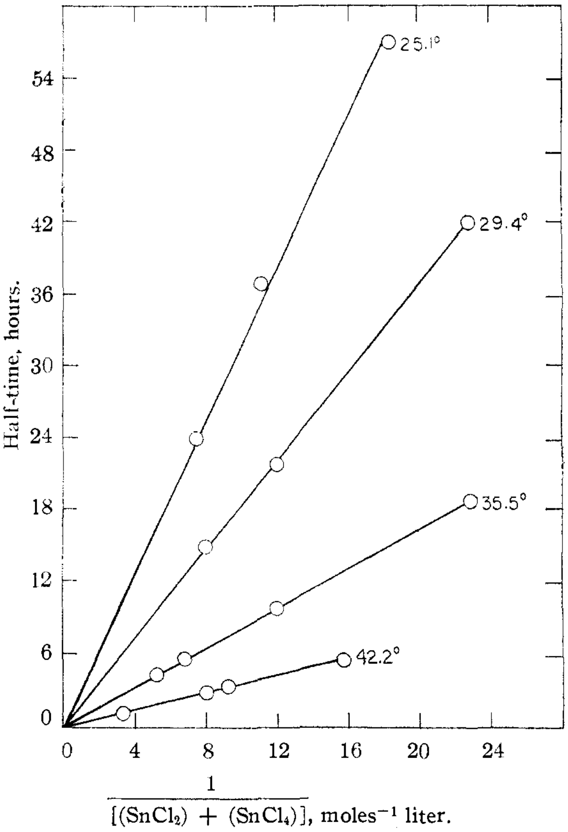

Fig. 2.—Effect of total tin concentration on the half-time of the exchange.

values for the velocity constant *k* against the reciprocal of the absolute temperature The experimental activation energy determined from this plot is 23,700 ± 800 cal.

The Rate Law.—From the foregoing discussion it appears that the exchange reaction is homogeneous and first order with respect to both the stannous chloride and stannic chloride concentrations over a temperature range from 25.1 to 42.2° and a concentration range from 0.0438 to 0.2725 *M* total tin. The rate law for the exchange reaction is

$$R = 5.02 \times 10^{16}e^{-23,700/RT}(SnCl_4)(SnCl_2)$$

where the units of *R* are moles liter^{-1} hr.$^{-1}$.

Discussion of Results

At least two mechanisms can be postulated which agree with the experimentally determined rate law and the known chemistry and structure of the tin chlorides. One mechanism is represented by equations (4) and (5).

$$SnCl_2 + \overset{*}{Sn}Cl_4 = Sn\overset{*}{Sn}Cl_6 \text{ (rapid equilibrium)} \quad (4)$$
$$\text{(activated complex)}$$

$$Sn\overset{*}{Sn}Cl_6 \longrightarrow \overset{*}{Sn}Cl_2 + SnCl_4 \text{ (rate determining step)} \quad (5)$$

Stannic chloride is a tetrahedral molecule with a tin–chlorine bond length of 2.30 Å.[8] According to[9] Lister and Sutton, the angle in stannous chloride is expected to be slightly larger than 90°, both from theory and measurements on related compounds; the tin–chlorine bond length is 2.42 Å. Conceivably, a stannic chloride molecule could approach a stannous chloride molecule in such a way as to form a configuration consisting of two tetrahedral stannic chloride molecules sharing two chlorine atoms along a common edge. Upon dissociation, this symmetrical activated complex would yield a radioactive tin atom with either two or four chlorine atoms.

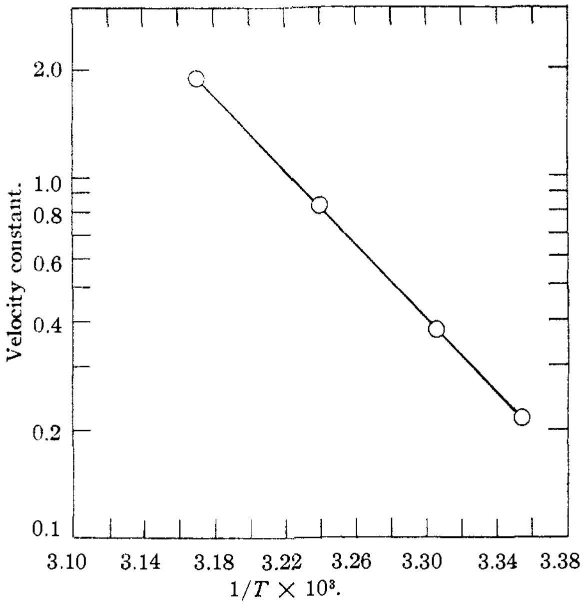

Fig. 3.—The temperature dependence of the exchange reaction.

It is quite possible that solvated tin chloride molecules are taking part in the exchange reaction and that the activated complex is solvated. Robiquet[10] obtained evidence for the existence of $SnCl_4 \cdot 2C_2H_5OH$, and the hydrate $SnCl_2 \cdot 2H_2O$ is well known. If the exchange reaction occurs between solvated molecules, a reasonable formula for the activated complex would be $Sn\overset{*}{Sn}Cl_6 \cdot 4C_2H_5OH$ wherein two octahedral $SnCl_4 \cdot 2C_2H_5OH$ molecules share two chlorine atoms along a common edge. Upon dissociation, such an activated complex would also yield a radioactive tin atom with either two or four chlorine atoms.

The second mechanism, which involves the same activated complex postulated in the foregoing discussion, is shown below. This mechanism is

$$\overset{*}{Sn}Cl_4 = \overset{*}{Sn}Cl_3{}^+ + Cl^- \text{ (rapid equilibrium)} \quad (6)$$

$$SnCl_2 + Cl^- = SnCl_3{}^- \text{ (rapid equilibrium)} \quad (7)$$

$$\overset{*}{Sn}Cl_3{}^+ + SnCl_3{}^- = Sn\overset{*}{Sn}Cl_6 \text{ (rapid equilibrium)} \quad (8)$$
$$\text{(activated complex)}$$

$$Sn\overset{*}{Sn}Cl_6 \longrightarrow \overset{*}{Sn}Cl_2 + SnCl_4 \text{ (rate determining step)} \quad (9)$$

dependent on the existence of $SnCl_3{}^+$ and $\overset{*}{Sn}Cl_3{}^-$ ions in alcohol. The former ion would result from the ionization of stannic chloride. Evidence which

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[8] L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

[9] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 406 (1941).

[10] Robiquet, *Jahresber.*, 560 (1854).

supports this hypothesis is derived from measurements of the conductivity of solutions of stannic chloride in alcohol. Wertyporoch and Altmann[11] measured the specific conductivities of solutions of stannic chloride in alcohol at 0°. Values of 2.53, 2.88 and 3.83×10^{-4} ohms^{-1} were obtained for stannic chloride concentrations of 0.0436, 0.0863 and 0.1293 mole per liter, respectively. According to Smyth,[12] the tin–chlorine bond in stannic chloride is almost electrovalent in character. According to Delwaulle and Francois,[13] and Prytz,[14] stannous chloride and chloride ion, in aqueous solutions, react to form the complex ion $SnCl_3^-$. It is assumed that this reaction would also take place in alcohol solutions.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. W. Spence and Mr. James Sattizahn of the Los Alamos Scientific Laboratory for irradiation of the samples of stannic chloride.

(11) E. Wertyporoch and B. Altmann, *Z. physik. Chem.*, **A168**, 1 (1934).

(12) C. P. Smyth, THIS JOURNAL, **60**, 183 (1938).

(13) M. L. Delwaulle and F. Francois, *Compt. rend.*, **211**, 65 (1940).

(14) M. Prytz, *Z. anorg. allgem. Chem.*, **172**, 147 (1928).

ALBUQUERQUE, NEW MEXICO RECEIVED MARCH 31, 1951

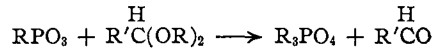
[CONTRIBUTION FROM THE PROCESS IMPROVEMENT AND DEVELOPMENT LABORATORIES, TENNESSEE EASTMAN COMPANY]

Reactions of Some Orthoesters with Phosphorus Pentoxide and Phosphorus Pentasulfide

BY KENT C. BRANNOCK[*]

The reactions of some aliphatic orthoesters with phosphorus pentoxide and phosphorus pentasulfide have been investigated. Ethyl orthoformate and phosphorus pentoxide yield triethyl phosphate, tetraethyl pyrophosphate and ethyl formate. Phosphorus pentasulfide and ethyl orthoformate react to give a triethyl dithiophosphate, ethyl formate and ethyl thionoformate. Phosphorus pentasulfide and ethyl orthothioformate give triethyl tetrathiophosphate and ethyl dithioformate, while under similar conditions phosphorus pentoxide and ethyl orthothioformate do not react. The scope and limitations of this type of reaction remain to be determined.

The preparation of trialkyl phosphates by the interaction of an alkyl metaphosphate and an acetal has been reported.[1] This may be illustrated as follows[2]



$$RPO_3 + R'\overset{H}{C}(OR)_2 \longrightarrow R_3PO_4 + R'\overset{H}{C}O$$

In view of this reaction, it seemed logical to investigate the reactions of the acetal-like alkyl orthoesters with compounds having a polyphosphate structure, such as phosphorus pentoxide. A literature survey disclosed that Staudinger and Rathsam[3] attempted to obtain ketene acetal by treating ethyl orthoformate with phosphorus pentoxide, but obtained ethyl formate instead. Similar results were obtained with ethyl orthoacetate and ethyl orthopropionate, and the reaction was thought to proceed as $RC(OEt)_3 \xrightarrow{P_2O_5} RCOOEt + Et_2O$. Although no ether was obtained, they speculated that it was formed but underwent further reaction with the phosphorus pentoxide. Under the conditions used by these authors any ether formed in the reaction should have been recovered, since the reaction of ether with phosphorus pentoxide at temperatures attainable under atmospheric pressure is very slow. For example, the preparation of ethyl metaphosphate from phosphorus pentoxide and excess ether at reflux temperature requires about 60 hours.[4]

It has been shown in the present investigation that ethyl orthoformate reacts with phosphorus pentoxide at elevated temperatures to give triethyl phosphate, tetraethyl pyrophosphate and ethyl formate. The over-all reactions may be illustrated by the equations

$$P_2O_5 + 2HC(OEt)_3 \longrightarrow 2HCOOEt + (EtO)_2P(O)OP(O)(OEt)_2$$

$$P_2O_5 + 3HC(OEt)_3 \longrightarrow 3HCOOEt + 2Et_3PO_4$$

Extending the reaction to the sulfur analogs, it was found that ethyl orthoformate and phosphorus pentasulfide at 95–150° give ethyl formate, ethyl thionoformate and a triethyl dithiophosphate. No chemical evidence was obtained to justify the assignment of a definite structure to the latter compound; therefore, it may be either O,O,S-triethyl dithiophosphate or O,S,S-triethyl dithiophosphate.

$$P_2S_5 + 3HC(OEt)_3 \longrightarrow 2HCOOEt + HCSOEt + 2Et_3PO_2S_2$$

Similarly, ethyl orthothioformate and phosphorus pentasulfide give triethyl tetrathiophosphate and, by analogy, ethyl dithioformate.

$$P_2S_5 + 3HC(SEt)_3 \longrightarrow 3HCSSEt + Et_3PS_4$$

Ethyl orthothioformate and phosphorus pentoxide do not appear to react at 150°.

The mechanism of this type of reaction as well as its scope and limitation remains to be determined.

Acknowledgment.—The author is indebted to Mr. Stanley A. Murray of these laboratories for his helpful discussions and the tetraethyl pyrophosphate analysis reported below.

Experimental[5]

Materials.—The phosphorus pentoxide and phosphorus pentasulfide used in this investigation were commercial products. Ethyl orthoformate was a redistilled Eastman

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[*] Department of Chemistry, Emory University, Ga.

(1) D. C. Hull and A. H. Agett, U. S. Patent 2,430,569 (1947).

(2) For the sake of simplicity the empirical formula of the alkyl metaphosphate is used, although it is known that these esters exist in a condensed or polyphosphate state. This is discussed briefly in G. M. Kosolapoff, "Organophosphorus Compounds," Chapter 12, John Wiley and Sons, Inc., New York, N. Y., 1950.

(3) H. Staudinger and H. Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

(4) K. Langheld, *Ber.*, **44**, 2076 (1911).

(5) All boiling points are uncorrected.