bromine. However, this effect is overshadowed by the fact that the more acidic N-2-bromoethyl-*p*-nitrobenzamide produces a greater number of ions than the unsubstituted benzamide homolog.

TABLE III

RATES OF ALKALINE METHANOLYSIS OF N-2-BROMOETHYLBENZAMIDES AND N-ARYL-4-BROMOBUTANAMIDES AT 22.90°

Compound	$k \times 10^3$, l. moles^{-1} sec.$^{-1}$
N-2-Bromoethyl-*p*-chlorobenzamide	4.53
N-*p*-Chlorophenyl-4-bromobutanamide	9.41
N-2-Bromoethylbenzamide	2.20
N-Phenyl-4-bromobutanamide	3.00

An alternate interpretation which will equally well accommodate the data is a concerted mechanism whereby the methoxide ion removes the proton while at the same time the oxygen is executing a nucleophilic displacement of the bromine. Finally, it is of interest to compare under the same experimental conditions the relative rates of alkaline solvolyses of the N-2-bromoethylbenzamides to form the oxazolines with the alkaline solvolyses of the N-aryl-4-bromobutanamides which give the N-arylpyrrolidones. These results are shown in Table III.

Evidently there is no great difference in the rate of O-alkylation to form oxazolines and N-alkylation to form pyrrolidones.

Acknowledgment.—The author wishes to thank the Dow Chemical Co., Midland, Mich., for a generous grant to carry out this study.

LEWISBURG, PENNSYLVANIA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Elemental Sulfur. I. The Uncatalyzed Reaction of Sulfur with Triarylphosphines[1]

BY PAUL D. BARTLETT AND GARBIS MEGUERIAN[2]

RECEIVED FEBRUARY 10, 1956

The uncatalyzed reaction between ordinary sulfur, S_8, and triphenylphosphine under nitrogen to yield triphenylphosphine sulfide is of the second order. Its rate is strongly increased by ionizing solvents and by electron-releasing substituents in the phenyl groups, the reaction having a value of $\rho = -2.5$ in the Hammett equation. It is concluded that this reaction begins as a nucleophilic displacement of sulfur on sulfur by the basic phosphine, with opening of the sulfur ring to a dipolar ion which then reacts rapidly in a series of follow-up reactions with more triphenylphosphine. Two other forms of elemental sulfur, the rhombohedral hexatomic form of Aten and the amorphous form produced by irradiation in solution, react immeasurably fast with triphenylphosphine, affording a titration method both for total sulfur and for S_8 in the presence of other forms.

Introduction.—The eight-membered ring structure of the common rhombic or monoclinic sulfur has been fully established by X-ray methods,[3] and an interesting explanation has been offered for the stability of this eight-membered ring in comparison to all other structural forms of sulfur.[4] At temperatures above the melting point the thermal interconversion of different molecular forms of sulfur proceeds readily, and in the neighborhood of 140° the equilibrium favors very high polymers of biradical[5] or cyclic[6] character. In sulfur vapor at much higher temperatures the equilibrium shifts back ultimately in favor of the species S_2 and S_1.[7]

Among the many reactions of elemental sulfur with organic compounds, the well-known processes of dehydrogenation and of the vulcanization of rubber take place at such high temperatures that rapid interconversion of a number of molecular forms of sulfur may be assumed. There are, however, certain reactions into which sulfur enters with organic compounds under such mild conditions that the mechanism by which the eight-membered ring is opened and the sulfur distributed to a number of different molecules presents a challenging problem. When sulfur acts as an inhibitor of the polymerization of olefinic substances[8,9] or reacts with triphenylmethyl radicals[10] or with liquid ammonia,[11] the conditions are so mild that the products must be formed by a series of steps commencing with the direct opening of the eight-membered ring of sulfur. While it is likely that the reactions of sulfur with free radicals are of the homolytic type, the importance of ammonia, hydroxy compounds, amines and sulfides as redistributors of sulfur[12,13] suggests that the sulfur ring may be opened also by heterolytic or polar mechanisms. The present work is concerned with a reaction clearly of this type.

The Reaction of Sulfur with Tertiary Phosphines.—Trialkylphosphines react vigorously with sulfur to yield trialkylphosphine sulfides.[14,15] Replacement of one alkyl by a phenyl group leaves the

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(1) This work was supported in part by a grant from the Research Corporation. Reported at the Fifth Conference on Reactions Mechanisms, Durham, N. H., September 10, 1954.

(2) Corina Borden Keen Fellow from Brown University, 1950–1951.

(3) B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935); S. C. Abrahams, *Acta Cryst.*, **8**, 661 (1955).

(4) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 495 (1949).

(5) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

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(7) G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

(8) P. D. Bartlett and H. Kwart, THIS JOURNAL, **74**, 3969 (1952).

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(11) F. W. Bergstrom, THIS JOURNAL, **48**, 2319 (1926).

(12) R. C. Fuson, C. C. Price, D. M. Burness, R. E. Foster, W. R. Hatchard and R. D. Lipscomb, *J. Org. Chem.*, **11**, 487 (1946).

(13) A. Smith and W. B. Holmes, *Z. physik. Chem.*, **54**, 255 (1906).

(14) A. Cahours and A. W. Hofmann, *Ann.*, **104**, 12, 23 (1857).

(15) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter 6.

rate still too fast for convenient measurement, less than 30 seconds being required for apparently complete reaction of dimethylphenylphosphine with sulfur at concentrations of 0.1 M in benzene.[16] Triphenylphosphine, however, reacts with sulfur at room temperature at a rate convenient for kinetic studies. Among the low temperature reactions of sulfur, this one is almost unique for its cleanness since the tertiary phosphine monosulfide is the only product observed.

Titration Method.—Triphenylphosphine can be titrated in the presence of triphenylphosphine sulfide by means of a moist solution of iodine, which converts the phosphine into triphenylphosphine oxide with formation of hydrogen iodide. In this work we used a standard solution of iodine in a solvent composed of benzene (75%) and 95% ethanol (25%), containing 5 g. of pyridine per liter. Triphenylphosphine sulfide is inert to the iodine solution and iodine can be titrated by the standard methods in the presence of triphenylphosphine oxide and sulfide.

Reproducibility of Rate Measurements.—When freshly prepared (within hours) solutions of triphenylphosphine were used, the rate of the uncatalyzed reaction between triphenylphosphine and sulfur in benzene, chlorobenzene and a number of mixed solvents was reproducible and accurately of the second order (first order with respect to each of the reactants). Dr. E. F. Cox has also obtained reproducible rate constants in cyclohexane and carbon tetrachloride and has explored the effects of oxygen and light upon the reaction (Part II of this series).[17] The kinetic experiments of the present paper were all made under nitrogen.

Effect of Solvent on Rate of Reaction.—The rate of the reaction is sharply dependent upon the solvent, a behavior generally noted for reactions involving transition states of ionic or highly polar character. Table I shows the second-order rate constants for the reaction in four rather non-polar solvents. For comparison there are included the relative rate constants, with benzene taken as 100, for these solvents and for a similar range of solvents in which the rate of formation of p-nitrobenzyltrimethylammonium chloride has been measured. *The sensitivity of the triphenylphosphine–sulfur reaction to solvent change is at least as great as that of quaternary salt formation*, in which the transition state must be something like half separated into ions.

TABLE I

EFFECT OF SOLVENT ON RATE OF REACTION OF SULFUR WITH TRIPHENYLPHOSPHINE IN COMPARISON WITH RATE OF FORMATION OF QUATERNARY AMMONIUM SALTS

	$k_2 \times 10^5$ (l./mole sec.) for formation of		Relative rate constant	
Solvent	Ph_3PS, 25°	p-O_2N-C_6H_4N-$(CH_3)_3^+Cl^-$,[a] 25°	Ph_3PS	p-O_2N-C_6H_4N-$(CH_3)_3^+$-Cl^-[a]
α-$C_{10}H_7Br$		23.8		960
C_6H_5Cl	3130 (35°)		260	
Benzene	458 (1130 at 35°)	2.5	100	100
CCl_4	93		20.3	
Cyclohexane	5.8		1.25	
Hexane		0.145		5.8

[a] H. v. Halban, *Z. physik. Chem.*, **84**, 129 (1913).

Mixtures of Benzene and Ionizing Solvents.—As suggested by this solvent sensitivity, the rate constant also responds to the presence in the solvent benzene of small amounts of acetonitrile, methanol or phenol. Benzene saturated with water afforded a rate constant consistently 15–20% higher than dry benzene. Figure 1 shows the bimolecular rate constant for the triphenylphosphine–sulfur reaction in benzene as a function of the amount of "ionizing" solvent added. The effects are large and are not linear in the added solvent; the curves all rise with increasing steepness as the concentration of ionizing solvent is increased. This is typical of the effects observed by Farinacci and Hammett[18] in the solvolysis of benzhydryl chloride and strengthens the similarity between the present reaction and an ionization process. A further point of similarity is that the effectiveness of the solvent is parallel to its hydrogen bonding power (its ability to solvate anions) but by no means to its dielectric constant, since the order of increasing effectiveness of acetonitrile, methanol and phenol is not the order of increasing dielectric constant. Figure 2 emphasizes this; the rate constants are plotted against the dielectric constants of the mixed solvents, estimated by assuming proportionality.

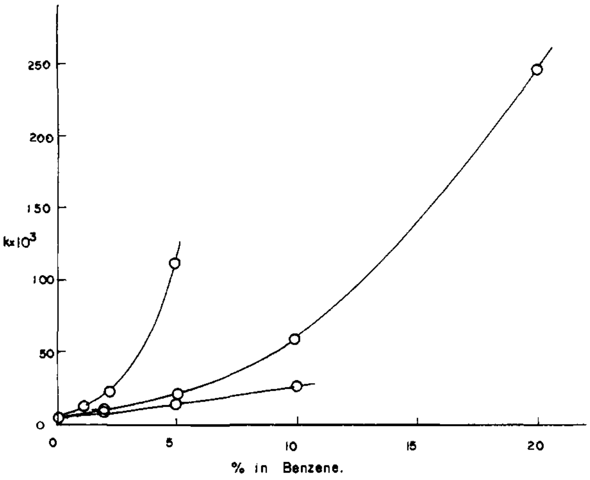

Fig. 1.—Effect of added substances on bimolecular rate constant for reaction of sulfur with triphenylphosphine in benzene at 25°: upper curve, phenol; middle curve, methanol; lower curve, acetonitrile.

The Effect of *para* Substituents in Triphenylphosphine.—One reasonable mechanism for the reaction between triphenylphosphine and sulfur is that it begins as a nucleophilic displacement of sulfur on sulfur by the phosphorus atom of the phosphine, opening the sulfur ring to a linear octasulfide with positive charge on the phosphonium phos-

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(16) W. C. Davies and W. P. Walters, *J. Chem. Soc.*, 1792 (1935).

(17) P. D. Bartlett and E. F. Cox, to be published.

(18) N. Farinacci and L. P. Hammett, THIS JOURNAL, **59**, 2542 (1937).

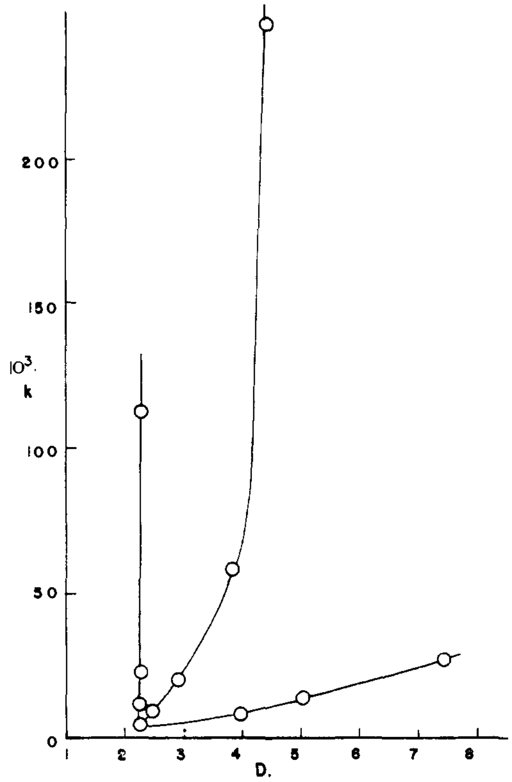
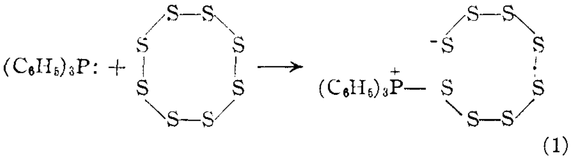


Fig. 2.—Same data as in Fig. 1, plotted against estimated dielectric constant of solvent mixture, showing specific dependence of rate on solvent: left-hand curve, phenol; middle curve, methanol; right-hand curve, acetonitrile.

phorus atom and negative charge on the displaced sulfur atom



(1)

This would make the reaction, in its rate-determining step, closely analogous to the Menschutkin reaction and would account for the favorable effect of anion-solvating solvents upon the rate of the reaction. This mechanism would respond to substitution in the phosphine in the same way as the basicity, being favored by electron-releasing and retarded by electron-attracting substituents. Table II lists the rate constants for tri-*p*-tolylphosphine and the mono-, di- and tri-*p*-chlorotriphenylphosphines, and Figure 3 shows the data so plotted as to test the applicability of the Hammett equation, log k being plotted against the sum of the σ-constants for all the substituents. The slope of this plot yields a value of $\rho = -2.5$; therefore polar substituents affect the rate of this reaction more than twice as strongly as they affect the ionization constant of benzoic acid.

TABLE II

EFFECT OF *para* SUBSTITUENTS ON RATE OF REACTION BETWEEN TRIPHENYLPHOSPHINE AND SULFUR IN BENZENE AT 25°

p-Substituent	Number	Total σ	$k \times 10^5$, l./mole sec.
CH_3	3	−0.51	6770
None		0	458
Cl	1	+0.227	100
Cl	2	+ .45	47
Cl	3	+ .68	5

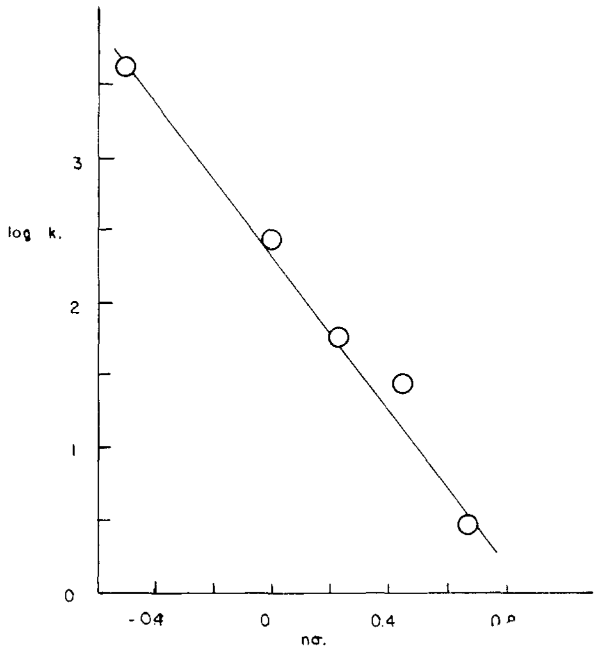


Fig. 3.—Application of the Hammett equation to the reaction of sulfur at 25° in benzene with triphenylphosphines containing *n para* substituents with the substituent parameter σ.

Mechanism of the Reaction.—Since the eight sulfur atoms in a molecule of sulfur are in eight different molecules of triphenylphosphine sulfide at the end of the reaction, the over-all reaction cannot have been accomplished without a succession of steps. If, like the rate determining step (1), each of these is only of the second order, then there must be seven rapid follow-up processes following the one measurable attack which results in the dipolar intermediate and which determines the rate. Each of the intermediates must possess a reactivity toward triphenylphosphine which exceeds that of the cyclic sulfur molecule itself.

Equation 1 may be followed by

$$(C_6H_5)_3P + (C_6H_5)_3\overset{+}{P}\ \overset{\downarrow}{S}SSSSSSS^- \longrightarrow (C_6H_5)_3PS + (C_6H_5)_3\overset{+}{P}\ SSSSSSS^-, \text{ etc.} \quad (2\text{-}7)$$

$$(C_6H_5)_3P + (C_6H_5)_3\overset{+}{P}\ SS^- \longrightarrow 2(C_6H_5)_3PS \quad (8)$$

According to this view the successive reactions of triphenylphosphine with sulfur and with the intermediate products are nucleophilic displacement reactions of sulfur on sulfur. Sulfenyl halides afford examples of nucleophilic displacement reactions on sulfur, showing that this is a favored type of reaction.[19]

Because of the special stability of the eight-membered ring of sulfur arising out of its favorable

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(19) N. Kharasch, C. M. Buess and S. I. Strashun, THIS JOURNAL, **74**, 3422 (1952), and previous papers.

dihedral angles,[4] this molecule is quite possibly more resistant to nucleophilic displacement than any other form of sulfur. The dipolar polysulfides pictured in the equations react relatively rapidly for this reason and also because a displacement at the sulfur atom marked with an arrow puts the displaced sulfur atom in the highly stable condition prevailing in a phosphine sulfide. No new anion solvation is required for this reaction, which fact should tend to make it rapid in non-polar solvents compared to the initial step. Only the final reaction (8), that between triphenylphosphine and the disulfide, looks as if there should be an electrostatic barrier to its accomplishment. Perhaps this is offset by the favorable energy change attending the formation of *two* phosphine sulfide molecules and the favorable entropy change attending the final release of the solvent molecules which have been held in solvation of the negatively charged sulfur atom.

Hexatomic Sulfur and Triphenylphosphine.—The same factors which make S_8 the preferred stable form of sulfur might affect its rate of reaction toward a general displacement reagent in comparison with other molecular forms of the element. The reddish-yellow, rhombohedral, hexatomic form of sulfur[20] is the only form differing from ordinary sulfur in its molecular makeup which is available in a pure crystalline state. It has been characterized by its cryoscopic molecular weight, crystal form, X-ray diffraction pattern and absorption spectrum.[21,22] In a number of attempts to measure the rate of reaction between triphenylphosphine and S_6 in benzene at 25°, the reaction appeared to have practically reached completion by the time of the first titration, when in a comparable reaction very little S_8 would have been consumed. Thus no information was available concerning the order of this reaction, but the surmise that forms of sulfur other than S_8 should be more readily attacked was strikingly confirmed.

Irradiated Sulfur and Triphenylphosphine.—It is known[23,24] that irradiation of concentrated solutions of rhombic sulfur in carbon tetrachloride, carbon disulfide or toluene precipitates amorphous sulfur, which in the dark reverts to S_8. By the use of solutions containing not over 0.1 gram-atom of sulfur per liter of benzene, we found that irradiation with a sunlamp or in direct sunlight produced a transient cloudiness but no precipitation. The resultant clear solution had an absorption in the visible and near ultraviolet which was more intense than that of S_8; the two spectra crossed at 317 mμ, the irradiated species absorbing less than S_8 until 256 mμ, where the curves again crossed. In this respect the spectrum of the irradiated sulfur resembles that of hexatomic sulfur, but the isosbestic points with the spectrum of S_8 occur at different places. One would suppose that irradiation might produce a random mixture of a number of polymeric forms of sulfur. If this is true the spectra show that different components of the irradiated sulfur are not formed at different rates, since a series of spectra taken after different lengths of irradiation of a sulfur solution in benzene show a steadily increasing intensity of absorption on the long-wave side of the isosbestic point without any shift in that point.

A solution of sulfur in benzene which had been irradiated in direct sunlight for 3 hr. was used in a kinetic determination with triphenylphosphine. It reacted in two stages: 78% of the sulfur was consumed with a rate constant at least 100 times as great as that of normal sulfur, the remainder showing the usual rate constant typical of S_8 (Fig. 4).

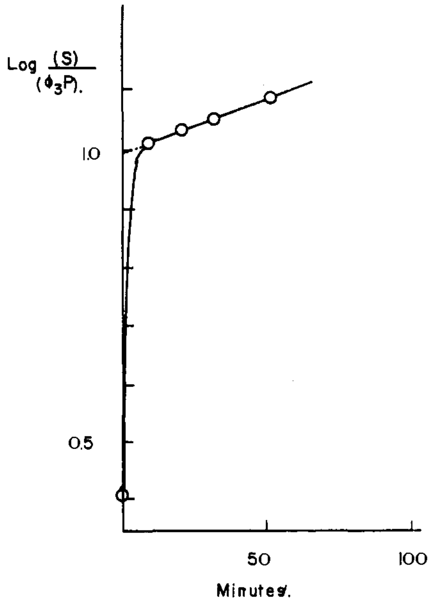

Fig. 4.—Reaction of solution of sulfur in benzene, after irradiation for 3 hr. in sunlight, with triphenylphosphine. The extrapolated intercept corresponds to a 78% content of fast-reacting sulfur.

The addition of a little tri-*n*-butylamine to a solution of irradiated sulfur in benzene caused rapid reversion to normal sulfur, as evidenced by the absorption spectrum of the solution and by its rate of reaction with triphenylphosphine.

Evaporation of irradiated solutions of sulfur in benzene gave a sticky yellow oil mixed with crystalline sulfur. The oil hardened slowly in the dark and faster in the light. Irradiation of sulfur solutions in alcohols gave solutions smelling of hydrogen sulfide and blackening lead acetate paper held in the vapor. No precipitation occurred.

One experiment showed that even amorphous sulfur precipitated in a finely divided state will react with triphenylphosphine more rapidly than dissolved S_8. A solution in carbon tetrachloride containing 0.13 gram-atom of sulfur per liter was irradiated with the appearance of a turbidity which did not disappear even on standing for 3 days in the dark. On addition of triphenylphosphine solution the turbidity disappeared and the solution became clear. Further irradiation produced a further turbidity, which was again dissolved by triphenylphosphine. This process could be repeated until enough triphenylphosphine had been added to react with all the sulfur in the solution.

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(20) H. W. Aten, *Z. physik. Chem.*, **88**, 321 (1914).

(21) R. E. Whitfield, Thesis, Harvard University, 1949.

(22) R. E. Whitfield and C. Frondel, *Acta Cryst.*, **3**, 242 (1950).

(23) Rankin, *J. Phys. Chem.*, **11**, 1 (1907).

(24) Wigant, *Z. physik. Chem.*, **77**, 423 (1913).

Triphenylphosphine as a Reagent for Titration.—It follows from the observations reported here that triphenylphosphine can be used both to titrate the total amount of elemental sulfur present in a solution and to differentiate between the usual form of sulfur, S_8, and all other forms of the element. For the first purpose time must be allowed for completion of a reaction which ordinarily proceeds at a slow and measurable rate; advantage may be taken of the powerful catalytic effect of ionizing solvents, added even in moderate amounts to a non-ionizing solvent. The conditions must be worked out with consideration to the rate constant of the reaction in the intended medium and the concentrations of reactants present. The differentiation between S_8 and other forms of sulfur is advantageously carried out in benzene; the "instantaneous" titer is obtained by extrapolation of several titrations which have stood for different lengths of time (dotted line in Fig. 4).

Experimental

Materials.—**Solvents**: Reagent grade (Merck) benzene and toluene and Eastman Kodak white label chlorobenzene were purified according to Fieser,[25] dried and distilled over calcium hydride in an atmosphere of nitrogen. Benzene and toluene were kept over sodium wire. **Sulfur**: Sublimed U.S.P. grade (Mallinckrodt) sulfur was crystallized twice from benzene. **Methyl Alcohol**: Reagent grade (Merck) absolute methanol was dried over Drierite. **Acetonitrile**: Eastman Kodak white label grade acetonitrile was distilled over phosphorus pentoxide. **Phenol**: Merck reagent grade phenol (loose crystals) was used without purification.

Preparation of Triaryl Phosphines.—Triphenylphosphine, m.p. 78–79°, tri-*p*-tolylphosphine, m.p. 146–147°, and tri-*p*-chlorophenylphosphine, m.p. 103–104°, were prepared from the respective aryl-magnesium bromides and phosphorus trichloride[28] in yields of 76, 68 and 55%, respectively.

In the case of tri-*p*-chlorophenyl phosphine, *p*-chlorophenylmagnesium bromide was preferred over the iodide (used by Mann and Chaplin) which requires extremely careful exclusion of air all through the reaction in order to avoid formation of the phosphine oxide. The formation of this oxide is due to the hydrolysis of Ar_3PI_2, which is formed from the phosphine and free iodine liberated during the hydrolysis of the Grignard reaction products in the presence of air.

Samples used for the kinetic runs were crystallized three times from 95% ethanol and dried under vacuum.

Phenyl-di-*p*-chlorophenylphosphine was prepared from *p*-chlorophenylmagnesium bromide and phenyl phosphorus dichloride (obtained from the Victor Chemical Works). A solution of 18 g. of phenylphosphorus dichloride in 100 ml. of anhydrous ether was added to a solution of *p*-chlorophenylmagnesium bromide prepared from 38.5 g. of *p*-chlorobromobenzene and 5 g. of magnesium in 500 ml. of ether. The reaction mixture was refluxed 2 hr., cooled in an ice-bath and hydrolyzed with a saturated solution of ammonium chloride. The ether layer was dried over calcium chloride. After removal of the ether by distillation at atmospheric pressure, the residue was distilled under reduced pressure in an atmosphere of nitrogen; yield 20 g. (60%) boiling at 227–229° under 5 mm. pressure.

Anal. Calcd. for $C_{18}H_{13}Cl_2P$: C, 65.28; H, 3.96; Cl, 21.41. Found: C, 65.32; H, 4.18; Cl, 21.34.

_p_-Chlorophenyldiphenylphosphine, b.p. 184–187° (4 mm.), was prepared by the same method from phenylmagnesium bromide and *p*-chlorophenyl phosphorus dichloride, yield 62%.

Anal. Calcd. for $C_{18}H_{14}ClP$: C, 72.86; H, 4.75; Cl, 11.95. Found: C, 72.70; H, 4.64; Cl, 11.72.

_p_-Chlorophenyl phosphorus dichloride was prepared by the method of Buchner and Lockhart.[27]

A mixture of 165 g. (1.2 moles) of phosphorus trichloride, 53.5 g. (0.4 mole) of aluminum chloride and 34 g. (0.3 mole) of chlorobenzene was heated gently for 2 hr. in a 3-necked flask while stirring. It was refluxed vigorously for 4 hr., when the evolution of hydrogen chloride had practically stopped. The heating was discontinued and while the reaction mixture was still hot, 61.5 g. (0.4 mole) of phosphorus oxychloride was added dropwise to it. After cooling, the mixture was extracted 6 times with 100-ml. portions of petroleum ether (b.p. 30–60°). The petroleum ether and excess phosphorus trichloride were distilled off at atmospheric pressure and in an atmosphere of nitrogen. The residue was fractionally distilled under reduced pressure. Forty-six grams of product, boiling at 119–122° (15 mm.), was collected; yield 72%.

Anal. Calcd. for $C_6H_4Cl_3P$: C, 33.76; H, 1.89; Cl, 49.83. Found: C, 33.63; H, 2.09; Cl, 49.35.

Kinetic Procedure.—The reaction flasks were of 125-ml. capacity, kept under a few millimeters positive pressure of nitrogen during the reaction and immersed in a thermostat controlled within ±0.005°.

Solutions of the triarylphosphines and sulfur, placed in glass stoppered volumetric flasks, were brought to temperature equilibrium with the bath. Twenty-five ml. of the phosphine solution (approximately 0.02 *M*) was transferred into the reaction flask and an equal volume of the sulfur solution was added rapidly while gently shaking the flask; shaking was continued for one minute after the addition of sulfur solution to assure thorough mixing. At intervals, 2- or 3-ml. aliquots were removed by means of calibrated pipets and placed in a 25-ml. flask containing a sufficient and known amount of a cooled iodine solution (approximately 0.01 *M*) to react with all the unreacted triarylphosphine and stop the reaction. The excess iodine was back titrated with a solution of triarylphosphine in benzene. A micro or semi-micro buret was used.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR REACTION OF TRIPHENYLPHOSPHINE WITH SULFUR (S_8) IN BENZENE

Temp., °C.	$[(C_6H_5)_3P]_0$, mole/l.	$[S_8]_0$, mole/l.	% of completion to which reacn. followed	*k*, l./mole sec. × 10^3
25.20	0.0141	0.00349	84	4.62
25.20	.0141	.00349	76	4.60
25.20	.0142	.00698	86	4.74
25.20	.00818	.00698	78	4.64
25.20	.00797	.00132	56	4.64
25.20	.00859	.00700	84	4.54
25.20	.00133	.00269	74	4.54
25.20	.0106	.00265	76	4.42
25.20	.01142	.00262	49	4.45
25.20	.00818	.00349	81	4.90
25.20	.0127	.00538	60	5.40
25.20	.0112	.00538	70	5.07
35.20	.0172	.00300	84	10.5
35.20	.0168	.00300	79	10.6
35.20	.00954	.00300	80	10.4
35.20	.00954	.00150	81	11.4[a]
35.20	.00928	.00150	65	10.5
35.20	.00954	.00751	83	11.5[a]
35.20	.00954	.00075	72	11.6[a]

[a] These rate constants were determined from solutions of sulfur which had stood for 3–5 days exposed to humid laboratory air. The increased rates are attributed to water catalysis.

The Analytical Method.—This method is based on the following reaction of R_3P with iodine.[28]

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[25] L. F. Fieser, "Experiments in Organic Chemistry," Part II, 2nd Ed., D. C. Heath & Co., Boston, Mass., 1941.

[26] Mann and Chaplin, *J. Chem. Soc.*, 527 (1937).

[27] B. Buchner and L. Lockhart, Jr., THIS JOURNAL, **73**, 755 (1951).

[28] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

$$R_3P + I_2 \rightleftharpoons R_3PI_2 \qquad (1)$$

$$R_3PI_2 + H_2O \longrightarrow R_3PO + 2HI \qquad (2)$$

The tertiary phosphine in any solvent can be titrated directly with a solution of iodine in 95% ethanol. The end-point is very sharp and is observed by the appearance of a bright yellow color. The alcohol and water in the titration solutions accelerate the sulfur–phosphine reaction in the aliquots during the direct titration with iodine. This caused an error which was most noticeable in the early part of a run. Such errors were eventually eliminated by quenching each aliquot in an excess of standard iodine solution and then back-titrating with standard triphenylphosphine; however, the rate constants so obtained were identical with those from the latter part of each direct-titration run, and such runs are included in Table III. The solutions of iodine and phosphine for titration were made in benzene containing 20–25% ethanol (95%). The concentration of the phosphine solution must be checked from time to time in order to avoid errors due to the oxidation of the phosphine. When tri-*p*-chlorophenylphosphine is used, oxidation does not occur at room temperatures; on the other hand, trialkyl phosphines cannot be used since they oxidize extremely rapidly in the presence of air. To minimize errors due to oxidation of the liberated HI, about 5 g. of pyridine was added to one liter of iodine solution. Using this method a sample of triphenylphosphine crystallized three times from 95% ethanol analyzed as 99.4% Ph_3P.

The presence of sulfur, phosphine sulfides, phosphine oxides or tertiary amines (in not very large amounts) does not introduce any error nor affect the end-point.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF WESTVACO CHLOR-ALKALI DIVISION OF FOOD MACHINERY AND CHEMICAL CORPORATION]

Structure of the Reaction Products of Fully Esterified Phosphorus(III) Acids and α-Halo Carbonyl Compounds[1]

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The products obtained by the reaction of α-halo carbonyl compounds and completely esterified acids of trivalent phosphorus were shown to be vinyl esters of pentavalent phosphorus acids by the independent synthesis of diethyl vinyl phosphate by the action of sodium hydride on diethyl 2-bromoethyl phosphate, by the addition of hydrogen, chlorine and bromine and by infrared absorption characteristic of the ethylenic double bond.

In a recent paper[2] the reaction products of α-halogenated carbonyl compounds and completely esterified acids of trivalent phosphorus were represented as vinyl esters of the corresponding pentavalent phosphorus acids, and the reasons for the structure assignment were stated briefly. We now wish to present in detail some of the experimental evidence for the vinyl ester structure. In the meantime other investigators[3] have published data supporting the vinyl ester structure and eliminating certain other structures originally thought possible, making a detailed description of some of our work unnecessary.

The vinyl ester structure is supported by a considerable body of evidence, the most important being (a) the independent synthesis of diethyl vinyl phosphate by the dehydrobromination of diethyl 2-bromoethyl phosphate and by the debromination by zinc of the bromine adduct of the product obtained from chloral and triethyl phosphite; (b) the addition of hydrogen, chlorine and bromine to certain members of the series to form saturated products; (c) the hydrolysis of the reaction product of chloral and triethyl phosphite to dichloroacetaldehyde; and (d) infrared absorption at 6.1 μ.

Upson[4] has described the preparation of diethyl vinyl phosphate and divinyl phenylphosphonate by the dehydrochlorination of the corresponding 2-chloroethyl esters. Upson[4b] reported the formation of a viscous polymeric diethyl vinyl phosphate when diethyl chloroethyl phosphate and triethylamine were refluxed for 84 hours, and although we obtained a similar product by the same procedure, neither of the two liquid phases obtained gave a positive test for chloride ion, indicating that triethylammonium chloride was not obtained. Furthermore, when triethylamine was refluxed for 84 hours with the product obtained from triethyl phosphite and chloroacetaldehyde a crystalline solid was obtained which appears to be an addition product of the two reactants. These results suggest that the Upson reaction does not give diethyl vinyl phosphate as an intermediate but that both reactions may involve alkylation (or vinylation in the case of the vinyl phosphate) of the amine. A 5% excess of triethylamine reacted with diethyl 2-bromoethyl phosphate in refluxing isopropyl ether to give a 46% yield of bromide ion and a small liquid fraction distilling at 81–110° (3 mm.) which decolorized bromine and presumably contained diethyl vinyl phosphate. Our efforts to repeat Upson's dehydrochlorination with ethanolic potassium hydroxide and other basic reagents resulted primarily in ethanolysis and degradation and only traces of unsaturated products were obtained.

An unexpected development occurred in an attempt to dehydrobrominate diethyl 2-bromoethyl phosphate with sodium *t*-butoxide in *t*-butyl alcohol. The product closely resembled the product obtained from triethyl phosphite and chloroacetaldehyde in physical properties, including infrared absorption, but the specific gravity and phosphorus content were significantly low, suggesting that the vinyl compound was contaminated with

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 11–16, 1955.

[2] J. F. Allen and O. H. Johnson, THIS JOURNAL, **77**, 2871 (1955).

[3] (a) W. F. Barthel, B. H. Alexander, P. A. Giang and S. A. Hall, *ibid.*, **77**, 2424 (1955); (b) A. M. Mattson, J. T. Spillane and G. W. Pearce, *J. Agr. Food Chem.*, **3**, 319 (1955); (c) W. Perkow, *Chem. Ber.*, **87**, 755 (1954); (d) W. Perkow, W. Krockow and K. Knoevenagel, *ibid.*, **88**, 662 (1955); (e) W. Lorenz, A. Henglein and G. Schraeder, THIS JOURNAL, **77**, 2554 (1955); (f) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

[4] (a) R. W. Upson, THIS JOURNAL, **75**, 1763 (1953); (b) R. W. Upson, U. S. Patent 2,557,805 (1951).