A Study of the Kinetics of the Sulfur-Transfer Reaction Between Triphenylphosphine Sulfide and Tributylphosphine[1]

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Because several reactions involving a direct transfer of a covalently bonded sulfur or oxygen atom between molecules have been reported as shown,

$$(CH_2{=}CHCH_2S)_2 + (C_6H_5)_3P \xrightarrow{\text{benzene}} (CH_2{=}CHCH_2)_2S + (C_6H_5)_3P(S)$$

(Challenger and Greenwood, 1950)

$$C_6H_5CS(N_3) + (C_6H_5)_3P \xrightarrow{\text{dioxane}} C_6H_5CN + N_2 + (C_6H_5)_3P(S)$$

(Horner and Gross, 1955)

$$P^{32}(O)Cl_3 + PCl_3 \xrightarrow{\text{xylene}} P^{32}Cl_3 + P(O)Cl_3 \qquad \text{(Grantham, 1959)}$$

$$P(S)Cl_3 + (RO)_3P \xrightarrow{\text{neat}} PCl_3 + (RO)_3P(S) \qquad \text{(Gottlieb, 1932)}$$

$$P(S)Cl_3 + C_6H_5PCl_2 \xrightarrow{\text{neat}} PCl_3 + C_6H_5P(S)Cl_2 \qquad \text{(Gottlieb, 1932)}$$

$$R_2P(S)X + (C_6H_5)_3P, (C_4H_9)_3P \xrightarrow{\text{neat}} R_2PX + (C_6H_5)_3P(S), (C_4H_9)_3P(S)$$

(Gottlieb, 1932)

it became of interest to determine the existence and facility of such a transfer reaction involving trialkyl- and triarylphosphines and their derivatives. It was anticipated that kinetic data might be obtained.

Tributylphosphine (TBP) (pK_a 8.34) (Steuli, 1960) and triphenylphosphine (TPP) (pK_a 2.75) (Steuli, 1960) and the corresponding oxides and sulfides were chosen for initial studies. It was found that no reaction occurred when tributylphosphine oxide (TBPO) or sulfide and TPP were heated in the absence of solvent.

$$(C_6H_5)_3P + (C_4H_9)_3P(O) \xrightarrow[N_2,\ 273\ C]{9\ \text{hr, neat}} \text{no reaction}$$

$$(C_6H_5)_3P + (C_4H_9)_3P(S) \xrightarrow[N_2,\ 220\ C]{\text{neat}} \text{no reaction}$$

It was not surprising, considering the thermal stability of triphenylphosphine oxide (TPPO) relative to trialkylphosphine oxides (Maier, 1963, 1965), that oxygen exchange was not observed when the arylphosphine

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$$(C_6H_5)_3P(O) + (C_4H_9)_3P \xrightarrow[N_2,\ 257\ C]{2\ hr,\ neat} \text{no reaction}$$

oxide was a reactant. However, when a 1:1 mixture of triphenylphosphine sulfide (TPPS) and TBP was heated at 200 C there occurred a quantitative transfer of sulfur to TBP to give tributylphosphine sulfide (TBPS) and TPP. Indeed, the reaction was found to proceed at 137 C in *p*-xylene in a manner conforming to second order kinetics. Side products were not detected when samples were analyzed in gas chromatographic units equipped with thermal and hydrogen flame detectors.

$$(C_6H_5)_3P(S) + (C_4H_9)_3P \xrightarrow[N_2,\ 200\ C]{2\ hr,\ neat} (C_6H_5)_3P + (C_4H_9)_3P(S)$$

quantitative

$$(C_6H_5)_3P(S) + (C_4H_9)_3P \xrightarrow[N_2,\ 137\ C]{p\text{-xylene}} (C_6H_5)_3P + (C_4H_9)_3P(S)$$

Subsequent runs were made to determine the rate constants and the activation energy using toluene and *m*-xylene as solvents. Temperature regulation was provided by heating solutions of the reactants in toluene and in *m*-xylene to the boiling point of the respective solutions under deoxygenated highly purified nitrogen (Arthur, 1964). The time required to reach the boiling point was about 15 min. It was found that the reaction rate did not change when TBP was added to the boiling solution of TPPS as compared to the rate observed after the solution of TBP and TPPS in toluene had been heated to boiling. Regulation of ± 0.04 to ± 0.10 degrees was achieved during that period in each run when samples used in the determination of the rate constant was based on concentrations of TPP and TPPS (see Calculations) as determined by gas chromatography (glc). Peak areas were measured with a planimeter (Scott and Grant, 1964). The effective volume of the reaction mixture during the reaction and the differing sensitivity of the detector to TPP and TPPS, knowledge of which was necessary for the calculation of $C_{TPPS}(C')$, were determined and used as described in the calculations.

From graphs of (C^{-1}_{TPPS}) $(=1/C')$ vs time (Figs. 1 and 2) the rate constant (k_2) for sulfur exchange at 110.8 C was found to be 1.19×10^{-4} l/mole-sec. This value is expectedly several magnitudes lower than the rate constant of the second order reaction between triphenylphosphine and elemental sulfur, which Bartlett and Meguerian (1955) report as 45.8×10^{-4} l/mole-sec at 25 C $(113.0 \times 10^{-4}$ l/mole-sec at 35 C) in benzene. They report also that the corresponding reaction of sulfur with short-chain alkylphosphines proceeds much more rapidly under the same conditions.

The energy (enthalpy), ΔH^* $(\simeq E_a)$, and entropy, ΔS^*, of activation at 124.8 C were calculated to be 22.3 ± 1.1 Kcal/mole and 0.135 Kcal/mole-K, respectively. The precision of the experiment was 5%. The accuracy of the data, presumably not better than 10%, is probably limited by the assumption of a value 1 for the transmission coefficient κ in the derivation of the equation

$$k_2 = (\kappa kT/h)e^{(-\Delta F^*/RT)}$$

from transition state theory (Frost and Pearson, 1961).

The mechanism of this transfer reaction can be discussed on a tentative basis. The relatively low value of E_a^* makes an ionic intermediate unlikely in the non-polar media used. A more plausible mechanism in-

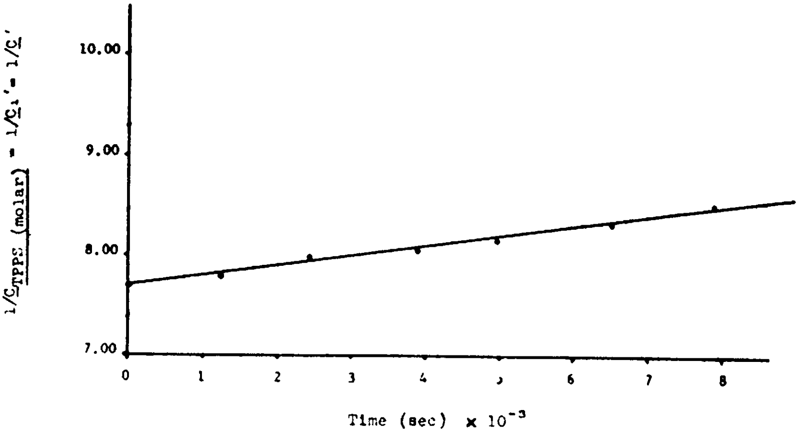


Fig. 1. Kinetic run 3 in toluene at 110.7 C

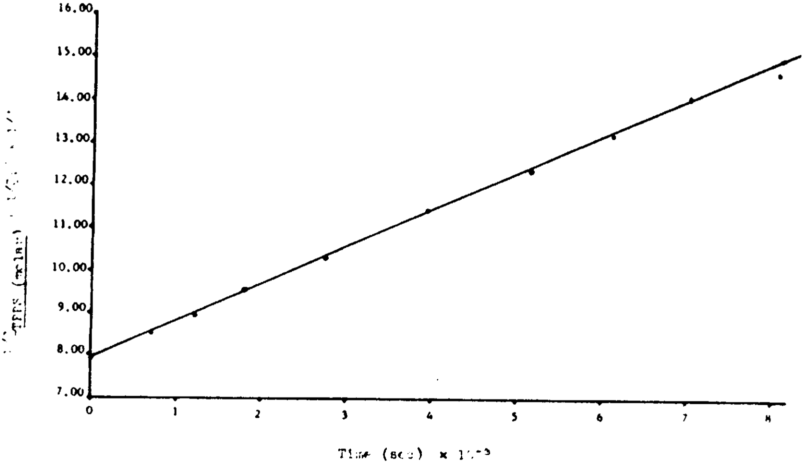
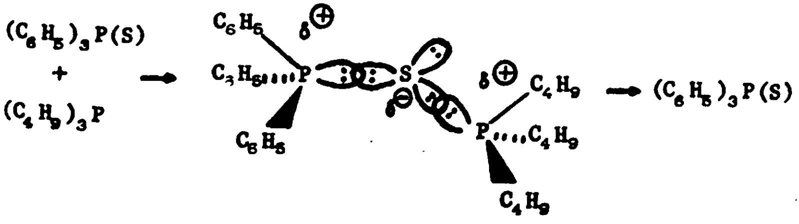


Fig. 2 Kinetic run 1 in *m*-xylene at 138.9 C

volves the direct transfer of a sulfur atom between phosphines. Such a process could involve an intermediate in which sulfur



assumes a bipyramidal configuration. Another possibility is that the sulfides dissociate to give free sulfur, the equilibrium for the alkylphosphine lying more toward its sulfide. This is the mechanism proposed by Grantham (1959)

$$(C_6H_5)_3P(S) \underset{\longleftarrow}{\xrightarrow{\Delta}} (C_6H_5)_3P + S$$

$$(C_4H_9)_3P + S \underset{\longleftarrow}{\xrightarrow{\Delta}} (C_4H_9)_3P(S)$$

for the exchange of oxygen between thiophosphoryl chloride and phosphorus trichloride, though a bimolecular exchange could not be eliminated on the evidence available. Indeed, the excellent agreement of our results with those expected of a second order reaction (Figs. 1 and 2), the large difference in the rates of reaction of tributyl- and triphenylphosphine with elemental sulfur (Bartlett and Meguerian, 1956), and the availability of *d* orbitals in sulfur strongly suggest that the bimolecular mechanism is the correct one for our example. If, indeed, a direct transfer is involved, the low value for ΔS^* implies a transition state that is not highly ordered. Examination of models does, in fact, suggest that rehybridization of the bonding orbitals on phosphorus in the reactants TPPS and TBP would not impose significant geometric deformations in a bipyramidal transition state. The large diffuse *d* orbitals in sulfur and phosphorus (assuming sp^3 hybridization of the non-bonded pairs of electrons on sulfur) should make for easy overlap and considerable freedom in the transition state. In view of the second order kinetics and the low positive entropy value, the reaction seems best described as a concerted process involving the pictured transition state.

The two-step process is less probable since the reaction rate constants for the reaction of TPP and TBP with sulfur, respectively, would have to be of the same order of magnitude. This is unlikely in view of the work of Bartlett and Meguerian (1956).

TERMS AND EQUATIONS

Throughout, C, A, S, and V represent respectively molar concentration, peak area (glc), standardization ratio (glc; molarity/peak area), and volume.

Standard solutions: C_0, A_0, S_0, V_0 refer to TPP standard, and C'_0, A'_0, S'_0, V'_0 to TPPS.

Samples: C_1 = TPP, hot; C'_1 = TPPS, hot; C_2 and A_2 = TPP, diluted; C'_2 and A'_2 = TPPS, diluted; V_1 = volume of hot sample removed; V_2 = volume of diluted cooled sample; V_3 = volume of diluted cooled sample injected (glc).

Reaction solutions: C = TPP solution; C' = TPPS solution; EV = effective solution volume; M = initial amount of TPPS = 0.0100 mole; $C_{TPPS(t)} = C + C'$ in solution at time t.

Rate constants: k_2 and k'_2 = respectively rate constants for the exchange process in toluene and *m*-xylene.

Equations for TPPS: $C'_2 = C'_0 \, (A'_2/A'_0) \, (V'_0/V'_3) = (C'_0V'_0/A'_0) \, (A'_2/V'_3) = S'_0 \, (A'_2/V'_3)$; $C' = C'_1 = C'_2 \, (V_2/V_1)$.

Similarly for TPP: $C_2 = C_0 \, (A_2/A_0) \, (V_0/V_3) = (C_0V_0/A_0) \, (A_2/V_3) = S_0 \, (A_2/V_3)$; $C = C_1 = C_2 \, (V_2/V_1)$.

The ratio $C/C' = C_t/C'_t = (A_t/A'_t)\ (V_sA'_sV_t/V'_sA_sV_t)\ (C_s/C'_s)\ (V_s/V_t)$ $(V_t/V_s) = (A_t/A'_t)\ (C_sV_s/A_s)\ (A'_s/V'_sC'_s)$. Let us define a total correction factor R (correlation factor between standards used and the diluted solution) as S_s and S'_s,

$$R = S_s/S'_s = (C_sV_s/A_s)/(C'_sV'_s/A'_s).$$

and hence R, were determined from three to ten injections of the standard solutions before and after injections of the diluted samples. R remained fairly constant for 6 to 8 hr. R was used to correct the area ratio actually measured, i.e.,

$$C/C' = C_t/C'_t = R(A_t/A'_t).$$

However, in Table I, R is not tabulated but is left in terms of S_s and S'_s for TPP and TPPS individually.

Now $C_t + C'_t = C_{TPPS\ (\text{dilute total})}$, since the amount of TPP available is the same as the amount of TPPS that has reacted. Since TPP + TPPS $= M = 0.0100$ mole at any time during the reaction and since EV is nearly constant as shown in Table I,

$$C + C' = C_t + C'_t = C_{TPPS(t)} = M/EV.$$

By algebraic combination, we may write

$$C' = C'_t = M/EV(1 + RA_t/A'_t) = C_{TPPS(t)}/(1 + RA_t/A'_t).$$

CALCULATIONS

Effective reaction volume—As samples were withdrawn from the reaction vessel, their volumes were quickly read on the calibrated 1-ml pipettes or syringe used before placing them in 2.00 ml (at a recorded temperature near room temperature) of freshly distilled toluene at 0 C. Taking the densities of the reaction mixture as those of the pure solvent[3] at the reaction temperature and at room temperature and comparing areas from the glc of the diluted sample ($V_s = 2.00$ ml $+ D_4^{T_s}\ V_t/D_4^{T_t}$) with those of the standard solutions of TPP and TPPS, C and C' could be determined in the reaction solution at times of sample withdrawal. In Table I is found the basic data for calculation of $C_{TPPS(t)}$ and EV to demonstrate the relative constancy of EV.

C_{TPPS} values used for determination of k_t and k'_t—Not all hot-sample solution volumes were determinable, as in some cases bubbles drawn into the pipette prevented quick (< 10 sec) sighting. Therefore, C' values used for the rate constant determination were calculated from $C_{TPPS(t)}$ (as determined from the analyses of samples having determinable dilution factors), through the relation $C_t + C'_t = C_{TPPS(t)}$, and the C/C' ratio in the reaction solution. The latter was obtained for each sample by taking the product of R and the peak area ratio A_t/A'_t. Thus, the differing sensitivity of the detector to TPP and TPPS was taken into account as was the difference in molecular weights of the two compounds.

Determination of k_t and k'_t—The rate constant for each run was determined from the slope of a graph of C^{-1}_{TPPS} (1/C′) vs time, as shown in Figs. 1 and 2.

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[3] Toluene: $D^{100.2}_4$, 0.77805, D^{25}_4, 0.8623; *m*-xylene, $D^{139.2}_4$, 0.7572, D^{25}_4, 0.8598 (Faraday and Freeborn, 1958).

TABLE I. SAMPLE DATA FOR CALCULATIONS OF $C_{TPPS(i)}$ IN DILUTE SOLUTION AND EFFECTIVE REACTION VOLUMES

	DATA FOR DILUTED SAMPLE									DATA FOR REACTION SOLUTION	
Run No.	Sample No.	Injection, V_s (µl)*	Avg (units) A_s	Avg (units) A'_s	Avg Standardization Ratio*† $\times 10^3$ S_s	Avg Standardization Ratio*† $\times 10^3$ S'_s	$C_s + C'_s = C_{TPPS}$ (dilute total) $\times 10^3$			$C_{TPPS(i)}$††	EV (ml)
Toluene 4	5	50.8 ± 0.1	31.0	143.7	1.85	1.50	9.41	36.8	46.2	$0.1\bar{4}85$	$6\bar{7}.2$
	6	50.7	35.8	141.2			10.8	36.8	47.6	0.1505	66.3
	7	50.7	41.0	134.8			12.4	34.5	46.9	0.1520	65.8
										(Avg $0.1\bar{5}0$)	(Avg 66.6)
m-Xylene 1	2	50.8 ± 0.1	33.5	136.3	1.59	1.36	9.49	39.5	46.0	0.151	66.2
	3	50.7	38.7	127.7			12.1	34.2	46.3	0.151	66.2
	4	50.6	45.0	119			14.3	32.3	46.6	0.153	65.3
										(Avg 0.152)	(Avg 65.8)

*The values for three injections of sample are averaged.

**Standard solution injections were made between sample injections throughout the analyses.

†Variation in values is due to slightly different chromatographic conditions.

††$C_{TPPS(i)} = C_{TPPS(dilute\ total)}\ (V_t/V_s)$. The bar over the digit indicates the last significant figure reading from left to right.

The data in Table II comprise data for run 3 in toluene and run 1 in *m*-xylene. $1/C'$ was plotted against time to give the rate constants k_2 and k'_2 for the second order reaction as shown in Figs. 1 and 2, respectively.

Calculation of E_a^*, ΔF^*, and ΔS^*.—From the average of the results of toluene runs 2, 3, and 4 ($k_2 = 1.19 \pm 0.1 \times 10^{-4}$ l/mole-sec at 383.9 K, 110.7 C) and of *m*-xylene runs 1 and 2 ($k'_2 = 8.68 \pm 0.1 \times 10^{-4}$ l/mole-sec at 412.1 K, 138.9 C), E_a^* was calculated to be 22.3 ± 1.1 Kcal/mole by use of the equation $d(\ln k_2)/dT = \Delta H/RT^2$ with the assumptions that $\Delta H^* = E_a^*$ was not a function of temperature over the range studied. With the same assumptions, ΔF^*, and hence, ΔS^*, were determined from the equation $k_2 = (\kappa kT/h)\, e^{(-\Delta F^*/RT)}$ at each temperature to be, respectively, —30.2 Kcal/mole, 0.132 Kcal/mole-K (110.7 C) and —32.0 Kcal/mole, 0.137 Kcal/mole-K (138.9 C). The transmission coefficient κ was taken as one (Table III).

EXPERIMENTAL

Analysis—Analysis for TPP and the corresponding sulfide were made in an Aerograph A-700 (Wilkens Instruments, Inc.) at 250-265 C using a column of 8% Silicone Rubber 30 on 60/80 acid-washed Chromosorb G (¼-in by 6-ft). Specific conditions for column temperatures of 252 C and 257 C are recorded in Table IV. Three (or more) injections were made for each sample used for rate calculation. Purity checks were made in a Hy Fi Aerograph apparatus (Wilkens Instruments, Inc.) with hydrogen flame detector using a column of 10% Silicone Rubber 30 on 60/80 acid-washed Chromosorb G (⅛-in by 8-ft).

Total phosphines in the reaction mixture were determined by titration of 1- or 2-ml samples of the hot solution with a 0.005 M I_2 solution for which 95% ethanol served as solvent (Bartlett and Meguerian, 1956). Usually the sample was placed in an excess of titrant. Then 2-5 ml of a standardized TPP solution (benzene solvent) was added and the excess was titrated with additional iodine solution.[4]

Standard solutions of TPPS and TPP in benzene were 0.100-0.010 M, these concentrations allowing 10-50-μl injections (without attenuation) under the same conditions as were being used for sample analyses.

Reaction solution components were identified by means of mixed injections with solutions of the pure compounds.

Triphenyl- and Tributylphosphine Sulfide — Sulfur (8.02 g, 0.250 mole) was added continually over a period of 30 min to a boiling solution of TPP (56.02 g, 0.214 mole) in 210 ml benzene contained in a 50-ml, three-necked flask equipped with an N_2 inlet, a thermometer, condenser, and motor-driven stirring assembly. The mixture was held at reflux 3 hr. The yellow-tinted white residue obtained from aspirator distillation of solvent gave pure crystals of mp 162.2-163.2 C when recrystallized from 5:1 benzene-ethanol (95%). The yield of pure compound was 55 g (87%). Horner and Gross (1955) report mp 159 C. A few grams of TBPS, bp 143.0-4.5 C/0.3 mm, n_D^{21} 1.4960, were prepared by the same general method. Reference values are bp 111 C/0.1 mm, n_D^{20} 1.5045 (Christen, Vander Linde, and Nooga 1959) and bp 137.8 C/1.1 mm, n_D^{25} 1.4945, d_4^{25} 1.0339 (Zingaro and McGlothlin, 1961).

Tributylphosphine oxide—Several grams were prepared by the general method of Berlin and Butler (1961). Vacuum distillation of the crude solid followed by vacuum-oven dehydration with phosphorus pentoxide gave 25 g (57% yield) of white, odorless, extremely hygroscopic crystals, mp 63-7 C (in air), bp 122-5 C/0.27 mm; Buckler (1962) reported mp 67-9 C.

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[4] See the fourth run in toluene concerning the accuracy of these titrations.

TABLE II. KINETIC DATA

Sample	Time (sec)	A_1/A'_2*	C/C'**	C' (moles/l)	$C^{-1}_{TPPS} = 1/C'$ (l/mole)
			Toluene Run 3†		
1	0	0.127	0.150	0.1305	7.66
2	1140	0.139	0.163	0.1288	7.77
3	2460	0.167	0.197	0.1253	7.97
4	3840	0.171	0.202	0.1246	9.03
5	4860	0.191	0.225	0.1223	8.17
6	6360	0.218	0.257	0.1193	8.37
7	7740	0.231	0.272	0.1178	8.50
			m-Xylene Run 1††		
1	0	0.165	0.195	0.127	7.88
2	720	0.245	0.289	0.118	8.48
3	1200	0.304	0.358	0.112	8.94
4	1800	0.376	0.444	0.105	9.53
5	2760	0.457	0.540	0.0987	10.3
6	3960	0.616	0.727	0.0880	11.4
7	5160	0.747	0.881	0.0807	12.4
8	6120	0.857	1.01	0.0756	13.2
9	6960	0.950	1.12	0.0717	14.0
10	8100	1.05	1.24	0.0679	14.7

*Three results are overaged for the diluted solutions injected at room temperature; the correction factors using S_i and S'_i are omitted but values shown in Table I are of the same order here. The R values are given below.

**$C_{TPP}/C_{TPPS} = RA_i/A'_t = C/C'$ †$R = 1.17$ ††$R = 1.18$

TABLE III. KINETIC RESULTS

Solvent	Run	Temp (C)	k_2 (l/mole-sec)	t ½ (hr)
Toluene	1*,**	110.0 ± 0.1	1.25×10^{-4}	15.5
	2	110.65 ± 0.05	1.30	14.2
	3	110.72 ± 0.06	1.09	17.0
	4	110.78 ± 0.04	1.19	15.6
m-Xylene	1	138.94 ± 0.1	8.57	1.97
	2	138.95 ± 0.05	8.78	2.05

$E_a = 22.3 \pm 1.1$ Kcal/mole

$t = 110.7$ C
$\Delta F^* = -30.2$ Kcal/mole
$\Delta F^* = 0.132$ Kcal/mole-K
Average values: $\Delta F^* = -31$ Kcal/mole

$t = 138.9$ C
$\Delta F^* = -32.0$ Kcal/mole
$\Delta S^* = 0.137$ Kcal/mole-K
$\Delta S^* = +0.135$ Kcal/mole-K

*The results of Run 1 were not used in rate constant calculations.

**Effective solution volume (*EV*) was assumed to be 75 ml (calcd by addition of approximately 5 ml of reactant solution and 70 ml of toluene at room temperature).

KINETIC PROCEDURE—TOLUENE

First run—The system consisted of a 100-ml, three-necked flask equipped with a thermometer and N_2 inlet (by way of a Y-joint), a 10-cm condenser (which was stoppered except during sample removal by means of a 2-ml pipette), a 20-cm straight condenser stoppered with a one-holed stopper, magnetic stirrer, and glass wool insulation. The reactants and

TABLE IV. CHROMATOGRAPHIC DATA FOR TRIPHENYL- AND TRIBUTYLPHOSPHINE AND THEIR DERIVATIVES

Temperature	(C)	Compound	Retention Time (sec)	He Flow Rate (ml/min)
Column	257	$(C_6H_5)_3P(S)$	264	240
Injector	302	$(C_6H_5)_3P(O)$	196	
Detector	303	$(C_6H_5)_3P$	94	
(Filament current	200 ma)			
		$(C_4H_9)_3P(S)$	37	
		$(C_4H_9)_3P(O)$	29	
		$(C_4H_9)_3P$	15	
Column	252	$(C_6H_5)_3P(S)$	514	100
Injector	306	$(C_6H_5)_3P(S)$	—	
Detector	301	$(C_6H_5)_3P$	165	
(Filament current	180 ma)	$(C_4H_9)_3P(S)$	65	
		$(C_4H_9)_3P(O)$	53	
		$(C_4H_9)_3P$	24	

solvent were placed in the system (N_2-flushed) in order: TPPS (2.94 g, 0.0100 mole) (mp 161.9-162.8 C), toluene (70.00 ml, freshly distilled), commercial TBP (2.02 g, 0.0100 mole, bp 148-50 C/50 mm) (Maier, 1963; bp 135-44 C/43 mm). The system was flushed for an additional 30 min before heating to reflux (this required 15 min), establishing temperature equilibrium, and beginning sample removal. Five 2-ml samples were taken at 30-min intervals. Six more aliquots were taken beginning 2.5 hr after the first five samples had been removed. Samples were placed in 3 ml of solvent at ice-bath temperature immediately, to be warmed to room temperature during analysis and comparison with fresh standard benzene solutions of TPPS and TPP. Analysis and subsequent calculation gave $k_2 = 1.25 \times 10^{-4}$ l/mole-sec at 110.0 ± 0.1 C for eleven samples.

Second run—Modifications used: (1) 99-201/0.01 C thermometer; (2) freshly distilled TBP which showed only a trace of impurity by analysis on the hydrogen flame unit; (3) nitrogen deoxygenated by the method of Arthur (1964); (4) samples of approximately 1 ml were removed with 1.000/0.01-ml pipettes and were placed in 2.00-ml aliquots of solvent at 0 C; (5) standard initial TPP and TPPS solutions were used to determine the concentration of the sulfide and thus the effective reaction volume. Analysis and calculation gave $k_2 = 1.30 \times 10^{-4}$ l/mole-sec at 110.65 ± 0.05 C for ten samples.

Third run—No modifications from the second run. Analysis and calculation gave $k_2 = 1.09 \times 10^{-4}$ l/mole-sec at 110.72 ± 0.06 C for eight samples.

Fourth run—Modifications from second run: (1) TBP used contained some impurity (3.00 ml of solution were taken, I_2 titration having indicated an additional 0.5 ml at 25 C would contain 0.010 moles); (2) phosphines in the reaction mixture were determined by pipetting a hot, 2.00-ml sample into a near excess of 0.005 M iodine titrant and titrating to a permanent yellow tint, calculation giving total phosphine content as 0.00857 moles and concentration as 0.128 M; (3) the TBP was added by means of a 5-ml hypodermic syringe fitted with an 8-inch needle to the boiling solution of 2.9434 g (0.0100 mole) TPPS in toluene; (4) five samples were taken at 15-20 min intervals, and then five more at 1-hr intervals. Analysis and calculations gave $k_2 = 1.19 \times 10^{-4}$ l/mole-sec at 110.78 ± 0.04 C. Effective reaction volume was 66.6 ml. Total phosphine content was, as noted above, 0.00857 mole. However, appreciable oxidation took place and this figure is low, hot alkylphosphines being highly reactive with atmospheric oxygen (Buckler, 1962).

KINETIC PROCEDURE—*M*-XYLENE

First run—Modifications from fourth run in toluene: (1) 30-cm condenser replaced 20-cm piece at center joint; (2) a septum and a 2.5-ml hypodermic syringe with an 8-inch needle replaced the 10-cm condenser and the pipettes for sample removal; (3) 2.50 ml (0.0100 M if pure, 0.00895 M by iodine titration of reaction mixture aliquots[4]) of TBP (bp 62.0-0.5 C/0.2-0.12 mm) were used; (4) 70.00 ml of reagent grade *m*-xylene were used; (5) samples were taken at 7-min and then 15-min intervals. Analysis and calculation gave $k'_2 = 8.57 \times 10^{-4}$ l/mole-sec at 138.9 ± 0.1 C for nine samples. Effective reaction volume was 65.8 ml. Total phosphine content was 0.00895 mole.[5]

Second run—Modifications: Same as fourth run in toluene except that 2.80 ml (calcd. 0.010 mole from titration data) TBP (bp 62.0-0.5 C/0.2-0.12 mm) were used. Analysis and calculation gave $k'_2 = 8.78 \times 10^{-4}$ l/mole-sec at 138.9 ± 0.05 C for ten samples. Effective reaction volume was 63.3 ml; total phosphine content was 0.00753 mole.[5]

Attempted reaction of triphenylphosphine with tributylphosphine sulfide—neat and in toluene—A 50-ml boiling flask equipped with a straight condenser, thermometer, and an N_2 inlet was charged with 1.04 g (0.0040 mole) TPP and 0.92 g (0.0040 mole) of orange-tinted (probably sulfur-containing) TBPS. The solution was heated to 200 C (1 hr), cooled, diluted with 28.0 ml toluene, heated to boiling (6 hr), cooled to room temperature for two weeks, and again heated to boiling (12 hr). Glc samples were removed just prior to the addition of toluene and after each period of reflux. The hot undiluted solution soon became decolorized upon heating. Glc analysis gave TPP/TPPS area ratios of 4.6, 4.4, and 4.4 for the samples in the order of their removal, implying no reaction except what may have occurred during the heating period when probable sulfur impurity was reacting with TPP.

Attempted reaction of triphenylphosphine sulfide and tributylphosphine at room temperature—Approximately 1 ml of TBP and 0.1 g of TPPS were placed in a 50-ml glass-stoppered Erlenmeyer flask under nitrogen and left for four days at room temperature with occasional shaking. No TPP was detected (by analysis in the A-700 glc unit).

Attempted reaction of triphenylphosphine oxide and tributylphosphine—A 50-ml boiling flask equipped as previously described was charged with 4.17 g (0.015 mole) TPPO and 3.03 g (0.015 mole) of TBP. The mixture was heated to boiling at 257 C for 7.5 hr. After cooling the mixture to room temperature, 25 ml of toluene was added and a sample taken for analysis in the A-700 instrument. No TPP could be detected.

No TPPO could be detected when the reverse reaction was attempted under the same conditions.

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[5] See the fourth run in toluene concerning the accuracy of those results.

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