TABLE II

STOICHIOMETRIC RESULTS (0°, 1 M $HClO_4$)

	Init concn, $M \times 10^3$		ΔA^a			Stoichiometric ratio	
	V(II)	Tl(III)	Obsd	Calcd^b	R^c	Obsd^d	Calcd^e
1	2.29	2.95	0.358, 0.361	0.359	0.99_7, 1.00_6		
2	2.29	3.65	0.357	0.359	0.99_4		
3	2.72	2.95	0.425, 0.428	0.427	0.99_5, 1.00_2		
4	3.51	2.95	0.454	0.463	0.98_1	0.98	0.979
5	4.09	2.95	0.454, 0.452	0.463	0.98_1, 0.97_6	0.98, 0.98	0.978
6	7.02	2.95	0.456	0.463	0.98_5	0.99	0.976
7	10.5	2.95	0.451	0.463	0.97_4	0.98	0.975
8	14.0	2.95	0.448	0.463	0.96_8	0.97	0.975
9	14.0	1.48	0.221, 0.224	0.231	0.95_7, 0.97_0	0.96, 0.97	0.975
10^g	4.09	2.95	0.455, 0.456	0.463	0.98_3, 0.98_5	0.99, 0.99	0.996
11^g	4.09	2.95	0.460	0.463	0.99_4	0.99	0.998
12	4.47	2.96	0.226^f	0.464	0.48_7	0.56	
13^g	2.98	2.96	0.236^f	0.464	0.50_9	0.58	

[a] Absorbance change in 10 cm when Tl(III) injected into V(II) solution, corrected for increase in volume. [b] Calculated assuming [V(IV)] formed equals the initial concentration of limiting reactant, based on average of first three lines where V(II) was limiting. [c] $R = \Delta A(\text{obsd})/\Delta A(\text{calcd})$. [d] Calculated from eq 10 using $(\epsilon_{V(II)} - \epsilon_{V(III)})/(\epsilon_{V(IV)} - \epsilon_{V(II)}) = 0.088$. [e] Calculated assuming $k_1/(k_1 + 2k_2) = 0.95$ and $k_4/k_3 = 10^{-6}$. [f] Chloride present, solution was 0.02 M HCl and 0.98 M $HClO_4$. [g] Initial concentration of V(III) is zero, except in expt 10 (2.68×10^{-3} M), 11 (6.71×10^{-3} M), and 13 (4.50×10^{-3} M).

calculation of the concentrations of reactants and products as a function of time for various initial concentrations and values of k_1, k_2, k_3, and k_5/k_4. The calculations were taken to essentially complete reaction and the ratio $[V(IV)]_{formed}/[Tl(III)]_{added}$ was calculated for comparison with the experimental stoichiometric ratios. The rate constant $(k_1 + 2k_2)$ was taken as 70 M^{-1} sec^{-1} in accord with Table I, while k_3 was taken as 310 M^{-1} sec^{-1}, obtained by interpolating published data.[5] Two sets of initial concentrations were chosen to correspond to line 8 and line 11 in Table II. The results of these calculations are summarized in Table III.

TABLE III

$[V(IV)]_{formed}/[Tl(III)]_{added}$ FOR VARIOUS VALUES OF k_5/k_4 AND $k_1/(k_1 + 2k_2)^a$

	$k_1/(k_1 + 2k_2)$				
k_5/k_4	0.0	0.4	0.8	0.95	1.00
0	0.529^b	0.711	0.901	0.975	1.000
	0.960^c	0.976	0.992	0.998	1.000
0.02	0.531	0.711	0.901	0.975	1.000
	1.015	1.027	1.041	1.047	1.049
0.1	0.540	0.715	0.902	0.975	1.000
	1.149	1.159	1.168	1.172	1.173
0.5	0.581	0.732	0.904	0.975	1.000
	1.405	1.407	1.409	1.410	1.410
2	0.671	0.776	0.911	0.976	1.000
	1.637	1.629	1.622	1.619	1.618
8	0.794	0.849	0.929	0.979	1.000
	1.788	1.769	1.752	1.746	1.744
10^3	0.981	0.984	0.991	0.997	1.000
	1.883	1.851	1.824	1.815	1.812

[a] For all calculations $k_1 + 2k_2 = 70$ M^{-1} sec^{-1} and $k_3 = 310$ M^{-1} sec^{-1}. [b] Upper figures apply to $[V(II)]_0 = 14 \times 10^{-3}$ M, $[V(III)]_0 = 0$, and $[Tl(III)] = 3.03 \times 10^{-3}$ M. [c] Lower figures apply to $[V(II)]_0 = 4.09 \times 10^{-3}$ M, $[V(III)]_0 = 6.71 \times 10^{-3}$ M, and $[Tl(III)] = 3.03 \times 10^{-3}$ M.

The results in the first column of the table show that a scheme consisting of reactions 2, 3, 4, and 5 is not consistent with both sets of data. However, if the two-electron oxidation, reaction 1, is considered to be important, much better agreement is obtained in the region of high values of $k_1/(k_1 + 2k_2)$ and low values of k_5/k_4. The rest of the data are also in agreement with the conclusion that the reaction is predominantly a two-electron oxidation of V(II) by Tl(III). The last column in Table II gives stoichiometric ratios calculated assuming $k_1/(k_1 + 2k_2) = 0.95$ and $k_5/k_4 = 10^{-6}$.

The effect of low concentrations of chloride is quite striking. Daugherty reported that chloride strongly inhibits the V(III)–Tl(III) reaction.[5] In agreement, we find an initial apparent second-order rate constant of 0.1 M^{-1} sec^{-1} in 0.02 M HCl–0.98 M $HClO_4$ solutions. In similar solutions V(II)–Tl(III) mixtures produce only about half as much V(IV) at about the same rate as in the absence of chloride. The stoichiometric ratios shown in lines 11 and 12 of Table II are consistent with the idea that although reaction 3 is strongly inhibited by chloride, reaction 2 is more strongly catalyzed than is reaction 1.

CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH AND
DEVELOPMENT CENTER, SCHENECTADY, NEW YORK

The Synthesis of Copper Disulfide

BY RONALD A. MUNSON

Received March 4, 1966

Over the years there have been a number of reported syntheses of copper polysulfides.[1] Gattow and Rosenberg,[2] who investigated these claims roentgenographically, conclude that all hitherto reported compounds of composition $CuS_{>1}$ were mixtures of CuS and sulfur and not distinct compounds of copper. In no case was synthesis attempted at both elevated

---

(1) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim/Bergstrasse, 1958, pp 483, 484.

(2) G. Gattow and O. Rosenberg, *Naturwissenschaften*, **51**, 213 (1964).

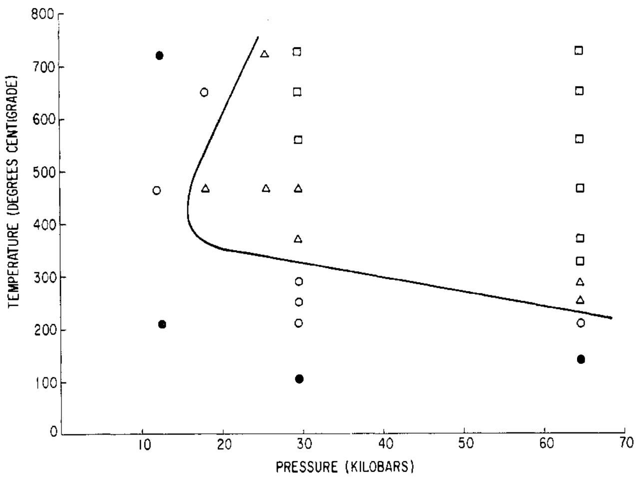

Figure 1.—Pressure–temperature diagram for the reaction of sulfur with covellite to form cubic copper disulfide. Two-minute runs produce the pyrite structure only, □; mostly pyrite structure, △; mostly covellite, ○; and no reaction, ●.

TABLE I

SPACING AND INDEXING OF THE REFLECTIONS OF CUBIC COPPER DISULFIDE[a]

d, A	*hkl*	Intens	*d*, A	*hkl*	Intens
3.32	111	m	1.054	521	m
2.89	200	vs	1.022	440	m
2.57	210	ms	1.005	522	w
2.35	211	ms	0.990	530	vw
2.04	220	s	0.978	531	m
1.92	300	w	0.963	600	m
1.86	310	vw	0.950	610	vw
1.73	311	s	0.939	611	m
1.66	222	m	0.913	620	m
1.59	320	m	0.903	621	m
1.54	321	m	0.895	541	w
1.40	410	mw	0.883	533	m
1.36	411	w	0.873	622	m
1.325	331	m	0.864	630	vw
1.291	420	m	0.854	631	m
1.260	421	m	0.828	700	m
1.231	332	w	0.819	710	m
1.180	422	mw	0.811	711	mw
1.158	500	w	0.804	640	ms
1.132	510	w	0.796	720	mw
1.112	511	ms	0.788	721	mw
1.073	520	m			

[a] Copper $K\alpha_1$ nickel-filtered radiation employed with a Norelco camera of diameter 114.59 mm.

temperature and pressure. This synthesis was carried out in the "belt" superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. The cell was calibrated at room temperature with the bismuth 25.5- and 27-kbar and the barium 58-kbar transformations. Temperatures were determined from the readings of a Pt—Pt-10% Rh thermocouple present during some of the runs. When a sample consisting of a mixture of CuS (covellite) and sulfur in a 1:1.2 mole ratio was subjected to the appropriate temperature and pressure conditions (Figure 1) and then washed with boiling CS_2 to extract the excess sulfur, a dark purplish red material was obtained. Chemical analysis indicated the formula $CuS_{1.9}$ and the X-ray reflections (Table I) showed that it had the cubic (NiS_2) pyrite structure, $a = 5.796$ A. The calculated density is 4.44 g cm^{-3}. The low pycnometric density, 4.24 ± 0.10 g cm^{-3}, may be ascribed to sulfur vacancies in the lattice. Between 200 and 300° in an inert atmosphere, CuS_2 decomposes to yield covellite, some digenite, and somewhat more than 1 mole of sulfur per mole of CuS_2. Further decomposition, which occurs between 400 and 475°, produces Cu_2S (chalcocite) and nearly 0.5 mole of sulfur.

Acknowledgment.—The author wishes to acknowledge the able assistance of D. R. Ochar in making the X-ray diffraction patterns and analyses and also helpful discussions with Dr. John S. Kasper. Dr. Lester Bronk performed the thermogravimetric measurement.

---

[3] H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

A Novel Synthesis of Arylphosphine Selenides. Reaction of Arylphosphines with Potassium Selenocyanate[1]

BY PHILIP NICPON[2] AND DEVON W. MEEK

Received March 14, 1966

Tertiary phosphine selenides have been prepared either by direct fusion of the tertiary phosphine with elemental selenium[3] or by refluxing the phosphine with selenium in an inert solvent.[4] We wish to report a novel synthesis of several arylphosphine selenides. Compared with the usual preparative routes for tertiary phosphine selenides, the reaction of a tertiary phosphine with potassium selenocyanate in acetonitrile is extremely simple (eq 1).

$$R_3P + KSeCN \xrightarrow{CH_3CN} R_3PSe + KCN \qquad (1)$$

Experimental Section

Reagent grade triphenylphosphine (Metal and Thermit) and potassium selenocyanate (Alfa) were not purified further. Acetonitrile was purified according to the procedure of Muney and Coetzee.[5]

Preparation of Triphenylphosphine Selenide.—The following preparation of $(C_6H_5)_3PSe$ illustrates a specific example of the synthetic procedure used to obtain tertiary phosphine selenides. To potassium selenocyanate (7.2 g, 0.05 mole) in 60 ml of acetonitrile was added rapidly, with stirring, triphenylphosphine (13.1 g, 0.05 mole) dissolved in 60 ml of warm acetonitrile. A white crystalline material began precipitating immediately. The reaction was stirred for 1 hr and then the solvent was evaporated. The solid residue was transferred to a sintered glass funnel and

---

[1] The authors gratefully acknowledge the financial support of Grant DA-ARO-(D)-31-124-G500 from the U. S. Army Research Office (Durham).

[2] Public Health Service Predoctoral Fellow, 1965–1966.

[3] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963).

[4] G. M. Kosolapoff, "Organophosphorous Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 98.

[5] W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).