

4. The surface tensions of aqueous camphor solutions change much less rapidly with concentration than do those of the aqueous solutions of borneol.

5. The presence of the dipentene and presumably of the other terpenes lowers the effectiveness of  $\alpha$ -terpineol as a frothing agent in so far as that property can be determined by surface and interfacial tension methods.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF VICTOR CHEMICAL WORKS]

## THE CATALYTIC EFFECT OF ALKALI AND ALKALINE EARTH SULFIDES ON THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR

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RECEIVED AUGUST 28, 1931

PUBLISHED FEBRUARY 5, 1932

In connection with work in this Laboratory on the preparation of phosphorus thiochloride, the reaction between phosphorus trichloride and sulfur as first reported by L. Henry<sup>1</sup> was investigated. A repetition of his experiment disclosed almost complete absence of reaction at 150° at the end of two hours and only partial reaction after eight hours' time.

Since such a reaction afforded a direct as well as simple means of preparing phosphorus thiochloride, it was hoped that further investigation would reveal a method of obtaining more complete reaction in shorter experimental periods.

### Experimental

**Sulfur.**—C. p. flowers of sulfur were used.

**Phosphorus Trichloride.**—The phosphorus trichloride was made by the direct combination of yellow phosphorus and dry chlorine gas. The crude product was re-distilled over fresh yellow phosphorus to remove any pentachloride. The boiling point of the final product was 76°.

**Sodium Polysulfide.**—Technical sodium monosulfide,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , was dehydrated by fusion. By heating together calculated quantities of anhydrous sodium monosulfide and sulfur, anhydrous sodium polysulfide was obtained. It was stored in a desiccator.

**Other Sulfides.**—The potassium, calcium and barium sulfides were of technical grade. They were dried before using.

**Procedure.**—The experiments at atmospheric pressure were carried out in an all-glass refluxing apparatus. The theoretical quantities of the reactants were placed in a 250-cc. round-bottomed flask attached to a reflux condenser by a ground-glass joint. At the top of the condenser was mounted a drying tube of phosphorus pentoxide to prevent moisture from entering the apparatus. At the end of the experiment the liquid in the flask was distilled from any residue into a distilling flask preparatory to determining its boiling range and gravimetric analysis.

When experimenting at elevated temperatures, sealed Pyrex tubes were used. The

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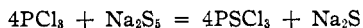
<sup>1</sup> L. Henry, *Ber.*, **2**, 638 (1869).

period of heating was controlled by placing the sealed tubes in preheated iron sheaths which were removed from the oven and quenched in cold water after the desired length of time.

Larger quantities of materials under pressure were handled in an oil-jacketed, steel autoclave which was equipped with a motor-driven agitator, extra-heavy pipe fittings, needle-valves and a pressure gage. Although iron was used throughout its construction, no signs of corrosion were evident after several runs. The product was distilled directly from the autoclave and redistilled in glass.

### Results

The effects of time, temperature and catalysts on the condensation of phosphorus trichloride and sulfur were studied. It was felt that if the sulfur were present in a more reactive form, such as an anhydrous alkali or alkaline earth polysulfide, the yield of phosphorus thiochloride would be increased. The equation for such a reaction may be written



This possibility as a solution to the problem was studied in conjunction with the direct reaction with sulfur.

In Table I are given the results of the experiments conducted at atmospheric pressure and at the boiling point of phosphorus trichloride.

TABLE I  
REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT THE BOILING POINT OF THE SOLUTION

Experiment	PCl <sub>3</sub> , g.	S, g.	Na <sub>2</sub> S <sub>5</sub> , g.	Time, hours	Boiling range of product, °C.
1	100	23.3	None	12	74- 79
2	100	23.3	None	24	74- 81
3	53.8	None	20.2	11	74- 85
4	120	None	45.0	24	105-122
5	39.4	9.2	0.5	11	74- 78

No reaction occurred when the two reactants were refluxed together for a reasonable length of time. When the calculated amount of sulfur was added in the form of anhydrous sodium polysulfide, Na<sub>2</sub>S<sub>5</sub>, a slow reaction took place as evidenced in Experiments 3 and 4. However, when a relatively small amount of the polysulfide was added to the phosphorus trichloride-sulfur mixture in an attempt to catalyze the direct reaction, the results were negative.

When higher temperatures were tried, namely 150°, an increase in the yield of phosphorus thiochloride was immediately apparent. In Table II, Experiments 6, 7 and 8 show the effect of time upon the reaction, which was still incomplete at eight hours. The next two experiments indicate that complete reaction may be obtained with the substitution of sodium polysulfide for the sulfur, while in Experiment 11 the presence of a small amount of polysulfide materially increased the rate of reaction between sulfur and phosphorus trichloride.

TABLE II  
REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT 150°

Experiment	PCl <sub>3</sub> , g.	S, g.	Na <sub>2</sub> S, g.	Time, hours	Boiling range of product, °C.
6	39.4	9.2	None	2	74- 78
7	39.4	9.2	None	4	75- 90
8	39.4	9.2	None	8	85-122
9	39.4	None	14.8	4	120-125
10	78.8	None	29.6	1	119-126
11	39.4	9.2	0.5	4	110-124

As a result of the above experiments, it appeared feasible to prepare phosphorus thiochloride from phosphorus trichloride and sodium polysulfide. It seemed more desirable, however, to develop the reaction between phosphorus trichloride and sulfur with the aid of the catalytic influence of small amounts of sodium sulfide. In continuing the investigation, the latter reaction was carried out on a slightly larger scale in a steel experimental autoclave. Sulfides of the other alkali and alkaline earth metals, namely, potassium, calcium and barium sulfides, were also tested for their effect upon the reaction.

The results of the experiments are presented in Table III. Experiments 12 and 13 were run as blanks with no catalyst present. They confirmed the slowness of reaction obtained in the experiments with sealed tubes. All the sulfides tried were effective catalysts. The alkaline earth sulfides appeared to have weaker catalytic activity than the alkali sulfides.

TABLE III  
REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT 150-160°

Charges consisted of 315 g. of phosphorus trichloride, 74 g. of sulfur and 3.9 g. (1%) of catalyst.

Experiment	Catalyst	Time, hours	Boiling range of product, °C.
12	None	4	78- 85
13	None	8	80-123
14	Na <sub>2</sub> S	5	118-124
15	Na <sub>2</sub> S	2	119-124
16	K <sub>2</sub> S	4	119-124
17	CaS	4	102-123
18	BaS	4	107-123

The boiling point of phosphorus trichloride is 76°, while that of phosphorus thiochloride is 123° at the barometric pressure under which the experiments were made. The boiling points were considered far enough apart to be used in judging the general extent of reaction. The thermometer readings given in the tables above are uncorrected.

In order to gain a more exact knowledge of the extent of reaction, gravimetric analyses of several of the products were made by the Carius method. The results are given in Table IV.

TABLE IV

## ANALYSIS OF REACTION PRODUCTS

Experiment	Calcd. for PCl <sub>3</sub> : P, 22.58. P found, %	Calcd. for PSCl <sub>3</sub> : P, 18.31; S, 18.88 S found, %	PSCl <sub>3</sub> (from S), %
6	22.47	0.61	3.23
7	21.19	6.19	32.74
8	19.81	12.68	67.16
9	18.53	19.14	100.0
14	18.69	18.29	96.87
15	18.62	18.72	99.15

The mechanism of the catalysis may well be explained by the intermediate compound theory in which the polysulfide is the active agent. Thus any basic substance with which sulfur easily reacts to give addition compounds would probably serve as a condensing agent for the reaction. For example, it has been observed that free caustic soda will catalyze the reaction. It was customary to clean the autoclave with hot caustic soda solution after each experimental run, and if the alkali were not thoroughly removed, reaction resulted in those experiments where no catalyst had been added.

## Summary

Phosphorus trichloride and sulfur do not react at atmospheric pressure and at the boiling point of the solution. At 150° a slow, partial reaction to form phosphorus thiochloride takes place.

Small amounts of alkali metal sulfides, alkaline earth metal sulfides or substances of like character which add on sulfur catalyze the reaction between phosphorus trichloride and sulfur so that conversion to phosphorus thiochloride is complete at 150° within a short period of time.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE PHOTOCHEMICAL DECOMPOSITION OF ORGANIC ACIDS<sup>1</sup>

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RECEIVED SEPTEMBER 1, 1931

PUBLISHED FEBRUARY 5, 1932

Quantitative studies have been made of the photochemical decomposition of aqueous solutions of oxalic,<sup>2</sup> formic,<sup>3</sup> lactic<sup>4</sup> and malonic<sup>5</sup> acids. Oxalic acid absorbs light of wave lengths below 365 mμ, decomposing to formic acid and carbon dioxide. The quantum yield is small. Formic acid de-

<sup>1</sup> A report of part of this work was presented at the Fall Meeting of the American Chemical Society at Minneapolis, 1929.

<sup>2</sup> Allmand and Reeve, *J. Chem. Soc.*, 129, 2834 (1926).

<sup>3</sup> Allmand and Reeve, *ibid.*, 129, 2852 (1926).

<sup>4</sup> Burns, *THIS JOURNAL*, 51, 3165 (1929).

<sup>5</sup> Pierce, Leviton and Noyes, *ibid.*, 51, 80 (1929).