# V. S. Abramov

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# On the Condensation of Dialkylphosphorous Acids with Derivatives of Carboxylic Acids

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The study of condensation reactions of dialkylphosphorous acids with carbonyl compounds has led us to the conclusion that aldehydes react most readily, and then ketones. Under the conditions for the condensation of dialkylphosphorous acids with aldehydes and ketones [1], as we reported [2], acids, acid amides, and esters do not react—not even formic acid esters, in which there is an aldehyde group bound to an alkoxy group. This is consistent with Watson' s series—the series of decreasing electrophilic capacity of carbonyl groups [3]. However, exploratory work on the interaction of dialkylphosphorous acids with derivatives of carboxylic acids continued. Experiments with derivatives of carbonic acid were successful; in particular, thiourea enters into reactions with dialkylphosphorous acids.

Thiourea has a basic character and can react with dialkylphosphorous acids with formation of a salt:

$$(RO)_2POH + NH_2CSNH_2 = (RO)_2P - ONH_3CSNH_2$$

Another possible course of the reaction is the addition of dialkylphosphorous acids at the $> C = S$ bond, by analogy with the addition of dialkylphosphorous acids to the carbonyl group, which may be represented by the scheme:

$$(RO)_2POH + C = S \begin{matrix} NH_2 \\ | \\ | \\ NH_2 \end{matrix} = (RO)_2P{-}C - SH \begin{matrix} \\ \\ \| \\ O \end{matrix} \begin{matrix} NH_2 \\ | \\ | \\ NH_2 \end{matrix}$$

In this case, esters of di-amino-sulfhydryl-methylphosphinic acid are formed.

As experiments have shown, thiourea enters into reaction with dialkylphosphorous acids when heated to a certain temperature, after which a vigorous reaction begins, with self-heating of the reaction mass—for example, with dimethylphosphorous acid. The reactions of dialkylphosphorous acids with thiourea proceed without a catalyst and the more readily and energetically, the smaller

the radical of the dialkylphosphorous acid: dimethylphosphorous acid reacts with thiourea at a temperature of 60°; diethyl-, dipropyl-, di-iso-propyl-, and di-ethoxy-ethylphosphorous acids react when heated on a water bath; dibutyl- and di-iso-butylphosphorous acids react at a higher temperature. The reactions were carried out in sealed tubes.

Salts of dialkylphosphorous acids belong to derivatives of trivalent phosphorus. They are characterized by addition reactions, for example, of sulfur [4]. If, in the interaction reaction of dialkylphosphorous acids with thiourea, salts are formed, then they should add sulfur and pass into derivatives of thiophosphoric acid; if, however, addition goes

dialkylphosphorous acids at the $> C = S$ bond and esters of di-amino-sulfhydryl-methylphosphinic acid are formed, then no interaction with sulfur should occur.

As experiments have shown, the reaction products of diethylphosphorous and dibutylphosphorous acids with thiourea do not add sulfur in benzene, aqueous alcohol, or dioxane. This circumstance enables us to make the preliminary conclusion that, in the reactions of dialkylphosphorous acids with thiourea, apparently salts are not formed; rather, the acids add at the $> C = S$ bond. However, further proof of the structure of the substances obtained, elucidation of the reaction mechanism, and study of their properties are necessary.

The constants of the products obtained are presented in Table 1.

**Table 1**

**Esters of di-amino-sulfhydryl-methylphosphinic acid**

| Product obtained | M.p., °C | P, % found | P, % calc. | Yield, % |
|---|---|---|---|---|
| $(CH_3O)_2P(=O)-C(NH_2)_2-SH$ | 113–114 | 16.44; 16.20 | 16.66 | 20.5 |
| $(C_2H_5O)_2P(=O)-C(NH_2)_2-SH$ | 109–110 | 14.30; 14.78 | 14.49 | 49.8 |
| $(C_3H_7O)_2P(=O)-C(NH_2)_2-SH$ | 103–104 | 12.76; 12.84 | 12.81 | 52.0 |
| $(C_4H_9O)_2P(=O)-C(NH_2)_2-SH$ | 114–115 | 11.65; 11.52 | 11.48 | 30.0 |

| Product obtained | M.p., °C | P, % found | P, % calc. | Yield, % |
|---|---|---|---|---|
| iso-$(C_4H_9O)_2P(=O)-C(NH_2)_2-SH$ | 144–145 | 11.28; 11.40 | 11.48 | 21.0 |

The condensation products are readily soluble in water, alcohol, and other solvents, from which they crystallize with difficulty. Recrystallization was carried out from dioxane. The esters of di-amino-sulfhydryl-methylphosphinic acid are greasy to the touch, paraffin-like crystals. Their melting point, which is preceded by shrinkage of the substance into lumps, is obtained as somewhat broadened. The yields of the crude products are good; however, during recrystallization large losses occur.

Preliminary experiments have shown that thiourea also enters into reaction with other phosphorous acids, for example, with acid esters of phenylphosphinic acid.

It has also been preliminarily established that urea, formamide, and other derivatives of carboxylic acids enter into reaction with dialkylphosphorous acids. Work in this direction is continuing.

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*Note: Figure translations are in progress. See original paper for figures.*