estimate the bond polarity by the value $\gamma = 1 - D_{cov}/D_{expt}$. Graphs for the relation between σ and γ for various halides are given in Fig. 1, from which graphs it can be seen that the energy estimate of the polarity γ is in agreement with the Pauling estimate σ.

The author thanks I. V. Stankevich for discussing the work.

CONCLUSIONS

The bond polarity, determined as the ionic component fraction of the bond energy, is related in a linear manner to the Pauling polarity value.

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SYNTHESIS OF THIOPHOSPHORIC ACID AMIDES

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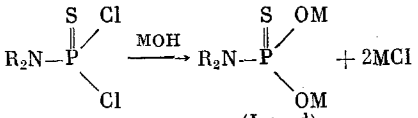
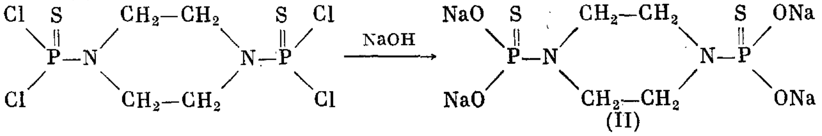
The chemistry of thiophosphoric acid has been studied in detail, but still hardly any literature data exists on the amides of thiophosphoric acid (ATA). The synthesis of some ATA by the alkaline hydrolysis of a diphenylamidothiophosphate was described [1], and also by the ammonolysis of $PSCl_3$ [2]. In the present paper we report the synthesis of some substituted ATA, which were obtained as the Na and NH_4 salts by treating the dichloride of the ATA with alkalis. The disodium and the mono- and diammonium cyclohexylamidothiophosphates (Ia-c), disodium piperididothiophosphate (Id), and tetrasodium piperazido-N',N"-bis-thiophosphate (II) were synthesized.



$$R_2N-P(S)Cl_2 \xrightarrow{MOH} R_2N-P(S)(OM)_2 + 2MCl$$

(I a—d)

$NR_2 = NHC_6H_{11}$, M = Na (a); $NR_2 = NHC_6H_{11}$, M = H and NH_4 (b); $NR_2 = NHC_6H_{11}$, $M = NH_4$ (c); $NR_2 = NC_5H_{10}$, M = Na (d)



(II)

It is known that the ATA are easily hydrolyzed, with cleavage of the P—N bond, to thiophosphoric acid, which then decomposes with the liberation of H_2S, in which connection an acid medium facilitates the hydrolysis [2]. The (I) and (II) compounds were synthesized in a homogeneous medium. The end products decomposed when the stirring was poor. The least stable of the obtained compounds, the cyclohexylamidothiophosphates (Ia-c), decomposed easily when the experimental conditions were not observed strictly, whereas piperidine (Id) and piperazide (II) were more stable.

EXPERIMENTAL

Cyclohexylamidothiophosphoric Acid, and Mono- and Diammonium Salts (Ib, c). With efficient stirring and using a dropping funnel equipped with a long tip, which descended into the alkaline solution layer, to a solution of 42 ml of 25% aqueous NH_3, 240 ml of water, and 550 ml of acetone was added at 0-5°C in 1 h a solution of 23.2 g (0.1 mole) of cyclohexylamido-

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thiophosphoryl dichloride in 50 ml of abs. acetone. An additional 300 ml of acetone was added and the obtained precipitate of diammonium salt (Ic) was filtered and dried in the air to give 19.01 g (83%) of product with mp 90° (the crystals change in appearance and become cloudy).

When 2.29 g (0.01 mole) of (Ic) was dried in a pistol dryer for 4 h at 70°, it lost 0.17 g (0.01 mole) of NH_3 and was converted to the monoammonium salt (Ib) (2.12 g, 0.01 mole) with mp 220-225°. Found: C 33.9; H 7.99; P 14.4; S 15.7%. $C_6H_{17}N_2O_2PS$. Calculated: C 34.0; H 8.00; P 14.6; S 15.1%.

Cyclohexylamidothiophosphoric Acid and Disodium Salt (Ia). With vigorous stirring, to a solution of 19.2 g (0.48 mole) of NaOH in 80 ml of 50% aqueous dioxane, heated to 80°, was added dropwise in 30 min a solution of 23.2 g (0.1 mole) of freshly prepared cyclohexylamidothiophosphoryl dichloride in 30 ml of dioxane using the above described dropping funnel and the heating at 80° was continued for 5 h, after which the mixture was cooled to 5° and 100 ml of EtOH was added to precipitate 8.1 g of Na_3PO_4. The addition of another 900 ml of EtOH gave 12.0 g (53.2%) of (Ia), which was reprecipitated from water solution with EtOH and dried in a vacuum-dessicator over P_2O_5. Found: N 5.3; P 13.0; S 13.5%. $C_6H_{12}NO_2PSNa_2$. Calculated: N 5.9; P 13.0; S 13.4%.

Piperididothiophosphoric Acid and Disodium Salt (Id). Using the above described conditions, from 20.0 g (0.1 mole) of piperididothiophosphoryl dichloride we obtained 18.6 g (80%) of (Id). Found: C 22.5; H 5.2; N 5.4; P 11.5; S 12.4%. $C_5H_{10}NO_2PSNa_2 \cdot 2H_2O$. Calculated: C 23.0; H 5.4; N 5.4; P 11.9; S 12.3%.

Piperazido-N',N"-bisthiophosphoric Acid and Tetrasodium Salt (II). In a similar manner, from 5.0 g (0.0142 mole) of piperazido-N',N"-bisthiophosphoryl tetrachloride we obtained 4.38 g (96.3%) of salt (II). Found: C 9.4; H 4.9; N 5.6; P 12.3; S 12.8%. $C_4H_8N_2O_4P_2S_2Na_4 \cdot 8H_2O$. Calculated: C 9.4; H 4.7; N 5.5; P 12.2; S 12.5%.

CONCLUSIONS

The cyclohexylamido- and piperididothiophosphoric acids were obtained for the first time, and also piperazido-N',N"-bisthiophosphoric acid as the Na and NH_4 salts.

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