method given in [4], with free aeration and using 0.005 M solutions of the corresponding acids. The exponential activity of the samples in the test solution was measured with an MST-17 end-window counter on B-2 and DP-100 A instruments. The Cu foil test samples had a thickness of 0.1 mm and a diameter of 20 mm, and after mechanical cleansing and degreasing with Eschke mixture were subjected to prior cathodic polarization in 1 N NaOH solution (current density 0.16 A/cm², 30 min).

In the adsorption experiments the polarization potential was maintained using a P-5827 potentiostat. A AgCl electrode was used as the reference electrode.

The cathodic polarization was studied at −0.25 V (when recalculated to the normal hydrogen electrode, while the anodic polarization was studied at 0.10 V.

The quantum-chemical calculations of the conformers of the studied anions were made using the CNDO/2 method as the sp and spd approximations with the parameters given in [5] (see [2] for details), and assuming that the discussed ions have a tetrahedral structure; $r_{P-O} = 1.54$, $r_{P-H} = 1.47$, $r_{O-H} = 1.0$ Å, ∠POH = 102°.

CONCLUSIONS

The radioactive isotope method was used to study the adsorption of various anions of phosphoric, phosphorous, and hypophosphorous acids on negatively and positively charged copper, and it was shown that the corresponding adsorption values change oppositely to the sums of the absolute values of the charges of all of the atoms of the anion, which were calculated by the CNDO/2 method.

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REACTION OF AMIDOPHOSPHITES WITH HYDROGEN CHLORIDE

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It is known that amidophosphites react with HCl to give amines and chlorophosphites [1]. It is postulated that the nitrogen atom of the amidophosphite is protonated. However, it proved that when hexamethyl triamidophosphite is reacted with CF_3COOH at low temperature the N-protonation products (amine and anhydride derivative) are accompanied by the formation of the P-protonated product [2]. In view of this it seemed of interest to study the reaction of the mono-, di-, and triamidophosphites with excess HCl by the ^{31}P NMR method at −70°C. In the case of the O,O-dialkyl amidophosphites the dialkyl chlorophosphite ($\delta_{^{31}P} = -165$ ppm) and amine are formed in the first step of the reaction. Under the influence of HCl the dialkyl chlorophosphite disproportionates to the alkyl dichlorophosphite ($\delta_{^{31}P}$ −177 ppm) and trialkyl phosphite, which appears in the ^{31}P NMR spectrum as its protonated form ($\delta_{^{31}P}$ −20 ppm, $J_{P-H} =$ 816 Hz). A similar disproportionation was also observed by us previously when dialkyl chlorophosphites are reacted with HCl [3]. A temperature above −40° leads to decomposition of the

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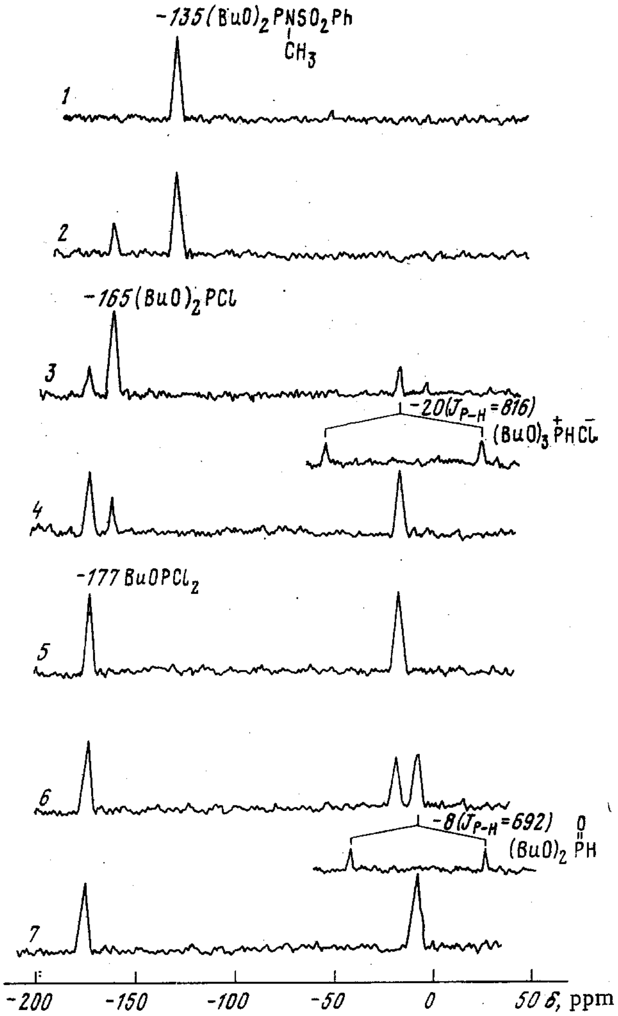
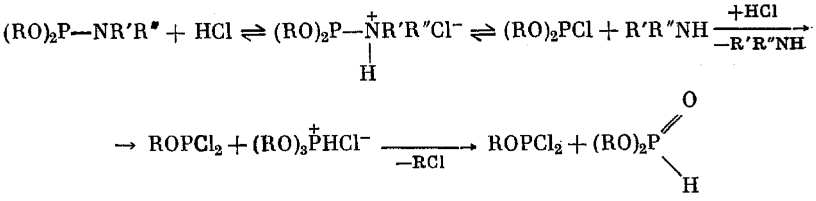


Fig. 1. NMR spectrum of reaction of $(BuO)_2P{-}NMeSO_2Ph$ + excess HCl at –70° (1-5) and –40° (6, 7).

protonated product to give the dialkylphosphorous acid ($\delta_{^{31}P}$ – 8 ppm, J_{P-H} = 692 Hz).

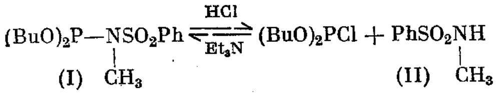


$$(RO)_2P{-}NR'R'' + HCl \rightleftharpoons (RO)_2P{-}\underset{\substack{|\\ H}}{\overset{+}{N}}R'R''Cl^- \rightleftharpoons (RO)_2PCl + R'R''NH \xrightarrow[-R'R''NH]{+HCl}$$

$$\rightarrow ROPCl_2 + (RO)_3\overset{+}{P}HCl^- \xrightarrow[-RCl]{} ROPCl_2 + (RO)_2P{\overset{\displaystyle O}{\diagup\!\!\diagup}}\!\!\underset{\displaystyle H}{\diagdown}$$

R = Et, R′ = R″ = Et, Bu; R = Bu, R′ = CH$_3$, R″ = SO$_2$Ph

The insertion of electron-acceptor substituents on the nitrogen atom, which lower its basicity substantially, fails to affect the direction of this reaction. When dibutylphosphorous acid N-methylbenzenesulfonamide (I) reacted with excess HCl in CH_2Cl_2 at –70° the products are N-methylbenzenesulfonamide (II) and dibutyl chlorophosphite, which under the influence of HCl undergo disproportionation by the above given scheme (Fig. 1). It should be mentioned that when this reaction is run at –70° using a 1:1 ratio of the starting reactants the reaction stops at the stage of forming dibutyl chlorophosphite and sulfonamide (II). The treatment of this mixture with an equimolar amount of triethylamine again leads to the formation of (I).



$$\underset{\text{(I)}}{(BuO)_2P{-}\underset{\substack{|\\ CH_3}}{N}SO_2Ph} \underset{Et_3N}{\overset{HCl}{\rightleftharpoons}} (BuO)_2PCl + \underset{\text{(II)}}{PhSO_2\underset{\substack{|\\ CH_3}}{N}H}$$

When the course of the reactions of tris(N-dialkylamido) phosphites and O-alkyl bis(N-dialkylamido) phosphites with HCl was checked by the ^{31}P NMR method at –70°, it was found that the P-protonated intermediate products are also not formed here. As a result, on the basis of the obtained results it may be assumed that when P(III) acid amides are reacted with HCl the nitrogen atom of the amido group is protonated, with subsequent nucleophilic replacement of the $H\overset{+}{N}R_2$ group on the tricoordinated phosphorus atom by chloride anion. The initial protonation of sulfonyl oxygen is not excluded when P(III) acid sulfonamides are used in this reaction.

EXPERIMENTAL

The chemical shifts of the ^{31}P nuclei were measured on a KGU-4 NMR spectrometer relative to 85% H_3PO_4.

Synthesis of Dibutylphosphorous Acid N-Methylbenzenesulfonamide. With stirring, to 37 g of dibutyl chlorophosphite in 100 ml of toluene was added 34 g of the Na salt of N-methylbenzenesulfonamide. The obtained precipitate was filtered. Fractional distillation of the filtrate gave 30 g (50%) of dibutylphosphorous acid N-methylbenzenesulfonamide with bp 136-140° (0.01 mm); n_D^{20} 1.5059; d_4^{20} 1.1087; $\delta_{^{31}P}$ –135 ppm. Found: N 3.48%. $C_{15}H_{26}NO_4PS$. Calculated: N 4.03%.

Reaction of Dibutylphosphorous Acid N-Methylbenzenesulfonamide with Hydrogen Chloride (1:1). Into a mixture of 4.3 g of dibutylphosphorous acid N-methylbenzenesulfonamide in 50 ml of ether was passed 0.67 g of dry HCl at –70°. Fractional distillation gave 1.76 g (84%) of the N-methylbenzenesulfonamide with bp 201-203° (10 mm); n_D^{20} 1.5328 and 1.32 g (50%) of dibutyl chlorophosphite with bp 98-100° (10 mm); n_D^{20} 1.4453; $\delta_{^{31}P}$ –166 ppm.

Reaction of N-Methylbenzenesulfonamide with Dibutyl Chlorophosphite in Presence of Triethylamine. To a mixture of 7.85 g of N-methylbenzenesulfonamide and 9.7 g of dibutyl chlorophosphite in 50 ml of ether was added 4.6 g of triethylamine in drops. The precipitate was filtered to give 6.0 g (95%) of $Et_3N \cdot HCl$ with mp 254°. Fractional distillation of the filtrate gave 8.0 g (51%) of dibutylphosphorous acid N-methylbenzenesulfonamide with bp 134-136° (0.01 mm); n_D^{20} 1.5054; $\delta_{^{31}P}$ –135 ppm.

CONCLUSIONS

The reaction of some mono-, di-, and triamidophosphites with HCl was studied at low temperatures. The amido group is replaced by chlorine in the first step of the reaction, apparently due to protonation of the nitrogen atom of the amidophosphite. The formation of P-protonated products in the case of the monoamidophosphites is due to the disproportionation of dialkyl chlorophosphites in excess HCl.

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