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## LETTERS TO THE EDITOR

# Synthesis on the Basis of Red Phosphorus of *O,O'*-Diisooctylthiophosphoric Acid Triethylammonium Salt, an Effective Inhibitor of Carbon Dioxide Corrosion of Steel

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The reactions of white phosphorus ($P_4$) and elemental sulfur with proton donor reagents readily proceed in the presence of amines, facilitating the opening of the phosphorus tetrahedron, with the formation of ammonium salts of phosphorous, hypophosphorous acids and diesters of dithiophosphoric acids [1–4]. The latter compounds were shown to be effective inhibitors of carbon dioxide and hydrogen sulfide corrosion of steel in a wide temperature range.

However, being highly toxic and easily flammable, white phosphorus requires special safety precautions in practical use. Red phosphorus, being less toxic and more stable than white phosphorus, has advantages over white phosphorus, that makes the synthesis of organo(thio)phosphorus compounds on the basis of red phosphorus an actual problem.

In the present work, we suggest a new method for the synthesis of ammonium salts of *O,O'*-dialkyldithiophosphoric acids, namely, the triethylammonium salt of *O,O'*-diisooctyldithiophosphoric acid, which showed high anticorrosive performance [4].

The reaction of red phosphorus with isooctanol was carried out in the presence of sulfur and triethylamine at 80–90°C in the course of 20 h. The reaction of the triad of red phosphorus $(P)_n$–amine–sulfur with alcohols follows the scheme earlier suggested by us for the reaction of white phosphorus, with participation of phosphide anion formed by successive rupture of the P–P bonds in the molecule of polymeric red phosphorus (Scheme 1).

As distinct from the method of synthesis of esters of dithiophosphoric acid by the reaction of phosphorus pentasulfide with alcohols, reaction (1) is followed by evolution of hydrogen rather than toxic hydrogen sulfide. Salt **I** is characterized by the signal in the $^{31}P$ NMR spectrum at $\delta_P$ 112 ppm.

**Scheme 1.**

$$P_n + Et_3\overset{+}{N}–S \ldots S_7^- \rightarrow Et_3\overset{+}{N}S–S_7–P^- + P_m, \quad (1)$$

$$Et_3\overset{+}{N}S–S_7–P^- \xrightarrow{i\text{-}C_8H_{17}OH} i\text{-}C_8H_{17}O–P–H$$

$$\xrightarrow{S} i\text{-}C_8H_{17}O–P–SH \xrightarrow{i\text{-}C_8H_{17}OH,\ S,\ Et_3N} (i\text{-}C_8H_{17}O)_2P(S)SH\cdot Et_3N + H_2. \quad (2)$$

**I**

The obtained salt **I** was investigated by the electrochemical method as an inhibitor of the carbon dioxide corrosion of steel. Using the procedures in [4] on the basis of potentiodynamic polarization curves and the method of linear polarization resistance the rates of corrosion were determined and the protecting effect of 92.0–95.9% was calculated, which coincided with that of the salt prepared from white phosphorus. It was also found that the protecting effect of salt **I** is increased with temperature and reaches 99.6% at 80ºC.

Therefore, a technological one-pot method of synthesis of triethylammonium salt of *O,O'*-diisooctyldithiophosphoric acid, a high-temperature inhibitor of the carbon dioxide corrosion, is suggested.

**Triethylammonium salt of diisooctylphosphoric acid (I).** To the mixture of 1 g of red phosphorus, 2 g of sulfur, and 9.2 g of isooctanol in 10 mL of toluene 3.3 g of triethylamine was added and stirred at 80–90ºC for 20 h. The unreacted reagents were filtered off, the solvent was removed in a vacuum, the residue was distilled in the apparatus for molecular film distillation at the temperature of the heater of 90ºC (0.01 mmHg) to give 7.2 g of salt **I** as a viscous substance, $n_D^{20}$ 1.4972. IR spectrum, ν, $cm^{-1}$: 680 (P=S). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.66 d [12H, $(CH_3)_2$, *J* 5.0], 1.06–1.07 m (16H, $CH_2$), 1.15–1.17 m (11H, $\underline{CH_3}CH_2$ and CH), 3.02 q (6H, $CH_3\underline{CH_2}$, *J* 7.2), 3.27–3.29 m (4H, $CH_2O$). $^{31}P$ NMR spectrum ($CH_3CN$), δ, ppm: 112. Found, %: C 57.34; H 10.57; N 3.37; P 6.53; S 14.53. $C_{22}H_{50}NO_2PS_2$. Calculated, %: C 58.02; H 10.98; N 3.08; P 6.81; S 14.06.

IR spectrum was registered on a Tensor 27 (Bruker) FTIR spectrometer in the range 4000–400 $cm^{-1}$. $^1H$ NMR spectrum was recorded on a Bruker MSL-500 spectrometer (500.13 MHz) with respect to the residual proton signals of the deuterated solvent. $^{31}P$ NMR spectrum was taken on a Bruker MSL-400 spectrometer (161.97 MHz). Elemental analysis for C, H, N, S was performed on a CHN-3 analyzer, the analysis for phosphorus, by the conventional pyrolysis method.

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