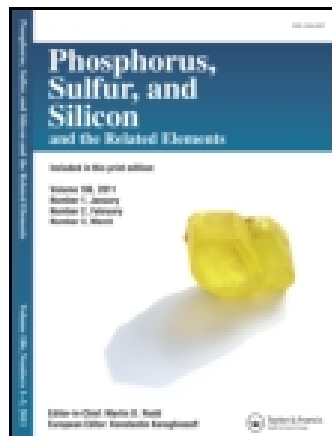


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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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Long-Chain Alkyl Esters of O,O-Dialkyl Dithiophosphoric and Thionophosphoric Acids Prepared on the Basis of Red Phosphorus, Elemental Sulfur, Alcohols, and Industrial Fractions of Higher Monoolefins

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Accepted author version posted online: 20 Aug 2014.



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To cite this article: Ilyas S. Nizamov, Radik R. Shamilov, Ramazan Z. Salikhov, Ilnar D. Nizamov, Yuriy P. Khodyrev & Elvira S. Batyeva (2015) Long-Chain Alkyl Esters of O,O-Dialkyl Dithiophosphoric and Thionophosphoric Acids Prepared on the Basis of Red Phosphorus, Elemental Sulfur, Alcohols, and Industrial Fractions of Higher Monoolefins, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 190:4, 484-493, DOI: [10.1080/10426507.2014.951999](https://doi.org/10.1080/10426507.2014.951999)

To link to this article: <http://dx.doi.org/10.1080/10426507.2014.951999>

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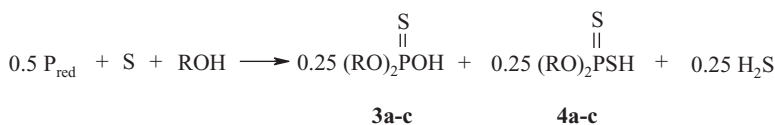
LONG-CHAIN ALKYL ESTERS OF *O,O*-DIALKYL DITHIOPHOSPHORIC AND THIONOPHOSPHORIC ACIDS PREPARED ON THE BASIS OF RED PHOSPHORUS, ELEMENTAL SULFUR, ALCOHOLS, AND INDUSTRIAL FRACTIONS OF HIGHER MONOOLEFINS

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GRAPHICAL ABSTRACT



R = Bu-*i* (**3a**, **4a**), Oct-*i* (**3b**, **4b**), Pr-*i* (**3c**, **4c**)

Abstract Mixtures of long chain *S*-alkyl *O,O*-dialkyl dithiophosphates, and *O*-alkyl *O,O*-dialkyl thionophosphates were obtained by the reaction of red phosphorus with elemental sulfur, alcohols, and industrial fractions of C_{16} – C_{18} and C_{20} – C_{26} of higher olefins in the presence of Lewis acid catalysts. The products obtained possess high anticorrosion activities toward mild steel.

Keywords Red phosphorus; sulfur; alcohols; higher olefins; anticorrosion activity

INTRODUCTION

The tetracoordinated phosphorus organic dithioacids as well as their esters and salts have found an expanding application as agricultural insecticide and pesticide derivatives,^{1–5} antiwear oil lubricant additives,⁶ surface-active agents, emollients, washing agents, wetting agents and detergents, dispersing agents, and versatile chelating ligands.^{7–10} The dithiophosphate derivatives have played a key role as corrosion inhibitors of mild steel.^{11–13}

Received 6 May 2014; accepted 2 August 2014.

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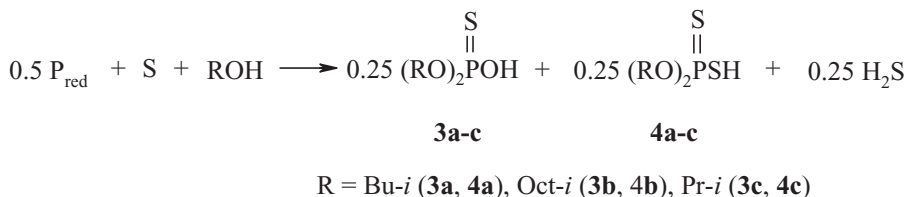
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These compounds involve nonpolar hydrocarbon chains as well as a S=P–S group. Low-chain *O,O*-dialkyl *S*-alkyl dithiophosphates were prepared by the reactions of *O,O*-dialkyl dithiophosphoric acids with hexadec-1-ene, octadec-1-ene, 2-methylpentadec-1-ene, 2-methylheptadec-1-ene, and 2-methylpent-1-ene in the presence of zinc chloride and under ultrasound irradiation.^{14–16} However, the chemical behavior of nonactivated simple higher (C_{16} and C_{18} and higher) α -monoolefins in the similar reactions appear to have attracted little attention. Thus, we have managed to obtain long chain *S*-alkyl *O,O*-dialkyl dithiophosphates by the addition of *O,O*-dialkyl dithiophosphoric acids at the carbon–carbon double bond of higher monoolefins of industrial fractions of C_{16} – C_{18} and C_{20} – C_{26} .¹² High inhibition efficiency has been found for long chain *S*-alkyl *O,O*-dialkyl dithiophosphates.¹² Taking into account that *O,O*-dialkyl dithiophosphoric acids have usually been prepared by the reaction of tetraphosphorus decasulfide with alcohols,¹⁷ we have decided to use mixtures of red phosphorus and elemental sulfur instead of tetraphosphorus decasulfide. We have already reported our preliminary results on the reaction of red phosphorus with sulfur, alcohols, and higher olefins of industrial fractions of C_{16} – C_{18} and C_{20} – C_{26} as an abstract of conference report¹⁸ without experimental details and structure identification. So in this article experimental details of this reaction are presented. The mixture of long chain *S*-alkyl *O,O*-dialkyl dithiophosphates and *O*-alkyl *O,O*-dialkyl thionophosphates were tested as inhibitors for carbon dioxide corrosion of mild steel using polarization curves.

RESULTS AND DISCUSSION

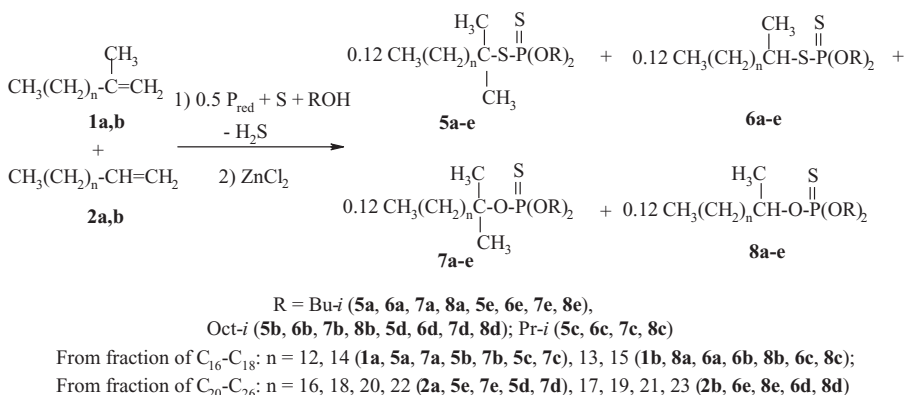
We have previously established content and structure of higher olefins of industrial fractions of C_{16} – C_{18} and C_{20} – C_{26} manufactured by Joint Stock Company “Nizhnekamskneftekhim” (Russian Federation) by ^1H NMR spectroscopy, mass spectrometry, and GC analyses.¹⁹ The fraction of C_{16} – C_{18} mainly includes vinylidene α -olefins **1a** 25.6%, linear C_{16} and C_{18} α -olefins **1b** 61.6%, and inner C_{16} and C_{18} olefins **1c** 12.8%. The fraction C_{20} – C_{26} mostly contains the olefins of C_{20} (the overall content of C_{20} is 31.7%), C_{22} (26.0%), C_{24} (16.4%), and C_{26} (12.9%) involving C_{28} (7.8%) and involves vinylidene α -olefins **2a**, linear α -olefins **2b**, and minor amounts of spatially hindered olefins with inner $\text{C}=\text{C}$ **2c**.¹⁹

It should be noted that the complicacy of the contents of industrial fractions C_{16} – C_{18} and C_{20} – C_{26} olefins can lead to intricate mixtures of the addition products of phosphorus thioacids into the $\text{C}=\text{C}$ bond. Ethanol, 1-propanol, 1-butanol, 1-pentanol, heptanol, 1-octanol, and 1-dodecanol have been reported to react with red phosphorus and sulfur in ratio of 1:1:1 at 100–150°C for 3–24 h to form mixtures of *O,O*-dialkyl dithiophosphoric acids (the main products) and *O,O*-dialkyl thionophosphoric acids (the minor products).²⁰ Indeed, we have confirmed that the reaction of red phosphorus and sulfur with *iso*-butanol, *iso*-octanol, and *iso*-propanol has been completed by heating the reactants at 100–110°C for 6–12 h with the minor formation of *O,O*-dialkyl thionophosphoric acids **3a–c** ($\delta_{\text{P}} = 64$ ppm) and the main formation of *O,O*-dialkyl dithiophosphoric acids **4a–c** ($\delta_{\text{P}} = 86$ ppm; Scheme 1). The ^{31}P NMR resonances at 64 and 86 ppm are typical for dithiophosphoric and thionophosphoric acids.²¹ It should be emphasized that the ratio of red phosphorus/sulfur/*iso*-butanol as 2:5:4 corresponds to the stoichiometry of the reaction of tetraphosphorus decasulfide with alcohols.²² At this ratio at 100°C for 10 h we have obtained mixtures of *O,O*-di-*iso*-butyl dithiophosphoric acids **4a** as main product (90%, $\delta_{\text{P}} = 86.8$ ppm) and *O,O*-di-*iso*-butyl thionophosphoric acids **3a** (10%, $\delta_{\text{P}} = 64.3$ ppm) as minor product.



Scheme 1

There is no need to isolate the thioacids **3a-c** and **4a-c**. The reaction mixtures obtained (see Scheme 1) were treated by olefins **1a-c** and **2a-c** in the presence of 2–3 wt% of ZnCl₂ as Lewis acid catalyst at 80°C for 4 h to form S-alkyl *O,O*-dialkyl dithiophosphates **5a-e** and **6a-e** ($\delta_P = 90$ and 94 ppm, respectively) and *O*-alkyl *O,O*-dialkyl thionophosphates **7a-e** and **8a-e** (Scheme 2).²³ The inner olefins **1c** and **2c** and minor amounts of phosphorus thioacids formed from these olefins are not shown in Scheme 2.



Scheme 2

The products **5**, **6**, **7**, and **8** were not isolated as individual compounds but characterized as the mixtures. Compounds **5c**, **6c**, **7c**, and **8c** (with *iso*-propoxy groups) were purified by column chromatography on silica gel. The ³¹P NMR signals of the intermediate products **3a-c** and **4a-c** disappeared when the reaction (Scheme 2) was completed. The ³¹P NMR spectra of minor thionophosphates **7a-e** and **8a-e** show signals in the field of $\delta_P = 69.1$ – 69.9 ppm. These signals are in accordance with literature data.²¹ Thus, *O*-*iso*-propyl *O,O*-diethyl thionophosphate and tri-*iso*-butyl thionophosphate are known to possess signals in the ³¹P NMR spectra at $\delta_P = 69.0$ and 68.3 ppm, respectively.²¹ In the reactions of red phosphorus, sulfur, *iso*-butanol or *iso*-octanol with olefins **1a-c**, the ratio between dithiophosphate **5a-e**, **6a-e**, and thionophosphates **7a-e**, **8a-e** is 2:1 whereas in the reactions of olefins **2a-c** with red phosphorus, sulfur, *iso*-butanol, the ratio between **5a-e**, **6a-e**, and **7a-e**, **8a-e** is 9:1.

The reactions studied (Scheme 2) have been found to bring about the formation of products as Markovnikov's adducts. The ¹H NMR spectra of all products **5**, **6**, **7**, and **8** show characteristic resonances due to the presence of the methyl protons of a CH₃CH₂CH₂ fragment. Thus, a large triplet at $\delta = 0.90$ ppm (³J_{HH} = 7.2 Hz) was assigned to the methyl protons of the CH₃CH₂CH₂ fragment of the main products **5c** and **6c**, whereas a little triplet

at $\delta = 0.97$ ppm ($^3J_{\text{HH}} = 7.2$ Hz) was attributed to the same protons of the minor products **7c** and **8c**. The ^1H NMR spectrum of **6a** exhibits a multiplet at $\delta = 3.03$ ppm for the methine proton of the $\text{PSC}(\text{CH}_3)\text{CH}_2$ fragment. A siglet observed at $\delta = 1.59$ ppm is assigned to the methine proton of the $\text{PSC}(\text{H})\text{CH}_2$ fragment of **5a**. The methylene protons attached to the oxygen atom [the $(\text{CH}_2\text{CH}_2\text{O})_2\text{P}$ fragment] of **5b**, **6b**, **7b**, and **8b** (with *iso*-octyloxy groups) appeared as two doublet of triplets at $\delta = 3.97$ and 4.05 ppm ($^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{PH}} = 5.1$ Hz, **5b**, **6b** and $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{PH}} = 5.8$ Hz, **7b**, **8b**). The methyl protons of the $[(\text{CH}_3)_2\text{CHO}]_2\text{P}$ fragment of **5c**, **6c**, **7c**, and **8c** (with *iso*-propoxy groups) appear as a doublet at $\delta = 1.38$ ppm ($^3J_{\text{HH}} = 6.3$ Hz). The methyl protons of the $[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_2\text{P}$ groups of **5e**, **6e**, **7e**, and **8e** (with *iso*-butoxy groups) reveal a doublet at $\delta = 0.98$ ppm ($^3J_{\text{HH}} = 6.4$ Hz).

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of **5a**, **6a**, **7a**, and **8a** show a doublet at $\delta = 36.7$ ppm that is being attributable to the carbon atom of the $\text{PSC}(\text{H})$ fragment of **6a** ($^2J_{\text{PC}} = 5.9$ Hz), a doublet at $\delta = 41.3$ ppm (PSC , **5a**, $^2J_{\text{PC}} = 5.5$ Hz), a singlet at $\delta = 67.4$ ppm ($\text{POCHCH}_2\text{CH}_2$, **8a**), and a singlet at $\delta = 70.0$ [$\text{POC}(\text{CH}_3)_2\text{CH}_2$, **7a**].

The ESI mass spectrum of **5a**, **6a**, **7a**, and **8a** exhibits the mass peak m/e 478.3 due to molecular ions $[\text{M}]^+$ of **7a** and **8a**, formed from olefins of C_{18} (calculated molecular mass **M 7a** and **8a** is 478.8). The peaks m/e 554.6 and 1009.6 were assigned to ions $[\text{M} + \text{Na} + \text{K}]^+$ and $[2\text{M} + \text{K}]^+$ where **M** is the molecular mass of **5a** and **6a** (**M** 466.8) resulting from C_{16} olefins. The esters **5a** and **6a** formed from C_{18} olefins give a peak m/e 1049.1 of ion $[2\text{M} + \text{Na} + \text{K}]^+$ (requires 494.8).

The bands at ν 675 and 553 cm^{-1} in the IR spectrum of **5a**, **6a**, **7a**, and **8a** are assigned to the $\text{P}=\text{S}$ and $\text{P}-\text{S}$ stretching vibrations. The band at ν 999 cm^{-1} is due to the stretching vibration of the $(\text{P})\text{O}-\text{C}$ bond. The band of the symmetrical deformation vibrations of the geminal $(\text{CH}_3)_2\text{C}$ group appeared at ν 1377 cm^{-1} .

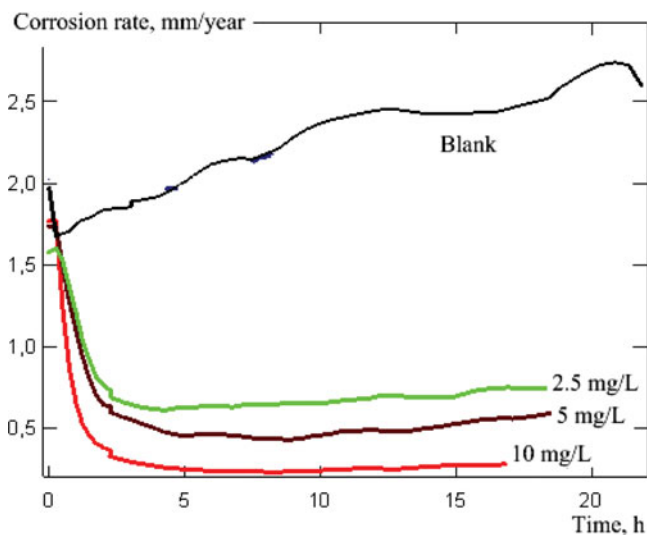
There is no need to prepare intermediate tetraphosphorus decasulfide or *O,O*-dialkyl dithiophosphoric acids. Long chain *S*-alkyl *O,O*-dialkyl dithiophosphates and *O*-alkyl *O,O*-dialkyl thionophosphates obtained possess thiophosphoryl and dithiophosphoryl groups which can coordinate to iron atoms.¹³ It is noteworthy that carbon dioxide corrosion of mild steel is a very serious problem in the oil and gas production industry.^{24,25} So we have decided to study the inhibition effectiveness upon CO_2 corrosion of mild steel for the mixtures of **5**, **6**, **7**, and **8**. Data of inhibition coefficient (γ) and inhibition efficiency (η) with different concentrations of **5**, **6**, **7**, and **8** are presented in Table 1. The inhibition efficiency reached 91.8% when compounds **5a**, **6a**, **7a**, and **8a** with *iso*-butoxy groups are introduced into the standard brine in a concentration of 10 mg L^{-1} after 16 h. At the same concentration, products **5c**, **6c**, **7c**, and **8c** with *iso*-propoxy groups reveal protection effects of 89.8%. As shown in Figure 1, the corrosion rate decreases with reduce of concentrations of compounds **5a**, **6a**, **7a**, and **8a** less than 10 mg L^{-1} . It is of interest to compare the inhibition efficiencies of **5a**, **6a**, **7a**, and **8a** with long chain *S*-alkyl *O,O*-diethyl dithiophosphates previously obtained by the reaction of *O,O*-diethyl dithiophosphoric acid with olefins **1a-c**¹² by the induction period after addition to the brine. The protection effect of latest compounds occurs 2–3 h after the introduction of inhibitor,¹² whereas the mixture of **5a**, **6a**, **7a**, and **8a** works as inhibitor at 1–1.5 h after introduction in brine. Thus, the synergistic effect of the mixture of red phosphorus and sulfur on inhibition efficiency of long chain *S*-alkyl esters of phosphorus thioacids was established.

Table 1 Inhibition coefficients γ and inhibition efficiencies η for different concentrations of compounds **5e**, **6e**, **7e** and **8e** at carbonaceous mild steel corrosion

Compounds	Dose, mg L ⁻¹	γ (16 h)	η , % (16 h)
5a, 6a, 7a, 8a	10	12.3	91.8
5a, 6a, 7a, 8a	5	5.5	82.0
5a, 6a, 7a, 8a	2,5	4.4	77.1
5b, 6b, 7b, 8b	10	1.8	45.7
5b, 6b, 7b, 8b	5	2.0	50.6
5c, 6c, 7c, 8c	10	9.8	89.8
5d, 6d, 7d, 8d	10	6.1	83.5
5d, 6d, 7d, 8d	5	5.3	81.3
5d, 6d, 7d, 8d	1	2.9	66.0
5e, 6e, 7e, 8e	10	5.7	82.5
5d, 6d, 7d, 8d	5	7.1	85.8

EXPERIMENTAL

The ³¹P NMR spectra were taken on a Bruker Avance 400 spectrometer (161.98 MHz; Bruker BioSpin GmbH, Rheinstetten, Germany) in C₆H₆ with 85% H₃PO₄ as an external reference. The ¹H NMR spectra were recorded at ambient temperature with a Bruker Avance 400 instrument (400 MHz; Bruker BioSpin GmbH, Rheinstetten, Germany) in CDCl₃. The ¹³C NMR spectra were run with a Bruker Avance-600 spectrometer (100.6 MHz; Bruker BioSpin GmbH, Rheinstetten, Germany) in CDCl₃. Chemical shifts δ are presented in ppm relative to residual resonance of solvent (¹H: 7.26 ppm), coupling constants J are given in Hz. FTIR spectra were obtained from films with a Bruker Vector 22 (400–4000 cm⁻¹, Bruker Optik GmbH, Ettlingen, Germany) and expressed in cm⁻¹, δ = the deformation

**Figure 1** Dependences of corrosion rate on time for mild steel in brine (blank) and in brine containing compounds **5e**, **6e**, **7e**, and **8e** in concentrations of 10, 5, and 2.5 mg L⁻¹.

vibration. The ESI mass spectra were determined on a Bruker Compass Data Analysis 4.0 mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany).

Red phosphorus was purified from residues of white phosphorus by refluxing with 7% aqueous solution of NaOH, washed by anhydrous diethyl ether and benzene and dried under vacuum (0.02 mm Hg) at 40°C. Sulfur was dried by refluxing in anhydrous benzene by means of a Dean-Stark trap. Olefins of industrial fractions of C₁₆–C₁₈ (TU 2411-067-05766801-97) and C₂₀–C₂₆ (TU 2411-068-05766801-97) were dried with CaCl₂.

Corrosion tests were carried out in a 1 L glass cell with three similar mild steel electrodes Pattern 44–1018MS of 30.7 mm length and 4.7 mm diameter, which were used in turn during subsequent experiments. Platinum mesh and Ag/AgCl/KCl saturated electrode (SSE) were used as counter electrode and reference electrode, respectively. The potential of this reference electrode at 25°C is 200 mV versus the standard H₂ electrode. All electrode potentials were thus expressed with reference to SSE. Before each experiment, the working electrodes were treated with abrasive paper (1200 grit SiC), etched with 10% HCl solution for 10 min, washed with distilled water, then acetone and dried by warm air, immediately afterwards placed into the cell.

Synthetic brine was used for experiments based on the ASTM D1141–90 standard (NaCl—24.5; MgCl₂—5.2; Na₂SO₄—4.09; CaCl₂—1.16; KCl—0.66; NaHCO₃—0.2 g L⁻¹). The solution was magnetically stirred at a speed of 500 rpm and carbon dioxide was bubbled through the solution. Upon the saturation with carbon dioxide, the pH of the brine was found to be 5.3. Experiments were carried out at 40°C, the temperature being controlled within ±1°C. The time of the introduction of electrodes was counted from the point when the equilibrium distribution of ions and hydrated particles, formed upon dissolution of CO₂, was reached, the equilibrium being controlled via the stability of the pH values.

Field Machine ICM Instruments (ACM Instruments, Cumbria, England) was used for inhibition efficiency tests, pH values were measured by a pH-meter HI 9025 Hanna Instruments (Woonsocket, Rhode Island, USA). The corrosion rates were determined by polarization curves and by means of linear polarization resistance (R_p). Value R_p was measured after the introduction of electrodes in the cell at an interval of 0.5 h (±6 mV respective to corrosion potential, scan rate of the potential being equal to 0.3 mV/s). Electrochemical impedance spectrum was recorded 16 h after the introduction of inhibitor in the frequency interval 1–30 kHz with 10 points per decade at corrosion potential applying the amplitude of alternating voltage 3 mV. Potentiodynamic polarization curves were recorded at the end of experiment, in most cases 22 h after the introduction of inhibitor into the brine in a range of –200 + 30 mV (0.5 cycle) for cathode and a range –30 + 250 mV (1 cycle) for anode regions respective to corrosion potential with the scan rate of 0.3 mV s⁻¹. The polarization resistance values were calculated as corrosion rates U_{cor} (mm y⁻¹), as follows:

$$U_{cor} = \frac{b_A b_C}{2.3(b_A + b_C) R_p(t)} \quad (1)$$

where b_A and b_C —Tafel coefficients determined graphically from potentiodynamic polarization curves; R_p —polarization resistance; t —time after introduction of inhibitor into the brine.

The inhibition efficiency (η) and inhibition coefficient (γ) were calculated using the following equations:

$$\eta = 100 (U_{cor}(0) - U_{inh}(t)) / U_{cor}(0) \quad (2)$$

$$\gamma = U_{cor}(0) / U_{inh}(t) \quad (3)$$

where $U_{\text{cor}}(0)$ —corrosion rates without inhibitor; $U_{\text{inh}}(t)$ —corrosion rates in time t after inhibitor introduction.

S-Alkyl *O,O*-Di-*iso*-butyl Dithiophosphates **5a** and **6a**, and *O*-Alkyl *O,O*-Di-*iso*-butyl Thionophosphates **7a** and **8a**

The mixture of red phosphorus (0.4 g), sulfur (0.81 g), and *iso*-butanol (1.87 g, 25.2 mmol) was heated for 12 h at 100–110° with stirring. Olefins **1a–c** (3.4 g, 14.3 mmol) and anhydrous ZnCl_2 (0.1 g, 0.7 mmol, 2.9 wt%) were added into the mixture and the stirring was continued for 4 h at 80°C. The mixture was filtered. The filtrate was evaporated under vacuum (0.02 mm Hg) at 60°C for 1 h and gave 2.7 g (90%) of a mixture of **5a**, **6a**, **7a**, and **8a**. n_D^{20} 1.4450. Anal. Found C 62.11; H 11.08, P 5.86; S 12.59. $\text{C}_{24}\text{H}_{51}\text{O}_2\text{PS}_2$ and $\text{C}_{26}\text{H}_{55}\text{O}_2\text{PS}_2$. Calcd. C 61.75–63.10; H 11.04–311.23; P 6.26–6.64; S 12.93–13.71% (there and then elemental analysis data for minor products **7** and **8** were not taken into account). IR: film, $\nu = 2957, 2924, 2854$ (CH_3 as, s; CH_2 as, s); 1466 δ (CH_3 as); 1377 δ [$(\text{CH}_3)_2\text{C}$ gem. s]; 999 [(P)O–C]; 964 (OC–C); 675 (P=S); 553 (P–S). ^1H NMR: $\delta = 0.86$ t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.5$ Hz, **7a**, **8a**); 0.91 t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.2$ Hz, **5a**, **6a**); 1.00 d {12Hxn, [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$] $_2\text{P}$, $^3J_{\text{HH}} = 6.8$ Hz}; 1.29 br s [$\text{C}(\text{CH}_2)_n\text{C}$]; 1.39 m [1Hxn, $\text{CH}(\text{CH}_3)_2$]; 1.52 d [3Hxn, $\text{CH}_3\text{C}(\text{H})\text{SP}$, $^3J_{\text{HH}} = 6.2$ Hz, **6a**]; 1.59 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **5a**]; 1.60 m [2Hxn, $\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$, **5a**, **7a**]; 1.67 m [2Hxn, $\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$, **6a**]; 1.70 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **7a**]; 2.00 m (2Hxn, $\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$, **5a**, **7a**); 2.07 t (2Hxn, $\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 6.8$ Hz, **5a**, **7a**); 3.03 m [1Hxn, $\text{PSC}(\text{CH}_3)_2\text{CH}_2$, **6a**]; 3.87 m {4Hxn, [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$] $_2\text{P}$, **5a**, **6a**}; 3.97 m {4Hxn, [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$] $_2\text{P}$, **7a**, **8a**}. The ^{13}C NMR (signal form in the ^{13}C -{ ^1H } NMR was brought in braces): $\delta = 14.1$ q (s) [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$, $^1J_{\text{HC}} = 125.0$ Hz, **5a**, **6a**, **7a**, **8a**]; 15.8 q (s) [$(\text{CH}_3)_2\text{CSP}$, $^1J_{\text{HC}} = 124.7$ Hz, **5a**, **7a**]; 17.9 q (s) (CH_3CHSP , $^1J_{\text{HC}} = 124.1$ Hz, **6a**, **8a**); 18.9 and 19.0 two q (two s) ($\text{CH}_3\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 125.5$ Hz, **5a**, **6a**, **7a**, **8a**); 22.7 t (s) ($\text{CH}_3\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 124.1$ Hz, **5a**, **6a**, **7a**, **8a**); 23.4–23.5, 24.3–24.7, 26.6–26.8 and 27.7–28.0 m (m) ($\text{CH}_2\text{CH}_2\text{CH}_2$); 28.9 t (s) [$\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 126.2$ Hz, **5a**]; 29.2 t (s) [$\text{PSC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 126.9$ Hz, **5a**]; 29.4 t (s) ($\text{CH}_3\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 123.2$ Hz, **5a**, **6a**, **7a**, **8a**); 29.6 t (s) ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 128.4$ Hz, **5a**, **6a**, **7a**, **8a**); 29.7 t (s) ($\text{CH}_2\text{CH}_2\text{CH}_2$, $^1J_{\text{HC}} = 124.7$ Hz, **6a**, **8a**); 31.9 t (s) ($-\text{CH}_2-$, $^1J_{\text{HC}} = 126.2$ Hz); 33.9 t (s) (CH_2 , $^1J_{\text{HC}} = 129.7$ Hz); 36.7 t (s) (POCHCH_2 , $^1J_{\text{HC}} = 120.3$ Hz, **7a**); 37.7 t (s) (POCCH_2 , $^1J_{\text{HC}} = 120.3$ Hz, **8a**); 39.5 m (s) (PSCCH_2 , **6a**); 39.8 t (s) (PSCCH_2 , $^1J_{\text{HC}} = 126.9$ Hz, **5a**); 36.7 m (d) (PSCCH_2 , $^2J_{\text{PC}} = 5.9$ Hz, **6a**); 41.3 m (d) (PSC , $^2J_{\text{PC}} = 5.5$ Hz, **5a**); 67.4 m (s) ($\text{POCHCH}_2\text{CH}_2$, **8a**); 70.0 m (s) [$\text{POC}(\text{CH}_3)_2\text{CH}_2$, **7a**]; 73.5 dt (d) [$\text{POCH}_2\text{CH}(\text{CH}_3)_2$, $^1J_{\text{HC}} = 170.9$ Hz, $^2J_{\text{PC}} = 7.7$ Hz, **7a**, **8a**]; 73.8 dt (d) [$\text{POCH}_2\text{CH}(\text{CH}_3)_2$, $^1J_{\text{HC}} = 170.2$ Hz, $^2J_{\text{PC}} = 6.6$ Hz, **5a**, **6a**]. ^{31}P NMR: $\delta_{\text{P}} = 98.9, 90.3$ and 69.0 in ratio 15:55:30. MS (ESI), m/e : 478.3 $[\text{M}]^+$, 501.4 $[\text{M} + \text{Na}]^+$ require 478.8 **7a**, **8a** (from C_{18}); 554.6 $[\text{M} + \text{Na} + \text{K}]^+$, 1009.6 $[2\text{M} + \text{K}]^+$ require 466.8 **5a**, **6a** (from C_{16}); 1049.1 $[2\text{M} + \text{Na} + \text{K}]^+$ requires 494.8 **5a**, **6a** (from C_{18}).

S-Alkyl *O,O*-Di-*iso*-octyl Dithiophosphates **5b** and **6b** and *O*-Alkyl *O,O*-Di-*iso*-octyl Thionophosphates **7b** and **8b**

The mixture of red phosphorus (0.79 g), sulfur (1.59 g) and *iso*-octanol (6.5 g, 49.9 mmol) was heated for 10 h at 100°C with stirring. Olefins **1a–c** (6.1 g, 25.6 mmol) and anhydrous ZnCl_2 (0.15 g, 1.1 mmol, 2.5 wt%) were added into the mixture and the stirring was continued for 4 h at 80°C. The mixture was filtered. The filtrate was diluted

with 10 mL of diethyl ether and washed with three portions of 20 mL of water. The organic layer was separated and dried with CaCl_2 for 1 day. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.5 mm Hg) at 40°C for 1 h and then under vacuum (0.02 mm Hg) at 40°C for 1 h and gave 7.2 g (96%) of the mixture of **5b**, **6b**, **7b**, and **8b**. Anal. Found C 66.49; H 11.43; P 5.12; S 10.77. $\text{C}_{32}\text{H}_{67}\text{O}_2\text{PS}_2$ and $\text{C}_{34}\text{H}_{71}\text{O}_2\text{PS}_2$. Calcd. C 66.37–67.26; H 11.70–11.82; P 5.11–5.35; S 10.55–11.05. IR: film, $\nu = 2959, 2955, 2855$ (CH_3 as, s; CH_2 as, s); 1464 δ (CH_3 as); 1379 δ (CH_3 s); 1038 [(P)O–C]; 972 (OC–C); 663 (P=S); 554, 544 (P–S). ^1H NMR: $\delta = 0.86$ t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.5$ Hz, **7a**, **8a**); 0.90 t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.2$ Hz, **5b**, **6b**); 0.93 d {12Hxn, [(CH_3)₂CH(CH_2)₄CH₂O]₂P, $^3J_{\text{HH}} = 7.2$ Hz}; 1.28 br s [C(CH_2)_nC]; 1.32 m (2Hxn, CH_2); 1.38 m [2Hxn, CH_2]; 1.39 s [6Hxn, (CH_3)₂CSP, **5b**]; 1.41 s [6Hxn, (CH_3)₂CSP, **7b**]; 1.49–1.69 m (2Hxn, CH_2); 1.99 m [1Hxn, (CH_3)₂CHCH₂]; 2.06 dt [2Hxn, PSC(CH_3)₂CH₂CH₂, $^3J_{\text{HH}} = 6.8$ Hz, **5b**, **7b**]; 3.13 m [1Hxn, PSC $\text{CH}(\text{CH}_3)\text{CH}_2$, **6b**]; 3.97 dt [4Hxn, ($\text{CH}_2\text{CH}_2\text{O}$)₂P, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{PH}} = 5.1$ Hz, **5b**, **6b**]; 4.05 dt [4Hxn, ($\text{CH}_2\text{CH}_2\text{O}$)₂P, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{PH}} = 5.8$ Hz, **7b**, **8b**]. ^{31}P NMR: $\delta_{\text{P}} = 69.7$ and 91.0 in ratio 77:23.

S-Alkyl *O,O*-Di-*iso*-propyl Dithiophosphates **5c** and **6c** and *O*-Alkyl *O,O*-Di-*iso*-propyl Thionophosphates **7c** and **8c**

Products **5c**, **6c**, **7c**, and **8c** were obtained in analogy to experiment (b) from red phosphorus (1.0 g), sulfur (2.1 g), *iso*-propanol (4.0 g, 58.7 mmol), and olefins **1a–c** (8.4 g, 35.2 mmol) with use of ZnCl_2 (0.3 g, 2.2 mmol, 3.6 wt%). Heptane was used instead of Et_2O . Yield 5.1 g (71%). Part of crude products (1.5 g) was chromatographed on a silica gel (0.060–0.200 micron) column with petroleum ether (bp. 40 – 70°C) as eluent, R_f 0.40 (petroleum ether). n_D^{20} 1.4490. Anal. Found C 61.66; H 11.06; P 6.76; S 14.72. $\text{C}_{22}\text{H}_{47}\text{O}_2\text{PS}_2$ and $\text{C}_{24}\text{H}_{51}\text{O}_2\text{PS}_2$. Calcd. C 60.23–61.75; H 10.80–11.04; P 6.64–7.06; S 13.71–14.62%. ^1H NMR: $\delta = 0.90$ t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.2$ Hz, **5c**, **6c**); 0.97 t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.2$ Hz, **7c**, **8c**); 1.28 br s [C(CH_2)_nC]; 1.36 d {12Hxn, [(CH_3)₂CHO]₂P, $^3J_{\text{HH}} = 6.3$ Hz}; 1.38 d {12Hxn, [(CH_3)₂CHO]₂P, $^3J_{\text{HH}} = 6.3$ Hz}; 1.52 s [6Hxn, (CH_3)₂CSP, **5c**]; 1.53–1.69 m (2Hxn, CH_2); 1.60 s [6Hxn, (CH_3)₂CSP, **7c**]; 1.62 d [3Hxn, $\text{CH}_3\text{C}(\text{H})\text{SP}$, $^3J_{\text{HH}} = 6.8$ Hz, **6c**]; 1.99 t [2Hxn, PSC(CH_3)₂CH₂CH₂, $^3J_{\text{HH}} = 6.8$ Hz, **5c**, **7c**]; 2.06 m [4Hxn, CH_2CH_2]; 3.33 and 3.49 two m [1Hxn, PSC $\text{CH}(\text{CH}_3)\text{CH}_2$, **6c**]; 4.03 and 4.12 two m [1Hxn, POCH(CH_3)CH₂, **8c**]; 4.90 m {2Hxn, [(CH_3)₂CHO]₂P}. ^{31}P NMR: $\delta_{\text{P}} = 92.9, 87.0$ and 64.1 in ratio 7:90:3.

S-Alkyl *O,O*-Di-*iso*-octyl Dithiophosphates **5d** and **6d** and *O*-Alkyl *O,O*-Di-*iso*-octyl Thionophosphates **7d** and **8d**

Products **5d**, **6d**, **7d**, and **8d** were obtained in analogy to experiment (b) from red phosphorus (4.0 g), sulfur (0.83 g), *iso*-octanol (3.36 g, 25.8 mmol), and olefins **2a–c** (4.0 g, 12.4 mmol) with use of ZnCl_2 (0.1 g, 0.7 mmol, 2.5 wt%). Yield 2.6 g (60%). n_D^{20} 1.4540. Anal. Found C 70.01; H 12.02; P 4.75; S 8.99. $\text{C}_{35}\text{H}_{75}\text{O}_2\text{PS}_2$, $\text{C}_{38}\text{H}_{79}\text{O}_2\text{PS}_2$, $\text{C}_{40}\text{H}_{83}\text{O}_2\text{PS}_2$ and $\text{C}_{42}\text{H}_{87}\text{O}_2\text{PS}_2$. Calcd. C 68.07–70.11; H 11.94–12.22; P 4.31–4.88; S 8.90–10.07%. IR: film, $\nu = 2957, 2924, 2853$ (CH_3 as, s; CH_2 as, s); 1464 δ (CH_3 as); 1378 δ (CH_3 s); 1035 [(P)O–C]; 966 (OC–C); 673 (P=S); 541 (P–S). ^1H NMR: $\delta = 0.90$ t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 6.9$ Hz, **5d**, **6d**); 0.92 d {12Hxn, [(CH_3)₂CH(CH_2)₄CH₂O]₂P, $^3J_{\text{HH}} = 7.8$ Hz}; 1.04 t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 8.0$ Hz,

7d, 8d]; 1.28 br s [$\text{C}(\text{CH}_2)_n\text{C}$]; 1.42 m (2Hxn, CH_2); 1.50 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **5d**]; 1.59 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **7d**]; 1.60 d [3Hxn, $\text{CH}_3\text{C}(\text{H})\text{SP}$, $^3J_{\text{HH}} = 7.3$ Hz, **6d**]; 1.65–1.80 m (2Hxn, CH_2); 2.02 m (2Hxn, $\text{PSCH}(\text{CH}_3)\text{CH}_2\text{CH}_2$, **6d**); 3.14 m [1Hxn, $\text{PSCH}(\text{CH}_3)\text{CH}_2$, **6d**]; 3.96 and 4.09 two m [4Hxn, $(\text{CH}_2\text{CH}_2\text{O})_2\text{P}$]; 4.26 m [1Hxn, $\text{POCH}(\text{CH}_3)\text{CH}_2$, **8d**]. ^{31}P NMR: $\delta_{\text{P}} = 91.0$ and 69.9 in ratio 2:1.

S-Alkyl *O,O*-Di-*iso*-butyl Dithiophosphates **5e** and **6e** and *O*-Alkyl *O,O*-Di-*iso*-butyl Thionophosphates **7e** and **8e**

Products **5e**, **6e**, **7e**, and **8e** were obtained in analogy to experiment (**b**) from red phosphorus (0.4 g), sulfur (0.83 g), *iso*-butanol (1.9 g, 25.6 mmol), and olefins **2a–c** (4.1 g, 12.7 mmol) with use of ZnCl_2 (0.1 g, 0.7 mmol, 2.4 wt%). Yield 2.1 g (58%), n_D^{20} 1.4610. Anal. Found C 67.14; H 11.66, P 5.18; S 10.29. $\text{C}_{28}\text{H}_{59}\text{O}_2\text{PS}_2$, $\text{C}_{30}\text{H}_{63}\text{O}_2\text{PS}_2$, $\text{C}_{32}\text{H}_{67}\text{O}_2\text{PS}_2$ and $\text{C}_{34}\text{H}_{71}\text{O}_2\text{PS}_2$. Calcd. C 64.32–67.27; H 11.37–11.79; P 5.10–5.92; S 10.56–12.27%. ^1H NMR: $\delta = 0.90$ t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 6.9$ Hz, **5e, 6e**); 0.98 d {12Hxn, [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$] $_2\text{P}$, $^3J_{\text{HH}} = 6.4$ Hz}; 1.04 t (3Hxn, $\text{CH}_3\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 7.8$ Hz, **7e, 8e**); 1.28 br s [$\text{C}(\text{CH}_2)_n\text{C}$]; 1.43 m [$(\text{CH}_3)_2\text{CH}$]; 1.51 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **5e**]; 1.60 s [6Hxn, $(\text{CH}_3)_2\text{CSP}$, **7e**]; 1.59–1.74 m (2Hxn, CH_2); 2.02 dt [2Hxn, $\text{PSCH}(\text{CH}_3)\text{CH}_2\text{CH}_2$, $^3J_{\text{HH}} = 6.9$ Hz, **6e**]; 3.02 m [1Hxn, $\text{PSCH}(\text{CH}_3)\text{CH}_2$, **6e**]; 3.85 and 3.95 two m {4Hxn, [$(\text{CH}_3)_2\text{CHCH}_2\text{O}$] $_2\text{P}$ }; 4.05 m [1Hxn, $\text{POCH}(\text{CH}_3)\text{CH}_2$, **8e**]. ^{31}P NMR: $\delta_{\text{P}} = 91.0$ and 69.6 in ratio 9:1.

FUNDING

The study was performed with financial support of the Russian Foundation for Basic Researches (grant no. 13-03-97043-a).

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