© 2017 IJSRST | Volume 3 | Issue 4 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

Oxidation of PH_3 By Redox Polymers – Convenient Method For Synthesis Organic Phosphorus Compounds

B. A. Mukhitdinova*[1], E. E. Ergozhin[1], G. S. Polimbetova[2], A. K. Borangazieva[2], K. Ch. Chakimbolatova[1], A. Tasmagambet[1], N. T. Dauletkulova[1]
[1]ISC, Institute of Chemical Sciences named after A.B. Bekturov, 106, Sh. Ualichanov Str.,050010 Almaty, Republic of Kazakhstan
[2]JSC Institute of Fuel, Catalysis and Electochemistry named after D.V. Sokolsky, 142, D.Kunaev Str., 050010, Almaty, Republic of Kazakhstan
*e-mail: mukhitdinovab@mail.ru

ABSTRACT

The synthesis of aminoquinoid redox polymers and their oxidation of a toxic gas of phosphine is described. An effect of the nature of solvents, catalysts, relationship between initial components, temperature and time modes of condensation of reactants on the yield and properties of redox polymers formed have been researched into by way of chemical modification of industrial weak-basic anion exchangers by quinones and their derivatives, in an environment similar to green chemistry positions. Synthesized redox-polymers have been tested as oxidants of toxic gas phosphine. The process is based on the oxidation of phosphine by quinones and redox polymers on their basis. Molecular iodine is used as a catalyst. Two-, three-, four- and multicomponent systems are studied in order to determine optimal conditions of the oxidation of phosphine. The rate and selectivity of reaction were monitored by the absorption of PH_3. As alcohols used aliphatic alcohols: BuOH, PrOH, EtOH, MeOH. Organophosphorus compounds were analyzed by a chromatographic method. Conversion of phosphine constitutes 80-86%.

Keywords: Redox Polymer, Quinone, Anion Exchanger, Phosphine, Oxidation, Green Chemistry

I. INTRODUCTION

Redox polymers (RP) or electron exchangers constitute polymeric materials, which have redox properties [1,2]. The range of reactions they may be involved in varies greatly. Such polymers enter successfully ionic, donor-acceptor and hydrophobic interactions. No wonder that these compounds raise equal interest in chemists and other professionals engaged in biochemistry, physics, medicine, electrochemistry, etc.

In the recent past, chemical modification of halogen methylated or aminated polyvinyl aromatic compounds by quinones was a common and most frequently used synthesis of redox polymers (RPs) [3,4]. The process proceeds through halogen methylation or nitration and subsequent reduction of macromolecules in harsh or corrosive environments, involving the use of toxic initial reagents and the release of harmful intermediate compounds.

A new direction in chemistry that has recently developed is green chemistry [5-8]. It offers another way: reducing the number of stages, excluding or minimizing the processes of destruction and recycling of waste products, etc. It certainly would affect the environmental and economic efficiency of the synthesis. In terms of green chemistry, a method based on applying industrial ready-made resins is promising as a starting template for modification. This involves weak-basic anion exchangers, which contain primary and/or secondary amino groups. Their application would allow reducing the number of stages in obtaining redox polymers.

II. METHODS AND MATERIAL

A. The Synthesis of Quinoid Redox Polymers on the Basis of Weak-Basic Anion Exchangers

The synthesis of redox polymers based on weak base anion exchangers (AE) and quinones (Q) was carried out in various solvents at various mole ratios of initial AE:Q reactants, and at various temperature and time modes [3,4,9]. The pH level was adjusted by adding ammonia, sodium hydroxide or sodium acetate. As soon as the reaction terminated, the polymer was separated, purified with methyl (ethyl) alcohol in a Soxhlet extractor, treated by 4% NaOH, washed until the wash water showed neutral reaction, where after the key physical and chemical properties were identified. As quinones the following were used: 1,4-benzoquinone (BQ), 1,2-naphthoquinone (NQ), 2,3-dichloro-5,6-dicyanobenzoquinone (DCLDCBQ); chloranil (ChA) or 2,3,5,6-tetrachloro-1,4-benzoquinone; chloranilic acid (ChAA), or 2,3-Dichloro-5,6-dihydroxybenzoquinone.

B. **Measurement of Physical-Chemical Characteristics**

The progress of the reaction was assessed in view of the data obtained by way of elemental analysis and IR spectroscopy, as well as by referring to redox capacity (RC) and static exchange capacity (SEC) upon the main groups of final products, and the values of potentiometric acid-base titration measured by DL50 titration apparatus Mettler Toledo at 250. IR-spectra of samples were taken on a spectrometer “Specord M-80/M-85 in tablets with KBr (200 mg of KBr + 1 mg of substances).

C. **Oxidation-Reduction Potentiometric Measurement**

The redox capacity of reduced samples was determined in the argon atmosphere under 0,1N solution of $Fe_2(SO_4)_3$. Oxidized-reduced potentiometric titration of the reduced polymers was carried out on a titrometer of the firm Mettler-Toledo in a thermostated cell in the argon flow by solution of $Ce(SO_4)_2$ in sulfuric acid, standartized with 0.1N solution of $Na_2S_2O_3$ in the presence of a calomel electrode with a smooth platinum electrode at the temperature of 25ºC. As mediator in the case of cross-linked redox polymers, 1/30N solution of Fe^{3+} in a buffer of $K_2SO_4+H_2SO_4$ at pH 0.6-0.7 was used [1].

D. The Oxidizing Ability of Redox polymers in Relation to Phosphine [10]

Syntheses based on PH_3 was carried out in a thermostated glass reactor type catalyst "duck" with a potentiometric device under vigorous stirring. The gas mix of Ar–PH_3 was obtained by acid decomposition of Zn_3P_2, then it was dried up by granulated NaOH. Alcohols were cleared by distillation. The analysis of gases on the content of PH_3 carried out iodometric and colorimetric methods. The rate of reaction was monitored by the absorption of PH_3. Chromatographic analysis for alcohols, acetals, dioxane, quinone, hydroquinone, and OPC was performed using a flame ionization detector and steel columns (300 x 0.3cm). The columns were filled with unsilaneted chromaton soaked with apiezon L (5%) in the chromatograph model 3700 and Chrom-5. For oxidative alkoxylation of PH_3 aliphatic alcohols (butyl – BuOH, propyl – PrOH, ethyl – EtOH, methyl – MeOH) in a mixture with dioxane, toluene or DMFA were used. Products of catalytic reactions of oxidation of PH_3 in butanolic solutions of benzoquinone, redox-polymers on its basis and iodine obtained with vacuum distillation at pressure of 2-5 mm mercury column. Obtained OPC identified GL chromatography methods, NMR^{31}P-, IR-spectroscopy, and also at temperatures of boiling and refraction indicators. IR-spectra obtained OPC registered on the Specord M80/M85, spectra ЯМР^{31}P - on "Bruker" AHM-400 and WP-80 spectrometer in relation to 75 % H_3PO_4, indicators of refraction (n_D^{20}) are established on the IRF-454 refractometer.

III. RESULTS AND DISCUSSION

The idea of using commercial anion exchange or cation exchange resins as carriers of redox groups is not new: it has been successfully implemented by Saldadze [11], Pashkov [12], Kozhevnikov [13] and others for the synthesis of electron-ion exchanges. Mixed valence metals were put on and then recovered on the surface and in the pores of an ionite matrix to reach a metallic state. By repeating such a process, materials with high metal content were obtained. Subsequent treatment of electron-ion exchangers by alkaline solution of sodium hydrogen sulphite provides redox properties. Examples include copper-, iron-, silver- and bismuth-containing redox polymers.

A. **The Synthesis of Quinoid Redox Polymers on the Basis of Weak-Basic Anion Exchangers**

Notably, the most cost-efficient way to obtain them is to use anion exchangers (AE) AB-16GS, EDE-10P, AN-31 and AN-2FN that obtain high redox capacity even after two covers with metal. This can be explained by the presence of polyethylene polyamine chains and the possibility to form ethylene-diamine complexes. Such oxidation-reduction polymers (ORP) are efficient to remove dissolved oxygen from demineralized water. However, when water runs through a layer of ORP, complex compounds are dissociated on the surface of anionite, and small amounts of metal ions move to the filtrate, thus lowering the redox capacity and polluting the filtrate.

Therefore, a covalent attachment of redox compounds to amino groups of a polymer anion exchanger matrix seems promising [4, 7, 8]. The interaction of quinones with amines is the same as that involving unsaturated α, β-diketones of open chain through restorative attachment of quinones to polyamines. In order to optimize chemical modification of industrial anion exchanger AN-31 by quinones (Q): 1,4-benzoquinone (BQ), 1,2-naphthoquinone (NQ), 2,3-dichloro-5,6-dicyanobenzoquinone (DCLDCBQ); chloranil (ChA) or 2,3,5,6-tetrachloro-1,4-benzoquinone; chloranilic acid (ChAA), or 2,3-Dichloro-5,6-dihydroxybenzoquinone − in an environment similar to green chemistry positions, the effect of nature of solvents and catalysts, the relationship between initial components, temperature and time modes of output condensation of reactants, and the properties RPs so formed have been studied.

Decent solubility of quinones and high expansibility of initial anionites in most organic solvents all provide a high conversion of primary and secondary amino groups of anion exchangers. However, following the green chemistry positions, the process has been further studied in green solvents, such as ethanol, water or equimolar mixture. This has allowed, due to their high polarity, achieving a high output of RPs. Furthermore, another green chemistry position is so implemented: the process proceeds without any emission of toxic intermediate products, which would require recycling or utilization, because HCl released is consumed to flavor quinoid nucleus, as applicable to benzoquinones and naphthoquinones. When anion exchanger condensates with chlorinated quinones, HCl released is consumed to form salt with nitrogen atoms of the product.

The effect of relationship between initial components has shown that an increase in AE:Q ratio would cause an increase in the output of RPs. Similarly, a change in temperature and time modes would have an effect. The redox capacity of samples of $Fe_2(SO_4)_3$ 0.1N solution is 1.3-2.9 meq/g, and the anion exchange capacity is 1.7-6.3 meq/g. It takes the highest values for RPs based on AN-31. The redox potential of RPs is consistent with the reported one and reaches for quinone 690 of mV, for the chlorreplaced quinones - 750-780 mV.

A change in the nature of IR-spectra of initial ions, as compared to condensation products, shows that the process runs as appropriate. The IR-spectra of RPs so based acquire characteristic bands of absorption of significant intensity that relate to valence vibrations C=O (1,653 cm-1) and valence vibrations of phenolic –C-O− (1,210 cm^{-1}) of quinoid ring, and links >C=C< (1,501 cm^{-1}), =NH- (1,580 cm^{-1}) and C-N (1,340 cm^{-1}), which confirms the formation amino-quinoid polymers.

B. **The Oxidizing Ability of Redox Polymers**

Phosphine (PH_3) is formed as toxic impurity during electro-thermal production of yellow phosphorus in processes with participation of phosphides of metals and when acetylene is obtained. Maximally admissible concentration of PH_3 in a working zone of production rooms is 0, 1 mg/m^3. In this regard the problem of purification of exhaust and technological gases from toxic phosphine is a topical issue from the ecological point of view.

At the same time phosphine is a universal raw material for obtaining valuable organophosphorus compounds (OPC) in a laboratory and industrial practice. Traditional methods for obtaining important classes of the OPC, including organic phosphines, phosphinhalkogenides, ethers of acids of phosphorus are based on aggressive and sensitive to moisture halogenides of phosphorus. Realization of these methods is accompanied by formation of significant amounts of a difficult utilized dangerous waste [14]. Therefore currently the increasing attention is given to the development of "non chlorine" methods of synthesis of OPC directly from the elemental phosphorus, phosphine and phosphides of transient metals as alternative phosphorylated agents [15, 16].

Generally, phosphine is considered very active in radical-chain of reactions and less active in heterolytic organic transformations [14]. The considerable number of publications are devoted to the chemistry of functional replaced phosphines and their derivatives – alkyl- and arylphosphines. The area of their application is extremely various [17-19]. However use of PH_3 for formation of P-O, P-C - bonds and synthesis organic and inorganic phosphines is very limited in the absence of effective technological methods of its obtaining. Known organic reactions of phosphine proceed in hard conditions: under the influence of high pressures, temperatures, the superacids, the superbases, and in the presence of initiators of free radicals. Synthesis, on the basis of PH_3, is used very rarely and it is not realized in the industry because there are no effective technological methods of its obtaining.

Phosphine can be used for obtaining various OPC which are important supplementary reagents, construction blocks, semi-products, and also ligands for metal complex catalysts, extragents and antipyrenes. High reactionary ability of phosphine is the objective precondition of its wider involvement in phosphor organic synthesis, despite many obvious advantages in comparison with phosphorus chlorides. In spite of the fact that hydride of phosphorus is quite strong reducing agent, in the absence of catalysts it does not oxidize with appreciable speed by any of known acceptors of electrons.

Research of oxidation of phosphine by redox polymers is a development of new ecologically safe catalytic synthesis of esters of phosphorus and phosphoric acids from PH_3. Ethers of phosphoric acid – dialkylphosphites are widely applied in organic synthesis for obtaining medicines and biologically active substances. Ethers of phosphoric acid – trialkylphosphates are used as extragents of rare and radioactive elements from mineral raw materials and wastes of nuclear power, solvents of varnishes and paints in printing industry, additives to combustive-lubricating materials, softeners, antipyrenes, etc. World production of OPC composes tens of thousands tons per year [14]

Therefore, synthesized RPs have been tested as oxidants of toxic gas phosphine, which evolves as a part of furnace gas (0.1-2.0%) at phosphate plants in Kazakhstan. Phosphine is characterized by inertness in acid-base reactions, and it is not absorbed by alkalis solutions. In the absence of catalyst, the oxidation reaction of PH_3 proceeds at a low rate. The reactivity of quinones and redox polymers on their basis in alcoholic solutions with respect to PH_3 has not been previously studied. On the other hand, the oxidation of phosphine is a convenient method for synthesizing valuable organic phosphorus compounds [14, 15].

In order to establish what effect a composition of reaction medium has on the speed and selectivity of the phosphine oxidation by 2,3-dichlor-naphtoquinone (2,3-DClNQ) and RPs on its basis, we have researched into two-, three- and four-component systems (see Table). As can be seen from the table, in the absence of Ct (iodine or copper salts) quinone solution in BuOH oxidizes PH_3 at low speed. No formation of OPC occurred (tests 1). Insignificant additives of I_2 or copper salts 0.40-2.2 mM in the testing NQ solution increases the speed of reaction and the amount of PH_3 absorbed. The yield of tributyl phosphate **2** is 80-86% (tests 2-3). Unlike iodine systems, alcohols containing quinone and copper salts are well regenerated by oxygen. The kinetic regularities of the oxidation reaction of PH_3 in alcohol solutions of quinoid redoxites are consistent with the laws obtained in the presence of quinone (tests 4-8).). In alcoholic solutions of $CuCI_2$ and redox polymers, a phosphoric acid ester **2** is produced with a yield of 50% (test 6). In the presence of copper acetates, a mixture of phosphorus acid esters is formed with a total yield of 68-85% (tests 7-8).

IV. CONCLUSION

Thus, quinoid redox polymers of high oxidizing ability have been obtained by way of covalent attachment between efficient oxidizing agents, such as quinones or their derivatives, and weak base anion exchangers, in an environment similar to green chemistry positions.

Synthesized quinoid redox polymers, based on weak-base anion exchangers, efficiently oxidize phosphine and form organic phosphorus compounds. Varying the

TABLE

Oxidation of phosphine in alchogol solutions 2,3-DClNQ (M), RP (on the basis of EDE-10P) and Ct

№	NQ, M RP, g	Ct, Mmol	$PH_3 \cdot 10^{-3}$, Pa	T°, C	$W_{PH3} \cdot 10^3$,M/min	$Q_{PH3} \cdot 10^2$, M	**1**,%	**2**,%
1	NQ,0.45	-	1,2	80	8,6	-	-	-
2	NQ, 1,5	$CuBr_2$ - 0.22	1,2	70	6,0	19,0	-	86
3	NQ,0.8	I_2- 0.6	1,7	60	13,0	12,0	-	80
4	NQ,0.2	-	1,0	50	0,2	0,2	-	-
5	RP, 0.2	I_2- 0.4	1,7	50	2,5	3,2	39	51
6	RP, 0.2	$CuCl_2$ -0,3	1,6	50	1,5	1,0	-	50
7	RP, 0.4	$Cu(OAc)_2$ -0,25	1,2	60	1,0	4,0	33	35
8	RP,0.4	$Cu(OAc)_2$ -1,0	0.5	60	1.2	6 .0	52	33

Condition of reaction: solvent ДМFA, C_7H_8; **1** -$(BuO)_2HPO$, **2** - $(BuO)_3PO$.

conditions of process allow for efficient regulation of the synthesis of organic phosphorus compounds.

V. REFERENCES

[1] Cassidy, H.J., Kun, K.A., (1967). Oxidation-reduction polymers, Chemistry: Leningrad.

[2] Ergozhin, E.E., Mukhitdinova, B.A., (1983). Redoxionites, Nauka: Alma-Ata.

[3] Ergozhin,E.E., Mukhitdinova, B.A., (2000). Oxidation-reduction ion exchangers, RIO VAK RK: Almaty.

[4] Ergozhin, E.E.; Mukhitdinova, B.A.; Stefanova,O.K.; Bakirova,R.Kh.; Rozhdestvenskaya,N.V.; (1991/1992). Redox polymers based on polyamines. Reactive Polymers, 16, 321-334.

[5] Anastas,P.T., Warner, J.C., (1998). Green Chemistry: Theory and Practice, Oxford University Press: New York.

[6] Cook, S.; (1999). Green chemistry – evolution or revolution. Green Chemistry. 10, G138-G140

[7] Mukhitdinova,B.A.;Ergozhin,E.E.; Nikitina, A.I.; (2013). Realization of some positions of Green Chemistry in the synthesis of redox-polymers. STEPI BOOK. Proceedings. Stepi 9. 9th European Technical Symposium on Polyimides&High Performance Functional Polymers. IAE. University Montpellier II. S.T.A. 246-251.

[8] Mukhitdinova, B.A.; Ergozhin, E.E.; (2015). Green chemistry conception in redox polymers synthesis. Intern. J. Chem. and Biomed. Sci., 1(2), 44-51

[9] Mukhitdinova,B.A.; Ergozhin, E.E.; Polimbetova G.S.; et al; (2016). Applying Certain Green Chemistry Positions During the Synthesis Of Redox-Polymers, as Sorbents and Oxidants, STEPI 10. 10th European Technical Symposium on Polyimides & High Performance Functional Polymers.@ IAE, Université Montpellier II, S.T.L.: June 6-8. Posters Session I-PI-7, Montpellier (France)

[10] Mukhitdinova, B.A.; Ergozhin, E.E.; Polimbetova, G.S.; Boangazieva, A.K.; (2012). The Synthesis of Organophosphorus Compounds from Phosphine and Alcohols in the Presence of Quinones and Redox Polymers on their Basis. Euras.Chem-Technol. J., 6, 191-199.

[11] Saldadze, K.M., (1967). Oxidation-reduction polymers and their application, Chemistry: Leningrad.

[12] Kruglikova, N.M., Pashkov, A.B., ibid, P. 14.

[13] Kozhevnikov,A.V., (1972). Electron ion exchangers, Chemistry: Leningrad.

[14] Purdela, D., Vilchanu, R., (1972). Chemistry of organic compounds of phosphor. Chimia: Moscow.

[15] Budnikova, Yu.G.; Gryaznova, T.V.; Кrasnov, S.A.; Magdeev, I.M.; Sinyashin, O.G.; (2007). Creation of ecologically safe and high electrochemical technologies. Electrochimiya, 43, 1291-1296.

[16] Polimbetova, G.S.; Abdreimova, R.R.; Faisova, F.Kh.; (2000). Catalytic synthesis of organophosphorus compounds from inorganic derivatives of low valence phosphorus. Eurasian Chem.Tech.J., 2, 21-27.

[17] Valentine,D.H., Hillhouse, J.H., (2003). Alkyl phosphines as reagents and catalysts in organic synthesis, Synthesis: Stuttgart, 3, 317-334.

[18] Honaker, M.T.; Hovland, J.M.; Salvatone, R.N.; (2007). The synthesis of tertiary and secondary phosphines and their applications in organic synthesis. Current Organic Synthesis, 4, 31-45.

[19] Ulah, E.; McNulty, J.; Sliwinski, M. R.; (2012). One step synthesis of reusable, polymer-supported tri-alkyl phosphine ligands. Application in Suzuki-Miyaura and alcoxycarbonylation reaction. Tetrahedron Letters, 53, 3990-3993.

[20] Erastov, O.E., Nikonov,G.N., (1986). Functional substituted phosphines and their derivatives, Science: Moscow.

[21] Kutyrev, A.A.; V.V Moskva V.V.; (1991). Nucleophilic reactions of quinones. Uspehi Chim.,60, 134-168.

This research was conducted with the financial support of the Committee of science of the Ministry of Education and Science of the Republic of Kazakhstan (a government grant No. 0500/GF4 issued under the budgetary program: 217 "Development of science", the subprogramme 102 "Grant financing of scientific research", on a priority: "Rational use of natural resources, processing of raw materials and production", on a subpriority: "Technology of receiving new materials".