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N. P. Tarasova^a; Yu. V. Smetannikov^a; I. M. Artemkina^a; A. S. Vilesov^a

^a D.I. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia

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Influence of Media on Processes of Radiation-Induced Polymerization of White Phosphorus

N. P. Tarasova, Yu. V. Smetannikov, I. M. Artemkina,
and A. S. Vilesov

D.I. Mendeleyev University of Chemical Technology of Russia, Miusskay
sq., 9, Moscow, 125047, Russia

Radiation-induced polymerization of elemental phosphorus in the presence of ionic liquids(IL) was investigated. Composition, structure, and properties of the products-phosphorus-containing polymers (PCPs)-were examined by the methods of physicochemical analysis. It was found that the structure of ionic liquid and its concentration in the media has a significant influence on the polymerization rate. Some kinetic properties of the radiation-induced polymerization process of the elemental phosphorus in the presence of ionic liquids in the mixed solvent “dimethylsulfate (DMSO)/benzene” were determined (reaction rate, effective rate constant, reaction orders).

Keywords elemental phosphorus; ionic liquid; kinetics; phosphorus-containing polymer; radiation-induced polymerization

INTRODUCTION

Many properties of the allotropic modifications of elemental phosphorus,^{1,2} capable of the transmutations,³ are determined by their electronic structure. White phosphorus depending on reaction conditions is capable to manifest as nucleophilic, so and electrophilic nature, which determines the spectrum of products, including polymeric, on its basis.^{4–7} The construction of polymer assumes participation in the process of reactive billets on the basis of tetraphosphorus. One of the examples of the reactions, in which it is possible to expect the appearance of clusters P_4 of different structure, is considered to be the bulk polymerization of white phosphorus into the red one. It is known that

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Address correspondence to N. P. Tarasova, D. Mendeleyev University of Chemical Technology of Russia, Miusskaya sq., 9, Moscow 125047 Russia. E-mail: tarasnp@muctt.edu.ru

the processes of obtaining the latter realized on an industrial scale lead to the end product with the badly reproducible physicochemical properties.⁸ They assume that one of the reasons for this is the manifestation of the special features of synthesis conditions of polymeric phosphorus.³ It is obvious that reaction conditions in the extreme case determine the probability of the breaking of bonds P–P in the cellular tetrahedral molecule of tetrphosphorus with the retention of tetratomic grouping. In this case the formation of polymers of red phosphorus both of linear and three-dimensional structure is possible.

From the point of view of the transformation of initial tetrphosphorus into the red phosphorus, polymerization reaction can be represented in the form of the following stages: the formation of reactive intermediates on the basis of tetrphosphorus, complicated, depending on the conditions of reaction medium, by interaction with the solvent formation the *n*-dimensional clusters of phosphorus and the formation of three-dimensional polymer. There are data, which confirm the flow of two last stages,⁹ whereas the information about the nature and the structure of those initiating the polymerization of particles is very limited.

It is understandable that the large number of allotropic modifications of element phosphorus is determined by its unique electronic system, the experimental study by which, however, is hindered by its high reactivity.

EXPERIMENTAL PARTY

In the work the following ionic liquids (ILs) were used (99.9% purity, the product of—"Merckh," Germany): 1-butyl-3-methylimidazolium-trifluoromethanesulfonate (I), 1-butyl-3-methylimidazolium tetrafluoroborate (II), 1-butyl-3-methylimidazolium hexafluorophosphate (III), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IV), 1-butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)imide (V), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)tri-fluorophosphate (VI)

The purification of white phosphorus was conducted employing the modified procedure.¹⁰ Solvents (benzene, dimethylsulfoxide (DMSO)) have been conditioned employing the standard procedures.¹¹

The polymerization of white phosphorus was conducted employing ampoule procedure. In the inert atmosphere the solutions were placed into the ampoules. Ampoules were irradiated with gamma-radiation of radionuclide ⁶⁰Co(absorbed dose rate 0.59 Gy/s). Temperature of the polymerization *T* = 298 K. After the irradiation of ampoule they revealed, the sediment was filtered. The residual concentration of phosphorus in the solution was determined by titrimetric method.¹²

IR-spectra were obtained on Fourier-IR spectrometer Tensor 27. Microphotographs were obtained on the electronic scanning microscope "Tesla BS 340." X-ray analysis was carried out on the instrument "DRON-3M."

CONSIDERATION OF THE RESULTS

The product of the reaction of the radiation-initiated polymerization of white phosphorus in the binary solvent DMSO/benzene in the presence of IL is the phosphorus-containing substance, which falls out into the sediment in the form of fine dispersed yellowish orange powder. The obtained product does not dissolve in any accessible polar or nonpolar solvent, what is characteristic for polymeric phosphorus. The study of product by the method of X-ray diffraction analysis showed its X-ray amorphism. According to the data of the elemental analysis, carried out by the method of combustion in oxygen, in the product depending on the absorbed dose on the average it is contained (in the mass percentages): $\sim 70\text{--}80\%$ P, $\sim 5\text{--}7\%$ C, $\sim 2\text{--}3\%$ H, $\sim 10\text{--}20\%$ O. For all phosphorus-containing samples depending on the type of IL in the samples used there are present N, S, F with the total content no more than 1% mass. The presence in the IR-spectra of the absorption bands, which correspond to chemical bonds P-OH (1460 cm^{-1}), P-O (1380 cm^{-1}), P-H (1150 and 970 cm^{-1}), P-C (720 cm^{-1}), attests to the fact that the organic fragments of the solvent are chemically bound with phosphorus. On the spectra the band of weak intensity (500 cm^{-1}) is also present, which can be attributed to the oscillations of P-P bonds. All the absorption bands enumerated above are characteristic also for the phosphorous-containing polymers, obtained earlier with radiation initiated polymerization of white phosphorus in the benzene.⁴

The estimation of the molecular mass of the polymer according to the number of the end fragments groups of the solvent testifies about the short-chain nature of the process with the degree of polymerization $n = 3\text{--}6$ ($(\text{P}_4)_{3-6}$).

The macro structural examination of the phosphorus-containing product (PCP), obtained in the benzene and in the mixture of DMSO/benzene in the presence of IL, by the methods of morphological analysis and electron microscopy, showed that, in the case of conducting the process in the polar solvent of DMSO/benzene, the particles are formed with average size of $0.25\text{ }\mu\text{m}$, which is considerably less than the size of the particles ($11\text{ }\mu\text{m}$), which are formed in the pure benzene.

The introduction of ILs (amphiphilic compounds, which possess the ability to participate in intermolecular interactions) into the reaction media (white phosphorus – benzene – DMSO) leads to an increase in

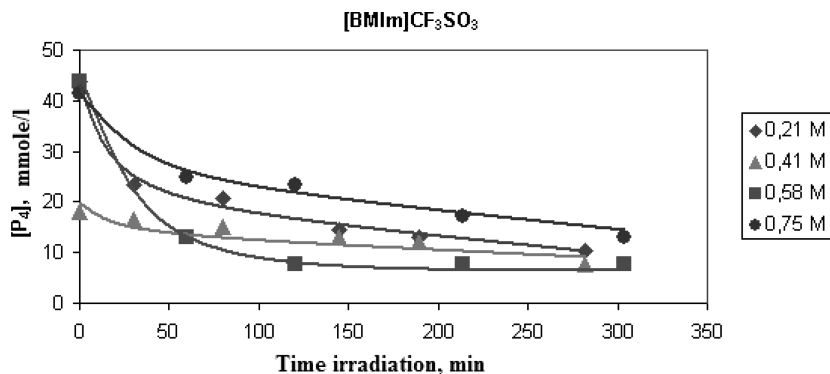


FIGURE 1 Dependence of the concentration of white phosphorus on the time of irradiation (reactions with the different content of IL in the reaction systems). $D = 0.59$ Gy/s, $T = 298$ K, $[[BMIm]^+[CF_3SO_3]-]_0 = 0.21, 0.41, 0.58, 0.75$ M.

the rate of the process and an increase in the degree of conversion, other conditions being equal, in comparison with the one in the absence of IL (Figures 1, 2).

The curved losses of white phosphorus in the course of time, rapidly fall in the initial sections and leave in the plateau with the values of absorbed dose on the order of 7.1 kGy.

The obtained curves are linearized in the coordinates of $1/[P_4] = f(t)$ (second order) and have, depending on type and concentration of ILs, different slope angle and, therefore, the different values of the effective reaction rate constants K_{eff} (Figure 3).

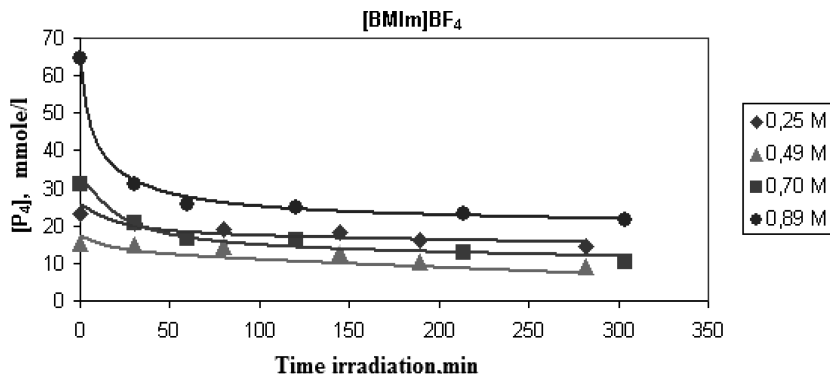


FIGURE 2 Dependence of the concentration of white phosphorus on the time of irradiation (reactions with the different content of IL in the reaction systems). $D = 0.59$ Gy/s, $T = 298$ K, $[[BMIm]^+[BF_4]-]_0 = 0.25, 0.49, 0.70, 0.89$ M.

TABLE I Dependence of the Effective Reaction Rate Constant of the Polymerization of White Phosphorus and G PCP on the Relationship of the Initial Concentrations of Elemental Phosphorus and Ionic Liquid (T = 298 K, D = 0.59 Gy/s, The Solvent of DMSO/benzene (1:1))

No	Ionic liquid	$\frac{[P_4]_0}{[IL]}$	K eff., $M^{-1} \cdot min^{-1}$	r^2	G PCP, molecule (P)/100 eV
I	[BmIm] ⁺ [CF ₃ SO ₃] ⁻	0.045	0.24 ± 0.02	0.883	21 ± 2
		0.055	0.16 ± 0.02	0.976	74 ± 7
		0.075	0.89 ± 0.09	1.000	455 ± 46
		0.206	0.25 ± 0.03	0.970	151 ± 15
II	[BmIm] ⁺ [BF ₄] ⁻	0.032	0.16 ± 0.02	0.928	11 ± 1
		0.044	0.16 ± 0.02	0.964	42 ± 4
		0.072	0.042 ± 0.004	0.852	47 ± 5
		0.092	0.089 ± 0.009	0.978	13 ± 1
III	[BmIm] ⁺ [PF ₆] ⁻	0.022	0.13 ± 0.01	0.947	11 ± 1
		0.035	0.53 ± 0.05	0.968	34 ± 3
		0.069	0.14 ± 0.01	0.915	69 ± 7
		0.201	0.17 ± 0.02	0.945	101 ± 10
IV	[EmIm] ⁺ [N(SO ₂ CF ₃) ₂] ⁻	0.215	0.14 ± 0.01	0.989	60 ± 6
V	[BMPyr] ⁺ [N(SO ₂ CF ₃) ₂] ⁻	0.081	0.19 ± 0.02	0.979	31 ± 3
		0.093	0.18 ± 0.02	0.988	80 ± 8
		0.105	0.46 ± 0.05	0.990	415 ± 42
		0.305	0.20 ± 0.02	0.986	128 ± 13
VI	[HmIm] ⁺ [(C ₂ F ₅) ₃ PF ₃] ⁻	0.049	0.18 ± 0.02	1.000	19 ± 2
		0.134	0.13 ± 0.01	0.948	32 ± 3
		0.148	0.11 ± 0.01	0.967	70 ± 7
		0.470	0.27 ± 0.03	0.970	237 ± 24
	Without IL	—	0.017 ± 0.002	0.939	8 ± 1

Table I gives the values of the effective reaction rate constants of the polymerization of white phosphorus and radiation chemical yield G of the polymeric product (PCP) in the dependence on the relationship of the initial concentrations of elemental phosphorus and ionic liquid.

A study of laws governing the radiation chemical synthesis of PCP in the mixed solvent benzene/DMSO (1:1) in the presence of ionic liquids by the method of formal kinetics revealed the essential dependence of effective constants on the concentration of IL. The possible explanations of the observed phenomena can be connected: with the formation of complex “white phosphorus—IL”, and with the ability of IL, due to intermolecular interactions, to structure solid and liquid solutions. For the four-component systems of benzene:DMSO:IL:P₄ the observed dependence of the concentration of white phosphorus in the system on the

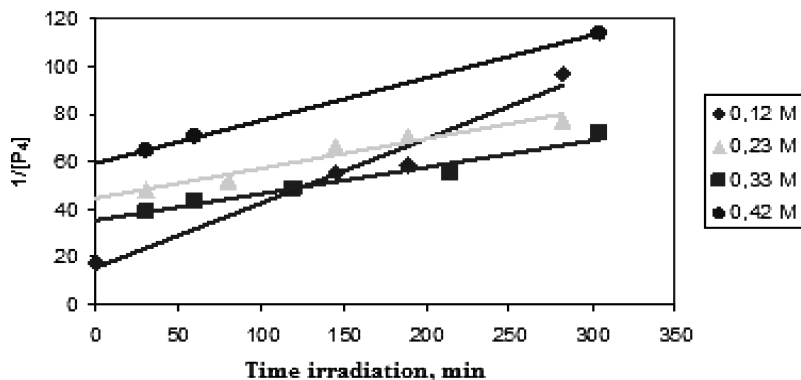


FIGURE 3 Linearization of the dependence of the concentration of white phosphorus on the irradiation time with the different content IL in the reaction system. $D^* = 0.59$ Gy/s, $T = 298$ K, $[[\text{HMIIm}]^+[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-]_0 = 0.12, 0.23, 0.33, 0.42$ M.

content of IL, is possibly, connected with the formation of fluctuations with different content of tetrphosphorus.

In the work¹³ it is shown that the ionic liquids based on 1-alkyl-3-methylimidazolium tetrafluoroborate-, hexafluorophosphate-, bistriflimide-, chloride ion) when mixed with the aromatic hydrocarbons form the liquid clathrates, which upon transfer into the solid state form the crystalline conjunctions of composition of 2:1 (e.g.—dimethylimidazolium hexafluorophosphate—benzene).

Work¹⁴ examines questions of the influence of solvation on the formation of polymers, clusters of metals and control of the processes of the formation of supramolecular structures.

It is known¹⁵ that in the very dilute solutions the amphiphilic ions (a special case—ionic liquids) behave as usual strong electrolytes, but if their concentration exceeds the so-called critical concentration of micelle formation, usually equal to 10^{-4} – 10^{-2} M, then spherical associates are formed. Such a control of chemical reactions, by means of the start of initial connections in the regulated associates, is one of the most important trends in development of the chemical technology.

Structuring is characteristic also for the benzene solutions. Besides the associates of benzene, there can be present its complexes with the molecules of the components of system and the associates of the molecules of these components¹⁶ can be present. In turn, liquid dimethylsulfoxide possesses the regular structure, which is destroyed in the range of temperatures of 313–333 K and is accompanied by a change in the physicochemical characteristics: the index of refraction,

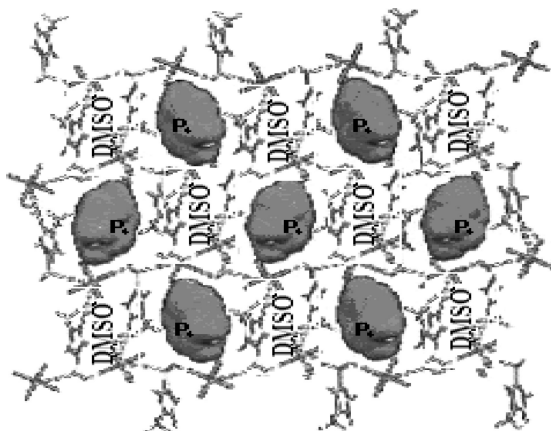


FIGURE 4 Topological (volumetric) model of the solution of white phosphorus in DMSO:benzene in the presence of IL

density, viscosity. In this respect DMSO resembles water, which manifests distinct changes in the structure of liquid. It is shown that in liquid dimethylsulfoxide there exist aggregates of the chain structure, caused by hydrogen bonds.^{17,18}

The analysis of literature data and experimental data, obtained in the work, made it possible to assume the existence in the system of benzene:DMSO:IL:P₄ of the fluctuations of the concentrations of white phosphorus, connected with the special features of solvation interactions in the system and to use topological ideas for describing the process (Figure 4).

In this case for the analysis of laws governing the formation of PCP there was used the equation, which describes the topochemical model of the compressive sphere¹⁹:

$$\ln(1 - \alpha^{1/3}) = \ln K_T + n \ln t,$$

where $\alpha = [P_4]/[P_4]_0$ – the degree of the transformation, K_T – the constant of the topochemical reaction, n – the constant, which characterizes reaction mechanism, t – the reaction time.

The results of kinetic analysis within the framework of topochemical model are represented in Table II.

In the majority of the cases the close values of parameter n , which characterizes the special features of topochemical process, testify about the uniformity of reactions occurring in the system. Substantial change of K_T depending on the concentration of IL makes it possible to speak about the influence of the structural organization of the solution on the polymerization of white phosphorus.

TABLE II Dependence of the Constant of Topochemical Reaction on the Concentration of IL, T = 298 K, D = 0.59 Gy/s

[BMIm] ⁺ [CF ₃ SO ₃] ⁻	C _{IL} , M	0.21	0.41	0.58	0.75
	lnK _T	-2.34 ± 0.23	-3.32 ± 0.033	-2.46 ± 0.25	-3.62 ± 0.36
	n	0.25 ± 0.03	0.35 ± 0.04	0.23 ± 0.02	0.36 ± 0.04
[BMIm] ⁺ [BF ₄] ⁻	C _{IL} , M	0.26	0.49	0.70	0.89
	lnK _T	-5.32 ± 0.53	-8.90 ± 0.89	-3.11 ± 0.31	-1.95 ± 0.20
	n	0.59 ± 0.06	1.25 ± 0.13	0.32 ± 0.03	0.14 ± 0.01
[BMIm] ⁺ [PF ₆] ⁻	C _{IL} , M	0.23	0.44	0.63	0.81
	lnK _T	-3.09 ± 0.31	-13.40 ± 1.34	-3.29 ± 0.33	-3.05 ± 0.31
	n	0.35 ± 0.04	2.19 ± 0.22	0.34 ± 0.03	0.27 ± 0.03
[HMIm] ⁺ [(C ₂ F ₅) ₃ PF ₃] ⁻	C _{IL} , M	0.12	0.23	0.33	0.43
	lnK _T	-3.62 ± 0.36	-5.87 ± 0.59	-2.00 ± 0.20	-2.19 ± 0.23
	n	0.46 ± 0.05	0.83 ± 0.08	0.19 ± 0.02	0.23 ± 0.02
[BMPyr] ⁺ [N(SO ₂ CF ₃) ₂] ⁻	C _{IL} , M	0.16	0.31	0.44	0.56
	lnK _T	-2.34 ± 0.23	-3.32 ± 0.33	-2.46 ± 0.25	-3.62 ± 0.36
	n	0.25 ± 0.03	0.35 ± 0.04	0.23 ± 0.02	0.36 ± 0.04

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