UDC 542.943.7; 546.18; 546.562

Zh.K. Kairbekov, D.N. Akbayeva*, Zh.T. Eshova
Al-Farabi Kazakh National University, Kazakhstan, Almaty
*E-mail: dnakbayeva@inbox.ru

Kinetics of the oxidative hydroxylation of tetraphosphorus in the presence of copper(II) chloride modified by humic (fulvo-) acid

Abstract. It was established that in mild conditions (50-70 oC, PO2 = 1 atm) white phosphorus effectively is oxidized by oxygen in water-toluene solutions of copper(II) chloride modified by humic (fulvo-) acid to give mainly phosphoric acid. Humic (fulvo-) acid was extracted from brown coal of domestic deposit Kiyakty. For determination of optimum parameters of fulvo-acid extraction the laboratory experiments were carried out using the method of experiment planning. The kinetics, intermediate and final products, optimum conditions of new catalytic reaction of P4 oxidation by oxygen in water medium were defined by kinetics, volumometry, redox-potentiometry, 31P{1H} NMR spectroscopy and titration.
Keywords: white phosphorus, oxidation, oxygen, humic (fulvo-) acid, hydroxylation, phosphoric acid, kinetics, optimum conditions.

Introduction

Phosphorus-containing inorganic derivatives, in particular, phosphorus acids play important role in the vital development and exchange and found application in inorganic and organic synthesis, as reducers, in production of heat-resistant plastic, fodder and technical phosphates, in food, medical and war industry. As an initial material for industrial production of valuable acids of phosphorus rather cheap and available yellow phosphorus (P_4) is used. Raw materials for obtaining valuable phosphorus-containing compounds in the industry using traditional technology are chlorine-containing derivatives of phosphorus PCl_3, PCl_5, $POCl_3$, $POCl_3$. Multiphase industrial process is accompanied by the yield of a large amount of hydrogen chloride, causing additional expenses on its neutralization and decrease in yield of target products, and also creates serious environmental problems. Selective disclosure of tetrahedral molecule P_4 and its direct functionalization gains the increasing value in connection with search of new non-polluting processes of obtaining phosphorus products. In turn, the Cu(II) complexes are widely used as reversible catalysts of oxidation of a number of inorganic and organic compounds by molecular oxygen with formation of oxygen-containing compounds [1, 2].

The purpose of this work is the development of effective catalysts of an oxidizing hydroxylation of tetraphosphorus in the presence of the copper(II) chloride modified by humic (fulvo-) acid, extracted from brown coal of domestic deposit Kiyakty for the purpose of obtaining phosphoric acid.

Materials and methods

The process of P_4 catalytic oxidation by oxygen in the aqueous environment carried out in the closed isothermal system with intensively stirred up reactor, supplied with the electrometric device and connected to gasometrical burette with oxygen. Deuterium oxide (D_2O) (Aldrich) for NMR experiments and $CuCl_2 \cdot 2H_2O$ are used without additional cleaning. Phosphinoxide TPPMSO is used as an internal standard in a nuclear magnetic resonance experiments, and was synthesized by a known technique [3]. Particles of P_4 weighed under water, and then dissolved in toluene (PhMe) at 45-50°C. Concentration of P_4 in the obtained toluene solution was determined by iodometric titration [4]. For determination of optimum parameters of fulvo-acid (FA) extraction the laboratory experiments were carried out using the method of experiment planning [5].

The matrix of the 4th factorial of experiment planning at the 4th level was constructed and optimal

conditions of transfer to alkaline solution of fulvo-acid from coal of a Kiyakty field were determined. The optimal conditions of extraction of fulvo-acid: X_1-extraction temperature – 80°C; X_2 – duration of experiment – 45 mines; X_3 – concentration of alkali – 1,0 %; X_4 – ratio of coal and alkali 1:25 solution. The experiment realized in these conditions was coordinated with sampled data. Determination of phosphoric and humic (fulvo-) acids concentration was carried out by acidic-alkaline titration according to a technique given in [6].

Results and discussion

It was established that in anaerobic conditions white phosphorus is oxidized in water-toluene solutions of $CuCl_2$ and $Cu(MeCO_2)_2$ at 90°C to give a mixture of deuterated phosphorous **IIa** (5-21 %), hypophosphorous **Ia** (27-75 %) and phosphoric **IIIa** (20-62 %) acids (1-3). At introduction of P_4 in water solutions of green $CuCl_2$ and $Cu(MeCO_2)_2$ the blackening of solutions is observed that indicates Cu(II) reduction to Cu(0) by white phosphorus.

$$P_4 + 6CuX_2 + 12D_2O \rightarrow 4P(O)D(OD)_2 + 6Cu + 12DX \quad (1)$$

Ia

$$P_4 + 2CuX_2 + 8D_2O \rightarrow 4P(O)D_2(OD) + 2Cu + 4DX \quad (2)$$

IIa

$$P_4 + 10CuX_2 + 16D_2O \rightarrow 4P(O)(OD)_3 + 10Cu + 20DX \quad (3)$$

IIIa

Oxidation of P_4 proceeds in the biphasic system P_4/PhMe-D_2O where the dissolved phosphorus is in the upper organic layer, and D_2O - in the bottom layer. In table 1 the conditions and yields of products of P_4 oxidation by CuX_2 complexes are given in the inert atmosphere in water toluene solutions at 90°C.

Table 1 – Oxidation of P_4 by the CuX_2 complexes at a ratio [Cu(II)]:[P_4] = 3,3 in water toluene solutions in the inert atmosphere

Experiment	[CuX_2], mmol	τ, h	η_{P4}, %	Yield of products, %		
				Ia	IIa	IIIa
1	$CuCl_2$ 0,8	1	96	75	5	20
2[a]	0,8	1	100	44	8	48
3[b,c]	0,8	1	72	68	12	21
4	$Cu(MeCO_2)_2$ 0,8	1	100	35	12	53
5[a]	0,8	1	77	27	11	62
6[b,c]	0,8	1	100	40	21	39
Conditions of reaction, mmol: [P_4] = 0,24; [D_2O] = 55,3; [PhMe] = 9,4; 90°C; argon. [a] [D_2O] = 83. [b] [Py] = 9,9. [c] without PhMe.						

^{31}P NMR spectra of reactive solutions after 1 h at 90°C under condition of a complete reduction of $CuCl_2$ and $Cu(MeCO_2)_2$ by white phosphorus to Cu(0) are completely identical and contain the signals indicating three deuterated acids **Ia**, **IIa** and **IIIa**. The triplet 1:1:1 in the weak field with the center at 5,7 ppm with coupling constant ^1J (P-D) = 102,5 Hz corresponds to **Ia**, a nonbinominal quintet at 13,54 ppm with coupling constant ^1J (P-D) = 85,6 Hz - **IIa** acid, and sharp singlet at 0,32 ppm of - to **IIIa** product. Singlet at 36,49 ppm match the internal TPPMSO standard.

In the picture 1 the $^{31}P\{^1H\}$ NMR spectrum of $CuCl_2$-D_2O-P_4-TPPMSO solution is presented at 20°C (experimental conditions 2 in table 2). The total yield of phosphorus acids after reaction with $CuCl_2$ and $Cu(MeCO_2)_2$ was 70-100 % (table 1, оп. 1-6). Irrespective of composition of reactionary solution the main product of reaction was **Ia** with the maximum yield of 75 % (table 1, exp. 1). Acids **IIa** (5-21 %) and **IIIa** (20-62 %) are formed with lower yields.

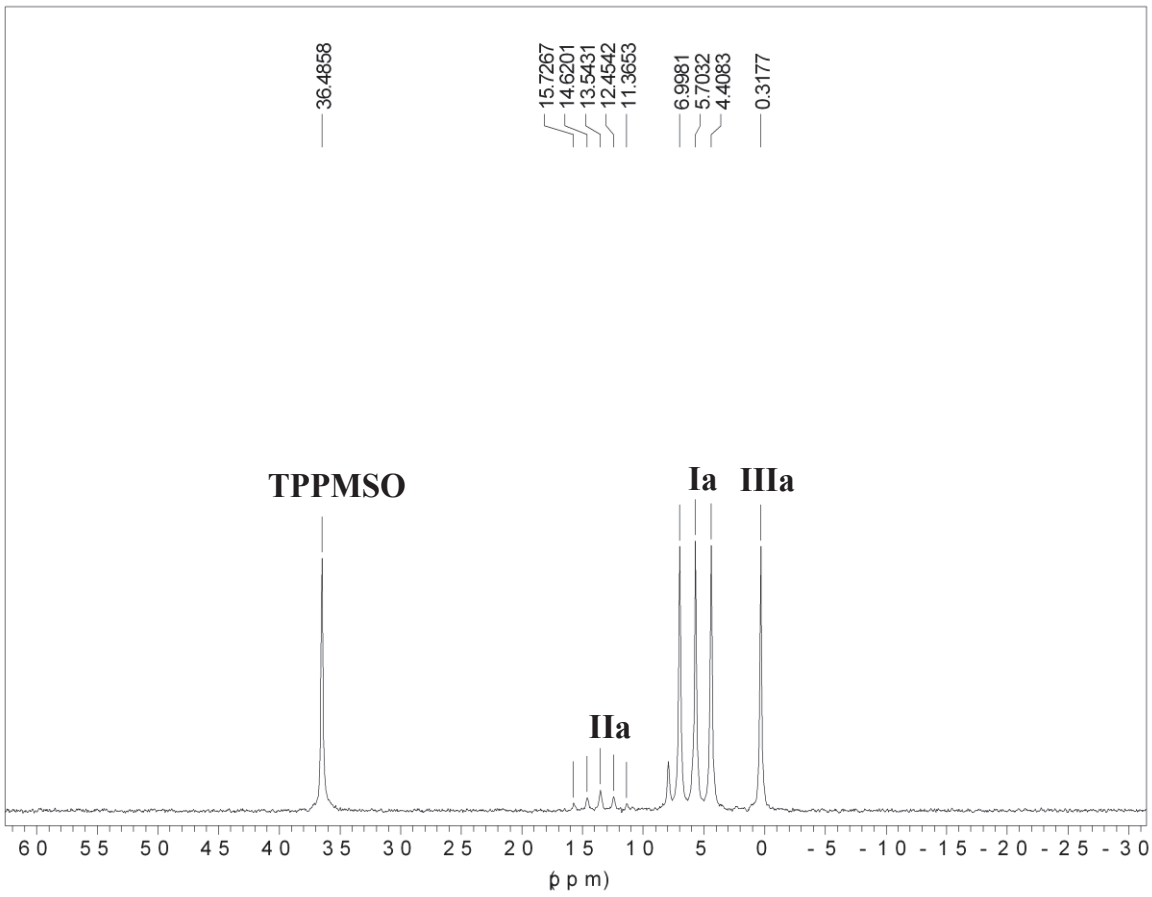


Figure 1 – $^{31}P\{^{1}H\}$ NMR spectrum of solution $CuCl_2$ (0,8 mmol) – D_2O (55,3 mmol) – P_4 (0,24 mmol) – TPPMSO (0,048 mmol) at 90°C (conditions of experiment 2 in table 2)

In the presence of oxygen the reactions (1-3) become catalytic. It was found that at oxidation of P_4 by oxygen in water solution of copper(II) chloride at 50-70°C phosphoric acid is formed:

$$P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4 \qquad (4)$$

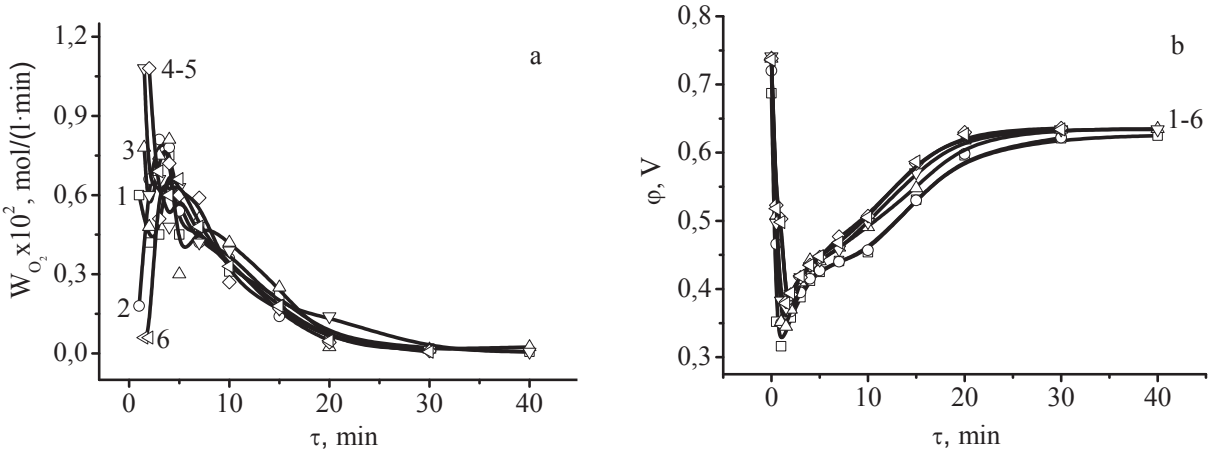
The concentration effect of components of the reactive medium and temperature for process velocity (1) is studied. The obtained experimental data are presented in picture 2 and given in table 2. In the absent of copper(II) chloride and fulvo-acid the oxidative hydrolysis proceeds with smaller velocity. The reaction conditions and products yields of tetraphosphorus oxidation by oxygen in water solution of $CuCl_2$ are presented in the table.

The green water solution $CuCl_2$ (2,1 mmol) at 60°C after addition of P_4 aliquote (0,08 mol) gradually changes color to brown, redox-potential is displaced in the cathodic side from 0,69 to the 0,32 V. Simultaneously the pressure decreasing occurs in the closed system and absorption of oxygen begins. At the beginning of experiment the velocity of O_2 absorption is small, then increases, passes through a maximum, and by the end of experience reduces to zero. After attaining the point of a maximum, the redox-potential defined by pair of Cu(II)/Cu(I) starts to come back to the anodic side, coming nearer to initial value, the quantity of absorbed O_2 corresponds to a stoichiometry of reaction (4) (picture 2).

The addition in a reactive mixture of water solution of fulvo-acid (0,03 mol) promotes the increase of reaction velocity. The increase of fulvo-acid concentration from 0,03 to 0,14 mol is accompanied by increase of reaction velocity and initial potential systems (picture 2). The yield of phosphoric acid is 81-100 %. Temperature decrease to 50°C and increase to 70°C at C_{FA} 0,08 mol is accompanied by decrease of reaction velocity.

Table 2 – Oxidation of P_4 by oxygen in water solutions of $CuCl_2$

exp. №	$[CuCl_2 \cdot 2H_2O]$ mmol (g)	[FA], mol (ml)	max $W_{O2} \cdot 10^2$ (mol/(l·min))	$Q_{O2} \cdot 10^2$ (mol/l)	Yield of H_3PO_4, %
1[a]	2,1	0,08 (3 ml)	0,6	5,0	81
2	2,1	0,08 (3 ml)	1,1	5,2	92
3[b]	2,1	0,08 (3 ml)	0,4	4,6	95
4[c]	2,1	0,08 (3 ml)	0,6	2,3	92
5[d]	2,1	0,08 (3 ml)	1,5	8,0	93
6	2,1	0,03 (1 ml)	0,8	5,3	99
7	2,1	0,06 (2 ml)	0,8	5,4	87
8	2,1	0,11 (4 ml)	1,1	5,5	87
9	2,1	0,14 (5 ml)	0,7	5,5	95
10	0,8	0,08 (3 ml)	1,0	4,7	92
11	4,2	0,08 (3 ml)	1,0	5,7	100
The note - $[P_4]$ 8,3 mmol; $[H_2O]$ 9 ml; $[C_7H_8]$ 1 ml; 60°C; P_{O2} 1 atm; reaction time 20-40 min. [a] 50°C. [b] 70°C. [c] $[P_4]$ 1,3 mmol. [d] $[P_4]$ 4,2 mmol.					



Reaction conditions, mol: $[CuCl_2]$ $2,1\times10^{-3}$; $[P_4]$ $8,3\times10^{-3}$; $[H_2O]$ 22,2-50; 60°C; P_{O2} 1 atm; [FA]: 1 – 0; 2 – 0,03; 3 – 0,06; 4 – 0,08; 5 – 0,11; 6 – 0,14.

Figure 2 – Kinetic (a) and potentiometric (b) curves of oxidative hydrolysis of P_4 by oxygen in the presence of copper(II) chloride modified by humic (fulvo-) acid extracted from brown coal of domestic deposit Kiyakty

Conclusion

Thus, the promoting influence of an added humic (fulvo-) acid obtained from brown coal of domestic deposit Kiyakty, on velocity of an oxidative hydroxylation of P_4 in the presence of copper(II) chloride is revealed. Optimum conditions of oxidation of a tetraphosphorus with formation of phosphoric acid are: temperature 60°C; P_{O2} = 1 atm; H_2O = 60 vol. %; FA = 30 vol. %; toluene = 10 vol. %; $CuCl_2/P_4$ = 1:4; FA/P_4 = 10.

Acknowledgements

The authors gratefully acknowledge the support of Ministry of Education and Science of Republic of Kazakhstan (№ 505 grant, on a priority 5.1. «Basic researches in the field of natural sciences», according to the program "The development of scientific bases of processing of combustible minerals and obtaining of new materials»).

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Ж.К. Қаирбеков, Д.Н. Ақбаева, Ж.Т. Ешова

Гумин (фульво-) қышқылымен модифицирленген мыс (II) хлориді қатысында тетрафосфорды тотықтыра гидроксилирлеудің кинетикасы

Жұмсақ жағдайларда (50-70°С, P_{O2} = 1 атм) сулы-толуолды ерітінділерде ақ фосфор гумин (фульво-) қышқылдарымен модифицирленген мыс (II) хлориді қатысында фосфор қышқылын түзе оттекпен тиімді тотығатыны айқындалды. Гумин (фульво-) қышқылы Қияқты кен орны қоңыр көмірінен бөлініп алынды. Гумин қышқылдарын бөліп алудың қолайлы әдістері тәжірибені ықтималды болжау әдісі қолданылып жүргізілді. Волюмометрия, редокс-потенциометрия, ЯМР $^{31}P\{^{1}H\}$-спектроскопия, кинетика, титрлеу әдістерімен аралық және соңғы өнімдер мен процесс кинетикасы зерттеліп, сулы ерітінділерде P_4 оттекпен тотықтырудың жаңа катализдік рекцияларының қолайлы жағдайлары анықталды.

Түйін сөздер: ақ фосфор, тотығу, оттек, гумин (фульво-) қышқылы, гидроксилдеу, фосфор қышқылы, кинетика, қолайлы жағдайлар.

Ж.К. Каирбеков, Д.Н. Акбаева, Ж.Т. Ешова

Кинетика окислительного гидроксилирования тетрафосфора в присутствии хлорида меди(II), модифицированного гуминовой (фульво-) кислотой

Установлено, что в мягких условиях (50-70°С, P_{O2} = 1 атм) белый фосфор эффективно окисляется кислородом в водно-толуольных растворах хлорида меди(II), модифицированного гуминовой (фульво-) кислотой, с преимущественным образованием фосфорной кислоты. Гуминовая (фульво-) кислота была выделена из бурого угля отечественного месторождения Киякты. Для определения оптимальных параметров извлечения гуминовых кислот проведены лабораторные опыты с использованием метода вероятностно-детерминированного планирования эксперимента. Методами кинетики, волюмометрии, редокс-потенциометрии, ЯМР $^{31}P\{^{1}H\}$-спектроскопии и титриметрии исследованы кинетика, промежуточные и конечные продукты, определены оптимальные условия новых каталитических реакций окисления P_4 кислородом в водных средах.

Ключевые слова: белый фосфор, окисление, кислород, гуминовая (фульво-) кислота, гидроксилирование, фосфорная кислота, кинетика, оптимальные условия.