Quantum-chemical study of activation of yellow phosphorus by copper (II) chloride

Akbayeva D.N.*, Tulegenov A.S.

Al-Farabi Kazakh National University,
Almaty, Kazakhstan
*E-mail: dnakbayeva@inbox.ru

Catalytic properties of Cu^{2+} ions in oxidation reactions of P_4 were investigated in present work using quantum-chemical methods. The geometric structures of several transition metal complexes were determined. The oxidation of P_4 molecules in reactions with alkane hydroxide compounds by means of interaction with Cu^{2+} ions is substantiated based on comparative analysis of energies. The mechanism of activation of P_4 molecular cations is studied. The possibility of occurrence of the reaction is shown based on thermodynamic parameters.

Keywords: yellow phosphorus; copper (II) halides; activation; quantum and chemical calculations; complexes.

Квантово-химическое исследование активации жёлтого фосфора хлоридом меди (II)

Акбаева Д.Н.*, Тулегенов А.С.

Казахский национальный университет им.
аль-Фараби, Алматы, Казахстан
*E-mail: dnakbayeva@inbox.ru

С использованием квантово-химических методов в работе исследованы каталитические свойства ионов Cu^{2+} в реакциях окисления P_4. Найдены геометрические конфигурации промежуточных комплексов. Окисление молекул P_4 в реакциях с гидрокси соединениями алканов посредством взаимодействия с ионами Cu^{2+} доказано на основе сравнительного анализа энергий. Исследован механизм активации молекулярных катионов P_4. Термодинамическая возможность протекания реакции показана на основе вычисления энергетических параметров реакции.

Ключевые слова: жёлтый фосфор; галогениды меди (II); активация; квантово-химические расчеты; комплексы.

Фосфор молекулалардың мыс иондар (II) арқылы белсендеудің кванттық химиялық зерттеу

Акбаева Д.Н. *, Тулегенов А.С.

Әл-Фараби атындағы Қазақ ұлттық
университеті, Алматы, Қазақстан
*E-mail: dnakbayeva@inbox.ru

Жұмыста Cu^{2+} иондарының P_4 тотығу реакциялардағы каталитикалық қасиеттер кванттық-химиялық әдістер арқылы зерттелінген. Бірнеше ауыспалы комплекстердің геометриялық құрылысы табылған. P_4 молекулалардың алкан гидроксидтер қосылыстармен реакцияларда Cu^{2+} иондармен әрекеттесу арқылы тотығу процесстеріне ұшырауы иондану энергиялардың салыстырмалы талдау бойынша дәлелденген. P_4 молекулярлы иондардың белсендеуінің механизмі зерттелінген. Реакция өтуінің термодинамикалық мүмкіншілігі реакцияның энергиялық параметрлер есептеу бойынша көрсетілген.

Түйін сөздер: сары фосфор, мыс (II) галогенидтер, белсендеу, кванттық-химиялық әдістер, комплекстер.

CHEMICAL BULLETIN

of Kazakh National University

http://bulletin.chemistry.kz/

UDC 541.1

http://dx.doi.org/10.15328/cb791

Quantum-chemical study of activation of yellow phosphorus by copper (II) chloride

Akbayeva D.N.*, Tulegenov A.S.

Al-Farabi Kazakh National University, Almaty, Kazakhstan
*E-mail: dnakbayeva@inbox.ru

1. Introduction

Development of chlorine-free methods of synthesis of derivatives of phosphorus directly from yellow phosphorus is one of the primary tasks of chemistry of phosphorus-containing compounds and chemical technology in connection to the increase of requirements of ecological purity and efficiency of industrial processes. This problem is particularly interesting for Kazakhstan as one of the largest producers of yellow phosphorus in CIS. In spite of the fact that in Kazakhstan there is mined the phosphorite ore and the production of yellow phosphorus is driven to the degree of functioning, the production of phosphorus acids directly from elementary P_4 is absent. Phosphorus-containing derivatives are characterized by a large variety of structures and properties, they play the main role in life sustaining processes of development and exchange [1]. Yellow phosphorus (P_4) is characterized by high reactive ability with respect to the range of organometallic substances. Coordination compounds of transition metals containing coordinated molecule P_4 are not numerous despite the high interest exhibited towards them [2-11]. For the present day the problem of coordination and activation of yellow phosphorus in coordination sphere of complexes of transition metals still attracts the insufficient attention.

In present work the problem was posed of determination of the mechanism of elementary stages of catalytic activation of yellow phosphorus in the reactions of hydroxylation and alkoxylation.

2. Experiment

Quantum-chemical computations of molecules were carried out using GAMESS [12] program in Hartree-Fock approximation (ROHF) using ahlrichs-vdz basis set. The values of energies are provided in atomic units, bond lengths are provided in Å. The series of computations directed towards the geometry optimization of several equilibrium structures were obtained for given initial optimization points. The obtained results were analyzed on the subject of energies magnitudes, atomic charges and interatomic distances. The mechanism of the reaction is studied by means of the comparative analysis of electronic energies in the course of formation of stable states.

3. Results and discussion

Earlier we found [13-20] that in the presence of individual catalysts CuX_2, FeX_3 (X = Cl, Br, NO_3, $MeCO_2$, $PrCO_2$, $StCO_2$) and mixed systems CuX_2-FeX_3, $PdCl_2/RuOHCl_3$-Cocat (Cocat = $FeCl_3$, $CuCl_2$, $NaNO_2$) the yellow phosphorus is quickly and selectively oxidized by oxygen in aqueous and alcohol solutions (R = H, Me, Pr, i-Pr, Bu, i-Bu, Am, i-Am) depending on the nature of acidic-ion and conditions of the reaction to phosphorous acid (1), threealkylphosphite (2), threealkylphosphate (3), dialkylphosphite (4).

$$P_4+6H_2O+5O_2 \rightarrow 4P(O)(OH)_3 \qquad (1)$$
$$P_4+12ROH+3O_2 \rightarrow 4P(OR)_3+6H_2O \qquad (2)$$
$$P_4+12ROH+5O_2 \rightarrow 4P(O)(OR)_3+6H_2O \qquad (3)$$
$$P_4+8ROH+3O_2 \rightarrow 4P(O)H(OR)_2+2H_2O \qquad (4)$$

In the result of study of the mechanism of the reactions (1-4) using the NMR methods ^{31}P-, IR-, ESR-spectroscopy, potentiometry and gas chromatography it is established that the character of products of the reaction P_4 with copper complexes (II) depends on the nature of ligands.

There were posed several tasks in present work with the objective of determining the mechanism of interaction of the P_4 molecule with copper (II) halides. For the assessment of the possibility of quantum-chemical computations there were carried out the series of computations for the estimation of the effects produced by ligand environment. As the benchmark the basis sets of Dunning were chosen of the series ccpNz which were compared against the computations in the basis of Ahlrihs [21]. The results of computations for the free molecule P_4 depending on the basis are provided in Table 1. The Ahlrichs's basis overestimates the energies and bond lengths of P_4 molecule, but it was chosen due to its relatively small size, good convergence properties exhibited for transition metals, low computational cost and possibility of making qualitatively correct estimates at non-empirical level of theory.

The main state of the molecule corresponds to the singlet state (Table 2). Positively charged cation P_4 present in state with multiplicity 2 does not undergo substantial changes and preserves the pyramidal shape close to tetrahedral, as is seen from the results of computations, provided in Table 3.

For the preliminary evaluation of thermodynamic possibility of the reaction of oxidation-reduction the structure of Cu^{2+}-P_4 complex was estimated. According to the results of computation the main state of a given complex is the state corresponding to the copper cation in the oxidation state +1 and P_4 cation in the oxidation state +1. As a rule, the formation of particles with the same sign of charge leads to the repulsion and in the result there is formed the complex with copper cation located at the considerable distance from the P_4^+ particle. According to the results of computation P_4^+ cation-radical is stable in free state and does not undergo substantial deformations in oxidized state (Table 4).

For the correctness of the considered models of interaction the primary condition is the conservation of charge, i.e. it is necessary to consider the interaction of copper cation, whose charge is balanced by the charges of the anions of counterion (halide) present in the model. In present work the mechanism was determined of elementary stages of interaction. The initial point of study was the determination of the number of particles responsible for the formation of activated complex. We consider two hypotheses – about the two-body and three-body interaction. The hypothesis about the two-body interaction assumes the occurrence of the two-step process – activation of P_4 and formation of hydroxyl phosphorus compound. The hypothesis about the three-body interaction supposes the

Table 1 – Dependence of P_4 properties on the basis

Basis	r(P-P), Å	E, atomic units	HOMO energy
Ccd	2.18378	-1363.00514	-0.3585
Cct	2.17359	-1363.05604	-0.3576
ahlrihs-dz	2.41799	-1362.33752	-0.3601
ahlrihs-tz	2.33935	-1362.7969321	-0.3629

Table 2 – Energies of multiplicity state of P_4 molecule. Dunning nCC basis

Basis	Singlet state	Triplet state
Ccd	-1363.005	-1362.951
Cct	-1363.056	-1362.999

Table 3 – Parameters of particle P_4

Property	P_4-neutral	P_4-cationic
Energy	-1363.0051	-1362.6498
P-P distance	2.115	2.184
Symmetry	Td	Td

Table 4 – Dependence of energy of complexes on the position of the ligand

Property	Localized	Distributed
Energy, a.u.	-3919.7478	-3919.7836
r(P-P), Å	2.438	3.2564
Charge on Cl atom	0.0490	-0.270950

Table 5 – Parameters of complexes R-OH...P_4...$CuCl_2$

Ligand type	Initial state	Final state	r(P-P), final	r(P-O), final	qP	qO
CH_3OH fin	-4034.6538	-4034.679	3.1862	1.7006	-0.168231	-0.964400
C_2H_5OH fin	-4073.6462	-4073.672	3.1887	1.6976	-0.171429	-0.977355
C_3H_7OH fin	-4112.6327	-4112.658	3.18885	1.697480	-0.172032	-0.979863
C_4H_9OH fin	-4151.6190	-4151.645	3.18866	1.697404	-0.172790	-0.980933

formation of activated three-body complex R-OH-P_4-$CuCl_2$ transforming into the products of the reaction.

The results of quantum-chemical computations have shown the correctness of both hypotheses. Within the model of two-body interaction there was considered the dependence of formation of the complex and oxidation of P_4 depending on the position of halide-anion. Two types of localization of halide-anion correspond to two different minima on the multidimensional potential energy surface. In case of dominating localization of halide-anion at the top of tetrahedron there occurs the activation of P_4 with the opening of tetrahedron. The reason of such difference in properties of structures may be the delocalization of charge and its effect on the ionization potential of P_4, polarization of P_4 increases in case of complex formation with delocalized counterions. These counterions act similarly to the analogy of oppositely charged hypothetic electrodes introducing the additional contribution to the destabilization of P_4 cation. Delocalization of two oppositely charged ions increases the overall dipole moment of their complex, hence, increasing their polarity. The question of the effects of delocalzation of charge produced on interaction energy was addressed in [22,23]. The equilibrium state of this three-body complex corresponds to the state of copper with the oxidation degree +1.

Comparative analysis of the state energies provided in Table 3 shows that the activated form of P_4 within the complex P_4...Cl...CuCl with the distributed localization of ions is the global minimum (state with lower energy) and non-active form of P_4 within the complex P_4...$CuCl_2$ with the localized localization of ions is the local minimum (state with relatively higher value of energy). The next step was the evaluation of the energy of three-body complexes and with inclusion into the model of the alcohol molecules and counterion of Cu^{2+} cation (Table 4). In the course of determination of the mechanism of elementary stages of catalytic activation of phosphorus in the reaction of hydroxylation and alkoxylation it was established that the initial act of reaction includes the three-body interaction in P_4-ROH-$CuCl_2$, which occurs in two stages. The first stage is the oxidation of the P_4 particle by copper cations Cu(II) coordinated with two chlorine anions. Further course of reaction is the activation of P_4 cation by the ligand environment of copper ion and alcohol molecules. Reactivity of P_4 cation is dependent on the activation corresponding to opening of the tetrahedron. The series of computational experiments have shown that the activation of P_4 depends on the configuration of ligand environment of a given cation. Two configurations of ligand environment of a given cation were considered – with the distributed and localized position of chlorine anions and copper cation. As in the model of two-body complex the activation of P_4 occurs only in case of distributed configuration of ions of the P_4 environment. Computational experiments were constructed for two configurations – the initial with the hydrogen bonds between the P_4 and R-OH and the final with the covalent bond P-O of the formed alkylphosphate and hydrogen chloride (Table 5). Comparison of energies of these states allows to make the conclusion about the thermodynamic possibility of the process

The initial and final state of the complex C_4H_9OH...P_4...$CuCl_2$ are shown in figures 1 and 2.

This fact is supported by the series of computational experiments directed towards the optimization of geometric structure and comparison of energy characteristics of

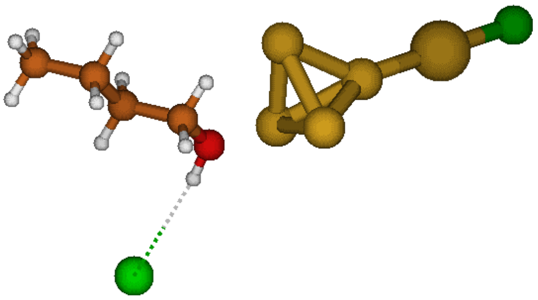

Figure 1 – Initial state of the $C_4H_9OH\cdots P_4\cdots CuCl_2$ complex

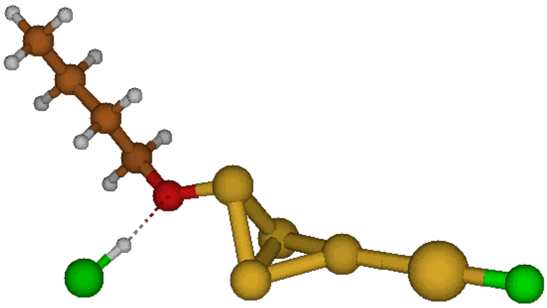

Figure 2 – Final state of the $C_4H_9OH\cdots P_4\cdots CuCl_2$ complex

various complexes, corresponding to the local minima on multidimensional potential energy surface. Comparative analysis of states shows that the activated form of P_4 within the complex P_4OR...HCl...CuCl with the distributed position of ions is the global minimum (state with the lowest energy) and the non-active form P_4 within the ROH...P_4...$CuCl_2$ complex with the localized position of ions is the local minimum (state with relatively higher value of energy).

4. Conclusion

The activation of P_4 molecule by copper(II) ions in the reaction with alcohols was studied in present work using quantum-chemical methods. The geometric structures of several transition complexes were determined. The mechanism of oxidation of P_4 molecules in reactions with alcohol compounds catalyzed by intermediate oxidation by Cu^{2+} ions is supported based on comparative analysis of energies. The conditions of activation of P_4 molecular ionic tetrahedra are studied leading to the conclusion that the distributed localization of ligand environment is preferrential for the further activation of P_4 particles. The possibility of occurrence of the reaction is shown based on comparison of ground state energies of the initial and final states.

Acknowledgements

The work has been carried out within the project of MES RK 3662/GF4 «Development of catalytic processes of oxidation and hydrogenation with the objective of obtaining organic substances from yellow phosphorus, alcohols and unsaturated hydrocarbons.

References GOST

1 Corbridge D.E.C. Phosphorus. Chemistry, biochemistry and technology. Sixth ed. – New York: CRC PressTaylor & Francis Group, 2013. – 1391 p.

2 Whitmire K.H. Main group – transition metal cluster compounds of the group 15 elements // Advances in Organometallic Chemistry. – 1998. – Vol. 42. – P. 2-130.

3 Scherer O.J. P_n and As_n ligands: A novel chapter in the chemistry of phosphorus and arsenic // Accounts of Chemical Research. – 1999. – Vol. 32, № 9. – P. 751-762.

4 Peruzzini M., De los Rios I., Romerosa A., Vizza F. Metal-assisted P-H bond formation: a step towards the hydrogenation of white phosphorus // European Journal of Inorganic Chemistry. – 2001. – № 3. – P. 593-608.

5 Scheer M. Metal element triple bonds of the heavier group 15 elements // Coordination Chemistry Reviews. – 1997. – Vol. 163. – P. 271-286.

6 Ehses M., Romerosa A., Peruzzini M. Aggregation and degradation of white phosphorus // Topics in Current Chemistry. – 2001. – Vol. 220. – P. 108-140.

7 Scherer O.J. Complexes with substituent-free scyclic and cyclic phosphorus, arsenic, antimony, and bismuth ligands // Angewandte Chemie-International Edition in English. – 1990. - Vol. 29, Is. 10. – P. 1104-1122.

8 Regitz M., Scherer O.J. Multiple bonds and low coordination in phosphorus chemistry. - Stuttgart: Thieme, 1990. – 478 p.

9 Scherer O.J. Phosphorus, arsenic, antimony, and bismuth multiply bonded systems with low coordination number – their role as complex ligands // Angewandte Chemie-International Edition in English. – 1985. – Vol. 24, № 11. – P. 924-943.

10 Luis P. L., de los Rios I., Peruzzini M. Synthesis and structural properties of mononuclear transition metal complexes containing naked tetraphosphorus, P_4, units as ligand // Phosphorus Research Bulletin. – 2001. – Vol. 12. – P. 167-180.

11 Di Vaira M., Stoppioni P., Peruzzini M. Naked phosphorus atoms and units in transition metal complexes // Polyhedron. – 1987. – Vol. 6, Is. 3. - P. 351-382.

12 Schmidt M.W., Baldridge K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., Koseki S., Matsunaga N., Nguyen K.A., Su S., Windus T.L., Dupuis M., Montgomery J.A. General atomic and molecular electronic structure system // Journal of Computational Chemistry. – 1993. – Vol. 14, Is. 11. – P. 1347-1363.

13 Дорфман Я.А., Абдреимова Р.Р., Левина Л.В., Петрова Т.В. Окислительное алкоксилирование тетрафосфора в присутствии пиридиновых комплексов меди (II,I) // Кинетика и катализ. – 1989. – Т. 30, № 6. – С. 1484-1486.

14 Дорфман Я.А., Абдреимова Р.Р., Левина Л.В., Петрова Т.В. Окисление тетрафосфора куприи купро-хлоридами в спиртовых растворах // Журнал общей химии. – 1989. – Т. 59, № 2. – С. 481-482.

15 Абдреимова Р.Р., Акбаева Д.Н., Фаизова Ф.Х., Айбасова С.М. Окислительное алкоксилирование белого фосфора в присутствии галогенидов Fe(III) // Известия МН-АН РК. Серия химическая. – 1998. – № 4. – С. 65-71.

16 Дорфман Я.А., Абдреимова Р.Р., Акбаева Д.Н. Кинетика и механизм окислительного алкоксилирования тетрафосфора в присутствии сульфатов и карбоксилатов Cu(II) // Кинетика и катализ. – 1995. – Т. 36, № 1. – С. 103-110.

17 Предварительный патент 6280 РК, МПК C07F 9/141. Способ получения триалкилфосфитов / Дорфман Я.А., Абдреимова Р.Р., Полимбетова Г.С., Акбаева Д.Н.; опубл. 15.06.1998.

18 Предварительный патент 6279 РК, МПК C07F 9/141. Способ получения диалкилфосфитов / Дорфман Я.А., Абдреимова Р.Р., Полимбетова Г.С., Акбаева Д.Н.; опубл. 15.06.1998.

19 Фаизова Ф.Х., Акбаева Д.Н., Алиев М.Б., Абдреимова Р.Р. Окисление белого фосфора кислородом в спиртовых растворах синергического $FeCl_3/CuCl_2$ катализатора // Известия НАН РК. Серия химическая. – 2006. – Т. 355, № 1. – С. 27-32.

20 Abdreimova R.R., Akbayeva D.N., Polimbetova G.S., Caminade A.-M., Majoral J.-P. Chlorine free synthesis of organophosphorus compounds based on the functionalization of white phosphrous (P_4) // Phosphorus Sulfur and Silicon and The Related Elements. – 2000. – Vol. 156. – P. 239-254.

21 Schafer A., Horn H., Ahlrichs R. Fully optimized contracted gaussian basis sets for atoms Li to Kr // The Journal of Physical Chemistry A. – 1992. – Vol. 97. – P. 2571.

22 Tulegenov A.S., Kenzhaliev B., Berkinbayeva A., Khusainov I.I. Prediction of thermodynamic stability constants of transition metal complexes // Вестник КазНУ. Серия химическая. – 2015. – № 2. – С. 54-60.

23 Tulegenov A.S, Abramova G.V., Avchukir Kh., Nauryzbayev M.K., Imanbekov K.I. Correlation models in the studies of structure and properties of amides // Вестник КазНУ. Серия химическая. – 2012. – № 2. – С. 164-170.

References

1 Corbridge DEC (2013) Phosphorus. Chemistry, biochemistry and technology. Sixth ed. CRC Press Taylor & Francis Group, New York, USA. ISBN 9781439840887

2 Whitmire KH (1998) Adv Organomet Chem 42:2-130. *https://dx.doi.org/10.1016/s0065-3055(08)60542-0*

3 Scherer OJ (1999) Accounts Chem Res 32:751-762. *https://dx.doi.org/10.1002/chin.199949241*

4 Peruzzini M, De los Rios I, Romerosa A, Vizza F (2001) Eur J Inorg Chem 3:593-608. *https://dx.doi.org/10.1002/1099-0682(200103)2001:3<593::AID-EJIC593>3.0.CO;2-N*

5 Scheer M (1997) Coordin Chem Rev 163:271-286. *http://dx.doi.org/10.1016/S0010-8545(97)00014-3*

6 Ehses M, Romerosa A, Peruzzini M (2001) Top Curr Chem 220:108-140.

7 Scherer OJ (1990) Angew Chem Int Ed 29:1104-1122. *https://dx.doi.org/10.1002/anie.199011041*

8 Regitz M, Scherer OJ (1990) Multiple bonds and low coordination in phosphorus chemistry. Thieme, Stuttgart, Germany. *https://dx.doi.org/10.1002/hc.520040117*

9 Scherer OJ (1985) Angew Chem Int Ed 24:924-943. *https://dx.doi.org/10.1002/anie.198509241*

10 Luis PL, de los Rios I, Peruzzini M (2001) Phosphorus Research Bulletin 12:167-180. *http://doi.org/10.3363/prb1992.12.0_167*

11 Di Vaira M, Stoppioni P, Peruzzini M (1987) Polyhedron 6:351-382. *http://dx.doi.org/10.1016/S0277-5387(00)80993-6*

12 Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347-1363. *http://dx.doi.org/10.1002/jcc.540141112*

13 Dorfman YaA, Abdreimova RR, Levina LV, Petrova TV (1989) Kinet Catal+ 30:1484-1486. (In Russian)

14 Dorfman YaA, Abdreimova RR, Levina LV, Petrova TV (1989) Russ J Gen Chem 59:481-482. (In Russian)

15 Abdreimova RR, Akbayeva DN, Faizova FKh, Aibassova SM (1998) News of NAS RK. Series chemistry and technology [Izvestiya NAN RK. Seriya himicheskaya] 310:65-71. (In Russian)

16 Dorfman YaA, Abdreimova RR, Akbaeva DN (1995) Kinet Catal+ 36:103-110. (In Russian)

17 Dorfman YaA, Abdreimova RR, Polimbetova GS, Akbayeva DN (2008) A method for trialkylphosphites obtaining [Sposob polucheniya trialkylphosphitov]. Preliminary Patent of the Republic of Kazakhstan No. 6280 [Predvaritelnyi patent Respubliki Kazakhstan Nomer 6280]. (In Russian)

18 Dorfman YaA, Abdreimova RR, Polimbetova GS, Akbayeva DN (1998) A method for dialkylphosphites obtaining [Sposob polucheniya dialkylphosphitov]. Preliminary Patent of the Republic of Kazakhstan No. 6279 [Predvaritelnyi patent Respubliki Kazakhstan Nomer 6279]. (In Russian)

19 Faizova FKh, Akbayeva DN, Aliev MB, Abdreimova RR (2006) News of NAS RK. Series chemistry and technology [Izvestiya NAN RK. Seriya himicheskaya] 355:27-32. (In Russian)

20 Abdreimova RR, Akbayeva DN, Polimbetova GS, Caminade AM, Majoral JP (2000) Phosphorus Sulfur 156:239-254. *http://dx.doi.org/10.1080/10426500008045007*

21 Schafer A, Horn H, Ahlrichs RJ (1992) Chem Phys 97:2571. *http://dx.doi.org/10.1063/1.463096*

22 Tulegenov AS., Kenzhaliev B, Berkinbayeva A, Khusainov II (2015) Chemical Bulletin of Kazakh National University 2:54-60. *http://dx.doi.org/10.15328/cb638*

23 Tulegenov AS, Abramova GV, Avchukir Kh, Nauryzbayev MK, Imanbekov KI (2012) Chemical Bulletin of Kazakh National University 2:164-170. *http://dx.doi.org/10.15328/chemb_2012_2164-170*