

- Эфрос, Л. С. Химия и технология ароматических соединений в задачах и упражнениях [Текст] / Л. С. Эфрос, И. Я. Квитко. – Л.: Химия, 1971. – 496с.
- Герчиков, А. Я. Кинетика окисления метилэтилкетона озонированным кислородом в водных растворах [Текст] / Герчиков А. Я., Курамшин Э. М., Комиссаров В. Д., Денисов Е. Т. // Кинетика и катализ. – 1974. – Т. 15, № 1. – С. 230-232.
- Герчиков, А. Я. Кинетика и продукты окисления метилэтилкетона озонированным кислородом в растворе четыреххлористого углерода [Текст] / Герчиков А. Я., Комиссаров В. Д., Денисов Е. Т., Кочемасова Г. Б. // Кинетика и катализ. – 1972. – Т. 13, № 5. – С. 1126-1130.
- Комиссарова, И. Н. Механизм окисления бензальдегида озонированным кислородом [Текст] / И. Н. Комиссарова, В. Д. Комиссаров, Е. Т. Денисов // Изв. АН СССР. Сер. хим. – 1978. - №9. – С. 1991-1996.
- Комиссаров, В.Д. Цепное разложение озона в системе $\text{CH}_3\text{CHO}-\text{O}_3-\text{O}_2$ [Текст] / В. Д.Комиссаров, И. Н.Комиссарова, Г. К.Фаррахова, Е. Т.Денисов // Изв.АН СССР сер.хим.-1979, № 6.-С.1205-1212.
- Розумовський, С. Д. Озон та його реакції з аліфатичними сполуками [Текст] / С. Д. Розумовський, Г. А. Галстян, М. Ф. Тюпало. – Луганськ: ВУНУ, 2000. – 272 с.
- Эммануэль, Н. М. Цепные реакции окисления углеводов в жидкой фазе [Текст] / Н. М. Эмануэль, Е. Т. Денисов, З. К. Майзус. – М. : Наука, 1965. – 375 с

Встановлено, що дегідратація 2,3 диметилбутан 2,3-діолу (ДО) проходить за двома послідовними стадіями: за першою в результаті відщеплення однієї молекули води утворюється проміжний продукт – 2,3 диметилбут 3 ен 2 ол, а за другою – при відщепленні ще однієї молекули води отримують 2,3 диметилбута 1,3 дієн (ДМБ).

Дегідратація гексагідрату 2,3 диметилбутан 2,3-діолу протікає в присутності молекул води, в результаті чого суттєво знижується енергетичний бар'єр реакції

Ключові слова: 2,3-Диметилбутан-2,3-діол / 2,3-Диметилбута-1,3-дієн / Квантово-хімічні розрахунки / МОРАС2009 / Winmostar / RM1

Установлено, что дегидратация 2,3 диметилбутан-2,3-диола (ДО) происходит в две последовательные стадии: в первой в результате отщепления одной молекулы воды образуется промежуточный продукт – 2,3 диметилбут-3-ен-2-ол, во второй – при отщеплении ещё одной молекулы воды получают 2,3 диметилбута-1,3-диен (ДМБ).

Дегидратация гексагидрата 2,3 диметилбутан- 2,3-диола протекает в присутствии молекулы воды, в результате чего существенно снижается энергетический барьер реакции

Ключевые слова: 2,3 диметилбутан-2,3-диол / 2,3 диметилбута-1,3-диен / квантово-химические расчеты / МОРАС2009 / Winmostar / RM1

UDC: 547.422.26, 66.093.48

QUANTUM-CHEMICAL RESEARCH OF MECHANISM OF THE REACTION DEHYDRATION OF 2,3-DIMETHYLBUTAN-2,3-DIOL AND IT'S HEXAHYDRATE

Ya. P. Kovalskiy

Research worker*

E-mail: yakovalskiy@polynet.lviv.ua

I. S. Kostiv

PHD student*

E-mail: kostiv.irina@gmail.com

O. I. Marshalok

Candidate of chemical sciences, an assistant

Department physical chemistry**

E-mail: ostoya@in.lviv.ua

N. M. Vytrykush

Candidate of engineering sciences, an assistant*

E-mail: natakarpiak@mail.ru

*Department analytical chemistry**

**Institute of chemistry and chemical technologies

National university Lviv Polytechnic

str. S.Bandery, 12, Lviv, Ukraine,79013

1. Introduction

2,3-Dimethylbuta-1,3-diene is the starting reagent and valuable monomer in organic synthesis used for the plastics producing, including metyl-rubbers. The alkylcyclohexen

derivatives, which can be widely used in chemical, perfume and food industries are received as a result of cyclization of this diene with alkylacroleins and alkylacrylics.

Both in laboratory practice and in industry the technologically perspective method of DMB receiving during

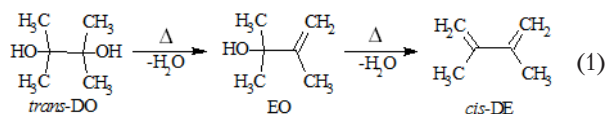
the catalytic dehydration of 2,3-dimethylbutane-2,3-diol is considered to be the one, to which the major attention is paid. [1 – 3]. Industrially available acetone is considered to be the original stuff in this process, which turns into 2,3-dimethylbutane-2,3-diol hexahydrate by reduction. The 2,3-dimethylbutane-2,3-diol hexahydrate is dehydrated by azeotropic rectification with benzene [4].

2. Purpose of work

In this work the quantum-chemical investigation of mechanism of 2,3-dimethylbutane-2,3-diol dehydration was conducted for the sake of the opportunity to identify the possibility of hexahydrate 2,3-dimethylbutane-2,3-diol usage without stage of prior dehydration.

3. Method of quantum-chemical calculations

The dehydration process of 2,3-dimethylbutane-2,3-diol (DO), or its industrially available analogue - hexahydrate 2,3-dimethylbutane-2,3-diol is endothermic. It is conducted in the result of heating and leads to creating of one water molecule and intermediate compound of 2,3-dimethylbut-3-en-2-ol (enol, EO) and is accompanied by subsequent splitting of another water molecule from EO and by 2,3-dimethylbuta-1, 3-diene (diene, DE) creating [5] (Fig. 1):



The quantum-chemical modelling of 2,3-dimethylbutane-2,3-diol (DO) and its hexahydrate dehydration was carried out by semiempirical program MOPAC2009 [6] and the graphic interface Winmostar [7]. Geometry optimization, at the same time as calculation of heats of molecular structures formation and activation systems in transition states of the reaction system were carried out by semiempirical method RM1 using unrestricted Hartree-Fock (UHF) with the coefficient for energy rationing (GNORM) within 0.01-0.5 kcal/mol. The dependence of system potential energy determination from coordinate of the reaction were conducted with the step of 0.02 Å (STEP = -0.02).

4. Results and Discussion

In Table 1 we can see energetic parameters for reactants and products of 2,3-dimethylbutane-2,3-diol dehydration (Fig. 1), i.e. heat of formation ($\Delta_f H^{298}$), electron energy (Eel), core-core repulsion energy (Ecore), dipole moment (D) and ionization potential (I).

The 2,3-dimethylbutane-2,3-diol dehydration is conducted through two consecutive stages. Fig. 1 gives energy profiles of two stages of dehydration. Figure 2 shows the reaction conditions model of it.

At the first stage the hydrogen atom H(11) comes to the hydroxy group atom of oxygen O(7) creating at the same time the tense of four membered rings C(1) N(11) O(7) C(2) (transitional state TS1), destruction of which leads to

creating of the enol EO and water molecule (state EO+H₂O). At the second stage, in the enol EO molecule, the hydrogen atom H(20) comes to the another hydroxy group atom of oxygen O(8) creating the strained four-membered rings C(6) H(20) O(8) C(3) (transitional state TS2) destruction of which leads to the splitting of the second water molecule and diene formation (state DE+2H₂O).

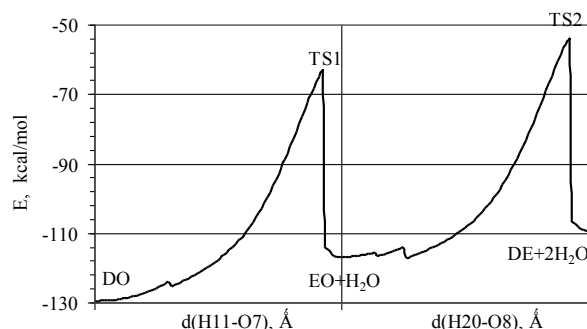


Fig. 1. Energy profiles of two stages of anhydrous diol DO dehydration

Table 1

Energy parameters of reactants for dehydration of anhydrous diol DO

Parameters	DO	EO	H ₂ O	DE
$\Delta_f H^{298}$, kcal/mol	-129.5	-57.7	-57.9	10.7
E _{el} , eV	-7774.75	-5675.30	-489.18	-3854.52
E _{core} , eV	6189.13	4435.86	143.61	2961.12
D, D	0.00	1.73	1.87	0.53
I, eV	10.73	9.58	12.26	9.22

As it has been shown at the graphic of diol DO dehydration energy profiles (Fig. 1) and in the data table 2 the difference between the power of formation of enol EO and diene DE molecular structure is positive what indicates on endothermic reaction. At the same time, the energy barriers of both stages are proportionate 65.6 and 61.8 kcal/mol, respectively.

$$\Delta_f H^{298} = 129.5 - 63.9 = 65.6 \text{ kcal/mol}$$

$$\Delta_f H^{298} = 117.2 - 55.4 = 61.8 \text{ kcal/mol}$$

Energy released value is about 54 kcal / mol, which is equal to the power of water molecule formation (Table 1).

$$\Delta_f H^{298} = 109.4 - 55.4 = 54 \text{ kcal/mol}$$

In addition, the formation of the transition state for these reactions goes closer to of the products formation and has the late character [8, 9]. This indicates that the destruction of C-H bond and the formation of O-H bond (transition the hydrogen atom from methyl group to the hydroxy group atom of oxygen) is faster than the destruction of O-C bond of enol with the formation of C=C bond of diene at once.

The water molecule H(11) O(7) H(21) are placed accordingly to enol molecule in such a way that it leads to the formation of the intermolecular complex EO:H₂O due to weak (C(6)-H(20) ... O(7)) and medium (O(7)- H(21) ... O(8)) hydrogen bonds (Fig. 3) [10].

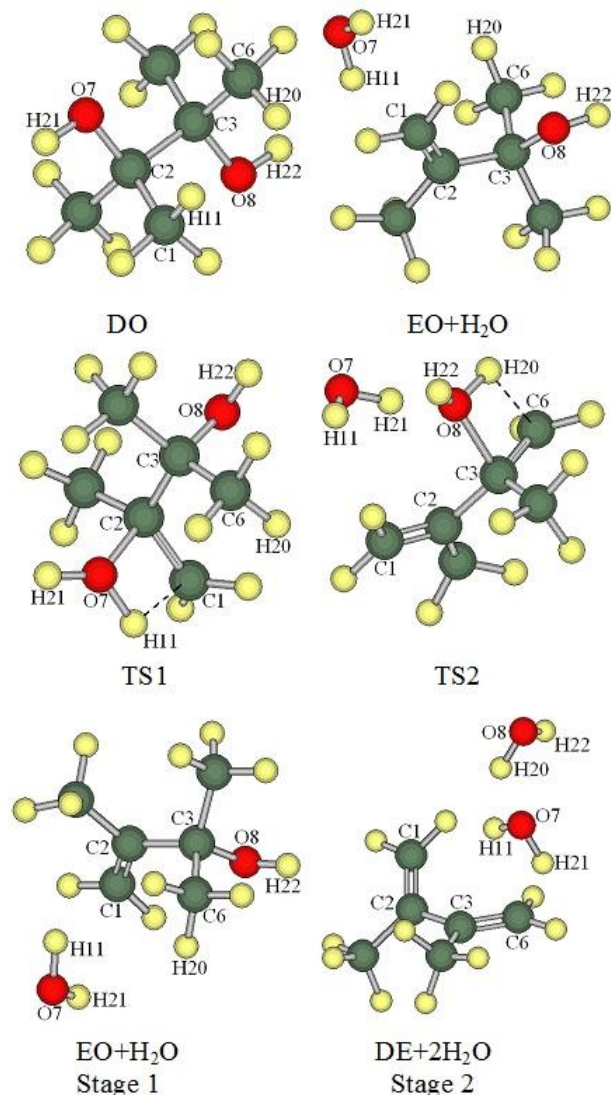


Fig. 2. Models of reaction states of anhydrous diol DO dehydration

Its formation is confirmed by the heat decreasing of formation state of EO: H₂O in comparison with the state of EO + H₂O after the first stage (Table 2).

The enol dehydration reaction modelling in the presence of water molecule (state EO : H₂O) was performed in the realm of two reaction coordinates $d(H(20)-O(7))$ and $d(H(21)-O(8))$ with the step of -0.02 \AA and potential energy of the reaction system was determinate at each point (Fig. 4).

At fig. 4 we can see that the enol dehydration, in the presence of water molecule, (state EO : H₂O) can be conducted as the concerted mechanism, when at the same time, up to achieving the saddle point transition state TS2 (H₂O), three pairs of bonds- (H(20)-O(7)), H(21)-O(8), C(6)-C(3)) - are being formed and three other pairs - (H(20)-C (6), H(21)-O(7), O(8)-C(3)) - are being decomposed, (Fig. 3). The formation of the transition state of this reaction also has the late character. We can judge about it by analysing smooth transforming bond order of atoms pairs reaction from the original (state EO: H₂O) to the transition state TS2 (H₂O) and by quickly transformation to the final products of the reaction DE (2H₂O) (Table 2). Pay attention that energy barrier of this stage (55.6 kcal/mol) is

significantly lower than the barrier of corresponding stage without water molecule (TS2).

$$\Delta_f H^{298} = 117.8 - 62.2 = 55.6 \text{ kcal/mol}$$

This indicates that water molecule H(11) O(7) H(21) in six membered ring transition state TS2 (H₂O) (Fig. 3) reduces ring tension in comparison with the four membered transition state TS2 (Fig. 1) for 6.2 kcal / mol.

$$\Delta_f H^{298} = 63.9 - 57.7 = 6.2 \text{ kcal/mol}$$

In the transition state TS2 (H₂O) it acts as an element of transmission. So, the atom of hydrogen H(20) from atom C(6) methyl group becomes the atom of oxygen O(7) and the atom of hydrogen H(21) transmits to atom of oxygen O(8) of enol molecule hydroxy group.

The dehydration of diol DO hexahydrate also runs in two stages, but, unlike dehydration of anhydrous diol DO, it is performed in the presence of water (DO:H₂O).

Table 2

Heat of formation ($\Delta_f H^{298}$, kcal / mol) and bonds order (n) for reactions states of anhydrous diol dehydration

Parameter	Reaction state							
	DO	TS1	EO+H ₂ O	TS2	DE+H ₂ O	EO:H ₂ O	TS2 (H ₂ O)	DE (2H ₂ O)
$\Delta_f H^{298}$	-129.5	-63.9	-117.2	-55.4	-109.4	-117.8	-62.2	-109.6
n(C2-C1)	0.968	1.342	1.944	1.938	1.931	1.948	1.928	1.917
n(C3-C2)	0.927	0.935	0.953	0.966	0.989	0.954	0.973	0.995
n(C4-C3)	0.968	0.964	0.964	0.980	0.996	0.962	0.986	0.996
n(C5-C2)	0.968	0.984	0.997	0.995	0.995	0.997	0.997	0.996
n(C6-C3)	0.968	0.968	0.959	1.319	1.922	0.962	1.267	1.924
n(O7-C2)	0.984	0.531	0.002	0.001	0.001	0.001	0.001	0.001
n(O8-C3)	0.984	0.985	0.986	0.537	0.000	0.981	0.470	0.001
n(H11-C1)	0.982	0.312	0.001	0.001	0.001	0.001	0.000	0.000
n(H20-C6)	0.982	0.979	0.981	0.318	0.000	0.982	0.297	0.000
n(H11-O7)	0.001	0.591	0.959	0.959	0.953	0.958	0.946	0.961
n(H20-O7)	0.000	0.000	0.000	0.000	0.002	0.000	0.563	0.951
n(H21-O7)	0.937	0.868	0.961	0.958	0.958	0.961	0.392	0.001
n(H20-O8)	0.001	0.001	0.001	0.577	0.959	0.001	0.008	0.001
n(H21-O8)	0.001	0.000	0.000	0.001	0.001	0.001	0.483	0.959
n(H22-O8)	0.937	0.937	0.936	0.875	0.959	0.935	0.933	0.960

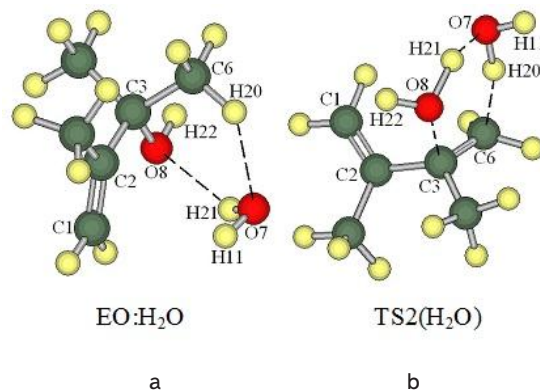


Fig. 3. Models of initial a - (EO: H₂O) and transitional b - (TS2 (H₂O)) states of enol EO dehydration in the presence of water molecule

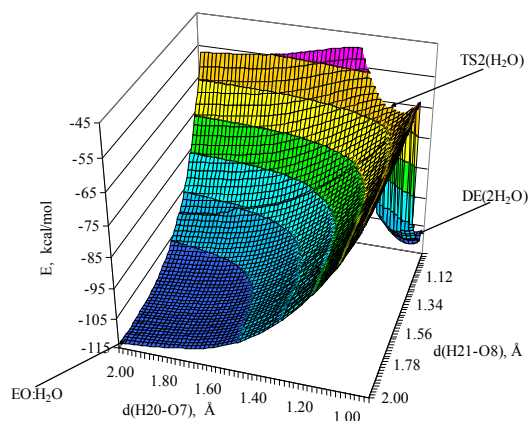


Fig. 4. Potential energy surface of enol dehydration in the presence of water molecule (EO: H₂O)

Water molecule of anhydrous diol DO:H₂O, similar to the dehydration of enol EO: H₂O water complex (Fig. 3), in both cases acts as an atom of hydrogen transmission element from the methyl group of DO through water hydroxy group atom of oxygen to the DO hydroxyl atom of oxygen. As a result less tense six membered ring (Fig. 5) was created comparing to much more tense four membered ring (Fig. 2 (TS1)).

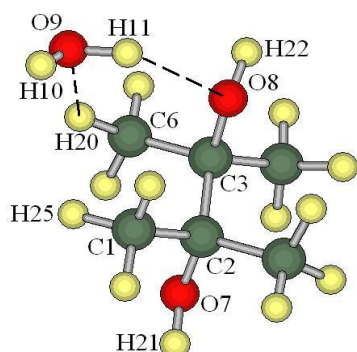


Fig. 5. Model of hydrated diol (DO: H₂O)

The creating of TS1 (H₂O) and TS2 (2H₂O) transition states (Fig. 6) of two stages hydrated diol DO:H₂O dehydration also runs by the concerted mechanism, as for complex EO:H₂O (Fig. 4), and potential energy surfaces for both stages also have the saddle points, energy barriers of which correspond to some transitional states (Table 3).

Energy barriers, during both stages of transition creating (first stage - TS1 (H₂O) from the initial complex DO : H₂O; second stage - TS2 (2H₂O from the intermediate complex EO: 2H₂O)) are 54.4 and 56.5 kcal / mol, respectively.

$$\Delta_f H^{298} = 184.2 - 129.8 = 54.4 \text{ kcal/mol}$$

$$\Delta_f H^{298} = 176.0 - 119.5 = 56.5 \text{ kcal/mol}$$

These values are significantly lower than the energy barriers of TS1 and TS2 stages of anhydrous diol DO dehydration (65.6 and 61.8 kcal/mol, respectively). This fact indicates that obtaining 2,3-dimethylbuta-1,3-diene from the 2,3-dimethylbutane-2,3-diol hydrated by its dehydration

instead of anhydrous 2,3-dimethylbutane-2,3-diol is more favoured.

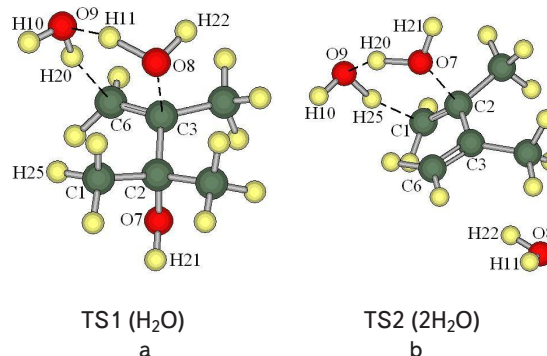


Fig. 6. Models of : a - TS1 (H₂O) and b - TS2 (2H₂O) transition states of two stages hydrated diol DO: H₂O dehydration

Table 3
Heats of molecular structures and transition states ($\Delta_f H^{298}$, kcal / mol) formation and bonds order (n) of two stages hydrated diol DO: H₂O dehydration

Parameter	Reaction state					
	DO: H ₂ O	TS1(H ₂ O)	EO+ 2H ₂ O	EO: 2H ₂ O	TS2(2H ₂ O)	DE+ 3H ₂ O
$\Delta_f H^{298}$	-184.2	-129.8	-178.2	-176.0	-119.5	-171.3
n(C2-C1)	0.967	0.968	0.959	0.962	1.262	1.927
n(C3-C2)	0.927	0.934	0.953	0.955	0.976	0.994
n(C4-C3)	0.970	0.987	0.998	0.996	0.996	0.996
n(C5-C2)	0.966	0.967	0.964	0.962	0.986	0.995
n(C6-C3)	0.970	1.293	1.944	1.948	1.928	1.922
n(O7-C2)	0.986	0.983	0.984	0.980	0.468	0.000
n(O8-C3)	0.972	0.461	0.000	0.000	0.000	0.000
n(H25-C1)	0.980	0.981	0.983	0.982	0.306	0.000
n(H20-C6)	0.961	0.290	0.002	0.000	0.001	0.000
n(H20-O7)	0.000	0.000	0.000	0.001	0.478	0.956
n(H21-O7)	0.936	0.936	0.937	0.934	0.936	0.957
n(H11-O8)	0.014	0.495	0.959	0.965	0.965	0.957
n(H22-O8)	0.933	0.936	0.960	0.965	0.964	0.958
n(H10-O9)	0.963	0.946	0.961	0.957	0.946	0.956
n(H11-O9)	0.936	0.381	0.001	0.000	0.000	0.000
n(H20-O9)	0.011	0.571	0.951	0.961	0.398	0.002
n(H25-O9)	0.000	0.000	0.000	0.000	0.554	0.950

5. Conclusions

In this work it has been established that in the result of quantum-chemical research the anhydrous mechanism of dehydration of 2,3-dimethylbutane-2,3-diol and its hexahydrate is passed two consecutive stages. The reaction is proceeded in the presence of water, which makes the transmission of methyl group atom of hydrogen to the DO hydroxyl atom of oxygen in the case of using hexahydrate DO for dehydration. This effect of transmission significantly reduces energy barriers stages of hydrated DO dehydration, in comparison with the anhydrous.

References

1. Potapova, V. M. Organikum. Workshop on Organic Chemistry [Text] / V. M. Potapova, S. V. Ponomarev. – Moscow, Publishing house Mir, 1979. – Vol. 2. – 121 p.
2. Francis, A. Organic Chemistry [Text] / A. Francis. – Ed. 7. – New York, NY 10020. Copyright. – 2007. – 1245 p.
3. George, S. Modern Organic Synthesis - An Introduction [Text] / S. George, H. Michael. – 2007. – 504 p.
4. Vaculyk, P. Chemistry of monomers v.1 translation from czech [Text] / P. Vaculyk. – M.: Publishing house IL, 1960. – 738 p.
5. Allen, C. F. H. Org. Synth. 2,3-dimethylbutadien [Text] / C. F. H. Allen, A. Bell // Synthesis of organic substances. – Publishing house foreign literature. – Moscow, 1952. – P. 189-191.
6. Stewart, J. J. P., Program Package MOPAC2009 [Electronic resource] / J. J. P. Stewart. – Available: \www/ URL: http://www.openmopac.net.
7. Senda, N. Program Package Winmostar [Electronic resource] / N. Senda. – Available: \www/ URL: http://winmostar.com.
8. Uryadov, V. G. Chemistry and computer modeling [Text] / V. G. Uryadov, E. N. Oficerov // Butlerov messages. – 2003. – № 1. – P. 1-8.
9. Jensen, F. Introduction to Computational Chemistry [Text] / F. Jensen // Wiley. – 2006. – 620 p.
10. Steiner, T. The hydrogen bond in the solid state [Text] / T. Steiner // Angew. Chem. Int. Ed. – 2002. – № 41. – P. 48.

Досліджено закономірності адіабатичного нітрування бензолу до нітробензолу з одночасною відгонкою продуктів реакції. Вивчено вплив на склад рідкої і парової фаз на виході: мольного вхідного співвідношення бензол - азотна кислота, тиску в системі, температури маси на вході. Показано, що проведення процесу під залишковим тиском дозволяє повністю перевести продукти в парову фазу за рахунок теплоти реакції

Ключові слова: адіабатичне нітрування, бензол, математична модель, склад фаз, тиск, температура, концентрація

Исследованы закономерности адиабатического нитрования бензола до нитробензола с одновременной отгонкой продуктов реакции. Изучено влияние на состав жидкой и паровой фаз на выходе: мольного входного соотношения бензол – азотная кислота, давления в системе, температуры массы на входе. Показано, что проведение процесса под остаточным давлением позволяет полностью перевести продукты в паровую фазу за счет теплоты реакции

Ключевые слова: адиабатическое нитрование, бензол, математическая модель, состав фаз, давление, температура, концентрация

УДК 66.095.81

МОДЕЛИРОВАНИЕ НЕПРЕРЫВНОГО АДИАБАТИЧЕСКОГО НИТРОВАНИЯ БЕНЗОЛА

А. А. Красильникова
Аспирант*

E-mail: krasina@list.ru

С. А. Кондратов

Доктор химических наук,
профессор, заведующий кафедрой
Кафедра высшей математики
и компьютерной технологии*

E-mail: kondratovsa@gmail.com

*Институт химических технологий

Восточноукраинского национального университета
им. Владимира Даля (г.Рубежное)
ул. Ленина, 31, г. Рубежное,
Луганская область, Украина, 93010

1. Введение

Нитробензол – важнейший продукт промышленного органического синтеза, основа для дальнейшего получения полимеров, красителей, лекарственных препаратов, взрывчатых веществ [1]. Мировой объем производства нитробензола превышает 2,5 млн тонн [2] и имеет тенденцию дальнейшего возрастания. Технология нитробензола характеризуется сравнительно высокой энергоемкостью, образованием значительного количества отходов: газовых выбросов и сточных вод, подлежащих очистке. Разработка новых подходов к

совершенствованию технологии этого продукта, основанная на использовании современных методов, в том числе, математического моделирования, является актуальной проблемой.

2. Анализ литературных данных и постановка проблемы

Все существующие на сегодняшний день подходы к разработке технологии получения нитробензола базируются, в основном, на реакции нитрования бензола азотной кислотой: