UDC 547.52/59.66-9

STUDY OF THE ARYLATION REACTION OF ETHYLENE BY TOLUENE**A.M.Aliyev, G.A.Ali-zadeh, M.G.Aliyeva, S.R.Mamedova, R.Yu.Agayeva***M.Nagiev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**ali-zadegula@mail.ru*

Received 26.01.2019

The arylation reaction of ethylene by toluene has been studied in the liquid phase with the using of the homogeneous catalytic system $\text{Pd}(\text{OAc})_2 + \text{Cu}(\text{OAc})_2 + \text{PPh}_3$, in the semibatch flask reactor under atmospheric pressure. Optimum conditions for the reactions were as follows: mole ratio of the components of the catalytic system $\text{Pd}(\text{OAc})_2 : \text{Cu}(\text{OAc})_2 : \text{PPh}_3 = 1:2:0.03$, concentration of the active mass of the catalytic system, $[\text{Pd}(\text{OAc})_2] = 6 \cdot 10^{-2} \div 10^{-3}$ mol/l, temperature $(95 \div 105)^\circ\text{C}$. In these conditions the yield of vinyltoluene is $(5 \div 8)$ wt.%. It has been proposed as a possible mechanism for the reaction including the formation of the intermediate complexes of palladium acetate with toluene, ethylene and triphenyl phosphine.

Keywords: arylation, ethylene, toluene, vinyltoluene, palladium acetate, triphenyl phosphine.

doi**Introduction**

The reaction of olefins arylation in the presence of salts of group VIII metals, an arylating agent (aryl-Hg-halide), was carried out first by Heck [1].

In works [2–11] it has been shown that not only metal organic but pure organic compounds as well, in particular aromatic hydrocarbons, may serve as donors of the aryl groups in the substitution reactions of olefins. It has been estimated [12] that addition of $\text{Cu}(\text{OAc})_2$ and AgOAc to the reaction mixture and in the presence of oxygen turns it in to a catalytic one at the expense of Pd^0 of regeneration reduction. The yield of alkenylaromatic hydrocarbons in this case does not exceed ~130 mol % based on $\text{Pd}(\text{OAc})_2$ in 8–10 hours. The low yield of alkenylaromatic hydrocarbons and settling out of the metal Pd^0 in the course of the reaction are the principal shortcomings of this process.

In the present work the problem on intensification of the reaction of ethylene arylation by toluene in the presence of the catalytic system $\text{Pd}(\text{OAc})_2 + \text{Cu}(\text{OAc})_2$ by means of addition of $\text{P}(\text{Ph})_3$ into the reaction mixture has been discussed and the mechanism of the reaction has been proposed as well.

Experimental part

The experimental study of the reaction of ethylene arylation by toluene was carried out in

the flask of 75 cm³ capacity, equipped with a high speed agitator, a reflux condenser and a thermometer. Ethylene and oxygen were introduced in to the reactor through a barbotage. To maintain the reaction temperature constant the reactor was placed into a glycerine bath, the temperature of which was controlled thermostatically to within $\pm 0.5^\circ\text{C}$.

Distilled and dried toluene was used as the original aromatic hydrocarbon. Ethylene and oxygen, before entering to the reactor, passed through several tubes filled with activated carbon, silica gel and calcium chloride.

$\text{Pd}(\text{OAc})_2$ was prepared from porous Pd and glacial acetic acid in the presence of concentrated nitric acid according to Wilkinson and co-authours [13].

The reaction mixture was filtered removing the catalyst in reverse. The filtrate was washed twice with distilled water removing the acetic acid. The organic layer was dried with anhydrous sodium sulphate and analysed using a gas-liquid chromatograph with a heat conductivity detector and a 3.5 m long packed column filled with spherochromium supporting polyethylene glycolsuccinate. Flow rate, at the inlet pressure 3.2 atm of the carrier-gas (helium), was 3 l/hour, temperature of the column was 90°C .

Results and discussion

A number of experiments have been carried out to estimate the effect of temperature,

ratio of the catalytic system, components of partial pressure of ethylene and oxygen, concentration of $\text{Pd}(\text{OAc})_2$ and $\text{P}(\text{Ph})_3$ upon the arylation reaction of ethylene by toluene.

There has been shown in Figure 1 a dependence of the vinyltoluenes yield on the reaction temperature at the molar ratio of components of the catalytic system $\text{Pd}(\text{OAc})_2:\text{Cu}(\text{OAc})_2:\text{P}(\text{C}_6\text{H}_5)_3=1:2:0.03$, partial pressure $p_{\text{C}_2\text{H}_4}=0.3$ atm, $p_{\text{O}_2}=0.2$ atm and concentrations of acetic acid and toluene in the reaction mixture $11.12 \cdot 10^{-3}$ mol/l and $3.42 \cdot 10^{-3}$ mol/l, respectively. The flow rate of gas mixture was 3.5 l/hour.

From Figure 1 it follows that an increase of temperature from 50 up to 105°C results an increase in of yields vinyltoluenes and 4,4-dimethylstilbene.

Further increases in temperature result in a sudden decrease of the reaction product yields. It may be explained by the lability of the intermediary complexes at high temperatures.

On the basis of the above one may draw the conclusion that 105°C is the optimum temperature at which the reaction may be realized.

Fig. 1. Dependence of the vinyltoluenes and 4,4-dimethylstilbene yields on the reaction temperature. 1, 2, 3 – yields of vinyltoluenes in 2, 4 and 8 hours respectively, 1', 2', 3' – yields of 4,4-dimethylstilbene in 2, 4 and 8 hours respectively; $[\text{Pd}(\text{OAc})_2]=6.0$ mol/l, $p=1$ atm, $p_{\text{N}_2}=0.5$ atm.

As it is seen from Figure 2 the maximum yields of vinyltoluene and 4,4'-dimethylstilbene occurs at a molar ratio $\text{Pd}(\text{OAc})_2:\text{Cu}(\text{OAc})_2=1:2$. Low yields of the reaction products at upper molar ratios than 1:2 may be explained by an insufficient amount of $\text{Cu}(\text{OAc})_2$ to assure reoxidation of the recovered Pd.

At molar ratios less than 1:2, the yield of vinyltoluenes and 4,4-dimethylstilbene decreases, probably stimulated by blocking of $\text{Pd}(\text{OAc})_2$ molecules by $\text{Cu}(\text{OAc})_2$ molecules.

Dependence of the vinyltoluene yield on ethylene partial pressure is shown in Figure 3. It follows from this plot that an increase of the ethylene partial pressure from 0 to 0.6 atm results in an abrupt increase of vinyltoluenes. Further increases in the ethylene partial pressure have almost no effect upon the reaction products yield.

This may be explained by the fact that ethylene, dissolved in the reaction mixture, participates in the reaction and an increase in the partial pressure above 0.6 atm has little effect upon the dissolving of ethylene.

Effect of the partial pressure of oxygen upon vinyltoluene yield is shown in Figure 4.

Fig. 2. Dependence of the vinyltoluenes and 4,4-dimethylstilbene yields on mole ratio $[\text{Pd}(\text{OAc})_2]/[\text{Cu}(\text{OAc})_2]$; $T=105^\circ\text{C}$, $[\text{Pd}(\text{OAc})_2]=6.0$ mol/l; $[\text{Pd}(\text{OAc})_2]/[\text{PPh}_3]=1:0.03$, $p_{\text{C}_2\text{H}_4}=0.3$ atm, $p_{\text{O}_2}=0.2$ atm (symbols as for Figure 1).

Fig. 3. Dependence of the vinyltoluenes yields on ethylene partial pressure; $P = 1$ atm, $T=105^{\circ}\text{C}$, $p_{\text{N}_2} = 0$ (the other parameters of the process and symbols as for Figure 1).

Fig. 4. Dependence of the vinyltoluenes yields on oxygen partial pressure. $T= 105^{\circ}\text{C}$, $p_{\text{N}_2}=0$, $P=1$ atm (the other parameters of the process and symbols as for Figure 1).

A partial pressure of oxygen of 0.2 atm corresponds to the maximum of these curves, after which vinyltoluene yield abruptly decreases. The shape of these curves is explained by the fact that at high partial pressures of oxygen the reaction proceeds mainly with the formation of benzyl alcohol and benzyl ether.

To estimate effect of the active component concentration on the arylation reaction of ethylene by toluene, a number of experiments were carried out under the optimum conditions shown above. The results of these experiments are shown in Figure 5, from which it follows that vinyltoluene and 4,4'-dimethylstilbene yields increase with rise in $\text{Pd}(\text{OAc})_2$ concentration up to 10^{-3} mol/l. Further increases in the concentration of the catalyst active mass do not effect on the yields of the reaction products. Such a dependence is explained evidently by the fact that the palladium complex dissolved in the reaction mixture catalyzes the ethylene arylation reaction by toluene and the highest rate of olefins arylation might be observed in the

saturated solution of the palladium complex. If the reaction is catalyzed by a suspended catalyst then the contacting surface increases with increases in its concentration in the reaction mixture and the yield of arylaromatic products should increase, that is, not seen on the basis of the experimental data.

The curves showing the dependence of vinyltoluene yields upon $\text{P}(\text{Ph})_3$ concentration after 2, 4, 6, 8 and 10 hours usage of the catalyst are shown in Figure 6. It follows from the figure that the maximum yields of vinyltoluenes in all the cases are obtained when the $\text{P}(\text{Ph})_3$ concentration is equal to $2 \cdot 10^{-3}$ mol/l. Low yields of vinyltoluenes, when the concentration of $\text{P}(\text{Ph})_3$ is above $2 \cdot 10^{-3}$ mol/l, may be explained by blocking of $\text{Pd}(\text{OAc})_2$ molecules by $\text{P}(\text{Ph})_3$ molecules.

On the basis of data available in literature on the intermediate complexes of the palladium salts with aromatic hydrocarbons, ethylene and $\text{P}(\text{Ph})_3$, we have suggested a possible mechanism for the liquid phase ethylene arylation by toluene in the presence of $\text{P}(\text{Ph})_3$:

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ETİLENİN TOLUOLLA ARILLƏŞDİRMƏ REAKSİYASININ ÖYRƏNİLMƏSİ**A.M.Əliyev, G.Ə.Əli-zadə, M.Q.Əliyeva, S.R.Məmmədova, R.Y.Ağayeva**

Etilenin toluolla arilləşdirmə reaksiyası atmosfer təziyində, yarım fasiləsiz reaktorda, maye-fazada, homogen katalitik sistemin iştirakı ilə $\text{Pd}(\text{OAc})_2 + \text{Cu}(\text{OAc})_2 + \text{PPh}_3$ öyrənilmişdir. Katalitik sistemin aktiv tərkibi, mol nisbəti $\text{Pd}(\text{OAc})_2 : \text{Cu}(\text{OAc})_2 : \text{PPh}_3 = 1:2:0.03$, katalitik sistemin aktiv kütləsinin konsentrasiyası $[\text{Pd}(\text{OAc})_2] = 6 \cdot 10^{-2} \div 10^{-3} \text{ mol/l}$, reaksiyanın temperaturu $(95 \div 105)^\circ\text{C}$ təyin edilmişdir. Bu şəraitdə viniltoluolun çıxımı $5 \div 8$ çək.% təşkil edir. Reaksiya zamanı asetat palladiumla toluol, etilen və trifenilfosfatla əmələ gələn aralıq komplekslər daxil olmaqla, reaksiyanın ehtimal olunan mərhələli mexanizmi təklif edilmişdir.

Açar sözlər: arilləşdirmə, etilen, toluol, viniltoluol, asetat palladium, trifenilfosfat.

ИЗУЧЕНИЕ РЕАКЦИИ АРИЛИРОВАНИЯ ЭТИЛЕНА ТОЛУОЛОМ**А.М.Алиев, Г.А.Али-заде, М.Г.Алиева, С.Р.Мамедова, Р.Ю.Агаева**

При атмосферном давлении в полунепрерывном реакторе, в жидкой фазе, в присутствии гомогенной каталитической системы $\text{Pd}(\text{OAc})_2 + \text{Cu}(\text{OAc})_2 + \text{PPh}_3$ изучена реакция арилирования этилена толуолом. Найден активный состав каталитической системы в мольных соотношениях $\text{Pd}(\text{OAc})_2 : \text{Cu}(\text{OAc})_2 : \text{PPh}_3 = 1:2:0.03$, концентрация активной массы каталитической системы $[\text{Pd}(\text{OAc})_2] = 6 \cdot (10^{-2} \div 10^{-3})$ моль/л. Температура реакции $T = (95 \div 105)^\circ\text{C}$. При этих условиях выход винилтолуола составляет $5 \div 8$ мас. %. Предложен вероятный механизм протекания реакции, включающий промежуточные комплексы ацетата палладия с толуолом, этиленом и трифенилфосфатом.

Ключевые слова: арилирование, этилен, толуол, винилтолуол, ацетат палладия, трифенилфосфат.