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А. А. Агаев (д.х.н., проф.), М. М. Мурадов (к.т.н., доц.), М. К. Назарова (к.х.н., доц.), И. Э. Гараева (к.х.н., доц.), С. Е. Турабханли (докторант)

ИЗУЧЕНИЕ РЕАКЦИИ АЛКИЛИРОВАНИЯ 2-МЕТИЛАНИЛИНА СПИРТАМИ C_1–C_3

Сумгаитский государственный университет,
кафедра нефтехимии и химической инженерии
AZ 5008, Республика Азербайджан, г. Сумгаит, 43-кв.; e-mail: Akber.Aqayev@sdu.edu.az; mailoglu@mail.ru

A. A. Agayev, M. M. Muradov, M. K. Nazarova, I. E. Garayeva, S. E. Turabkhanli

STUDY OF THE ALKYLATION REACTION OF 2-METHYLANILINE WITH C_1–C_3 ALCOHOLS

Sumgait State University
43-rd quarder, AZ 5008, Sumgait, Republik of Azerbaijan; e-mail: Akber.Aqayev@sdu.edu.az; mailoglu@mail.ru

Представлены результаты исследования реакции алкилирования 2-метиланилина метанолом, этанолом и пропанолами в проточном реакторе с неподвижным слоем палладий-модифицированного Н-морденита. При использовании в качестве алкилирующего агента метанола получают метилгомологи 2-анилина, а в случае этанола при взаимодействии с пропанолами – этильные производные *о*-толуидина, а также пропильные и изопропильные производные. В каталитическом процессе электрофильное замещение происходит на азотных (N-) и углеродных (C-) участках молекулы 2-метиланилина, и в зависимости от условий реакции эти механизмы конкурируют. Оба направления реализуются посредством последовательного механизма. В реакции алкилирования 2-метиланилина ортоселективность преобладает во всех спиртах и увеличивается с повышением температуры. Однако по мере увеличения молекулярной массы спирта доля *о*-алкилирования уменьшается, а образование других изомеров постепенно увеличивается. Проведен сравнительный анализ показателей, характеризующих реакцию алкилирования 2-метиланилина спиртами C_1–C_3, выявивший каталитические свойства каждого спирта и определивший их практическое значение в синтезе алкилпроизводных ароматических аминов.

Ключевые слова: алкилирование; 2-метиланилин; морденит; электрофильное замещение

The results of the study of the alkylation reaction of 2-methylaniline with methanol, ethanol and propanols in a flow-type reactor with a fixed-bed palladium-modified H-mordenite catalyst are presented. When methanol is taken as the alkylating agent, methyl homologues of 2-aniline are obtained, and in the case of ethanol, ethyl derivatives of *o*-toluidine are obtained by the interaction with propanols, and propyl and isopropyl derivatives are obtained. In the catalytic process, electrophilic substitution occurs in the 2-methylaniline molecule at nitrogen (N-) and carbon in the nucleus (C-), and depending on the reaction conditions, these mechanisms are in competition. Both directions occur by a sequential mechanism. In the alkylation reaction of 2-methylaniline, ortho-selectivity prevails in all alcohols and increases with increasing temperature. However, as the molecular weight of the alcohol increases, the share of *o*-alkylation decreases and the formation of other isomers gradually increases. As a result, a comparative analysis of the indicators characterizing the alkylation reaction of 2-methylaniline with C_1–C_3 alcohols was carried out, the catalytic properties of each alcohol were revealed and their practical importance in the synthesis of alkyl derivatives of aromatic amines was determined.

Key words: alkylation; electrophilic substitution; 2-methylaniline; mordenite

Low molecular weight alkyl derivatives of analine are valuable intermediates in the production of a number of important products, including dyes, acid corrosion inhibitors, and antioxidants. Some alkoxy- and halogenated derivatives of these compounds have a wide range of liquid crystalline mesophases and high dielectric constants and optical anisotropy. Therefore, these valuable intermediates are used in various types of display structures [1–3] successfully.

In the synthesis of methyl-, ethyl-, propyl- and isopropyl derivatives of aniline, along with other alkylating agents, monoatomic alcohols are taken and the application of effective catalytic systems is preferred. Based on analogous technology and with

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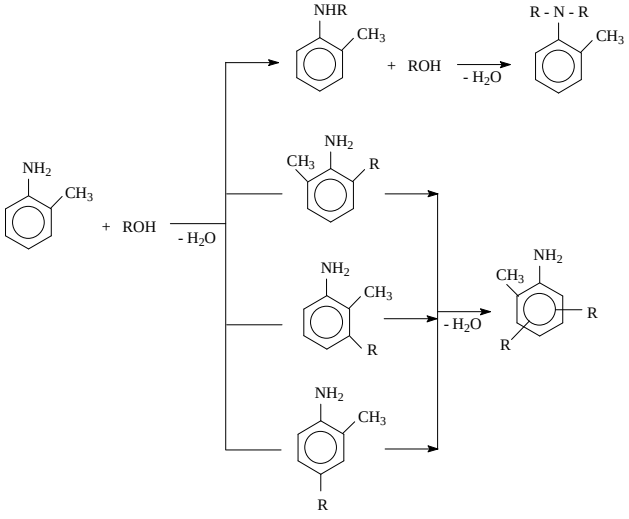
the participation of such universal catalysts, it is possible to increase the range of synthesized products by changing the alkylating reagent (alcohol) and achieve the synthesis of valuable alkylanilines with a simple technological operation under selected reaction conditions.

The article presents the results of the study of the alkylation process of 2-methylaniline with methanol, ethanol and propanol, the results of the comparison and obtained results obtained of analysis.



R = - CH_3 ; - C_2H_5 ; *n*-C_3H_7 ; *i*-C_3H_7

The experiments were carried out in a laboratory setup reactor with a fixed-bed catalyst. The volume of the zeolite catalyst in the reactor was 10 cm^3, and the duration of the reaction was 1 hour. The reaction products were analyzed in a gas-liquid chromatograph (chromium-5). In the chromatograph column, 6% SE-30 (silicon elastomer) impregnated on chromate N-AW was used as a phase, the detector was of the flame-ionization type. The relative error is not more than 3.0%.

The Spectral analysis of the obtained alkylanilines was performed on a German Bruker AV-300 (300 MHz, H'NMR) device. Some of the results of the analysis are given in Tab. 1. They basically coincide with those known in the literature [4] and unambiguously confirm the structure and composition of the synthesized alkylanilines.

The modulus value of Pd,H-mordenite was 25, and the palladium concentration was 10% mass. This catalytic system was synthesized by known methods [5, 6].

The results of the alkylation of 2-methylaniline with methanol, ethanol and propanol are reflected in Tab. 2.

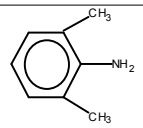
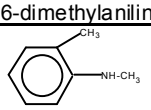
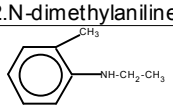
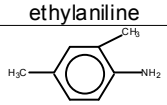
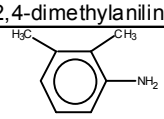
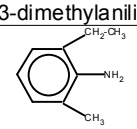
As can be seen from the comparison of the results of the alkylation of 2-methylaniline with C_1–C_3 alcohols in the presence of a Pd,H-mordenite catalyst, the main reaction products, regardless of the structure and composition of the alcohol, include N-alkyl-2-methylaniline, N,N-dialkyl-2-methylaniline, 2-alkyl-6-methylaniline, 2-methyl-4-alkylaniline, a mixture of 2-methyl-3-alkyl- and 2-methyl-5-alkylanilines, and dialkyl-2-methylaniline. When methanol is taken, methyl derivatives of 2-methylaniline are obtained, and in the presence of ethanol, ethyl derivatives of *o*-toluidine are obtained. When propyl and isopropyl alcohol interact with 2-methylaniline, the alkylation products are its propyl and isopropyl derivatives, respectively. The scheme of the interaction of 2-methylaniline with C_1–C_3 alcohols is given above. In the alkylation process, electrophilic substitution occurs at the nitrogen (N-) and carbon (C-) sites in the 2-methylaniline molecule, and they compete depending on the temperature. On the other hand, alkylation at the N- and C-sites occurs in both cases according to a sequential mechanism. In other words, at low temperatures (300 °C), N-alkyl-2-methylanilines (50–92.0 %) are first formed from N-alkylation, while at 340 °C, N,N-alkylmethyl and diethyl derivatives of *o*-toluidine are formed (15.5–18.0 %). In this case, the selectivity of N-monoalkyl-2-methylanilines decreases significantly (20.0–30.0 %). Unlike methanol and ethanol, the selectivity of N,N-dialkyl-2-methylanilines obtained when alkylating with C_3 alcohols changes little with the above-mentioned increase in temperature in the case of *p*-propanol and is only 2.0%. In the alkylation process with 2-propanol, N,N-diisopropyl-2-methyl anilines are practically not obtained. This can be explained by the fact that the process proceeds in different directions depending on the acid-base properties of the catalyst, the structure and composition of the alcohol. Raising the temperature to 380 °C also significantly reduces the share of sequential alkylation due to nitrogen in other alcohols and reduces it to zero in the case of ethanol.

Alkylation of 2-methylaniline with low molecular weight alcohols due to the carbon in the benzene nucleus is also observed with different indicators depending on the composition, structure and reaction temperature of the alcohol.

First *ortho*-selectivity prevails in the alkylation reaction of 2-methylaniline in all alcohols and this indicator increases with increasing temperature. However, as the molecular weight of the alcohol increases, the share of *o*-alkylation decreases. Although the selectivity of *o*-alkyl-2-methylalkyls is higher compared to other alkyl isomers, the selectivity of the process for *m*- and *p*-alkyl isomers gradually increases due to the decrease in its share. Thus, the selectivity of 2,6-dimethylaniline obtained from methanol at 380 °C is 78.5%, and the selectivity of 2-ethyl-6-methylaniline formed when ethanol is taken is 41.0%. When alkylation is carried out with 2-propanol, the calculated yield of 2-isopropyl-6-

Table 1

Results of PMR spectra of some synthesized alkylanilines

№	Alkylaniline	Chemical shift of protons of proton-withdrawing groups and aromatic nucleus, δ, m.h.											
		Ph-NH_2	Ph-NH-CH_3	Ph-N-CH_2-C	Ph-N-C-CH_3	Ph-CH_3	Ph-CH_2-C	Ph-C-CH_3	C_2-H (*ortho*)	C_3-H (*meta*)	C_4-H (*para*)	C_5-H (*meta*)	C_6-H (*orto*)
1	 2.6-dimethylaniline	3.5 (c)	-	-	-	2.2 (c)	-	-	-	6.90	6.65	6.90	-
2	 2.N-dimethylaniline	3.50 (c)	2.82(c)	-	-	2.22(c)	-	-	-	6.95	6.80	6.95	6.65
3	 2-methyl-N-ethylaniline	3.54 (c)	-	3.30 (kv)	1.24 (tp)	2.20(c)	-	-	-	6.93	6.80	6.93	6.60
4	 2,4-dimethylaniline	3.64 (c)	-	-	-	2.18(c)	-	-	-	7.05	-	7.05	6.62
5	 2,3-dimethylaniline	3.65 (c)	-	-	-	2.20(c)	-	-	-	-	6.70	7.00	6.58
6	 2-methyl-6-ethylaniline	3.50	-	-	-	2.20(c)	250	1.2(tp)	-	6.60	6.90	6.60	-

methylphenol obtained based on the converted *o*-toluidine is only 37.0%. In the latter case, the selectivity for 2-methyl-4-isopropyl and 2-methyl-3-isopropyl anilines is 29.0 and 18.5 %, respectively. The selectivities of formation of *o*- and *p*-alkyl-2-methylanilines in the alkylate obtained from the alkylation of 2-methylaniline with ethanol at a temperature of 380 °C are 41.0 and 49.0 %, respectively, which is a different result compared to other alcohols. Although *o*-selectivity (52.5%) prevails in the alkylation process of 2-methylaniline with 1-propanol, the selectivity of formation of 2-methyl-4-propyl-aniline is quite high (35.0%).

Most likely, in the presence of Pd,H-mordenite, whose acid-base properties are regulated, as the molecular mass of the alcohol increases, its partial conversion into an olefin and its participation in *p*-alkylation cannot be ruled out. On the other hand, increasing the temperature not only increases the rate of *p*-alkylation, but also accelerates the isomerization of alkyl derivatives of 2-methylaniline in the reaction mixture.

The rate of sequential alkylation increases with temperature and branching of the molecular weight of the alcohol and the structure of the C_3 alcohol. Thus, while the selectivity of dialkyl-2-methyl-anilines obtained when normal alcohols are taken is 3.0%, the calculated yield of dialkyl *o*-toluidine in alkylation with 2-propanol with respect to the converted 2-methylaniline increases by 7.0% with an increase in temperature of 80 °C to 12.0%.

In general, the side transformations of alcolols in catalytic alkylation also vary depending on their composition, structure and reaction conditions. In the case of methanol, diethylether is obtained, in the case of ethanol and 1-propanol, diethylether, dipraylether, ethene and propane are obtained, and in the case of 2-propanol, mainly propane and party 2-propanol, mainly propane and parthy 2-izopropylether are obtained, and with increasiky temperature, the formation of olefins increases. With increasing temperature and the stable operation of the catalytic system in the stationary mode, it also decreases somelishat.

In general, the side reactions of alcohols in catalytic alkylation also vary depending on their composition, structure and reaction conditions. In the case of methanol, diethylether is obtained, in the

Table 2

Comparative results of the alkylation of 2-methylaniline with alcohols in the presence of Pd,H-mordenite

Reaction conditions: υ = 1.0 st^{-1}, ν =1:3 mol/mol

Name	methanol			ethanol			1-propanol			2-propanol		
Temperature, °C	300	340	380	300	340	380	300	340	380	300	340	380
Conversion of 2-methylaniline	77.0	90.5	98.0	82.0	94.0	99.0	91.0	95.0	100	88.0	100	100
Yield of reaction products calculated based on converted 2-methylaniline, %:												
N-alkyl-2-methylaniline	92.0	30.0	7.5	90.0	25.0	5.0	80.0	20.0	4.0	50.0	20.5	2.0
N,N-dialkyl-2methylaniline	7.0	18.0	2.0	6.0	15.5	1.0	4.0	2.0	-	-	-	-
2-alkyl-6-methylaniline	0.5	55.0	78.5	2.5	38.0	41.0	13.0	48.0	52.5	38.0	29.5	37.0
2-methyl-4-alkylaniline	-	3.0	7.0	-	17.5	49.0	1.0	25.0	35.0	3.5	25.0	29.0
2-methyl-3-alkylaniline *	-	-	1.0	-	2.0	5.0	-	1.5	4.0	2.0	13.0	18.5
dialkyl-2-methylanilines	-	2.0	3.0	-	-	3.0	-	1.0	3.0	5.0	10.5	12.0

** Mixture with 2-methyl-5-alkylaniline*

case of ethanol and 1-propanol, diethylether, dipropylether, ethene and propene are obtained, and in the case of 2-propanol, mainly propene and partly 2-isopropylether are obtained, and with increasing temperature, the formation of olefins increases. With increasing temperature and the stable operation of the catalytic system in the stationary mode, it also decreases somewhat.

Thus, as a result of the conducted, studies a comparative analysis of the indicators characterizing the alkylation reaction of 2-methylaniline with C_1–C_3 alcohols was carried out, the catalytic properties of each alcohol in the alkylation process were revealed, and their role and impertance in the synthesis of alkyl derivatives of aromatic amines was determined.

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