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CASE STUDY ON 4-ISOPROPYL-*ORTHO*-XYLENE PRODUCTION

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Abstract. *We have experimentally studied the alkylation reaction of o-xylene with propylene under kinetic control conditions followed by realkylation under thermodynamic control conditions. The paper provides an analysis of the alkylation reaction products obtained under kinetic control as well as kinetic analysis and thermodynamic analysis of the overalkylation process. The authors have considered the methyl group migration reactions during overalkylation and have given kinetic analyses of these reactions. We found that the optimal method for the preparation of 4-isopropyl-o-xylene is to conduct the process in two stages. The first one is a liquid-phase alkylation of o-xylene under kinetic control at 353 K. The second stage is liquid-phase realkylation of the obtained alkylation reaction mass until reaching thermodynamic equilibrium at a temperature range of 303-353 K under certain conditions. These conditions should ensure minimal migration of methyl groups, i.e. with minimum contact time and alkyl-/aryl- < 0.5 ratio in the reaction products.*

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Introduction

Friedel-Crafts alkylation reaction is one of the most important chemical methods for the production of alkylaromatic hydrocarbons (HCs), which are widely used to produce stabilisers, fuel additives, pharmaceuticals, and agricultural chemicals.

The most common large-tonnage process based on this method is the production of alkylaromatic HCs (isopropylbenzenes, isopropyltoluenes, cyclohexylbenzene) required for the corresponding phenols and ketones production by hydroperoxide method [1].

Many publications have been devoted to the laws of isopropylaromatic HC production by alkylation catalysed by Lewis and Branstead acids under homogeneous or heterogeneous conditions; we have analysed several of them in [2]. However, the process of isopropylxylenes production is one of the least studied of all known technological processes for the alkylaromatic hydrocarbons production.

Therefore, this paper is devoted to a special case of isopropylxylene production - the process of alkylation of *o*-xylene with propylene. On the one hand, this is due to theoretical interest, since it is possible to study the whole complex of transformations occurring during Friedel-Crafts alkylation of xylenes. On the other hand, the results of the study have important applications, as they open a potential way to obtain the intermediate 3,4-xylenol via 4-isopropyl-*o*-xylene (4-IPOX). 3,4-Xylenol is widely used for the production of various pesticides, such as 3,4-dimethylphenyl-*N*-methylcarbamate [3], and, equally with other xylenols, for the production of trixylylyl phosphates, components of flame-retardant oils [4].

The complexity of the alkylation process of *o*-xylene with propylene and realkylation of isopropyl-*o*-xylenes is based on the possibility of migration reactions of the isopropyl group in xylenes.

The patent [5] discusses a method for *p*-xylene alkylation with propylene and isopropyl alcohol in the presence of sulfuric acid and $BF_3 \times H_3PO_4$. The results show that $BF_3 \times H_3PO_4$ yields an equilibrium mixture consisting of 56% of 1,4-dimethyl-2,5-diisopropylbenzene. The only by-product reported by the authors is 1,4-dimethyl-2-isopropylbenzene. The formation of *o*-, *m*-xylene and polymethylbenzene derivatives has not been described.

The paper [6] presents data on alkylation of *o*-xylene with propylene on cationite KU-2 and aluminium chloride. It is shown that methyl group migration takes place in the presence of aluminium chloride. However, no conclusions about reaching equilibrium in the isopropyl-*o*-xylene system are drawn from the data obtained, and no practical ways of suppressing undesirable migration of methyl groups are discussed.

Paper [7] describes the isomerisation of mono- and diisopropyl derivatives of *o*-xylene, but there are no data on the realkylation of di-isopropyl-*o*-xylene to *o*-xylene. Also, this paper does not consider the possibility of methyl group migration.

Papers [8-9] describe the *o*-xylene alkylation with isopropanol in the presence of various solid catalysts. The authors report the achievement of high yield of 4-IPOC. Additionally, [9] shows the possibility of formation of isopropyltoluenes and trimethylbenzenes under experimental conditions. But chemical equilibrium was apparently not reached in these studies. Thus, there are no data on the equilibrium compositions of isomeric isopropyl-*o*-xylenes.

The patent [10] describes a method for the preparation of 4-IPOC by *o*-xylene alkylation with propylene in the presence of an $AlCl_3$-CH_3NO_2 catalyst. Information on the reaction masses composition does not allow us to draw a definite conclusion as to whether chemical equilibrium in the system has been reached. Moreover, there are no data on methyl group migration side reactions.

One of the main problems to be solved in the alkylation of *o*-xylene with propylene is the process conditions under which the methyl group migration is minimised. Failing to observe this restriction inevitably leads to formation in the reaction mass not only of isopropyltoluenes and polymethylbenzenes, but also of isopropyl-*m*- and *p*-xylenes.

Isopropyl-*m*- and *p*-xylenes have close boiling points to the target 4-IPOX. Respectively, their presence in the reaction mass can significantly reduce the cost-effectiveness of the technology due to the complex block of target product isolation included in it.

The purpose of this study is to solve fundamental issues of extremely selective production of 4-isopropyl-*o*-xylene from available petrochemical feedstock - *o*-xylene and propylene.

Main body

We used as initial substances: *o*-xylene, purity not less than 99.5% wt. according to gas-liquid chromatography (GLC); propylene - industrial sample with the content of the main substance 99.5% wt. produced by JSC "Novokuibyshevskaya petrochemical company (NPC)"; anhydrous technical aluminium chloride with the content of the main substance 99.5% wt. produced by JSC "Kaustik"; sulphocationite Amberlyst 36 Dry produced by Dow Chemical, which before the experiments was dried from moisture by thermostatisation at 378 K to constant weight.

We performed studies on the isopropyl-*o*-xylene equilibrium transformation as follows:

We obtained a non-equilibrium mixture of isopropyl-*o*-xylenes by *o*-xylene alkylation with propylene in the presence of 5 wt% Amberlyst 36 Dry cationite at a temperature of 353 K and a contact time of 0.2-1.5 h. We conducted the reaction in a metal thermostatted reactor ($V = 500$ cm^3 at a pressure ensuring the presence of the reactants in the liquid state. Under these conditions the propylene conversion was 100%.

We realkylated the obtained mixture in the presence of 1-3% wt% of anhydrous $AlCl_3$ based catalyst complex at temperatures of 303-333 K until reaching the equilibrium composition of the reaction mass.

We studied the isomerisation chemical equilibrium in the isopropyl-*o*-xylene system at atmospheric pressure in the liquid phase in an isothermal glass reactor ($V = 20$ cm^3) under vigorous stirring (300 rpm) in the presence of an $AlCl_3$-based catalyst complex. We provided the temperature constancy by circulation of the coolant in the reactor jacket. We varied the composition in the range of molar ratios "isopropyl-/aryl-", which is 0.2-1.8. We took samples from the upper hydrocarbon layer after switching off the stirrer motor and complete precipitation of the catalytic complex. We treated the samples with 10% caustic soda solution and water to deactivate the dissolved catalyst.

The main method for analysing reaction mixtures is GLC. We analysed the samples on a Crystal 2000 M instrument with the Chromatek-Analytical hardware and software system equipped with a flame ionisation detector, a carrier gas flow divider, and a quartz capillary column (60 m × 0.25 mm) with a grafted SE-30 stationary phase. Helium was used as the carrier gas. The pressure of the carrier gas at the column inlet was 42.5 kPa. The evaporator temperature was 473 K and the detector temperature was 503 K. *N*-butanol was used as an internal standard. The temperature regime of the analysis ensured complete separation of all reaction mass components.

The identification of all mixture components involved setting up a special chemical experiment and chromatography-mass spectrometric analysis, which was performed on an Agilent 6850 gas chromatograph, equipped with an Agilent 19091S-433E capillary column (30 m×0.25 mm×0.25 μm) with a stationary phase (5% diphenylpolysiloxane + 95% dimethylpolysiloxane) and an Agilent 5975C VL MSD mass-selective detector at an ionising voltage of 70 eV.

We conducted the process of obtaining 4-IPOX in two stages. In the first stage we conducted alkylation of *o*-xylene with propylene under kinetic control conditions, and in the second stage we conducted isomerisation of the alkylation reaction mass until liquid-phase equilibrium was reached in the "*o*-xylene-isopropyl-*o*-xylene" system.

Alkylation of o-xylene with propylene on Amberlyst 36 Dry sulphocationite

The task solved at the alkylation stage was to obtain isopropyl-o-xylenes as selectively as possible. To prevent the migration of methyl groups in the aromatic nucleus, alkylation should be performed on proton catalysts that allow the process to be conducted in the kinetic range. Currently, the most promising of such catalysts are macroporous sulphocationites such as Amberlyst, Lewatit, Tulsion, Purolite, and others.

According to the study [11], the Amberlyst 36 Dry catalyst allows us to obtain mixtures of cymols with predominance of para- and ortho-isomers with high selectivity. Therefore, this catalyst was also chosen for the alkylation of o-xylene.

We performed the alkylation at a temperature of 353 K; contact time 0-120 min, in the range of isopropyl-/aryl- ratios for the alkylation products of 0.02-1.0 mol/mol. At the alkylation stage we considered the following series-parallel transformations:

o-xylene + propylene → 4-isopropyl-o-xylene (4-IPOX) (1)
o-xylene + propylene → 3-isopropyl-o-xylene (3-IPOX) (2)
4-IPOX + propylene → 4,5-di-isopropyl-*o*-xylene (4,5-DIPOX) (3)
4-IPOX + propylene → 3,5-di-isopropyl-*o*-xylene (3,5-DIPOX) (4)
3-IPOX + propylene → 3,5-di-isopropyl-*o*-xylene (3,5-DIPOX) (5)

By statistics, the probabilities of formation of products by reactions (1) and (2) are equal. Reactions (3), (4), and (5) are also equally likely to occur. Thus, theoretically, the expected composition of the alkylation reaction mass should be dominated by 3-IPOX, since 4-IPOX is consumed in two reactions: (3) and (4), and 3,5-DIPOX should be doubly dominated by 4,5-DIPOX.

However, the experimental results indicate that in the reaction mass the predominant isomer is 4-IPOX, while the product of its further alkylation (4,5-DIPOX) is significantly inferior to the amount of 3,5-DIPOX (by a factor of six at a propylene/*o*-xylene molar ratio of 0.8). Figures 1 and 2 show the data on their concentration ratios.

We can assume that such component distribution of the reaction mass composition is explained by the difference in the ratio of rate constants for two parallel reactions - alkylation of 4-IPOX and alkylation of 3-IPOX - arising due to the presence of steric hindrance of adjacent isopropyl groups during the formation of 4,5-DIPOX.

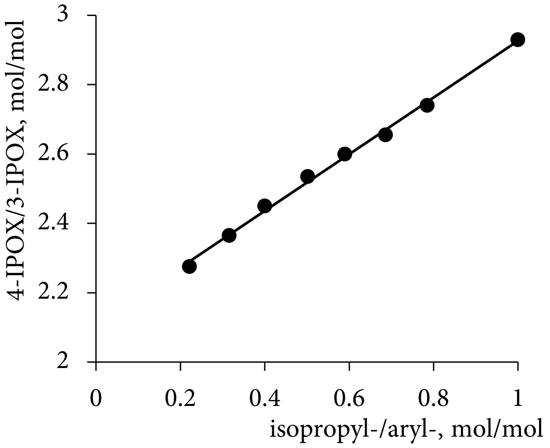

Fig. 1. Concentration ratio of mono-IPOX in the process of *o*-xylene alkylation with propylene alkylation on "Amberlyst 36 Dry" sulphocationite at 353 K

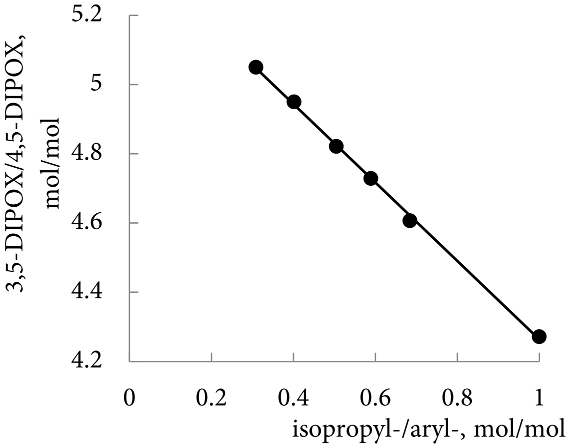

Fig. 2. Concentration ratio of di-IPOX in the process of *o*-xylene alkylation with propylene alkylation on "Amberlyst 36 Dry" sulphocationite at 353 K

Experimentally we found that the alkylation process has 100% selectivity for the sum of isopropyl-*o*-xylenes (Fig. 3). It was found the formation of two isomers in the group of monosubstituted *o*-xylenes: 4-IPOX and 3-IPOX. Their maximum concentrations in the reaction mass are reached at a propylene/*o*-xylene molar ratio equal to 1. For 4-IPOX the concentration was 35.7% mol, for 3-IPOX it was 12.4% mol. Two isomers, 4,5-DIPOX and 3,5-DIPOX, with concentrations of 4.1% mol and 17.5% mol, respectively, are also formed in the group of disubstituted *o*-xylenes.

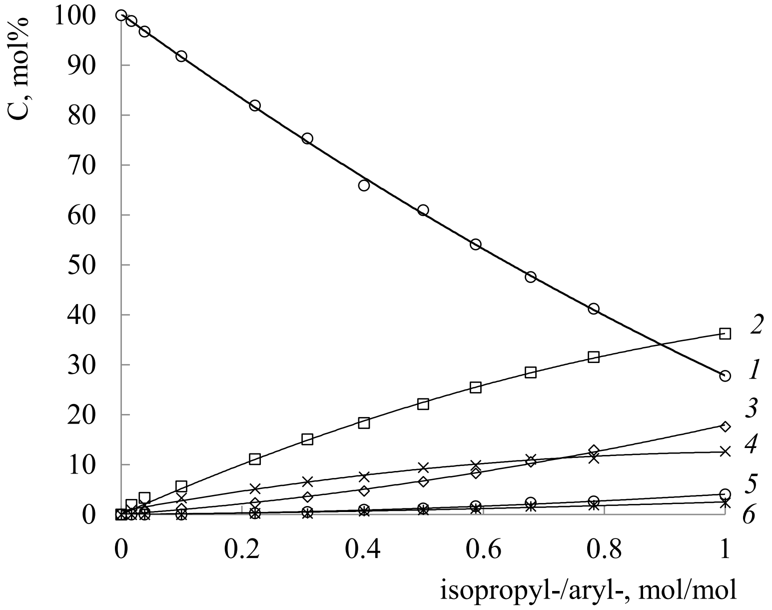

Fig. 3. Composition of reaction mass for alkylation of *o*-xylene with propylene on "Amberlyst 36 Dry" at 353 K: 1 - *o*-xylene; 2 - 4-IPOX; 3 - 3,5-DIPOX; 4 - 3-IPOX; 5 - 4,5-DIPOX; 6 - TRIIPOX

Isomerisation and realkylation of the o-xylene alkylation reaction mass with propylene. Thermodynamic analysis of isomerisation and overalkylation

The system "o-xylene - isopropyl-o-xylene" was represented by five components. We chose three independent reactions to describe the equilibrium:

$$\text{3-IPOX} \leftrightarrow \text{4-IPOX} \tag{6}$$
$$\text{4,5-DIPOX} \leftrightarrow \text{3,5-DIPOX} \tag{7}$$
$$\text{3,5-DIPOX} + \text{OX} \leftrightarrow \text{4-IPOX} + \text{4-IPOX} \tag{8}$$

Table 1 summarizes the results of the equilibrium study obtained.

Table 1. Study results of the reactions equilibrium (6), (7) and (8)[a]

T, K	t_n, min	t_{equal}, min	Alkyl/Aryl, mol/mol	$AlCl_3$ content, % wt.	K_x	$t_{0,05}S$
3-IPOX ↔ 4-IPOX (6)						
303	400	1200	0,07	1,6	119	4,75
303	300	1500	0,08	1,8	163	8,88
303	360	900	0,18	2,1	116	6,47
303	900	1700	1,01	2,3	132	3,30
318	360	600	0,27	1,6	107	1,35
318	480	1200	1,81	1,9	103	0,37
318	540	1200	0,77	2,3	108	0,26
333	180	420	0,06	1,8	81,5	1,68
333	180	600	0,24	2,5	101	1,11
333	180	660	0,30	1,5	97,7	1,41
333	180	660	0,63	2,4	93,6	1,19
333	180	600	0,43	2,2	92,9	0,20
333	210	720	0,82	2,1	99,5	1,26
333	180	540	1,02	1,8	96,2	1,45
333	240	660	1,27	2,0	100,0	1,20
333	150	720	1,39	2,2	92,0	0,85
353	60	300	0,39	2,3	81,1	1,57
353	45	600	0,98	6,7	76.8	0,38
373^b		65			70,0	16,74
393^b		50			34,3	4,38
413^b		38			31,0	6,46
4,5-DIPOX ↔ 3,5-DIPOX (7)						
303	900	1700	1,01	2,3	6,65	0,04
303	900	2700	1,00	2,3	6,78	0,07
318	480	1200	1,81	1,9	6,48	0,08
318	540	1200	0,77	2,3	6,71	0,05
333	180	600	0,43	2,2	7,59	0,16
333	210	720	0,82	2,1	5,71	0,13
333	180	540	1,02	1,8	6,70	0,08
333	240	660	1,27	2,0	7,81	0,21
333	150	720	1,39	2,2	7,44	0,18
353	45	600	0,98	6,7	6,64	0,05
353^b					6,5	0,3
373^b		65			5,59	0,55
393^b		50			5,50	0,46
413^b		38			5,90	0,53
3,5-DIPOX + OX ↔ 4-IPOX + 4-IPOX (8)						
303	900	1700	1,01	2,3	318	7,78
318	360	600	0,27	1,6	275	13,76
318	480	1200	1,81	1,9	230	4,23
318	540	1200	0,77	2,3	255	3,89
333	180	660	0,30	1,5	197	4,45

T, K	t_n, min	t_{equal}, min	Alkyl/Aryl, mol/mol	$AlCl_3$ content, % wt.	K_x	$t_{0,05}S$
333	180	660	0,63	2,4	206	9,26
333	180	600	0,43	2,2	203	4,49
333	210	720	0,82	2,1	194	5,35
333	180	540	1,02	1,8	218	4,82
333	240	660	1,27	2,0	210	4,55
333	150	720	1,39	2,2	204	4,36
353	60	300	0,39	2,3	173	6,61
353	45	600	0,98	6,7	179	2,59

[a] Symbols: t_n - time for the system to reach equilibrium; t_{eq} - time for studying the system under equilibrium conditions; K_x - ratio of equilibrium concentrations of reaction products in mole fractions to equilibrium concentrations of initial substances; $t_{0.05}S$ - confidence interval for the significance level of 0.05;

[b] [12].

Table 2 shows the enthalpic and entropic effects of reactions (6), (7) and (8) obtained by linear approximation of the equilibrium constants (ln K_x) as a function of inverse temperature $10^3/T$.

Table 2. Enthalpic ($kJ \cdot mol^{-1}$) and entropic ($J \cdot mol^{-1} \cdot K^{-1}$) characteristics of the studied reactions in liquid phase

No. of reaction	$T_н$-$T_к$	$\Delta_r H_T^0(l)$	$t_{0,05}S$	$\Delta_r S_T^0(l)$	$t_{0,05}S$
6	303–413	-12.6	2.6	-0.6	7.9
7	303–413	-1.8	1.3	10.1	3.9
8	303–353	-10.5	1.2	13.0	3.6

The values of gas-phase equilibrium constants (K_r) are calculated in the Raul's law applicability approximation as:

$$K_p = K_x\left(\Pi P_{vp(product)}/\Pi P_{vp(initial)}\right),$$

where $P_{vp(initial)}$ is saturated vapour pressure of initial reagents; $P_{vp(product)}$ is saturated vapour pressure of reaction products. The saturated vapour pressures for all components were calculated using the Ambrose-Walton method.

Table 3 shows the enthalpic and entropic effects of reactions (6)-(8) obtained by linear approximation of the equilibrium constants (ln K_p) as a function of inverse temperature $10^3/T$.

Table 3. Enthalpic ($kJ \cdot mol^{-1}$) and entropic ($J \cdot mol^{-1} \cdot K^{-1}$) characteristics of the studied reactions in the gas phase

No. of reaction	$T_н$–$T_к$	$\Delta_r H_T^0(g)$	$t_{0,05}S$	$\Delta_r S_T^0(g)$	$t_{0,05}S$
6	303–413	-13.2	2.6	-1.0	7.7
7	303–413	-1.8	1.4	9.6	4.0
8	303–353	-8.7	1.1	14.8	3.4

According to data presented, reaction (7) is characterised by an unexpectedly low enthalpy, despite the *ortho*-effect of the two isopropyl groups in 4,5-DIPOX. However, Table 3 shows the "triple" enthalpy effect of *Me-Me-isopropyl-* in 3-DIPOX is a very significant value of 13.2 $kJ \cdot mol^{-1}$ for reaction (6). We assume the same data for reaction (7), leading to mutual compensation of *ortho*-effects.

The composition of the equilibrium mixture for the system "*o*-xylene - isopropyl-*o*-xylene" (Fig. 4) was calculated by solving a system of five equations with five unknowns (three equations are expressions for equilibrium constants of reactions (6)-(8)) with experimental values of K_x, and two material balance equations - for aromatic nuclei and for isopropyl substituents). The equilibrium calculation was performed at temperatures of 318, 333, and 353 K. As a result, it was found that when the system reaches liquid-phase equilibrium with increasing isomerisation temperature from 303 to 353 K, the concentration of target 4-IPOC decreases from 89 to 86% mol. at the alkyl-/aryl- ratio equal to 1 mol/mol.

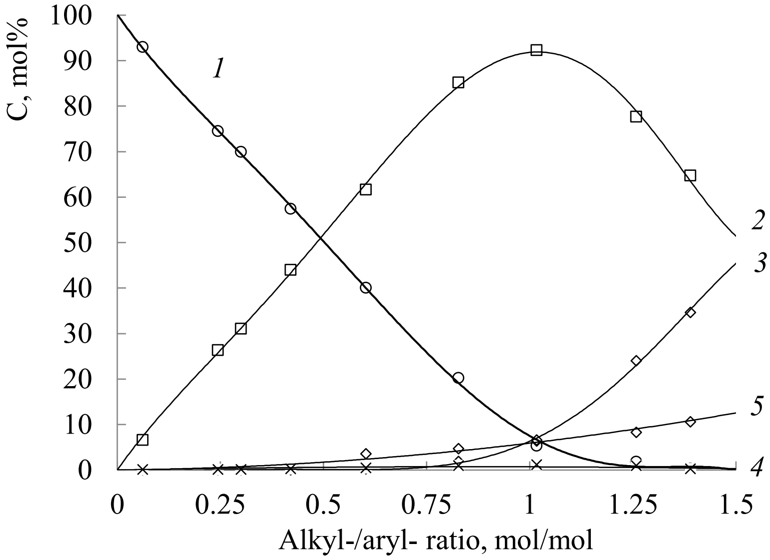

Fig. 4. Composition of the equilibrium mixture in the system "*o*-xylene + isopropyl-*o*-xylene" at 333 K: 1 – *o*-xylene; 2 – 4-IPOX; 3 – 3,5-DIPOX; 4 – 3-IPOX; 5 – 4,5-DIPOX

The presented data indicate that the process of obtaining 4-IPOX should be performed under conditions when the reaction mass reaches thermodynamic equilibrium in the isopropyl-*o*-xylene group.

Kinetic analysis of methyl group migration in the Isopropyl-o-xylene isomerisation process

The main purpose of the analysis was to establish the formation pathways of 5-isopropyl-*m*-xylene (5-IPMX), pseudocumene, 3-isopropyltoluene (3-IPT), and 4-isopropyltoluene (4-IPT), the by-products of the reaction mass isomerisation of the *o*-xylene alkylation with propylene.

Isomerisation by-products are obtained by the following reactions:

4-IPOX → 5-IPMX (9)
o-xylene ↔ *m-xylene* (10.1)
m-xylene +4-IPOX → *5-IPMX + o-xylene* (10.2)
o-Xylene + 4-IPOX → *Pseudocoumol + 4-IPT* (11)
4-IPT ↔ 3-IPT (12)

The most difficult to separate from 4-IPOX is 5-IPMX, since the normal boiling points of these compounds differ only by 7 K. For this reason, its appearance in the isomerisation reaction mass should be under control. 5-IPMX has two ways of accumulation in the reaction mass. The first one is by reaction (9) upon isomerisation of the methyl group position in 4-IPOX, the second one is by the sequential reactions (10.1) and (10.2) through the *m*-xylene formation. The depth of *o*-xylene alkylation with propylene depends on the predominance of one or another way of 5-IPMX formation.

We analysed the kinetic data by comparing the compositions of isomerisation reaction masses at a temperature of 333 K, alkyl-/aryl- ratios of 0.24 and 0.63 mol/mol, and catalyst amounts of 2.5 and 2.4 wt%, respectively. As a result, it was found that 5-IPMX was predominantly formed by the isomerisation reaction of the methyl group position from 4-IPOX (reaction (9)). It is evidenced by the higher rate of its accumulation in the case when the reaction mass with a higher alkyl-/aryl- (mol/mol) ratio undergoes isomerisation (Fig. 5). However, the amounts of pseudocoumol, 3-IPT and 4-IPT when the system reaches equilibrium on the isopropyl-o-xylene group are insignificant at 0.09, 0.04 and 0.01% mol, respectively.

The concentration of side-formed pseudocumene, 3-IPT and 4-IPT is higher at lower alkyl-/aryl- ratio of 0.24 (mol/mol) after reaching equilibrium concentrations in the isopropyl-*o*-xylene group.

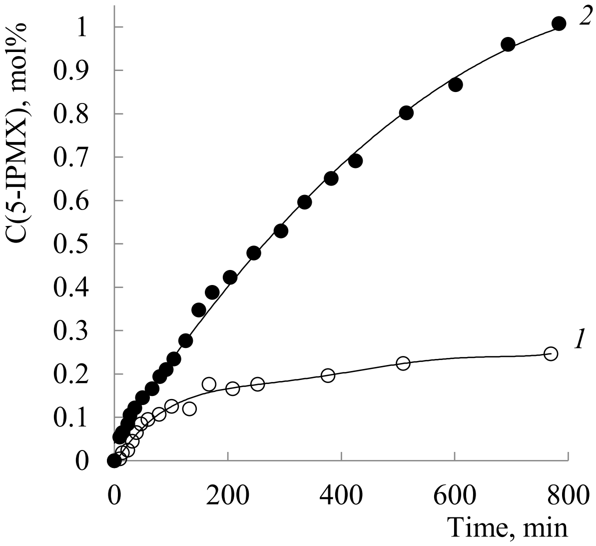

Fig. 5. Concentration of 5-IPMX during isomerisation of reaction mass alkylation of *o*-xylene with propylene at 333 K: 1 - alkyl-/aryl- = 0.24; 2 - alkyl-/aryl- = 0.63

Thus, the minimum amount of by-products will be achieved by shallow alkylation of *o*-xylene with propylene (i.e., if the ratio of alkyl-/aryl- ≤ 0.5 mol/mol in the reaction products is maintained), and the subsequent isomerisation step of the reaction mass under conditions ensuring the equilibrium in the isopropyl-*o*-xylene group at low contact time.

Conclusions and recommendations

Hence, we found that the alkylation of *o*-xylene with propylene on Amberlyst 36 Dry sulfocationite proceeds in the kinetic region with 100% selectivity for the sum of isopropyl-*o*-xylenes. Nevertheless, it was impossible to ensure high yield of target 4-IPOX under these conditions.

It is shown to obtain the maximum yield of 4-IPOX a realkylation step under thermodynamic equilibrium conditions is necessary.

Equilibrium transformations of isomeric isopropyl-*o*-xylenes have been studied in the presence of an $AlCl_3$-based catalytic complex during the realkylation of reaction masses. Thermodynamic characteristics of the realkylation reactions are given. The kinetic analysis of methyl group migration reactions catalysed by $AlCl_3$-based complex was also performed. The condition for minimal formation of 5-IPMX is the contact time not exceeding the time of reaching the equilibrium of the system "*o*-xylene - isopropyl-*o*-xylene", as well as obtaining the initial alkylation reaction mass with a low alkyl-/aryl- ratio.

The following conditions for the selective production of 4-IPOX were determined as a result of this study:

The first stage of the process is the liquid-phase alkylation of *o*-xylene under kinetic control conditions at the minimum temperature from the operating range of the sulfocationic acid, which for most catalysts of this type is 353 K;

The second stage is liquid-phase realkylation of the obtained alkylation reaction mass until reaching thermodynamic equilibrium at a temperature range of 303-353 K under certain conditions. These conditions should ensure minimal migration of methyl groups, i.e. with minimum contact time and alkyl-/aryl- < 0.5 ratio in the reaction products.

The results obtained can be used for a more detailed study of the continuous two-stage process conditions for the production of 4-IPOX (temperature, pressure, volume feed rate of raw materials, features of the alkylation design and re-alkylation reactors), and further development of this product production technology.

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