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Theory and Practice of the Preparation of Adamantylarenes

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Abstract—The adamantylation of diphenyl oxide and phenol with 1-chloro(bromo)adamantanes in a liquid phase has been studied. The reaction has been performed under kinetic control and under the conditions of reaching chemical equilibrium using the following catalysts: Amberlyst 36 Dry, in situ HBr, and $AlCl_3$. The kinetics of isomerization of (1-adamantyl)- and (2-adamantyl)diphenyl oxides has been studied at 333 and 417 K in the presence of $AlCl_3$ and Amberlyst 36 Dry, respectively. The equilibrium of the positional and structural "bridge–bridgehead" isomerization has been studied in the range of 333–523 K. It has been found that high selectivity of the adamantylation of diphenyl oxide or phenol can be achieved in the case of the use of sulfonated cation-exchange resins as a catalyst. In the presence of aluminum halides or HBr, the reaction mixture has been represented by all the possible isomers and adamantane.

Keywords: isomerization, kinetics, chemical equilibrium, adamantane, sulfonated cation-exchange resins, acids

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Starting from 1957 and to the present day, a lot of methods for the preparation of adamantylarenes have been developed. Most of them have no fundamental differences from the alkylation of arenes. Compounds with 1- and 2-adamantyl substituents are prepared via the adamantylation of the corresponding aromatic substrate with 1- and 2-haloadamantanes [1, 2] or 1- and 2-adamantanols [3–5] in the presence of various acidic catalysts including Lewis superacids [1] and solid superacids of the Nafion-H type [2]. To date, a wealth of sulfonated cation-exchange resins and zeolites with different catalytic activity have been tested as catalysts. A retrospective (up to 2009) analysis of the potential fields of application of sulfonated cation-exchange resins was performed by Alexandratos [6].

Together with the conventional methods for the adamantylation of arenes, other approaches are considered. Butov et al. [7, 8] believe that 1,3-dihydroadamantane (1,3-DHA) is a very promising adamantylating agent. In the presence of catalytic amounts of sulfuric acid, selective preparation (the yield is 83–96 wt %) of *p*-(1-adamantyl)benzenes [7] and *p*-(1-adamantyl)phenols is possible with the use of 1,3-DHA as an adamantylating agent [8]. In the absence of an acidic catalyst, diatomic phenols react with 1,3-DHA to form 1-adamantyl phenyl ethers (the yield is 80–88%) and the products of C-adamantylation are byproducts (with a yield of 8–10%) [8].

The result of adamantylation will probably be fundamentally different in the case of running the process under the conditions of kinetic or thermodynamic control by analogy with the alkylation of arenes with branched pentenes or halopentanes [9]. Systematic studies on these problems are extremely scarce. More or less general studies include the following works. Olah et al. [1] investigated the adamantylation of benzene and toluene with 1- and 2-halo(fluoro, chloro, and bromo)adamantanes or 1-adamantanoyl chloride and the isomerization of monoaryladamantanes in the presence of superacids in a medium of various solvents. The adamantylation of benzene and toluene with 2-halo(chloro and bromo)adamantanes in a dichloromethane medium is accompanied by intensive isomerization ("bridge–bridgehead" and in the aromatic ring), and the concentration of the initially formed 2-Ad derivatives decreases at room temperature within 60 min to 6% for a mixture of Ad-benzenes and to 10–20%, for Ad-toluenes. The change of the type of superacids selected in [10] had no influence on the result of the adamantylation of toluene.

The study with superacids was continued by Laali et al. [11], who showed that the process is characterized by high *p*-(1-Ad)toluene selectivity, which reaches 90–100% of total products. The yield of adamantane and *m*-(1-Ad)toluene did not exceed 5% in each of the experiments.

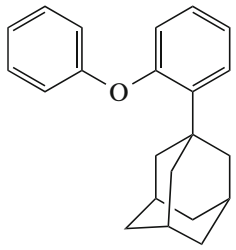
The use of sulfonated cation-exchange resins (Amberlyst XN 1010 and Dowex X2-100) instead of superacids [12] allowed Olah to increase the selectivity for the *p*-Ad derivatives to 100% in the adamantylation of monosubstituted benzenes.

The adamantylation of phenols was studied in the presence of the sulfonated cation-exchange resins Amberlite 200 and Amberlite IR120 [13] and trifluoroacetic acid [14] or without catalysts whatsoever [15, 16], with unsubstituted phenols giving a mixture of *ortho*- and *para*-derivatives with the isomer ratio that depends on the process conditions [17].

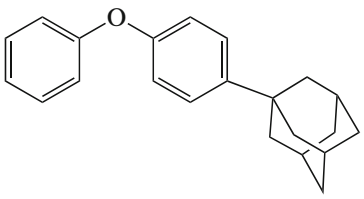
Irrespective of the field of application of adamantylarenes, 1-adamantyl derivatives are preferable, and only such structures can be used in some cases [18]. The selective preparation of these structures requires the possession of reliable data on the kinetics of adamantylation and equilibrium of the transformations of adamantylarenes, first of all, their isomerization.

Despite the fact that there is already a considerable number of works on the adamantylation of arenes, there is almost no information on the kinetics of the processes. The only papers on the issue by Pimerzin and Sarkisova [19, 20] are devoted to the systematic study of the equilibrium of the transformations of adamantylarenes. They studied the equilibrium of the bridge–bridgehead isomerization in the liquid- phase for adamantylarenes (benzenes, toluenes, and *ortho*- and *meta*-xylenes). There is no information of this kind for compounds of other classes.

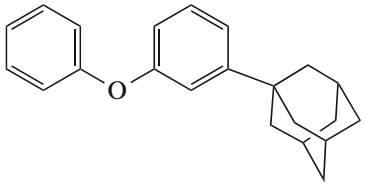
This research is aimed at the reduction of the aforementioned gaps in information on the kinetics and thermodynamics of the adamantylation of arenes and the interconversion of adamantylation products. The compounds under consideration in this work are presented below:



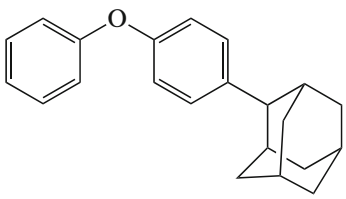
o-(1-Adamantyl)DPO



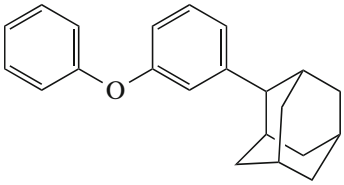
p-(1-Adamantyl)DPO



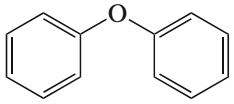
m-(1-Adamantyl)DPO



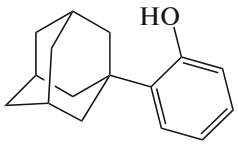
p-(2-Adamantyl)DPO



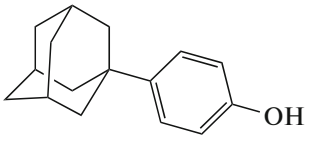
m-(2-Adamantyl)DPO



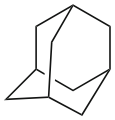
DPO



o-(1-Adamantyl)phenol



p-(1-Adamantyl)phenol



Adamantane

EXPERIMENTAL

Diphenyl oxide (DPO) (Vekton, Russia) with the purity of more than 99 wt % according to GLC data was used for the synthesis of AdDPO. Phenol 99.9 wt % (purchased from the Novokuibyshevsk Petrochemical Company NNK, Russia) was used for the preparation of adamantylphenols (AdP) without additional purification.

1-Chloro- and 1-bromoadamantanes (1-ClAd and 1-BrAd) containing trace amounts of adamantane were used as an alkylating agent. The alkylation of DPO and phenol was performed using Amberlyst 36 Dry sulfonated cation-exchange resin (Dow Chemical) as the catalyst (provided by NNK, Russia). Prior to the experiments, the catalysts were dried in a thermostat at 105°C to constant weight. The alkylation was performed in a glass jacketed reactor, equipped with a stirrer and a reflux condenser, in the temperature range of 80–150°C. The reactor was thermostated at an appropriate temperature with a heat-transfer fluid (benzene, toluene, *o*-xylene, or *n*-nonane) boiling in the jacket.

The reactor was charged with diphenyl oxide or phenol and the catalyst in an amount of 30 wt %, the mixture was stirred at the temperature of the experiment for 30 min, then 1-ClAd was introduced, and sampling started. To preclude the formation of diadamantyl derivatives, the alkylation was performed with an excess of the substrate. The 1-ClAd/substrate molar ratio was varied in the range of 0.01–0.7.

The isomerization equilibrium of adamantyl diphenyl oxides (AdDPO) was studied in the liquid phase using the static method and catalysis with $AlCl_3$ or $AlBr_3$.

The reaction mixture obtained via alkylation over the sulfonated resin was freed from the catalyst, placed into an airtight glass reactor, and heated to the reaction temperature; then, 1–5 wt % $AlCl_3$ was introduced and the reactor was thermostated with an accuracy of ±1°C in a SNOL-58/350 air bath oven. The time of the experiment was counted from this moment on. Samples were collected with a microsyringe from the liquid phase by piercing the seal in the lid of the reactor. The sample taken was immediately quenched with water, extracted with toluene, dried over calcium chloride, and chromatographically analyzed.

The experiment consisted of series of measurements. The temperature, the initial composition, and the type and amount of the catalyst remained constant within each series, only the duration of the experiment varied. The series differed between each other only in the composition of the initial mixture and the amount of the catalyst.

The isomerization equilibrium of adamantylphenols was studied in the presence of 20–30 wt % A-36 sulfonated cation-exchange resin. The experimental procedure was similar to that used for the isomerization of AdDPO except that the samples taken were not subjected to any special treatment; they were just diluted with toluene and analyzed.

The main method for the analysis of the reaction mixtures was gas–liquid chromatography. The chromatographic analysis was performed on a Kristall 2000 M chromatograph with a Chromatec-Analitik software–hardware complex equipped with a flame ionization detector, a carrier gas splitter, and a quartz capillary column (60 m × 0.25 mm) with the bonded SE-30 stationary phase. Helium was used as the carrier gas. The carrier gas pressure at the inlet to the column was 3 atm, the stability of the pressure was provided via double reduction. The column temperature modes were individually selected for each system and were maintained accurate to within ±0.1°C. The evaporator temperature of was 543 K, and the detector temperature was 573 K.

The identification of all the components of the mixtures included both a chemical experiment and a chromatographic–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 an HP-5MS stationary phase (5% diphenylpolysiloxane + 95% dimethylpolysiloxane) and an Agilent 5975C VL MSD mass selective detector at an ionizing energy of 70 eV.

RESULTS AND DISCUSSION

The adamantylation of DPO with 1-chloro(bromo)adamantanes in the presence of A-36 (30 wt %) and at a haloadamantane/DPO molar ratio not exceeding 0.25 is quite a rapid process; it is completed within 60–90 min over the operating temperature range of the sulfonated cation exchanger. The selectivity of the process for *p*-(1-Ad)DPO is high, being at the level of 96–94%.

In the low-temperature region (353–383 K) of the use of the cation-exchange resins, *o*-(1-Ad)DPO is the only impurity to *p*-(1-Ad)DPO. Note this fact is characteristic not only for the alkylation step, but also for the subsequent isomerization up to 270 min, with the *o*-(1-Ad)DPO concentration changing by no more than 2%.

The high-temperature region (≥417 K) of the use of the cation-exchange resins is characterized by the noticeable progress of the isomerization of two types:

• in the aromatic ring, resulting in a change in the *o*-(1-Ad)DPO concentration and the formation of *m*-(1-Ad)DPO and

• in the adamantyl substituents, resulting in the appearance of *p*-(2-Ad)DPO and a further growth in its concentration.

In this region, the rate of formation of *p*-(2-Ad)DPO keeps the fivefold higher value relative to the rate of formation of *m*-(1-Ad)DPO over the entire time span of the study.

The values of the rate constants obtained for the isomerization of a *p*-(1-Ad)DPO + DPO mixture over A-36 (30 wt %) at 417 K are presented in Table 1. The kinetic information was processed by the Runge–Kutta method using recommendations set out in [23].

Therefore, the high selectivity of the adamantylation of DPO over sulfonated cation-exchange resins becomes explainable—forming *o*-(1-Ad)DPO rapidly transforms into target *p*-(1-Ad)DPO. It was experi-

Table 1. Rate constants for the isomerization of AdDPO over A-36 at 417 K

Reaction	Reaction symbol	k_i, min^{-1}	k_i/k_{-1}	k_i/k_{-i}
o-(1-Ad)DPO $\xrightarrow{k_1}$ *p*-(1-Ad)DPO	1.Ad	5.05E-04	30	30
p-(1-Ad)DPO $\xrightarrow{k_{-1}}$ *o*-(1-Ad)DPO	−1.Ad	1.68E-05	1	
p-(1-Ad)DPO $\xrightarrow{k_2}$ *m*-(1-Ad)DPO	2.Ad	2.70E-05	1.6	
p-(1-Ad)DPO $\xrightarrow{k_3}$ *p*-(2-Ad)DPO	3.Ad	2.35E-04	14	
p-(2-Ad)DPO $\xrightarrow{k_{-3}}$ *p*-(1-Ad)DPO	−3.Ad	5.04E-03	300	21

mentally found that adamantane was not formed as a byproduct during the adamantylation of DPO over the A-36 resin and the subsequent isomerization of the products over the same catalyst in the range of 333–424 K for 6 h.

Practice shows that like phenol and anisole [15, 16], DPO possesses sufficient reactivity to react with halo(chloro and bromo)adamantanes even in the absence of an added catalyst. Higher temperatures are required for the reaction.

In the range of 523–623 K, the reaction of DPO with bromoadamantane proceeds almost instantaneously. The *p*-(1-Ad)DPO selectivity of the process is at the level of 90–92% for several minutes. Then follows intensive development of the isomerization with the predominant formation of all mono(1-Ad)DPO and establishment of equilibrium between them (Figs. 1a and 1b) with the prevalence of *m*-(1-Ad)DPO in the equilibrium mixture.

Thus, the high-temperature adamantylation of DPO with 1-bromoadamantane can be considered as an alternative method for the preparation of *m*-(1-Ad)DPO.

The analysis of the results obtained in this study shows that in the group of 2-AdDPO, the concentration of the *para*-isomer stabilizes quite rapidly (within 16 h at 523 K) (Fig. 1a) and the concentration of the *meta*-isomer increases (Fig. 1b). It is noteworthy that the *p*-(1-Ad)DPO/*p*-(2-Ad)DPO and *m*-(1-Ad)DPO/*p*-(1-Ad)DPO concentration ratios almost simultaneously reach their equilibrium levels, which remain unchanged in the case of a tenfold increase in the residence time under the conditions of the experiment at 523 K. At the same time, the *m*-(1-Ad)DPO/*m*-(2-Ad)DPO concentration ratio decreases, slowly approaching the equilibrium value.

The total concentration of the *ortho*-isomers in the monoAdDPO group did not exceed 7% regardless of the conditions of adamantylation. The possibility for the formation of diAdDPO in this work was limited for practical reasons; it was eliminated by running the processes in excess DPO.

The adamantylation of DPO over Lewis acids is accompanied by the fast formation of all the possible isomers of AdDPO and accumulation of adamantane in the reaction mixture (Fig. 2).

The values of the rate constants found by studying the kinetics of the transformations of AdDPO in a DPO medium (80–5 mol %) over $AlCl_3$ (4.9 wt %) at 333 K are presented in Table 2.

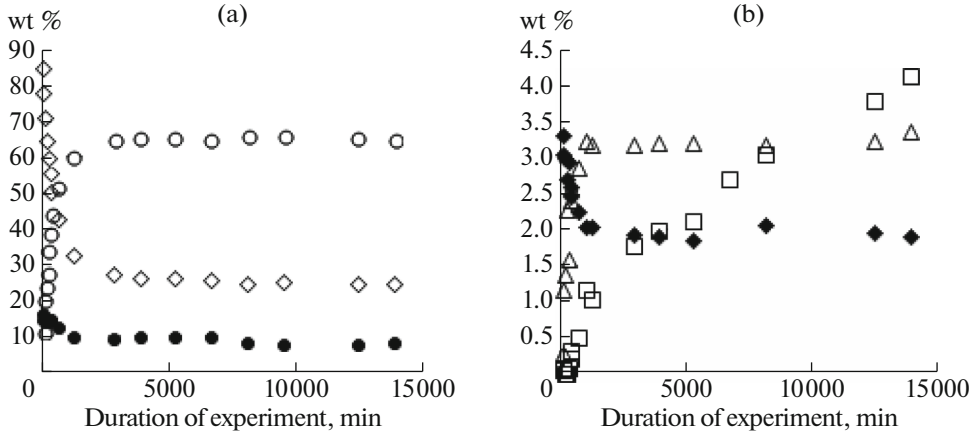


Fig. 1. Isomerization of *p*-(1-Ad)DPO at 523 K, catalysis with in situ HBr: (◊) *p*-(1-Ad)DPO, (○) *m*-(1-Ad)DPO, (◆) *o*-(1-Ad)DPO, (□) *m*-(2-Ad)DPO, (△) *p*-(2-Ad)DPO, and (●) degree of conversion of DPO.

The values of the rate constants of reactions (1.Ad)–(3.Ad) over $AlCl_3$ exceed k_i values for the same processes over A-36 by more than an order of magnitude, despite the fact that the process temperature in the experiment with $AlCl_3$ is lower by 84 K as compared to A-36. The analysis of the ratios of the rate constants (Table 2) shows that it is hardly possible to expect the selective preparation of any AdDPO over $AlCl_3$.

The following findings also deserve attention:

• the rate of *p*-(1-Ad)DPO decomposition to form adamantane (Table 2, reaction (6.Ad)) is higher by a factor of 1.8 than the rate of the coupled isomerization reaction of *p*-(1-Ad)DPO to *p*-(2-Ad)DPO (reaction (3.Ad)) and sixfold higher than the rate of formation of *m*-(1-Ad)DPO (reaction (2.Ad));

• the rate of decomposition of *m*-(1-Ad)DPO is sevenfold higher than the rate of decomposition of *p*-(1-Ad)DPO; and

• the decomposition reactions of AdDPO are reversible (Fig. 2, Table 2).

Apparently, a similar situation should be expected for other Lewis acids and, possibly, for strong acids of other types.

Thus, it was experimentally found that the AdDPO transformations of the types of *ortho–para* in the aromatic ring, *para–meta* in the aromatic ring, and bridge–bridgehead in the adamantane cage are significantly different in terms of kinetics.

The *ortho–para* transformations in the aromatic ring are characterized by the highest rate under otherwise equal conditions. By selecting the type of the catalyst and conditions of the process, the transformation *o*-(1-Ad)DPO ↔ *p*-(1-Ad)DPO (1.Ad) can be singled out from the set of all the reactions not only in the case of the kinetic control of the process, but also up to the point of reaching the equilibrium. In the high-temperature operating region of the cation-exchange resins, the equilibrium of reaction (1.Ad) is reached within several minutes (5–7 min over 30 wt % A-36 at 417–424 K) and is selectively maintained up to 150 min. At equilibrium, the concentration of *p*-(1-Ad)DPO is 30 times that of *o*-(1-Ad)DPO. Reaction (1.Ad) over the cation-exchangers can reach the equi-

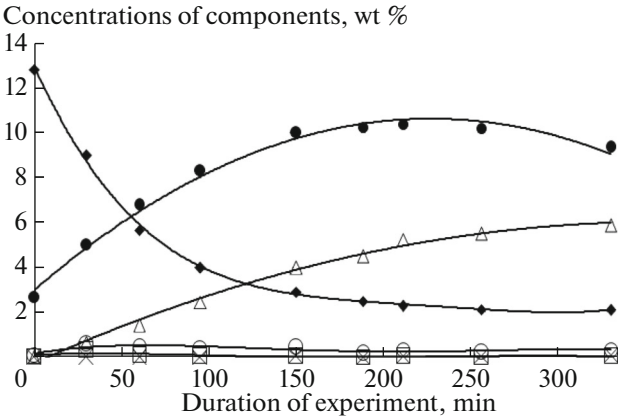


Fig. 2. Transformations of AdDPO over $AlCl_3$ at 333 K: (●) adamantane, (□) *o*-1-AdDPO, (△) *m*-1-AdDPO, (×) *m*-2-AdDPO, (◆) *p*-1-AdDPO, and (○) *p*-2-AdDPO.

Table 2. Rate constants of the isomerization of AdDPO over $AlCl_3$ at 333 K

Reaction	Reaction symbol	k_i, min^{-1}	k_i/k_{-1}	$k_i(AlCl_3)/k_i$(A-36)
o-(1-Ad)DPO $\xrightarrow{k_1}$ *p*-(1-Ad)DPO	1.Ad	5.79E-03	71	11
p-(1-Ad)DPO $\xrightarrow{k_{-1}}$ *o*-(1-Ad)DPO	−1.Ad	8.16E-05	**1**	
p-(1-Ad)DPO $\xrightarrow{k_2}$ *m*-(1-Ad)DPO	2.Ad	2.49E-03	30	92
m-(1-Ad)DPO $\xrightarrow{k_{-2}}$ *p*-(1-Ad)DPO	−2.Ad	9.10E-04	11	
p-(1-Ad)DPO $\xrightarrow{k_3}$ *p*-(2-Ad)DPO	3.Ad	8.02E-03	98	34
p-(2-Ad)DPO $\xrightarrow{k_{-3}}$ *p*-(1-Ad)DPO	−3.Ad	1.29E-01	1582	
m-(1-Ad)DPO $\xrightarrow{k_4}$ *m*-(2-Ad)DPO	4.Ad	1.08E-02	133	
m-(2-Ad)DPO $\xrightarrow{k_{-4}}$ *m*-(1-Ad)DPO	−4.Ad	1.74E-01	2127	
p-(2-Ad)DPO $\xrightarrow{k_5}$ *m*-(2-Ad)DPO	5.Ad	1.04E-02	127	
m-(2-Ad)DPO $\xrightarrow{k_{-5}}$ *p*-(2-Ad)DPO	−5.Ad	5.19E-03	64	
p-(1-Ad)DPO $\xrightarrow{k_6}$ Adamantane + DPO	6.Ad	1.43E-02	175	
Adamantane + DPO $\xrightarrow{k_{-6}}$ *p*-(1-Ad)DPO	−6.Ad	2.03E-04	2.5	
m-(1-Ad)DPO $\xrightarrow{k_7}$ Adamantane + DPO	7.Ad	9.81E-02	1202	

Table 3. Results of studying the AdDPO isomerization equilibrium

T, K	n^a	m^b	Catalyst, wt %	Time, min	$K_x \pm t_{0.05}s$	K_x^σ	Composition of reaction mixture
o-(1-Ad)DPO ↔ *p*-(1-Ad)DPO (1.Ad)							
353	6	1	$AlCl_3$, 6%	15–210	52.1 ± 5.6	104	All AdDPO isomers
393	7	1	$AlCl_3$, 3%	20–180	37.8 ± 5.2	75.6	All AdDPO isomers
417	9	1	A-36, 30%	5–300	28.2 ± 0.9	56.4	No *m*-AdDPO
417	8	1	$AlCl_3$, 5%	1–260	29.2 ± 2.6	58.4	All AdDPO isomers
424	9	1	A-36, 30%	7–150	33.1 ± 0.8	66.2	*o*- and *p*-(1-Ad)DPO
424	3	1	A-36, 30%	90–270	30.1 ± 1.8	60.2	Other AdDPO < 5%
523	11	1	HBr, in situ	960–13800	14.0 ± 1.0	28.0	2-AdDPO < 5%
p-(1-Ad)DPO ↔ *m*-(1-Ad)DPO (2.Ad)							
333	4	1	$AlCl_3$, 3%	188–3270	2.57 ± 0.18	1.29	All AdDPO isomers
353	3	1	$AlBr_3$, 5%	290–530	2.79 ± 0.04	1.40	All AdDPO isomers
353	10	1	$AlCl_3$, 3%	125–600	2.64 ± 0.26	1.34	All AdDPO isomers
353	6	1	$AlCl_3$, 6%	15–210	2.82 ± 0.09	1.41	All AdDPO isomers
383	3	1	$AlBr_3$, 5%	140–270	2.75 ± 0.03	1.38	All AdDPO isomers
393	7	1	$AlCl_3$, 3%	20–180	2.93 ± 0.31	1.47	All AdDPO isomers
417	4	1	$AlCl_3$, 5%	90–260	2.67 ± 0.03	1.37	All AdDPO isomers
523	4	1	HBr, in situ	8040–13800	2.62 ± 0.02	1.31	2-AdDPO < 5%
p-(2-Ad)DPO ↔ *p*-(1-Ad)DPO (3.Ad)							
353	3	1	$AlCl_3$, 6%	90–210	13.3 ± 0.1		All AdDPO isomers
383	3	1	$AlBr_3$, 5%	140–270	12.1 ± 0.5		All AdDPO isomers
393	6	1	$AlCl_3$, 3%	30–180	10.4 ± 0.8		All AdDPO isomers
417	9	1	$AlCl_3$, 5%	1–260	8.9 ± 1.7		All AdDPO isomers

[a] The number of determinations; [b] the number of sets of experiments; $K_x \pm t_{0.05}s$ are respectively the equilibrium constant and the confidence interval at the significance level of 0.95.

librium at lower temperatures as well. In that case, the residence time increases (≥30 min at 383 K).

Under otherwise equal conditions, the reaction *p*-(2-Ad)DPO ↔ *p*-(1-Ad)DPO (2.Ad) has a lower rate in comparison with reaction (1.Ad) and cannot be singled out from the set of AdDPO transformations. However, these two reactions can be accomplished up to reaching equilibrium by them providing that all the other isomeric transformations are almost completely ruled out. The equilibrium concentration of *p*-(1-Ad)DPO 9–13 times that of *p*-(2-Ad)DPO in the temperature range examined. Reaction (3.Ad) proceeds at an even lower rate; its equilibrium is reached only in the case of a significant residence time and the established equilibrium of reactions (1.Ad) and (2.Ad).

The values of the equilibrium constants presented in Table 3 are approximated by a linear equation, the coefficients of which and the enthalpies and entropies calculated on their basis for reactions (1.Ad)–(3.Ad) are presented in Table 4. The errors of all the quantities are presented by confidence intervals for the significance level of 0.05.

The value of the enthalpy effect of reaction (1.Ad) gives evidence for a significant *ortho*-interaction of the (PhO) and (1-Ad) substituents on the aromatic ring, which destabilizes the (1-Ad)-DPO molecule. On the assumption of the absence of interaction between the (PhO) and (1-Ad) substituents in the *p*-(1-Ad)DPO molecule, the value of the enthalpy term of the *ortho*-effect for the same substituents is 11.8 ± 1.4 kJ/mol (for the liquid state). It is interesting that, this term obtained similarly for the *ortho*-effect of the interaction of the (OH) and (1-Ad) substituents in adamantylphenols has a high value of 15.0 ± 1.0 kJ/mol.

Reaction (2.Ad) characterizes the bridge–bridgehead transition in the adamantyl moiety of the *p*-AdDPO molecule. The enthalpy of this reaction is 7.7 ± 1.7 kJ/mol.

Sarkisova [22] obtained the following values of enthalpy for identical transformations in studying liquid-phase isomerization equilibria:

−9.6 ± 0.6 kJ/mol for (2-Ad)benzene ↔ (1-Ad)benzene,

Table 4. Thermodynamic characteristics of the liquid-phase transformations studied

Reaction symbol	T_{in}–T_{fin}, K	T_m, K	Coefficients of equation $\ln(K_x) = a + 1000b/T$		$\Delta_r H_m^0(l)$, kJ/mol	$\Delta_r S_m^0(l)$, J mol^{-1} K^{-1}
			a	b		
1.Ad	353–523	405	–0.0101	1.4232	–11.8 ± 1.4	0.0 ± 3.5
2.Ad	333–523	389	0.9722	0.0111	–0.1 ± 0.4	8.1 ± 1.1
3.Ad	353–417	387	–0.0107	0.9292	–7.7 ± 1.7	–0.1 ± 4.5

$\Delta_r H_m^0(l)$ and $\Delta_r S_m^0(l)$ are respectively the enthalpy and the entropy of the reaction in the liquid phase.

–10.5 ± 0.8 kJ/mol for *m*-(2-Ad)toluene ↔ *m*-(1-Ad)toluene, and

–11.2 ± 1.1 kJ/mol for *p*-(2-Ad)toluene ↔ *p*-(1-Ad)toluene.

These values are somewhat lower than the value obtained in the present study. Moreover, there is a certain trend in the dependence of the enthalpy on the structure of the molecule is emerging. However, it was noted [21, 22] that the Allinger molecular mechanics method with a force field (MM2-1991) gives a single value $\Delta_r H_{298.g}^0 = -7.28$ kJ/mol for all the reactions in question. It is believed [21, 22] that this value cannot be used for the determination of the enthalpies of reactions involving aryladamantanes; to eliminate the discrepancy, it is proposed to correct the constants of the Allinger method. Nonetheless, the coincidence of the value obtained in the study with the one predicted by the Allinger method suggests that this issue is still an open question.

The data (Table 4) obtained for reaction (3.Ad) supplement the quite vast database on the thermodynamics of the *meta–para* transformation of aromatic hydrocarbons with new structures and is in good agreement with the information accumulated to date.

It was experimentally found that both *ortho–para* and *meta–para* transformations can be selectively accomplished for 1-AdDPO under equilibrium conditions. The results of this study (Table 4) made it possible to find the temperature dependence of the composition of equilibrium mixtures in the groups of these isomers (Fig. 3).

Thus, under the equilibrium between *ortho–para* transformations is established (Fig. 3), the concentration of *p*-(1-Ad)DPO decreases with an increase in temperature, remaining at a high level, which reaches 99% at 300 K.

In the system represented by *p*-(1-Ad)DPO, *m*-(1-Ad)DPO, and *p*-(2-Ad)DPO, the dominating isomer is *m*-(1-Ad)DPO. Its concentration slightly depends on temperature to be at the level of 71 ± 1%, the concentration of *p*-(1-Ad)DPO is 26 ± 1%, and *p*-(2-Ad)DPO makes no more than 5%.

We found (Table 4) that the equilibrium is selectively reached in both the systems: over the entire

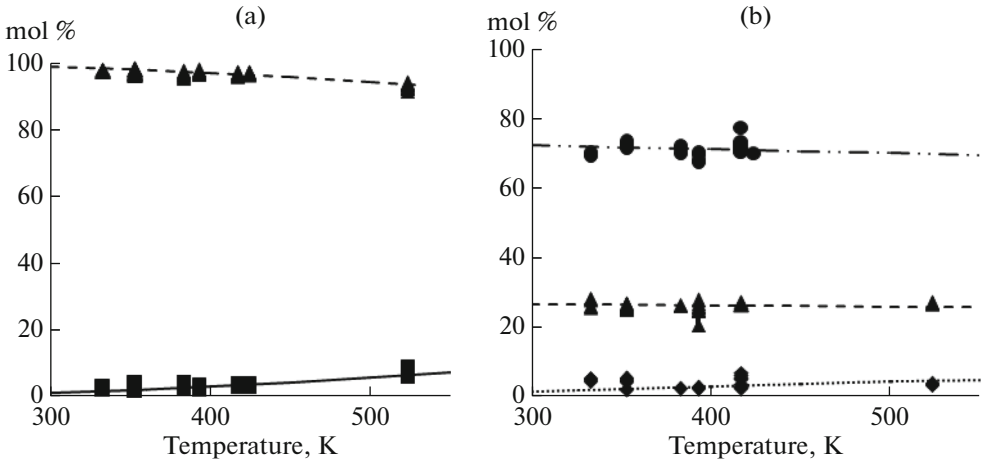


Fig. 3. Temperature dependence of the composition of the equilibrium mixture (a) in *o*- and *p*-(1-Ad)DPO; the curves and symbols refer to the calculated and experimental values of concentrations, respectively: (▲) *p*-(1-Ad)DPO, and (■) *o*-(1-Ad)DPO. (b) Temperature dependence of the composition of the equilibrium mixture in *m*- and *p*-(1-Ad)DPO and *p*-(2-Ad)DPO. The curves and symbols refer to the calculated and experimental values of concentrations, respectively: (▲) *p*-(1-Ad)DPO, (•) *m*-(1-Ad)DPO, and (♦) *p*-(2-Ad)DPO.

Table 5. Results of studying the isomerization equilibrium of adamantylphenols

T, K	n[a]	m[b]	Catalyst, wt %	Time, min	$K_x \pm t_{0.05}s$	$\Delta_r H_m^0(l)$, kJ/mol	$\Delta_r S_m^0(l)$, J mol^{-1} K^{-1}
o-(1-Ad)phenol ⇄ *p*-(1-Ad)phenol (1.AdP)							
373	27	3	H_2SO_4, 5–10	2–36	110.1 ± 0.1	−15.0 ± 1.0	−1.1 ± 2.3
403	10	1	A-36, 30	8–32	75.2 ± 2.5		
403	36	3	H_2SO_4, 5–10	0.5–20	77.4 ± 0.1		
413	8	1	A-36, 30	5–22	69.8 ± 3.4		
453	52	5	H_2SO_4, 1.0–1.5	0.5–18	50.4 ± 0.1		
523	44	5	H_2SO_4, 1.0	0.08–8	26.4 ± 0.04		
573	34	3	H_2SO_4, 0.5–1.0	0.08–8	20.7 ± 0.04		

[a] The number of determinations; [b] the number of sets of experiments; $K_x \pm t_{0.05}s$ are respectively the equilibrium constant and the confidence interval at the significance level of 0.95; $\Delta_r H_m^0(l)$ and $\Delta_r S_m^0(l)$ are respectively the enthalpy and the entropy of the reaction in the liquid phase.

operating range on the sulfonated resins in the or at 523 on HBr K for *ortho–para* transformations and at 343–447 K on aluminum halides and at 523 K on HBr for *meta–para* transformations.

The adamantylation of phenol with (1-chloro/bromo)adamantanes or 1-adamantanol over protic catalysts is also a quite selective process with respect to *p*-(1-Ad)phenol. The concentration of *p*-(2-Ad)phenol did not exceed 0.3% (of total isomers) in all the experiments (over A-36 or H_2SO_4). Adamantane almost did not form in this case, and adamantane initially introduced into the system transformed into Ad-phenols. The *p*-(1-Ad)phenol/*o*-(1-Ad)phenol ratio substantially depends not only on the temperature of the process, but also on the residence time. In the low-temperature region of the operating range of the sulfonated cation-exchangers (333–363 K), the concentration of the *o*-isomer at the onset of adamantylation exceeds 30 wt % in the mixture of *o*- and *p*-(1-Ad)P; however, the system starts approaching the equilibrium quite rapidly (within 2–4 h). Increasing the temperature shortens this period. In addition, the concentration of *p*-(2-Ad)P changes slightly even under the conditions of stable equilibrium for reaction (1.AdP). The results obtained by Karlina [25] and in this study of the AdP isomerization equilibrium of are presented in Table 5' from the data in the table, it follows that the *p*-(1-Ad)P selectivity can reach 99% when the phenol adamantylation process is performed under the conditions of established equilibrium.

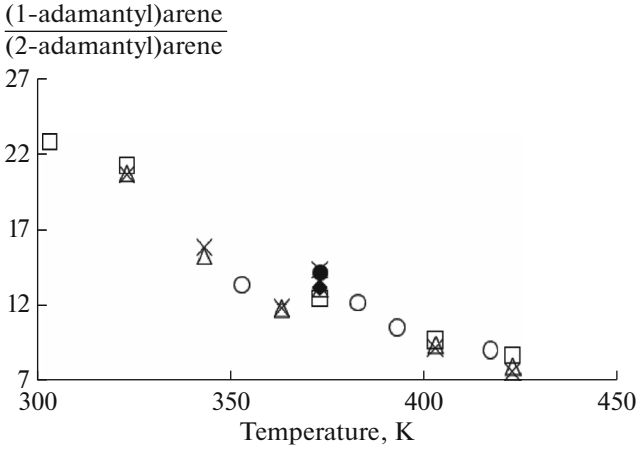


Fig. 4. Temperature dependence for the equilibrium constants of the bridge–bridgehead isomerization in the liquid phase of adamantylbenzenes and diphenyl oxides: (○) *p*-2-AdDPO ⇄ *p*-1-AdDPO, (□) (2-Ad)benzene ⇄ (1-Ad)benzene, (△) *m*-(2-Ad)toluene ⇄ *m*-(1-Ad)toluene, (×) *p*-(2-Ad)toluene ⇄ *p*-(1-Ad)toluene, (◆) *4*-(2-Ad)-*o*-xylene ⇄ *4*-(1-Ad)-*o*-xylene, and (●) *5*-(2-Ad)-*m*-xylene ⇄ *5*-(1-Ad)-*m*-xylene.

Regarding adamantylbenzenes, there are published results of a targeted study by Pimerzin and Sarkisova [19, 20] on the equilibrium of bridge–bridgehead type isomerization. In the context of this work, it would be interesting to compare the results of their study and the data that we obtained for AdDPO. These data arrays are collated in Fig. 4, showing that the values of the liquid-phase equilibrium constants of the bridge–bridgehead isomerization do not differ fundamentally for the systems of benzenes and diphenyl oxides and depend on temperature, decreasing almost threefold with its increase from 303 to 423 K.

Since benzenes and DPO exhibit fundamentally different reactivities in electrophilic substitution reactions, this result can be extended to a significant series of adamantylation substrates. This means that under equilibrium conditions, the selectivity of processes for preparing sterically unstrained (1-adamantyl)arenes significantly increases with a decrease in the synthesis temperature.

Despite the fact that , the data of targeted kinetic and thermodynamic studies on the adamantylation of benzenes are limited, important experimental information has been obtained so far for answering at least two questions considered below.

One of them concerns the ratio of the concentrations of the isomers in the aromatic ring in the case of adamantylation of substituted arenes under the conditions of thermodynamic control. The results obtained by Olah [1] for the adamantylation of toluene and isomerization of adamantyltoluenes on boron tris(triflate) lead to the conclusion that the isomeric composition of (1-adamantyl)arenes can be assessed on the basis of the same approaches which are applied to tertiary alkylarenes [25]. Similar parallels between alkylbenzenes and (2-adamantyl)arenes are still impossible to draw because of the absence of necessary information. However, the values of the rate constants presented in Table 2, which yield the equilibrium constant of 2.00 for the *para*–*meta* isomerization of (2-Ad)DPO (reaction (3.Ad)), give grounds to expect that there is analogy in the behavior of (2-adamantyl)arenes and secondary alkylbenzenes [25] as well. Unlike positional isomers of aromatic compounds, structural isomers in the classes of adamantyl- and alkylarenes fundamentally differ with in their relative thermodynamic stability. Indeed, at follows from the data in Fig. 4, (1-Ad)arene has more than 20-fold higher stability than (2-Ad)arene at 300 K. At the same time, the tertiary isomer in the case of branched pentylbenzenes is fivefold less stable than secondary (1,2-dimethylpropyl)arene [9]. This fact should be reckoned with.

The second question concerns adamantane that is formed during the adamantylation of arenes and isomerization of Ad-arenes in an amount comparable to that of the main product or even exceeding it [1, 11, 12]. The essence of the question is evident. The selectivity of such processes cannot be considered satisfactory. Nonetheless, adamantane barely formed as a byproduct during the adamantylation of phenol or DPO over the sulfonated cation-exchange resins or in the absence of a catalyst. This fact has been established in the present study and reported in [15, 16]. However, passing to $AlCl_3$ in the study of AdDPO isomerization dramatically changes the situation (Table 2), namely, the adamantane formation and AdDPO isomerization rates turn to be comparable even at a relatively low temperature (333 K). Therefore, the cornerstone of success in the adamantylation of arenes centers is the selection of an appropriate catalyst.

CONCLUSIONS

The adamantylation of phenol and diphenyl oxide with 1-chloro(bromo)adamantanes in the presence of aluminum halides and the sulfonated cation-exchange resin Amberlyst 36 Dry has been performed. The study of the reaction under the conditions of kinetic control or after establishment of chemical equilibrium has shown that the selectivity of the adamantylation of arenes significantly depends on the choice of the catalyst. Thus, it has been found that:

(1) the high selectivity of the adamantylation of DPO at the *para*-position is provided by using sulfonated cation-exchange resins as a catalyst. Carrying out the reaction in the low-temperature range of operation of the cation-exchange resin (353–383 K) leads to inhibition of the positional and structural "1-adamantyl–2-adamantyl" isomerization. The selectivity for 1-AdDPO reaches 94–96% even within 6 h of isomerization;

(2) the replacement of the catalyst by aluminum halides or HBr not only increases the rate of isomerization, but also yields a reaction mixture with all the possible isomers. When these catalysts are used, the formation of adamantane is also observed. This means that it is challenging to obtain any of the AdDPO isomers as an individual product in the case of adamantylation over aluminum halides;

(3) chemical equilibrium can be selective established in the following reactions: *ortho*–*para* isomerization in the presence of A-36 in the range of its operability (353–417 K) or HBr at 523 K and *para*–*meta* isomerization on aluminum halides at 343–447 K or HBr at 523 K. Under equilibrium conditions, 1-adamantylated products predominate over 2-adamantyl derivatives in concentration; and

(4) the adamantylation of phenol can be selectively performed with 1-haloadamantane in the presence of protic catalysts (A-36, H_2SO_4) to yield *p*-(1-adamantyl)phenol. The *p*-1-adamantylphenol selectivity can be as high as 99%.

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