



Azoxybenzene rearrangement catalyzed by solid acids

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ABSTRACT

For the first time, the potential of acidic cation-exchange resin (sulfonated polystyrene) to catalyze the Wallach rearrangement of azoxybenzene into 4-hydroxyazobenzene has been proved. This finding reveals an alternative reaction path possible in a heterogeneous process using solid acids and may help to clear some doubts concerning the rearrangement mechanism postulated so far. The resin-induced reaction was found to proceed exclusively in a non-polar medium. Reasonable yield was obtained particularly in isooctane due to favorable distribution of azoxybenzene throughout the resin's matrix. On the contrary, the HY type zeolite did not activate the rearrangement, most probably because of steric hindrance. Experimental results favor the hypothesis of a quinoid intermediate controlling the chemistry of azoxybenzene conversion, which also follows from thermodynamic considerations involving DFT calculations.

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1. Introduction

Isomerization of azoxybenzene, **1**, to 4-hydroxyazobenzene, **2a**, occurring in concentrated solutions of sulfuric acid is known as the Wallach rearrangement [1] (Scheme 1).

This acid-catalyzed intermolecular transformation may be considered in terms of aromatic nucleophilic substitution by OH group formed by the medium [2]. Rearrangement of [¹⁵N]-azoxybenzene indicated that both of the para-carbons might be migration targets, hence, a symmetrical intermediate was suggested [3]. Its structure is still controversial and has been assumed to be either a dication **3** [4] or *N,N'*-diphenyloxadiaziridine **4** [5]. A quinoid intermediate **5**, as a different alternative, has also been proposed [6] (Scheme 2).

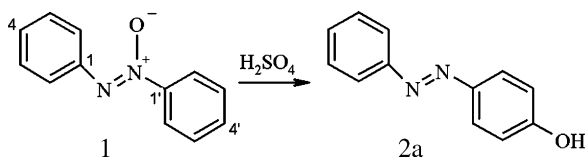
In a recent monograph dedicated to the “azoxy” compounds and their rearrangements the so-called dicationic mechanism involving **3** was claimed to be the most adequate explanation of the reaction shown in Scheme 1 [7]. This statement was based in principle on a previous report maintaining that cation-exchange resins do not catalyze the Wallach rearrangement [8]. It was concluded, that such resins have no potential to induce double-protonation of **1** and hence to produce the dication intermediate **3**, considered essential for the rearrangement. However, analysis of experimental conditions applied in [8] brings up some questions regarding both the results and conclusions. Similarly, the validity of other reports, seemingly supporting the hypothesis of **3**, including exper-

iments with ¹⁵N [9] and ¹⁴C [10] isotope-labeled azoxybenzene **1** was discussed elsewhere [10,11]. The only certain fact emerging from these investigations is that under homogenous reaction conditions both benzene rings have been equally activated for the nucleophilic attack. This would imply that formation of a symmetrical intermediate and hence double-protonation may not be necessary to realize the Wallach rearrangement, for instance in a heterogeneous process exploiting cation-exchange solid acids such as zeolites or polymeric resins. Indeed, HY-type acid zeolite was reported to catalyze this reaction [12]. The product included the 4-hydroxyazobenzene, **2a**, along with the 2-hydroxy derivative, **2b**. The authors proposed a novel mechanism involving formation of a cyclic compound, **4**, following the idea of a symmetrical intermediate (Scheme 2).

An alternative mechanism involving the quinoid form, **5** (Nu = HSO₄⁻), was proposed on the base of empirical studies [6,13], which proved the “azoxy” group in **1** may equally activate both of the benzene rings for a nucleophilic attack, despite of their quasi-nonequivalence. This idea found reasonable support in theoretical calculations, which revealed that formation of the quinoid intermediate **5** was thermodynamically and kinetically much more favorable than the other structures proposed instead, i.e. **3** and **4** [14]. Nevertheless, another theoretical study has promoted the dication **3** as the most probable structure, although no comparative results concerning **4** and/or **5** have been included [15].

Since the results reported so far apply exclusively to the homogeneous Wallach process (except [12]), we felt reasonable to propose our view upon the discussed problems, on the basis of data obtained from experiments carried out under heterogeneous conditions. It has been the intention of this work to help clearing some

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Scheme 1.

nuances in understanding of the studied reaction mechanism and to trigger off further discussion, involving similar processes, as well. Therefore, the following targets have been particularly addressed to, namely (i) do acidic cation-exchange resins and zeolites induce protonation of azoxybenzene and its substituted derivatives; (ii) does rearrangement of protonated azoxybenzene and its derivatives take place in the presence of ion-exchange resins and zeolites; and (iii) do any of the literature-postulated intermediates meet the thermodynamic requirements for the Wallach rearrangement (estimated by using the DFT calculation method).

2. Experimental

The substrate **1** and products **2a** and **2b** have been characterized in detail in [Supporting Information](#). Lewatit K-2629 (Fluka) cation-exchange resin cross-linked polystyrene matrix with sulfonic acid groups was used. Specification: H⁺-form, strongly acidic, macroporous, pore size 65 nm, specific surface area approximately 40 m²/g, spherical particles 0.4–1.3 mm; preheated at 110 °C for 12 h. NH₄Y zeolite (Aldrich, 334413-100 G) heated at 500 °C for 12 h (to produce the HY type) was used. All solvents used in this study were reagent grade.

2.1. Rearrangement of azoxybenzene, **1**, on the Lewatit resin

Most operations were carried out under dark conditions (and for comparison under typical laboratory scattered light conditions). 30 mg (0.15 mmole) of **1** was dissolved in 100 ml of a suitable solvent in a glass flask and 3.0 g of Lewatit resin K-2629 was added. The flask was wrapped in aluminum foil and heated under reflux for 24 h. The post-reaction mixture was filtered and the filtrate was analyzed by HPLC and GC–MS. The Lewatit resin was washed with several portions of methanol (in total 100 ml) and the filtrate was analyzed by HPLC, GC–MS and UV–vis. Next the resin was washed out directly on the funnel with few portions of 85% H₂SO₄ (in total 20 ml) and the liquid was collected in a vessel containing 180 ml of water; this diluted acid solution (8.5% H₂SO₄) was extracted by three 50 ml portions of CH₂Cl₂. The extract was washed with water and dried over anhydrous CaCl₂. Next, the solvent was distilled off in a rotary vaporizer; afterwards, the solid residue was dissolved in 10 ml of CH₃OH and analyzed (HPLC, GC–MS). Results have been presented in [Table 1](#). It must be emphasized, that in experiments in which the rearrangement was successfully performed, the total amount of the target product (**2a** + **2b**) found in the sulfuric acid extract was less than 0.2%. However, the same extract contained the bulk of the polymeric by-product. Thus, the applied acid-extraction has proved an effective way to free the resin of the post-reaction residues and allows the re-use of it.

Table 1
Azoxybenzene rearrangement on Lewatit resin and HY zeolite

M ^a	Solvent	T (°C)	AZB _{solv} ^b	δ _{AZB} ^c	Reaction yield ^d	
					2a	2b
R	Methanol	65	80	16	0	0
R	20% MeOH + water	90	20	57	0	0
R	2-Propanol	82	62	11	0	0
R	Acetic acid	118	93	4	0	0
R	DMF	146	93	5	1.8	2.4
R	CCl ₄	77	51	14	0.6	0.2
R	<i>n</i> -Heptane	98	2	89	11.3	5.2
R	Isooctane	100	0	90	36.2	11.4
R	Isooctane	20 ^e	86	5	0	0
Z	Methanol	65	91	8	0	0
Z	Isooctane	100	0	11	0	0

^a Solid matrix type, where R = resin and Z = zeolite.

^b Concentration of azoxybenzene remaining in the post-reaction solvent (mass%).

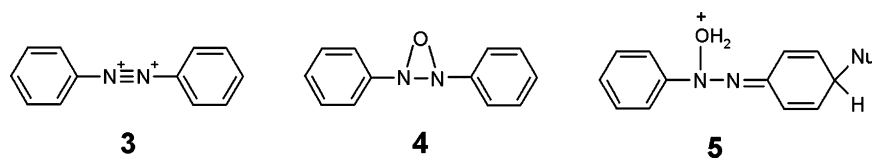
^c Conversion degree of azoxybenzene (%), δ_{AZB} = [(m₀ – m_r)/m₀] × 100%, where m₀ and m_r denote the mass of azoxybenzene in the studied system before and after reaction, respectively.

^d Reaction yield (mass%) has been referred to m₀.

^e Reaction time: 168 h; in all other cases the reaction was stopped after 24 h.

2.2. Rearrangement of azoxybenzene, **1**, on the HY zeolite

NH₄Y zeolite (Aldrich, 334413-100 G) was heated at 500 °C for 12 h. Such obtained acidic zeolite of the HY type (300 mg) was added into a solution of **1** (30 mg, 0.15 mmole) in 100 ml of a suitable solvent. The flask was wrapped in aluminum foil and heated under reflux for 24 h. The post-reaction mixture was filtered off on a funnel with a glass sinter and the filtrate analyzed by HPLC, GC–MS and UV–vis. Only **1** was identified in the methanol solution, however in isooctane neither **1** nor the rearrangement products were found. After being filtered off, the HY zeolite was refluxed with 100 ml of CH₂Cl₂ for 12 h. The extract was dry-evaporated in a rotary vaporizer; the residue was dissolved in 10 ml CH₃OH and analyzed by UV–vis and GC–MS. In both cases (methanol or isooctane starting solution), neither **1** nor its rearrangement products were identified. The filtered-off zeolite was washed with few portions of 85% H₂SO₄ (in total 20 ml) and the liquid collected in a vessel containing 180 ml of water. The diluted filtrate (8.5% H₂SO₄) was extracted by three 50 ml portions of CH₂Cl₂. The extract was washed with water and dried over anhydrous CaCl₂. The solvent was distilled off and the solid residue dissolved in 10 ml of methanol and analyzed by UV–vis and GC–MS. Neither **1** nor any rearrangement product was found, no matter which solvent was initially used for the reaction. Since the method applied to isolate the reaction products adsorbed on the zeolite (according to [12]) did not appear efficient a new procedure consisting in destruction (dissolution) of the zeolite's structure was elaborated. After the solvent (methanol or isooctane) was filtered off, the zeolite was dissolved in 30 ml of 4 M NaOH. Next, 70 ml water was added and the liquid acidified with 3 M HCl to achieve pH ≈ 3. This solution was next extracted by three 50 ml portions of CH₂Cl₂; the extract was washed with water and dried over anhydrous CaCl₂. After the solvent had been distilled off, the solid residue was dissolved in 20 ml of CH₃OH and analyzed by UV–vis, HPLC and GC–MS. In either case only the presence of **1** was proved.



Scheme 2.

2.3. Quantitative analysis

HPLC was applied in quantitative determination of the principal reaction components (**1** and the all products), using the standard calibration curve method.

2.4. Theoretical calculations

The density functional (DFT) method with the Gaussian 03 package [16] was used to estimate the relative Gibbs free energies of formation (ΔG) of potential intermediates considered important for the Wallach rearrangement mechanism. Geometry optimization and vibrational analysis of the studied compounds were performed without constraints on isolated molecules with the Becke3LYP density functional hybrid method [17,18] in combination with the standard basis set 6-31+G^{**}. This model allows calculation of free energies of organic molecules with standard deviation of 0.38 kcal/mol [19]. Zero-point energies (ZPE) were calculated using analytical second derivatives and scaled down by a factor of 0.9804 [20]. Thermal correction to enthalpy was determined from equation: $\Delta E_{\text{corr}}(T) = \Delta E_{\text{rot}} + \Delta E_{\text{trans}} + \Delta E_{\text{vib}} + RT$. Appropriate Z-matrices have been provided in Supporting Information. For comparison, the polarizable continuum model (PCM) developed by Tomasi and co-workers [21] was applied to assess the effect of solvation in water upon the rearrangement thermodynamics for the reaction involving the dicationic intermediate **3**. In the water ambient the structures were fully optimized and the vibrational frequencies were calculated by the B3LYP/6-31+G^{**} method.

3. Results and discussion

Quantitative data concerning the progress in the studied reaction under different solvent conditions, obtained from HPLC analyses, have been presented in Table 1. These results are different from those reported elsewhere [7,8,12,15]. First, the conversion of azoxybenzene **1** into 4-hydroxyazobenzene **2a** proved possible on the cross-linked sulfonated polystyrene resin and this work is probably the first one reporting a successful resin-catalyzed Wallach rearrangement. Second, no rearrangement products were formed when HY zeolite was used instead of the resin. Besides, the scattered laboratory light was found not to influence the course of the studied reaction in a particular way.

3.1. Resin-activated rearrangement

Attempts to carry out the rearrangement of azoxybenzene in the presence of a cation-exchange resin proved that in polar sol-

vents (methanol, methanol–water, 2-propanol, and acetic acid) the reaction stopped at the stage of azoxybenzene monoprotection. This fact has been confirmed by a characteristic absorption band at 384 nm, displayed in the UV–vis spectra of methanol solutions of **1** in the presence of the resin [8]. In the final reaction product, except azoxybenzene, **1**, neither 4-hydroxyazobenzene (**2a**) nor 2-hydroxyazobenzene (**2b**), as well as no other aromatic compounds with the azobenzene skeleton were identified. One exception to the rule was DMF, however in this case the conversion degree of azoxybenzene and the reaction yield were very poor, as well. The fact the reaction in DMF was initiated at all, one may attribute to the thermal activation rather (at 146 °C) than to the effect of the resin. This conclusion has been reflected by extremely high concentration of unreacted **1** ($AZB_{\text{solV}} = 93\%$) found in the post-reaction medium.

Application of a non-polar solvent, isooctane, resulted in the classic Wallach rearrangement yielding **2a** in average of 36.2% as well as some quantity of **2b** (11.4%). Since the post-reaction solvent contained no azoxybenzene as well as its **2a** and **2b** derivatives, it is obvious the rearrangement occurred within the bulk of the resin (see Fig. 1). The reaction must be thermally activated, otherwise the process would fail (Table 1, isooctane, 20 °C). Sub-products constitute ca. 47% of the bulk and approximately the half of this amount was determined as azobenzene. The rest remained unknown, however from our attempts (GC–MS analysis) it follows, that this part of the product represents an aniline-derivative polymeric material, as suggested elsewhere [12,22].

These results are in agreement with the primary Wallach reaction. Under typical homogeneous conditions (in concentrated H₂SO₄) the yields reported for **2a** fall between 40 and 60% [12,23]. The only quoted side-products have been azobenzene and the so-called “unidentified polymeric material”, the latter one making up even 34% of the total reaction product [12].

The both rearrangement products were identified also in the other non-polar solvents used and particularly in *n*-heptane the reaction yield (in total 16.5%) was quite acceptable, although significantly lower when compared with isooctane. However, CCl₄ proved no efficient medium for the studied process and hence the yield was very poor. This may be due to disadvantageous distribution of azoxybenzene, **1**, between the solid phase and the liquid, as indicated by the amount of **1** left in the solvent after the process was finished (51% in CCl₄).

These findings do challenge the concept of the dicationic Wallach rearrangement mechanism involving **3**, strongly postulated for the homogeneous reaction [7,8]. However, in the studied heterogeneous system the mechanism could have changed with the changing conditions. It was suggested, that the structure of a

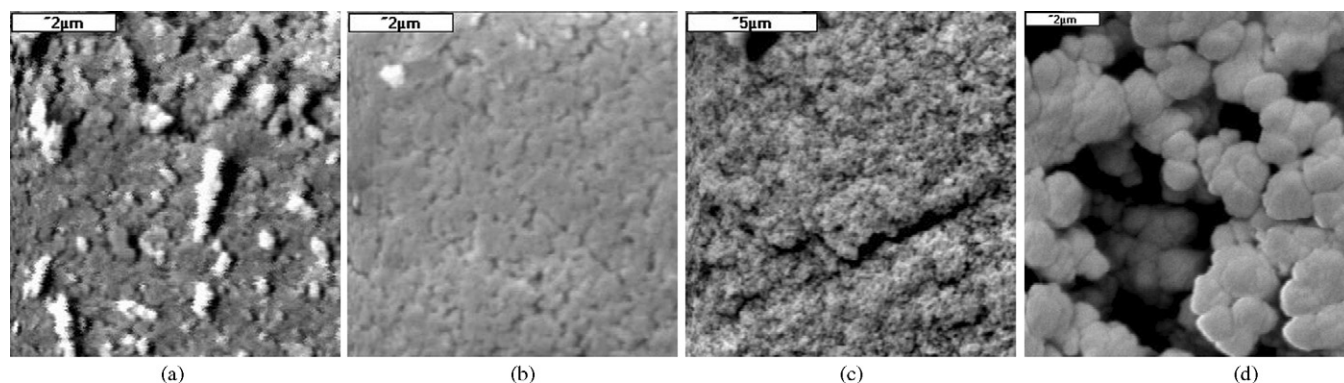


Fig. 1. Morphology (SEM) of the solid acid bed used in reaction with azoxybenzene in isooctane solution. (a) Resin's surface before reaction, 10 000 \times . (b) Resin's surface after reaction, 10 000 \times . (c) Inside of resin's matrix covered by reaction products, 5000 \times . (d) Zeolite HY surface after reaction with azoxybenzene, 10 000 \times .

macroporous resin does not allow a single azoxybenzene molecule adsorbed to be anchored by two sulfonic groups at the same time [8]. In fact, the rigid matrix of the sulfonated polystyrene chains cross-linked by divinylbenzene (DVB) particles [24] does not seem to favor a simultaneous contact of **1** with two sulfonic groups, separated from each other to a distance exceeding the size of **1**, even at the molecular level. Moreover, mutual interactions between the non-polar part of the reactant and the resin's matrix during catalysis on an ion-exchange resin prevent the azoxybenzene molecule from double-protonation [25]. However, due to such interactions the azoxybenzene solution may freely penetrate into the resin's pores.

It must be emphasized, that changing the solvent's polarity entails a change in the distribution coefficient of the "azoxy" compound between the solvent and the resin's matrix. On the other hand, polarity of the solvent influences the dissociation of the resin's sulfonic groups, increasing its acidity and catalytic activity when non-dissociated. This may explain the results reported in Table 1, which prove that the resin-catalyzed Wallach rearrangement evidently occurs in the non-polar isooctane or *n*-heptane, whereas it is not being observed in methanol and other polar solvents used. Trace amounts of water present in the system allow the hydration of sulfonic group protons, which next give rise to the monoprotection of **1**. Finally, it must be noticed, that benzenesulfonic acid is considered almost as strong as H₂SO₄ and hence it has become a rather popular catalyst. The catalytic activity of *p*-toluenesulfonic acid was confirmed also for the Wallach rearrangement under homogeneous conditions [26]. Thus, one might have expected a similar result produced by the Lewatit resin in a heterogeneous reaction.

3.2. Zeolite-activated rearrangement

Experiments designed to perform the conversion of **1** into its **2a** derivative on a HY type zeolite bed gave no positive results and furthermore proved the Wallach rearrangement was not possible under reaction conditions according to the procedure reported in literature [12]. Nevertheless, non-polar isooctane allowed very efficient adsorption of **1** at the zeolite surface compared with methanol, Table 1. However, in both cases it appeared difficult to

discharge the products from the solid substrate by typical extraction. Only after dissolving the post-reaction solid bed in NaOH, it was possible to retrieve the compounds adsorbed by the zeolite during the process and estimate the yield (see Section 2 for details). Examination of the product freed from the zeolite revealed that no rearrangement had occurred and only the substrate, **1**, was determined in the post-reaction extract. Interestingly, in the cited work [12], comparable amounts of the **2a** and **2b** derivatives were obtained with the HY zeolite. From the other hand it is well known, that under solar or UV light azoxybenzene is preferably converted into **2b** even while in solid state [5], however no contribution of the photochemical mechanism to the zeolite-catalyzed rearrangement observed in [12] was reported.

3.3. Solid acid structure-related effects

Solids of the resin and HY zeolite used in our work are characterized by completely different space structures and this fact proved crucial for their catalytic activity against the reaction substrate. The size of a single azoxybenzene molecule, **1**, fits a frame of ca. 12 Å × 5 Å and the both rearrangement products fit that of ca. 13 Å × 5 Å. Hence, the resin containing pores of ca. 650 Å in diameter, which may easily be penetrated by molecules of **1**, appeared efficient in the studied case. In contrast, acidic zeolite of the HY type, characterized by channels and cavities being few Å in diameter (100 times narrower compared with the resin) has proved ineffective to induce the azoxybenzene rearrangement. Furthermore, the resin's system remains porous even after the reaction has been completed, as follows from SEM investigations, Fig. 1. The outer surface of the resin beads (Fig. 1b) appears quite smooth and is uniformly covered by a thin layer of **1**, as revealed by the line scan and EDAX analyses (Fig. 2a). A very similar pattern was obtained for surface-adsorbed **1** at 20 °C, when no reaction occurred. In isooctane, due to a particularly favorable distribution coefficient (liquid phase–resin's matrix) the once adsorbed reagent molecules seem to be quite firmly held inside of the porous matrix and do not tend to migrate back into the outer liquid phase, whereas a reversed trend was observed in case of the polar solvents used (Table 1). However, this may reduce to some extent the diffusion of the substrate toward the resin's active sites and in consequence be crucial to the reaction yield. At the same

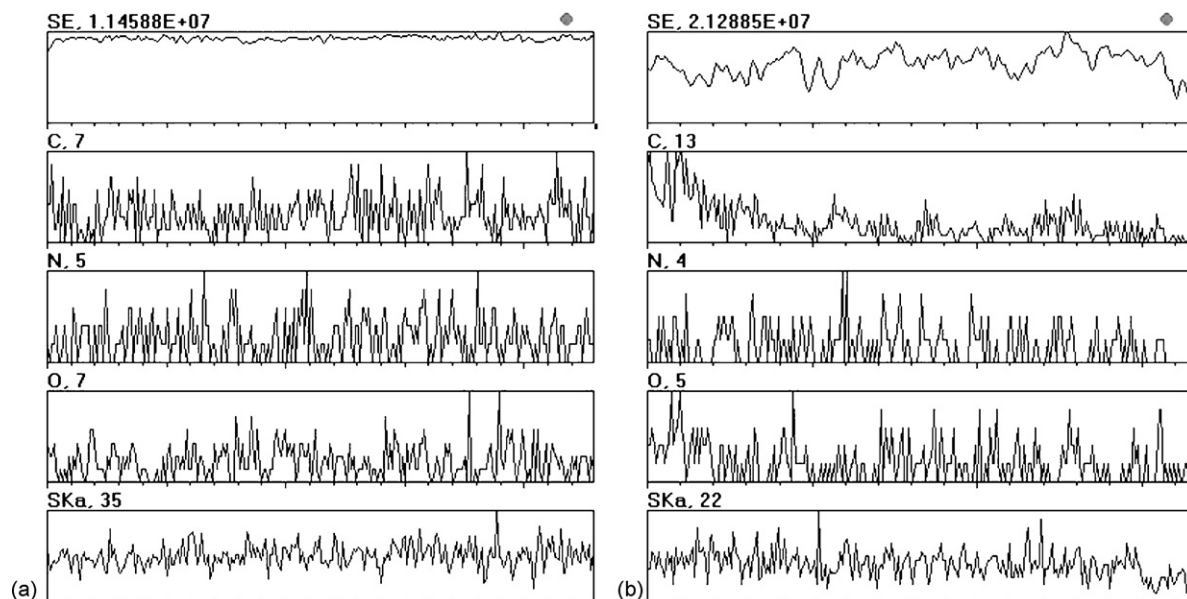
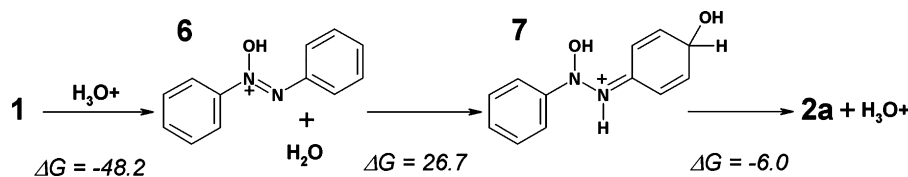


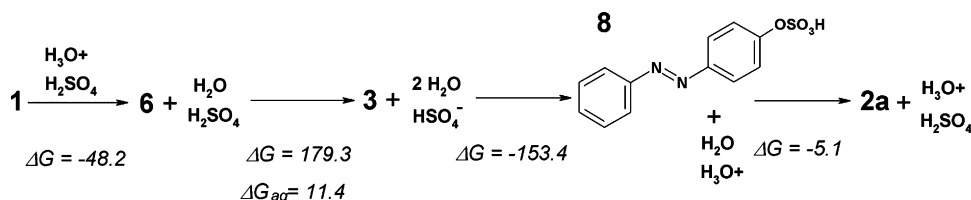
Fig. 2. SEM linescan; performed for resin solids after the reaction was completed. (a) Surface (refer to Fig. 1b). (b) Inside of the resin's matrix (refer to Fig. 1c).

Table 2
Energies and enthalpies of structures involved in the Wallach rearrangement

Compound	E_{elec} (a.u.)	ZPE (kcal/mol)	ΔE_{corr} (kcal/mol)	H^{298} (a.u.)	G^{298} (a.u.)
1	-647.9854	120.5	7.6	-647.7812	-647.8287
2a	-648.0271	119.7	8.0	-647.8237	-647.8726
3	-572.0936	116.9	7.5	-571.8953	-571.9423
3 in water	-572.3620	115.5	7.2	-572.1665	-572.2132
6	-648.3359	127.6	8.0	-648.1198	-648.1678
6 in water	-648.4212	125.7	7.9	-648.2083	-648.2567
7	-724.7467	144.0	9.2	-724.5026	-724.5556
8	-1271.8186	128.3	10.7	-1271.5972	-1271.6575
9	-1348.1750	144.7	11.8	-1347.9256	-1347.9896
H ₂ O	-76.4341	13.1	2.3	-76.4095	-76.4304
H ₂ O in water	-76.4481	12.5	2.3	-76.4245	-76.4455
H ₃ O ⁺	-76.7078	21.1	2.4	-76.6703	-76.6926
H ₂ SO ₄	-700.2332	23.5	3.8	-700.1897	700.2235
H ₂ SO ₄ in water	-700.2685	21.5	3.7	-700.2283	-700.2618
HSO ₄ ⁻	-699.7301	16.0	3.7	-699.6987	-699.7329
HSO ₄ ⁻ in water	-699.8384	15.1	3.2	-699.8092	-699.8416



Scheme 3. Rearrangement involving the *N,N'*-diphenyloxadiaziridine intermediate (ΔG , kcal/mol).



Scheme 4. Rearrangement involving the dicationic intermediate (ΔG , kcal/mol).

time parallel and/or consecutive reactions resulting in the polymeric material and azobenzene may be prompted. Nevertheless, clearly both the products and unreacted **1** have been distributed throughout the resin's matrix in such a way that no pore clogging occurred (Figs. 1c and 2b). Hence, there is still sufficient space left to allow relative easy solvent-extraction of the adsorbed compounds from the post-reaction system. In the case of HY type zeolite, a layer of **1** was formed probably only at the surface of the solids making up the bed (Fig. 1d) and therefore no reaction could proceed. Unfortunately, we were not in position to investigate the interior of the zeolite matrix due to its specific structure and very small grain size.

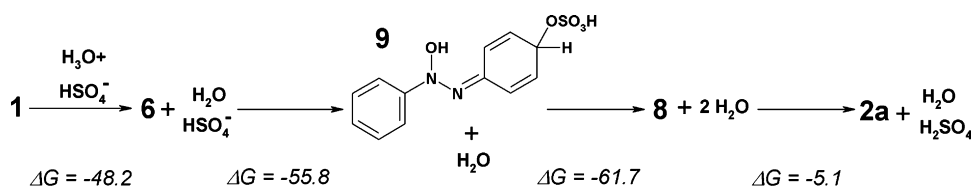
3.4. Theoretical calculations

The DFT method was applied in this work only to estimate the thermodynamic reliability of the hypothetical intermediates **3**, **4**

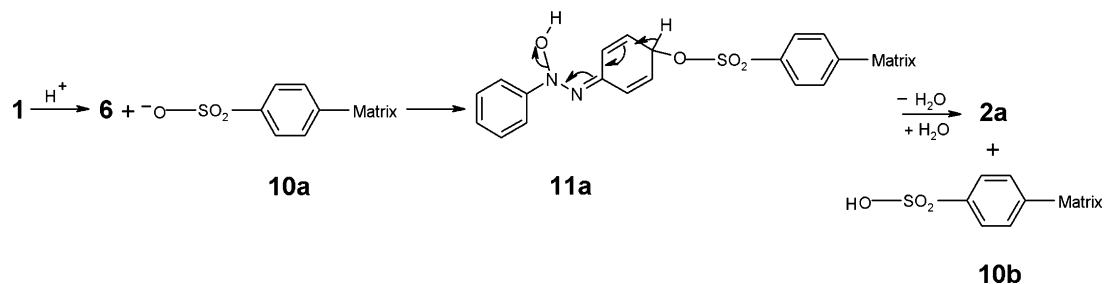
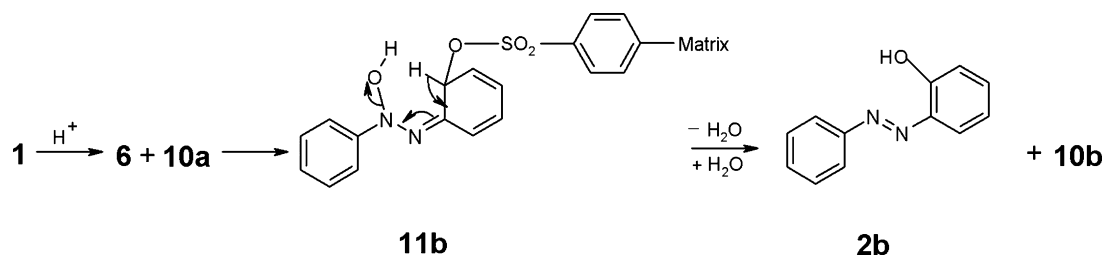
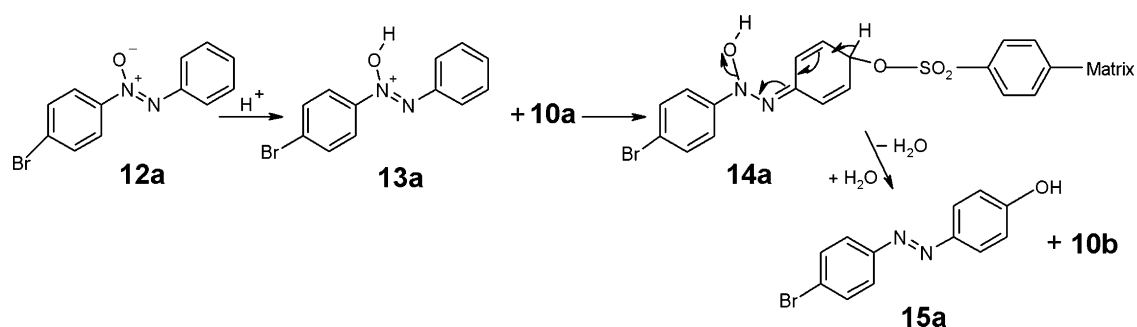
and **5**, considered important for the studied rearrangement. Thus, calculated relative free enthalpies of formation (ΔG) were used to justify it. However, at this stage it had not been our objective to submit a complete mechanistic model. Hence, our conclusions referring to the most probable reaction course are supposed to be considered merely as a preliminary step in preparation of a comprehensive theoretical study to be reported in a follow-up paper.

The choice of DFT calculations and the level of theory used seem adequate for the studied reaction to provide the most realistic energy values, as stated elsewhere [16–19]. Results have been collected in Table 2 and included in Schemes 3–5. The enthalpies of the studied molecules have been computed using the following expression:

$$H^{298} = E_{elec} + ZPE_{scaled} + \Delta E_{corr}(T)$$



Scheme 5. Rearrangement involving the quinoid intermediate (ΔG , kcal/mol).

Scheme 6. Resin-activated formation of 4-hydroxyazobenzene, **2a**.Scheme 7. Resin-activated formation of 2-hydroxyazobenzene, **2b**.Scheme 8. Resin-activated rearrangement of trans-4-bromo-NNO-azoxybenzene, **12a**.

where E_{elec} represents the electronic energy, ZPE_{scaled} the scaled zero-point energy and $\Delta E_{\text{corr}}(T)$ the thermal correction to enthalpy (see Section 2 for details).

A comparison of the azoxybenzene rearrangement energetics for the mechanisms discussed above has proved that only the quinoid intermediate **9** would be thermodynamically favored, in contrast to the other ones (**3** and **7**), as shown in Schemes 3–5. In particular, formation of the dicationic species **3** appeared to be a highly endoergic process ($\Delta G = +179.3$ kcal/mol), which means the equilibrium of this reaction lies strongly in favor of the reactants. In addition, the free enthalpy of formation of **3** including the solvation effect (ΔG_{aq}) also appeared positive. This implies the dicationic mechanism of the Wallach rearrangement is not favored even in a polar solvent.

3.5. Explanation of the resin-catalyzed mechanism

Experimental results and thermodynamic considerations suggest, that the most realistic explanation of the chemistry in resin-activated rearrangement of azoxybenzene is offered by assuming the reaction proceeds via the quinoid intermediate **9**. The postulated general reaction mechanisms presented in Schemes 6 and 7 explain the formation of the both hydroxyazobenzene isomers (**2a** and **2b**), observed under experimental conditions excluding the possibility of a photochemically induced rearrangement. It is obvious that the quantity ratio of the both isomers

depends on the stability of the particular quinoid intermediates **11a** and **11b** and presumably on the solvent properties and reaction temperature, as well. Since the structure **11a** is supposed to be considerably more stable, hence the higher yield of the **2a** isomer in the applied non-polar solvents (Table 1).

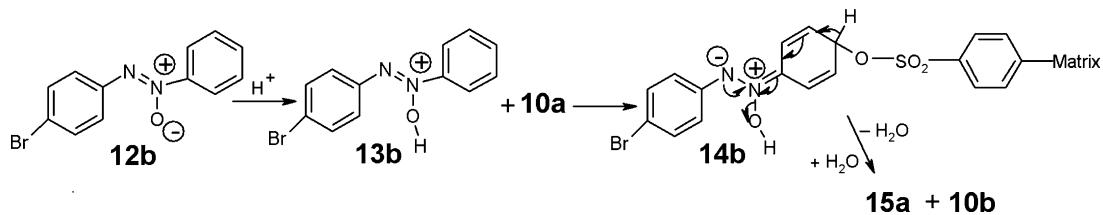
Direct kinetic measurements were not possible for the studied heterogeneous reaction. Nevertheless, by considering the entropic contribution to the theoretically estimated ΔG term one may assume the rate determining step to occur rather before the quinoid intermediate is formed ($T\Delta S \approx -12$ kcal/mol) than after this stage ($T\Delta S \approx +11$ kcal/mol). This may have indicated for a bimolecular reaction act controlling the rearrangement kinetics. From the other hand, as mentioned above, the diffusion of reactants at the resin–liquid interface is probably critical to the rearrangement chemistry and may particularly affect the initial stages of activation of **1**.

Table 3
Resin-activated rearrangement of para bromo-azoxybenzene isomers in isoctane

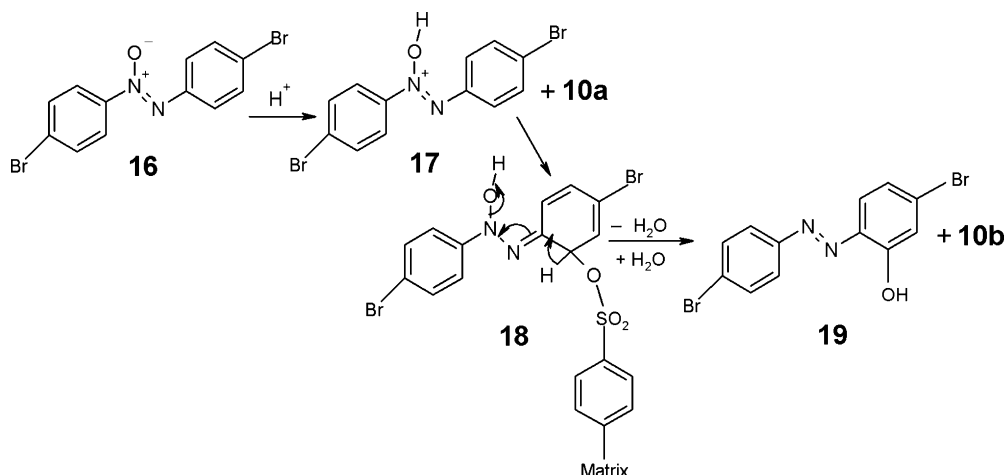
Substrate	δ_s^a	Reaction yield ^b	
		15a	4bazb
12a	19	15	4
12b	23	15	8

^a Substrate conversion degree (%).

^b mass% (see Table 1).



Scheme 9. Resin-activated rearrangement of trans-4-bromo-ONN-azoxybenzene, **12b**.



Scheme 10. Resin-activated rearrangement of 4,4'-dibromoazoxybenzene, **16**.

Additionally, to confirm the postulated heterogeneous Wallach mechanism, the Lewatit resin was applied to para bromo-substituted azoxybenzene isomers **12a** and **12b** (synthesis of, see [27]), in a process carried out in boiling isooctane under similar conditions as in the case of **1**. As expected, each of the individual bromo-derivatives yielded the same hydroxy-compound, namely 4-bromo-4'-hydroxyazobenzene, **15a**, and interestingly, in the same quantity (Table 3). The lower rearrangement yield (15%) in comparison with the principal reaction (47.6% in total, Table 1) was due to the considerably less reactive bromo-substrate. The only side-product identified was 4-bromoazobenzene (4bazb). No 2-hydroxyazobenzene bromo-derivative was found in the product. This result is consistent with the experimental data previously published for homogenous systems [26,28]. A probable reaction mechanism is shown in Schemes 8 and 9.

It is worth to mention, that 4,4'-dibromoazoxybenzene (**16**) in 92% H₂SO₄ rearranged exclusively into 4,4'-dibromo-2-hydroxyazobenzene (11% of yield) [26]. Similarly, in a resin-catalyzed process, by using the same substrate **16** we have solely obtained the 2-hydroxy derivative (16% of yield, $\delta_S = 50\%$). A hypothetical mechanism is presented in Scheme 10.

4. Conclusions

The experimental and theoretical results presented in this work confirm that the “azoxy” group does not distinguish the benzene rings in **1** and hence both are equally susceptible to interactions involving the nucleophilic resins' sulfonic group. In our opinion this is the fundamental reason making the rearrangement possible also in heterogeneous systems. This fact was proved in the successfully performed reactions using the brominated isomers of **1**, as described in Schemes 8 and 9. It is clear, that the position of the oxygen atom does not affect the reaction product. In addition, by regarding the structure-related restrictions imposed by the resin [24,25] it seems, that formation of an absolutely symmetrical

intermediate (e.g. **3**) may not be necessary to realize the thermodynamic and kinetic terms essential for the Wallach rearrangement, at least in the studied case. Thus, for the resin-catalyzed heterogeneous reaction the postulated quinoid mechanism looks plausible and complies with a previously proposed theory [13].

Summarizing, we would like to emphasize the principal importance of a proper solvent choice for a resin-activated reaction. In our opinion the effect of the solvent generally deserves much more detailed research to be carried out. Moreover, we feel that other factors, which have been highlighted here, e.g. structural features of the solid substrate, reaction temperature, water content and influence of light may also be significant for the reactivity of the solid acid-azoxybenzene system. In addition, the catalytic properties displayed under specified conditions by the sulfonated polystyrene resin may also be of interest in the case of other reactions involving acidic activation.

Supporting information available

General experimental: synthesis and characterization of the substrate and products (for reference) and Z-matrices for the structures considered in theoretical calculations are provided via the Internet.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.05.016.

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