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# Thermal and photochemical Wallach rearrangement of azoxybenzene in zeolite cages

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## Abstract

Acidic zeolites HY and CaY catalyse the Wallach rearrangement of azoxybenzene (**I**) leading mainly to the formation of *para*-hydroxyazobenzene (**II**) and *ortho*-hydroxyazobenzene (**III**). In this transformation, increasing the loading level of **I** results in the formation of a larger amount of *para*-isomer. As observed in isotropic media, photochemical Wallach rearrangement in the presence of various cation-exchanged faujasites results in the predominant formation of the *ortho*-isomer from the $S_1$ state and this rules out any appreciable heavy atom effect. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Azoxybenzene; Wallach rearrangement; Acidic zeolites; Irradiation

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## 1. Introduction

Azoxybenzene (**I**), when treated with strong sulfuric acid solutions either for a longer time at room temperature or for a shorter time at higher temperature, rearranges to para-hydroxyazobenzene (**II**) and this is known as Wallach rearrangement [1]. This intermolecular transformation, as proved by carrying it out in $^{18}$O-labelled sulfuric acid and $^{18}$O-labelled (**I**) [2,3], also takes place in chlorosulfonic acid [4,5]. Unlike the closely related Bamberger rearrangement, the Wallach rearrangement takes place only in strong acid solutions, as the course of the reaction involves acceptance of two protons by **I** (a weak base) from the medium to form a dicationic intermediate. The existence of dication mechanism is supported by the inability of strongly acidic cation exchange resins (which are unable to form the dication intermediate) to catalyse the Wallach rearrangement [6]. In this rearrangement, by-products like ortho-hydroxyazobenzene (**III**), azobenzene (**IV**) and some polymeric materials of aniline and sulfonic acids are also formed in very small amounts (Scheme 1).

A small increase in the amounts of **IV** and polymeric materials is observed with an increase in acidity [7]. Compound **I**, when heated at higher temperature (245–250°C), gives **IV** as the major product with small amounts of **II**, **III** and *para*-hydroxyazoxybenzene [8]. Thus, it is obvious that the nature of the products depends on the reaction conditions.

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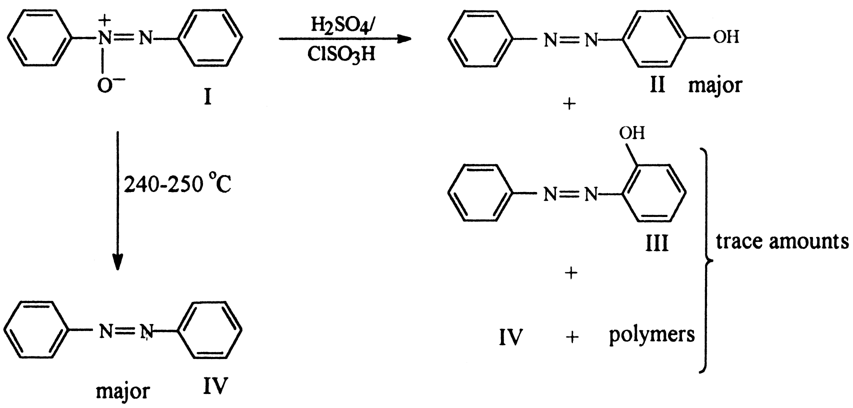
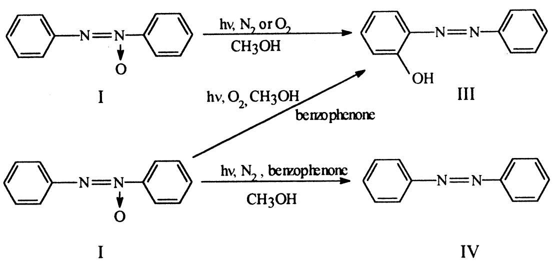


Scheme 1.

In the photochemical rearrangement of **I** in solution, it has been reported [3,9,10] that **III** is the major product (Scheme 2) and the transformation proceeding from the singlet state of **I** involves an intramolecular process. The presence of oxygen does not affect the product distribution in the absence of a sensitizer. The triplet chemistry, however, is different and the product obtained in the case of benzophenone sensitized irradiation in nitrogen atmosphere is **IV** [11]. This deoxygenation, analogous to the conversion of pyridine-*N*-oxide to pyridine is common in α-diaza compounds [12–14]. In some cases, it may involve oxaziridine intermediate, which transfers oxygen to suitable substrate. The reaction also depends on the hydrogen-bonding ability of the solvent. In many reactions such as hydroxylation of aromatics, alkanes, epoxidation of alkenes, etc., *N*-oxides are employed as useful oxidants [15–17]. Quenching of triplet of **I** by molecular oxygen results in the formation of **III** [11].



Scheme 2.

Zeolites are efficient solid acids whose acidity can be controlled and therefore act as excellent replacements for conventional mineral acids [18–23]. Other advantages of using the acidic zeolite catalysts are improved selectivity and reactivity, easier work-up, reusability, milder reaction conditions and easier modulation of acidity levels by suitable exchange of cations, etc. Recently, we have employed zeolites for the efficient protection of carbonyl groups [24], and zeolite impregnated reagents are used for deprotection of carbonyl derivatives [25]. This prompted us to carry out the rearrangement of **I** in the presence of the acidic zeolites HY and CaY and the photochemical Wallach rearrangement of **I** in the presence of various non-acidic cation exchanged zeolites. The results of these studies are discussed below.

## 2. Experimental

Zeolite HY was obtained by the thermal deammonification of $NH_4Y$ (Aldrich) at 500°C and other cations of interest were exchanged into the NaY (Aldrich) powder by stirring with the corresponding nitrate (10%) solution at 70°C for about 12 h. The exchange was repeated at least four times. Each time, after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. All these cation-exchanged zeolites were activated at 500°C for about 10 h prior to use. Compound **I** was prepared and purified by reported procedure [26].

To a known amount of **I** in iso-octane, 300 mg of zeolite activated at 500°C was added and refluxed with stirring. After that, the iso-octane portion was filtered and the zeolite portion was extracted overnight with a polar solvent namely, dichloromethane. Both the fractions after removal of the solvent were analysed and bulk of the reaction mixture (~ 95%) was found to be present in the zeolite portion. The combined iso-octane and zeolite portions were analysed by GC (Netel Chromatograph) using OV-1 column (FID detector) with unreacted starting material as the internal reference. Products were identified by their melting points, $^1$H-NMR spectra and also by coinjection with authentic samples. Mass balances in all the entires presented in Tables 1 and 2 were greater than 90% and this ruled out the formation of any significant amount of polymeric products (which is formed only with conc. $H_2SO_4$).

Table 2
Product distribution (in %) in photochemical Wallach rearrangement[a]

| Medium | % Conversion | **III** | **IV** | **III/IV** ratio |
|---|---|---|---|---|
| $CH_3OH$[b] | 89.0 | 100 | – | – |
| $CH_3OH + Ph_2CO/O_2$[b] | 77.0 | 99.0 | 1.00 | – |
| $CH_3OH + Ph_2CO/N_2$[b] | 85.0 | 12.0 | 88.0 | 0.13 |
| LiY[c] | 24.0 | 73.0 | 27.0 | 2.70 |
| NaY[c] | 22.0 | 81.0 | 19.0 | 4.23 |
| KY[c] | 17.0 | 85.0 | 15.0 | 5.58 |
| RbY[c] | 17.0 | 91.0 | 9.00 | 10.4 |
| CsY[c] | 10.7 | 91.0 | 9.00 | 10.2 |

[a] Error Limit ±5%. Analysed by GC.

[b] From Ref. [11] (the results are reproducible in our experimental conditions also).

[c] A 30 mg of **I** loaded in 300 mg of zeolite, irradiated as hexane slurry under $N_2$ atmosphere for 4 h.

Photochemical rearrangements were performed by adding the activated zeolites to the solution of **I** and the slurry was irradiated in nitrogen atmosphere using a 400-W medium pressure mercury lamp ($\lambda = 365$ nm) for 4 h.

Table 1
Product distribution (in %) in the thermal Wallach rearrangement of **I**[a]

| Medium | Amount of **I** (mg) | % Conversion | Time (h) | **II** | **III** | **IV** | Aniline |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$[b] | 30 | 80.0 | 2 | 72.0 | – | 28.0 | – |
| $H_2SO_4$[c] | 30 | 100 | 2 | 21.0 | – | 45.0 | – |
| NaY | 30 | nil | 6 | – | – | – | – |
| None[d] | 30 | 9.00 | 6 | 6.00 | 15.0 | 79.0 | – |
| HY | 30 | 17.0 | 6 | 39.0 | 34.0 | 11.0 | 16.0 |
| HY | 15 | 37.0 | 20 | 38.0 | 36.0 | 12.0 | 14.0 |
| HY | 30 | 28.0 | 20 | 35.0 | 31.0 | 10.0 | 24.0 |
| HY | 60 | 18.0 | 20 | 63.0 | 13.0 | 2.00 | 22.0 |
| HY[e] | 30 | 15.0 | 20 | ≤ 1 | ≤ 1 | 98.0 | – |
| CaY | 30 | 5.00 | 6 | 37.0 | 31.0 | 16.0 | 16.0 |
| CaY | 30 | 11.0 | 20 | 41.0 | 26.0 | 8.00 | 25.0 |
| CaY[f] | 30 | nil | 20 | – | – | – | – |

[a] Refluxed for 20 h with stirring in iso-octane. Analysed by GC; Error Limit ±5%. For structures **I**–**IV**, refer to Scheme 1.

[b] Treated with conc. $H_2SO_4$ at room temperature for 2 h (earlier reports show that **II** is the major product in $H_2SO_4$ and the amount of **IV** increases with increase in acidity).

[c] Heated with conc. $H_2SO_4$ at 90°C for 2 h (remaining products are unidentified, may be the polymeric materials formed from aniline and sulfonic acids).

[d] Solid **I** heated at 120°C in the absence of zeolite.

[e] Solid **I**–HY complex heated at 120°C.

[f] Unactivated CaY. Refluxed in iso-octane.

After irradiation, the products were separated and analysed as mentioned above.

## 3. Results and discussion

### 3.1. Thermal Wallach rearrangement

Products distribution in the case of Wallach rearrangement in the presence of acidic zeolites like HY and CaY is given in Table 1. It is observed that under similar conditions, there is no rearrangement in the presence of the non-acidic zeolite, NaY, and the reaction is facile only in the presence of acidic zeolites HY and CaY. Unlike in $H_2SO_4$, where only **II** is obtained as a major product, the zeolite mediated Wallach rearrangement is distinctly different, since in addition to (**II**) and (**IV**), (**III**) and small amount of aniline are also formed. In the conventional Wallach rearrangement with conc. $H_2SO_4$, aniline is formed as a polymeric material along with sulfonic acids.

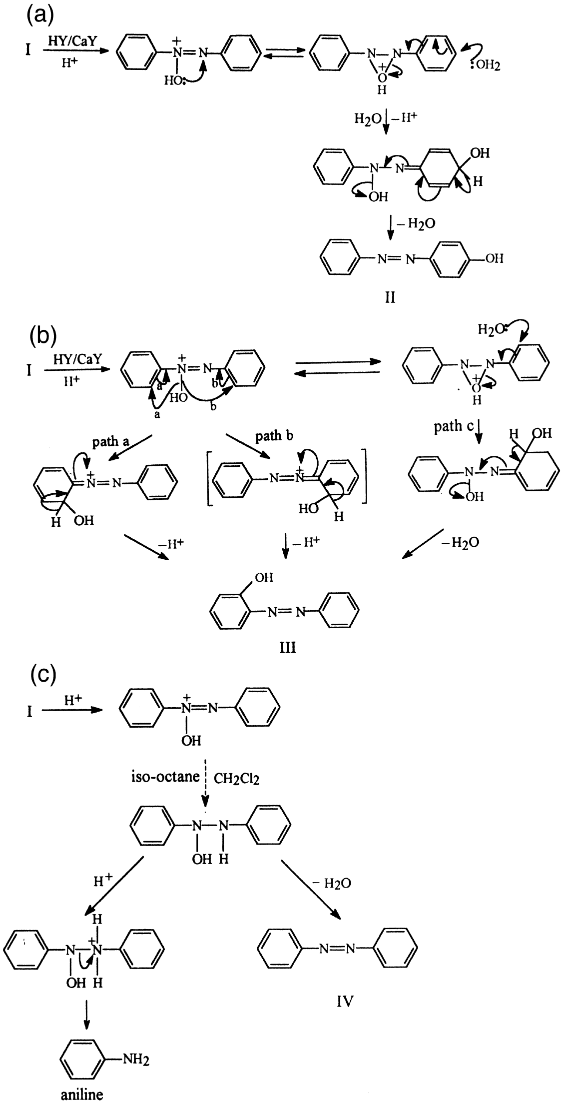
Loading level of **I** into the zeolite and also the reaction time influence the products distribution and also the percentage conversion. With a lower loading (15 mg of **I** in 300 mg of HY), the conversion is significant and the *ortho*-isomer is formed almost in equal amounts to *para*-isomer. When the amount of **I** is increased (from 15 to 60 mg), keeping a constant amount of HY (300 mg), the conversion decreases whereas the amount of *para*-isomer increases. Also, there is a significant decrease in the amount of **IV** in the case of higher loading. Heating the solid complex of **I** with HY at about 120°C in an oil bath results in the formation of **IV** as the major product with negligible amounts of **II** and **III**. Thus, the results demonstrate the efficiency of solid HY zeolite as an attractive alternative for the corrosive liquid $H_2SO_4$ catalyst. The zeolite-catalysed reaction is not only smooth but also controlled to get varying amounts of the different products. With CaY zeolites, which also possess acidic sites, products similar to those obtained in NaY are formed, indicating the significance of Brönsted acidity in this rearrangement. The percentage conversion, however, is lesser, reflecting its weaker acidic character compared to HY.

Formation of **II** and **IV** in zeolite-catalysed Wallach rearrangement has been explained by proposing suitable mechanisms by analogy with the mechanistic details of conc. $H_2SO_4$-catalysed Wallach rearrangement. Protonation of **I** followed by cyclization leads to the formation of a cyclic intermediate [27–29], which in turn, undergoes nucleophilic attack of water molecule to give **II** (Scheme 3a). As water is regenerated in the final step, only catalytic quantity is needed, which may be either zeolite bound or present as solvent impurity. As the intermediate is symmetrical, the attack of water molecule can take place at either of the *para*-positions leading to the formation of **II**.

Formation of the *ortho*-isomer by an intramolecular mechanism (Scheme 3b) involves the nucleophilic attack of the protonated azoxy oxygen on the *ortho*-position of the nearer ring (path a-minor) or of the farther ring (path b-major). An intermolecular water attack at the *ortho*-position (path c) may also be visualised. At this stage, it is not possible to conclude whether the formation of **III** in zeolite cavities is intramolecular or intermolecular. The formation of **IV** and aniline can also be explained (Scheme 3c). Protonated **I** binds strongly with zeolite walls and can undergo reduction when extracted with dichloromethane. Similar reduction of a wide range of olefins in acidic zeolite is well documented [30,31].

### 3.2. Photochemical Wallach rearrangement

In the present study, photochemical Wallach rearrangement has also been investigated. A previous study in isotropic media indicates that **III** is the major product in direct and benzophenone-sensitized irradiation (in oxygen-purged solution) and **IV** is the predominant product in the sensitized irradiation under nitrogen atmosphere [11]. Thus, it is obvious that **III**



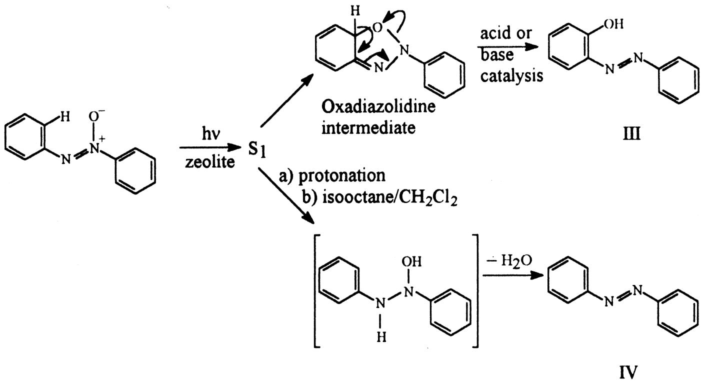
Scheme 3. (a) Formation of **II**, (b) formation of **III**, (c) formation of aniline and **IV**.

is the major product from $S_1$ state and **IV** is the major product from $T_1$ level, and oxygen quenches efficiently the $T_1$ state of **I** (cf. Scheme 2).

The results of the present study given in Table 2 show that **III** is the major product with a small amount of **IV**. The absence of any *para*-isomer rules out a blank thermal reaction. The inherent zeolite polarity results in adsorption of the polar substrate into/onto the cages and this rules out any significant reaction in the liquid phase. This is supported by the recovery of $> 95\%$ of the reaction mixture from the zeolite portion.

The increase in the size of the cations present in the zeolites decreases the conversion with the concomitant increase in the amount of **III** at the expense of **IV**. In fact, amount of **IV** formed is considerable in LiY and decreases with an increase in cation size. The absence of significant amounts of **IV** in RbY and CsY rules out any appreciable heavy atom effect. Also, only a 2.5-fold decrease in percentage conversion from LiY to CsY is observed (cf. Table 2). Based on the known precedents of heavy atom effects in zeolites with its reactive singlet/unreactive triplet manifold contributions, the absence of any dramatic decrease in CsY can also be construed as additional evidence of absence of significant heavy atom effect. Smaller cations, with their higher electrostatic fields, bind readily with the negatively charged oxygen atom in **I** and results in a reduction in its conversion to the oxadiazolidine intermediate leading to **III**. This explains the observed increase in **III**/**IV** ratio on moving from LiY to CsY. The "cation size effect" may also play a role in controlling the product ratio. While the transition state for the formation of **III** involves minimal change in nuclear positions, the alternative pathway of protonation, hydrogen abstraction from the solvent followed by subsequent water elimination needs more space and, hence, is less favoured in the case of faujasites exchanged with bulkier cations.

From the singlet state, the reaction proceeds by attack of azoxy oxygen on the *ortho*-position of the farther ring (Scheme 4), forming an oxadiazolidine intermediate which rearranges to **III** [17]. An alternative acid–base mechanism similar to the one proposed in Scheme 3c (leading to the formation of **IV**) may also be visualised. Protonation, followed by hydrogen abstraction from a suitable donor preferably from the solvent, followed by dehydration leads to



Scheme 4.

**IV**. It is relevant to note that hydrogen abstraction from alkanes is reported from the excited states of *N*-oxides and is a general route for hydroxylation of aromatics and alkanes [15,17].

## 4. Conclusion

Thus, the present work explains the use of acidic zeolites as efficient reagents in the place of mineral acids. While stringent acidic conditions involving diprotonation of **I** are necessary with mineral acids, zeolite-mediated reactions involve only monoprotonation. With the use of zeolites as heterogeneous catalysts, the product separation is easily achieved by simply filtering the catalyst that can be reused after activation. The formation of a significant amount of *ortho*-isomer that is not formed with the conventional Brönsted acids, the significant reduction in the yield of **IV** while increasing the loading level of **I**, and the suppression of the formation of polymeric products that are significant in the case of sulfuric acid-catalysed rerarrangement are the advantages in this zeolite-catalysed rearrangement. The photochemical rearrangement in cation exchanged zeolites originates from the $S_1$ state, giving the *ortho*-isomer as the predominant product. Heavy atom effect is absent and cation size effect plays an important role in product formation.

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