Electron transfer-induced dehydrogenation reactions within methyl viologen-supported zeolite Na-Y under non-irradiative conditions

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Received 22 May 2001; revised 5 July 2001; accepted 12 July 2001

Abstract—Methyl viologen-supported zeolite Na-Y is a unique and very efficient medium for carrying out electron transfer-induced reactions in the absence of an irradiation source (spontaneously). Several monoterpenes loaded within the supported zeolite are dehydrogenated to \( p \)-cymene. The reaction occurs even in the open air with formation of minor amounts of ascaridole depending on the substrate. It is proposed that the radical cations of the monoterpenes are formed by single electron transfer to Na-Y, with methyl viologen acting as a promoter. © 2001 Elsevier Science Ltd. All rights reserved.

Radical ion pairs are orders of magnitude longer-lived within the pores and the channels of zeolites\(^1\) than in solution, where rapid back electron transfer takes place. Therefore, the confined interior of zeolites should be an ideal medium to carry out electron transfer reactions of organic compounds. However, this aspect of intrazeolite chemistry, especially for zeolite Na-Y, has attracted little attention. The only known examples so far are photosensitized processes. Ramamurthy and coworkers have reported photoinduced \([2+2]\) dimerizations of aryl-alkenes sensitized by cyanoaromatic and ionic sensitizers.\(^2\) Furthermore, in triphenylpyrilium supported zeolites, photosensitized electron transfer isomerization of stilbenes\(^3\) and \([4+2]\) or \([2+2]\) dimerization of 1,3-cyclohexadiene have been found.\(^4\)

It is well known that methyl viologen (MV\(^{2+}\)) supported within zeolite Na-Y forms a charge transfer complex with the interior framework of the zeolite. Inclusion of an arene donor into the cages results in the formation of arene/MV\(^{2+}\) charge transfer complexes.\(^1\) Upon photostimulation of the arene/MV\(^{2+}\) charge transfer bands, the radical cations of arene and methyl viologen (MV\(^{+}\)) are formed.\(^5\)

In a representative example, 5 mg of limonene (3, 99% pure) dissolved in 5 mL of dry hexane was added to 0.5 g of MV\(^{2+}/Na-Y\). After 30 min of stirring under argon either in the dark, or under ambient light, 5 mL of moistened THF was added and the slurry was stirred for 2 h and then filtered. Analysis by GC or by GC/MS revealed that the products were 60% \( p \)-cymene 6, 15% terpinolene 4, 10% \( \gamma \)-terpinene 2, 10% \( \alpha \)-terpinene 1, and approximately 2–4% of alcohols with the molecular formula \( C_{10}H_{18}O \).

Keywords: zeolite Na-Y; electron transfer; terpenes.

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Table 1.

<table>
<thead>
<tr>
<th>Terpene</th>
<th>Conversion* (%)</th>
<th>1 (%)</th>
<th>2 (%)</th>
<th>4 (%)</th>
<th>6 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Terpinene, 1</td>
<td>&gt;95</td>
<td>–</td>
<td>4</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>γ-Terpinene, 2</td>
<td>66</td>
<td>12</td>
<td>–</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>Limonene, 3</td>
<td>&gt;98</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>Terpinolene, 4</td>
<td>70</td>
<td>8</td>
<td>7</td>
<td>13</td>
<td>73</td>
</tr>
<tr>
<td>α-Phellandrene, 5</td>
<td>&gt;98</td>
<td>7</td>
<td>–</td>
<td>16</td>
<td>73</td>
</tr>
</tbody>
</table>

* Typical intrazeolite experiment: to 0.5 gr of MV\(^{2+}\)/Na-Y was added 5 ml of each monoterpene dissolved in 5 ml of dry hexane. After 30 min of stirring under argon in the dark, 5 ml of moistened THF was added. The resulting slurry was stirred for 2 h and then filtered. Analysis of the products was performed by GC on a 50 m HP-5 capillary column and by GC/MS. The C10-alcohols (2–4%) and other isomeric monoterpenes with less than 2% contribution are not shown.

If stirring continues for a further 30 min, only p-cymene and the minor alcoholic component were detected. Surprisingly, the reaction can be efficiently performed in the open air with formation, in addition to p-cymene and the isomeric terpenes, of varying amounts (3–15%) of ascaridole, and some other minor (<4%) unidentified products depending on the substrate.

It is worthy to note that under photochemical conditions, the rates of the reactions are similar to those in the absence of the light source. By adding two identically prepared samples of limonene to MV\(^{2+}\)/Na-Y, and stirring either in the dark or by irradiation with a 400 W Xenon lamp, both reactions proceeded to the same extent. This indicates that even upon irradiation the reaction occurs by a non-photochemically driven electron transfer pathway. Although zeolite Na-Y was reported to be slightly acidic, we found by GC–MS that by adding a hexane solution of the monoterpenes to non-supported dried Na-Y, only minor amounts of C10-alcohols (1–2%) appear after 1 h as new products. The alcohols are probably formed via addition of H\(_2\)O, still present in the cages, to the double bonds of the terpenes. Furthermore, methyl viologen adsorbed on the surface of silica gel was inefficient in performing the isomerisation/dehydrogenation reaction sequences, which probably indicates that transformation of the monoterpenes to p-cymene occurs in the interior, rather than at the surface of zeolite Na-Y.

To test the generality of this dehydrogenation reaction, 1,2-dihyronaphthalene \(8\), and 9,10-dihydroanthracene \(9\), were loaded within the zeolite and gave naphthalene and anthracene, respectively (Scheme 1), in around 30% yield after 30 min of stirring followed by extractive workup.

Formation of p-cymene from α- and γ-terpinene is known in their photoinduced electron transfer reactions in solution. Based on this, we propose that the double dehydrogenation reactions of monoterpenes within Na-Y to form 6 arises through the formation of their radical cations. Considering that spontaneous electron transfer from the zeolite framework to the MV\(^{2+}\) occurs, it is likely that the monoterpane radical cation is formed via single electron transfer from the monoterpene to the radical cation of the zeolite framework. The monoterpane radical cations either isomerize to form other terpenes, or expel a proton to form an allylic radical. In a second step, a hydrogen atom is lost forming p-cymene. The possibility that the allylic radical can be oxidized to the carbocation which in turn expels a second proton cannot be excluded. This mechanistic rational is shown in Scheme 2 for the case of the radical cation of α-terpinene. Furthermore, this radical cation can be captured by traces of water to form alcohols, or by superoxide ion if the reaction is carried out in the open air to form ascaridole. It is also notable that oxygen does not interfere significantly with...
the progress of the reaction, since minor amounts of ascaridole are formed compared to p-cymene. A similar observation has been reported by Garcia, Miranda and coworkers \(^3\) for an intrazeolite photoinduced electron transfer reaction.

Spontaneous intrazeolite electron transfer reactions are so far known to occur within ZSM-5 \(^1\) and Ca-Y. \(^1\) To the best of our knowledge, this paper describes the first example of the spontaneous formation of radical cations within Na-Y. The advantages of the MV\(^{2+}/\text{Na-Y}\) compared to the ZSM-5 is that for zeolite Y, the void space of the supercages is significantly larger, and they can host organic molecules even the size of a steroid. Also Ca-Y is acidic, while Na-Y is almost neutral.

In summary, we have presented a simple and effective system for performing spontaneous electron transfer reactions under very mild conditions, in the absence of irradiation. Further uses of MV\(^{2+}/\text{Na-Y}\) are currently under investigation.

Acknowledgements

This work was supported in part by the Greek Secretariat of Research and Technology (Program 1476), and by the EIIAEEK program ‘Isolation and synthesis of natural products with biological activity’. We thank Professor G. J. Karabatsos for valuable comments.

References

6. The doped zeolite used in this study was prepared by stirring 10 g of zeolite Na-Y (Degussa) in 1 L of deionized water containing 35 mg of methyl viologen dichloride for 24 h. The supported-zeolite was filtered, dried in the air and then washed with water in a Soxhlet apparatus for 2 days. Finally, it was dried under vacuum for several hours at 120°C, until the white powder turned to light blue, indicative of the formation of the radical cation of methyl viologen. We estimate that the doped zeolite contains approximately less than one MV\(^{2+}\) molecule per 10 supercages.
7. Ascaridole was prepared by reaction of singlet oxygen with \(\alpha\)-terpinene (CH\(_2\)Cl\(_2\)/methylene blue), and was purified by flash column chromatography using chloroform/hexane = 1/1 as eluent. The relative amounts of ascaridole formed if the intrazeolite reactions are carried out in the open air depend on the substrate, and are as follows: for 1, 15%, for 2, 5%, for 3, 6%, and for 4, 3%.