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Thermal transformation of monoterpenes within thionin-supported zeolite Na-Y. Acid-catalyzed or electron transfer-induced?†

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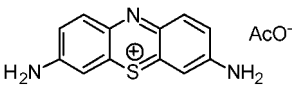
ABSTRACT: Several monoterpenes (monocyclic, bicyclic or acyclic) isomerize and finally transform to *p*-cymene in the dark upon loading within thionin-supported zeolite Na-Y. The same reactions occur in Na-Y dried under the same conditions as thionin/Na-Y. It is postulated that the thermal treatment of Na-Y generates 'electron holes' (probably acidic sites). The transformation of monoterpenes occurs more likely via an electron transfer-induced reaction subordinated to the occurrence of the acidic sites. The radical cation of the more thermodynamically stable monoterpene, α-terpinene, eventually dehydrogenates to *p*-cymene. For comparison, the same reactions were performed within methyl viologen-supported Na-Y. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: zeolite Na-Y; acid catalysis; electron transfer; terpenes

INTRODUCTION

In recent years, photooxygenation of alkenes adsorbed within thionin or methylene blue-supported zeolite Y has attracted considerable mechanistic and synthetic attention.[1] The major problem in carrying out intrazeolite ene hydroperoxidation reactions is that the reactant alkenes and the oxygenated products undergo structural isomerizations and decompositions which were attributed[2] to the few Brønsted acid sites[3] present in Na-Y. For example, in the intrazeolite photooxygenation of limonene, Ramamurthy and co-workers[2] successfully used pyridine or diethylamine to prevent those rearrangements. To examine the role of thionin and the zeolite in those isomerizations we present in this paper our studies on the thermal transformation of several monoterpenes (monocyclic, bicyclic and acyclic) within thionin-supported zeolite Na-Y. The results indicate that probably within Na-Y an electron transfer pathway is subordinated[4,5] to the presence of acidic sites.



thionin acetate

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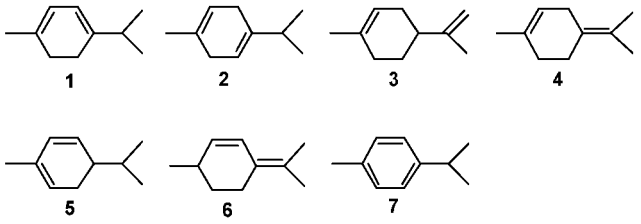
RESULTS AND DISCUSSION

Upon loading the monocyclic monoterpenes **1**–**5** (Table 1) within thionin/Na-Y under argon or even in the open air, immediate isomerization occurs, with formation of α-terpinene (**1**), γ-terpinene (**2**) and isoterpinolene (**6**) as the major products (thionin-supported Na-Y was prepared exactly as described in Refs 1a and 1e; it was heated in an oil-bath to 120 °C at 4 mbar for 4–8 h until it turned from purple to light blue, which requires, for a 5–8 g of the zeolite, around 6–8 h; it is estimated that it contains one thionin cation per 100 supercages of Na-Y). The isomeric monoterpenes **1**, **2** and **6** lead to the final oxidation product *p*-cymene (**7**). It is notable that reduced monoterpenes with the molecular formula $C_{10}H_{18}$ are formed in 1–5% relative yield and their amount is disproportional to the formation of the oxidation product *p*-cymene.

The results are similar to those found[6] recently upon loading of **1**–**5** within methyl viologen (MV^{2+})-supported Na-Y. However, the isomerization–dehydrogenation reaction sequence is much slower within thionin/Na-Y compared with the MV^{2+}/Na-Y medium. For example, limonene affords *p*-cymene within MV^{2+}/Na-Y in >70% yield after 30 min, and after 2 h is the only product. The loading level of the methyl viologen used in those experiments was approximately an order of magnitude higher. By using MV^{2+}/Na-Y with loading levels of the organic cations identical with those for thionin/Na-Y, very similar rates of isomerization–dehydrogenation are obtained. On the other hand, zeolite Na-Y with around a 10 times higher loading of thionin compared with that

Table 1. Transformation of monocyclic monoterpenes within thionin/Na-Y



Terpene	Conversion (%)[a]	**1** (%)	**2** (%)	**6** (%)	**7** (%)
α-Terpinene, **1**	75	25	4	32	36
γ-Terpinene, **2**	40	10	60	10	17
Limonene, **3**	>97	20	22	25	29
Terpinolene, **4**	>97	25	10	33	28
α-Phellandrene, **5**	>97	36	3	30	27

[a] Intrazeolite reaction time of 30 min at room temperature. If stirring is continued for a further 2 h, *p*-cymene is by far the major product. The C_{10} alcohols (2–4%) and other isomeric monoterpenes with less than 2% contribution are not shown. For details on the intrazeolite experiments, see the Experimental section.

used in the experiments presented in Table 1 does not improve the rate of the transformations. Approximately 2–4% of alcohols with the molecular formula $C_{10}H_{18}O$ are also formed under the reaction conditions, via hydration of the monoterpenes. The mass balance for all reactions, as measured by using *n*-nonane or *n*-dodecane as internal standards, was always >80%. The reactions can be performed efficiently in the open air with the formation, in addition to *p*-cymene and the isomeric terpenes, of trace amounts (~1%) of the endoperoxide of α-terpinene (ascaridole). The open-air reactions were carried out strictly in the dark to avoid the formation of singlet oxygen ene-type adducts[1] or ascaridole (up to 15%), which are produced slowly even in the ambient light of the laboratory.

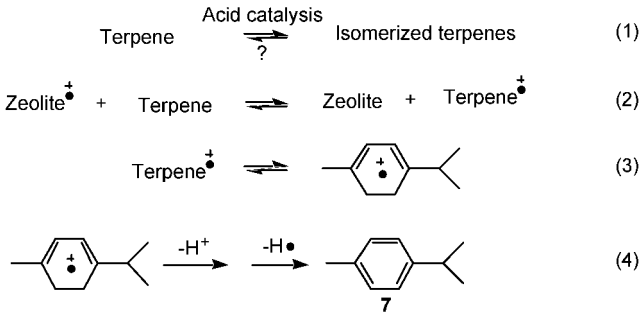
Note that in our previous work within MV^{2+}/Na-Y[6] we reported that terpinolene (**4**) is formed as one of the intermediate terpenes that finally lead to *p*-cymene. Careful re-examination of the products revealed that isoterpinolene (**6**) is formed instead. Unfortunately, terpinolene and isoterpinolene have identical retention times in GC, even on a 50 m capillary column, and that led to the wrong product assignment. Compound **6** is formed within thionin/Na-Y in appreciable amounts (see Table 1), and we were able to characterize it properly, after isolation by preparative GC. [Isoterpinolene (**6**) has the following ^{1}H NMR data in $CDCl_3$: 6.41 (dd, $J_1 = 10$ Hz, $J_2 = 2.2$ Hz, 1H), 5.55 (d, $J = 10$ Hz, 1H), 2.51 (m, 1H), 2.13 (m, 2H), 1.83 (m, 2H), 1.77 (s, 3H), 1.73 (s, 3H), 1.01 (d, $J = 7.2$ Hz, 3H). Its fragmentation pattern in the mass spectrum is identical with that reported in the literature.] Nevertheless, **6** also ends up as *p*-cymene after prolonged intrazeolite reaction time.

The above-mentioned transformations of **1**–**6**, or isomerizations of other simple alkenes within thionin-supported Na-Y, do not occur in Na-Y as obtained from commercial sources. Upon heating the zeolite at 120 °C under vacuum for 1–2 h, a slight formation (<4%) of the isomeric products is observed in 30 min, whereas after heating for at least 6–10 h, Na-Y has almost the same properties as thionin/Na-Y, and gives very similar results to those presented in Table 1. Prolonged drying for 24 h does not improve the efficiency of Na-Y in performing faster isomerization–dehydrogenation reactions. These results indicate that thionin, a well known electron acceptor,[8] does not participate in these intrazeolite reactions.

From the first point of view, the isomerization reactions seem to proceed by acid catalysis, attributable to the few Brønsted acid[3] sites present in Na-Y. However, this explanation is questionable. The acid-catalyzed skeletal isomerization of monoterpenes having the molecular formula $C_{10}H_{16}$ within porous materials and zeolites is well known and affords not only various amounts of *p*-cymene, but also reduced products with the molecular formula $C_{10}H_{18}$, such as *p*-menthenes.[9] This disproportionation reaction occurs by hydride transfer from a neutral monoterpene molecule to the carbocation generated by addition of a proton to another monoterpene molecule. The low percentage of $C_{10}H_{18}$ terpenes, or even their absence, indicates that *p*-cymene is formed by an alternative pathway. In addition, thionin/Na-Y neither dehydrates nor racemizes optically active *sec*-phenylethanol. [In a competing reaction, (±)-*sec*-phenylethanol and several monoterpenes used this study were treated in cyclohexane with the acidic catalyst Amberlyst 15. The alcohol was dehydrated at rates significantly higher to the isomerization of the monoterpenes.] Only the highly unstable α,α-dimethylbenzyl alcohol dehydrates to α-methylstyrene in 82% yield after 30 min of stirring with thionin/Na-Y.

The dehydrogenation of monoterpenes such as **1**–**6** to *p*-cymene is identical with their transformation within MV^{2+}/Na-Y,[6] in photosensitized electron-transfer reactions in solution,[10,11] on metal oxides surfaces upon irradiation,[12] or by catalytic amounts of the mixed-addenda heteropolyanion $PV_2Mo_{10}O_{40}^{5-}$.[13] These oxidation reactions have been attributed to proceed via formation of the radical cations of the monoterpenes. We postulate that during the thermal dehydration treatment of Na-Y, acidic sites within the cages[14] and/or extra-lattice aluminum species[15] are activated and catalyze these rearrangements. For example, Lewis acid sites within zeolites are known to act as 'electron holes'[16] and accept one electron from substrates with low ionization potential. For the thionin/Na-Y system we propose the mechanistic rationale shown in Scheme 1.

The terpenes may isomerize due to the acidic environment [Eqn. (1)]. On the other hand, the 'electron holes' within Na-Y could also accept an electron from the monoterpene [Eqn. (2)], whose radical cations can isomerize to the more stable radical cation of α-terpinene



Scheme 1

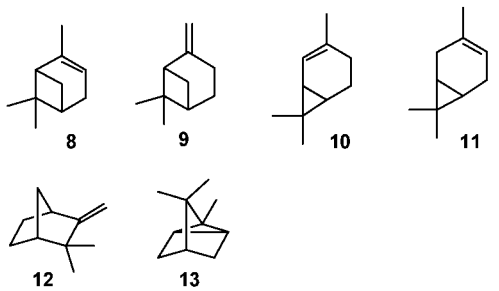
[Eqn. (3)]. This radical cation in turn dehydrogenates[10–13] to *p*-cymene [Eqn. (4)]. Therefore, both acid and electron transfer catalysis are probably involved in these transformations. Crockett and Roduner, based on an EPR study, reported[17] that within the highly acidic H-mordenite, the radical cations of *trans*-isolimonene and α-pinene are formed, that transform spontaneously to the radical cation of α-terpinene. This transformation is not catalyzed by Brønsted but rather by Lewis acidity. Recent work,[18] however, has shown that it is difficult to probe the reactivity of the Lewis and Brønsted acidic sites within Na-Y. Hence we are unable to distinguish among Lewis or Brønsted sites as being responsible for these transformations.

Within MV^{2+}/Na-Y, the isomerization–dehydrogenation reactions are much more efficient. For this system, extra 'electron holes' are generated thermally on the zeolite lattice as found by Yoon and co-workers,[19] since methyl viologen, an excellent electron acceptor, can abstract an electron from the zeolite and form $MV^{+\cdot}$ [The MV^{2+}/Na-Y was dried under a vacuum (120 °C at 4 mbar) until it turned light blue, due to the formation of the $MV^{+\cdot}$; this requires approximately 6–10 h]. Thionin is probably less efficient at accepting an electron from the zeolite lattice to form thionin radical. ESR examination of a thionin/Na-Y slurry in dry hexane showed no signal due to the thionin radical.

We further examined the intrazeolite transformation of four bicyclic monoterpenes [α-pinene (**8**), *β*-pinene (**9**), 2-carene (**10**) and 3-carene (**11**)] by using either thionin/Na-Y or MV^{2+}/Na-Y. Both zeolitic systems afford identical products, but the extent of the transformations is higher within MV^{2+}/Na-Y, as found for substrates **1–5**. The results after 30 min of stirring with thionin/Na-Y are shown in Table 2. Within MV^{2+}/Na-Y, *p*-cymene is formed in significantly higher amounts (e.g., 43% from **8**, 42% from **9** and 42% from **10**), with the same reaction time of 30 min.

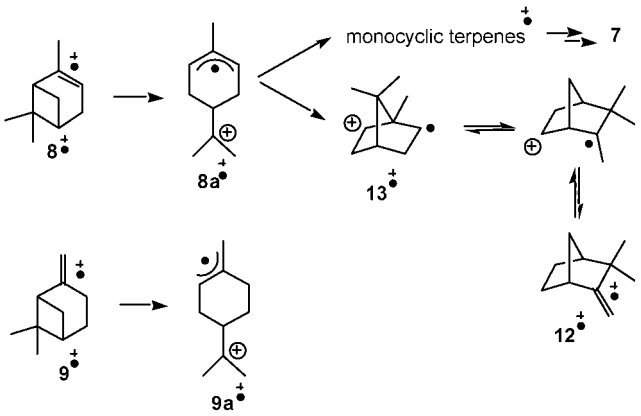
Formation of the products from α- and *β*-pinene can be explained by considering the same acid catalysis/electron transfer rationalization. Acids are well known to transform these bicyclic terpenes to their monocyclic isomers via formation of carbocationic intermediates. In Scheme 2 we present only a possible electron transfer-induced mechanism, although this isomerization pathway may not be the only one. From $\mathbf{8}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$, the distonic radical cations $\mathbf{8a}^{+\cdot}$ and $\mathbf{9a}^{+\cdot}$ can be formed. In $\mathbf{8a}^{+\cdot}$ a bonding interaction between the cation and the central carbon atom of the allylic radical leads to $\mathbf{12}^{+\cdot}$ via $\mathbf{13}^{+\cdot}$. Similarly, rearrangement of the radical cation of *β*-pinene ($\mathbf{9}^{+\cdot}$) to $\mathbf{9a}^{+\cdot}$ affords the same products as α-pinene. Tricyclene (**13**) and camphene (**12**) are in equilibrium, and they cannot form the monocyclic isomers **1–5** or *p*-cymene. Camphene, after 30 min of intrazeolite treatment, affords tricyclene (9%), isoborneol (6%) and 2% of an unidentidified C_{10}- alcohol. The alcohols are probably formed by hydration of **12** and **13** from the traces of water present in the zeolite.

Table 2. Transformation of bicyclic monoterpenes within thionin/Na-Y



Terpene	Conversion (%)[a]	**1** (%)	**2** (%)	**6** (%)	**12** (%)	**13** (%)	**11** (%)	**7** (%)
α-Pinene, **8**	>97[b]	20	18	20	20	2	—	16
β-Pinene, **9**	>97[b]	24	14	26	16	1	—	15
2-Carene, **10**	>96	25	2	40	—	—	10	18
3-Carene, **11**	13	<1%	—	3	—	—	88	7

[a] Intrazeolite reaction time of 30 min, at room temperature.
[b] After a further 1 h of reaction, the relative ratio **13**/(**1** + **2** + **6** + **14** + **7**) is almost unchanged; however, the ratio **7**/(**1** + **2** + **6**) increases considerably.

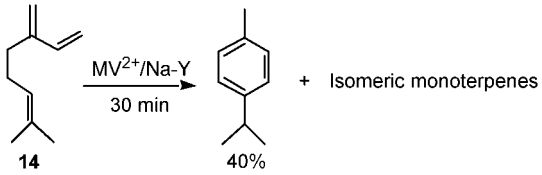


Scheme 2

3-Carene (**10**) reacts smoothly (95% conversion), and affords after 30 min the monocyclic monoterpenes **1, 2** and **6**, the isomeric 2-carene (**11**) and *p*-cymene. 2-Carene is very unreactive (only 13% conversion after 30 min), and affords mostly *p*-cymene (7%) and isoterpinolene (3%). Considering again radical ion pairs, for 3-carene, rearrangement of $\mathbf{10}^{+\cdot}$ to $\mathbf{10a}^{+\cdot}$ may occur readily (Scheme 3) whereas $\mathbf{10a}^{+\cdot}$ is expected to afford other monocyclic monoterpenes and eventually *p*-cymene. By contrast, $\mathbf{11}^{+\cdot}$ cannot rearrange to a distonic radical cation such as $\mathbf{10a}^{+\cdot}$, but transforms slowly to $\mathbf{10}^{+\cdot}$, which affords the typical products obtained from the radical cation of 3-carene. That is in agreement with the low reactivity of 2-carene within Na-Y.

We also tested the efficiency of thionin/Na-Y and MV^{2+}/Na-Y to aromatize acyclic monoterpenes such as myrcene (**14**). Myrcene was completely consumed after 30 min, and gave *p*-cymene in 22% relative yield with thionin/Na-Y and in 40% with MV^{2+}/Na-Y (Scheme 4). The rest was a mixture of monocyclic and acyclic isomeric monoterpenes, which on prolonged reaction time (2 h for MV^{2+}/Na-Y) also convert to *p*-cymene with >70% yield.

Therefore, thionin-supported zeolite Na-Y is a dual system that, depending on the conditions, can give acid-catalyzed, electron transfer or energy transfer-driven reactions. Upon visible light irradiation it can sensitize the formation of singlet oxygen via an energy transfer process from the triplet excited state of the dye to the triplet molecular oxygen. A competing electron transfer-induced pathway subordinated[4] to the occurrence of acidic sites can also take place. Pyridine and triethylamine used in the past[1d,1e,2] to minimize the unwanted rearrangements of the reactants within thionin/Na-Y probably react with the acidic sites, thus destroying the 'electron holes.'



Scheme 4

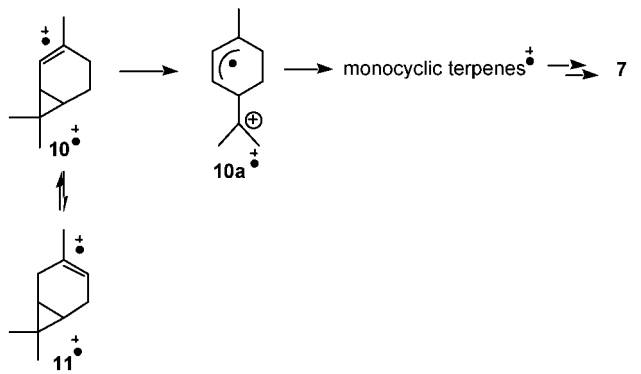
In conclusion, we have presented evidence that the transformation of monoterpenes and the skeletal isomerization of alkenes within thionin/Na-Y probably occur by a combination of acid catalysis and electron transfer. Further applications of cation-exchanged zeolite Y in organic chemistry are currently under examination.

EXPERIMENTAL

All monoterpenes were purchased from commercial sources and their purity was examined by GC–MS and ^{1}H NMR spectroscopy (500 MHz). Zeolite Na-Y was supplied by Degussa. Hexane was distilled from CaH_2 and THF from Na–benzophenone. For the preparation of thionin-supported zeolite Na-Y, see the Results and Discussion section. Non-supported zeolite Na-Y was thermally activated under exactly the same conditions as thionin/Na-Y.

Intrazeollte transformation of monoterpenes

To 0.5 g of thionin-supported zeolite Na-Y were added 5 µl of the monoterpene dissolved in 5 ml of dry hexane. After 30 min of stirring under argon or in the open air in the dark, 5 ml of moistened tetrahydrofuran were added. The resulting slurry was stirred for 2 h and then filtered. Analysis of the products was performed by ^{1}H NMR spectroscopy, by GC on a 50 m HP-5 capillary column and by GC–MS. It is notable that no transformation of the monoterpenes occurs within the Na-Y slurry if the solvent is moistened tetrahydrofuran. To calculate the mass balance, n-dodecane was used as an internal standard. Approximately equimolar amounts of n-dode-



Scheme 3

cane and the terpene were treated with thionin-supported zeolite Na-Y as described above. After extractive work-up, the mixture was analyzed by GC.

Acknowledgements

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REFERENCES

1. (a) Li X, Ramamurthy V. *J. Am. Chem. Soc.* 1996; **118**: 10666–10667; (b) Robins RJ, Ramamurthy V. *J. Chem. Soc., Chem. Commun.* 1997; 1071–1072; (c) Clennan EL, Sram JP. *Tetrahedron Lett.* 1999; **40**: 5275–5278; (d) Stratakis M, Froudakis G. *Org. Lett.* 2000; **2**: 1369–1372; (e) Shailaja J, Sivaguru J, Robbins RJ, Ramamurthy V, Sunoj RB, Chandrasekhar J. *Tetrahedron* 2000; **56**: 6927–6943; (f) Clennan EL, Sram JP. *Tetrahedron* 2000; **56**: 6945–6950; (g) Stratakis M, Rabalakos C. *Tetrahedron Lett.* 2001; **42**: 4545–4547; (h) Stratakis M, Kosmas G. *Tetrahedron Lett.* 2001; **42**: 6007–6009.
2. Ramamurthy V, Lakshminarasimhan PH, Grey CP, Johnston L. *J. Chem. Soc., Chem. Commun.* 1998; 2411–2418.
3. Jayathirma Rao V, Perlstein DL, Robbins RJ, Lakshminarasimhan PH, Kao H-M, Grey CP, Ramamurthy V. *J. Chem. Soc., Chem. Commun.* 1998; 269–270.
4. Pitchumani K, Joy A, Prevost N, Ramamurthy V. *J. Chem. Soc., Chem. Commun.* 1997; 127–128.
5. Casades I, Alvaro M, Garcia H, Espla M. *J. Chem. Soc., Chem. Commun.* 2001; 982–983.
6. Stratakis M, Stavroulakis M. *Tetrahedron Lett.* 2001; **42**: 6409–6411.
7. McCormick JP, Barton DL. *Tetrahedron* 1978; **34**: 325–330.
8. Reid GD, Whittaker DJ, Day MA, Creely CM, Tuite EM, Kelly JM, Beddard GS. *J. Am. Chem. Soc.* 2001; **123**: 6953–6954.
9. (a) Stanislaus A, Yeddanapalli LM. *Can. J. Chem.* 1972; **50**: 61–74; (b) Lopez CM, Machado FJ, Rodriguez K, Mendez B, Haseqawa M, Pekekar S. *Appl. Catal. A* 1996; **173**: 75–85.
10. Roth HD, Weng H, Herbertz T. *Tetrahedron* 1997; **53**: 10051–10070.
11. Climent M-J, Miranda MA, Roth HD. *Eur. J. Org. Chem.* 2000; 1563–1567.
12. Fox MA, Sackett DD, Younathan JN. *Tetrahedron* 1987; **43**: 1643–1660.
13. Neumann R, Levin M. *J. Am. Chem. Soc.* 1992; **114**: 7278–7286.
14. Lange JP, Gutsze A, Karge HG. *J. Catal.* 1988; **114**: 136.
15. Freude D, Hunger M, Pfeifer HZ. *J. Phys. Chem.* 1987; **152**: 429.
16. Liu X, Iu K-K, Thomas JK, He H, Klinowski J. *J. Am. Chem. Soc.* 1994; **116**: 11811–11818.
17. Crockett R, Roduner E. *J. Chem. Soc., Perkin Trans. 2* 1994; 347–350.
18. Herwijnen van HWG, Brinker UH. *Tetrahedron* 2002; **58**: 4693–4697.
19. (a) Yoon KB. *Chem. Rev.* 1993; **93**: 321–339; (b) Park YS, Um SY, Yoon KB. *J. Am. Chem. Soc.* 1999; **121**: 3193–3200.