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Chemoselective hydroperoxidation of alkenylarenes within thionin-supported zeolite Na-Y

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Abstract—Photooxidation of several 1-aryl-2-methylpropenes within the thionin-supported zeolite Na-Y affords the *ene* type allylic hydroperoxides in a highly chemoselective manner. This is in contrast to their photooxygenation reaction in solution, where the *ene* pathway is less favorable compared to the [4+2] or [2+2] pathways. Cation- π interactions are likely to be responsible for this selectivity. © 2001 Published by Elsevier Science Ltd.

The photooxygenation of organic compounds adsorbed within the dye-supported zeolite Na-Y¹ and other constrained media² has recently attracted considerable attention primarily due to the significant enhancement of product selectivity. So far it is recognized that in the intrazeolite (Na-Y) photooxygenation of geminal dimethyl trisubstituted alkenes, formation of the new double bond in the ene adduct occurs preferentially at the methyl groups³ (Markovnikov selectivity). Specific deuterium labeling of the anti methyl group in a series of such trisubstituted alkenes, independently by us⁴ and Clennan,⁵ showed that the well known 'cis effect'⁶ selectivity in solution does not operate within the zeolite. It was proposed that electrostatic interaction between the intermediate perepoxide and an alkali metal cation⁷ plays a significant role in dictating the distribution of the ene products. Similarly, in contrast to the reaction in solution, an anti 'cis effect' selectivity was found in the intrazeolite photooxygenation of 1methylcycloalkenes.8

As part of our continuing interest in the regioselectivity and stereoselectivity of singlet oxygen reactions in homogeneous and heterogeneous media, we report in this communication our preliminary results on the intrazeolite photooxygenation of 1-aryl-2-methylpropenes. It is well known that reaction of alkenylarenes with ${}^{1}O_{2}$ in solution affords products arising mainly from [4+2] or [2+2] addition to the double bond.⁹ The *ene* pathway is less favorable or even absent. For

Keywords: zeolite Na-Y; ene reactions; singlet oxygen; zwitterions. * Corresponding author. Fax: +30-81-393601; e-mail: stratakis@ chemistry.uoc.gr example, β , β -dimethylstyrene (1) affords¹⁰ the *ene* adduct **1a** in approximately 20% yield, benzaldehyde (**1b**), and mainly the two diastereomeric diendoperoxides¹¹ **1d** and **1e** in a 68/32 ratio; di-endoperoxides arise from initial [4+2] addition of ¹O₂ to **1**, followed by a second addition of ¹O₂ to the newly formed diene endoperoxide **1c** (Scheme 1). Also, for 1-(2-methylpropenyl)naphthalene (**2**), originally it was reported that only the 1,4-endoperoxide **2b** is formed.¹² However, the same group reported later¹³ that the *ene* adduct **2a** is also formed in various yields (24–40%) depending on solvent polarity (Scheme 1). We repeated this reaction (CH₂Cl₂/methylene blue) and found that the *ene* product is formed in low yield (around 15%).

Intrazeolite photooxygenation of alkenylarenes 1-6 within the thionin-supported zeolite Na-Y afforded surprisingly the *ene* adducts $1a-6a^{14}$ as the major or only products (Table 1). This is in contrast to their reactions in solution where the allylic hydroperoxides are formed as secondary adducts (5-20% yield).¹⁵ In a typical experiment, 10 mg of the alkenylarene dissolved in 10 mL of hexane were added into a tube containing 1 g of dry thionin-supported Na-Y.16 The tube was immediately irradiated for 5 min under constant flow of oxygen. Short irradiation time and low loading levels of the alkene into zeolite are the optimum conditions for performing intrazeolite photooxygenations.3b,5 After extractive work up as described earlier,⁴ the solvent was removed under a vacuum and the products were analyzed by ¹H NMR.

Apart from the *ene* allylic hydroperoxides, minor amounts (3-6%) of aldehydes resulting from the cleavage of the alkene double bond are also produced.

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Formation of the aldehydes probably arises via a nonphotochemically induced electron-transfer pathway, which competes with the energy-transfer pathway that produces singlet oxygen.¹⁷ It is interesting that the substrates had been completely consumed within 5 minutes of irradiation, whereas the same amounts of alkenylarenes (~ 10 mg) in solution require reaction for 1–3 h to go to completion. The mass balances, as



Scheme 1.

Table 1. Photooxygenation of alkenes 1-6 within the thionin-supported zeolite Na-Y



^a Di-endoperoxides 1d and 1e are also formed in 8% combined yield.
^b For compound 5 the reaction was performed on a 50 mg scale using 2.5 g of the supported zeolite and the pure *ene* hydroperoxide was isolated in 88% yield.

 $^{\rm c}$ A minor product, not found in the reaction with 1O_2 in solution, is also formed in 12% yield. This product was not isolated or characterized.



Scheme 2.

estimated by GC using several calibration compounds (2-phenylethanol, 2,6-di-tert-butyl-p-cresol or transdecahydronaphthalene) depending on the substrate, were >85% for substrates 1 and 4-6, whereas for 2-3 they were $\sim 75\%$. Equimolar amounts of the alkenylarene and the appropriate calibration compound were subjected to reaction. After the workup, the reaction mixtures were analyzed by ¹H NMR or alternatively triphenylphosphine was added to reduce the hydroperoxides to alcohols and the relative amounts of the alcohols versus the calibration compounds were found by GC. To establish further our results, the four products from the reaction of ${}^{1}O_{2}$ with 1 in solution (ene, benzaldehyde and the two di-endoperoxides) were added to thionin-supported Na-Y and then irradiated under a constant flow of oxygen for 5 minutes. After extractive workup and analysis by ¹H NMR, the ratio of the oxygenated adducts before and after irradiation was almost unchanged.

As a reasonable mechanistic rationalization for the observed chemoselectivity, we consider that the [4+2] and [2+2] products in the reactions of arylalkenes with singlet oxygen are formed in a step-wise manner, via a common open 1,4-zwitterionic intermediate.¹⁸ On the other hand, the ene products arise from a perepoxide intermediate or an exciplex with the structural require-ments of a perepoxide.^{1d,6} It is reasonable that Na⁺ binding to the electron rich aryl ring¹⁹ within the cages of Na-Y results in destabilization of the open zwitterionic intermediate (ZI), because the aryl ring upon complexation is losing electron density and is less able to stabilize the positive charge at the benzylic position of ZI, as shown in Scheme 2 for substrate 1. On the other hand, in the perepoxide intermediate the benzylic carbon has only a partial positive charge;¹⁰ thus, complexation of the aryl ring to the cation is expected to cause significantly less destabilization compared to the zwitterion.

An alternative explanation of the product chemoselectivity could be that the simultaneous complexation of the Na⁺ to the aryl ring and to the alkene double bond within the cages, places the aryl group at an inappropriate conformation for a concerted [4+2] reaction to occur; the alkene double bond and the aryl ring cannot be coplanar. This rationalization, however, is less likely, since it requires a synchronous mechanism for ${}^{1}O_{2}$ addition to the diene moiety of the alkenylarene forming the endoperoxide.

Similar lack of formation of [4+2] products, in contrast to their reaction in solution, was reported in the photo-oxygenation of stilbene and 4,4'-dimethoxystilbene.²⁰ The 1,2-dioxetane was formed instead and the selectivity was attributed to an electron transfer mechanism.

Further work to determine the relative reactivity of the *syn* and *anti* methyl groups of a series of geminal dimethyl alkenylarenes are under way in order to shed more light on the mechanistic rationalization of this highly chemoselective *ene* reaction.

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- 14. ¹H NMR data of the allylic hydroperoxides; compound 1a: 7.95 (s, 1H, OOH), 7.30-7.38 (m, 5H), 5.38 (s, 1H), 5.13 (br. s, 1H), 5.08 (br. s, 1H), 1.69 (s, 3H). Compound 2a: 8.21 (s, 1H, OOH), 8.14 (d, J=8.3 Hz, 1H), 7.89 (d, J=7.8 Hz, 1H), 7.86 (d, J=8.3 Hz, 1H), 7.58 (d, J=7.1Hz, 1H), 7.48–7.55 (m, 3H), 6.15 (s, 1H), 5.21 (br. s, 2H), 1.79 (s, 3H). Compound 3a: 8.09 (s, 1H, OOH), 7.84-7.87 (m, 4H), 7.46-7.51 (m, 3H), 5.55 (s, 1H), 5.20 (br. s, 1H), 5.13 (br. s, 1H), 1.74 (s, 3H). Compound 4a: 8.03 (s, 1H, OOH), 7.59-7.62 (m, 4H), 7.43-7.49 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 5.44 (s, 1H), 5.18 (br. s, 1H), 5.12 (br. s, 1H), 1.75 (s, 3H). Compound 5a: 8.09 (s, 1H, OOH), 7.64 (d, J=8.1 Hz, 2H), 7.49 (d, J=8.1 Hz, 2H), 5.44 (s, 1H),5.12 (br. s, 1H), 5.11 (br. s, 1H), 1.70 (s, 3H). Compound **6a**: 7.99 (s, 1H, OOH), 7.29 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 5.33 (s, 1H), 5.14 (br. s, 1H), 5.08 (br. s, 1H), 3.81 (s, 3H), 1.70 (s, 3H).
- 15. The reaction of alkenes 3-6 with ${}^{1}O_{2}$ in solution, apart from the *ene* adducts which are formed in low yield, affords mainly other oxygenated products which were not isolated or characterized.
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