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Photodimerization of *trans*-2-styrylpyridine in zeolite cages

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Abstract

The photochemical behaviour of *trans*-2-styrylpyridine in various cation-exchanged faujasite zeolites has been investigated. At a lower loading level, *trans–cis* isomerization is the only process. When the loading level is increased, in addition to isomerization, significant amounts of dimerization and cyclization products are also observed with the products distribution depending on the free volume available inside the cage. Acidic zeolites such as HY and MgY are found to catalyse the thermal reaction of 2-styrylpyridine. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: *trans*-2-Styrylpyridine; Faujasite zeolites; Irradiation; Isomerization; Dimerization

1. Introduction

Photocyclization and dimerization reactions in solution phase are limited by a lack of stereo/regiochemical control whereas many photodimerization reactions in solid host systems result in the selective transformation due to the specific packing of the monomers inside these solid host systems [1–7]. Microheterogeneous media such as micelles, cyclodextrins and zeolites also serve as hosts for controlling such photochemical reactions.

Photolysis of *trans*-2-styrylpyridine (2-SP) in benzene solvent under nitrogen atmosphere results in *cis–trans* isomerization, whereas the irradiation in the solid state in oxygen atmosphere results in the formation of significant amounts of photooxidation products [8]. A small amount of dimer (2.6%) is also obtained. However, when *trans*-2-SP is irradiated as its hydrochloride or methiodide, the dimer is obtained as the major product in the solid state as well as in benzene suspension [8,9]. The type of the dimer produced is influenced by steric and charge interference factors. Irradiation of *trans*-2-SP in cyclohexane in the presence of oxygen results in the rapid *trans–cis* isomerisation and subsequent cyclization to dihydrobenzo[f]quinoline which is oxidised to benzo[f]quinoline, in addition to the formation of a small amount of 1-phenyl-2-(2-pyridyl) ethanol [10].

The dependence of photobehaviour on molecular environment is clearly demonstrated by studying the selectivity obtained in the dimerization of 4-styrylpyridinium cations over organized assemblies like micelles, crystals and monolayers [6]. In contrast to homogeneous photolysis, wherein 13% of the *cis*-isomer and 60% of the *syn*-head-to-tail dimer are formed, the irradiation of *trans*-4-styrylpyridinium cations in reversed micelles formed from hexane–aerosol OT-water, leads to an efficient and selective formation of *syn*-head-to-head dimer [11]. 4-Styrylpyridinium cations give selectively the *syn*-head-to-tail dimers when irradiated between clay interlayers [12]. Recently, we have established that the photolysis of α- and β-cyclodextrin complexes of *trans*-2-SP in the solid state leads to unimolecular reactions (photoisomerization and/or photocyclization) and γ-cyclodextrin complex to bimolecular reaction (photodimerization) [13].

Zeolites are crystalline aluminosilicates made up of corner-sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra and the framework contains a large number of pores, channels and cages of various dimensions that can accommodate organic molecules of right size. As the zeolites are photo-inert, the confined environment in their framework can be successfully utilized to attain remarkable selectivity in photochemical reactions. We have already reported [14] the effect of various cation exchanged faujasite zeolites on the selective *trans–cis* isomerization of α,β-unsaturated sulfones. This prompted us to study the irradiation of free base of *trans*-2-SP inside the cages of faujasite zeolites. As the double bond in 2-SP is more polar than that of stilbene, dimerization is expected to be more facile even with unsubstituted 2-SP. It will be of interest to study whether it is possible to

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control the product of photolysis towards unimolecular or bimolecular reactions by changing the loading level of the substrate and by using different cation-exchanged zeolites.

2. Experimental details

trans-2-SP was prepared as reported in the literature [15]. Cations of interest were exchanged into the NaY (Aldrich) powder by stirring with the corresponding nitrate (10%) solution at 70°C for ca. 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. Based on an earlier report, exchange levels are assumed to be between 62 and 84% [16].[2] All these cation-exchanged zeolites were activated at 500°C for ca. 10 h prior to use. Solid complexes of *trans*-2-SP and zeolites were prepared by stirring the required quantity of *trans*-2-SP and the appropriate zeolite in hexane followed by filtration. Complexes were irradiated either as a hexane slurry with continuous stirring (under nitrogen atmosphere for 2 h) or as solids (for 15 h) using 400 W medium pressure mercury lamp. Then, the products were extracted with $CHCl_3$ after breaking the zeolite framework with 4 N HCl and the percentage of products were determined by preparative TLC for higher loading level. The photostationary state composition at the lower loading level was determined from the absorption spectra of the reaction mixture in which only *cis*- and *trans*-isomers are present. The products were characterized by their characteristic ^1H-NMR spectra. The NMR pattern of the *syn*-head-to-tail dimer (**3**) (m.p. 189–190°C) obtained is given below: ($CDCl_3$, 300 MHz) 4.93 (2H,t), 5.10(2H,t), 7.11–7.59(16H,m,) and 8.66 (2H,d). The cyclized product (**4**) (m.p. 89°C) has the following NMR features: 7.48–7.33 (3H), 7.89–8.01 (3H), 8.58–8.68 (1H), 8.89–9.00 (2H) [10].

3. Results and discussion

Our studies on irradiation of *trans*-2-SP (λ_{max}=307 nm) in methanol under nitrogen atmosphere results only in isomerization and neither dimerization nor cyclization is observed. A photostationary state, PSS, (reached in 80 s) richer in *cis*-isomer (95%, λ_{max}=288 nm) is obtained and this is in accordance with the report in benzene [8]. The presence of only two absorbing species is evident from an isobestic point at 253 nm (Fig. 1). In the benzil-sensitized irradiation of *trans*-2-SP (the triplet energies of benzil and *trans*-2-SP are 54.3 and 49.0 kcal/mol, respectively [17,18]), the absence of an isobestic point and presence of a hypsochromic shift of λ_{max} indicate that from the triplet state in addition to *trans*- and *cis*-isomers, others derived from *cis*-isomer may also be formed. A 10-fold excess of the sensitizer is used and its absorption is subtracted by placing a solution of identical concentration in the reference cell.

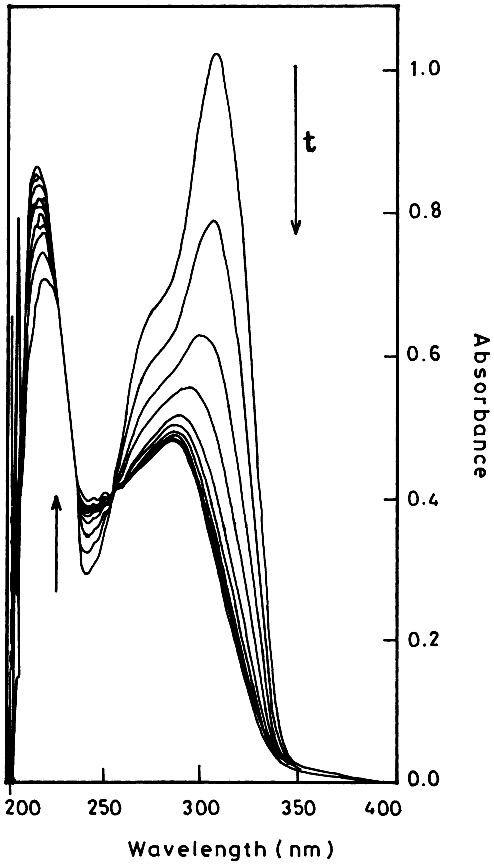

Fig. 1. Absorption spectra of *trans*-2-SP in methanol at different time intervals (10 s) of irradiations in nitrogen atmosphere.

Irradiation of *trans*-2-SP included within zeolite cages is carried out at two different loading levels of the guest molecule. A lower loading level (approximately one molecule per supercage) irradiation as a hexane slurry leads only to *cis*–*trans* isomerization (Table 1). With the variation in zeolite cations, the PSS composition also varies. In the

Table 1
Products distribution (PSS) (in %) in the irradiation of zeolite–*trans*-2-SP complexes at lower loading level[a]

Medium	Percentage of	
	cis-2-SP	*trans*-2-SP
Methanol	95	5.0
LiY	93 (75)[b]	7.0 (25)
NaY	88 (66)	12 (34)
KY	63	37
RbY	73	27
CsY	73 (36)	27 (64)

[a] Twenty milligram of *trans*-2-SP in 300 mg of zeolite irradiated as hexane slurry in nitrogen atmosphere for 2 h. Percentages are calculated from UV–Vis spectra.

[b] Data in parantheses represent the products distribution in irradiation of solid zeolite–*trans*-2-SP complexes for 15 h.

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[2] Exchange levels are reported as follows: LiY 64%; KY 84%; RbY 68%; and CsY 62%.

Table 2
Products distribution (in %) in the photolysis of zeolite–*trans*-2-SP complexes at higher loading level[a,b]

Medium	Loading level	*trans*-2-SP (**1**)	*cis*-2-SP (**2**)	Dimer (**3**)	Benzo[f]-quinoline (**4**)	X[c]
LiY	1.97	22 (49)[d]	18 (30)	34 (12)	16 (9.0)	10 (–)
NaY	1.91	20	35	30	6.0	9.0
KY	1.79	12	18	29	35	6.0
RbY	1.58	30	13	17	30	6.0
CsY	1.54	39 (68)[d]	13 (18)	12 (6.0)	29 (8.0)	7.0 (–)

[a] Loading level: number of molecules per super cage.
[b] Irradiated as solid complexes for 15 h; analysed by TLC.
[c] Unidentified products.
[d] Data in parantheses represent the products distributions in slurry irradiations for 2 h.

Table 3
Products distribution of thermal and photochemical reaction of *trans*-2-SP in the presence of acidic zeolites[a]

Medium	Loading level[b]	*trans*-2-SP (**1**)	*cis*-2-SP (**2**)	Dimer (**3**)	Benzo[f]-quinoline (**4**)	X[c]
HY (thermal)	2.10	70	6.0	11	10	3.0
HY ($h\nu$)	2.10	55	10	18	10	7.0
MgY (thermal)	1.78	57	11	11	13	8.0
MgY ($h\nu$)	1.78	45	20	25	8.0	2.0

[a] Irradiated as solid complexes for 15 h; analysed by TLC.
[b] Number of molecules per super cage.
[c] Unidentified products.

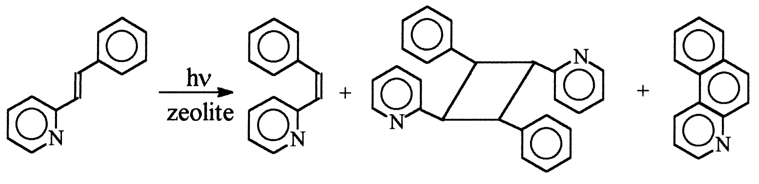
photostationary state with LiY and NaY, the *cis*-isomer is found to be the major component and resembles the PSS in homogeneous media. While going from KY to CsY, the amount of *cis*-isomer decreases considerably. This is due to the considerable restrictions imposed by the reduction in cavity free volume (due to the presence of larger cations) on the rotation of the π-bond. With larger cations, presence of only *cis*- and *trans*-isomers rules out any significant reaction from the triplet state of *trans*-2-SP. That cavity free volume plays a major role, is also consistent with our earlier report, [13] wherein, with α-cyclodextrin, the amount of *cis*-isomer is reduced compared to that of homogeneous solution and this is attributed to the restriction imposed by the α-CD cavity on the photoisomerization of *trans*-2-SP [13].

Irradiation of solid zeolite–*trans*-2-SP complexes (at a lower loading level, with approximately one molecule per supercage) has also been carried out in LiY, NaY and CsY as representative examples. In all the cases, the percentage of *cis*-isomer in the PSS is less compared to slurry irradiations (Table 1). It is likely that, in the solid-state irradiations, in the absence of solvent molecules in between (which act as lubricants), binding of the *trans*-2-SP with the zeolite framework is stronger and this acts as an impediment to *trans*–*cis* isomerization.

Irradiation is also extended to a 'low' loading level (2 mg of *trans*-2-SP in 300 mg of zeolite, corresponding to a loading level of ~0.08 molecule per super cage in the case of NaY). Only unimolecular *cis*–*trans* isomerization is observed and the PSS composition is similar to that reported for a loading level of 20 mg of the substrate in 300 mg of zeolite.

At higher loading levels, with approximately two guest molecules per cage, the irradiations are carried out on solid complexes so as to facilitate dimerization. A different product distribution is obtained (Tables 2 and 3), and in addition to isomerization, dimerization and cyclization are also observed (Scheme 1).

The dimer formed in the irradiation of zeolite–*trans*-2-SP complex is identified as the *syn*-head-to-tail dimer based on its characteristic NMR spectrum and is the same as obtained in the irradiation of the hydrochloride or methiodide [8,9]. The absence of other dimers show that the



1 **2** **3** **4**

Scheme 1. Photochemical reactions of *trans*-2-SP in zeolites.

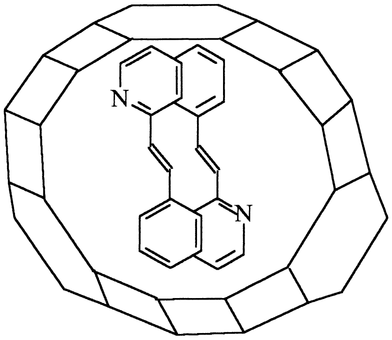
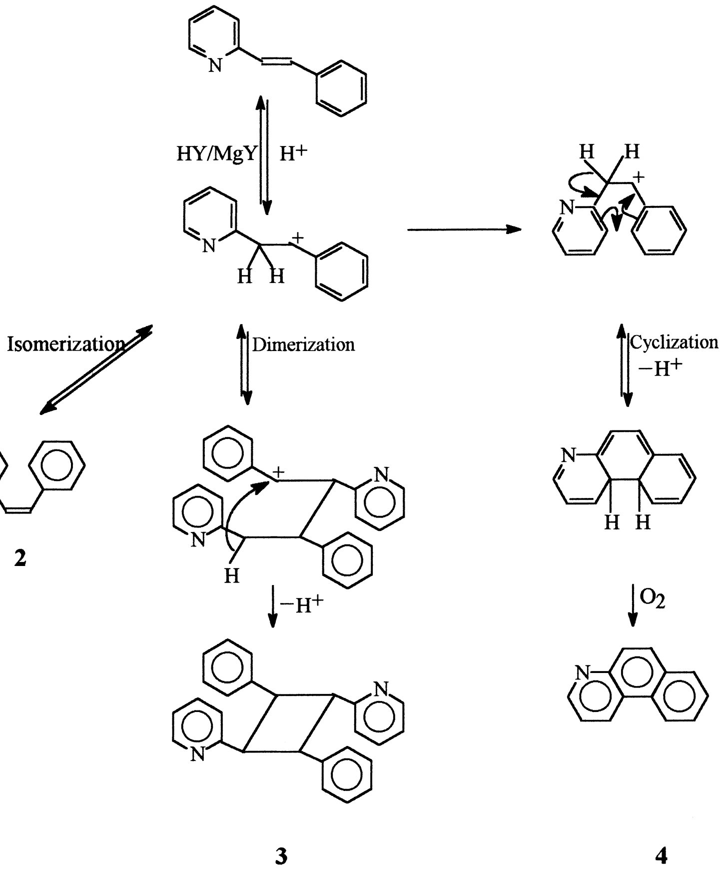


Fig. 2. Preferred *syn*-head-to-tail orientation of *trans*-2-SP molecules inside the zeolite cages.

heterocyclic rings, obviously, prefer to dimerize in alternate positions of *trans*-2-SP so as to reduce steric hindrance and also charge interference (Fig. 2). Dimerization is significant with LiY and NaY. Stronger binding of the smaller cations (Li^+ and Na^+) with nitrogen is likely which will increase the electron deficiency and crowding at the heteroatom. The resultant steric and charge interference, coupled with subsequent increase in the polarity of the double bond, enhance dimerization in a head-to-tail orientation. Electrostatic interaction between light alkali ion with olefinic/aromatic systems [19,20] has been reported in the gas phase. Recent reports [21–24] also predict that ions such as Li^+ can accelerate rearrangement reactions of certain olefins, implying interaction between the two. Presence of such an interaction between aromatic molecules and alkali ions within the zeolite supercage has been inferred from neutron diffraction and NMR studies [25–28]. Cation dependent Norrish types I and II photochemistry of α,α-dialkylphenyl ketones in M^+X and M^+Y (Li, Na, K, Rb and Cs) zeolites is reported [29]. Smaller cations yield higher yield of α-cleavage products by binding strongly with the carbonyl chromophore, thereby impeding type II hydrogen abstraction. Though no clue to the binding interaction between the cation and the ketone is obtained from the absorption spectra, thermogravimetric analyses have indicated that the temperature required to desorb these ketones from LiX is much higher than from CsX. Therefore, it is presumed that there will be a stronger binding of the smaller cations with nitrogen. This stronger binding may lead to anchoring of the *trans*-2-SP onto the walls of the zeolites through the cations. It is also likely that, nitrogen atom of *trans*-2-SP interacts with the zeolite framework through hydrogen bonding, thereby facilitating dimerization.

An increase in cation size causes a decrease in the percentage of the dimer while the unimolecular reaction to give **4** is facilitated. It is reasonable to expect that an increase in



Scheme 2. Proposed mechanism of reaction of *trans*-2-SP inside acidic zeolites.

cation size, causes a subsequent decrease in the cage free volume. The binding interaction between *trans*-2-SP with the cations is also very weak as the increase in cation size increases their basicity. This puts severe restrictions on the packing of *trans*-2-SP in the parallel orientation inside the supercage, thus, causing a decrease in yield of the dimer.

For comparison irradiation as a hexane slurry of zeolite–*trans*-2-SP complexes (with a higher loading level of *trans*-2-SP) are also carried out with LiY and CsY zeolites as representative examples. The slurry irradiations are distinguished by reduced conversion, lower yield of dimer and increased yield of *cis*-isomer compared to solid irradiations and this is attributed to the inability to preorganize in the hexane slurry. It is also marked by the absence of unidentified products which are significant in solid irradiations. As the unidentified products are present in small amounts, no attempt is made to isolate and characterise them. It is relevant to recall that, in solid irradiations, in the absence of nitrogen atmosphere, contact charge transfer (CCT) complexes of olefins such as stilbene, with oxygen is likely [30] which undergo subsequent oxidation.

In addition, thermal reaction of *trans*-2-SP is also observed inside the cages of acidic zeolites like HY and MgY. Protonation of the olefinic double bond, followed by subsequent reactions (isomerization/cyclization/dimerization) leads to the observed products distribution. A plausible mechanism is presented in Scheme 2.

It is interesting to note that, in these acidic zeolites dimer formation is observed even without irradiation. However, irradiation improves the conversion to some extent, by increasing the polarity of *trans*-2-SP thereby facilitating H^+ abstraction, causing an increase in the yield of dimer whereas the amount of benzo[f]quinoline remains unchanged.

4. Conclusion

The present study demonstrates the efficiency and utility of zeolite cages as ‘microscopic reaction vessels’. With suitable choice of zeolites, it is possible to control the reactivity of *trans*-2-SP towards either isomerization, dimerization or cyclization. Loading levels and size of cations play significant roles in this regard.

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