

Effect of Co-adsorbed Water on Photodimerization and Photooxygenation of 4-Methoxystyrene Included in NaY

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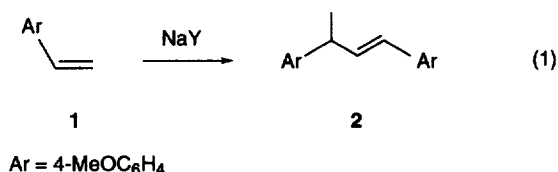
Abstract: Irradiation of 4-methoxystyrene (**1**) in zeolite NaY under vacuum, dry oxygen, and wet air yielded dimers and oxygenation products dependent on the atmosphere and co-adsorbed water. Head-to-head *cis*- and *trans*-cyclobutane dimers of **1** were produced at the isomer ratio of 91/9 under vacuum through excimer of **1** and 38/62 under wet air through cation radical of **1**, respectively. However, 4-methoxybenzaldehyde was a primary product under dry oxygen at the expense of production of the dimers (*clt* = 81/19). These results show significant differences in the photochemical behavior of **1** in solution and in NaY. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Dimerization; Oxygenation; Photochemistry; Zeolites

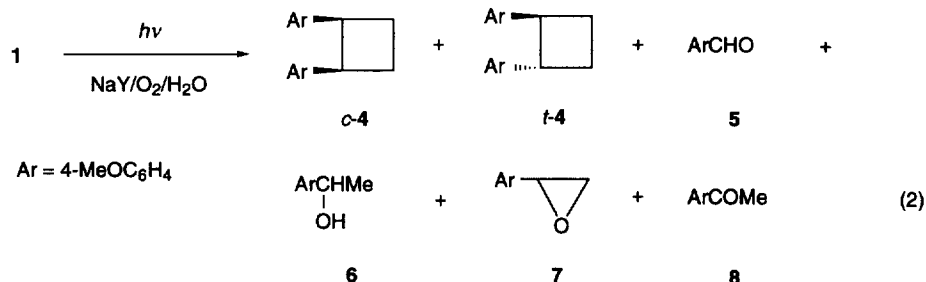
It is likely that zeolite cavities have considerable potential as new photochemical reaction vessels [1]. One of the recent trends in photochemical research on zeolite cavities focuses on the way in which the restricted spaces influence the regioselectivity [2] and stereoselectivity of products [3, 4], and the enhanced molecular interaction of guest molecules [5-7]. Another interesting feature is the way in which metal ions in the cavities affect the acceleration of the process of intersystem crossing [8] and the potential energy surface of guest molecules [9]. However, the fact that protonation and electron transfer reactions often occur without light at Brønsted and Lewis acid sites particularly in proton-exchanged zeolites [10-12] poses difficulties for photochemists. In order to determine the factors affecting the excited species generated in zeolites, it is essential in the first instance to distinguish between dark and photochemical reactions. We report here that co-adsorbed water plays an important role in the dimerization and oxygenation of 4-methoxystyrene (**1**) in both dark and photochemical reactions.

It has been found that when **1** is adsorbed into dehydrated NaY, an acyclic dimer **2** is predominantly produced through monomer and dimer carbocations of **1**, as shown in eq 1 [12]. In the case of CaY, in particular, the carbocations have been observed as very stable species by means of diffuse reflectance absorption spectra. Under our conditions, 9% of **1** was converted to give **2** and an unknown dimer **3** (**2/3** = 94/6; relative yield, 87%). However, irradiation of **1** included in NaY under vacuum using a 400-W high-pressure mercury lamp through a Pyrex filter at room temperature for 2h yielded head-to-head *cis*- (**c-4**) and *trans*-

cyclobutane dimers (*t*-4) of **1** as primary products (conversion of **1**, 28%; **4**: 30%, *c/t* = 91/9); in addition, **2** isomerized to **3** (**2/3** = 60/40) [13]. Similar irradiation of **1** in NaY under dry oxygen gave 4-methoxybenzaldehyde (**5**, 31%) as the major product at the expense of production of **4** (3%, *c/t* = 81/19), together with 1-(4-methoxyphenyl)ethanol (**6**, 6%), 4-methoxystyrene oxide (**7**, 8%), and 4-methoxyacetophenone (**8**, <1%) as by-products as shown in eq 2 and Table 1.



One of the present authors has reported that selective irradiation of the contact charge-transfer (CCT) complex comprising **1** and the oxygen molecule (O₂) in MeCN gives *t*-4, through electron transfer reaction, as the predominant dimer (24%, *c/t* = 4/96) as well as the formation of **5** (68%) [14]. It should be noted that the selectivity for the formation of *c*- and *t*-4 in NaY differs significantly from that in MeCN. Thus, as shown in Scheme 1, it is likely that the predominant formation of *c*-4 in NaY in the absence or presence of O₂ under dry conditions occurs through the excimer of **1** and that the cation radical of **1** (1⁺) generated by excitation of the CCT complex in NaY reacts selectively with superoxide anion radical (O₂^{•-}), before diffusion of 1⁺ into zeolite cavities, to produce the dioxetane of **1**, which readily decomposes to **5** as in the case of stilbenes [7].



When the NaY samples containing **1** were left in air in the dark for 2h, the sample weight increased approximately 1.2 times by adsorbing moisture. Surprisingly, under the conditions, a high proportion of **1** was consumed (63%) to yield alcohol **6** (27%) and dimers **2** and **3** (45% and 5%, respectively) together with **5** (7%) and **7** (16%), without producing cyclobutane dimers **4**. Irradiation of the 1/NaY sample in the presence of co-adsorbed water under air for 20 min gave **4** (4%, *c/t* = 38/62) as significant photoproducts. Further irradiation of the zeolite sample caused increase in the yield of **4** (9%) and decrease in the yield of **2** (34%), while the conversion of **1** did not change. Moreover, it was found that the ratio of *c/t* changed slightly to become 30/70.

The mechanism for the formation of *t*-4 is explained as shown in Scheme 2. In the presence of co-adsorbed water, protonation of **1** readily occurs without light to give monomer carbocation A. Addition of **1** to A yields dimers **2** and **3** as the major products [12], probably following polymerization. However, irradiation of the dimers produced in NaY in the presence of co-adsorbed water causes selective decomposition of **2**, to give **1** and the monomer

Table 1

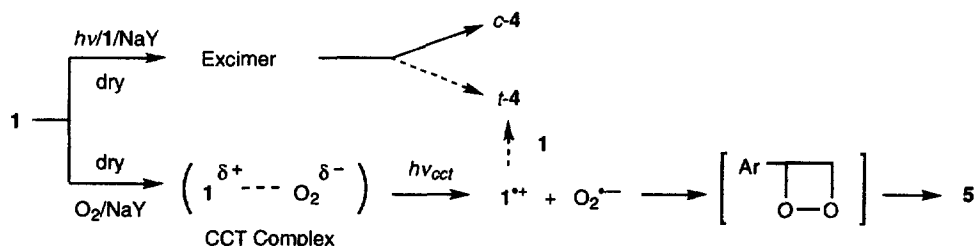
Distribution of products obtained by irradiation of 4-methoxystyrene (**1**) adsorbed within zeolite NaY

Condition	Conv ^a /%	Total yield ^b /%	Distribution of products/%						Isomer ratio	
			2 and 3	4	5	6	7	8	c-4/t-4	2/3
Dark/dry ^c	9	85	87	-	4	4	5	Trace	-	94/6
Vacuum/2h ^d	28	37	65	30	2	2	1	Trace	91/9	60/40
O ₂ /dry/2h ^e	22	64	52	3	31	6	8	<1	81/19	81/19
Dark/wet/2h ^f	63	13	50	-	7	27	16	<1	-	90/10
Air/wet/20 min ^g	92	12	48	4	10	26	12	<1	38/62	83/17
Air/wet/1h ^h	93	12	44	9	13	25	9	<1	30/70	78/22

^a Conversion of **1**.^b Total yield of products.^c Sample dried under vacuum immediately after preparation.^d Irradiated under vacuum for 2h with a high-pressure mercury lamp.^e Irradiated under dry oxygen for 2h with a high-pressure mercury lamp.^f Sample kept under atmosphere in dark for 2h. The conversion depended on the amount of moisture.^g Irradiated under air in the presence of co-adsorbed water for 20 min with a high-pressure mercury lamp.^h Irradiated under air in the presence of co-adsorbed water for 1h with a high-pressure mercury lamp.

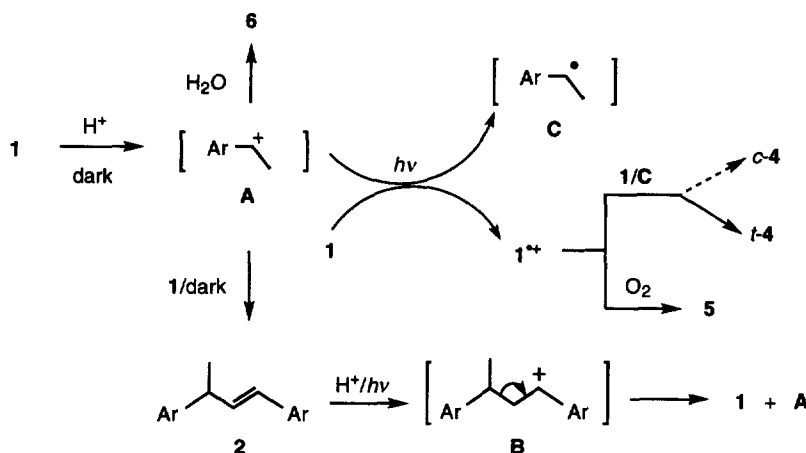
carbocation **A** through dimer carbocation **B**; in contrast, **3** was stable under the conditions. Subsequently, photoinduced electron transfer (PET) from **1** to **A** generates **1⁺⁺** and free radical **C**, as in the case of PET reaction of 1,1-bis(4-methoxyphenyl)ethene and its carbocation in solution [15]. Generated **1⁺⁺** reacts with **1** to give its dimer cation radical. Return electron transfer from radical **C** to the dimer cation radical finally produces *t*-**4** selectively, reproducing carbocation **A**. In addition, it is probable that oxygenation of **1⁺⁺** by O₂ increases the yield of **5**. The difference in the photoproduct distribution between NaY and MeCN indicates that the reaction processes shown in Schemes 1 and 2 compete in NaY. In fact, the control experiment showed that H₂O (0.5 M) did not influence the dimerization and oxygenation of **1** through PET reaction of its CCT complex with O₂ in MeCN; namely, no alcohol **4** was produced under the conditions.

It has been found, by means of absorption and fluorescence spectroscopy, that co-adsorbed water controls the aggregation of dyes such as thionin and methylene blue in NaY [16] and also prompts displacement of phenanthrene and anthracene from the internal to the external surface of the zeolite [17, 18]. Thus far, however, only one example of the effect of hydration on photoproducts has been found, i.e. that of the photolysis of dibenzylketone in X zeolites

Scheme 1: Photodimerization and oxygenation of **1** in NaY under dry conditions.

reported by Ramamurthy et al. [1]. The present results greatly emphasize that the effect of hydration is an important factor controlling the photochemical behavior of guest molecules included in zeolite cavities.

We have already noticed that co-adsorbed water also accelerates dark reactions in NaY for 1-arylcyclopentenes and 1-arylcyclohexenes (Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄). Metal-ion exchanged zeolites promise unique opportunities for photochemical catalysis because they have less active Brønsted and Lewis acid sites compared to proton-exchanged zeolites. However, before photochemists can exploit these characteristics further, it is essential to confirm if there is a hydration effect on the photospectroscopic and photochemical behavior of guest molecules within the zeolites.



Scheme 2: Photodimerization and oxygenation of 1 in NaY in the presence of co-adsorbed water.

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