

Modification of the Photochemical Reactivity of Cyclic Ethylene Acetal of α -Bromopropiophenone by Adsorption within Zeolites. A Combined Contribution of Lewis Acidity and Cage Effect in the Formation of a 2-Phenylpropanoate via 1,2-Phenyl Shift

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Introduction

Irradiation of organic substrates adsorbed on solid surfaces constitutes a general methodology to control the chemical reactivity of excited states and divert the pathways undergone by the reaction intermediates.¹ Zeolites are useful host materials for this purpose since they fulfill important requirements such as complete photochemical stability, wide range of chemical compositions, and a large diversity of crystalline structures.² Interestingly, depending on the guest molecular size, the internal channels and cavities of these microporous aluminosilicates can be accessible to organic molecules. In these cases, the crystalline framework acts as a vessel of microscopic walls ("microscopic reactor"),³ and the course of the photochemical reaction can be altered compared with that observed in solution due to the steric constraints imposed to the reacting species ("cage effect")⁴ and by interaction of the guest molecules with the charge-compensating cations present inside the zeolite internal voids.⁵

In the present work, we report that the photochemical reactivity of the cyclic acetal of 2-bromopropiophenone (1) can be modified by performing its photolysis adsorbed within large pore zeolites. Moreover, evidences are presented showing that the 1,2-phenyl shift pathway leading to 2-phenylpropanoate 8 arises from the combined contribution of the cage effect and Lewis acid interaction of 1 with the metal ion.

Results and Discussion

The results obtained in the photolysis of cyclic acetal 1 under the different conditions studied are contained in Table I. It can be seen there that when the irradiation of 1 was carried out in cyclohexane solution a complex reaction mixture was obtained. Besides the acetals 1, 5, and 9, and their corresponding ketones 2, 6, and 10, cyclohexyl benzoate (3) and the 2-phenylpropanoate 8 were formed, together with small amounts of cyclohexanol and cyclohexanone.

A likely rationalization to account for this result is outlined in Scheme I. Thus, after light absorption 1*

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Table I. Photolysis of Acetal 1 in Organic Solution and Adsorbed on Solid Supports

| conditions ^a | mass balance (%) ^b | conversion, % | products (selectivity, %) |
|---|-------------------------------|---------------|---|
| I, c-C ₆ H ₁₂ | 95 | 46 | 3 ^c (25), 5 ^d (6), 6 (22), 8 ^e (24), 9 ^e (13), 10 ^f (10) |
| I, DMSO | 78 | 54 | 8 (40), 9 (60) |
| II, NaX | 72 | 52 | 8 (38), 9 (62) |
| II, HY ^g | 93 | 72 | 6 (8), 8 (17), 10 (75) |
| II, ZnNaX | 70 | 100 | 8 (100) |
| II, ZnNaY | 96 | 98 | 3 (4), 6 (7), 8 (87), 10 (1) |
| II, Zn ₂ Cl ₂ ·SiO ₂ | 87 | 66 | 8 (54), 9 (46) |

^a I: solution, solvent; II: slurry of c-C₆H₁₂, host. ^b Recovered material (Σ mol)/starting material (mol) \times 100. ^{c-f} References 14-17. ^g Acetal hydrolysis of 1 to 2 occurs to some extent even in the dark.

undergoes an homolytic C-Br bond breaking to give 4[•] and a Br atom (i). Hydrogen abstraction from the solvent (iv) would explain the formation of acetal 5 and cyclohexyl radicals which by combination with molecular oxygen would afford cyclohexanol and cyclohexanone. Alternatively, the primary radical pair can undergo single electron transfer affording a bromide anion and the carbocation 4⁺ (vi), from which the unsaturated acetal 9 and the 1,2-phenyl migration product 8 would result. Related precedents for the occurrence of homolytic bond breaking followed by electron transfer are well documented in the photochemistry of alkyl halides.^{6,7} Acid catalysis by the photochemically generated hydrobromic acid can explain the occurrence of some hydrolysis of the acetals 1, 5, and 9, affording the corresponding propiophenones 2, 6, and 10.

In order to ascertain the origin of benzoate 3, which implies the C-C bond rupture of the lateral side chain, photolysis of 2-bromopropiophenone (2) was investigated. Under the same experimental conditions, 3 was formed in high yields together with propiophenone (6). This fact supports the assumption that 3 is a secondary product derived, at least in part, from the primary 2-bromopropiophenone (2).

By contrast, when complexes of 1 and NaX were submitted to photolysis a much simpler reaction mixture was obtained. In this case 1,2-phenyl migration and elimination of hydrogen bromide leading to 8 and 9 were the only processes observed.

A reasonable explanation to account for the absence of radical products is based on the inclusion of 1 within the voids of NaX. The cyclic ethylene acetal of α -bromopropiophenone (1) can reach the faujasite supercavities (12.4 Å, α cages) through 12-membered ring windows of 7.2 Å. The initial 4[•]/Br[•] radical pair entrapped in the faujasite supercavities undergoes a more efficient electron transfer, probably due to the steric limitations imposed to the diffusion. The local electrostatic fields experienced inside the NaX would favor this pathway.

Alternatively, other processes such as direct heterolytic bond rupture (ii) or a concerted bromide elimination and 1,2-phenyl migration (iii) from 1 in its excited state might also be feasible, specially if a strong complexation of 1 with the metal ion is enhancing the polarity of the C-Br bond.

In order to get experimental support to our proposal, photolysis of cyclic acetal 1 was carried out in DMSO. It

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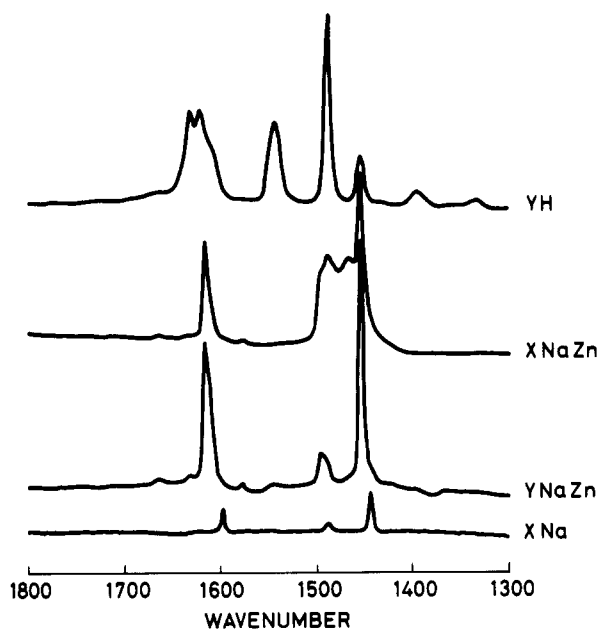


Figure 1. IR spectra of pyridine in NaX, XNaZn, YNaZn, and YH zeolites after adsorption at room temperature on dehydrated samples and subsequent evacuation at 523 K and 10^{-2} Torr for 1 h.

efficient in the ZnNaX sample due to the enhanced cage effect provided by the zeolite micropores.

In conclusion, the photochemical reactivity of cyclic ethylene acetal 1 is altered when this compound is adsorbed within the faujasite micropores. Thus, the homogeneous cyclohexane photolysis gives rise to products arising mostly from the radical pathways. By contrast, the photochemical pattern found when 1 is adsorbed within zeolites is better rationalized by assuming the intermediacy of carbenium ions 4^+ and 7^+ . In this case the unprecedented photochemical 1,2-phenyl migration to the 2-phenylpropanoate 8 is the most characteristic pathway. A cooperation between the cage effect due to the zeolite framework and the Lewis acid interaction with the charge-compensating cations present in the zeolite has been disclosed to be responsible for these results.

Experimental Section

Materials. Two samples of sodium faujasite in their X and Y form were obtained from Union Carbide (zeolites 13X and LZ52, respectively). They are called here NaX and NaY respectively. Both samples have the same structure (faujasite) and the most important difference lies in the chemical composition, i.e. the framework Si/Al ratio (which is 1.2 for NaX and 2.5 for NaY). When the countercations Na^+ were exchanged by protons in the Y zeolite, the sodium NaY form was converted into the acid HY form. This exchange was carried out in an

indirect way in order to avoid zeolite structure damages. Thus Na^+ was exchanged by NH_4^+ , producing a NH_4Y zeolite which upon calcination produced the decomposition of NH_4^+ into NH_3 and H^+ , the proton remaining as countercation. Details on the preparation procedure are given elsewhere.¹³ When a part of the Na^+ in the NaX and NaY samples was exchanged by Zn^{2+} , ZnNaX and ZnNaY zeolites resulted. This exchange was carried out using a 1 M aqueous solution of $\text{Zn}(\text{NO}_3)_2$ in a solid to liquid ratio of 1:10 at 353 K for 2 h. Chemical analysis showed that the Zn^{2+} content of these samples were 19% (ZnNaX) and 12% (ZnNaY) w/w.

Impregnation of the ZnCl_2 on SiO_2 was performed by stirring at room temperature a solution of ZnCl_2 (0.5 g) in distilled water (15 mL) and SiO_2 (Broden) (1 g) for 2 h. Finally the water was removed under vacuum.

Cyclic ethylene acetal of α -bromopropiophenone¹⁴ was prepared by heating a mixture of α -bromopropiophenone (2 g), ethylene glycol (5 mL), and 4-toluenesulfonic acid (150 mg) in toluene (100 mL) using Dean-Stark equipment.

Irradiation Procedure. Adsorption was accomplished by stirring at room temperature for 2 h a suspension containing the acetal 1 (95 mg), cyclohexane (15 mL), and the corresponding zeolite (400 mg), previously dehydrated by thermal activation (423 K, 1 Torr, 2 h). The organic solution was separated by centrifugation and evaporated to dryness. The amount of 1 adsorbed (typically about 35 mg) was calculated by difference between the weight of the residue and the initial amount of 1. A volume of fresh cyclohexane (5 mL) was added to the zeolite and this new suspension was irradiated through quartz for 2 h at room temperature, under continuous magnetic stirring, using a 125-W medium pressure mercury lamp. Only trace amounts of 1 or reaction products could be detected in the liquid phase, but fairly good mass balances (see Table I) were obtained after continuous solid-liquid extraction of the zeolite using CH_2Cl_2 as solvent. Analyses of the reaction mixtures were performed by GC (25-m capillary column of crosslinked 5% phenylmethylsilicone), GC-MS (HP 5988A), and GC-FTIR (HP 5965A). The estimated analytical error is ca. 5% of the stated values. Characterization of cyclohexyl benzoate 3 and phenylpropanoate 8 was carried out by comparison with authentic samples prepared by esterification of benzoic acid with cyclohexanol using *N,N*-dicyclohexylcarbodiimide as condensing agent and by thermal transposition of the acetal,¹⁴ respectively. The solvents used throughout this work were of the commercially available highest purity. Control experiments showed that except for the HY sample (see footnote g in the Table I) no reaction takes place in the dark.

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