

Photolysis of Benzyl Chloride included in NaY Zeolite: Product Study Evidence for the Implication of Benzyl Cation

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The photochemical behaviour of benzyl chloride is strongly altered by inclusion within the zeolite micropores; evidence is presented for the existence of an ionic pathway in zeolites which is not present when the photochemical reaction occurs in liquid media.

In the last decade a number of articles have been published showing how zeolites can be used as 'microscopic reactors' to alter the photophysical and photochemical behaviour of organic molecules hosted within the channels and cavities of these microporous solids,¹ which are photostable and provide a wide variety of chemical and topological environments.² The photochemistry of benzyl chloride (BC) has also attracted considerable attention, as a model for the operation of radical vs. ionic pathways, depending upon the reaction conditions.³

Benzyl radicals, generated by photolysis of dibenzyl ketones, have been extensively used as probes to explore the internal surfaces of medium and large pore zeolites.⁴ It has been found that the percentage of geminate recombination can be strongly dependent on the zeolite pore size, charge compensating cations and reaction conditions. In particular, it has been reported that photolysis of dibenzyl ketone adsorbed on NaY gives rise to diphenylethane as the major product (83%).⁵

Here we report that the strong electrostatic fields experienced within the zeolite cavities can also enhance ionic pathways when chlorine is associated with the benzyl radical.

A solution (15 ml) of BC (40–80 mg) was poured onto NaY zeolites (Union Carbide LZ-Y52, 1.00 g) previously activated

by calcination at 773 K for 12 h. The suspension was stirred for 1 h and centrifuged. The amount of BC included was calculated by difference between the initial and the recovered weights. Direct photolyses were carried out by resuspending the BC hosted in NaY, in fresh solvent (5 ml), with the quartz-filtered light of a 250 W medium pressure mercury lamp, for 1 h. Analysis by GC established that only traces of organic compounds were present in the liquid phase. At the end of the irradiation, the solid was thoroughly extracted with CH₂Cl₂ and the mixture analysed by GC-MS and GC-FTIR. As a general rule, authentic samples were prepared by alternative synthesis for comparison.

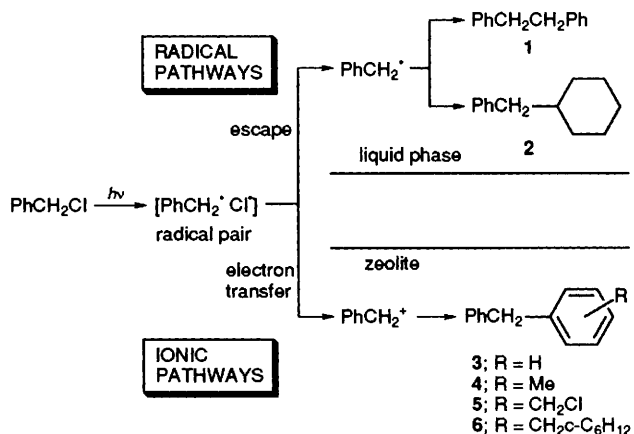
The results achieved in the homogeneous, and slurry photolysis of benzyl chloride adsorbed within NaY zeolite at three different loading ratios are summarized in Table 1. Control experiments showed that none of the products considered in Table 1 are formed in the dark.

It can be seen in Table 1 that the photolysis of BC in cyclohexane slurries led to the formation of diarylmethanes 4–6 not observed under the same conditions in homogeneous solution (runs 1, 3–5). The formation of products 4–6 is indicative of aromatic alkylation, which is a bimolecular reaction with respect to BC; by contrast, radical coupling

Table 1 Photolysis of benzyl chloride in homogeneous solution and adsorbed on NaY zeolite at different loading ratios

Run	Conditions ^a	Solvent	Conversion (%)	Mass balance ^b (%)	Products (selectivity %) ^c	Radical coupling: Ar alkylation ^d
1	A, 6.3 × 10 ⁻²	c-C ₆ H ₁₂	>95	73	1 (11), 2 (89)	100:0
2	A, 6.3 × 10 ⁻²	PhH	35	91	1 (87), 3 (13)	87:13
3 ^e	B, 80:400	c-C ₆ H ₁₂	90	88	2 (5), 4 (20), 5 (71), 6 (4)	23:77
4 ^e	B, 60:400	c-C ₆ H ₁₂	79	76	2 (35), 4 (31), 6 (34)	60:40
5 ^e	B, 40:400	c-C ₆ H ₁₂	35	93	2 (54), 5 (6), 6 (30)	69:31
6	B, 80:400	PhH	75	85	1 (50), 3 (50)	50:50

^a A: homogeneous solution, initial BC concentration (mol dm⁻³); B: slurry (5 ml solvent), amount of BC to NaY (mg:mg). ^b Includes recovered BC. The rest was formed by polymers and oligomers (mainly polybenzylated and polyhalogenated products); it may also include undetectable amounts of toluene. Part of the starting BC was consumed in a thermal reaction induced by NaY, leading to dibenzyl ether. ^c Solvent derived products not possessing a benzylic moiety (cyclohexene, cyclohexyl chloride, cyclohexylcyclohexane, biphenyl, etc.) are not considered. ^d Calculated as (1 + 2 + 4 + 6):(3 + 4 + 5 + 6) and normalized to 100. ^e Cyclohexyltoluenes were also observed in the reaction mixture.



Scheme 1 Photochemistry of benzyl chloride in the liquid phase and within NaY zeolite

leading to **2** is unimolecular with respect to BC. This explains why the ratio between both processes strongly depends on the zeolite loading, bimolecular processes being favoured at higher BC-to-NaY ratios.

Likewise, photolysis of BC in benzene solution gave rise to the formation of some aromatic alkylation product **3**, but adsorption within NaY zeolite increased dramatically the selectivity of diphenylmethane formation (runs **2** and **6**).

The results observed in the photolysis of BC adsorbed within NaY can be rationalized assuming that, due to the chemical nature of the chlorine atom, which accompanies the

benzyl radical after light absorption and homolytic C–Cl bond breaking, the cage effect and the electrostatic fields provided by the zeolite microenvironment favour a subsequent single electron transfer (Scheme 1).

In conclusion, in the present communication we have shown that the photochemistry of BC is strongly altered by inclusion within the zeolite micropores, the differences being rationalizable assuming the intermediacy of the benzyl cation.

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References

- V. Ramamurthy, in *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, Verlag Chemie, New York, 1991, ch. 10, pp. 429–493.
- Introduction to Zeolite Science and Practice*, eds. H. van Bekkum, E. M. Flanigen and J. C. Jansen, Elsevier, Amsterdam, 1991; *Preparative Chemistry Using Support Reagents*, ed. P. Laszlo, Academic Press, New York, 1987; *Solid Supports and Catalysts in Organic Synthesis*, ed. K. Smith, Ellis Horwood, Chichester, 1992; W. Hölderich, M. Hesse and F. Näumann, *Angew Chem., Int. Ed. Engl.*, 1988, **27**, 226.
- S. J. Cristol and B. E. Greenwald, *Tetrahedron Lett.*, 1976, 2105; S. J. Cristol and T. H. Brindel, *J. Am. Chem. Soc.*, 1981, **103**, 7287; D. C. Appleton, B. Brocklehurst, J. McKenna, J. M. McKenna, M. J. Smith, P. S. Taylor, S. Thackeray and A. R. Walley, *J. Chem. Soc., Chem. Commun.*, 1977, 108.
- N. J. Turro and M. A. Garcia-Garibay, in *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, Verlag Chemie, New York, 1991, ch. 1, pp. 1–38.
- N. J. Turro and P. Wan, *J. Am. Chem. Soc.*, 1985, **107**, 678.