

Photo-Fries Rearrangements of 1-Naphthyl Esters in Cation-Exchanged Zeolite Y and Polyethylene Media

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Using the photo-Fries rearrangements of three 1-naphthyl phenylacrylates (**1–3**; Scheme 1), we demonstrate here that limiting the constraining space of a reaction cavity in an organized medium^{1,2} can be less important than wall–guest interactions in determining the selectivity of guest reactions. Reaction cavities of the media employed, cation-exchanged Y zeolites,³ and a high-density polyethylene film of 71% crystallinity⁴ possess very different properties.

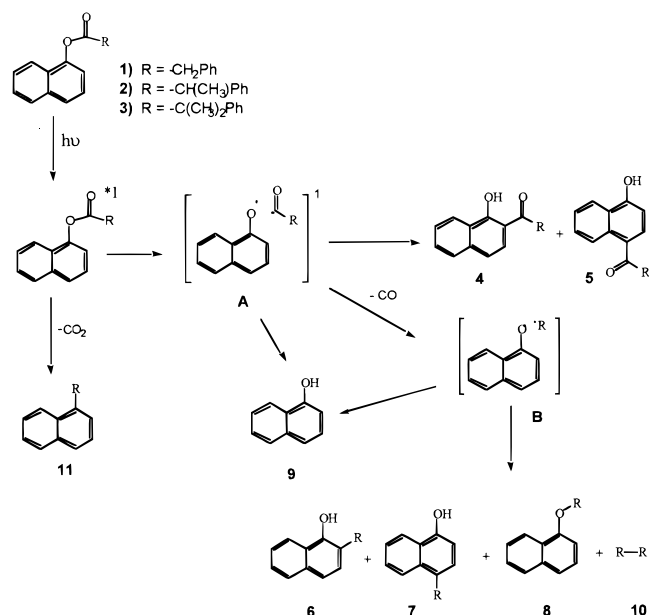
The cavity “walls”² of zeolites are not “passive”. Cations help anchor reactants, intermediates, and products to the surfaces. In addition, the walls are very “hard”, so that the shapes and volumes of the cavities do not change as guest molecules react. The cavities of Y zeolites (supercages of ~12 Å diameter²) are much larger than necessary to accommodate a molecule of **1–3** or their rearrangement photoproducts. Supercages are connected *directly* to each other by 7.4 Å diameter windows; there are no constricted “tunnels” into which an ester **1–3** (or their radical fragments; Scheme 1) can be placed in their entirety.

Cavities of polyethylene are less well-defined in size and shape.⁵ Their free volumes are smaller than the van der Waals volumes of **1–3**.⁶ Although the cavity walls of polyethylene are “passive” and “softer” than those of zeolites, they must exert more pressure on guest molecules during reactions. The correspondence between the relaxation times of the polyethylene chains constituting the walls and the lifetimes of the intermediates in the photo-Fries processes determines which products are formed.

Both zeolites and polyethylenes can exert significant control over the courses of photo-Fries reactions, *but for apparently very different reasons*. Irradiation of 2-naphthyl myristate in a polyethylene film yields 6-myristoyl-2-naphthol and mostly 3-myristoyl-2-naphthol, a product *not* observed in solution;⁷ *none* of the major photoproduct from solutions, 1-myristoyl-2-naphthol, was detected. It was argued that this radical pair **A** (like in Scheme 1) is held in a cavity shaped like the starting ester and whose walls relax more slowly than the radicals recombine. The preferred solution product is too different in shape from the starting ester to be formed.

Irradiation of 1-naphthyl acetate or 1-naphthyl benzoate within alkali metal cation-exchanged X and Y zeolites gives a single photo-Fries photoproduct, 2-acyl-1-naphthol.⁸ In hexane solutions,

Scheme 1



the 2- and 4-isomers are formed in comparable yields. Selectivity in the zeolites was suggested to result from restrictions imposed on the naphthoxy and acyl radicals by cations along the cavity walls.⁸ In support of this, acetyl radicals (from 1-naphthyl acetate) live for >10⁻⁵ s at room temperature within Na Y!⁹ The excellent yields of 2-acetyl-1-naphthol from 1-naphthyl acetate and the long radical lifetimes imply that the radical pairs **A** (R = methyl) are held tightly in place by cations before rejoining; they have the time and space, *but not the mobility*, to undergo other rearrangements.

The absence of products from direct irradiations of **1–3** within heavy-cation exchanged zeolites¹⁰ and our inability to sensitize the rearrangements of **1** with benzophenone in hexane are consistent with excited singlet state reactions.¹¹ Homolytic cleavage¹² gives geminate radical pair **A**. It is followed by in-cage recombination (**4** and **5**) or cage escape (**9** and/or **10**). Fast rates of phenylacetyl decarbonylation (*vide infra*) allow some radical pairs **A** from **1–3** to form radical pairs **B**, the source of **6–8** (Scheme 1).

When **1–3** were irradiated in hexane to ≤30% conversion, the 8 photoproducts in Scheme 1 were detected (Table 1). The photoproduct distributions from polyethylene (Table 1)^{13a} or a Y zeolite (Table 2)^{13b} are drastically different from those in solution. Cage-escape products are absent in both constraining media. The

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(12) Decarboxylation, yielding **11**, occurs to a small extent, also.

(13) (a) Cleaned polyethylene films were immersed in chloroform solutions of the esters for periods adequate to obtain the desired concentrations. They were rubbed gently with a tissue soaked in hexane, dried under a stream of nitrogen, irradiated (>300 nm; N₂ atmosphere), and extracted exhaustively. Photoproduct ratios were constant to 30% conversion. Mass balances were >90%. (b) Typically, an activated zeolite (300 mg) and 0.01 mol of ester in hexane were stirred for a protracted period, and the powder was washed with hexane and dried under reduced pressure (~10⁻⁴ Torr). The loading level is one ester molecule per 13 supercages. The solid was slurried in hexane and irradiated (>300 nm). Absence of reactants in the hexane layer was established by GC analyses and UV absorption spectra. Products were extracted with 5% water in THF. Mass balances were 85–90%. All analyses were by GC.

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Table 1. Relative Yields of Photoproducts from Irradiations of **1–3** in Hexane and Polyethylene Films at Room Temperature under N₂

ester	medium ^a	4	5	6	7	8	9	10	11
1	hexane	43	15	8.9	11	1.7	14	4.6	1.8
	PE	88	5.8	0.9	1.3	0	2.4	0	1.2
2	hexane	44	13	8.4	18	3.6	6.1	6.2	0.7
	PE	79	7.0	1.1	5.0	2.9	3.7	0	1.3
3	hexane	28	15	9.0	14	0	13	15	6.0

^a Concentrations were 3–7 mmol/kg in polyethylene (PE) and 2 mM in hexane.

Table 2. Relative Yields of **4** from Irradiations of **1–3** in Cation-Exchanged Y Zeolites

medium	ester			medium	ester		
	1 ^a	2 ^a	3		1 ^a	2 ^a	3
LiY	97	>99	>99	RbY	92	95	<i>b</i>
NaY	97	>99	>99	CsY	<i>c</i>	87	<i>b</i>
KY	96	93	>99	TIY	<i>b</i>	<i>b</i>	<i>b</i>

^a The remainder, **9**, is from a parallel dark reaction. ^b No loss of **1–3** detected after prolonged irradiation. ^c Only ~2% of **9** detected. CsY is known to be very basic.²³

selectivity and absence of decarbonylation products in the zeolites is remarkable, and reduction in the number of products from eight to one is rare, if not unprecedented.

Photorearrangements were very rapid in the Li⁺, Na⁺, and K⁺ Y zeolites, sluggish within the Rb⁺, and not observable in the Cs⁺ and TI⁺. Furthermore, the fluorescence intensity decreased at the expense of phosphorescence emission as the cations became heavier (Figure 1).¹⁰

Despite their large volume, zeolite supercages must limit drastically radical-pair motions. Although selective formation of **4** was expected,⁸ the lack of decarbonylation products **6–8** was not: the rates of decarbonylation of the phenylacetyl radicals from **1–3**^{14,15} are >10⁷ times that of acetyl.¹⁶ Rearrangement of radical pair **A** to **4** is apparently no faster within a zeolite than in solution,⁹ but decarbonylation and formation of the secondary radical pair **B** still do not occur!¹⁷ The large dimensions of the supercages and the windows joining them make spatial factors unimportant. However, cation binding to acyl radicals is expected to give them some cationic character: RC[•]=O M⁺ ↔ RC[•]=O^{δ+}...M^{δ+}.⁹ Such

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(17) The rate of decarbonylation of the phenylacetyl radical in methanol is ca. 3× slower than in alkane media.¹⁵ Decarbonylation in the "super polar" environments of zeolite supercages¹⁵ must be *much* slower than in hydrocarbon solution. (a) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *Photochem. Photobiol.* **1992**, *56*, 297. (b) Iu, K. K.; Thomas, J. K. *Langmuir* **1990**, *6*, 471.

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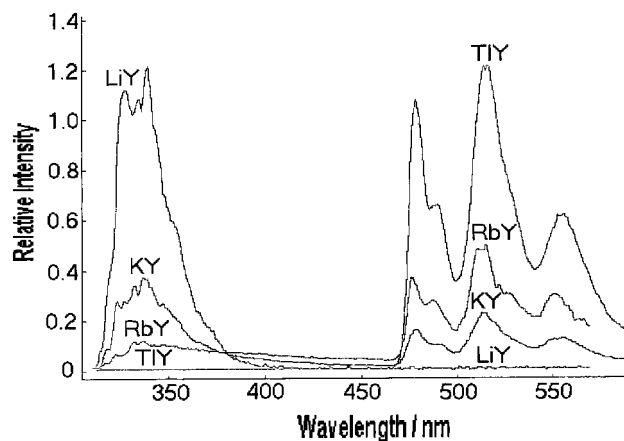
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**Figure 1.** Emission spectra of **3** (not normalized) in LiY, KY, RbY, and TIY. Compare relative intensities of fluorescence and phosphorescence within one spectrum only.

a species is unlikely to lose CO readily. Indeed, photolyses of dibenzyl ketones and phenyl phenylacetates also yield much more rearranged than decarbonylated products within M⁺ Y and M⁺ X zeolites^{18,19} or a Nafion membrane.²⁰

Results for **1** or **2** in hexane and polyethylene indicate that reaction cavities of the latter limit greatly the ability of radical pair **A** to move during its lifetime. The absence of **10** in polyethylene demonstrates that there are no out-of-cage recombinations. Since **6–8** are formed and acyl decarbonylation rates do not appear to be sensitive to solvent viscosity,^{15,21} the lifetime of radical pair **A** in polyethylene must be ≤10⁻⁶ s (vide ante). In acetonitrile, the lifetime of a naphthoxy and acetyl singlet radical pair is <1 ns.^{11a} Comparison between the **4/5** ratios (>10) and the **6/7** ratios (<1) in polyethylene suggests that radical pair **B** is able to "equilibrate" spatially before yielding products although **A** is not.

The cavity walls of polyethylene are much harder than those of hexane and much softer than those of zeolites. From NMR studies, the rotational correlation time of a guest of comparable size to the naphthyl esters is estimated to be ≤50 ns in polyethylene.²² This is the same time scale as reaction by radical pair **A** based on the small relative yields of decarbonylated products.

Thus, we believe that the more limited control exerted by polyethylene over the reactivity of the radical pairs from **1–3** is due primarily to wall stiffness and limitations on the available space within a cavity. The passive nature of the walls does not allow them to orient radical pair partners via the strong interactions available in cation-exchanged zeolites. The fact that the space in a zeolite supercage is much larger than the van der Waals volume of a naphthyl ester is of secondary importance in determining medium constraints when there are hard walls with active sites to act as templates for the radical pairs. In topological and energetic terms, we believe that surface interactions between radicals and the walls of a zeolite cavity are largely "two-dimensional" and attractive while escape by radical pairs from polyethylene cavities may be inhibited by "three-dimensional" pressures exerted by the surrounding chains in largely repulsive interactions. No single explanation can describe how constraints by different types of organized media influence the dynamics of guest molecules.²

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