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Heavy cation effect on intersystem crossing between triplet and singlet phenylacyl and benzyl geminate radical pairs within zeolites

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Abstract

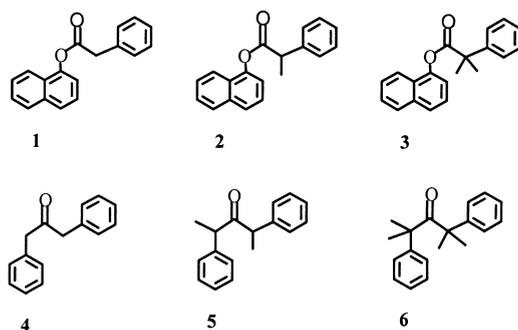
The difference in product selectivity observed between dibenzyl ketones and naphthyl esters in zeolites is due to the difference in spin of the radical pairs formed from these precursors. Heavy cations present in zeolites can enhance intersystem crossing between triplet and singlet geminate radical pairs. © 2000 Elsevier Science Ltd. All rights reserved.

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We showed recently that 1-naphthyl acetate and 1-naphthyl benzoate when irradiated within an alkali metal cation exchanged X and Y zeolites gave selectively a single isomer (2-substituted naphthol) as a result of photo-Fries rearrangement.¹ In solution both 2- and 4-substituted naphthols are formed. Selectivity was attributed to restriction imposed on the naphthoxy and acyl (benzoyl) radicals, the primary intermediates, by the cations present within a zeolite. Evidence in favor of the presence of an interaction between a Na⁺ ion and the acetoxy radical within NaY has since been provided by Vasenkov and Frei through FT-IR spectroscopy.² These authors also reported that the acetyl radicals have a lifetime of several microseconds at room temperature within a zeolite. Such a long lifetime implies that the two 'reactive fragments', namely naphthoxy and acetyl radicals, are held in place by cations for a long time before they combine selectively at the two position to yield 2-acetoxy naphthol. This suggests that, provided an opportunity arises before the rearrangement, the two radical fragments could undergo other reactions.

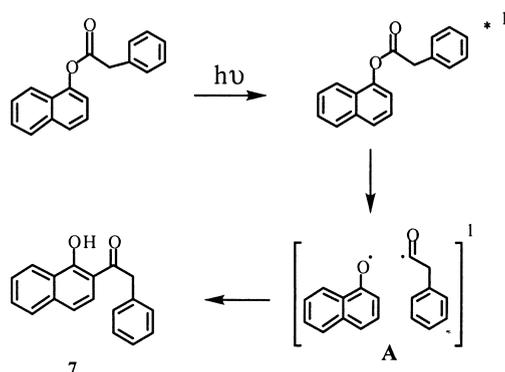
To test the above hypothesis we investigated the photobehavior of three 1-naphthyl benzyl esters **1–3** within zeolites (Scheme 1).³ In solution these three esters undergo facile decarbonylation after an initial photocleavage affording a wider range of rearrangement and coupling products

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Scheme 1.

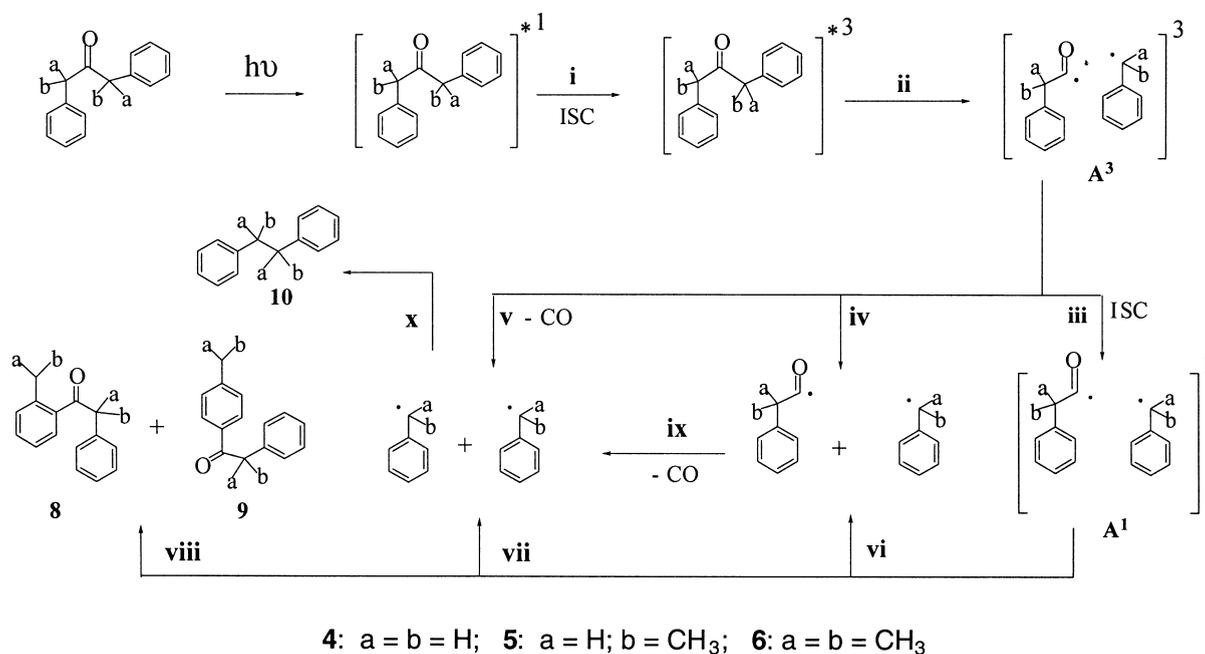
(eight products in total). Remarkably, when irradiation of **1–3** included within MY zeolites was conducted, a single product **7**, the 2-substituted naphthol (Scheme 2) was obtained. Within zeolites, the phenylacetyl radical generated from naphthyl esters **1–3** did not undergo decarbonylation. Most likely this is the result of singlet radical pairs recombining faster than the decarbonylation. To test this possibility, we have examined the photochemical behavior of dibenzyl ketones **4–6** (Scheme 1) included in alkali cation and Pb^{2+} exchanged Y zeolites. Although both naphthyl ester and dibenzyl ketone (DBK) generate phenylacetyl radical, the spin states of the primary radical pairs differ; the former produces the geminate radical pairs in the singlet (Scheme 2) while the latter generates it in the triplet spin state (Scheme 3). As expected, the products from the two systems are different and remarkably the cations present in a Y zeolite control the product distribution by influencing intersystem crossing (ISC) between the triplet and singlet radical pairs in the case of DBKs (A^3 and A^1 in Scheme 3).



Scheme 2.

A previously reported experimental procedure was adopted to include and irradiate the reactants and to extract and analyze the photoproducts.^{1–3} The product distribution obtained in alkali cation exchanged zeolites and in PbY are provided in Table 1.

The well-established mechanistic Scheme 3⁴ is utilized to rationalize the results presented in Table 1. Accordingly, DBK in its triplet excited state undergoes α -cleavage to yield the primary triplet radical pairs A^3 . In the absence of geminate recombination the radical pair diffuses apart (path iv), decarbonylates, and couples to yield dibenzyl ketone **10**. An ideal situation for this



Scheme 3.

would be an isotropic solution. However, in a medium such as zeolite where diffusional separation (path iv) has restraints, the primary radical pair A^3 may undergo ISC (path iii) to the singlet state A^1 from where rearrangement to products **8** and **9** could occur. A fast ISC from A^3 to A^1 , long lifetime of the geminate radical pair and slow decarbonylation rate are important for the formation of **8** and **9**.

Examination of Table 1 reveals that phenylacyl radicals derived from DBKs **4** and **5** yield both diphenyl alkane **10** (decarbonylated product) and the rearranged products **8** and **9**. Most interestingly, the yields of the decarbonylated and rearranged products depend on the cation present in the supercages of Y zeolite. Variations in the yield of the rearranged products from DBK **4** within MX zeolites have been rationalized earlier on the basis of 'size effect' ('lebensraum effect').⁵ It is unlikely, however, to play a role in Y zeolites which contain a lesser number of cations. While supercages of both X and Y zeolites contain four type II cations, the absence of type III cations in the latter provides room for the guest DBKs (Fig. 1).⁶

We believe the results presented in Table 1 reflect the ability of the cation to induce spin-orbit coupling between the A^3 and A^1 radical pairs. If the free volume within a cage (cation 'size effect') alone is important one would have expected the most and the least amounts of rearranged products from the bulkier DBK **6** and the smaller DBK **4**, respectively. This is not the case. The combined yields of rearranged products **8** and **9** from DBK **4** show a direct relationship with the spin-orbit coupling parameters of the cations (Table 1). The cation size alone cannot account for the difference in the combined yield of **8** and **9** between KY and TIY. Both cations differing in their spin-orbit coupling parameters by two orders of magnitude are of the same size. Owing to the doubly charged nature of the cation, the supercages in PbY are expected to have more free volume than any other zeolite shown in Table 1 (there should only be two instead of four type II cations). In spite of the presence of a large free volume within the supercages, highest yields of **8**

Table 1
Product distribution upon irradiation of dibenzylketones **4-6** within cation exchanged zeolites

Zeolite	Ionic radius of cation Å ^a	Spin-orbit coupling constants ^b for the corresponding atom ζ cm ⁻¹	DBK 4 ^{c,d,e}			DBK 5 ^{c,d,e}			DBK 6 ^{c,d,e}
			8	9	10	8	9	10	10
LiY	0.86	0.23	1	4	95	-	-	99	99
NaY	1.12	11.5	2	8	90	-	-	99	99
KY	1.44	38	7	17	76	-	-	99	99
RbY	1.58	160	3	18	79	-	9	91	99
CsY	1.84	370	13	54	33	2	14	84	99
TlY	1.40	3410	57	22	21	18	7	75	99
PbY	1.33	5089	46	43	11	24	13	63	99

- Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, V ed., Wiley-Interscience: New York, 1988, p. 124 and 209.
- The number for the ion might vary but the trend is expected to remain the same. Numbers taken from Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, Marcell Dekker: New York, 1993, pp. 338-341.
- For structures of reactant and products see Scheme 3. The structures of **8**, **9** and **10** contain additional methyl groups when they are derived from **5** and **6**.
- Product yields are based on GC analysis and are average of at least four independent runs; error limit $\pm 2\%$. The data are based on $\sim 30\%$ conversion but the ratio of the products remained the same in the conversion range 20 to 80%. Mass balance as monitored by GC with a calibration compound was $\sim 85\%$.
- Occupancy level was maintained at one molecule per eight supercages.

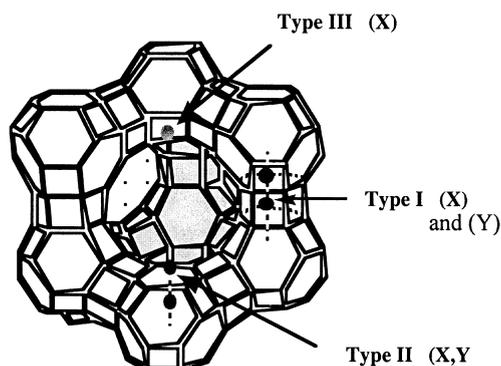


Figure 1.

and **9** were observed within the PbY. Large yields of **8** and **9** within PbY are consistent with the high spin-orbit coupling constant associated with Pb^{2+} . It is remarkable that Tl^+ and Pb^{2+} are able to exert a large external spin-orbit coupling influence enabling the ISC from A^3 to A^1 to compete with the decarbonylation process (rate of decarbonylation: $6.4 \times 10^6 \text{ s}^{-1}$ for phenylacetyl radical derived from DBK **4**)⁷. The cation effect must, however, not be strong enough to such

competition in the case of 1,1'-dimethyl 2-phenylacetyl radical derived from DBK **6** whose rate of decarbonylation is estimated to be near $1.5 \times 10^8 \text{ s}^{-1}$.⁷ The cation effect, yield of rearranged products and the rate of decarbonylation of 1-methyl 2-phenylacetyl radical in the case of DBK **5** is intermediary between those in DBK **4** and **6** (Table 1).

The results of the above study on DBK allows us to understand the selectivity observed during the photolysis of naphthyl esters **1–3**. Comparing the behavior of DBK **4** and naphthyl ester **1** both generating the phenyl acyl radical brings out a difference in behavior when included in NaY. While **1** quantitatively rearranges to **7** (Scheme 2), **4** gives only 10% of the rearranged products **8** and **9**, the difference which we believe is the result of the spin state of the geminate radical pair. The possibility to spin interconversion provided by TIY and PbY alters the yield of the rearranged products from 10 (NaY) to 89% (PbY) suggesting that the spin barrier is the main reason for the lack of rearrangement in **4** in NaY. An insight into the process is gained by comparing the behavior of naphthyl ester **3** and DBK **6**. While the former gives quantitatively the rearranged product **7**, the latter does not give any rearrangement product. In this case, due to the presence of α -methyl groups, the decarbonylation occurs 50 times faster than in unsubstituted phenyl acyl radical.⁷ Since we would have detected 1% of the rearranged product by GC, we believe that the rate of cation (Ti^+ and Pb^{2+}) induced ISC in the geminate pair (A^3 to A^1 ; Scheme 3) in the presence of heavy cations must be $\sim 10^6 \text{ s}^{-1}$. Thus, a comparison of the results observed with DBK systems and naphthyl esters suggests the lack of decarbonylation products in the case of naphthyl esters **1–3** to be due to the formation of primary radical pair A in the singlet state.

The results reported here unequivocally establish that heavy cations present within zeolites can have a remarkable influence on ISC of geminate radical pairs. Use of this technique to control product distribution during photochemical reactions involving triplet radical pairs, radical ion pairs and diradicals is a possibility that is currently being explored by us.

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