Tetrahedron Letters,Vol.30,No.29,pp 3761-3764,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

MAGNETIC ISOTOPE AND MAGNETIC FIELD EFFECTS ON THE PRODUCT DISTRIBUTIONS OF PHOTOLYSES OF DIBENZYL KETONE ADSORBED ON ZEOLITES

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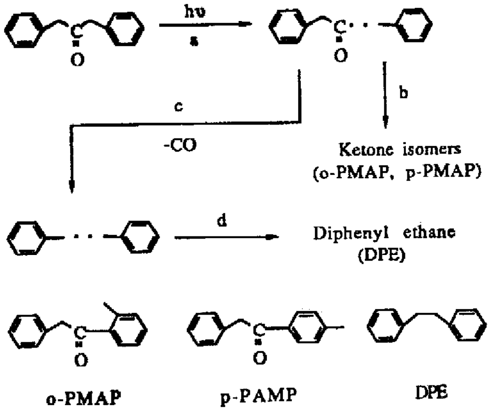
ABSTRACT: The photolysis of dibenzyl ketone adsorbed on faujasite zeolites results in product distributions that depend on the cation density and cation type, and, in two cases, were significantly modified by magnetic effects.

INTRODUCTION

The extent and nature of geminate pair reactions, which occur in competition with diffusional separation and free radical reactions, depend on the structure of exchangeable cations and on the cation density of zeolites.[1,2] Geminate radical pairs encapsulated in restricted spaces[1] are subject to unusually large magnetic effects.[3,4] We report large magnetic effects on the reactions of geminate radical pairs generated on the internal surfaces of zeolites and the influence of exchangeable cations on the occurrence or absence of magnetic effects.

EXPERIMENTAL STRATEGY AND METHODS

The paradigm for the photolysis of DBK[2] is given in Scheme I. If the space available in the supercage allows rapid diffusional separation of the primary geminate pair, then decarbonylation and eventual formation of diphenyl ethane (DPE) results. If the space available in the supercage restricts diffusion, but allows rotation of the radical pairs relative to one another, then isomeric products resulting from para (p-PMAP) or ortho (o-PMAP) coupling (followed by hydrogen migration) result. The product ratios thus serve as probes of the degree of diffusional and rotational motion available to the primary geminate pair. The zeolites selected for investigation were the Li, Na and K forms of the X and Y faujasites. Each zeolite possesses a 13 Å spherical "supercage" in which the DBK is adsorbed. The amount of void space in an X zeolite steadily decreases on going from LiX to NaX to KX. There is little variation in 13 Å void space on going from LiY to NaY to KY, because of the small cation density of MY zeolites.



SCHEME I. Schematic representation of the photolysis of dibenzyl ketone (DBK)

RESULTS

The results are summarized in Table 1. The following contrasts in the product distributions as a function of the experimental variables (cation, cation density, isotopic composition and magnetic field) were observed: (1) There is no difference, within the experimental error, in the product ratio for changes in any of the variables for photolysis on any of the MY or the LiX zeolites; (2) There is a significant 13-C isotope and magnetic field effect on the product distribution for photolysis of DBK adsorbed on NaX; (3) There are significant magnetic field effects on the product ratio for photolysis of DBK adsorbed on NaX and KX, (although there is a negligible magnetic isotope effect in the latter system); (4) There is a significant 2-H isotope effect on the product distribution for the photolysis of DBK adsorbed on NaX, but no such isotope effect is observed for photolysis on LiX, KX, or MY; i.e., the 2-H isotope effect follows the same pattern as the 13-C isotope effects observed with DBK.

Table 1. Photolysis of DBK in zeolites.

system	DPE	o-PMAP	p=PMAP
LiX			
DBK-^{12}CO	81% [85%][b]	3% [3%]	16% [12%]
DBK-^{13}CO (90%)[a]	81% [85%]	3% [2%]	16% [13%]
DBK-d_{10}(95%)	79%	2%	19%
NaX			
DBK-^{12}CO	56% [65%]	17% [13%]	26% [22%]
DBK-^{13}CO (90%)	27% [33%]	37% [25%]	36% [42%]
DBK-d_{10}(95%)	67% [59%]	10% [13%]	23%
KX			
DBK-^{12}CO	40% [68%]	40% [14%]	16% [18%]
DBK-^{13}CO (90%)	45% [62%]	32% [13%]	20% [25%]
DBK-d_{10} (95%)	45%	35%	20%

a. the number in the parenthesis ( ) is the isotope content;

b. the number in the parenthesis ( ) is the product yield of photolysis of DBK in the presence of 2000 G external magnetic field. The results for MY zeolites (Si/Al=2.36) are similar under all conditions (90-100% of DPE, very little isomers). See earlier paper[2] for experimental details.

DISCUSSION

We interpret the data in Table 1 on the basis of the lebensraum paradigms for reactions of radical pairs in zeolites[2] for magnetic effects on biradicals.[5] The amount of space available in the supercage determines the reaction pathways of the radical pair produced by photolysis of DBK by controlling the competition between the diffusional and rotational motions of the radical pair.[2] The <u>average separation</u> of the odd electron centers of primary geminate radical pairs will also depend on the space available in the supercage. Most space is available in the LiX and the MY supercages, least space in the KX supercage, and NaX is intermediate. There is an analogy between the effects induced on average separations of odd electron centers of the radical pairs by the size of the space in the supercage, and the average separation of the odd electron centers of a flexible biradical by the number of bonds connecting the radical centers (Figure 1b). This analogy allows us to inspect the interpretations of magnetic isotope and magnetic field effects on the reactions of flexible biradicals and to transfer these interpretations to radical pairs in the supercages of zeolites. The size of the supercage of an X or Y zeolite is approximately 13 Å in diameter, exclusive of the space occupied by the exchangeable cations. Thus, the radical pairs in the LiX and MY supercages are analogous to very long biradicals (>10 Å separation of radical centers), the NaX supercage is analogous to an intermediate size biradical (7-10 Å separation of the radical centers) and the KX supercage is analogous to a small biradical (3-5 Å separation of the radical centers). Figure 1a shows how the singlet-triplet gap and the mechanism of triplet-singlet intersystem crossing vary for a biradical as a function of the separation of the radical centers. Three limiting cases are examined, a long, medium and short biradical, where long, medium and short refer to average separations at which spin-lattice, hyperfine coupling or spin-lattice coupling determine intersystem crossing.

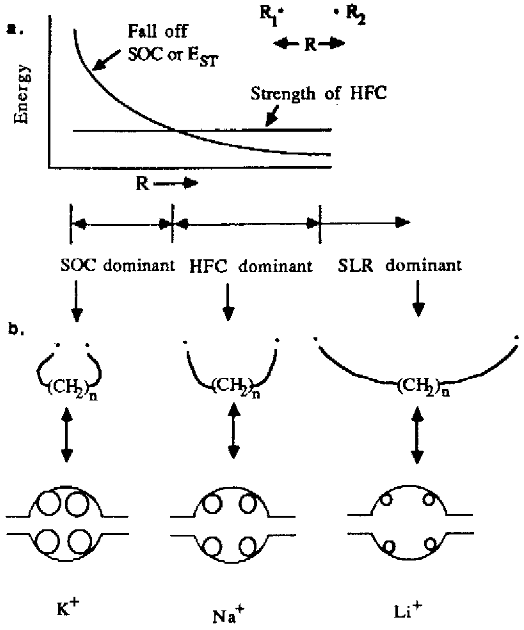


FIGURE 1. (a) Schematic representation of the S-T gap and the mechanism of T-S intersystem crossing as a function of the separation of the radical centers;

(b) Schematic representation of an analogy between a biradical and a radical pair generated in the zeolites.

No magnetic isotope effects or magnetic field effects are expected in such a limiting case of a very long biradical (which is essentially identical to the expectations for a freely diffusing radical pair in homogeneous solution). The photolysis of DBK in LiX and MY zeolites approaches the expectations of this limit. DPE is by far the major product (80-100%), due to the ease and extent of separation of the radical centers and to decarbonylation while the centers are separated. The lack of magnetic isotope or magnetic field effects for photolyses in LiX or MY zeolites is consistent with the postulate of rapid diffusional separation of the primary geminate pair into "free radicals" within the zeolite internal surface.

For a medium biradical, the singlet-triplet gap is small (ca. 10-100 Gauss), but not zero. In this case, intersystem crossing may be controlled by weak nuclear-electron hyperfine couplings, which are isotope dependent, and magnetic fields may inhibit intersystem crossing by splitting T_+ and T_- levels away from the S state of the biradical. Thus, both isotope and magnetic field effects are expected in such a limiting case. The photolysis of DBK in NaX approaches the expectations of the limit of a medium length biradical. For the unlabeled ketone (12-C DBK) the yields of DPE and isomers are comparable (56% and 44%, respectively). However, for 13-C DBK the yield of DPE drops sharply (to 27%) and the isomers become the major products (73%). On the other hand, the relative yield of DPE increases (to 67%) for 2-H DBK. The direction of the isotope effects is that expected for magnetic isotope effects: 13-C induces a faster intersystem crossing in the radical pair relative to the 12-C DBK (for which only the protons provide a hyperfine mechanism for intersystem crossing) and 2-H induces a slower intersystem crossing in the radical pair. The observation of a magnetic field effect on the yield of DPE is consistent with the conclusion that the radical pairs are, on average, separated by distances for which the singlet-triplet splitting is of the order of hyperfine couplings. An important observation is seen in the dramatic change in the ratio of the isomers upon substituting 13-C for 12-C at the carbonyl carbon: the ortho PMAP increasing substantially for the 13-C labeled compound. *This remarkable result is consistent with a faster intersystem crossing in the 13-C radical pair, that favors the formation of the ortho-isomer, since formation of the latter requires less rotational motion than formation of the para isomer.*

For a short biradical, the singlet-triplet gap is larger (*ca.* 500-1000 Gauss) than the strength of the hyperfine coupling and only spin-orbit coupling, which is isotope independent, possesses sufficient strength to induce intersystem crossing. Although no isotope effect is expected in such a situation, magnetic field effects are permissible if the singlet-triplet gap is smaller than the value of the externally applied field. The photolysis of DBK in KX approaches the expectation of this limit. There is no 2-H or 13-C isotope effect for the different DBKs (DPE yields 40-45% for each isotopically substituted DBK), but significant magnetic field effects are observed, e.g., DPE yield of 40% and 68% for 12-C DBK in the earth's field and in a field of 2000 Gauss, respectively. Above, it was postulated that the competition between intersystem crossing and rotation are competitive for radical pairs in NaX. A similar competition would lead to enhanced ratios of the para isomer relative to the ortho isomer in the presence of an applied field, as is observed (for 12-C DBK para/ortho - 0.4 and 1.3 in the earth's field and in an applied field of 2000 Gauss, respectively). Similar, but smaller, magnetic field effects are observed for the photolyses of isotopic DBKs on NaX.

CONCLUSION

The photolysis of isotopically substituted DBKs adsorbed on zeolites shows that magnetic isotope and magnetic field effects can be fine tuned by varying the cation size, which influences the amount of space available in the supercages in which the radical pairs are adsorbed. The competition between intersystem crossing and relative rotational and diffusional motions of the radical fragments can result in large magnetic isotope and magnetic field effects on the ratio of ortho and para isomers produced in the photolyses.

ACKNOWLEDGEMENTS

The authors thank NSF, AFOSR, DOE and the IBM Corporation for their generous support of this research.

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(Received in USA 6 April 1989)