

Triplet-triplet energy transfer between organic molecules trapped in zeolites

Kasi Pitchumani,^a Janet N. Gamlin,^b V. Ramamurthy*^a and John R. Scheffer*^b

^a Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA

^b Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1Z1

Double loading of a zeolite with a triplet energy donor and a triplet energy acceptor followed by selective irradiation into the donor absorption band leads to characteristic triplet state reactivity of the acceptor.

Zeolites are capable of including more than one organic molecule within the same supercage,¹ and by double loading techniques whereby first one guest molecule and then a second are introduced into the zeolite, it is possible to situate two dissimilar organic molecules near one another within a well ordered supramolecular environment. Previous research from our two laboratories has shown that such double loading techniques can be used to carry out photochemical asymmetric induction reactions in zeolites.² In that work, an optically active inductor molecule was first introduced into the zeolite followed by an achiral probe molecule capable of forming a chiral product upon photolysis, and irradiation of the resulting supramolecular assemblies gave products with low to moderate enantiomeric excesses.² In principle, the zeolite double loading technique should be applicable to the study of a wide variety of bimolecular processes, and here we report a novel extension of this concept to the process of triplet-triplet energy transfer, the goal of the work being to expand the range of photochemistry and photophysics that can be studied in zeolites.

To demonstrate triplet-triplet energy transfer in a zeolitic environment, we required not only a triplet energy donor but a probe molecule as well—a triplet energy acceptor whose own triplet state behaviour would be diagnostic of successful energy transfer. As the probe molecule we selected 11-hydroxymethyl-9,10-dihydro-9,10-ethenoanthracene **1**,³ a compound whose photochemistry is multiplicity-dependent, so that a relatively simple measurement of the singlet-triplet product ratio by gas chromatography indicates the extent of triplet-triplet energy transfer. Thus triplet-sensitized irradiation of **1** in acetone through Pyrex afforded the characteristic di- π -methane regioisomers **3** (55%) and **4** (45%),⁴ whereas direct irradiation of **1** in acetonitrile at 254 nm gave nearly complete conversion to the cyclooctatetraene derivative **2** (95%) along with very small amounts of **3** and **4**.[†] Such behaviour is typical of 11-alkyl substituted 9,10-ethenoanthracene derivatives.⁵

The sensitizers chosen for investigation were acetophenone, *p*-methoxyacetophenone and α -aminoacetophenone hydro-

chloride. These were introduced into the activated (*ca.* 480 °C) zeolite KY⁶ by stirring hexane solutions of the sensitizers in the presence of anhydrous KY followed by filtration and through washing with hexane.‡ The vacuum-dried complexes were then transferred to hexane solutions of 9,10-ethenoanthracene derivative **1** and again stirred, filtered, washed and dried. In every case, the filtrates and washings contained no residual guest material, indicating complete incorporation of sensitizer and probe within the zeolite cages. The amount of material introduced onto the zeolite—the loading level—was varied from 25 to 85, a loading level of 25 referring to an average of one molecule of sensitizer and one probe molecule for every 25 supercages.§

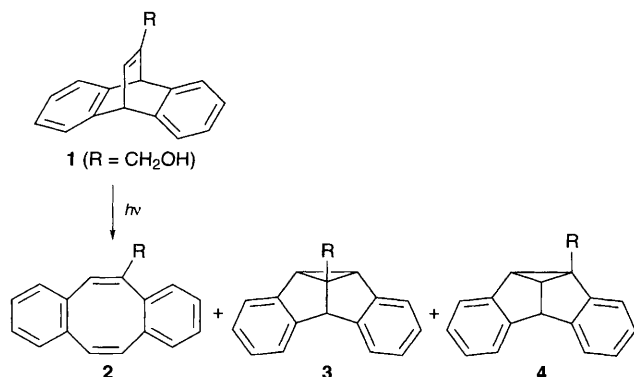
The double loaded zeolite complexes were photolyzed at $\lambda > 290$ nm (Pyrex) in the absence of oxygen, both as dry powders and as hexane slurries. Under these conditions, the sensitizers absorb most of the incident light. The slurry runs were much faster than those conducted in the solid state, requiring 2.5 h to achieve conversions of approximately 25% compared to 20 h for the powders. Following photolysis, the organic materials were extracted from the zeolites with diethyl ether and analysed by capillary gas chromatography. Mass balances were excellent, indicating that the photoproduct ratios were not skewed by selective inclusion of one of the products. The results of the triplet-triplet energy transfer experiments are compiled in Table 1. The table also contains the results of a control run, in which zeolite KY was single loaded with probe compound **1** and irradiated at 254 nm as a slurry and in the solid state.

The results summarized in Table 1 clearly reveal that (i) triplet-triplet energy transfer has occurred within the zeolite medium, (ii) *p*-methoxyacetophenone is the sensitizer of choice among those tested and (iii) the dry powder technique leads to

Table 1 Product distribution from photolysis of **1** under various conditions^a

Medium	Loading level ^b	Solution			Slurry ^c			Solid ^d		
		2	3	4	2	3	4	2	3	4
MeCN		95	04	01						
Acetone		<1	45	55						
KY	33				77	19	04	84	15	01
KY	25				20	54	26	07	65	28
Acetophenone	40				22	49	29	13	63	24
	85				81	11	08	20	52	28
KY	25				07	59	34	<1	54	45
<i>p</i> -Methoxyacetophenone	40				12	54	34	<1	61	38
	85				46	34	20	<1	55	44
KY	5				03	37	60	<1	43	56
α -Aminoacetophenone	25				51	21	28	32	32	36
HCl	40				63	13	24	68	14	18

^a A product distribution similar to that shown for **1** (R = CH₂OH) was also obtained in the case of **1** (R = CH₂OCH₂CO₂Me). To conserve space, the data for the latter compound have been omitted. ^b Loading level refers to the average number of supercages per guest molecule. For example, a value of 25 indicates one probe molecule and one sensitizer molecule per 25 supercages. ^c Samples irradiated for 2.5 h as suspensions in hexane. ^d Samples irradiated for 20 h as powders.



greater triplet-triplet energy transfer than the slurry method. The finding that *p*-methoxyacetophenone is an excellent sensitizer in zeolites parallels similar results in solution, where its relatively long π,π^* triplet lifetime and the sluggishness of this triplet toward hydrogen atom abstraction are prime factors in facilitating energy transfer.⁷¶

Not surprisingly, the extent of triplet-triplet energy transfer generally increases as the number of molecules per supercage is increased (that is the loading level, as defined here, is decreased), but what is somewhat surprising is that energy transfer is seen even at loading levels as low as one sensitizer molecule and one probe molecule in 85 supercages. The quantitative energy transfer from *p*-methoxyacetophenone at this loading level in the solid state is nothing short of remarkable.

Qualitatively, it appears that there are at least three factors that could contribute to efficient energy transfer under such 'dilute' conditions: selective donor-acceptor aggregation in the same supercage, long triplet lifetime of the donor, and/or rapid intrazeolite diffusion. Of these, rapid diffusion is probably least important, as rates of diffusion in zeolites are known to be slow.⁸ A related question concerns possible reasons for the greater degree of triplet-triplet energy transfer in the powders than in the slurries. Here it seems likely that an increased triplet lifetime of the sensitizer in the solid state,⁹ and a reduced diffusional mobility between donor and acceptor when the zeolite channels are filled with hexane¹⁰ play important roles. Attempts to obtain quantitative evidence on these points are under way.

Among the three sensitizers used in this study, α -aminoacetophenone hydrochloride is unique. Since it is anchored to the surface of the zeolite *via* an ionic bond, the photoproducts can be selectively removed from the zeolites leaving the sensitizer intact. This feature has allowed us to reuse the α -aminoacetophenone hydrochloride-exchanged KY for at least five runs without any deterioration of the performance. However, this advantage is offset by the poor mobility of the sensitizer. This results in the need to use relatively high amounts of the sensitizer. For example, with a loading level of 25, the triplet product formation in the case of α -aminoacetophenone hydrochloride is only approximately 70%, whereas for *p*-methoxyacetophenone and acetophenone, it is >99 and *ca.* 90%, respectively.

The results presented above open the door to further energy transfer studies in zeolites and greatly expand the range of photochemical processes that can be investigated in zeolitic media. Given the success of the sensitization studies, competitive concentration-dependent quenching studies of reactive excited states should also be possible, and with this comes the attractive possibility of obtaining kinetic information for excited state processes carried out in this important supra-molecular host medium. The approach described here should also allow us to conduct enantioselective triplet state photo-reactions by using optically active sensitizers.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (J. R. S. and V. R.). Financial support by the Natural Sciences and Engineering Research Council of Canada (J. R. S.) and the Office of Energy

Research, US Department of Energy (V. R.) is also gratefully acknowledged.

Footnotes

† Photoproducts **2**, **3** and **4** gave satisfactory elemental analyses and exhibited spectroscopic data fully in accord with their assigned structures. Exactly analogous results were obtained for compound **1** for which R = CH₂OCH₂CO₂Me. To conserve space, only the results for **1** (R = CH₂OH) are reported. Direct irradiation (254 nm) of the acetate of compound **1** (R = CH₂OH) has been reported to lead to a 4:1 ratio of 2-OAc and 3-OAc.¹¹

‡ Methanol was used for α -aminoacetophenone hydrochloride. The zeolite KY was chosen owing to the fact that it caused the least perturbation of the singlet-triplet photoproduct ratio compared to the results obtained in solution. When compound **1** was photolysed in other alkali metal exchanged zeolites, extensive triplet state behaviour was observed even in the absence of a sensitizer molecule. These results will form the subject of a future publication.

§ The sensitizer to reactant ratio was kept the same so that relative absorption of the incident light by the two remains constant at all loading levels. The loading level was varied by changing the amount of zeolite used for inclusion.

¶ The triplet lifetimes of acetophenone and *p*-methoxyacetophenone in dry NaX are 6 and 60 μ s, respectively.¹²

References

- 1 V. Ramamurthy, in *Surface Photochemistry*, ed. M. Anpo, Wiley, New York, 1996, pp.65; E. S. Brigham, P. T. Snowden, Y. I. Kim and T. E. Mallouk, *J. Phys. Chem.*, 1993, **97**, 8650; M. Borja and P. K. Dutta, *Nature*, 1993, **97**, 8650; K. B. Yoon, S. M. Hubig and J. K. Kochi, *J. Phys. Chem.*, 1995, **99**, 7042.
- 2 M. Leibovitch, G. Olovsson, G. Sundarababu, V. Ramamurthy, J. R. Scheffer and J. Trotter, *J. Am. Chem. Soc.*, 1996, **118**, 1219.
- 3 S. J. Cristol and A. L. Noreen, *J. Org. Chem.*, 1976, **41**, 4016; S. J. Cristol, G. C. Schloemer, D. R. James and L. A. Paquette, *J. Org. Chem.*, 1972, **37**, 3852.
- 4 For a recent, general review of the di- π -methane photorearrangement, see: H. E. Zimmerman, *Organic Photochemistry*, ed. A. Padwa, Marcel-Dekker, New York, 1991, vol. 11, ch. 11.
- 5 J. R. Scheffer and J. Yang, *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC Press, Boca Raton, FL, 1995, ch. 16.
- 6 D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, New York, 1974; H. van Bekkum, E. M. Flanigen and J. C. Jansen, *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, 1991; A. Dyer, *An Introduction to Zeolite Molecular Sieves*, Wiley, Chichester, 1988.
- 7 N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser and R. Dusenberry, *J. Am. Chem. Soc.*, 1967, **89**, 5466.
- 8 J. Kager and D. M. Ruthven, *Diffusion in Zeolites*, Wiley, New York, 1992, pp. 392-444.
- 9 M. V. Baldovi, A. Corma, H. Garcia and V. Marti, *Tetrahedron Lett.*, 1994, **35**, 9447; M. V. Baldovi, F. L. Cozens, V. Fornes, H. Garcia and J. C. Scaiano, *Chem. Mater.*, 1996, **8**, 152.
- 10 U. Hong, J. Karger and H. Pfeifer, *J. Am. Chem. Soc.*, 1991, **113**, 4812; P. Stilbs, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1987, **19**, 1.
- 11 S. J. Cristol, D. Braun, G. C. Schloemer and B. J. Vanden Plas, *Can. J. Chem.*, 1986, **64**, 1081.
- 12 L. J. Johnston and V. Ramamurthy, unpublished results.

Received, 23rd April 1996; Com. 6/02891H