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Controlling the reactive state through cation binding: photochemistry of enones within zeolites

Sundararajan Uppili,[a] Shinsuke Takagi,[a] R. B. Sunoj,[b] P. Lakshminarasimhan,[a] J. Chandrasekhar[b,]* and V. Ramamurthy[a,]*

[a]*Department of Chemistry, Tulane University, New Orleans, LA 70118, USA*
[b]*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India*

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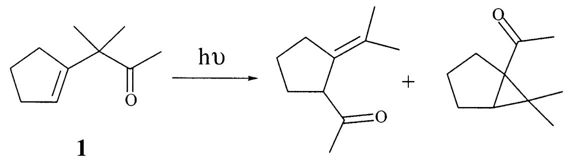
Abstract—The nature of the lowest triplet state of enones is altered by the cations present within Y zeolites. Alkali metal ions, such as Li^+, are predicted to interact with the carbonyl unit of enones in a collinear fashion and significantly lower both the p-type n and π-2 orbitals. Excited state energies, estimated at the CIS(D)/6-31+G* level, show that the lowest triplet is n-π* in character for the enones, but switch to π–π* on coordination with Li^+. Observed product distribution within zeolite is consistent with this theoretical prediction. © 2001 Elsevier Science Ltd. All rights reserved.

Photoreactions of molecules containing a carbonyl chromophore can occur from both the n-π* and π–π* excited triplet states if they are fairly proximal so that an equilibrium exists between these two states at ambient temperature.[1] Since the chemical reactivity of the two triplet states can differ markedly, the nature and yield of the products obtained depend on: (a) the relative rates of reaction from the two excited states, and (b) the energy gap between the two reactive states. Solvent polarity strongly influences the relative energies of n-π* and π–π* states of carbonyl compounds,[2] and can be employed to control the selectivity in product distribution.[3] However, this approach has limited value because most organic compounds do not dissolve in the most polar solvent, water. We believe zeolites offer a convenient polarizable environment[4] in which most organic molecules, insoluble in water, can be readily included, if the dimensions of the supercage window (diameter ~8 Å) permit. Further, cations present in zeolites can interact with the included carbonyl compounds[5,6] and potentially alter the excited state energetics. We now demonstrate that enones, which are known to give different products from the n-π* and π–π* triplets in the solution phase,[7] can indeed be directed to react preferentially via the π–π* triplet by employing a zeolite as the reaction medium. We also offer computational evidence that Li^+ complexation leads to a reversal of triplet state ordering in enones, accounting for the observed selectivity.

Triplet sensitization of 3-methyl-3-(1-cyclopentenyl)-butan-2-one, **1**, yields the 1,3-acyl migration product **2** from the n-π* triplet (and n-π* singlet) and the oxa-di-π-methane product **3** from the π–π* triplet (Scheme 1).[7c,d] In the present investigation, accumulation of the 1,3-acyl migration product from the excited singlet state was avoided by using the triplet sensitizer, 4-methoxy-acetophenone. Triplet sensitization of **1** by 4-methoxy-



1 (nπ*) **2** (ππ*) **3**

Medium	%2	%3
hexane	100%	0%
methanol	78	22
acetonitrile	76	24
KX/hexane	25	75
KY/hexane	26	74

Scheme 1.

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* Corresponding authors. Tel.: 504 862 8135; fax: 504 865 5596; e-mail: murthy@tulane.edu

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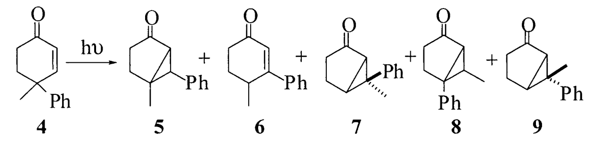
acetophenone in hexane gave exclusively the product from the n-π* triplet, **2**. However, in polar solvents, such as methanol and acetonitrile, a mixture of **2** and **3** was obtained (Scheme 1). The solvent dependence of product distribution can be rationalized on the basis of a two-state model.[7d] In hexane, the lowest triplet of enone **1** is n-π* in character and the next π–π* triplet is much higher in energy. The products are derived exclusively from the n-π* triplet. In polar solvents, the π–π* state is relatively stabilized enabling an equilibrium to be established with the n-π* triplet, resulting in products from both states. It is of interest to explore the effect of zeolites in controlling the relative energetics of n-π* and π–π* states and, in turn, the product distribution.

Enone **1** and the triplet sensitizer 4-methoxyacetophenone included (2 mg **1** and 5 mg of sensitizer in 300 mg of zeolite) in various M^+ exchanged X and Y zeolites were irradiated as a hexane slurry (450 W medium pressure mercury lamp, Pyrex filter, continuous nitrogen bubbling, 15 min, 15% conversion).[8] The oxa-di-π-methane product **3** was obtained in higher yield within the zeolite than in the non-polar hexane or in other polar solvents used in this investigation (Scheme 1). The results obtained in zeolites are consistent with the π–π* triplet being near the n-π* triplet state. In the absence of rates and efficiencies of reactions from these two states we cannot be certain about which of the two states is lower in energy. The selectivity in favor of the π–π* triplet product observed in zeolites is unmatched in any organic solvent, attesting to the uniqueness of zeolites.

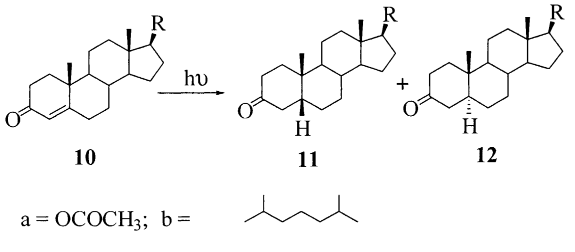
The above strategy of controlling product distributions by inclusion in a zeolite was also attempted with 4-methyl-4-phenyl-2-cyclohexenone **4**. As shown in Scheme 2, of the several products (**5**–**9**) that this molecule gives upon excitation, **5** and **6** have been established to arise from the n-π* triplet and products **7**–**9** from the π–π* triplet.[9] The ratio of the two sets of products [(**7**+**8**+**9**)/(**5**+**6**)] has been reported to depend on solvent polarity (Scheme 2).[9] Similar to enone **1**, in a non-polar hydrocarbon solvent, products from the n-π* triplet alone were obtained suggesting that the lowest triplet is n-π* in character and the second π–π* triplet is not close enough to establish an equilibrium and react. With increasing polarity, the two states apparently are brought closer in energy such that products from both states are formed (Scheme 2). Consistent with the behavior of enone **1**, direct irradiation of **4** included within MY and MX zeolites (6 mg of enone in 300 mg of zeolite, 450 W medium pressure mercury lamp, Pyrex filter, zeolite–hexane slurry, 5 h irradiation, 15% conversion) gave higher yields of products **7**–**9** derived from the π–π* triplet (Scheme 2) than in non-polar benzene (0%) or moderately polar acetonitrile (42%).[10] In LiY the combined yield of [(**7**+**8**+**9**)] was >85%, even higher than in a 30% water–methanol mixture (75%). The results obtained in Y-Sil and MCM-41 (25% of [(**7**+**8**+**9**)]), zeolites with no cations, reveal the key role of cations in enhancing the yield of π–π* triplet products.

The final examples involve steroidal cyclohexenones, testosterone acetate, **10a**, and cholestenone, **10b** (Scheme 3).[11] These enones, upon excitation in hexane, are unreactive. On the other hand, irradiation of **10a** and **b** in 2-propanol results in *cis*- and *trans*-fused hydrogen addition products **11** and **12**.[12] The absence of reduction products in hexane is consistent with the expectation that the rate of hydrogen abstraction from hexane by the triplet enone would be low. On the other hand, the solvent 2-propanol is a good hydrogen donor and reduction products as observed are anticipated. Based on reported studies on related systems, 4a-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrenone, and 4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphtha-



Medium	[7+8+9]	[5+6]
benzene	0 %	100%
ethanol	33	67
acetonitrile	42	58
LiY/hexane	87	13
NaY/hexane	70	30
NaX/hexane	71	29

Scheme 2.



	10a		10b	
Medium	11a	12a	11b	12b
2-propanol	27	73	15	65
NaY/hexane	85	15	80	10

Scheme 3.

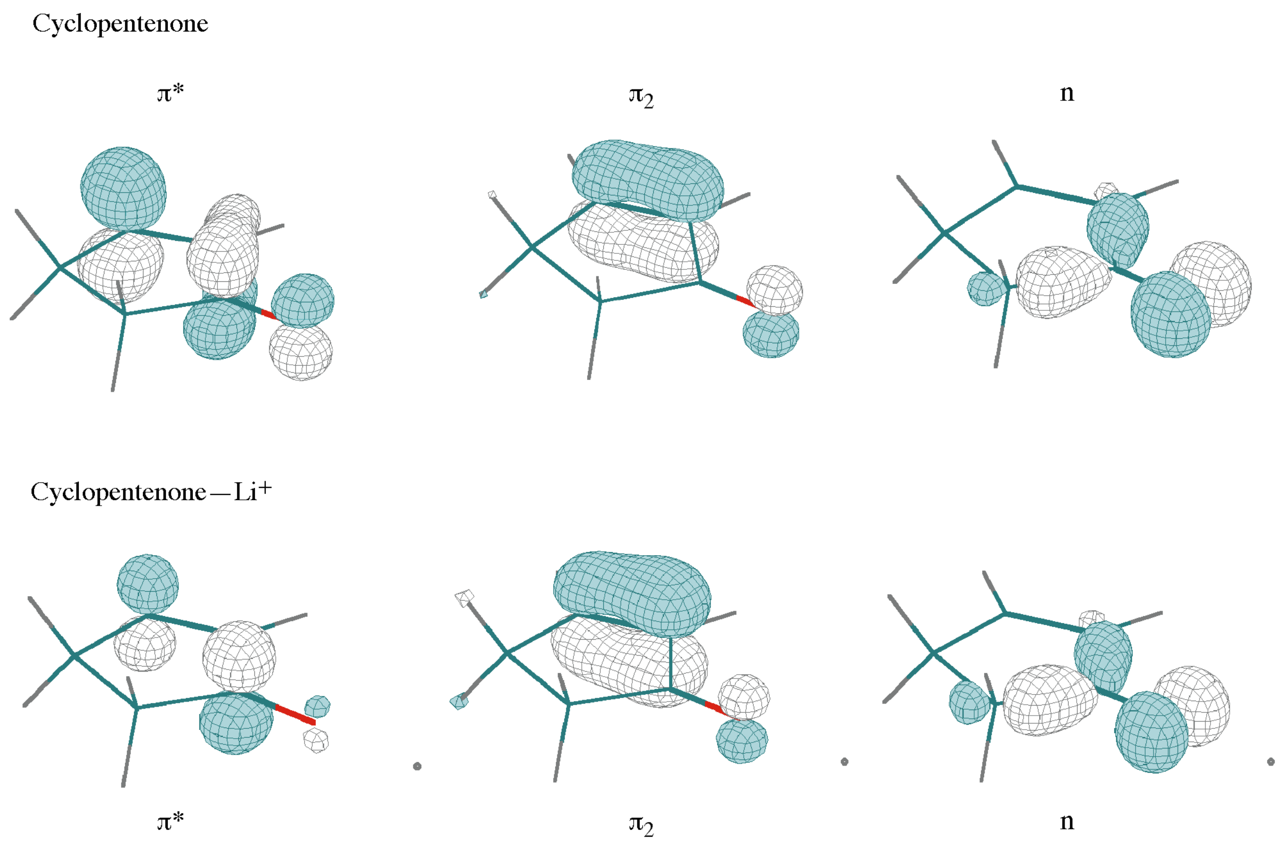


Figure 1. From right to left: schematic representations of n, π_2 and π^* orbitals of cyclopentenone (top) and cyclopentenone–Li^+ complex (bottom).

lenone,[13] we assume that products **11** and **12** arise from the π–π* and n-π* triplet states, respectively. In 2-propanol the major products from **10a** and **b** were **12a** and **b**, respectively, derived from the n-π* triplet. Formation of **11** along with **12** suggests that in 2-propanol the π–π* and n-π* triplets are near one another and hydrogen abstraction by both states occur. Thus, these molecules are, once again, ideal examples for exploring the use of zeolites to alter the energetic ordering of n-π* and π–π* triplet states. As shown in Scheme 3, when the irradiation was conducted in NaY (5 mg of enone in 300 mg of zeolite, 450 W medium pressure mercury lamp, Pyrex filter, zeolite–hexane slurry, continuous nitrogen bubbling, 5 h irradiation, 15% conversion),[10] consistent with the behavior of enones **1** and **4**, the major product switched from **12** to **11** (from n-π* to the π–π* triplet product). Interestingly, the steroidal enones **10a** and **b** abstract hydrogen from the solvent hexane only when they are present within the NaY zeolite. The absence of photoreduction of **10** in Y-Sil and MCM-41 zeolites suggests that cations are required for hydrogen abstraction from the co-guest hexane.

The observed changes in product distributions, shown in Schemes 1–3, reflect the remarkable influence of the zeolite medium on the location of the n-π* and π–π* triplets of enones. A simple interpretation involves the local polarity within zeolites. Based on measurement with at least five independent probes, the micropolarity of M^+Y and M^+X zeolites has been determined to be similar to the polarity of bulk water.[4] Hence, the included substrate is exposed to a highly polar or polarizable environment. By analogy with the known solvent dependency of photoreactions of enones, the π–π* triplet state is expected to be preferentially stabilized. In addition, we suggest that the cations present in zeolites play a direct role. The binding energies for Li^+ to formaldehyde and acetone have been experimentally measured to be ~36 and 45 kcal mol^{-1}, respectively.[5] Although the corresponding data for enones are not available, the values are likely to be in a similar range. At the MP2/6-31G* level,[14] we compute the binding energies of Li^+ to cyclopentenone and cyclohexenone to be 54 and 54.5 kcal mol^{-1}, respectively (for reference, the corresponding value for acetone is computed to be 48 kcal mol^{-1}). Although the strength of interaction is likely to be reduced due to the presence of oxyanionic counterions, enones adsorbed within a zeolite are expected to be bound to M^+ ions. We therefore probed the effect of metal ion complexation on the orbital and excitation energies of the model systems, cyclopentenone and cyclohexenone, along with acetone for comparison.

As in earlier studies on simple carbonyl compounds,[15] the Li^+ ion is computed to be aligned nearly collinear with the C=O bond, suggesting a primarily ion–dipolar electrostatic interaction between the metal ion and the enone (Fig. 1). While the nature and relative coefficients of the MOs are not altered in any significant

Table 1. Ground state orbital energies (HF/6-31G*) and energies of triplet states relative to the ground state (CIS(D)/6-31+G*) for carbonyl compounds and their Li^+ complexes

Molecule/ion	Orbital energy (eV)			Triplet energy (eV)[a]	
	π	n	π^*	n-π^*	π–π^*
Acetone	−13.03	−11.19	4.28	4.04 (4.41)	6.28 (5.19)
Acetone + Li^+	−18.45	−16.67	−2.08	4.51 (5.16)	6.63 (6.38)
Cyclopentenone	−10.21	−10.86	2.93	3.69 (4.33)	4.23 (3.36)
Cyclopentenone + Li^+	−14.31	−15.99	−1.99	4.35 (5.29)	4.10 (3.43)
Cyclohexenone	−10.08	−10.90	2.80	3.50 (4.13)	4.05 (3.17)
Cyclohexenone + Li^+	−14.03	−15.74	−2.02	4.15 (5.11)	3.84 (3.19)

[a] Results obtained at CIS/6-31+G* level (without doubles corrections) are given in parentheses.

manner, all the MOs are shifted to lower energies through coordination. The key MOs of importance in the present context are the p-type n orbital on the carbonyl oxygen, the filled π (higher lying π_2 for the enones) and the vacant π^* orbitals (shown in Fig. 1 for cyclohexenone). The n orbital is stabilized by Li^+ complexation to a greater extent than the π MO in the model enones (Table 1), suggesting that the n-π^* triplet will be relatively shifted to higher energy due to cation binding. However, orbital energies are not always a reliable guide for deriving excited state energetics. In order to obtain more accurate estimates, configuration interaction calculations were carried out using the MP2/6-31G* optimized geometries. After including all single excitations (CIS), the effect of double excitations was taken into account in a size-consistent second-order perturbative treatment.[16] These CIS(D) calculations were carried out using the larger 6-31+G* basis set. Since the two triplet states of interest and the ground state singlet correspond to the lowest roots of their spin and spatial symmetry types, the relative energies are likely to be fairly reliable.

The CIS(D)/6-31+G* calculations confirm that the n-π^* triplet is the lowest energy triplet in the three model systems (Table 1). While this is expected for acetone on the basis of orbital energies, the trend prevails in the enones in spite of the fact that the n orbital is below the π_2 HOMO. Interestingly, the greater stability of the n-π^* triplet, which is consistent with experimental trends noted above, is obtained only after the inclusion of doubles corrections. More significant in the present context is the effect of Li^+ coordination on the energies of the triplet states. While the n-π^* triplet is clearly shifted to higher energy, the π–π^* triplet is marginally stabilized in the enones. The lower energy triplet is now calculated to be the π–π^* state. The switch in the ordering of the triplet states and their relative energies are both qualitatively consistent with the observed product selectivities in photoreactions of enones in zeolites.

In summary, the high polarity and cation–carbonyl interactions enable the zeolite medium to control the product distribution from photoreactions of enones by influencing the energetic ordering of the reactive excited states.

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temperature. The zeolite was transferred to dry hexane inside a dry box, sealed with rubber septa, bubbled with dry nitrogen for 30 min (outside the dry box) and irradiated (>300 nm) for 15 min. The products were extracted by stirring the zeolite with dichloromethane and analyzed by GC. The mass balance, as estimated by GC using a calibration compound, was ~85%. X and Y zeolites used in this study were obtained from the PQ Corporation, Valley Forge, PA. The source of the zeolites was Zeolyst International, The Netherlands.

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