



# Triplet photochemistry within zeolites through heavy atom effect, sensitization and light atom effect

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**Abstract**—Methods to generate triplets of organic molecules within zeolites have been established by employing the Zimmerman rearrangement of barrelenes, oxa-di- $\pi$ -methane rearrangement of  $\beta,\gamma$ -unsaturated ketones and photodimerization of acenaphthylene as probe reactions. The two methods, heavy cation effect and triplet sensitization, are well established solution techniques and these work well within zeolites. The Zimmerman rearrangement of dibenzobarrelene is enhanced even within  $\text{Li}^+$  and  $\text{Na}^+$  exchanged zeolites and these are believed to be the result of slowing of the rearrangement to dibenzocyclooctatetraene from  $S_1$  through cation- $\pi$  interaction. The methods described here provide an opportunity to explore the control afforded by the zeolite environment on triplet reactions.

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## 1. Introduction

Early work by Kasha and Lewis had postulated the existence of a phosphorescent triplet state and the important role it plays in photochemical processes of organic molecules.<sup>1</sup> The use of external heavy atoms to increase singlet–triplet transition probabilities, first reported by Kasha in 1952, quickly became a common practice.<sup>2</sup> Spin–orbit coupling, induced by heavy atoms, provides the crucial mechanism, which allows the otherwise forbidden interconversion between singlet and triplet states. Molecules that are employed to influence the singlet–triplet interconversion include oxygen, alkyl halides, organo-metallic compounds, and rare gases such as xenon.<sup>3</sup> We reasoned that if a heavy atom perturber and an organic molecule could be ‘closeted’ within a constrained environment, such as zeolites, the interactions between them could be strengthened, leading to stronger heavy atom effects. In this context, reports on enhanced intersystem crossing and phosphorescence yields in the case of aromatics, olefins and azoalkanes included in heavy cation (e.g.  $\text{Cs}^+$ ,  $\text{Tl}^+$ ) exchanged faujasites are note worthy.<sup>4</sup>

By employing the Zimmerman rearrangement of dibenzobarrelene (**1**) and benzobarrelene (**5**)<sup>5</sup> and photodimerization of acenaphthylene (**8**)<sup>6</sup> as probe reactions we show in this report that the heavy cation technique could also be used to control photoproduct distributions within zeolites (Scheme 1). For dibenzobarrelene and benzobarrelene, the Zimmerman rearrangement proceeds solely from the triplet

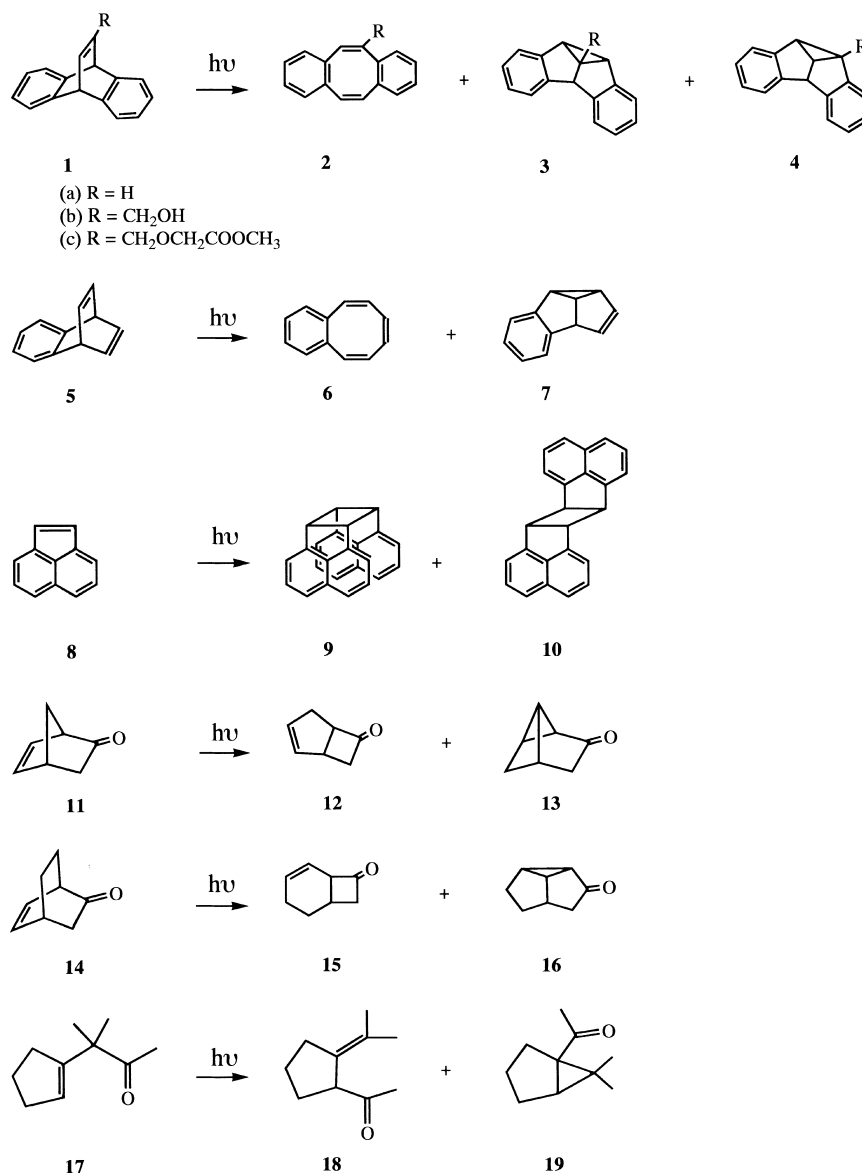
state giving semibullvalenes **3**, **4** and **7**. From excited singlet state these molecules yield cyclooctatetraene derivatives **2** and **6**. Acenaphthylene upon excitation undergoes photodimerization to give both *cis* and *trans* dimers. Of the two, the *trans* dimer (**10**) is derived only from the triplet state while the *cis* dimer (**9**) from both the triplet and excited singlet states. The product distributions obtained in these three systems within a zeolite would therefore, be a reflection of the extent of intersystem crossing under a given condition. Employing the photochemistry of  $\beta,\gamma$ -unsaturated ketones **11**, **14**, and **17**<sup>7</sup> we were able to establish the limitations of the zeolite based heavy cation technique. These molecules yield products of 1,3-acyl (**12**, **15** and **18**) and 1,2-acyl shifts (**13**, **16** and **19**; oxa-di- $\pi$ -methane rearrangement) predominantly from  $S_1$  and  $T_1$  states, respectively (Scheme 1). The  $\alpha$ -cleavage leading to 1,3-acyl migration occurs both from  $S_1$  and  $T_1$  of  $n\pi^*$  character while oxa-di- $\pi$ -methane rearrangement leading to 1,2-acyl shift occur essentially from  $\pi\pi^*$  triplet. Since no significant heavy cation effect was observed with  $\beta,\gamma$ -unsaturated ketones, we felt it important to establish a general method to generate triplets of molecules within zeolites. To this effect we have explored the well-known triplet sensitization technique within zeolites.<sup>8</sup> Results of heavy cation and triplet sensitization methods to generate reactive triplets within zeolites are presented below.

## 2. Results

Results of photolysis of barrelenes **1** and **5** in various media are presented in Tables 1–3. In isotropic solution medium, there is a preference for cyclooctatetraene (**2** and **6**). In

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Scheme 1.

presence of a triplet sensitizer (acetone for **1** and acetophenone for **5**), under conditions where only the sensitizer absorbed the light only semibullvalenes **3**, **4** and **7** were obtained. Zeolite loaded barrelenes were irradiated in the form of solid powder and hexane-slurry. For the solid irradiations, reactant 'loaded' zeolite samples were transferred to quartz/pyrex tubes and photolyzed directly as a powder. For the slurry irradiations, the loaded zeolite samples were transferred into fresh hexane and photolyzed as a hexane slurry with continuous stirring. Cation exchanged X zeolites were used as media.

The ratio of products derived from excited singlet and triplet states varies with the cations present within a zeolite. Mainly triplet derived products were obtained from **1** and **5** within Tl<sup>+</sup> exchanged zeolites. Unexpectedly, in the case of dibenzobarrelene higher yields of the triplet products were obtained even within LiX and NaX as compared to KX (Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> < Rb<sup>+</sup> < Cs<sup>+</sup> < Tl<sup>+</sup>). As shown in Table 3, this unusual phenomenon also occurs with two substituted

dibenzobarrelenes **1b** and **1c** (Table 3). Ability of Li<sup>+</sup> and Na<sup>+</sup> in bringing out triplet chemistry decreased when water was used as the co-adsorbent. In 'wet' zeolites the yield of the triplet product gradually increased with the atomic number of the cation (Li<sup>+</sup> ~ Na<sup>+</sup> < K<sup>+</sup> < Rb<sup>+</sup> < Cs<sup>+</sup> < Tl<sup>+</sup>). As opposed to dibenzobarrelene, benzobarrelene did not yield significant amounts of semibullvalene **7** within Li<sup>+</sup> and Na<sup>+</sup> exchanged zeolites. Also in this case (benzobarrelene) only Tl<sup>+</sup> was able to induce significant triplet reactivity.

In Table 4 results of solid state irradiation of acenaphthylene included in alkali ion exchanged Y zeolites are presented. Photochemistry of acenaphthylene in solution has been extensively investigated.<sup>6</sup> Direct excitation gives the *cis* dimer while triplet sensitization yields both *cis* and *trans* dimers in the ratio ~1:2 (methanol). From the table, it is clear that the ratio of the *trans* to the *cis* dimer depends on the cation. Essentially, the *cis* dimer was obtained in LiY while in RbY a mixture of *trans* and *cis* dimers were formed

**Table 1.** Product distribution upon irradiation of dibenzobarrelene (**1a**)

Medium	Conversion (%)	Slurry <sup>a</sup> (%)		Solid <sup>a</sup> (%)	
		2a	3a	2a	3a
Acetonitrile		77	23		
Acetone		0	100		
LiX	4(23) <sup>b</sup>	33{80} <sup>c</sup>	67{20}	18{57}	82{43}
NaX	6(20)	38{72}	62{28}	25{44}	75{56}
KX	17(30)	53{57}	47{43}	38{42}	62{58}
RbX	16(26)	25{31}	75{69}	16{24}	84{76}
CsX	24(41)	13{17}	87{83}	6{12}	94{88}
TiX	98(88)	<1{<1}	>99{>99}	<1{<1}	>99{>99}
Sensitizer	Loading level <sup>d</sup>				
Acetophenone in KY	25	5	95	1	99
	40	11	89	2	98
	85	25	75	5	95
4-Methoxy acetophenone in KY	25	<1	>99	<1	>99
	40	4	96	<1	>99
	85	13	87	<1	>99
$\alpha$ -Aminoaceto phenone HCl	25	8	92	5	95
	40	16	84	10	90
Xanthone in KY	25	5	95	2	98
	40	8	92	2	98
	85	20	80	23	77

<sup>a</sup> Slurry irradiations (hexane as solvent) were carried out for 2 h. Solid state irradiations were carried out for 20 h. Conversions are comparable since all irradiations were conducted under identical conditions.

<sup>b</sup> Numbers in bracket are for solid state irradiations.

<sup>c</sup> Numbers in parentheses are for zeolite co-adsorbed with water.

<sup>d</sup> Loading levels refer 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.

**Table 2.** Product distribution upon photolysis of benzobarrelene (**5**)

Medium	Conversion (%)	Slurry <sup>a,b</sup> (%)		Solid <sup>a,b</sup> (%)	
		6	7	6	7
Hexane		96	4		
Sens <sup>c</sup>		0	100		
LiX	70(31)	90	10	95	5
NaX	64(25) <sup>d</sup>	95	5	93	7
KX	74(13)	89	11	82	18
RbX	76(20)	90	10	84	16
CsX	63(25)	86	14	82	18
TiX	79(25)	8	92	5	95
Sensitizer	Loading level <sup>e</sup>				
Acetophenone in KY	13	17	83	6	94
	25	27	73	8	92
	40	47	53	12	88
4-Methoxy acetophenone in KY	13	10	90	1	99
	25	34	66	2	98
	40	51	49	20	80
$\alpha$ -Aminoaceto phenone Hcl in KY	13	39	61	18	82
	25	54	46	63	37
Xanthone in KY	13	21	79	5	95
	25	44	56	18	82
	40	68	32	28	72

<sup>a</sup> The product ratios are independent of % conversion within the estimated error limits of  $\pm 2\%$  and represent an average of at least 5 independent runs.

<sup>b</sup> Slurry irradiations were conducted in hexane for 2 h. Solid irradiations were carried out for 8 h.

<sup>c</sup> Acetophenone sensitization in hexane solution.

<sup>d</sup> Numbers in parentheses are for solid state irradiations.

<sup>e</sup> Loading levels refer 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.

**Table 3.** Product distribution upon irradiation of dibenzobarrelenes **1b** and **1c** under dry conditions

Medium	Conversion (%) <sup>a,b</sup>	Slurry <sup>c</sup>			Solid <sup>c</sup>		
		2b/c	3b/c	4b/c	2b/c	3b/c	4b/c
<b>Reactant 1b</b>							
Acetonitrile		95	4	1			
Acetone		–	55	45			
LiX	40(29)	21	74	5	36	29	35
NaX	36(24)	29	58	13	60	38	2
KX	43(15)	51	39	10	68	31	1
RbX	46(36)	20	66	14	22	57	21
CsX	54(11)	3	78	19	26	72	2
TiX	34	<1	>99		<1	>99	
<b>Reactant 1c</b>							
Acetonitrile			73	25	2		
Acetone		–	65	35			
LiX	12(8)	21	71	8	30	66	4
NaX	14(2)	45	55	3	51	46	3
KX	68(14)	55	44	1	67	23	10
RbX	73(47)	18	78	4	12	77	11
CsX	37(37)	12	82	6	10	83	7
TiX	87(52)	<1	>99		<1	>99	

<sup>a</sup> Loading level refers to number of available supercages per single molecule of the substrate/sensitizer. For direct irradiations, loading level was kept near 25 (20–25), i.e. one molecule per 25 supercages.

<sup>b</sup> Numbers in bracket are for solid state irradiation.

<sup>c</sup> Slurry irradiations (hexane as solvent) were carried out for 2.5 h. Solid state irradiations were carried out for 20 h. Conversions are comparable since all irradiations were conducted under identical conditions.

in nearly 1:1 ratio. Consistent with the conclusion that the *trans* dimer comes from the triplet state, irradiation of the RbY samples under oxygenated conditions gave only the *cis* dimer. Also, when the triplet quencher ferrocene was co-included (along with acenaphthylene) within RbY the *trans* dimer was selectively quenched (Table 4). These suggested that while in LiY acenaphthylene reacts only from S<sub>1</sub>, within RbY dimerization occurs from both S<sub>1</sub> and T<sub>1</sub>. Further confirming the role of heavy cation in favoring the *trans* dimerization the ratio of *trans* to *cis* dimer was

**Table 4.** Photodimerization of acenaphthylene within zeolites dependence of *cis* to *trans* dimer ratio on the condition of irradiation

Zeolite	Condition <sup>a,b</sup>	<i>cis/trans</i> Dimer ratio
	Hexane solution, 5 mg in 5 mL	<i>cis</i> only
LiY		16(25) <sup>c</sup>
NaY		2.3(25) <sup>c</sup>
KY		1.6(25) <sup>c</sup>
RbY		0.6(25) <sup>c</sup>
CsY		1.1(6.0) <sup>c</sup>
RbY	Ferrocene, 20 <sup>d</sup>	1.9
RbY	Ferrocene, 10 <sup>d</sup>	3.2
RbY	Ferrocene, 5 <sup>d</sup>	4.3
RbY	Ferrocene, 2 <sup>d</sup>	8.0
NaY	0% Cs <sup>+</sup>	25
NaY–CsY	0.1% Cs <sup>+</sup>	22
NaY–CsY	1.0% Cs <sup>+</sup>	18
NaY–CsY	8.0% Cs <sup>+</sup>	3.3

<sup>a</sup> Loading level of acenaphthylene in all cases was maintained at one molecule per five supercages.

<sup>b</sup> All irradiations were conducted as solid samples under deaerated conditions; for exception see footnote c.

<sup>c</sup> Numbers in parenthesis refers to irradiation under oxygen-saturated conditions.

<sup>d</sup> The number refers to loading level, which is defined as number of supercages per molecule. The number 10 means 1 molecule per 10 supercages.

found to depend on the % of Cs<sup>+</sup> ion content in NaY (Table 4). While in NaY the ratio of *cis* to *trans* dimer was 25, that in 8% Cs<sup>+</sup> exchanged NaY was 3.3. These observations suggest that the heavy cation such as Rb<sup>+</sup> and Cs<sup>+</sup> favor the production of triplet acenaphthylene.

Unlike reactants **1**, **5** and **8** there was no significant difference in product distribution upon photolysis of β,γ-unsaturated ketones **11**, **14** and **17** included in KX and TiX (Table 5). In these systems even the heavy Ti<sup>+</sup> ion failed to produce significant amount of oxa-di-π-methane rearrangement product that is believed to derive only from T<sub>1</sub> (ππ\*). This prompted us to examine the triplet sensitization technique within zeolites. Triplet sensitization experiments were conducted for substrates **1**, **5**, **11**, **14** and **17** in KY zeolite using acetophenone, 4-methoxy acetophenone, xanthone and α-aminoacetophenone hydrochloride as sensitizers. In these experiments, only two products were formed, one from S<sub>1</sub> and the other from T<sub>1</sub>. To monitor the efficiency of triplet energy transfer all samples were irradiated under identical conditions for the same length of time. We wish to highlight that sensitization occurs even under very low loading levels and sensitization is a reliable technique by which triplets of organic molecules could be produced within a zeolite. Results of these sensitization experiments are included in Tables 1, 2 and 5. In these tables, loading level corresponds to the number of supercages available for one molecule of the substrate and the sensitizer. For substrates **1** and **5**, it was evident that even at very 'low' loading levels like 85 (one molecule of the reactant and one molecule of the sensitizer per 85 supercages) yield of the triplet product was still very high within zeolites, suggesting efficient sensitization. 4'-Methoxy acetophenone was found to be the best sensitizer among the ones investigated. For example, even at a low loading level of 85, 87% triplet product yield was obtained during the photolysis of dibenzobarrelene (**1**) as a hexane slurry (Table 1). For the same loading level, triplet product yields were 75, 84 and 80 with acetophenone, α-amino acetophenone hydrochloride and xanthone as sensitizers (Table 1). In general, sensitization was more effective in the solid state than in hexane slurry. For example, at a loading level of 25, with 4'-methoxy acetophenone as the sensitizer, yield of the triplet product from **5** was 98% in the

**Table 5.** Product distribution upon irradiation of β,γ-unsaturated ketones **11**, **14** and **17** within zeolites under direct and sensitized conditions

Reactant	Conditions for irradiation	Product (%)	
		<b>12</b>	<b>13</b>
<b>11</b>	KX	>99	< 1
	TiX	89	11
	KX with 4-methoxy acetophenone	3	97
<b>14</b>		<b>15</b>	<b>16</b>
	KX	>99	< 1
	TiX	>99	< 1
<b>17</b>	KX with 4-methoxy acetophenone	18	82
		<b>18</b>	<b>19</b>
	KX	75	25
	TiX	79	21
	KX with 4-methoxy acetophenone	19	81

solid state, while it was only 66% in the slurry mode (Table 2). As shown in Table 5, the triplet sensitization technique satisfactorily worked also for  $\beta,\gamma$ -unsaturated ketones **11**, **14** and **17**. Thus triplet sensitization is fairly general within zeolites. To examine whether the sensitization occurs by a dynamic or a static process, the triplet lifetime of the sensitizer 4'-methoxy acetophenone was monitored (by following the decay of the triplet-triplet absorption of 4'-methoxy acetophenone, 350–450 nm) with increasing concentration of the quencher benzobarrelene. The triplet lifetime decreased in a linear fashion from 16 to 2.1  $\mu\text{s}$  when the loading level of benzobarrelene was varied between 0 molecule and 1 molecule per five supercages.

### 3. Discussion

#### 3.1. Heavy atom effect

As seen in Table 2, in the case of benzobarrelene, the percentage of benzosemibullvalene (triplet product) increased from 5% in NaX to 92% in TiX. Similarly, for **1a**, within wet zeolites the yield of dibenzosemibullvalene (triplet product) increased from 20% in LiX to 99% in TiX under slurry irradiations and from 43 to 99% under solid irradiation conditions (Table 1). Similar observations were also made with substituted dibenzobarrelenes (Table 3). The observed abundance of semibullvalenes as photoproducts in heavy cation exchanged zeolites, we believe, is the result of enhanced intersystem crossing rates in presence of heavy cations such as  $\text{Cs}^+$  and  $\text{Ti}^+$ . The increase in intersystem crossing (and the yield of triplet product) between  $\text{Li}^+$  and  $\text{Ti}^+$  exchanged zeolites is consistent with the difference in spin-orbit coupling parameter for the corresponding atoms ( $\text{Li}$ :  $0.23\text{ cm}^{-1}$  and  $\text{Ti}$ :  $3410\text{ cm}^{-1}$ ).<sup>9</sup> Examination of the photobehavior (especially under wet conditions) of dibenzobarrelene (Table 1) in various alkali ion exchanged zeolites reveal that the relative yield of the triplet product is dependent on the spin-orbit coupling parameter of the cation. The amount of triplet product increases in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Ti}^+$ . It is important to note that the spin-orbit coupling parameter for the corresponding atoms also increase in the same order ( $0.23, 11.5, 38, 160, 370$  and  $3410\text{ cm}^{-1}$ , respectively).<sup>9</sup> Similar observations were made with dibenzobarrelenes **1b** and **1c** (Table 3). However, in the case of benzobarrelene only  $\text{Ti}^+$  was most effective in bringing about triplet reactivity.

Results obtained with acenaphthylene establish unequivocally that the heavy cations present in zeolites could be used to control triplet production. Photolyses of dry solid inclusion complexes of acenaphthylene in various cation ( $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$ ) exchanged Y zeolites gave the *cis* and *trans* dimers. As seen in Table 4, the *cis* to *trans* dimer ratio is dependent on the cation. Absence of the *trans* dimer in LiY and NaY is consistent with the solution behavior in which the intersystem crossing yield from  $\text{S}_1$  to  $\text{T}_1$  is reported to be near zero ( $\Phi=0.00\pm 0.02$ ).<sup>6</sup> Exclusive formation of the *cis* dimer within LiY and NaY suggests that in these media the excited singlet state is trapped by the ground state acenaphthylene prior to intersystem crossing to the triplet state. Formation of the *trans* dimer in K, Rb and CsY is consistent with the expectation that the rate of

intersystem crossing from  $\text{S}_1$  to  $\text{T}_1$  would be enhanced in these media. Supporting the conclusion that the *trans* dimer is derived from  $\text{T}_1$ , its formation within RbY is quenched by the triplet quenchers oxygen and ferrocene (Table 4). The possibility of an enhanced heavy atom effect within the constrained zeolite cages has been previously established through photophysical studies.<sup>4</sup> Examples presented above establish that the same effect could also be employed to control photoproduct distributions.

While the heavy cation effect worked nicely with molecules containing aromatic and olefinic chromophores, it failed in the case of enones **11**, **14** and **17**. In these cases, the relative yields of products due to oxa-di- $\pi$ -methane rearrangement are an indication of the effectiveness of the heavy cations. Similar product distributions obtained within KX and TiX suggest that the heavy cation  $\text{Ti}^+$  is unable to enhance the rate of intersystem crossing with respect to  $\alpha$ -cleavage reaction from  $\text{S}_1$ . Given that the primary intermediate formed via the  $\alpha$ -cleavage process is an allyl radical, the rate of  $\alpha$ -cleavage in  $\beta,\gamma$ -unsaturated ketones **11**, **14** and **17** (Scheme 1) from  $\text{S}_1$  must have high rates. Further, considering the rules of intersystem crossing rates ( $\text{S}_1$  to  $\text{T}_1$ ) in organic molecules formulated by El Sayed, absence of heavy cation effect in  $\beta,\gamma$ -unsaturated ketones is not a surprise.<sup>10</sup> The rate of intersystem crossing from  $\text{S}_1$  to nearby triplet is inherently larger when the states involved have different characters ( $n\pi^*$  and  $\pi\pi^*$ ). In  $\beta,\gamma$ -unsaturated ketones the intersystem crossing is believed to be between  $\text{S}_1$  ( $n\pi^*$ ) and triplet of mixed  $n\pi^*$  and  $\pi\pi^*$  character.

#### 3.2. Triplet sensitization within zeolites

By using the heavy cation effect we could not improve the yields of the triplet products in the case of  $\beta,\gamma$ -unsaturated ketones **11**, **14** and **17** (Scheme 1) within zeolites. This prompted us to explore a general method that would enable one to produce triplets of all classes of molecules within zeolites. With this in mind we have examined the triplet sensitization of barrelenes and  $\beta,\gamma$ -unsaturated ketones within KY (Tables 1, 2 and 5). As seen from the results presented in Tables 1 and 2 sensitization is very efficient within zeolites.<sup>11</sup> The triplet sensitization technique satisfactorily worked also for  $\beta,\gamma$ -unsaturated ketones **11**, **14** and **17**. Loading level in the tables refers to the number of supercages per reactant and sensitizer molecules. Energy transfer was efficient (87% triplet product from **1a**) even at loading levels of one molecule of the sensitizer and substrate in 85 supercages. Generally, solid state irradiations were more efficient than slurry irradiations. For example, at the same loading level of 85, with 4'-methoxy acetophenone as the sensitizer, solid irradiation of **1a** gave 99% of the triplet product while slurry irradiation yielded only 87%. Of the four sensitizers used 4'-methoxy acetophenone was most effective. A point to note is that the only other product formed under the sensitization conditions was that from  $\text{S}_1$ .

Qualitatively, there could be three factors contributing to the observed efficiency of energy transfer within zeolites: intrazeolite diffusion of the donor and the acceptor, long triplet lifetime of the sensitizers and selective donor-acceptor aggregation in the same supercage. Importance of



diffusion in the process of energy transfer is revealed by the transient studies where the lifetime of the triplet of 4'-methoxy acetophenone was monitored in presence of benzobarrelene. The triplet lifetimes were 16, 14, 12, 8.1 and 2.1  $\mu\text{s}$  at 0, 0.02, 0.04, 0.07 and 0.2 molecules per supercage. If the energy transfer occurs via a static process the lifetime of the donor 4'-methoxy acetophenone would not be influenced by variation in the loading level of benzobarrelene. The fact that the triplet lifetime of 4'-methoxy acetophenone within KY was dependent on the loading level of benzobarrelene suggests that the energy transfer process was taking place predominantly via a diffusion-controlled processes. At a loading level of 1 molecule of the sensitizer and 1 molecule of the acceptor in 80 cages, the two are expected to be separated by  $\sim 40 \text{ \AA}$ .<sup>12</sup> At this loading level the two molecules would have to travel  $\sim 15 \text{ \AA}$  before energy transfer can occur. The details of energy transfer phenomenon within zeolites will be addressed in a future publication.

The importance of intrazeolite diffusion was suggested also by the results of different sensitizers under solid and slurry conditions. Both xanthone and  $\alpha$ -amino acetophenone hydrochloride would not be expected to be very mobile within a zeolite; the former due to size and the latter due to ionic interaction with the surface. Implying that diffusion is important for efficient energy transfer the yields of triplet product from **5** at a loading level of 13 under identical conditions of irradiation were 61 and 79% with  $\alpha$ -amino acetophenone hydrochloride and xanthone as sensitizers, while with 4'-methoxy acetophenone the yield was 90%. Due to reduced mobility of the acceptor and the sensitizer in presence of solvent molecules sensitization was less effective during slurry irradiations.

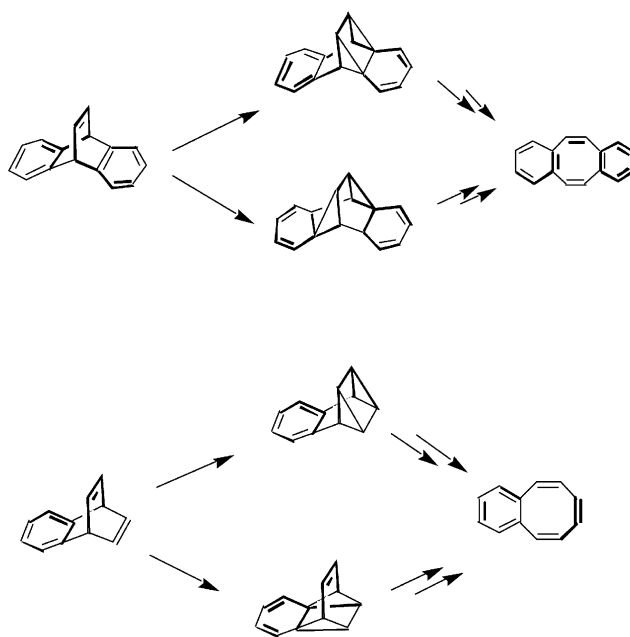
### 3.3. Light atom effect

Based on the photobehavior of aromatics and olefins we expected that dibenzobarrelene would not yield products from the triplet state in light cation exchanged zeolites. On the contrary, we isolated larger than expected amounts of dibenzosemibullvalenes, the triplet derived products, from three dibenzobarrelene systems in LiX and NaX than in KX. For example, during solid state irradiation of **1a** included in LiX, NaX and KX the yields of dibenzosemibullvalene were 82, 75 and 62%, respectively. A similar trend was observed also during slurry irradiations in X zeolites (67, 62 and 47%) (Table 1). Perusal of Table 3 indicates that substituted dibenzobarrelenes **1b** and **1c** also show a similar trend. The decreasing trend (as opposed to the increasing trend based on heavy cation effect) in the triplet product yield from Li<sup>+</sup>X to K<sup>+</sup>X zeolites in all three systems suggested that the cation binding to dibenzobarrelenes is likely to play an important role in this process. Importance of cation–dibenzobarrelene interaction became apparent when the irradiation was conducted in presence of co-adsorbed water molecules. As would be expected based on classical heavy atom effect the yield of the triplet product increased: LiX, 43%; NaX, 56%; KX, 58%; RbX, 76%; CsX, 88% and TlX 99% (solid irradiation). The above phenomenon of increased triplet product formation in presence of Li<sup>+</sup> and Na<sup>+</sup> is unusual and in the absence of a better term we call this the 'light atom effect'. An important point to note is that

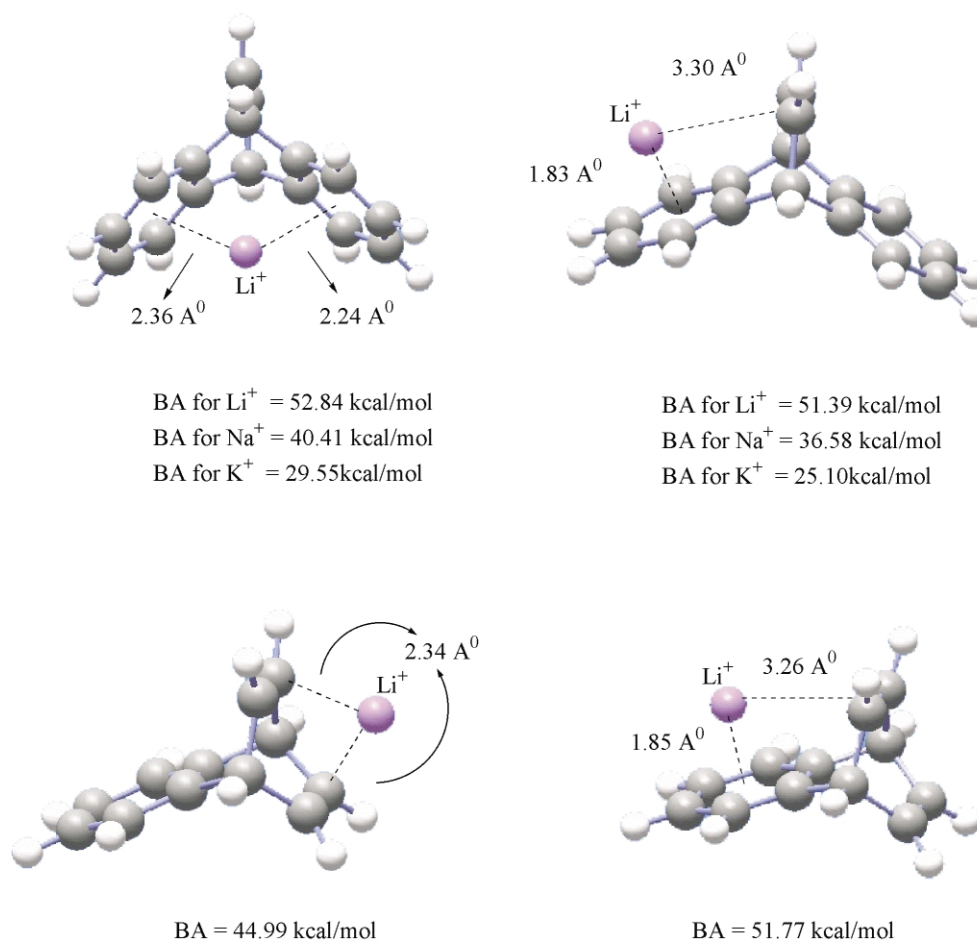
the 'light atom effect' did not operate in the case of benzobarrelene.

Any discussion of the likely origin of the light atom effect in the case of dibenzobarrelene should also address absence of it in the case of benzobarrelene. The increased yield of triplet product could either be due to the increased rate of intersystem crossing from S<sub>1</sub> to T<sub>1</sub> or due to the decreased rate of the rearrangement in S<sub>1</sub>. In the absence of any known mechanisms by which light cations could increase the rate of intersystem crossing from S<sub>1</sub> to T<sub>1</sub>, we believe that increased yield of triplet product formation is due to the decreased rate of rearrangement of dibenzobarrelene to dibenzocyclooctatetraene from S<sub>1</sub>. Proposed mechanisms for conversion of dibenzobarrelene to dibenzocyclooctatetraene shown in Scheme 2 involve initial benzo–vinyl bridging.<sup>5,13</sup> On the other hand, the rearrangement of benzobarrelene to benzocyclooctatetraene could proceed via either benzo–vinyl bridging or vinyl–vinyl bridging (Scheme 2).<sup>14</sup> Clearly benzobarrelene has an additional pathway (vinyl–vinyl bridging), which is lacking in dibenzobarrelene.

In order to explore whether the cation–aromatic/olefin  $\pi$  interaction within zeolites is responsible for the decreased reactivity in S<sub>1</sub>, we computed the structures of Li<sup>+</sup> complex with benzobarrelene and dibenzobarrelene at RB3LYP/6-31G(d) level.<sup>15</sup> The computed structures are shown in Figure 1. In the case of benzobarrelene two structures were identified. The one where Li<sup>+</sup> is interacting with the aryl part is much more stable than the one in which Li<sup>+</sup> is interacting with the vinyl part. Further, Li<sup>+</sup> binds preferentially to the phenyl rather than co-operatively to both phenyl and vinyl chromophores. Assuming that within zeolites the same trend prevails, benzobarrelene would be bound within zeolites through Li<sup>+</sup>···phenyl interaction and the vinyl parts would not be influenced by the cation. Such type of ion-bound benzobarrelene would be expected to react equally efficiently through vinyl–vinyl bridging as the



Scheme 2.



**Figure 1.** Optimized structures for  $\text{Li}^+$  complexes of dibenzobarrelene (top) and benzobarrelene (bottom) at RB3LYP/6-31G(d) level. Binding affinities are included at the bottom. Two structures were identified in each case.

unbound benzobarrelene. Because of this one would not expect the light cations to influence the rate of the rearrangement of benzobarrelene to benzocyclooctatetraene. This prediction is consistent with the observed results. On the other hand, in the case of dibenzobarrelene two structures nearly of equal energies were computed (Fig. 1). In one  $\text{Li}^+$  interacts selectively with one phenyl group and in the other co-operatively with both phenyl groups. Reactivity of the phenyl groups in both structures would be lower than that in free dibenzobarrelene. We believe that such a reduction in reactivity could enhance the triplet yield and thereby favor the formation of benzosemibullvalene at the expense of dibenzocyclooctatetraene. The computed binding energies of the alkali ion to dibenzobarrelene decrease in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  (Fig. 1). One would expect the influence of the cation to decrease in the same order as the binding energy. The yields of dibenzosemibullvalene within dry  $\text{LiX}$ ,  $\text{NaX}$  and  $\text{KX}$  follow the expected trend (Table 1). The above gas phase computational data provide a clue to what is likely to be responsible for the observed enhancement of triplet products within light alkali cation exchanged zeolites. While one might question the validity of using gas-phase computational data to understand the chemistry that occurs within a more complex environment, we believe that this is a good starting point.

We have recently established that light cation effect also

operates in the case of carbonyl systems.<sup>16,17</sup> Light cations such as  $\text{Li}^+$  and  $\text{Na}^+$  preferentially bind to the carbonyl chromophore and by so doing alter the nature of the lowest excited state. For example alkali ion bound acetophenone has  $\pi\pi^*$  as the lowest triplet whereas, the cation free acetophenone has  $n\pi^*$  state as the lowest triplet. Similar phenomenon was also established in the case of  $\alpha,\beta$ -unsaturated enones.<sup>17</sup> No detailed calculations were performed to establish that this is occurring in  $\beta,\gamma$ -unsaturated ketones. A likelihood of this possibility has been suggested earlier.<sup>18</sup>

#### 4. Conclusion

Heavy atom effect, light atom effect and sensitization methods have been explored to generate the excited triplet states of organic molecules within zeolites. Heavy atom effect as expected worked well with two systems whose excited states have  $\pi,\pi^*$  character. Sensitization, a technique commonly employed to generate the triplet states of organic molecules in isotropic media works well with several systems within zeolites. The light atom effect unique to dibenzobarrelenes, having limited potential, is mechanistically interesting. Our studies in zeolites continue to bring out the importance of alkali ion-organic interactions in controlling excited state chemistry.

## 5. Experimental

NaY and NaX zeolites were obtained from Aldrich. Monovalent cation exchanged ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Tl}^+$ ) zeolites were prepared by stirring 10 g of NaY or NaX with 100 mL of a 10% aqueous solution of the corresponding metal nitrate for 12 h with continuous refluxing. The zeolites were filtered and washed thoroughly with distilled water. This procedure was repeated for three times. The cation exchanged zeolite was then heated in an oven at 120° C for about 6 h. Acetophenone, 4'-methoxy acetophenone, xanthone and  $\alpha$ -aminoacetophenone hydrochloride and ferrocene were used as obtained from Aldrich. Acenaphthylene (Aldrich) was recrystallized thrice from ethanol prior to use. Commercially available metal nitrates were used for exchanging the zeolites.

Dibenzobarrelenes (**1a–c**), benzobarrelene (**5**), 5-norbornen-2-one (**11**), bicyclo[2.2.2]octenone (**14**), and 3-methyl-3-(cyclopent-1-enyl)butan-2-one (**17**) were prepared following literature procedures.<sup>19</sup> Spectral data of photoproducts from **1a–c**, **5**, **8**, **11**, **14** and **17** prepared by solution irradiation were compared with that of authentic samples reported in the literature.<sup>6,20</sup> The photoproducts thus prepared and identified were used to identify the peaks in the GC traces.

### 5.1. Photolysis procedures

The procedures adopted for the irradiation of barrelenes, and  $\beta,\gamma$ -enones were the same. Therefore, a general procedure is provided below.

### 5.2. Direct irradiation—slurry mode

The reactants (2–5 mg) were stirred with 300 mg of activated (500°C overnight under aerated conditions)  $\text{M}^+\text{Y}$  or  $\text{M}^+\text{X}$  zeolite in 10 mL of hexane for about 10 h. The zeolite was washed twice with 10 mL portions of hexane and the combined washings were concentrated and analyzed. Absence of the reactants in the washings was taken to indicate that it has been included into the zeolite. Reactant– $\text{M}^+\text{Y}$  complex was irradiated, as a slurry, in 4 mL of hexane after purging with nitrogen for 15 min. It was then extracted with 20 mL of diethyl ether for a period of 5 h and the concentrated ether extract was analyzed by GC (Hewlett–Packard 5890 series II fitted with HP5 capillary column). Absence of either the starting material or the photoproducts in the hexane portion after irradiation, excluded the possibility of any of them escaping the cage during the slurry irradiation. The material balance in all cases was >90%.

### 5.3. Direct irradiation—solid phase

For solid irradiations, the zeolite after stirring in hexane was filtered and washed with hexane. The solid complex thus obtained was degassed on a vacuum line ( $10^{-4}$  Torr) for more than 10 h and the dry powder was irradiated by exposing new surface every 30 min by manually rotating the sample tube. Rest of the procedure was the same as above.

### 5.4. Direct irradiation under 'wet' conditions

For experiments where 'wet' zeolites were used, water was co-adsorbed into the reactant loaded zeolite sample using the following procedure: The dry zeolite adsorbed with the reactant molecules was placed on a piece of weighing paper (10 cm×10 cm) on a balance. A 50 mL beaker full of water was placed next to the zeolite sample. After 7 mg of water was absorbed by the zeolite (corresponding to a loading level of 3 molecules of water per supercage), the sample was transferred to fresh hexane, purged with nitrogen and photolyzed as hexane slurry. Rest of the procedure was the same as above.

### 5.5. Sensitization experiments

Known amount of the sensitizer and activated (450°C, air oven) zeolite (300 mg) KY were stirred in hexane, filtered, washed with excess hexane and dried under reduced pressure ( $10^{-4}$  Torr). In case of  $\alpha$ -aminoacetophenone hydrochloride the sensitizer was first exchanged into the zeolite using the cation exchange procedure described under materials. Above sensitizer loaded zeolite was used to adsorb the reactants **1** and **2**. Known amounts of the reactants and 300 mg of the zeolite–sensitizer composite were stirred for 6 h, filtered, washed with hexane and dried. The loading level of the sensitizer to the substrate was always maintained at 1:1. The dried samples were then irradiated (450 W medium pressure mercury lamp, pyrex vessels) as a solid (solid irradiation) or as slurry in hexane (slurry irradiation). The hexane slurry was purged thoroughly with nitrogen before photolysis. Irradiations were carried out to about 30% conversion in all cases. This conversion was achieved in 2 h with slurry irradiations, 8 h with the solid irradiations. Rest of the procedure was the same as above.

### 5.6. Irradiation of acenaphthylene included in zeolites

Acenaphthylene and dried zeolites (furnace 500°C overnight) were stirred in trimethylpentane for about 10 h. Slightly yellowish solids were collected by filtration, washed with hexane and dried under nitrogen stream. These were degassed under vacuum (10–4 mm) and irradiated with two 450 W mercury lamps for 2 h. Samples were stirred by rotation every 30 min. Acenaphthylene dimers were extracted with ether and drops of con. HCl stirring overnight. Samples were analyzed by GC. Samples were also irradiated under oxygen. For this purpose, oxygen was admitted to the degassed samples on a vacuum line.

Irradiation of acenaphthylene in presence of ferrocene: complexes of acenaphthylene (5 mg) in hexane with Rb Y (250 mg) was prepared by stirring in hexane for an hour. The color due to acenaphthylene molecules (ANY) were not seen in solution and this observation led us to believe that all acenaphthylene molecules were adsorbed within zeolites. At this stage ferrocene was added from stock solution corresponding to 0, 2, 4, 6, 8, 10 mg and stirred. Solid complexes were collected by usual filtration etc. and diffuse reflectance spectra recorded. Spectra revealed the presence of both ANY and ferrocene inside. Samples degassed in two tubes (125 mg each) and irradiated for



3.5 h. Dimer isolated by acid/ether extraction and analyzed by GC.

Laser flash photolysis of zeolite samples: laser flash photolysis studies were carried out at National Research Council of Canada, Ottawa in the laboratory of L. J. Johnston. The experimental set up and procedure was provided by L. J. Johnston and K. J. Thomas. The laser flash photolysis system used for diffuse reflectance studies was equipped with a Lumonics EX-510 excimer laser (XeCl, 308 nm, 6 ns/pulse; <30 mJ/pulse) for sample excitation (located at the laboratory of L. J. Johnston, National Research Council of Canada, Ottawa). A pulsed 75-W xenon lamp with a PTI housing and power supply was used as the monitoring beam. The diffusely reflected analyzing beam was collected and focused on the entrance slit (typically 1.5 mm) of a Digikron 240 monochromator. It is important to ensure that the specular reflections from both the lamp and laser do not strike the collection lense. A Burle 4840 photomultiplier tube in a six-dynode stage housing was attached to the exit slit of the monochromator. A home built computer controlled power supply was used with the photomultiplier. The signal from the photomultiplier was connected via 93 ohm cable (with two 93-ohm terminators) to a back-off circuit, which measures the light intensity before the laser pulse and then offsets the voltage to zero. The signal then goes to a Tektronix 7912 AD digitizer equipped with 7A16P amplifier and 7B90P time base plug-ins. The digitizer is connected via a GPIB interface to a PDP 11/55 computer for data storage and processing. A Stanford Research Systems digital delay/pulse generator (DG235) provided TTL trigger pulses to control the timing for the laser, lamp and digitizer. Scimetrics Instruments Labmate data acquisition and control system is used to read voltages and provide TTL pulses to open and close shutters.

The zeolite samples were dried before the laser experiments. The zeolite samples were taken in 3×7 mm<sup>2</sup> quartz cells and were purged with either nitrogen or oxygen immediately prior to laser excitation. These samples were moved in the cell holder and shaken frequently in order to provide fresh zeolite surface and minimize complications due to product formation. For each transient profile, five or more laser shots were averaged. Benzobarrelene possesses no significant absorption at 308 nm. The absorption due to the substrate was minimal in all studies. This was confirmed by exciting zeolite samples containing the substrate at the highest concentration in the absence of sensitizer. Such experiments did not yield any signal indicating that no transients are formed by the direct excitation of the substrates. *p*-Methoxyacetophenone was used as the sensitizer for the energy transfer experiments. The zeolite used was KY for all these experiments. All the measurements were repeated until consistent readings were obtained. The concentration of benzobarrelene for these studies were found to be from 0.02 and 0.2 molecules per superpage. The concentration of sensitizer was kept at 0.02 molecules per superpage for all quencher concentrations.

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