Communications to the Editor

Organic Reactions in Zeolites. 1. Photooxidations of Sulfides in Methylene Blue Doped Zeolite Y

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The use of zeolites during photochemically initiated oxidations of hydrocarbons with both singlet[1−3] and triplet oxygen[4−11] has recently been reported. These studies were inaugurated with the expectation that the restricted space and high internal electrostatic fields present in these microscopic reaction vessels would dramatically affect these reactions which proceed, in many cases, via polar intermediates with significant charge separation. These expectations have been realized. Frei and co-workers[5−10] have demonstrated that the high electrostatic fields in the supercages of zeolite Y significantly stablize oxygen/olefin charge-transfer complexes allowing irradiation with visible rather than with ultraviolet energy, thereby enhancing the selectivity of the oxidation. Ramamurthy and co-workers[1,2] have demonstrated that the restricted space in zeolites can be used to direct singlet oxygen selectively to one face of an olefin. Tung and co-workers[3] have shown that zeolites can be used to restrict approach of the sensitizer to olefins and dienes and amplify singlet oxygen at the expense of electron transfer initiated photooxidation pathways. We report here that zeolites can also modify the selectivity of sulfide photooxidations and initiate oxidations which have no solution counterpart.

Photooxidations of pentamethylene sulfide, **1**, thiolane, **2**, and diphenyl sulfide, **3**, were conducted by adding 0.3 g of dry Methylene Blue (MB) exchanged NaY,[12] with an average occupancy ($\langle S \rangle$) of 0.0015 or 0.01 molecules of MB per supercage, to 5 mL of hexane containing the substrate. The hexane slurries were saturated with oxygen and stirred for 15 min and then irradiated under continuous oxygen agitation with a 600 W tungsten−halogen lamp for 1 h through 1 cm of a 12 M NaNO$_2$ filter solution. The products were isolated by continuous extraction (3 h) with THF and analyzed by gas chromatography. The mass balances were greater than 98% in all cases.

The sulfoxide, **1SO**, and the sulfone, **1SO$_2$**, are formed during photooxidations of **1** in both the zeolite (Table 1) and homogeneous solution (CH$_3$CN). However, the sulfone/sulfoxide ratio

Table 1. Photooxidations of **1** in NaY/MB ($\langle S \rangle = 0.0015$)

[**1**], M[a]	% adsorption	n^b	% conversion	[**1SO$_2$**]/[**1SO**]
0.01	97.0	0.26	100	53.6/46.4
0.02	96.1	0.51	91.6	46.0/54
0.04	97.5	1.04	100	31.8/68.2
0.07	94.3	1.75	12.0	11.6/88.4
			(80.5)[c]	(17.9/82.1)[c]
0.10	96.0	2.57	4.6	12.8/87.1
			(59.0)[c]	(13.8/86.2)[c]

[a] Concentration of **1** in 5 mL of hexane prior to the addition of NaY/MB. [b] n = loading level of **1** = molecules/supercage = ([**1**](volume of hexane, L)(adsorption %100)(1594 g))/(g of zeolite) where the weight of the unit cell (Na$_{56}$(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$) is 12 752 g with 8 supercages per unit cell. (12752 g/8 = 1594 g). [c] Using NaY/MB ($\langle S \rangle = 0.01$).

Scheme 1
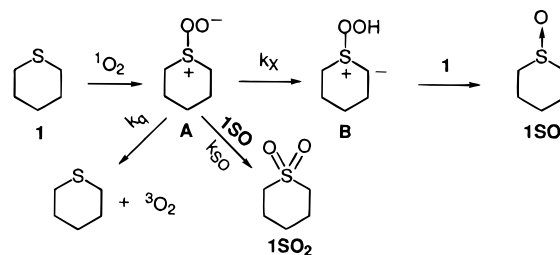
and its sensitivity to the concentrations of **1** is much greater in the zeolite than in CH$_3$CN. This phenomenon is a result of oxidation within the supercage of the zeolite rather than on its external surface since the sensitivity of the sulfone/sulfoxide ratio to the concentrations of **1** was not observed with use of MB adsorbed on silica gel as the sensitizer. The insensitivity of the sulfone/sulfoxide ratio to the concentration of **1** in CH$_3$CN (Supporting Information) is understandable in the context of the generally accepted mechanism for sulfide photooxidations depicted in Scheme 1.[13] In this scheme, the sulfide, **1**, intercepts the second intermediate and does not competitively inhibit the predominate sulfone forming pathway, k_{SO}.

The results in the zeolite, however, are inconsistent with the mechanism depicted in Scheme 1 but are consistent with competitive trapping of a single intermediate by both adventitious sulfoxide, **1SO**, and **1**. Consistent with this suggestion is the observation that the formation of **4**, which emanates from the second intermediate, **B**, by a Pummerer rearrangement during photooxidation of thiolane **2**[14] is completely suppressed in the zeolite. It appears that the persulfoxide, **A**, is stabilized in the highly electrostatic environment of the zeolite supercage and the hydrogen abstraction necessary to convert it to the second intermediate, **B**, is precluded.

Irradiation of a 0.04 M CH$_3$CN solution of diphenyl sulfide, **3**, containing 6 × 10^{-5} M MB for 1 h resulted in quantitative recovery of the starting material. This is consistent with earlier studies which took advantage of the lack of reactivity of **3** to use it as a trapping agent for peroxidic intermediates in $^1O_2$ reactions.[15] Remarkably, a 1-h irradiation of a 0.04 M hexane slurry of **3** encapsulated in NaY/MB ($\langle S \rangle$ MB = 0.01) resulted in greater than

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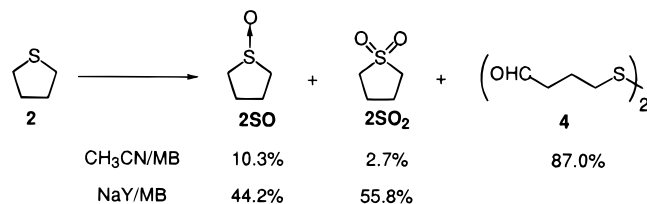(11) Myli, K. B.; Larsen, S. C.; Grassian, V. H. *Catal. Lett.* **1997**, *48*, 199−202.
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	2SO	**2SO$_2$**	**4**
CH$_3$CN/MB	10.3%	2.7%	87.0%
NaY/MB	44.2%	55.8%	

Table 2. Photooxidations of **3** in NaY/MB and in Cation Exchanged MY/MB

MY/MB[a]	[3], M[b]	[3], M[c]	% adsorption	% conversion	[3SO$_2$]/[3SO]
NaY	0.01	0.24	100	98.7	11.2/88.8
NaY	0.02	0.48	100	95.8	10.9/89.1
NaY	0.04	0.95	99.7	60.4	5.9/94.1
NaY	0.07	1.66	99.4	31.2	3.7/96.3
NaY	0.10	1.99	83.7	27.9	4.0/96.0
LiY	0.02			95.2	8.4/91.6
KY	0.02			38.3	4.8/95.2
RbY	0.02			4.8	0/100
CsY	0.02			0.5	0/100
BaY	0.02			50.8	1.4/98.6

[a] Photooxidation conducted with MB loading levels of $\langle S \rangle = 0.01$ in 5 mL hexane slurries for 1 h. *[b]* Concentration of **3** in 5 mL of hexane prior to addition of zeolite. *[c]* Concentration of **3** in the zeolite calculated using a interior volume of 0.07 mL per 100 mg of zeolite. Cozens, F. L.; O'Neill, M.; Schepp, N. P. *J. Am. Chem. Soc.* **1997**, *119*, 7583−7584.

60% conversion to a mixture of the sulfoxide and sulfone. (Table 2). We suggest that the reaction in the zeolite occurs by electron transfer from **3** to $^1O_2$ to give a sulfide radical cation superoxide ion pair that collapses to the persulfoxide.[16−18] Diphenyl persulfoxide suffers the same fate as the persulfoxides formed in the reactions of **1** and **2** and is competitively trapped by **3** and, albeit with reduced efficiency, by **3SO** (Scheme 2)

The experimental and computational data which support the mechanism depicted in Scheme 2 include the following: (1) The reaction in the zeolite did not occur in the absence of either MB or oxygen. (2) Bleaching of NaY/MB did not occur. (3) The oxidation of **3** was quenched in the presence of 2,3-dimethyl-2-butene as anticipated for a $^1O_2$ reaction. (4) The molecular volume[19] of **3** is approximately 238 Å^3 suggesting that up to 3 molecules can be accommodated in the 827 Å^3 vacant space within the NaY supercage.[20] (5) The allylic hydroperoxide formed from the reaction of $^1O_2$ with 2,3-dimethyl-2-butene was quenched by **3**. (6) The extent of reaction is a sensitive function of the identity of the cation exchanged zeolite used in the reaction, decreasing in the order LiY ≈ NaY > BaY > KY > RbY > CsY (Table 2). This is consistent with stabilization of the transition state leading to the ion pair since the electrostatic potential in the supercage decreases in the order BaY > LiY > NaY > KY > RbY > CsY.[21] The unusual behavior in BaY reflects a dichotomy between the size of the cation, which reduces the supercage free volume and decreases the rate of the reaction, and the electrostatic field, which enhances the reaction rate. A similar effect with counterion exchanged zeolites was not observed during photooxidations of **1**. (7) The competitive photooxidations of **2SO** and **3** generate **2SO$_2$** despite the fact that **2SO** does not react in the absence of **3**. Furthermore, the ratio [3SO]/[2SO$_2$] changes as a function of **3** and **2SO** as described by eq 1, which was derived for the mechanism depicted in Scheme 2.

Scheme 2

$$\frac{[3SO]}{[2SO_2]} = \frac{2 k_S [3]}{k_{SO} [2SO]} + 1 \qquad (1)$$

Factors which allow this unprecedented electron transfer initiated oxidation of **3** include the following: (1) the lack of reactivity of **3** toward $^1O_2$, (2) the very favorable reduction potential of dioxygen in the zeolite supercage, estimated to lie close to −0.4 V versus SCE,[22] (3) the rapid collapse of the sulfide radical cation superoxide ion pair to the persulfoxide that competes effectively with back electron transfer, and (4) the remarkable polarization effects in the interior of the zeolite which stabilize the ion pair.

Supporting Information Available: Diffuse Reflectance Spectra of NaY/MB at various stages of drying, plots according to eq 1, and sulfone/sulfoxide ratios for photooxidation of **1** in CH$_3$CN (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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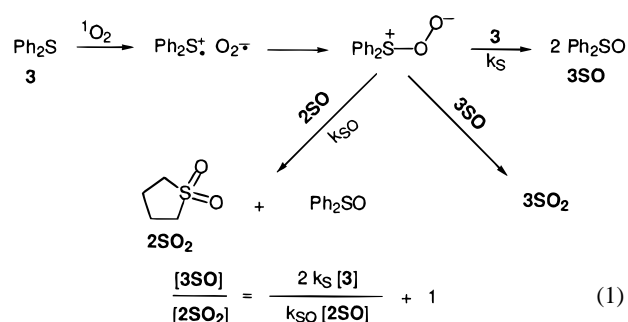(21) Vasenkov, S.; Frei, H. *J. Phys. Chem. B* **1998**, *102*, 8177−8182.
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