temperatures must indicate competition with other interfacial events likely to take place only in mixtures of nonspherical, polar, or amphiphathic molecules. Colloidal association and micellization are events of this type and the resulting buffered water-rich interface cannot be driven through the second-order transition, by means of which a phenol-rich film thickness as the two-liquid region is drawn near. The orientational arrangement that takes place at the interface only favors the formation of a monolayer and not that of a macroscopic wetting film. On the other hand, foams of phenol-water solutions are not persistent, an implication that their liquid films cannot be drained to a stable structure of two close adsorbed layers of phenol. This behavior is consistent with a bulk phase diagram that does not exhibit lamellar lyotropic liquid crystal phases. Careful observation of a foam column may develop into one of the simplest experimental methods to detect interfacial singularities associated to wetting, aggregation, micellization, and other related phenomena.

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Registry No. Phenol, 108-95-2.

# Photoassisted Oxygenation of Olefins: An Exchanged Zeolite as a Heterogeneous Photosensitizer

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 $Ru(bpy)_3^{2+}$  exchanged into zeolite Y acts as an effective, heterogeneous singlet oxygen sensitizer. The photogenerated singlet oxygen freely diffuses to solution where it reacts with normal selectivity. The photocatalyst has high catalytic turnover, and its high stability permits its reuse.

## Introduction

Heterogeneous photosensitizers have a number of practical advantages over soluble analogues. For example, sensitizer molecules held in a defined environment are site-isolated, decreasing self-quenching and side reactions. In addition, supported sensitizers can sometimes function in solvents where the dye itself is inactive and can be easily separated from the reaction mixture either by filtration or sedimentation.<sup>1</sup>

These heterogeneous photosensitizers are usually prepared in one of three ways: by covalent attachment to cross-linked polymers or other solid supports, by adsorptive immobilization on a solid surface, or by incorporation into a polymeric film. We report here the use of a heterogeneous photosensitizer prepared in an alternate way, by inclusion within a zeolitic cavity, and describe its activity in generating singlet oxygen.

Exchanged zeolites<sup>2-8</sup> have recently been investigated as heterogeneous photocatalysts. As an extension of our interest in heterogeneous photoreactions,<sup>9</sup> we have prepared zeolites exchanged with an organometallic complex,  $Ru(bpy)_3^{2+}$ , tris(2,2'-bipyridine)ruthenium(II), 1, and have studied its use as a photosensitizer.

The inclusion of 1 in a zeolite was first reported by Lunsford in 1980.<sup>7</sup> The complex was synthesized in the zeolite cavity by allowing 2,2'-bipyridine to react with  $\text{Ru}(\text{NH}_3)_6^{3+}$ -exchanged zeolite Y. The spectroscopic properties of the intrazeolitic complexes were similar to those exhibited by 1 complexes in aqueous solution. Faulkner and co-workers studied 1 in zeolite X prepared by impregnation.<sup>8</sup> They reported that the complex stays intact and can undergo one-electon transfer with N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD), 10-phenylphenothiazine (10-PP), and tetrabromo-*o*-benzoquinone (TBBQ), maintaining solution redox properties in the zeolite cavity. The size of 10-PP prevents it from entering the zeolite pores, accounting for the different redox chemistry when compared with TMPD. The bimodal decay of the excited state in luminescence quenching studies was attributed to the complex occupying two different sites in the zeolite. These studies were directed toward the characterization of the zeolite, leaving potential photocatalytic applications unexplored.

In solution, excited **1** produces singlet oxygen,<sup>10</sup> which can then undergo an "ene" reaction with olefins to form allylic hydroperoxides.<sup>11</sup>

## **Experimental Section**

Zeolite Preparation. In accord with published procedures,<sup>12</sup> 35-60-mesh LZ-Y52 zeolite powder (Union Carbide) was stirred at room temperature for 24 h in a 7 mM solution of 1 buffered by tris(hydroxymethyl)aminomethane (pH 8.2). The exchange solution was filtered with a fine glass frit, and the filtrate was analyzed by absorption spectrophotometry. The concentration difference between the filtrate and starting solution was attributed to the exchange of the complex for Na<sup>+</sup> in the zeolite. The loading levels were also obtained by spectrophotometric analysis of the exchanged zeolites dissolved in a solution of 1 M citric and hydrofluoric acid. Filtration with a fine glass frit yielded a light yellow, exchanged zeolite that was washed with water and

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TABLE I: Product Distributions in Singlet Oxygenation of 1-Methyl-1-cyclohexene

	product yield, %		
method of singlet oxygen sensitization	OH OH	Ŏ-	ОН
homogeneous <sup><i>a,b</i></sup>	50	17	31
1-exchanged zeolite <sup>a,b</sup>	51	16	33
dicyanoanthracenec	53	7	40
Rose Bengal <sup>c</sup>	45	14	41
radical oxidation <sup>c</sup>	12	40	36

<sup>a</sup> Products from the sensitized reaction of 410 mg of MCH in methanol at room temperature for 20 h. <sup>b</sup> The irradiation procedure was parallel to that described in the Experimental Section for homogeneous sensitization. <sup>c</sup> Reference 15.

## methanol and then air-dried at room temperature.

General Photolysis Procedure. A methanolic solution of the desired olefin (tetramethylethylene or 1-methylcyclohexene, approximately 0.1 M) was placed in a Pyrex test tube to which was added either 1 or the exchanged zeolite.<sup>12</sup> The system was sealed with a septum, saturated with oxygen, and maintained under positive  $O_2$  pressure of 100–300 mmHg. Illumination from a Hanovia Hg–Xe lamp operated at 675 W, with a 0.5 M CuSO<sub>4</sub> filter (>310 nm) solution, was employed. The filter thus ensured the absence of direct excitation of the organic substrate. After a defined irradiation period, trimethyl phosphite (approximately 3 equiv) was added to reduce the hydroperoxides to the respective alcohols before analysis by gas chromatography.

Homogeneous reactions were sampled and analyzed directly by gas-liquid chromatography (50-m BP-1 capillary column), while the zeolite reaction required centrifugation before analysis of the soluble reaction mixture. For preparative reactions, the volume of the reaction mixture was reduced to a few milliliters and was then partitioned between water and carbon tetrachloride. After the aqueous phase was extracted with  $CCl_4$  again, the organic layers were combined and stripped of solvent for spectroscopic analysis.

### **Results and Discussion**

The reaction of tetramethylethylene (TME) gives only one product in either experiment.<sup>13</sup> The extent of a 1-h photoreaction was comparable in the homogeneous and heterogeneous reactions

(86% and 88%, respectively) as determined by gas chromatography with isoamyl alcohol as an internal standard. The products (characterized by NMR and IR spectroscopy) agreed with literature values.<sup>14</sup> Quantitative comparison of the rates of homogeneous with the heterogeneous reactions shows that the efficiency of singlet oxygen production is not hindered by the photosensitizer being held within the zeolite cavity.

In a typical experiment, millimole quantities of the olefin were oxidized on zeolites containing micromole quantities of the exchanged complex. From a worst case ratio of product to complex, we calculate catalytic turnover numbers consistently greater than 300. Furthermore, the catalyst retained a substantial fraction (90%) of its original photoactivity after repeated use. We conclude therefore that the photoreaction is catalytic and that the complex is not consumed by the redox sensitization.

The product distribution of 1-methyl-1-cyclohexene (MCH) has been used as a criterion for the generation of singlet oxygen.<sup>15</sup> Photooxygenation of MCH with 1-exchanged zeolites yields a similar distribution of the three possible products as do other singlet oxygen sensitizers (Table I). Also, the chemical yields for the zeolite-immobilized complex were similar to those obtained by the homogeneous sensitization (65% and 58%, respectively). We assume thus that singlet oxygen can diffuse from the sites within the zeolite where it is formed into solution where its usual reactivity pattern is observed.

We conclude that 1-exchanged zeolites can sensitize singlet oxygen formation. This reactive oxidant can migrate freely from the cavity and react in normal fashion with singlet oxygen traps. The advantages afforded by the zeolite-supported sensitizer are in its ease of preparation, its high reactivity and stability, and its easy removal and workup. Investigations are continuing in our laboratory to determine whether additional selectivity can be afforded by substrate size selection. We also hope to further delineate the usefulness of zeolites as organized assemblies for organic photochemistry.

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**Registry No. 1**, 15158-62-0; O<sub>2</sub>, 7782-44-7; tetramethylethene, 563-79-1; 1-methyl-1-cyclohexene, 591-49-1; 1-methyl-3-cyclohexen-1-ol, 33061-16-4; 2-methyl-2-cyclohexen-1-ol, 20461-30-7; 2-methylenecyclohexanol, 4065-80-9.

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<sup>(13) 280</sup> mg of TME was used as received from Aldrich in 30 mL of distilled methanol for a 1-h illumination at room temperature.