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A New Experimental Protocol for Intrazeolite Photooxidations. The First Product-Based Estimate of an Upper Limit for the Intrazeolite Singlet Oxygen Lifetime

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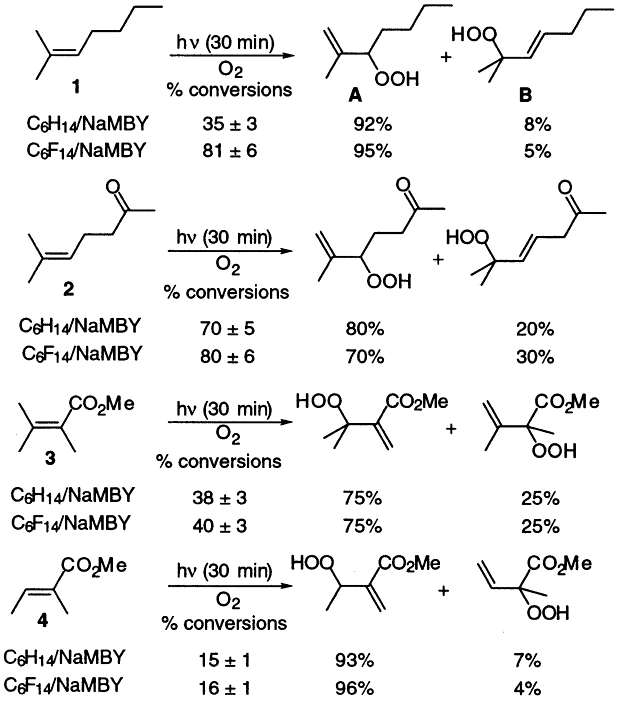
In 1996, Ramamurthy and Li[1] reported that the regioselectivity of the singlet oxygen ($^1O_2$; $^1\Delta_g$) ene reaction could be dramatically altered and enhanced by conducting the reaction in the interior of a zeolite.[2] This discovery provided an important new tool for the controlled introduction of O_2 into organic substrates.[3] It soon became apparent, however, that intrazeolite photooxidations suffer from the same experimental limitations exhibited by their homogeneous analogues.[4] In particular, intrazeolite Type I and Type II photooxidations compete, sensitizer bleaching occurs, and over-photooxidations can generate complicated reaction mixtures.

All of the previously reported intrazeolite photooxidations were conducted in hexane slurries. The disadvantages of this experimental protocol include the facts that hexane is not a chemically inert solvent[5] and that many substrates under these conditions exhibit low affinity for the interior of the zeolite. In this communication, we report the results of a study designed to explore the use of perfluorohexane slurries as an alternative reaction medium. Potential advantages of this solvent include the absence of any report of its intrazeolite chemical reactivity and its ability to enhance the lifetime of $^1O_2$.[6] In addition, the reduced solubility of organic compounds[7] in fluorinated in comparison to hydrocarbon solvents should also promote substrate migration into the zeolite.

$^{19}F/^{23}Na$ cross polarization (CP) MAS NMR has been used to convincingly demonstrate the ability of zeolite Y (NaY) to absorb hydrofluorocarbons.[8] In this study, we have used capillary column gas chromatography to demonstrate both the migration of perfluorohexane into NaY and its ability to promote absorption of the substrate 2-methyl-2-heptene, **1**. In the latter experiments, 300 mg of methylene blue-doped zeolite Y ($\langle S \rangle_{MB} = 0.01$; number of molecules of methylene blue per supercage) was added to 5 mL of a 0.04 M solution of **1**. The hexane and perfluorohexane solvents were then monitored as a function of time by capillary column gas chromatography. These studies (see Supporting Information) demonstrate that the fluorophobicity of **1** leads to a quantitative migration into the interior of the zeolite. On the other hand, the higher solubility of **1** in hexane decreases its affinity for the interior of the zeolite by 50−55%.

In contrast, similar loading studies with carbonyl containing substrates, **2**−**4**, reveal quantitative migration into the zeolite in both hexane and perfluorohexane. The higher affinity of **2**−**4** for the interior of the zeolite is presumably a function of the greater thermodynamic stabilities of the intrazeolite cation/substrate complexes. This suggestion is supported by the observation that the interaction of Li^+ with ethylene (24.3 kcal/mol) is 21 kcal/mol less favorable than that with acetone.[9]

Scheme 1. Product Ratios in Intrazeolite Photooxidations



Typical intrazeolite photooxidation conditions involved presaturation of these heterogeneous slurries (5 mL of 0.04 M substrate and 300 mg of NaMBY) with oxygen and then irradiation with a 600 W tungsten−halogen lamp under continuous oxygen agitation through 1 cm of a 12 M $NaNO_2$ 400 nm cutoff filter. After irradiation, the solvent was separated by centrifugation and analyzed by capillary gas chromatography. The zeolite powder was then extracted by stirring for a total of 9 h with three different 5 mL portions of acetonitrile. The extracts were then combined and analyzed by NMR or reduced with an excess of triphenylphosphine and analyzed by capillary gas chromatography, using in both cases triphenylmethane as an internal standard. The results from the intrazeolite photooxidation of **1**−**4** in both hexane and perfluorohexane slurries are depicted in Scheme 1.

Examination of Scheme 1 reveals that the ene regiochemistries are experimentally indistinguishable in hexane and perfluorohexane slurries. In addition, the % conversions during photooxidations of **2**−**4** under the two reaction conditions are nearly identical. Because **2**−**4** are encapsulated quantitatively and have the same intrazeolite

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Table 1. Intrazeolite Photooxidation of **1**

slurry[a]	$h\nu$ (min)	% conversion[c]	A/B[b] ratio	MB[c]
hexane	10	15	83/17	91
	20	14	98/2	97
	30	19	97/3	94
	70	35	92/8	96
perfluorohexane	10	30	93/7	88
	20	43	98/2	78
	30	62	97/3	83
	70	81	95/5	82

[a] [**1**] = 0.04 M in slurry so that $\langle S \rangle = 1.0$ in perfluorohexane and approximately 0.5 in hexane. [b] See Scheme 1 for the structures of A and B. [c] Mass balance reproducible to ±7−8%.

concentration in both reactions (vide supra), these results indicate that the reaction rates are approximately the same in hexane and perfluorohexane slurries. This is a remarkable outcome given the fact that the lifetime, τ_Δ, of $^1O_2$ is more than 2000 times longer in perfluorohexane (6.8×10^{-2} s)[10] than in hexane (3.1×10^{-5} s).[11] A control reaction in solution verifies that the % conversion is enhanced in perfluorohexane in comparison to hexane to an extent consistent with the lifetime difference (see Supporting Information).

The rate of alkene consumption is given by eq 1 and depends on the concentrations of both the alkene and the $^1O_2$. The concentration of the alkene in the interior of the zeolite at a loading level of $\langle S \rangle = 1.0$ (one molecule per supercage or eight molecules per unit cell) can be estimated from the volume of the unit cell (1.5×10^4 Å^3)[12] as 0.9 M. Under the constant irradiation conditions utilized in these photooxidations, $^1O_2$ reaches and maintains a steady-state concentration given by eq 2. In this equation, κ is the rate of $^1O_2$ formation, and k_T is the rate constant for alkene-induced removal, k_d is the rate constant for solvent-induced removal, and k_q^{zeolite} is the rate constant for zeolite-induced removal of $^1O_2$ from solution. Solving for $[^1O_2]$ and insertion into eq 1 gives eq 3.

$$-\frac{d[\text{alkene}]}{dt} = k_T[\text{alkene}][^1O_2] \tag{1}$$

$$\frac{d[^1O_2]}{dt} = 0 = \kappa - k_T[\text{alkene}][^1O_2] - k_d[^1O_2] - k_q^{\text{zeolite}}[^1O_2] \tag{2}$$

$$-\frac{d[\text{alkene}]}{dt} = \frac{\kappa k_T[\text{alkene}]}{k_T[\text{alkene}] + k_d + k_q^{\text{zeolite}}} \tag{3}$$

It is tempting to suggest that the high concentration of the alkene in the interior of the zeolite quantitatively traps all of the $^1O_2$ such that $k_T[\text{alkene}] \gg (k_d + k_q^{\text{zeolite}})$. Consequently, the lifetime of $^1O_2$ ($\tau_\Delta = 1/k_d$) would have no influence on the rate of product formation. If this scenario is correct, the rate of alkene consumption should also be independent of the concentration of the alkene (eq 3). However, examination of Table 1 shows that doubling the intrazeolite concentration of **1** by changing the slurry solvent from hexane to perfluorohexane nearly doubles the % conversion. In addition, comparing $k_T[\mathbf{4}]$ (6.1×10^3 s^{-1})[13] to k_d for hexane (3.2×10^4 s^{-1}) and perfluorohexane (1.47×10^1 s^{-1}) demonstrates that $k_T[\text{alkene}]$ cannot be greater than $(k_d + k_q^{\text{zeolite}})$, at least in hexane.

As an alternative explanation, we suggest that $k_q^{\text{zeolite}} > k_d$, which would also have the effect of removing any influence of the identity of the slurry solvent on the reaction rate. We believe that the framework aluminum tetrahedra, AlO_4^-, are responsible for the deactivation, k_q^{zeolite}, of $^1O_2$. Other anions such as azide (N_3^-, $k_q = 4.8 \times 10^9$ M^{-1} s^{-1} in CH_3CN)[14] are known to be potent charge-transfer quenchers[15] of $^1O_2$.

To effectively suppress the influence of the solvent, k_q^{zeolite} should be approximately 4 times as large as k_d for hexane (i.e., $4 \times [3.2 \times 10^4$ s$^{-1}]$; see Supporting Information). This corresponds to a zeolite-leveled upper limit for the lifetime of $^1O_2$ of 7.5 μs. This is slightly less than twice the lifetime of $^1O_2$ in water (4.2 μs).[16] Using the Einstein equation ($\langle x^2 \rangle = 6Dt$; where $\langle x^2 \rangle$ is the mean square molecular displacement)[17] and a very conservative estimate of the diffusion coefficient, D, for migration of oxygen,[18] one can calculate that $^1O_2$ can migrate approximately 370 Å within its lifetime. This implies that $^1O_2$ can sample many of more than 5000 zeolite supercages surrounding the locus of its generation.

The absence of a dramatic solvent effect on the regiochemistries of the intrazeolite $^1O_2$ ene reactions is consistent with the very minor solvent effect observed in homogeneous media.[3]

We anticipate that this new synthetic protocol for zeolite photooxidations will greatly extend the synthetic potential of intrazeolite photooxidations especially for substrates with low affinity for the interior of the zeolite. Preparative scale (500 mg) photooxidations (see Supporting Information) have now been conducted. In addition, higher intrazeolite concentrations of the substrate will inhibit competitive overphotooxidations,[4] and both the zeolite and the perfluorohexane can be recycled with little loss of activity.

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Supporting Information Available: A plot of % **1** in the zeolite as a function of equilibration time in hexane and perfluorohexane, estimation of k_q^{zeolite}, and full experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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