6004 *J. Org. Chem.* **1995,** *60,* 6004−6005

Photooxidation Kinetics in Heterogeneous Media

Edward L. Clennan* and Ming Fang Chen

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070

Received June 9, 1995

The rates of reactions of singlet oxygen with organic substrates covalently bound to silica or polymeric matrices are in general not available. This deplorable situation exists despite well-documented examples of photooxidations of organic substrates on surfaces and in restricted geometries. For example, Ito, Ikeda, and Ichimura[1] have reported a novel imaging system utilizing the dye-sensitized photooxidation of oxazole groups attached to a polymer backbone and Blatter and Frei[2,3] have reported the very novel photooxidations of small alkenes in zeolites. Photooxidation kinetic data are also needed for organic pollutants found both free and absorbed on particulate matter as necessary input for environmental modeling studies.[4]

Iu and Thomas[5,6] have reported a kinetic study of the photooxidations of amines physically absorbed to a silica surface, but a study of the photooxidations of *covalently* bound silica supported substrates using direct time resolved detection of singlet oxygen is still lacking. We report here the first successful attempt to measure the rates of photooxidations of organic substrates covalently bound to a porous silica and a method to compare these rates to those in homogeneous media.

Amicon[7] 30 μm Matrex silica with a 275 m^2/g specific surface area, a 250 Å nominal pore diameter, and a specific pore volume of 1.75 mL/g was chosen as the support material for this study. The kinetic data for the interaction of singlet oxygen with this silica and with several modified silicas are depicted in Table 1.

The siliceous materials examined included a trimethylsilylated silica, **1**, a decylated silica, **2**, a pure phase sulfenylated silica, **3**, and two mixed phase silicas, **4** and **5**, that were synthesized by adding approximately 1:1 and 1:16 mixtures of **3-Cl** and decyl dimethylsilyl chloride, **2-Cl**, to the Amicon silica. The sulfenylated modifier was synthesized as shown in Scheme 1. The hydrosilylation was the critical step in this sequence, and it was best accomplished using chloroplatinic acid as a catalyst in an argon atmosphere.[8]

Scheme 1

$$\begin{gathered}
\mathrm{CH_2{=}CH(CH_2)_8OH} \xrightarrow[\text{py}]{\text{TsCl}} \\
= \underset{77.5\%}{\mathrm{CH_2{=}CH(CH_2)_8OTs}} \xrightarrow[\text{EtOH}]{\mathrm{NaSCH_3}} \\
\underset{86.5\%}{\mathrm{CH_2{=}CH(CH_2)_8SCH_3}} \xrightarrow[\mathrm{H_2PtCl_6{\cdot}6H_2O,\ CHCl_3,\ Ar}]{\mathrm{ClSi(CH_3)_2H}} \\
\underset{\mathbf{3\text{-}Cl},\ 88.4\%}{\mathrm{ClSi(CH_3)_2(CH_2)_{10}SCH_3}}
\end{gathered}$$

The modified silicas were synthesized by taking the appropriate silyl chloride and pyridine and adding them under an argon atmosphere to a methylene chloride slurry of the silica gel which had been pretreated by heating at 150 °C for 10 h in a vacuum oven. The resulting mixtures were allowed to stir for 2 h at room temperature and reflux for 7−8 h. After an additional time interval of 12 h at room temperature the reaction mixtures were worked up by filtering, washing with methylene chloride, and drying at 60 °C for 3 h. The sulfenylated silicas were characterized by combustion analysis allowing determination of the surface coverage, given as N = (moles of substrate)/(g of modified silica) and Γ = (moles of substrate)/(m^2 of surface area) in Table 1.[9] The surface coverage, N, for silica **3** is the average value calculated from sulfur (5.67×10^2 μmol/g) and carbon (5.78×10^2 μmol/g) combustion analysis data using eq 1. Γ was calculated from eq 2 in which S_a is the specific surface area of the Amicon silica and where $W_s = 1 - N\mathrm{MW}_{\text{substrate}}$ = (g silica)/(g of modified silica) and $\mathrm{MW}_{\text{substrate}}$ is the molecular weight of the bound substrate.

$$N = \frac{\%(\text{S or C})/100}{(32 \text{ or } 12)(\text{no. of S or C atoms/molecule of substrate})} \tag{1}$$

$$\Gamma = \frac{N}{W_s S_a} \tag{2}$$

The kinetic samples were prepared by addition of various amounts of the silica or substrate bound silicas to 1 mL of oxygen-saturated benzene containing 3×10^{-5} M tetraphenylporphyrin (TPP) in a 2 mL cuvette.[10] The samples were stirred with a micro stirring bar in order to keep the slurry as uniform as possible. The lifetime of singlet oxygen was monitored by examining the decay of its emission at 1270 nm as described previously for homogeneous reactions.[11,12] The experimental lifetimes ($1/\tau$) were then plotted versus the weight of silica (g/L) used in the experiment (Figure 1). The slopes of these lines are the k_T values in L g^{-1} s^{-1} reported in Table 1.[13] The k_T values in solution-like units of M^{-1} s^{-1} were calculated for the sulfenylated silicas, **3** and **4**, from these values by dividing by N in units of mol/g (eq 1).

The unmodified native silica is a 2.5−4.5 times more effective quencher of singlet oxygen than is the chloro-

---

[1] (a) Ito, H.; Ikeda, T.; Ichimura, K. *Makromol. Chem.* **1993**, *194*, 2215−2224. (b) Ito, H.; Ichimura, K. *Macromol. Chem. Phys.* **1995**, *196*, 995−1003.

[2] Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501−7502.

[3] Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812−1820.

[4] Tratnyek, P. G.; Hoigné, J. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 153−160.

[5] Iu, K.-K.; Thomas, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 3319−3325.

[6] Iu, K.-K.; Thomas, J. K. *J. Photochem. Photobiol. A. Chem.* **1993**, *71*, 55−60.

[7] Amicon, Inc. (a Grace Company), 72 Cherry Hill Drive, Beverly, MA 01915-1087.

[8] Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974−979.

[9] Feibush, B.; Cohen, M. J.; Karger, B. L. *J. Chromatogr.* **1983**, *282*, 3−26.

[10] All the kinetic samples were prepared as illustrated below for **3**. Six samples were prepared by adding 25, 50, 75, 100, 150, and 200 mg of **3** (from the same batch of siliceous material for which combustion analysis data was available) to 1 mL of benzene containing 6.3×10^{-3} M pyridine and 3×10^{-5} M TPP in a 2 mL cuvette. The resulting slurries were then stirred with a micro stirring bar and agitated with a continuous stream of oxygen for 20 min prior to irradiation. The samples were then irradiated (average of 200 experiments) with a Spectra-Physics DCR11 Nd:YAG pulsed laser, and the emission of singlet oxygen collected at 1207 nm using the apparatus and data workup are described in refs 11 and 12.

[11] Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581−3584.

[12] Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080−5085.

0022-3263/95/1960-6004$09.00/0

Table 1. Rate Constants for Singlet Oxygen Deactivation by Native and Modified Silicas

modifier	k_T (L g^{-1} s^{-1})	k_T (M^{-1} s^{-1})	$N \times 10^{-2}$ (μmol/g)	Γ (μmol/m^2)
none	17.2 ± 1.4^b	$7.8 \times 10^{3\,a,b}$		"8"[a]
$ClSiMe_3$ (**1**)	3.6^b			
	6.7^c			
$ClSiMe_2(CH_2)_9CH_3$ (**2**)	5.3^c			
$ClSiMe_2(CH_2)_{10}SMe$ (**3**)	27.7^b	$4.8 \times 10^{4\,b}$	5.73	2.42
	29.8^c	$5.2 \times 10^{4\,b}$		
1 $ClSiMe_2(CH_2)_{10}SMe^i$	39.3^b	$5.9 \times 10^{4\,d}$	3.94^f	1.69^f
1 $ClSiMe_2(CH_2)_9CH_3$ (**4**)		$1.0 \times 10^{5\,e}$	2.75^g	1.18^g
			6.69^h	2.87^h
1 $ClSiMe_2(CH_2)_{10}SMe$ 16 $ClSiMe_2(CH_2)_9CH_3$ (**5**)	35.8			

[a] Calculated assuming an OH coverage in the untreated silica of 8 μmol/m^2 after heating at 150 °C for 10 h.[16] [b] In the presence of pyridine. [c] In the absence of pyridine. [d] Calculated using the total coverage N, [k_T = (39.3 L g^{-1} s^{-1})/(0.669 × 10^{-3} mol/g)]. [e] Calculated using the sulfur chain coverage only, N_S, [k_T = (39.3 L g^{-1} s^{-1})/(0.394 × 10^{-3} mol/g)]. [f] Sulfur chains only. [g] Carbon chains only. [h] Total coverage. [i] Synthesized by mixing the two modifiers in a 1:1 mixture. Combustion analysis, however, suggests a ratio of 58.9%/41.1% (sulfide chain/hydrocarbon chain), perhaps revealing a difference in reactivity with the surface.

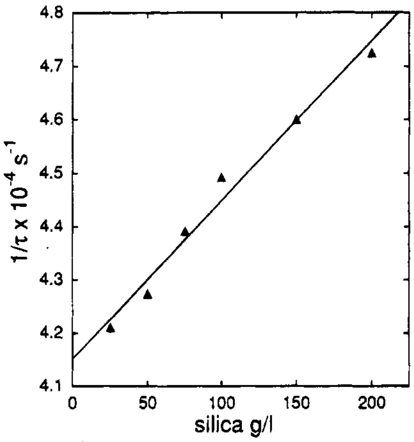

Figure 1. A plot of the [lifetime of $^1O_2$]$^{-1}$ as a function of silica **3** "concentration" in the absence of pyridine. Slope = 29.79 L g^{-1} s^{-1}; intercept = 41 516 s^{-1}.

trimethylsilane-modified silica, **1** (Table 1). This is consistent with electronic-to-vibronic energy transfer from singlet oxygen to the OH and CH oscillators via an exchange energy transfer mechanism.[14] Hydroxyl groups with higher vibrational frequencies are more effective quenchers than are the C−H bonds in the methyl groups of trimethylsilylated silica.[15] Addition of pyridine to the trimethylsilylated silica results in a decrease in the quenching rate from 6.7 to 3.6 L g^{-1} s^{-1} and is consistent with hydrogen bonding of pyridine to the residual hydroxyl groups on the surface.[5] A similar but reduced effect is observed with the sulfenylated silica **3**. In this case the hydroxyl groups are buried in the "hydrocarbon grass" on the surface and are less accessible.

The sulfenylate silica **3** quenches singlet oxygen nearly twice as fast as the native silica and nearly six times as fast as the decylated silica **2**, which is consistent with quenching by the sulfide group. Covalent bonding of the sulfide substrate to the silica decreased its reactivity by more than a factor of 600 in comparison to its homogeneous analogue, $Me_3Si(CH_2)_{10}SCH_3$ **6** (k_T = 3.32 × 10^7 M^{-1} s^{-1} in benzene). In addition to this significant reduction in reactivity the rate constants for reactions of the sulfenylated silicas are compressed to such an extent that the magnitudes of the rate constants are nearly independent of sulfide coverage.

In summary, we have developed a technique to measure the reactivities of substrates which have been covalently bound to a silica surface. We anticipate that this new technique will provide a valuable tool to explore how surfaces modify reactivities of bound substrates and potentially provide valuable morphological information.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research. We also thank Amicon, Inc., for their generous donation of the silica gel.

Supporting Information Available: Synthesis and spectral data for 9-decenyl methyl sulfide, **2-Cl**, and **6** (2 pages).

JO951051V

---

(13) The k_T (L g^{-1} s^{-1}) values in Table 1 are the least-square slopes of plots similar to Figure 1. Each point (lifetimes) in the plot is the average of three determinations and is reproducible to within ±15%. The linear regression equations, number of points, and regression coefficients (r) for the silicas containing the following modifiers are as follows: none, run 1, $y = 41\,978 + 17.928x$, 5 points, $r = 0.9188$; run 2, $y = 41\,914 + 15.859x$, 5 points, $r = 0.975\,48$; run 3, $y = 40\,243 + 17.881x$, 5 points, $r = 0.971\,13$; $ClSiMe_2$ (**1**), in the presence of pyridine, $y = 42\,063 + 3.608x$, 5 points, $r = 0.99672$, in the absence of pyridine, $y = 42\,261 + 6.6531x$, 4 points, $r = 0.925\,29$; $ClSiMe_2(CH_2)_9CH_3$ (**2**), $y = 40\,592 + 5.3206x$, 5 points, $r = 0.954\,26$; $ClSiMe_2(CH_2)_{10}SCH_3$ (**3**), in the presence of pyridine, $y = 39\,762 + 27.681x$, 5 points, $r = 0.9856$; in the absence of pyridine, $y = 41\,516 + 29788x$, 6 points, $r = 0.990\,53$; 1:1 $ClSiMe_2(CH_2)_{10}SCH_3/ClSiMe_2(CH_2)_9CH_3$ (**4**), $y = 39\,720 + 39.28x$, 6 points, $r = 0.995\,57$; 1:16 $ClSiMe_2(CH_2)_{10}SCH_3/ClSiMe_2(CH_2)_9CH_3$ (**5**), $y = 39\,388 + 35.819x$, 6 points, $r = 0.977\,12$. The inverse of the intercepts are the lifetimes of singlet oxygen in pure benzene and are independent of the siliceous material and are all within the range of values reported in the literature.

(14) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760.

(15) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201–6205.

(16) Unger, K. K. *Porous Silica its Properties and Use as Support in Column Liquid Chromatography*; Elsevier Scientific Publishing Company: Amsterdam, The Netherlands, 1979; Vol. 16, p 336.