J. Am. Chem. Soc. **1990**, *112*, 3319-3325

Quenching of Singlet Molecular Oxygen ($^1\Delta_gO_2$) in Silica Gel/Cyclohexane Heterogeneous Systems. A Direct Time-Resolved Study

Kai-Kong Iu and J. K. Thomas*

Contribution from the Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556.
Received October 25, 1989. Revised Manuscript Received December 20, 1989

Abstract: Direct time-resolved studies of singlet molecular oxygen ($^1\Delta_gO_2$) phosphorescence ($^3\Sigma_g^-O_2$ ($\nu = 0$) ← $^1\Delta_gO_2$ ($\nu = 0$); 1270 nm) in heterogeneous silica gel/cyclohexane systems are presented. Singlet molecular oxygen ($^1\Delta_gO_2$) is created through a photosensitization process on silica gel surfaces. The experimental results show that the lifetimes of singlet molecular oxygen ($^1\Delta_gO_2$) in both porous and compressed fumed silica/gel cyclohexane systems are significantly less than that in liquid cyclohexane. The shortened singlet molecular oxygen lifetime is due mainly to quenching by adsorbed water and silanol groups on the silica gel surface. In addition, monoamines coadsorbed on the silica gel surface do not quench singlet molecular oxygen ($^1\Delta_gO_2$); however, diamines such as DABCO or piperazine maintain their quenching activity, but the quenching kinetics are not of the Stern-Volmer type. The singlet molecular oxygen lifetime increases on loading the porous silica gel/cyclohexane system with monoamine. Coadsorption of piperazine increases quenching of $^1\Delta_gO_2$ by DABCO. These data suggest that at least two adsorption sites exist for diamine adsorption on the porous silica gel surface. Low monoamines and diamines adsorption, where all nitrogen lone pairs are bound to silica gel surface ("double" adsorption), leads to a low efficiency for quenching of $^1\Delta_gO_2$. Increasing the loading of diamine, or coadsorption of other nonreactive diamines, leads to saturation of the double adsorption sites, giving rise to adsorption at sites where only one nitrogen of the diamine is attached to the silica gel surface; increased $^1\Delta_gO_2$ quenching is observed under these conditions.

Direct detection of singlet molecular oxygen ($^1\Delta_gO_2$) phosphorescence ($^3\Sigma_g^-O_2$ ($\nu = 0$) ← $^1\Delta_gO_2$ ($\nu = 0$)) at 1270 nm has provided much insight into the interactions between ground-state molecular oxygen and excited organic molecules.[1] Furthermore, the long-lived singlet molecular oxygen is a unique experimental probe for oxygen diffusion and adsorption in polymer matrixes.[2] Although oxygen quenching of photoexcited species on Vycor glass[3] and silica gels[4] have been reported and the generation of singlet molecular oxygen in gas/solid[5] and liquid/solid[6] heterogeneous systems is well-established, a direct time-resolved study in a heterogeneous silica gel/cyclohexane system is still lacking. In this report, we present direct time-resolved observations of singlet molecular oxygen phosphorescence ($^3\Sigma_g^-O_2$ ($\nu = 0$) ← $^1\Delta_gO_2$ ($\nu = 0$); 1270 nm) in heterogeneous systems of both porous and fumed silica gel/cyclohexane. This experimental approach provides insight into oxygen diffusion and quenching of singlet oxygen on silica gel surfaces, information which is of use in catalysis surfaces.

Experimental Section

Silica Gel Samples Preparation. Silica gel (Davisil, 150-Å pore size, 100-200 mesh), cyclohexane (HPLC grade), 2-acetonaphthone (99%), piperazine (99%), DABCO (1,4-diazabicyclo[2.2.2]octane), tributylamine (Gold label), dipropylamine (Gold label), and diisopropylamine (Gold label) were obtained from Aldrich. Fumed silica gel was ordered from Cabot Corp. (CAB-O-SIL, HS-5) for DABCO quenching studies and from Dugussa Corp. (AEROSIL 380) for compression studies. All chemicals and silica gels were used as received. Silica gel was activated at 130 ± 5 °C for 3 h prior to adsorption from a stock cyclohexane solution of 2-acetonaphthone and amine(s). The silica gel and cyclohexane mixture was then stirred and kept overnight in the dark. The silica gel was washed twice with cyclohexane, and the subsequent cyclohexane supernatant was checked by UV-vis spectrophotometry (Perkin-Elmer Model 552) to ensure that all 2-acetonaphthone or amine(s) had been adsorbed onto the silica gel. In the preparation of the compressed fumed silica gel samples, the cyclohexane supernatant was evaporated under vacuum after loading of the sensitizer.[7] Sensitizer-loaded dry fumed silica gel was transferred to a hydraulic ram and was compressed with a pressure of 11.4K lb/in.^{2} (1 ton/($^1/_2$-in. diameter)) into a $^1/_2$-in.-diameter disk. The sample disk was finally broken into small pieces, washed twice, and used for further study. The concentrations of 2-acetonaphthone used were $<2 \times 10^{-6}$ mol/g for porous and $<1 \times 10^{-5}$ mol/g for fumed silica gel.

The adsorption isotherm of DABCO on 150-Å pore size Davisil silica gel was done by adding different amounts of stock DABCO cyclohexane solution to 0.15 ± 0.0005 g of silica gel, which had been treated at 130 °C for 3 h. The mixture was then stirred for 12 h. Finally, the equilibrium [DABCO] of this mixture was determined by UV-vis spectrophotometry.

Singlet Oxygen ($^1\Delta_gO_2$) Phosphorescence Measurement. A germanium near-IR detection system had been constructed in a manner similar to that reported previously.[8] Basically, a 3-mm-diameter p-n junction Ge diode (Germanium Power Devices Corp., GM7) coupled with a preamplifier (PMI, OP-37) was used as the detector unit. The analog signal from the detector unit was subsequently transferred to a digitizer (Tektronix 7912HB) equipped with a 7A16 plug-in amplifier. Three different load-resistor sets were used for this detection system to produce the necessary speed and sensitivity: (i) $\tau_{RC} = 500$ ns; (ii) $\tau_{RC} = 1.3$ μs; and (iii) $\tau_{RC} = 30$ μs (used for $^1\Delta_gO_2$ emission spectra measurements). In all cases, the speed of the detector is at least 6 times faster than the time-resolved $^1\Delta_gO_2$ decay signal to be determined, which eliminates the procedure of deconvoluting the observed signal. The digitizer was interfaced to an IBM PC-AT compatible computer (Zenith Z-238) for data processing. The routines for data handling have been described else-

---

* To whom correspondence should be addressed.

[1] Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1988**, *92*, 4662-4666, and references cited therein.

[2] Clough, R. L.; Dillon, M. P.; Iu, K.-K.; Ogilby, P. R. *Macromolecules* **1989**, *22*, 3620-3628.

[3] Wolfgang, S.; Gafney, H. D. *J. Phys. Chem.* **1983**, *87*, 5395-5401.

[4] (a) Wellner, E.; Rojanski, D.; Ottolenghi, M.; Huppert, D.; Avnir, D. *J. Am. Chem. Soc.* **1987**, *109*, 575-576. (b) Drake, J. K.; Levitz, P.; Turro, N. J.; Nitsche, K. S.; Cassidy, K. F. *J. Phys. Chem.* **1988**, *92*, 4680-4684. (c) Drake, J. K.; Levitz, P.; Klafter, J.; Turro, N. J.; Nitsche, K. S.; Cassidy, K. F. *Phys. Rev. Lett.* **1988**, *61*, 865-868.

[5] (a) Nilsson, R.; Kearns, D. R. *Photochem. Photobiol.* **1974**, *19*, 181-184. (b) Grigor'ev, E. I.; Myasnikov, I. A.; Tsivenko, V. I. *Zh. Fiz. Khim.* **1982**, *56*, 1748-1752. (c) Gohre, K.; Miller, G. C. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 793-800.

[6] (a) Tamagaki, S.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 1573-1576. (b) Cao, Y.; Zhang, B. W.; Ming, Y. F.; Chem, J. X. In *Studies in Organic Chemistry Vol. 33-The Role of Oxygen in Chemistry and Biochemistry*, Ando, W., Moro-oka, Y., Ed.; Elsevier Science: Amsterdam, 1988, pp 57-66. (c) Zhang, B. W.; Chen, J. X.; Cao, Y. *Huaxue Xuebao* **1989**, *47*, 502-505.

[7] The method of sensitizer loading in our studies might form dimers or microcrystals that could quench $^1\Delta_gO_2$. However, we do not observe any quenching of $^1\Delta_gO_2$ even at a sensitizer loading 3 times higher than that in the studies reported here (see Results and Discussion).

[8] (a) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 1611-1617. (b) Iu, K.-K.; Scurlock, R. D.; Ogilby, P. R. *J. Photochem.* **1987**, *37*, 19-32.

0002-7863/90/1512-3319$02.50/0

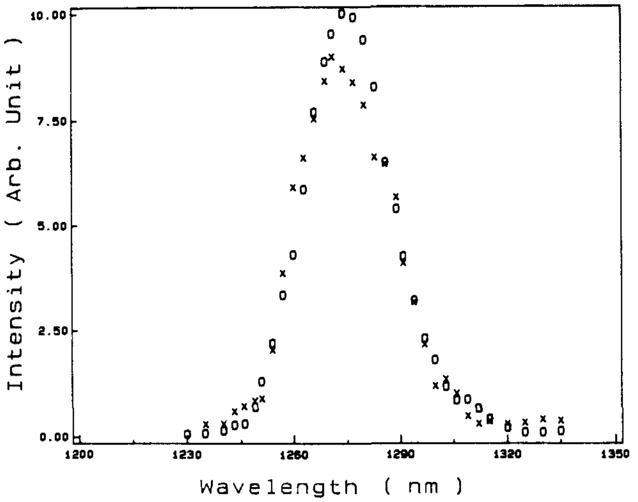


Figure 1. Singlet molecular oxygen ($^3\Sigma_g^-O_2$ (ν = 0) ← $^1\Delta_gO_2$ (ν = 0); 1270 nm) emission spectra: O, emission in cyclohexane solution with sensitizer (pyrene) concentration of 6.7×10^{-5} M; ×, emission in a 150-Å pore size Davisil silica gel/cyclohexane heterogeneous system with sensitizer (2-acetonaphthone) concentration of 2×10^{-6} mol/g. The spectrum for the heterogeneous system had been rescaled for the convenience of comparison. A τ_{RC} = 30 μs detector was used for these spectra.

where.[9] The detector unit was located inside a metal box, which provided an environment free of RF and stray light. A RG-1000 IR-transmitting glass filter and a custom interference filter (center at 1270 nm, fwhm = 50 nm, obtained from Barr Associate) were placed in front of the Ge detector to cut off unwanted scattered laser light. A curved mirror and an optical condensing system were used to focus the signal light onto the Ge detector. A Bausch & Lomb monochromator with a near-IR grating (IR No. 1, 675 lines/mm, blaze at 1000 nm) was also used in place of the interference filter to collect spectral data. The slit width of the monochromator was set to a band-pass of 18 nm.

The excitation source was a XeCl excimer laser (308 nm, Lambda Physik Model EMG100) with a pulse width of 10 ns and a pulse energy density of 10 mJ/cm^2. A diaphragm was used to block stray laser light, which produced a 0.9-cm-diameter laser beam to illuminate the front surface of the sample cuvette. A 2-Hz triggering device with variable time delay function was used to control the trigger system of the digitizer and excimer laser. In order to avoid photoproducts that could act as quencher(s), all silica gel samples were exposed to a maximum of 64 laser shots. The singlet molecular oxygen ($^1\Delta_gO_2$) emission spectrum in 150-Å pore size Davisil silica gel/cyclohexane system is an average of several samples adjusted with the proper normalization. The normalization was carried out by measuring a signal at 1271 nm for every sample, which was then used as a reference. Every data point in Figure 1 is a signal average of 20 laser shots. Standard 1-cm^2 quartz cuvettes were used for containing the samples, and all experiments were performed at room temperature (22 ± 1 °C).

Results and Discussion

Singlet Oxygen Emission. A submicrosecond Ge near-IR detection system was used to observe near-IR signals of $^1\Delta_gO_2$ at 1270 nm. Singlet molecular oxygen ($^1\Delta_gO_2$) was produced by a photosensitized reaction on SiO$_2$ surfaces in heterogeneous systems of silica gel/cyclohexane. The near-IR signal is due to the phosphorescence of singlet molecular oxygen, which was verified by the following observations: (1) The emission spectrum of the near-IR signal is identical with that of the emission of singlet molecular oxygen in cyclohexane (Figure 1). (2) The signal is diminished if the system is deoxygenated by bubbling with nitrogen (Figure 2). (3) An established singlet oxygen quencher–DABCO (1,4-diazabicyclo[2.2.2]octane) coadsorbed on the silica gel quenches the signal (see Figure 5B, C). (4) Irradiation of a sensitizer-free oxygenated system fails to give the signal. (5) Depletion of the oxygen concentration causes the signal intensity to decrease.

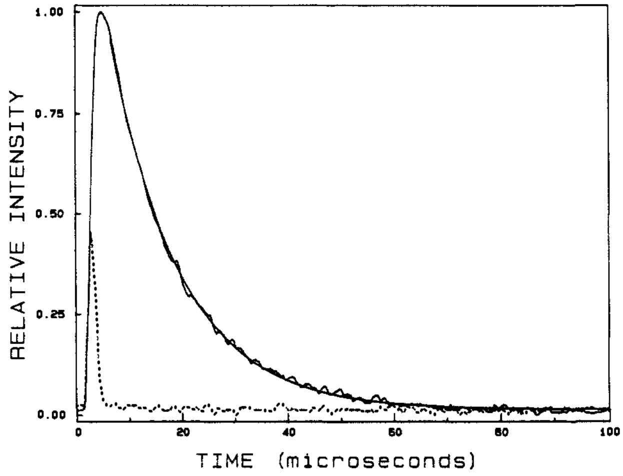


Figure 2. Time-resolved singlet molecular oxygen phosphorescence (1270 nm) signal from a photosensitized reaction in a 150-Å pore size Davisil silica gel/cyclohexane heterogeneous system: solid line, aerated; dashed line, background scattered light of a nitrogen-saturated (N$_2$ bubbling for 90 min) system. A single-exponential fit (smooth line on the raw data, τ = 13.4 μs) is also provided for the aerated system. The sensitizer was 2-acetonaphthone, and the loading concentration was 2×10^{-6} mol/g. A τ_{RC} = 500 ns detector was used for this experiment.

Table I. Singlet Molecular Oxygen ($^1\Delta gO_2$) Decay Rate Constants in a 150-Å Pore Size Davisil Silica Gel/Cyclohexane Heterogeneous System at Different Pretreated Temperatures[a]

temp (°C)	water loss (%)[b]	k_{obs} (s^{-1})[c]
125	5.10	73 800 ± 250
187	5.60	72 382 ± 100
300	5.73	71 542 ± 180
400	6.10	66 999 ± 50
550	7.15	56 878 ± 231

[a] This is the activated temperature of SiO$_2$ before the loading of 2-acetonaphthone. The period of activation was 3 h. [b] Starting material was 1 ± 0.0005 g. [c] An average value of the single-exponential decay fit from two different time scales.

The origin of the singlet molecular oxygen is the silica gel surface at the site of the adsorbed sensitizer molecule. No detectable near-IR signal was observed when the unadulterated cyclohexane supernatant was irradiated. The reasons for choosing 2-acetonaphthone as a photosensitizer are (a) it exhibits poor quenching for singlet molecular oxygen[10] and (b) it is strongly adsorbed on the silica gel surface. The 2-acetonaphthone concentration has no effect on the lifetime of singlet molecular oxygen, even at loadings of 2-acetonaphthone[12] up to 6×10^{-6} mol/g for porous and 3×10^{-5} mol/g for fumed silica gel. The amine quenchers all absorb weakly in the UV regime (e.g., $\lambda < 270$ nm, $\epsilon < 3000$ cm^{-1} M^{-1}) and are not directly excited by the laser. The supernatant used in the amine adsorption gave no detectable UV absorption signal of the amine. In addition, the decay rate of singlet molecular oxygen in the cyclohexane supernatant was identical with that in cyclohexane. This was done by adding 2-acetonaphthone to the supernatant to give a concentration of 2-acetonaphthone $\cong 1 \times 10^{-4}$ M, which generated $^1\Delta_gO_2$ phosphorescence through photosensitization. These results show that there is no amine(s) remaining in the cyclohexane supernatant even at the highest [amine(s)] reported here.

Singlet Oxygen Lifetime on Silica Gel/Cyclohexane Mixtures. Figure 2 shows the time-resolved near-IR signal from a photo-

---

(9) Liu, X.; Iu, K.-K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120–4128.

(10) In ref 11, a concentration of 2-acetonaphthone at ~10^{-2} M in benzene had been used without a significant quenching of $^1\Delta_gO_2$ lifetime. Indeed, we have measured the $k_q \leq 2 \times 10^5$ M^{-1} s^{-1} for 2-acetonaphthone in cyclohexane with a two-data-point experiment. Because 2-acetonaphthone is immovable on the silica gel surface, the quenching rate (k_q) will be less than 2×10^5 M^{-1} s^{-1}.

(11) Gorman, A. A.; Hamblett I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679–4682.

(12) Although we prefer to use the unit of mole per gram, the unit can be transformed to (moles per liter of SiO$_2$) by using the silica gel density = 2.2 g/mL of SiO$_2$. The conversion factor is 10^{-8} mol/g = 2.2×10^{-5} mol/L of SiO$_2$.

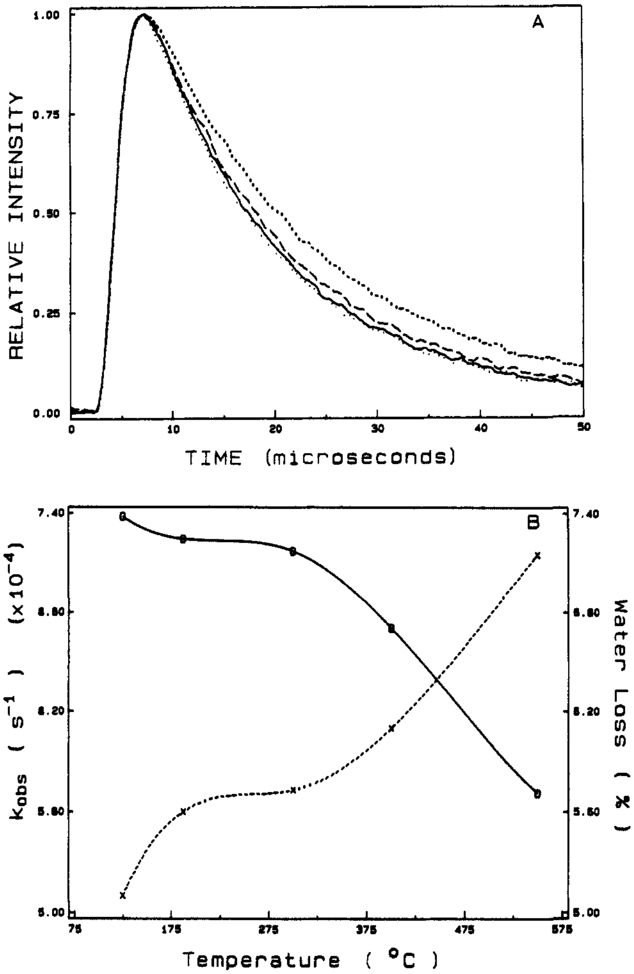


Figure 3. (A) Time-resolved singlet molecular oxygen decay traces at different pretreated temperatures: 550 °C (short dashed line), 440 °C (long dashed line), 300 °C (solid line), and 187 °C (dotted line). The trace of 125 °C is not shown because of the congestion. (B) Double y-axis plot for k_{obs} (O with solid line curve) and water loss (× with dashed line curve) as a function of pretreated temperature. The samples were 150-Å pore size Davisil silica gel/cyclohexane with a loading of 2-acetonaphthone of 2×10^{-6} mol/g. A $\tau_{RC} = 1.3$ μs detector was used for this experiment.

Scheme I

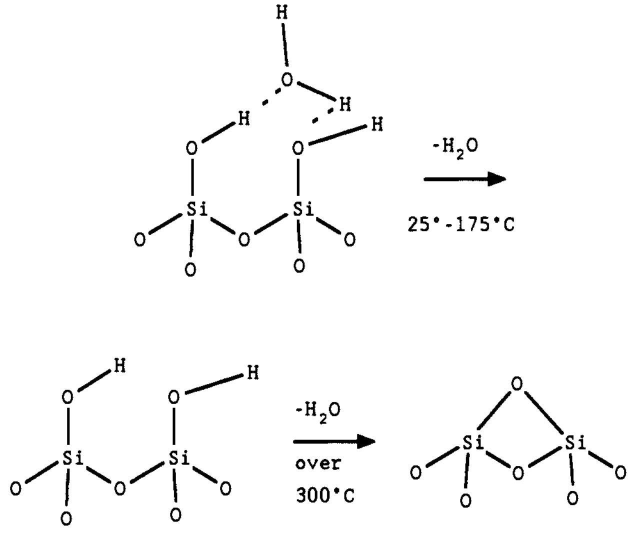


Table II. Calculated Adsorbed Water Quenching Rate Constants for Singlet Molecular Oxygen ($^1\Delta_gO_2$) in a 150-Å Pore Size Davisil Silica Gel/Cyclohexane Heterogeneous System at Different Pretreated Temperature Ranges[a]

temp range (°C)	$\Delta[H_2O]^b$ (mol/L of SiO_2)	calcd k_q^c ((mol/L of SiO_2)$^{-1}$ s^{-1})
125–187	0.610 ± 0.061	2324 ± 806
187–300	0.159 ± 0.061	5283 ± 3789
300–400	0.452 ± 0.061	10051 ± 1865
400–550	1.283 ± 0.061	7889 ± 594

[a] See footnote a of Table I. [b] Calculated from the amount of water loss (mol/g) and then converted (mol/L of SiO_2)[12]. The uncertainty of $\Delta[H_2O]$ is determined by the error of the starting material weighting (see footnote b of Table I). [c] Calculated from eq 2 in text.

sensitized reaction in the 150-Å pore size Davisil silica gel/cyclohexane system; the background scattered light of a nitrogen saturated sample is also shown for comparison.[13] The lifetime of this signal is 13.4 μs, which is much shorter than the lifetime of singlet molecular oxygen in cyclohexane ($\tau = 24 \pm 0.5$ μs).[15] In addition, we have verified that oxygen quenching of the triplet sensitizer[16] gives rise to the near-IR signal of singlet molecular oxygen.[17] The significant shortening of the singlet molecular oxygen lifetime is due to quenching on the silica gel surface; this has been suggested by Ogryzlo in gas–solid systems.[18] Figure 3A shows the time-resolved singlet molecular oxygen phosphorescence signal at different pretreated temperatures for 150-Å pore size Davisil silica gel. Figure 3B shows the plots of first-order decay rates and the amounts of water lost at different pretreated temperatures. The results are summarized in Table I, and they indicate that there is less quenching at higher pretreated temperatures. A number of hydroxyl groups exist on the silica gel surface (e.g., water adsorbed via hydrogen bonding and silanol groups). The adsorbed water can be eliminated simply by pumping under vacuum or mild heating (e.g., 25 °C < temperature < 175 °C); however, the dehydroxylation of the silanol groups occurs at much higher temperature (e.g., temperature > 300 °C).[19] Scheme I shows these reactions.

The decrease in the observed first-order decay rate constant is concomitant with the loss of adsorbed water and supports the concept that quenching on the silica gel surface is related to the adsorbed water. The observed first-order decay rate constant (k_{obs}) can be written as follows

$$k_{obs} = k_0 + k_q[H_2O] \qquad (1)$$

where the k_0 is the decay rate constant of totally dehydroxylated silica gel surface and k_q is the quenching rate constant with adsorbed water, the concentration of which is expressed as moles per liter of SiO_2. The k_q can be calculated by subtracting the values at any two temperatures with eq 2, and the results are listed

$$k_{obs}(\text{high temp}) - k_{obs}(\text{low temp}) = k_q\Delta[H_2O] \qquad (2)$$

in Table II. The calculated k_q is close to the bimolecular quenching rate of water (k_q(water) = 4290 M^{-1} s^{-1}),[20,21f] and it

---

(13) This scattered light may be the breakthrough of the laser light or luminescence of the optics after absorbing scattered laser light.[14] Nevertheless, it is very fast and follows the detection system response.

(14) Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Photochem.* **1987**, *37*, 247–255.

(15) This value was determined in our laboratory with 1×10^{-4} M 2-acetonaphthone in cyclohexane under an experimental condition described in the Experimental Section.

(16) The ^{3}(2-acetonaphthone)* lifetime at the aerated condition is less than 1 μs in both porous and fumed silica gel/cyclohexane systems. A 10-ns response photomultiplier tube was used for the determinations above. These data will be published in the forthcoming paper.

(17) It is unnecessary to deconvolute our observed time-resolved $^1\Delta_gO_2$ signals in order to determine an accuracy $^1\Delta_gO_2$ lifetime because both the detector response and decay of ^{3}(2-acetonaphthone)* – the $^1\Delta_gO_2$ precursor are at least 6 times faster than the $^1\Delta_gO_2$ decay in every study reported here. We, however, do not intend to draw any conclusion on the $^1\Delta_gO_2$ formation rate with the Ge detector used for these studies, particularly with the influence of the background scatter light (see Figure 2).

(18) Ogryzlo, E. A. cited by: Scheffer, J. R.; Ouchi, D. M. *Tetrahedron Lett.* **1970**, *3*, 223–226.

(19) Iler, R. K. *The Chemistry of Silica and Silicates, Polymerization, Colloid, and Surface Properties and Biochemistry*; Wiley: New York, 1979; p 626.

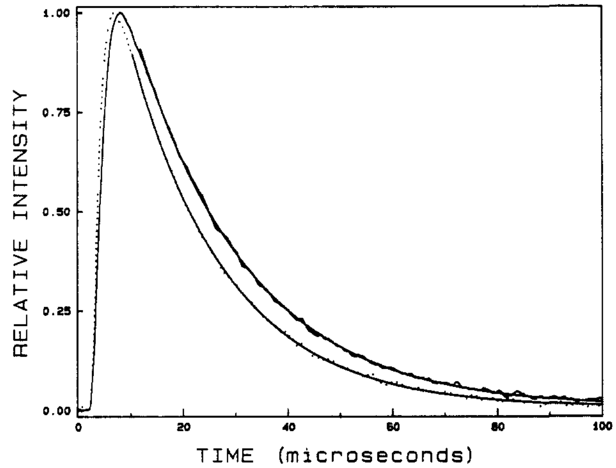


Figure 4. Effect of compression on a time-resolved singlet molecular oxygen (${}^1\Delta_gO_2$) phosphorescence (1270 nm) signal in an AEROSIL 380 fumed silica gel/cyclohexane heterogeneous system: dotted line, compressed silica gel sample (11.4K lb/in.^{2}); solid line, without compression. A single-exponential fit (smooth line on raw data) is applied on each sample (τ = 21.5 and 18.5 μs for uncompressed and compressed systems, respectively). A τ_{RC} = 1.3 μs detector was used for this experiment. The loading of 2-acetonaphthone was 9.5 × 10^{-6} mol/g.

further supports the hydroxyl groups quenching mechanism. The k_q value at low pretreated temperature (125–187 °C) is less than those at high pretreated temperatures. This indicates that the hydroxyl groups on SiO_2 surface after treatment at higher temperatures tend to quench ${}^1\Delta_gO_2$ more effectively. The hydroxyl group quenching of ${}^1\Delta_gO_2$ is primarily due to an electronic to vibrational (E → V) energy-transfer mechanism.[21] Hydroxyl groups with higher vibrational frequencies quench ${}^1\Delta_gO_2$ more effectively. Isolated silanol groups, which predominate on high-temperature pretreated SiO_2 surface, exhibit higher vibrational frequencies (3650–3750 cm^{-1}).[22] However, adsorbed water on the SiO_2 surface, which predominates on low-temperature pretreated SiO_2 surface, exhibits lower vibrational frequencies (3400–3500 cm^{-1}).[22] Therefore, our observation of effective ${}^1\Delta_gO_2$ quenching on high-temperature pretreated SiO_i surface is the result of quenching of ${}^1\Delta_gO_2$ by hydroxyl groups with high vibrational frequencies.

Effect of Compression on ${}^1\Delta_gO_2$ Lifetime in AEROSIL 380 Fumed Silica Gel. Figure 4 shows the effect of compression on the singlet molecular oxygen lifetime in the AEROSIL 380 fumed silica gel/cyclohexane system. The decay of singlet molecular oxygen becomes faster in the compressed silica gel system (τ = 18.5 ± 0.6 μs compared to τ = 21.5 ± 0.8 μs in the uncompressed system). A characteristic of the fumed silica gel is its colloidal aggregate, which is a composition of many primary particles (diameter ~80 Å).[23] For the uncompressed system, due to its dispersed character, the singlet molecular oxygen created from a photosensitization process on the initial fumed silica gel surface may not reencounter another SiO_2 surface after leaving the initial surface. However, artificial pores can be created by packing the gel particles together in a compressed system.[24] Here, singlet molecular oxygen may repeatedly reencounter the silica gel surface inside the pores; the lifetime of singlet molecular oxygen (${}^1\Delta_gO_2$)

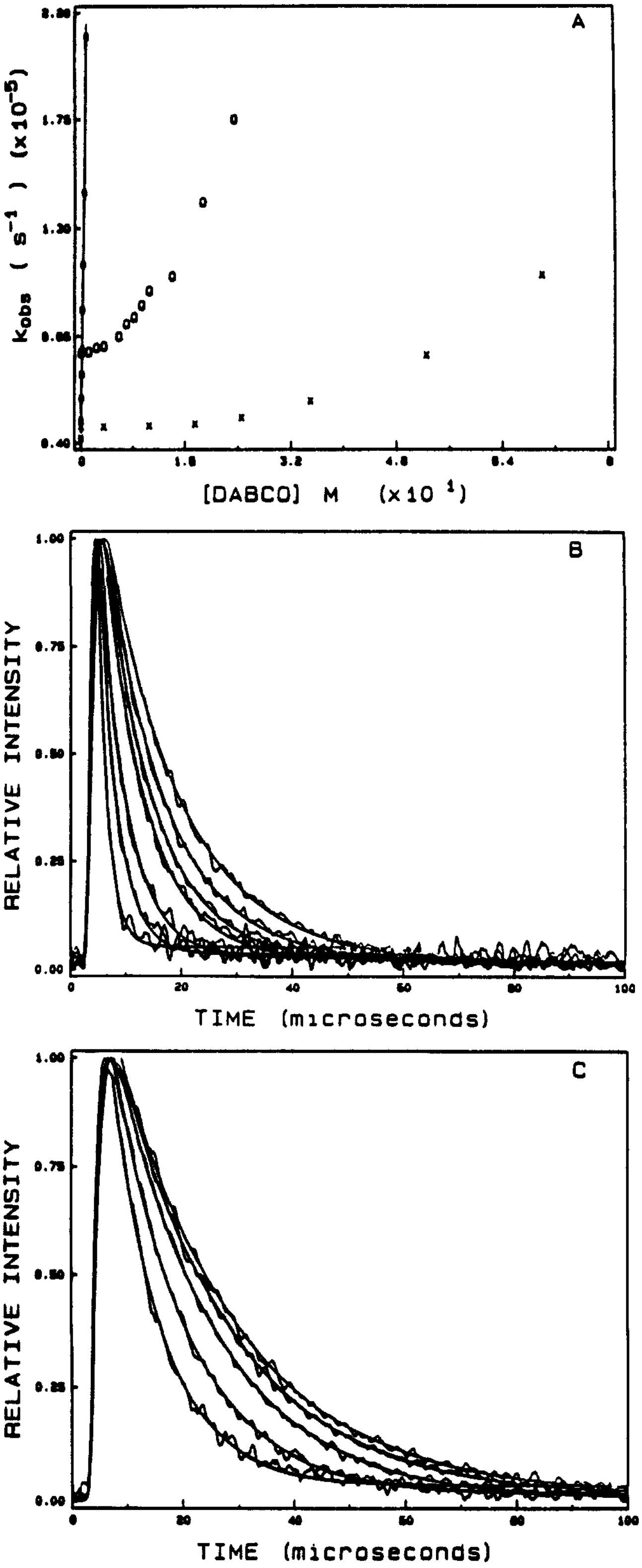


Figure 5. (A) DABCO quenching of singlet molecular oxygen in different silica gel/cyclohexane systems: * (linear fit), cyclohexane solution-phase data with [2-acetonaphthone] = 2 × 10^{-4} M; ○, 150-Å pore size Davisil silica gel/cyclohexane; ×, uncompressed CAB-O-SIL fumed silica gel/cyclohexane systems. The DABCO concentration unit for silica gel samples is mole per liter of SiO_2. (B) Time-resolved singlet molecular oxygen signal in a 150-Å pore size Davisil silica gel/cyclohexane system at different loading [DABCO]. The slowest decay is that wihtout DABCO, and others contain DABCO, at the six highest concentrations in A. (C) Time-resolved singlet molecular oxygen signal in an uncompressed CAB-O-SIL fumed silica gel/cyclohexane system at different loading [DABCO]. The slowest decay is that without DABCO, and others contain DABCO, at the four highest concentrations in A. A τ_{RC} = 500 ns detector was used for these experiments.

---

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

(21) (a) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244–7253. (b) Salokhiddinow, K. I.; Byteva, I. M.; Gurinowich, G. P. *Zh. Prikl. Spektrosk.* **1981**, *34*, 892–897. (c) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430. (d) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760. (e) Schmidt, R.; Brauer, H.-D. *J. Am. Chem. Soc.* **1987**, *109*, 6976–6981. (f) Schmidt, R. *J. Am. Chem. Soc.* **1989**, *111*, 6983–6987. We thank one of the reviewers who commented on this matter.

(22) Reference 19, pp 638–642.

(23) (a) Pigments (Basic Characteristics); Technical Bulletin No. 11; Degussa Corp.: Teterboro, NJ, 1987. (b) CAB-O-SIL Fumed Silica Properties and Functions; Cabot Corp.: Tuscola, IL, 1987.

(24) Conner, W. C.; Lane, A. M.; Ng, K. M.; Goldblatt, M. *J. Catal.* **1983**, 336–345.

Table III. Rate Constants for the Quenching of Singlet Molecular Oxygen ($^1\Delta_gO_2$) by Amines in Cyclohexane[a]

amine	k_q (10^{-5} M^{-1} s^{-1})[b]
tributylamine	300 ± 2
DABCO	211 ± 7
dipropylamine	97 ± 1
piperazine	17 ± 1
diisopropylamine	8.8 ± 0.1

[a] The sensitizer (2-acetonaphthone) concentration was 2 × 10^{-4} M. [b] Within 95% confidence limit.

then decreases. This billiard ball type diffusion mechanism of oxygen molecule between silica gel surfaces has also been invoked by Turro et al. in their studies of oxygen quenching of triplet excited states in porous silica.[4b]

Quenching of $^1\Delta_gO_2$ by Amines on SiO_2 Surface. Figure 5A shows DABCO quenching of singlet molecular oxygen in silica gel/cyclohexane systems; the cyclohexane solution phase data (symbol * with a linear fit) are also shown for comparison. Parts B and C of Figure 5 show the time-resolved DABCO quenching of singlet molecular oxygen phosphorescence in aerated 150-Å pore size Davisil silica gel/cyclohexane and uncompressed CAB-O-SIL fumed silica gel/cyclohexane systems, respectively. The decay of singlet molecular oxygen follows first-order decay kinetics at all DABCO concentrations studied. For the porous silica gel, the quenching is much less effective than in solution, but much more effective than in fumed silica gel. Unlike the solution phase, where both quencher and singlet molecular oxygen can move freely and rapidly, the quencher (DABCO) is anchored on the silica gel surface, and the quenching action occurs if singlet molecular oxygen encounters the DABCO molecule at the silica gel surface. The adsorbed molecules are located on the external surface of the aggregates of CAB-O-SIL fumed silica gel, but inside the pores of the porous silica gel. The average distance between surfaces inside the pore of the porous SiO_2 in this study is about 150 Å; however, the average distance between aggregates in fumed silica is much larger than 150 Å. The difference in DABCO quenching between porous and fumed silica gel is basically due to the different distance between surfaces (or aggregates, in the case of fumed SiO_2). The dispersed character of fumed silica gel decreases the reencounter frequency between surfaces during the singlet molecular oxygen lifetime. It is interesting to note that DABCO quenching of singlet molecular oxygen in silica gel/cyclohexane system does not follow Stern–Volmer kinetics (vide infra).

A series of aliphatic amines were used to quench singlet molecular oxygen in 150-Å pore size Davisil silica gel/cyclohexane system. Figure 6A shows quenching by these amines in the cyclohexane solution phase, and the quenching rate constants (k_q, the slope of the linear fit) are reported in Table III. It is noteworthy that the trend reported in Table III does not hold in the porous silica gel/cyclohexane systems. Figure 6B shows the results of the amine quenching of $^1\Delta_gO_2$ in porous silica gel/cyclohexane systems. Monoamines are unreactive on SiO_2, which can be rationalized as due to a binding of the lone-pair electrons on the nitrogen atom to a surface site. The lone pair is essential for the charge-transfer quenching mechanism[25] and is not available for $^1\Delta_gO_2$ quenching if the electron pair is connected with the silica gel surface. Further, the decrease of the singlet molecular oxygen decay rate as the loading of [monoamine] increases suggests a change in surface character (Figures 6B,C and 7B). This is due to binding of the free hydroxyl groups on the surface by the adsorbed amine.[26] This leads to a decrease quenching of $^1\Delta_gO_2$ on adsorption of monoamine to the SiO_2 surface. However, diamines (e.g., DABCO and piperazine) maintain their quenching activity on the silica gel surface, and piperazine is a less effective quencher compared to DABCO (also see Table III). The above

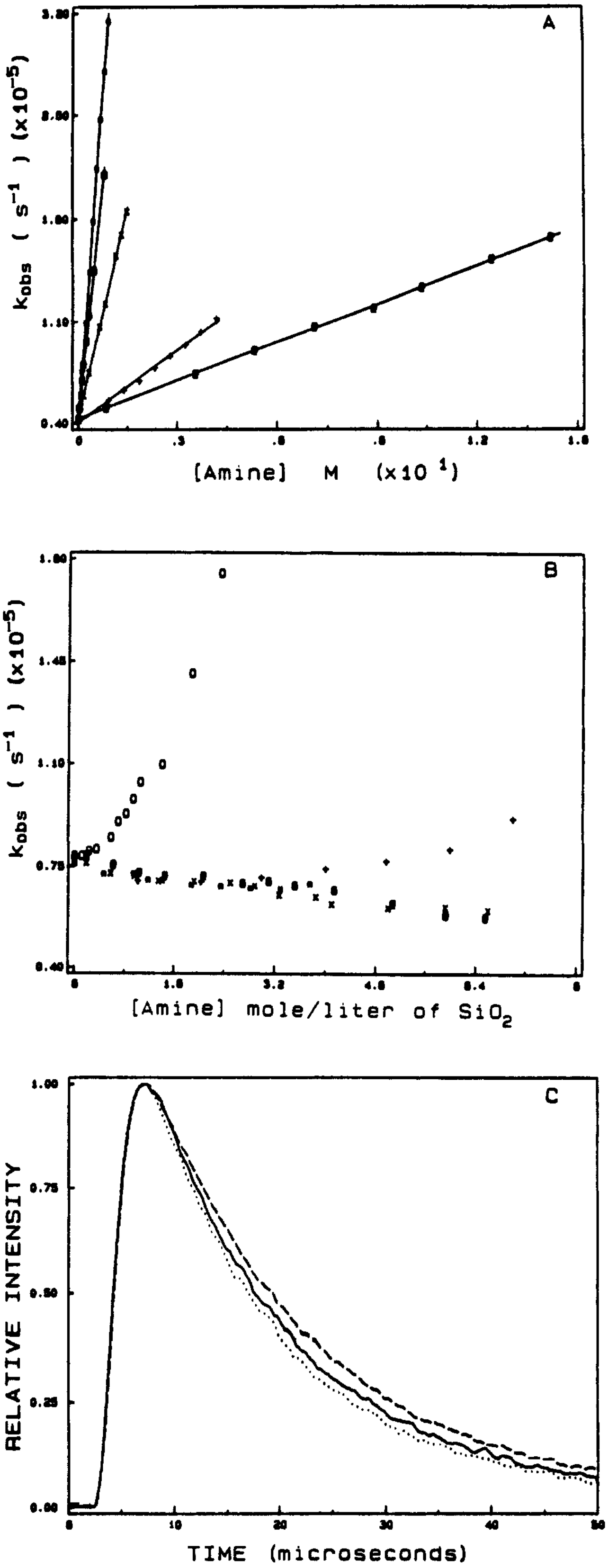


Figure 6. (A) Amines quenching of singlet molecular oxygen in cyclohexane solution with 2 × 10^{-4} M 2-acetonaphthone: *, tributylamine; O, DABCO; ×, dipropylamine, +, piperazine; @, diisopropylamine. The slope of each fit (k_q) is reported in Table III. (B) Amines quenching of singlet molecular oxygen in a 150-Å pore size Davisil silica gel/cyclohexane system. Symbols are the same as in A. (C) Time-resolved singlet molecular oxygen traces at different $(i\text{-Pr})_2NH$ loadings in a 150-Å pore size Davisil silica gel/cyclohexane system: long dashed line, 3.1 × 10^{-4} mol/g; solid line, 1.68 × 10^{-4} mol/g; dotted line, no loading. A τ_{RC} = 500 ns detector was used for A and B, but a τ_{RC} = 1.3 μs detector for C.

---

[25] (a) Ogryzlo, E. A.; Tang, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4034–4036. (b) *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press Inc.: Boca Raton, FL, 1985; Vol. 1, pp 194–197.

[26] Reference 19, p 655.

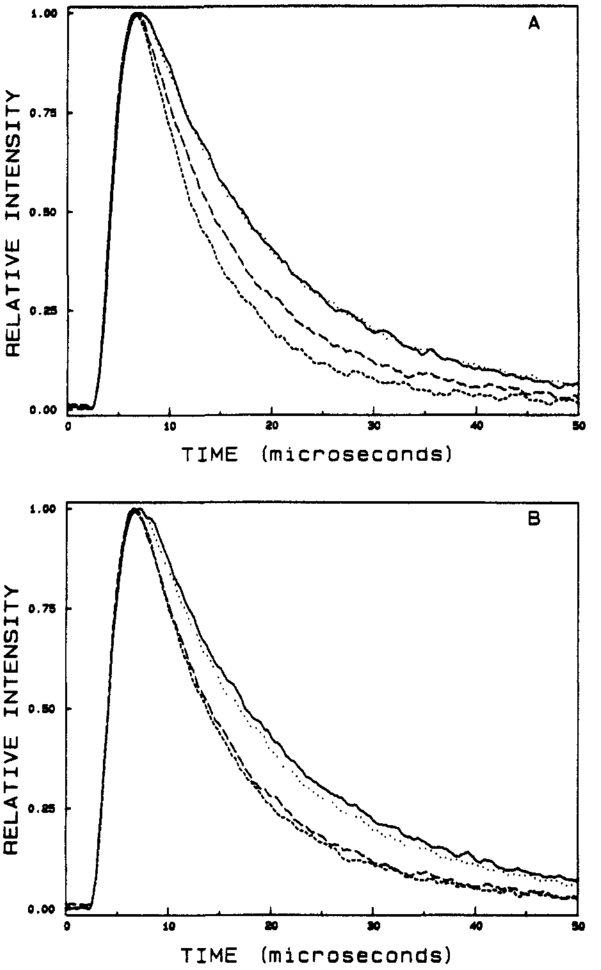
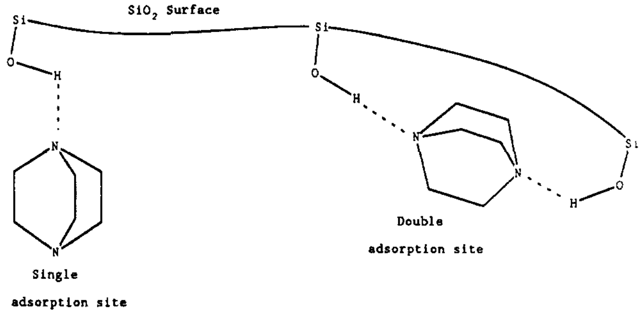


Figure 7. Effect of coadsorbed amine on DABCO quenching singlet molecular oxygen time-resolved signal in a 150-Å pore size Davisil silica gel/cyclohexane system. (A) Key: dotted line, sample with sensitizer (2-acetonaphthone, 2×10^{-6} mol/g) only; solid line, sample with sensitizer and piperazine (1.264×10^{-4} mol/g); long dashed line, sample with sensitizer and DABCO (4×10^{-5} mol/g); short dashed line, sample with sensitizer, piperazine (1.264×10^{-4} mol/g), and DABCO (4×10^{-5} mol/g). (B) Key: dotted line, sample with sensitizer (2-acetonaphthone, 2×10^{-6} mol/g) only; solid line, sample with sensitizer and $(i\text{-Pr})_2NH$ (1.68×10^{-4} mol/g); long dashed line, sample with sensitizer and DABCO (4×10^{-5} mol/g); short dashed line, sample with sensitizer, $(i\text{-Pr})_2NH$ (1.68×10^{-4} mol/g), and DABCO (4×10^{-5} mol/g). A τ_{RC} = 1.3 μs detector was used for these experiments.

results of mono- and diamine quenching confirm that the quenching of the coadsorbed amine on the silica gel surface is related to the lone electron pair of the nitrogen atom.

The quenching data with diamines do not follow simple Stern–Volmer kinetics. Nevertheless, the data show that inefficient quenching at low diamine concentration is due to diamine adsorbed at a double-adsorption site where both electron lone pairs of the diamine are bound to the surface; this suggestion is confirmed below. Figure 7A shows a loading of piperazine on the 150-Å pore size Davisil silica gel/cyclohexane system such that the decay of $^1\Delta_gO_2$ is unaffected and is essentially that of the free surface. Coadsorption of the same amount of piperazine to a DABCO sample markedly increases the $^1\Delta_gO_2$ quenching efficiency, over and above that due to DABCO alone. In contrast, monoamine such as $(i\text{-Pr})_2NH$ coadsorbed to a DABCO sample does not increase the rate of decay of $^1\Delta_gO_2$, as shown in Figure 7B. This is interpreted as follows: initial adsorption of DABCO occurs at sites where both nitrogen lone pairs are bonded to the silica gel surface. This situation is similar to the case of monoamines where little quenching is observed (vide ante). Higher concentrations of DABCO or piperazine saturate the sites of "double-adsorption", and adsorption now occurs at sites where only one nitrogen lone pair per molecule is bonded to the silica gel surface, i.e., "single-adsorption". Under the latter condition the unbounded nitrogen lone pair quenches the $^1\Delta_gO_2$.

A pictorial representation of these adsorption sites is shown as below:



On the basis of this two-adsorption-site model and the results of amines studies, DABCO quenching of $^1\Delta_gO_2$ in porous silica gel/cyclohexane system can be simply described as eq 3,

$$k_{obs} = k_0' + k_{S1}[S_1\cdots DABCO] \quad (3)$$

where k_{obs} is the observed single exponential decay rate of $^1\Delta_gO_2$, k_0' is the singlet oxygen decay rate without DABCO, k_{S1} is the DABCO adsorbed single-adsorption-site quenching rate of singlet oxygen, and $[S_1\cdots DABCO]$ is the DABCO-adsorbed single-adsorption-site concentration. The $[S_1\cdots DABCO]$ can be extracted by assuming an equilibrium between single- and double-adsorption sites as follows

$$S_2\cdots DABCO + S_1 \rightleftharpoons S_2 + S_1\cdots DABCO \quad (4)$$

and

$$K_{eq} = \frac{[S_2][S_1\cdots DABCO]}{[S_2\cdots DABCO][S_1]} \quad (5)$$

where $[S_2\cdots DABCO]$ is the DABCO-adsorbed double-adsorption-site concentration and K_{eq} is the equilibrium rate constant. From the proposed two-adsorption-site model, $[S_1\cdots DABCO]$ can be further expressed as a function of K_{eq}, $[-OH]_{total}$ (total accessible –OH by DABCO on surface), [DABCO], and $[S_1]_0$ (concentration of single-adsorption site accessible by DABCO on silica gel surface).[27] After substitution and rearrangement, eq 5 can be rewritten as

$$\begin{aligned}&(K_{eq} - 1)[S_1\cdots DABCO]^2 + \\ &\quad(\tfrac{1}{2}[S_1]_0 + [DABCO] - \tfrac{1}{2}(\text{const}) - K_{eq}([DABCO] + \\ &\qquad[S_1]_0))[S_1\cdots DABCO] + K_{eq}[S_1]_0[DABCO] = 0 \quad (6)\end{aligned}$$

Equation 6 is a typical quadratic equation, and the positive real root of this equation can be placed into eq 3 for computer fitting routines.

The [–OH] (total accessible –OH by DABCO on surface, mole/liter of SiO_2) can be calculated from the hydroxyl group density on SiO_2 surface (a constant = 5 $-OH/nm^2$)[28] and the accessible surface area of DABCO on 150-Å pore size Davisil silica gel. The value (300 m^2/g) supplied by the manufacturer,[29] which is determined by the N_2-BET method, is usually larger than the accessible surface area of the bigger absorbate.[30] We have determined the DABCO adsorption isotherm (Figure 8A,B) for the studied 150-Å pore size Davisil silica gel according to the Langmuir isotherm method.[31] The reciprocal of the slope (0.95 ± 0.01 mmol/g of SiO_2) in Figure 8B is the DABCO monolayer capacity for the studied 150-Å pore size Davisil silica gel. From

---

(27) In order to do this derivation, four more conditions have to be satisfied, and they are the following: (a) $[S_1] = [S_1]_0 - [S_1\cdots DABCO]$; (b) $[S_2] = [S_2]_0 - [S_2\cdots DABCO]$; (c) [–OH] (total accessible –OH by DABCO on surface) = $2[S_2]_0 + [S_1]_0$; and (d) $[DABCO] = [S_1\cdots DABCO] + [S_2\cdots DABCO]$. $[S_1]_0$ and $[S_2]_0$ are the concentrations of single- and double-adsorption sites accessible by DABCO on silica gel surface, respectively. Other variables have been described in text.

(28) Zhuravlev, L. T. *Langmuir* **1987**, *3*, 316–318.

(29) Aldrich Chemical Catalog, 1988–1989.

(30) We thank one of the reviewers who commented on this matter.

(31) Dharmaraja Iyer, K. P.; Wariyar, N. S. *Chem. Ind.* **1967**, *7*, 30–31.

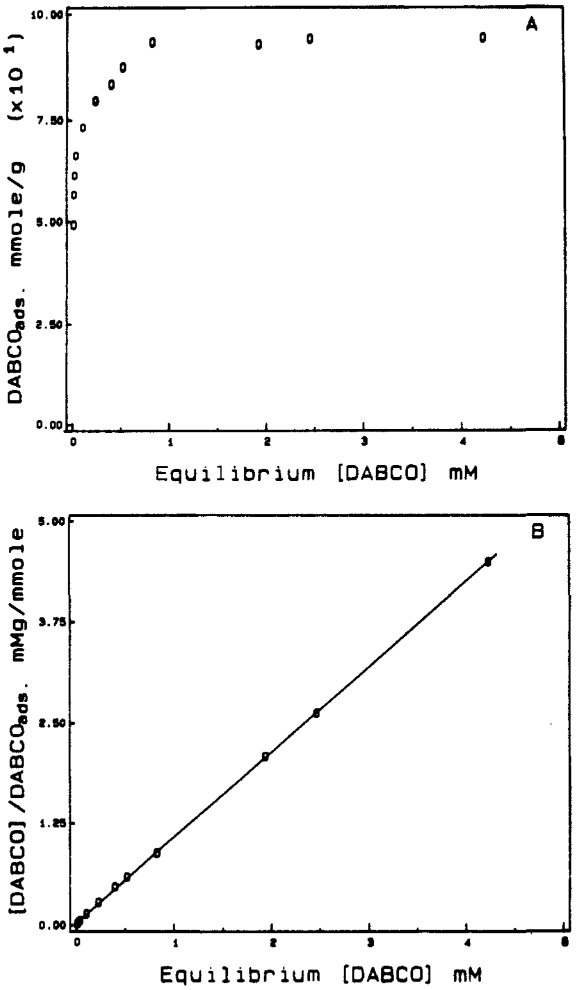


Figure 8. (A) Adsorption of DABCO on 150-Å pore size Davisil silica gel from cyclohexane solution. (B) Langmuir isotherm for adsorption of DABCO on 150-Å pore size Davisil silica gel from cyclohexane solution. A linear least-squares fit on data yields a slope of 1.05 ± 0.01 g/mmol.

Table IV. Results of Both Three-[a] (k_{S1}, K_{eq}, and $[S_1]_0$) and Four-Variable (k_0', k_{S1}, K_{eq}, and $[S_1]_0$) Least-Squares Fit on DABCO Quenching of Singlet Molecular Oxygen ($^1\Delta_gO_2$) in a 150-Å Pore Size Davisil Silica Gel/Cyclohexane Heterogeneous System[b]

	k_0' (s^{-1})	k_{S1} ((mol/L of $SiO_2)^{-1}$ s^{-1})	k_{eq}	$[S_1]_0$ (mol/L of SiO_2)
three-variable	78 061	976 056	0.009 62	2.405
four-variable	77 366	970 695	0.009 72	2.410
average	77 714	973 376	0.009 67	2.408
deviation	±347	±2 680	±0.000 05	±0.003

[a] The three-variable computer fit treats the k_0' equal to the decay rate without DABCO loading. [b] The derivation of the computer fitting is based on eqs 3–6 in text.

this value and the calculated cross-section area of DABCO (26.5 ± 3 Å^2),[32] we determine the accessible surface area for DABCO on the studied Davisil silica gel to be (151.6 ± 18.2 m^2/g) and the [–OH] (total accessible –OH by DABCO on surface) to be 2.77 ± 0.33 mol/L of SiO_2 (or 1.26 ± 0.15 mmol/g).

Both, three-(k_{S1}, k_{eq}, and $[S_1]_0$; solid line curve) and four-variable (k_0', k_{S1}, k_{eq}, and $[S_1]_0$; dashed line curve) least-squares fits of data on a 150-Å pore size Davisil silica gel/cyclohexane system are shown in Figure 9. The results are listed in Table IV, and the discrepancy between three- and four-variable fits is small. The computer fittings demonstrate that the proposed two-adsorption-site model can describe the kinetics of DABCO quenching $^1\Delta_gO_2$ in this porous silica gel/cyclohexane system. Since the [–OH] (total accessible –OH by DABCO on surface) is 2.77 ± 0.33 mol/L of SiO_2 and the $[S_1]_0$ is 2.408 ± 0.003 mol/L of SiO_2 on the studied Davisil surface accessible by DABCO, the difference is the concentration of double-adsorption-site $[S_2]_0$. In other words, the double-adsorption site for DABCO is 13.1 ± 3.2% of the total –OH accessible by DABCO on 150-Å pore size Davisil silica gel.

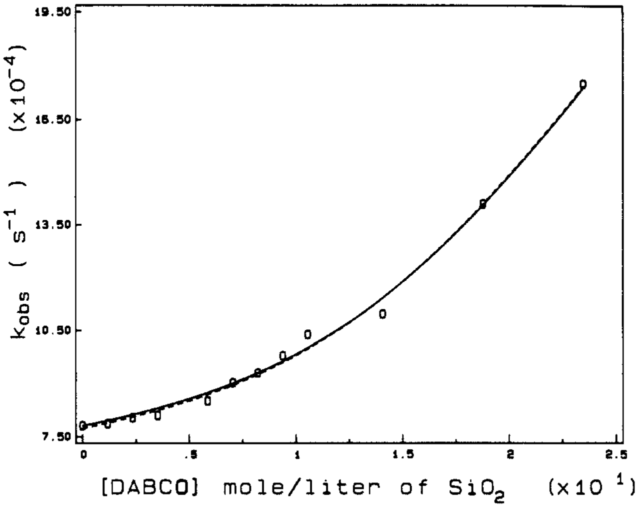


Figure 9. Three- (k_{S1}, K_{eq}, and $[S_1]_0$; solid curved line) and four-variable (k_0', k_{S1}, K_{eq}, and $[S_1]_0$; dashed curved line) least-squares fits based on two-adsorption-site model (eqs 3–6 in text) applied to DABCO quenching of $^1\Delta_gO_2$ in a 150-Å pore size Davisil silica gel/cyclohexane system. The data were taken from Figure 6B.

Adsorption of amines on the surface decreases the hydroxyl group content available for $^1\Delta_gO_2$ quenching and, hence, decreases the observed decay rate (k_{obs}) as seen for the monoamines. The DABCO quenching of $^1\Delta_gO_2$ on porous silica system is significantly faster than the natural decay by reaction with surface –OH group ($k_{S1} \gg k_q$(water), vide ante), and no correction for elimination of the surface –OH by amine is made.

Conclusion

Studies are reported for the time-resolved phosphorescence (1270 nm) of singlet molecular oxygen generated by a photosensitized reaction in silica gel/cyclohexane heterogeneous systems. The experimental results demonstrate that hydroxyl groups (e.g., adsorbed water and silanol groups) on the surface of silica gel quench singlet molecular oxygen and that this quenching becomes more significant in the case of porous and compressed fumed silica gel systems. These phenomena support that singlet molecular oxygen, following creation on the silica gel surface, rebounds between the silica gel surfaces inside the pores. Quenching of singlet molecular oxygen in porous silica gel/cyclohexane system by monoamines is much less effective than that in homogeneous solution and leads to a modified silica gel surface where fewer free –OH groups are available for reaction. Diamines, however, maintain their quenching activity especially at high loading conditions, at which more diamine molecules are adsorbed at the single-adsorption sites and quench $^1\Delta_gO_2$.

Acknowledgment. We thank the National Science Foundation for support of this work. K.-K. Iu thanks Jim Griffith for helping to develop the print circuit board of the Ge detector. We also thank Professor F. Wilkinson for a helpful discussion.

Registry No. DABCO, 280-57-9; O_2, 7782-44-7; cyclohexane, 110-82-7; dipropylamine, 142-84-7; tributylamine, 102-82-9; piperazine, 110-85-0; diisopropylamine, 108-18-9.

---

[32] This is calculated from the known bond lengths and bond angles.