

Benzophenone Triplet Quenching by Oxygen at the Gas/Solid Interface: A Target Annihilation Reaction in the Restricted Pore Geometry of Silica

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We have investigated, by diffuse reflectance time-resolved laser spectroscopy, the quenching of triplet-state benzophenone by oxygen in the Knudsen regime within the restricted pore geometry of a homologous series of silica gels. The quenching dynamic is modeled as a target annihilation reaction in 3D. A general scaling behavior is reported that relates the rate of annihilation (k_q) to the characteristic mean pore size of the silica (R_p). The scaling behavior observed is shown to be predicted by a simple random-walk picture of the oxygen diffusion within the pore space.

Introduction

Recently there has been considerable interest in molecular dynamics in restricted geometries. Results have been reported for molecular diffusion,^{1,2} exciton transport,^{3,4} direct energy transfer,^{5,6} and photodissociation.⁷ A variety of porous materials have been used as model systems of restricted geometries including Vycor glass, silica gel, membranes, and zeolites. These experiments are complimented by a growing number of theoretical works dealing with reactions in disordered solids⁸ and fractals.⁹

Heterogeneous reactions, in particular those at the gas/solid interface, have been widely studied, and many reaction systems have been discussed in the catalysis literature. For reactions that occur on a surface, we must in general consider the overall kinetics to involve some combination of consecutive or simultaneous processes: (a) diffusion of the reactant(s) to the surface, (b) adsorption of the reactant(s), (c) reaction at the surface site, (d) desorption of the product(s), and (e) diffusion of the product(s) away from the surface. The first step may involve either gas-phase diffusion or surface diffusion. The problem of surface diffusion has been discussed by Freeman and Doll¹⁰ and by Cukier.¹¹ What is important to notice about this reaction scheme is the major role of Langmuir type adsorption/desorption processes. Reaction systems that involve these adsorption/desorption processes have been characterized as being either Langmuir-Rideal (Eley-Rideal) or Langmuir-Hinshelwood. Reaction between gas-phase and surface-adsorbed molecules are Langmuir-Rideal,¹² and those reactions involving two adsorbed molecules are Langmuir-Hinshelwood.¹³ The work we describe is predominantly Langmuir-Rideal in character and is discussed as a target annihilation reaction by a random walker, using the theoretical work by Blumen et al.¹⁴ on target annihilation reactions.

We describe here the results of a "target annihilation reaction" between benzophenone and oxygen for a homologous series of silica gels of varying pore size. The reaction system studied involves a gas-phase ground-state triplet oxygen molecule (the random walker, or quencher) and a surface-bound excited-state triplet benzophenone molecule (the target). The annihilation reaction was studied at low oxygen partial pressures to keep the mean free path (λ) of oxygen much larger than the mean pore diameter ($2R_p$) of the silica gel (the Knudsen regime). In the Knudsen regime, where the Knudsen number (K_n) is given by

$$K_n = \frac{\lambda}{2R_p} > 1 \quad (1)$$

we can consider the diffusion of oxygen in the pore network of silica as a random walk in which each successive step of the walk is terminated by a collision with the pore boundary.¹⁵ Over the typical pressure range studied the mean free path of oxygen is greater than R_p , as calculated from

$$\lambda = \frac{kT}{2^{1/2}\pi\sigma^2P_{O_2}} \quad (2)$$

Taking a value for σ of 3.45 Å, at 250 Torr of oxygen the mean free path is 2200 Å. The observable in our experiment is the survival probability ($\Phi(t)$) of the target which is the lifetime of the excited benzophenone triplet (τ_1). From measurements of $\Phi(t)$ for different oxygen partial pressures, an overall annihilation rate (k_q) was measured for each silica. The results indicate that a general scaling relationship exists between R_p and k_q for each homologous series of silica gels. It is shown that in the Knudsen regime, where the annihilation rate is dominated by ballistic collisional quenching by gas-phase oxygen, the rate of reaction (k_q) increases linearly with the mean pore size (R_p). This scaling result is shown to be obtainable from a simple random-walk model in the limiting case of negligible quenching by oxygen surface diffusion and for porous silica gels with the same morphological pore structure.

Experimental Section

The reaction dynamics of triplet quenching by oxygen was measured by exciting (308 nm, 20 ns, fwhm excimer laser pulse),

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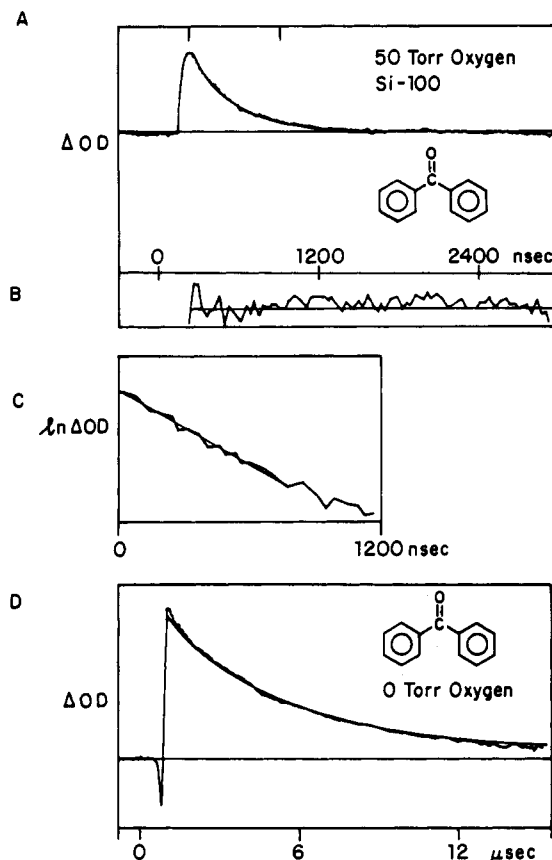


Figure 1. A: Benzophenone triplet annihilation decay for Si-100 lichrospher silica at 50 Torr of oxygen, where the two small lines above the curve denote the range for the first exponential fit of the data; B is the residuals from the first exponential fit of the data shown in C. D is the decay of the benzophenone triplet adsorbed on the same silica without added oxygen gas.

a small fraction of the surface-bound benzophenone to the triplet state via conventional (picosecond) intersystem crossing from the singlet manifold. The survival probability was determined by measuring the relaxation of the benzophenone triplet population with time-resolved diffuse reflectance transient absorption (TRDR). The experimental arrangement is essentially the same as that described by Wilkinson et al.¹⁶

The change in the triplet-state population of benzophenone was followed by probing the triplet-triplet absorption of benzophenone at 520 nm. The time dependence of the reflected signal at 520 nm is linearly related to the change in absorbance for weakly absorbing samples. The signals shown in Figure 1 are reported as relative changes in absorption of the reflected signal (OD). Two series of silica gels were used, each composed of silicas having different mean pore sizes but sharing the same morphological structure. The silica gels were prepared by E. Merck (Darmstadt, West Germany). These silicas are used primarily as chromatographic supports.

The lichrospher series has a pore structure derived from random packing of nearly monodispersed spheres of radius R_b with partially sintered interfaces. The interface of these spheres appears smooth at lengths greater than 10 Å. For this type of pore morphology it has been shown that $R_b \approx R_p$.¹⁷ The lichrospher silicas include Si-100, Si-300, Si-500, and Si-1000 with a mean particle size of 10 μm, having Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of 409, 228, 68, and 48 m²/g, and R_p of 34, 60, 200, and 286 Å, respectively. The second series of silicas are similar in structure to lichrospher but exhibit a hierarchical growth morphology. The primary building blocks of radius R_B associate, forming a secondary particle of radius R_B^* (where R_B^* is between

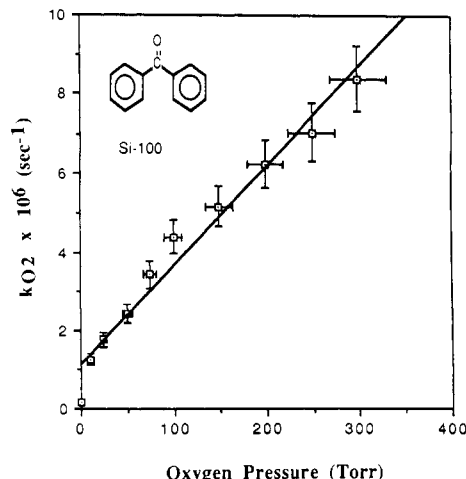


Figure 2. Decay rate of benzophenone triplet adsorbed on Si-100 lichrospher silica at various pressures of oxygen.

500 and 2500 Å) which aggregate further forming the macroscopic particle 120 μm in diameter. The silicas Si-40, Si-60, and Si-100 have S_{BET} of 768, 391, and 281 m²/g and R_p of 18, 35, and 60 Å.¹⁷

The samples were prepared by adsorbing benzophenone from pentane solution, giving surface concentrations of less than 5×10^{-5} mol/g of silica. The benzophenone molecules are adsorbed and strongly anchored to the silica surface during the triplet lifetime. The solvent was removed by initially placing the sample in a stream of warm air and then placing it under vacuum. The spatial distribution of the benzophenone is unknown and defined by the active sites of the interior pore surface of the silica. The evacuated sample cell, containing benzophenone on silica, was equilibrated with varying partial pressures of oxygen or other gases.

Results and Discussion

The benzophenone triplet annihilation rate constant (k_q) was measured for each silica by measuring $\Phi(t)$ as a function of oxygen pressure. The $\Phi(t)$ decays (see Figure 1) were fit to a single exponential as

$$\Phi(t) \propto \exp(-k_{O_2}t) \quad (3)$$

where

$$k_{O_2} = \frac{1}{\tau_1} + k_q P_{O_2} \quad (4)$$

and τ_1 is the triplet-state lifetime of the adsorbed benzophenone. The exponential form of $\Phi(t)$ is predicted by the target annihilation picture of Blumen et al.¹⁴ in the limit where the target concentration is much less the quencher concentration. The data for $\Phi(t)$, at low oxygen concentration (see Figure 2, lichrospher Si-100, 50 Torr of O₂) appear to fit an exponential reasonably well. However, in some cases of high oxygen partial pressures $\Phi(t)$ appears to be nonexponential. The fits become more difficult because as the rate of quenching increases, the signal-to-noise decreases and there are fewer data points to fit. This problem is particularly pronounced for the silicas with large R_p and small surface areas. It is important to keep the number of targets small. Therefore, the signal-to-noise problem cannot be solved by simply increasing the surface concentration of benzophenone and creating more targets. In addition to the experimental limitations, as the oxygen pressure is increased, there is an increase in the fractional surface coverage of oxygen (θ_{O_2}). For Langmuir adsorption the value of θ_{O_2} is given by

$$\theta_{O_2} = \frac{K P_{O_2}}{1 + K P_{O_2}} \quad (5)$$

where K is the equilibrium constant defined by the ratio of the adsorption/desorption rates for oxygen on silica gel at 25 °C. We have not determined the adsorption isotherms for oxygen on each

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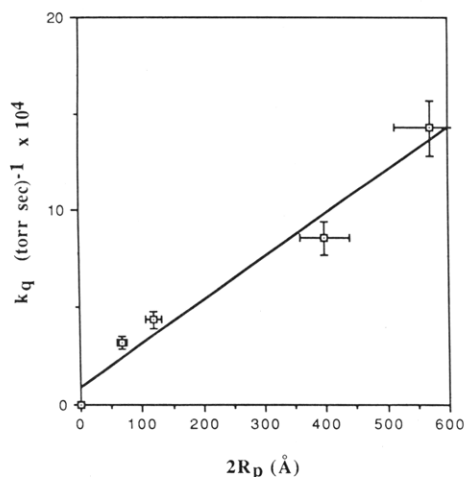


Figure 3. Quenching rate of benzophenone triplet k_q by oxygen versus the mean pore diameters for a series of Lichrospher silicas at low surface coverage θ_{BZP} : Si-100 = 3.15×10^4 mol/m², Si-300 = 4.37×10^4 mol/m², Si-500 = 6.63×10^4 mol/m², and Si-1000 = 7.00×10^4 mol/m².

of these silicas, but work by Markham and Benton¹⁸ indicates that substantial oxygen can be adsorbed on silica in the temperature range between 0 and 100 °C. Therefore, P_{O_2} in our experiment is a complex variable that determines the quencher concentration both in the pore and on the surface. As the limiting surface coverage of oxygen is approached, for some silicas a second annihilation reaction is present and is occurring concurrently with the ballistic quenching reaction. The second reaction is of the Langmuir-Hinshelwood type and is due to surface diffusion of oxygen to nearest-neighbor sites occupied by excited benzophenone. In this limit of the oxygen pressure, the form of $\Phi(t)$ is nonexponential, and the annihilation reaction goes from predominantly a reaction in three dimensions (3D) to having a component in 2D,¹⁴ where $\Phi(t)$ is of the form

$$\Phi(t) \approx \exp(-k^*t/\ln t) \quad (6)$$

Therefore, the quenching data presented are fit only to the exponential portion of the decay, and the characteristic rates are reported by recognizing these overall limitations and the inherent error in fitting only part of $\Phi(t)$. What we attempt to show is that the 3D ballistic quenching process dominates under the conditions for which our results are derived.

From the P_{O_2} versus k_{O_2} data, where k_{O_2} is the inverse of the measured lifetime of the benzophenone triplet population, a value of k_{O_2} was obtained for each silica gel (see Figure 2). At the oxygen pressure used, k_{O_2} increases linearly with P_{O_2} . The observed ($P_{\text{O}_2} = 0$) triplet-state lifetime for benzophenone ranged from 0.9 to 5.5 μs for the samples studied. As shown in Figure 2, for silica gel 100, the measured zero-pressure lifetime is longer than the interpolated lifetime obtained from the intercept value of the fit to the quenching data. These data represent a typical extreme observed in the benzophenone lifetime data. These observed fluctuations in the zero-pressure lifetimes are believed to be caused by differences in the chemical heterogeneity of the local surface of each silica and variations in sample preparation (i.e., dissolved oxygen in the pentane, sample handling, etc.) leading to different concentrations of surface-adsorbed oxygen (θ_{O_2}). Evidence for this can be seen in Figure 1D for silica gel 100. The best-fit line to the triplet relaxation data, when extrapolated to early times, underestimates the initial rate, suggesting a "static-like" quenching due to an oxygen/benzophenone nearest-neighbor surface complex.

The value of the slope of the plot of k_{O_2} versus P_{O_2} is the target annihilation rate (k_q). In Figure 3 we present k_q versus R_p for a Lichrospher series of silica gels. What is most striking about these data is the strong dependence of k_q on R_p . This linear scaling relationship holds for the Lichrospher series of silica gels over nearly a decade in R_p ($2R_p$ between 68 and 572 Å).

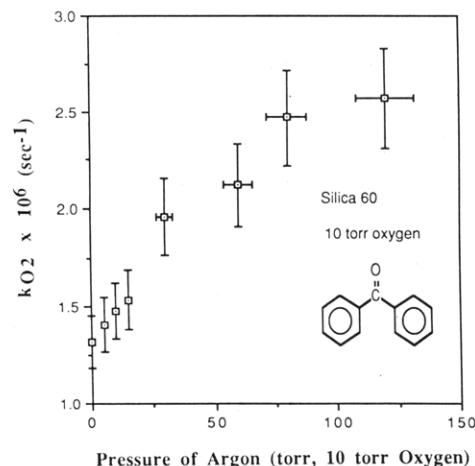


Figure 4. Rate of decay of benzophenone triplet adsorbed on Si-60 silica with 10 Torr of oxygen and varying pressures of argon.

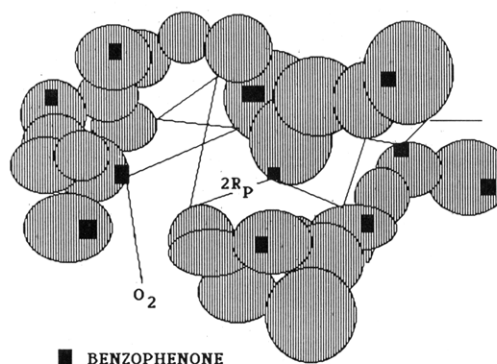


Figure 5. Random walk of oxygen for the target annihilation of benzophenone adsorbed on a porous solid with mean pore radius of R_p and net molecular displacement of R_N .

These general scaling results are most pronounced and clearly show the overriding dependence of k_q on R_p in the Knudsen regime. This scaling behavior holds for all oxygen pressures even though it is evident from $\Phi(t)$ that the surface diffusion annihilation by oxygen, which would be independent of R_p , is present at some oxygen pressures. Therefore, the annihilation rate is dominated in the Knudsen regime by a ballistic quenching mechanism that we suggest can be described by the 3D random walk of oxygen in a restricted geometry defined by the pore space of silica.

In an effort to establish that the annihilation reaction is dominated by ballistic collisional quenching, we performed a second series of experiments using both oxygen and a variety of inert buffer gases (i.e., He, Ar, and N₂). It was first established that in the absence of oxygen the addition of buffer gas did not affect the lifetime of triplet benzophenone. Then the partial pressure of oxygen was set to 10–15 Torr, and the buffer gas pressure was increased incrementally to a final pressure of 50–400 Torr depending on the sample. As the buffer gas pressure was increased, the rate of quenching increased (see Figure 4). We interpret these results using a modified form of the Langmuir adsorption equation, (5), for two noninteracting adsorbing gases¹⁸ to produce

$$\theta_{\text{O}_2} = \frac{K P_{\text{O}_2}}{1 + K P_{\text{O}_2} + K' P_{\text{B}}} \quad (7)$$

where K' is the equilibrium constant for the buffer gas. P_{B} is the partial pressure of buffer gas; however, the values of P_{B} shown in Figure 4 are in fact the total gas pressures as both buffer gas and oxygen are present in the pore volume. From eq 7 we see that as the buffer gas pressure increases, the fractional surface coverage of oxygen decreases, making more oxygen molecules available for quenching from the gas phase. If the quenching process was dominated by oxygen surface diffusion, the buffer gas would hinder the surface reaction as more and more surface

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sites became blocked by adsorbed buffer gas. We recognize that these observations may lend themselves to other interpretations. However, they are consistent with the gas-phase quenching picture that we are presenting.

On the basis of these results, we present a model for the annihilation reaction that confirms the scaling observed between k_q and R_p . The random walk of oxygen is depicted in Figure 5. After N reflections from the pore boundaries, the net molecular displacement is

$$R_N = \sum_{i=1}^N r_i \quad (8)$$

The average displacement is then given by

$$\langle R_N^2 \rangle = \sum_{i,j} \langle r_i r_j \rangle \quad (9)$$

If the oxygen molecule is diffusely scattered and at the same time its velocity is thermalized, we can assume that the reflections from the pore boundaries randomize the molecular velocities according to a Maxwellian distribution. Therefore

$$\langle r_i r_j \rangle = \delta_{ij} \langle r_i^2 \rangle \quad (10)$$

and R_p is therefore directly correlated to

$$R_p \propto \langle r_i^2 \rangle^{1/2} \quad (11)$$

In addition, we must include a geometric factor $g > 0$, which connects the value of R_p to the local morphological organization of the pore space and describes the tortuosity of the pore medium on the length scale of the random walk. Then we set

$$\langle r_i^2 \rangle = (gR_p)^2 \quad (12)$$

After N steps the total flight of an oxygen molecule (L) can be expressed by

$$L = NgR_p \approx \langle v \rangle t \quad (13)$$

where $\langle v \rangle$ is the oxygen mean molecular velocity given as

$$\langle v \rangle = \left(\frac{8kT}{\pi M_{O_2}} \right)^{1/2} \quad (14)$$

and t is the average flight time of an oxygen molecule. From eq 8–14 we obtain

$$\langle R_N^2 \rangle = gR_p \langle v \rangle t \quad (15)$$

which permits us to deduce an approximate expression for the diffusion coefficient (D_{KN}) of oxygen in the Knudsen regime inside the pore space of silica:

$$D_{KN} = \frac{1}{6} \frac{d\langle R_N^2 \rangle}{dt} = \frac{1}{6} gR_p \langle v \rangle \quad (16)$$

Except for the factor g , this expression is very close to the expression for the Knudsen diffusion coefficient for a gas in an infinite-length capillary tube.¹⁹

We consider the case of porous solids, for which the mean free path of the quencher obeys $\lambda \gg R_p$. If the pore surface fills the pore space uniformly but is not described by a regular geometry, then the target annihilation reaction can be treated as a homogeneous reaction in a 3D space.²⁰ From this argument we can write the kinetic expression for the benzophenone triplet population (N_T^*) in the form of a Smoluchowski equation relating N_T^* to the diffusion coefficient (D_{KN}):

$$-\frac{dN_T^*}{dt} = 4\pi\alpha r_{AB} D_{KN} \frac{P_{O_2}}{kT} N_T^* + \frac{N_T^*}{\tau_1} \quad (17)$$

where α is the efficiency of the annihilation reaction ($\alpha \ll 1$) for oxygen quenching benzophenone on silica, r_{AB} is the capture radius for the reactants, and the other terms have been previously defined. Substituting eq 16 in eq 17, we obtain

$$-\frac{dN_T^*}{dt} = \frac{4}{6} \pi \alpha r_{AB} g R_p \frac{P_{O_2}}{kT} N_T^* + \frac{N_T^*}{\tau_1} \quad (18)$$

where k_q is given by

$$k_q = \frac{4}{6} \pi \alpha r_{AB} g R_p \frac{\langle v \rangle}{kT} \quad (19)$$

This result predicts directly the observed scaling between k_q and R_p that was found experimentally, in the Knudsen limit ($\lambda \gg R_p$) for porous silicas of nearly the same g .

A second limiting case is when $\lambda \ll R_p$. Then the quenching process must be considered as a heterogeneous reaction. The quenchers strike the pore boundary just after a collision with another gas-phase molecule. In this limit the pore volume has no real influence on the annihilation process. If on the length scale of λ the pore boundary appears as a smooth surface, we may rewrite eq 17 as

$$-\frac{dN_T^*}{dt} = \frac{1}{4} \alpha \langle v \rangle \sigma_{BZP} \frac{P_{O_2}}{kT} N_T^* + \frac{N_T^*}{\tau_1} \quad (20)$$

where $\langle v \rangle P_{O_2}/kT$ is related to the number of quencher molecules striking the wall per unit time and per unit area, and σ_{BZP} is the average cross section of an adsorbed benzophenone. From eq 20 we can estimate k_q in this limit by

$$k_q = \frac{1}{4} \frac{\alpha \langle v \rangle \sigma_{BZP}}{kT} \quad (21)$$

It is clear that when $R_p \gg \lambda$, k_q becomes independent of R_p . Comparing the overall reaction rates for the two limits, $k_q = (k_q)_K$ when $R_p \ll \lambda$ and $k_q = (k_q)_g$ for $R_p \gg \lambda$, using eq 19 and 21, we have

$$\frac{(k_q)_K}{(k_q)_g} = g R_p \frac{r_{AB}}{\sigma_{BZP}} \quad (22)$$

and letting $(r_{AB})^2 = \sigma_{BZP}$, eq 22 becomes

$$\frac{(k_q)_K}{(k_q)_g} = g \frac{R_p}{(\sigma_{BZP})^{1/2}} \quad (23)$$

Here, the value of g is slightly greater than 1,²¹ and for the case of an infinite cylinder, g is found to be 4. Generally, $(k_q)_K$ is larger than $(k_q)_g$, except when R_p approaches $(\sigma_{BZP})^{1/2}$. In this limit there are excluded volume effects that prevent benzophenone from accessing the interior pore surface of the porous particle. The annihilation experiment then becomes more sensitive to oxygen quenching on the macroscopic external surface. This limit may be reached in porous silicas with micropores and/or when there is a screening effect on very rough surfaces.²²

For all the silica samples we have studied there are both internal and external surfaces. We describe two populations of triplet benzophenone: $(N_T)_I$ for the benzophenone on the interior pore surface and $(N_T)_E$ for the population on the external surface. In general, although TRDR probes both surface regimes simultaneously, the signal from $(N_T)_E$ is assumed to be negligible and therefore does not contribute to the observed $\Phi(t)$. This is likely to be a good assumption for those silicas where the internal surface is much greater than the external surface. If this condition were not met, we would expect to observe a biexponential decay for $\Phi(t)$, with the exponents associated with the different quenching rates for the two surface regimes.

For the lichrospher series, where the morphological structure is based on a nearly monodispersed building block, the observed

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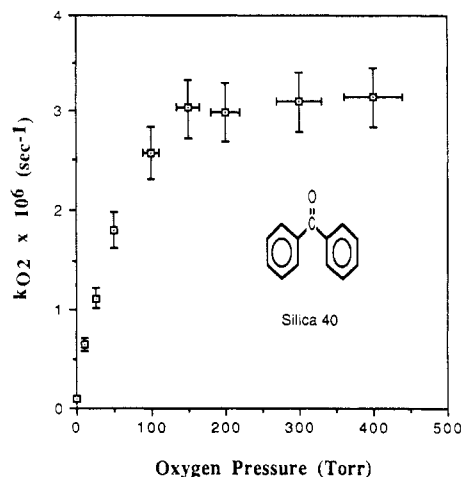


Figure 6. Rate of decay of benzophenone adsorbed on Si-40 silica as a function of oxygen pressure.

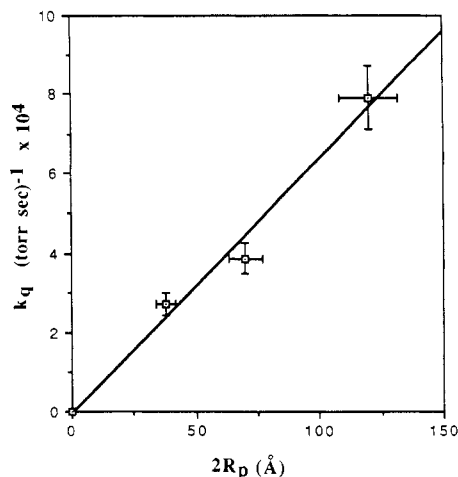


Figure 7. Quenching rate of benzophenone triplet by oxygen for a series of silicas with a hierarchical growth morphology as a function of the mean pore diameter of the silica.

quenching rate is associated with the benzophenone population on the interior surface. However, for the second series of silicas, Si-40, Si-60, and Si-100, which have a bimodal pore size distribution due to their hierarchical growth morphology, the existence of two surface regimes are evident in the quenching reaction.

When we measured the pressure dependence of k_{O_2} for Si-40, to obtain k_q , the quenching rate appeared to saturate at oxygen pressures greater than 100 Torr (see Figure 6). If we interpret this dramatic change in k_{O_2} above 100 Torr of oxygen as a crossover in the quenching mechanism to non-Knudsen diffusion ($K_N \leq 1$), this would correspond to an oxygen mean free path of 5500 Å, suggesting that the mean pore radius in the quenching regime is near 2700 Å. This is inconsistent with a $R_p = 36$ Å for Si-40, if k_{O_2} is for benzophenone on the interior pore surface defined by the primary pores building blocks. (To observe a crossover to non-Knudsen-like quenching in the primary pores of Si-40 would require an oxygen pressure of close to 14 000 Torr.) Therefore, we propose that the $(k_q)^*K$ for Si-40, measured by the tangent to the low-pressure quenching, is for benzophenone on the external surface of the secondary building blocks. Furthermore, the $(k_q)_K$ obtained from the quenching data above 100 Torr of oxygen is for benzophenone on the surface of the primary building blocks. The magnitude of the annihilation rate scales linearly with R_p , therefore

$$\frac{(k_q)^*K}{(k_q)_K} \propto \frac{R_p^*}{R_p} \approx 125 \quad (24)$$

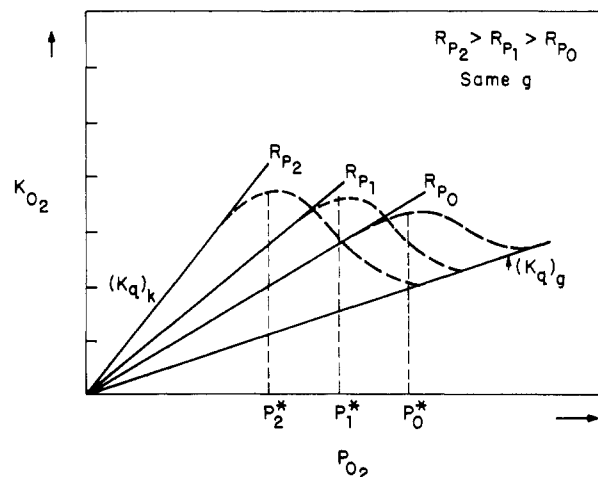


Figure 8. Annihilation rate, k_{O_2} , for a homologous series of porous materials characterized by mean pore sizes, R_p . The annihilation rate scales with mean pore size with a slope of $(k_q)_K$. At the transition period, denoted by P^* , non-Knudsen diffusion predominates, and the annihilation rate decreases to an asymptotic rate given by $(k_q)_g$ and independent of R_p .

for Si-40, and similar behavior is expected for Si-60 and Si-100. In Figure 7, we show the scaling of $(k_q)^*K$ with R_p for Si-40, Si-60, and Si-100. Again, as with the lichrosper series, $(k_q)^*K$ increases with R_p . The fact that $(k_q)^*K$ scales with R_p suggests that $R_p \sim \beta R_p^*$, where β is a constant relating the size scaling between the primary and secondary building blocks. At this time we lack a detailed understanding of scaling between the two morphological regimes. But the crossover to non-Knudsen diffusion is strongly suggestive of two benzophenone triplet populations distributed in two surface regimes, which is consistent with our current understanding of the structure of these silicas.¹⁷

We can generalize our results qualitatively as shown in Figure 8 for a homologous series of porous materials. Each material is defined by a characteristic pore size, which is made up of a distribution of pore sizes, that is finite and narrow, such that $R_{p0} < R_{p1} < R_{p2}$. For each silica the annihilation rate should increase linearly with the partial pressure of oxygen with the slope given by $(k_q)_K$ (eq 19). As the value of R_p approaches λ , a transition region is reached. This region is defined by the transition oxygen pressure, $P_{O_2}^*$, which is inversely proportional to R_p . Above $P_{O_2}^*$, the annihilation rate decreases to reach an asymptotic rate given by $(k_q)_g$ (eq 21), which is independent of R_p . In the crossover regime, where $\lambda = R_p$, there would be a plateau in the k_{O_2} versus P_{O_2} data.

Conclusions

For the reaction system of excited triplet benzophenone on silica gel quenched by ground-state triplet oxygen, the annihilation rate of benzophenone scales linearly with the mean pore size of the silica. This scaling is observed for oxygen pressures where the mean free path is greater than the mean pore size (Knudsen regime). In the Knudsen regime the annihilation reaction can be modeled by a random-walk picture in 3D. The scaling behavior observed dominates the results even though there is the possibility that there may be some quenching by the surface diffusion of oxygen. We are currently extending these experiments to understand the role of surface-adsorbed oxygen and (by improving the measurement sensitivity) to better characterize the survival probability of triplet benzophenone at long times.

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