

## Gas-Phase Quenching of Excitations as a Probe of Dynamics in Porous Silicas

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The quenching of an electronically excited adsorbed molecule by gas-phase quenchers within the pore network of several porous silicas has been studied. It is proposed that the early-time quenching rate should scale with the mean pore size,  $R_p$ , for gas pressures in the Knudsen regime. We have experimentally observed such scaling in what we believe is the first study of these quenching reactions in a homologous series of morphologically similar porous silicas.

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There has been a growing effort devoted to understanding dynamical processes of excited molecules embedded in restricted geometries. The emphasis has been on distributing molecular probes in porous materials having pore geometries with dimensions on length scales small enough to influence molecular dynamics. These materials include Vycor glass,<sup>1-4</sup> membranes,<sup>5</sup> porous silicas,<sup>6-9</sup> and many others. Common to these examples is that the molecules participating in photophysical or photochemical processes occupy sites or move subject to spatial restrictions imposed by the pore structure. It has been recently demonstrated that luminescent probes may serve as sensors of complex structures of microenvironments and also probe differences between global and local motions within confined spaces.<sup>1-10</sup> The idea is to focus on those observables which are sensitive to the geometrical aspects of the porous materials. Translational diffusion, rotational diffusion, excimer formation, and intermolecular energy transfer have been studied and have led to new insights into the complexity of these systems.

We have previously studied self-diffusion of dye molecules on scales large enough to be dominated by the tortuosity of the pore structure.<sup>2</sup> Smaller length scales have been recently probed on a family of porous silicas with direct energy transfer.<sup>6</sup> In the latter experiments an excited adsorbed molecule (donor) loses its energy to quenching molecules (acceptors), which are also randomly adsorbed on the pore network interface, because of long-range dipolar interactions. From the temporal decay pattern of the initially excited donor one obtains information about the underlying morphology. It has been realized that in the family of porous silicas which have been investigated the *mean pore size*  $R_p$  is a *significant length*.  $R_p$  partly characterizes the local pore structure<sup>6,8,9,11</sup> as has been strongly supported<sup>8,9</sup> by small-angle x-ray scattering of the same silicas, surface-area measurements, and electron micrographs.

In this Letter we report on experimental systems in which the quenching molecules move. Their motion, within the spatial confinement of the pore network, leads to quenching of the excited adsorbed donor encounter. In order for the pore geometry to play a major role one has to make sure it is not molecule-molecule collisions among the quenchers that dominate the diffusion, but rather the scattering of the individual quenchers off the pore boundaries. Such a behavior is expected for quenchers in the gas phase in the Knudsen regime.<sup>12-15</sup> The criterion for Knudsen diffusion is that the mean free path due to gas-phase molecule-molecule scattering,  $\lambda$ , is larger than the mean pore size,  $R_p$ ,

$$\lambda \gg R_p, \quad (1)$$

where  $\lambda = k_B T / \sqrt{2} \pi \sigma^2 P$ ,  $\sigma$  is the collision diameter of the molecules, and  $P$  is the gas pressure. We are then in the limit of relatively small pores where the quenchers collide more often with the pore walls than with each other. The problem of donor quenching due to Knudsen diffusion is complementary to the direct-energy-transfer problem.<sup>6</sup> In the energy-transfer case the boundaries restricted the *location* of the adsorbed quenchers. Here the same boundaries restrict the *motion* of the quenchers. In both cases it is possible to relate morphological information to dynamical process (decay of the donor).

The problem of calculating the survival probability of the donor, due to quenchers in the Knudsen regime, can be cast in a framework similar to that of the target model<sup>16</sup> which provides a random-walk description of reactions of the type  $Q + T \rightarrow Q$ .  $T$  is a static target (our donor) quenched by the diffusing quenchers  $Q$ . We assume that the pore space in porous silicas can be viewed as a three-dimensional homogeneous, yet tortuous, network. The quenching of a low concentration of randomly adsorbed donors by gas-phase quenchers can then be modeled through a three-dimensional target picture where (a) the quencher diffusion is determined by col-

lisions with the solid walls of the material, (b) the porosity and tortuosity are folded into the diffusion as a structure factor, and (c) possible contributions from surface diffusion of adsorbed quenchers are negligible. In the early-time small-density limit, the leading term in the survival of the donor is given as an exponential in terms of a Smoluchowski-type decay rate,<sup>16,17</sup>

$$\Phi(t) = \exp(-Kt), \quad (2)$$

with

$$K = k_q + \tau^{-1}. \quad (3)$$

Here  $\tau^{-1}$  is the triplet lifetime decay rate of the isolated donor and  $k_q$  is the Smoluchowski-type expression for the donor annihilation by the quenchers,

$$k_q \sim nDr_{AB}, \quad (4)$$

where  $n$  is the quencher-gas density and  $r_{AB}$  is a reaction radius.  $D$  is an averaged Knudsen diffusion coefficient of the quencher which has been shown to scale with the mean pore size<sup>12-15</sup>

$$D(R_p) = g\bar{v}R_p, \quad (5)$$

where  $\bar{v}$  is the mean quencher's velocity and  $g$  is a structure factor which depends on porosity, tortuosity, and other structural details.<sup>18</sup> With the assumption of ideal gas conditions,  $\bar{v} = (8k_B T/\pi m)^{1/2}$  and  $n = P/k_B$ , where  $m$  is the quencher's molecular mass and  $P$  is the gas pressure. If the structure factor  $g$  varies only slowly within a homologous series of silica as supported by small-angle x-ray-scattering measurements,<sup>8</sup> then the above assumptions and Eqs. (4) and (5) yield

$$k_q \sim gn\bar{v}R_p r_{AB} = (g\bar{v}r_{AB}/k_B)R_p P, \quad (6)$$

and the initial donor decay rate scales with the mean pore size of the silicas and with the gas pressure. Equation (6) can also be derived by our calculating the frequency of collisions of an ideal gas of density  $n$  with a section of length  $r_{AB}$  on the wall of a cylinder of radius  $R_p$ . This frequency is<sup>12</sup>  $(1/2\pi)n\bar{v}R_p r_{AB}$  and is directly related to the decay rate of the adsorbed donor. Both approaches describe the same geometry-dependent mechanism of the quenching process. However, a cylindrical pore is not necessary for the interpretation.<sup>15</sup>

In the opposite limit, where the molecule-molecule mean free path is smaller than the mean pore size,  $\lambda \ll R_p$ , Knudsen diffusion is not important. In this limit one should consider simple diffusion of the quenchers towards the excited target. Such a situation also occurs in the case of a solvent-filled porous system so that the quenchers' diffusion is determined by their interactions with the solvent. In this case another spectroscopic method has been proposed by de Gennes<sup>19</sup> in order to probe the pore surface morphology. The idea has been to follow the relaxation of diffusing excited molecules

quenched by traps bound to the surface. The predicted time evolution in this limit differs from our Knudsen behavior.

Experimentally we have studied the quenching of initially excited triplet benzophenone by oxygen molecules.<sup>20</sup> The reaction dynamics of triplet quenching by oxygen was measured by exciting (308 nm, 20-ns FWHM excimer-laser pulse) a small fraction of surface bound benzophenone to the triplet state via intersystem crossing from the singlet manifold. The survival probability was determined by the measurement of the relaxation of the benzophenone triplet population with time-resolved diffuse reflectance transient absorption. The experimental arrangement is essentially the same as that described in a paper by Wilkinson and Willsher.<sup>21</sup> A family of silica gels was used in which each silica had a different mean pore size while they shared the same morphological structure. The silica gels (lichrospher) were prepared by Merck (Darmstadt, Germany). The lichrospher series is characterized by a pore structure derived from random packing of nearly monodisperse spheres with partially sintered interfaces. The interface of these spheres appears smooth at lengths greater than 10 Å.<sup>8</sup> The lichrospher silicas we used were Si-100, Si-300, Si-500, and Si-1000 with a mean particle size of 10 μm, and with  $R_p$  values of 34, 60, 200, and 286 Å, respectively. The samples were prepared by the adsorption of benzophenone from pentane solution which yields surface concentrations of less than  $5 \times 10^{-5}$  moles per gram of silica. The solvent was removed by initially placing the sample in a stream of warm air and then placing it under vacuum. The evacuated sample cell, containing benzophenone on silica, was equilibrated with varying partial pressures of oxygen, or other gases. The benzophenone molecules were adsorbed and strongly anchored to the silica surface during the triplet lifetime. At the range of pressures and temperatures of the experiment (room temperature) the mean free path  $\lambda$  is much larger than any  $R_p$ , i.e., for  $\sigma = 3.45$  Å and  $P = 250$  Torr Eq. (1) yields  $\lambda \approx 2200$  Å. We are, therefore, safely within the Knudsen limit.

The benzophenone-triplet quenching rate  $K$  was measured for each silica as a function of oxygen pressure. The decays of the benzophenone were fitted to a single exponential according to Eq. (2). In some cases of high oxygen partial pressure, however,  $\Phi(t)$  appears to be nonexponential. Deviation from exponentiality could be generally attributed to a decreasing signal-to-noise ratio as the rate of quenching increases,<sup>21</sup> to an increase in the fractional surface coverage of oxygen, or to a contribution from a pore size distribution. We did not determine the adsorption isotherms for oxygen on each of these silicas, but there are indications that substantial oxygen can be adsorbed on silica in the temperature range between 0 and 100°C. Therefore,  $P$  in our experiment was a complex variable which determined both the quencher con-

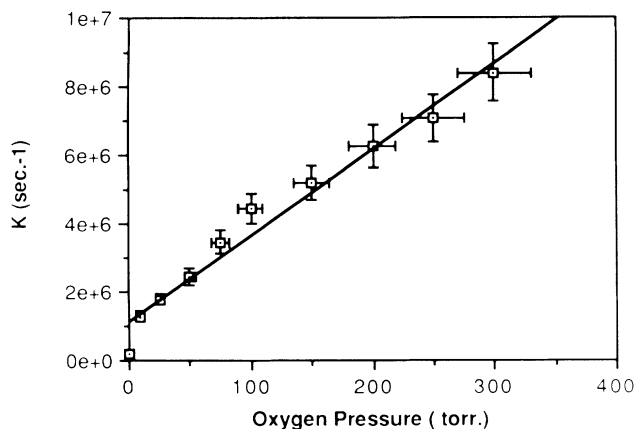


FIG. 1. The decay rate of benzophenone triplet adsorbed on Si-100 lichrospher silica at various pressure of oxygen.

centration in the pore and on the surface. As the limiting surface coverage of oxygen was approached for some silicas, a second quenching channel might have been present concurrent with the Knudsen quenching reaction. The second quenching could have been of the Langmuir-Hinshelwood-type 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 expected to be nonexponential and the benzophenone decay should then cross over from predominantly a three-dimensional Knudsen type to a two-dimensional surface diffusion component at later times. The donor decay laws analyzed were fitted to an exponential only in their *early-time* portion. The characteristic rates were reported recognizing these overall limitations and the inherent error in fitting only a part of  $\Phi(t)$ .

At the oxygen pressures used, the rate  $K$  increased linearly with the pressure  $P$  as expected (Fig. 1). The intercept at  $P=0$  was found to vary from sample to sample mainly because of differences in the amount of oxygen adsorbed on the surface. (This depended on sample preparation which was difficult to control, i.e., dissolved oxygen in pentane, sample handling, adsorbed  $H_2O$ , etc., but also possibly as a result of sample-dependent  $g$  values.) Although we cannot demonstrate conclusively at this time, we believe that small variations in the local surface environment of the adsorbed benzophenone influences its triplet lifetime. In Fig. 2 we present the rate  $K$  vs  $R_p$  for the lichrospher series of silicas. It is quite evident that  $K$  shows a linear dependence on  $R_p$  over nearly a decade of mean pore sizes ( $2R_p$  varies between 68 and 572 Å). These scaling results provide a strong supportive evidence for the dominance of the Knudsen-diffusion mechanism in our case.

In an effort to establish that the annihilation reaction is dominated by Knudsen collisional quenching we performed a second series of experiments using both oxygen and a variety of inert buffer gases (i.e., He, Ar, and  $N_2$ ).

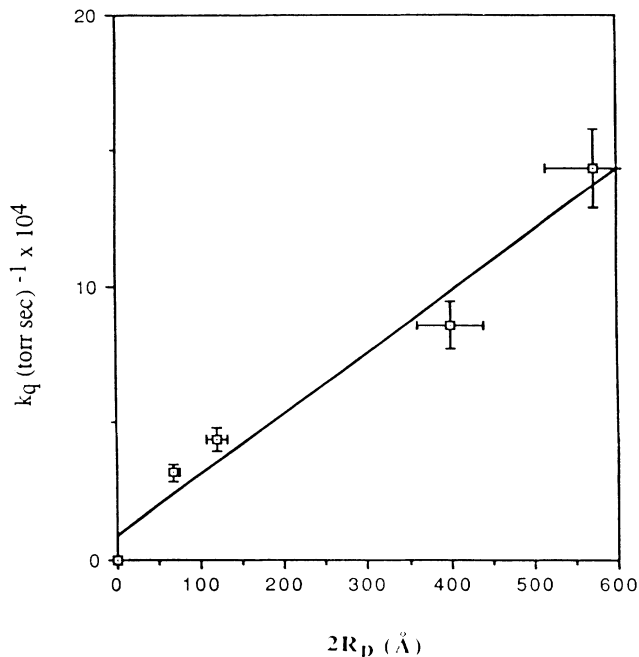


FIG. 2. The quenching rate of benzophenone triplet  $k_q$  by oxygen vs the mean pore diameters for a series of lichrospher silicas at low surface coverage of benzophenone on Si-100 ( $3.15 \times 10^{-5}$  mole/m<sup>2</sup>), Si-300 ( $4.37 \times 10^{-5}$  mole/m<sup>2</sup>), Si-500 ( $6.63 \times 10^{-5}$  mole/m<sup>2</sup>), and Si-100 ( $7.00 \times 10^{-5}$  mole/m<sup>2</sup>).

It was first determined 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 (Fig. 3). We interpret these results by assuming that as the buffer-gas pressure increases the fractional surface coverage of oxy-

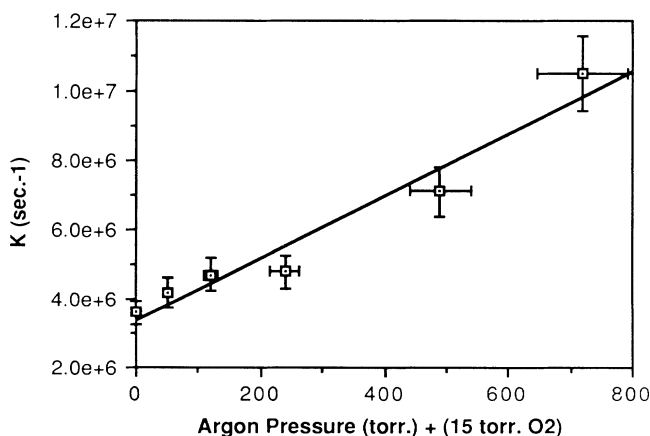


FIG. 3. Rate of decay of benzophenone triplet adsorbed on silica with 15 Torr of oxygen and varying pressures of argon.

gen decreases, making more oxygen molecules available for quenching from the gas phase. If the quenching process were dominated by oxygen surface diffusion, the buffer gas would hinder the surface reaction as more and more surface 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 which we are presenting.

We have studied excitation quenching in the framework of the Knudsen diffusion and have presented what we believe are the first quenching reactions of this type in a homologous series of morphologically similar porous silicas. The reaction rate is geometry sensitive and scales with mean pore size and with oxygen pressure. As in previous studies<sup>6,8</sup>  $R_p$ , the mean pore size, appears as a relevant length for processes within a homologous series of silicas in spite of the complexity of these systems.

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