

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,¹⁻⁴ membranes,⁵ porous silicas,⁶⁻⁹ 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.¹⁻¹⁰ 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.² Smaller length scales have been recently probed on a family of porous silicas with direct energy transfer.⁶ 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^{6,8,9,11} as has been strongly supported^{8,9} 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.¹²⁻¹⁵ The criterion for Knudsen diffusion is that the mean free path due to gas-phase molecule-molecule scattering, λ , is larger than the mean pore size, R_p ,

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

where $\lambda = k_B T / \sqrt{2} \pi \sigma^2 P$, σ 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.⁶ 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 model¹⁶ 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-

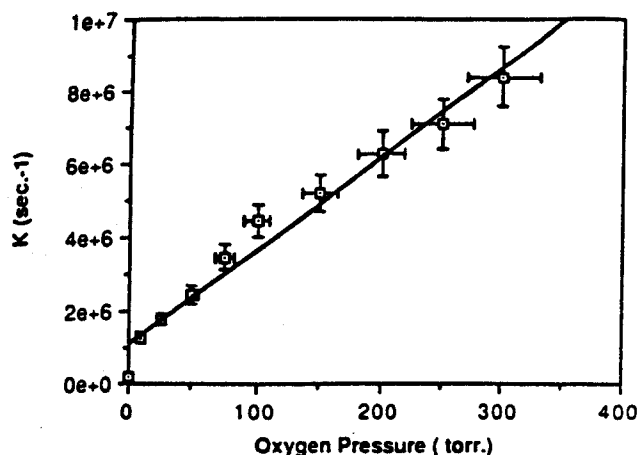


FIG. 1. The decay rate of benzophenone triplet adsorbed on Si-100 lichrospher silica at various pressure of oxygen.

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).

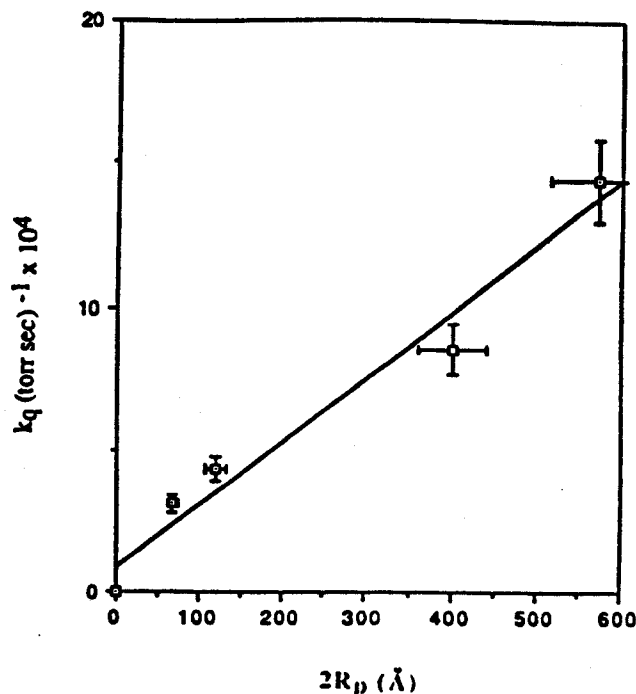


FIG. 2. The quenching rate of benzophenone triplet k_q by oxygen vs the mean pore diameters for a series of lichrospher silicas at low surface coverage of benzophenone on Si-100 (3.15×10^{-5} mole/m²), Si-300 (4.37×10^{-5} mole/m²), Si-500 (6.63×10^{-5} mole/m²), and Si-100 (7.00×10^{-5} mole/m²).

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-

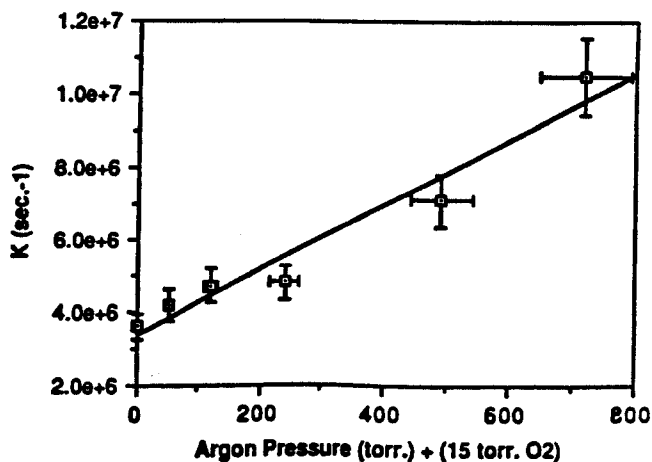


FIG. 3. Rate of decay of benzophenone triplet adsorbed on silica with 15 Torr of oxygen and varying pressures of argon.