INTERPARTICLE DIFFUSION OF AROMATIC HYDROCARBONS ON AEROSIL SURFACE

I. G. Tarasov, V. P. Kondilenko, and A. M. Eremenko

It has been demonstrated by the photobleaching method that the photostability of pyrene molecules on the surface of pyrogenic nonporous SiO₂ (aerosil) is independent of the surface concentration of the fluophor. Through a kinetic analysis of the recovery of fluorescence of the luminophore and solution of the two-dimensional diffusion equation, coefficients of interparticle diffusion were estimated for the molecules of pyrene and N,N-dimethylaniline.

In recent decades, interest has increased considerably in the investigation of diffusion-controlled photochemical processes involving charge transfer in homogeneous and heterogeneous systems. Mutual motion of the molecules ensures that the components will approach and that a collision complex will be formed, and this means that the distance will be brought down to that required for charge transfer [1]. In studying this sort of process, therefore, particular attention is being given to matters involving the diffusion component.

According to the theory of molecular diffusion in homogeneous media [2, 3], based on the laws of classical thermodynamics, we can estimate the diffusion coefficients of the molecules by using macroscopic characteristics of the medium.

Thus far, however, there is no single model that can be used as the basis for calculating coefficients of lateral diffusion of molecules on a silica surface. In such a theory, it is necessary to account for energy inhomogeneity of the surface [4], inhomogeneity in the distribution of adsorption centers, the presence of pores [5], and so on; we can speak only of mechanisms of shifts of molecules between adsorption centers of the surface [6]. Experimental methods used to estimate the diffusion coefficients of molecules on a surface [7] can yield only some sort of resultant coefficient that is a superposition of the diffusion coefficients characteristic for each mechanism individually. It should be expected that these diffusion coefficients will differ substantially, since activation of a diffusion process through the gas phase requires that the molecule must overcome a larger potential barrier than in the case of "sliding" along the silica surface.

Bjarneson et al. [8] were the first to propose an experimental method for the direct determination of the diffusion coefficient of polyacene molecules on the surface of porous SiO₂. By means of these methods, based on photobleaching of adsorbed molecules, diffusion coefficients were estimated for the diffusion of naphthacene on the surface of a single particle of silica gel.

The dimensions of the primary particles are considerably different for silica gel and aerosil; therefore, information can be obtained on shifts of organic molecules between aerosil particles — information that is extremely important in terms of understanding of the mechanism of formation of a donor—acceptor complex of the exciplex type in the adsorbed state on the surface of nonporous SiO₂. The work reported here was aimed at determining coefficients of interparticle diffusion of organic molecules on the surface of a nonporous, finely divided silica known as aerosil, by means of a photobleaching method.

The sorbent used in this work was a nonporous pyrogenic silica, aerosil Grade A-300 (surface area 260-300 m²/g, mean particle diameter 100-200 Å). Before use in the adsorption experiments, the aerosil surface was dehydrated at 500°C.

The fluophors used in this work were pyrene (Py) in special-purity grade and N,N-dimethylaniline (DMA), which, before use, was redistilled several times under reduced pressure in nitrogen vapor. The adsorption of the molecules was...
The kinetics of the processes of photobleaching and recovery of fluorescence intensity by the Py and DMA were recorded by means of a spectroscopic-kinetic unit that was automated on the basis of KAMAK and an S7-17 stroboscopic oscillograph. Excitation was provided by radiation from an LGI-21 nitrogen laser (power in pulse no greater than 3 kW, pulse length 10 nsec, beam diameter 6 mm, pulse follower frequency 100 Hz).

The photobleaching procedure that was used in this work consisted essentially of the following. A focused laser beam was directed onto the surface of a specimen containing Py or DMA molecules. In order to reduce the initial divergence of the laser beam (10^{-3} rad), it was passed through an 8-power quartz telescope. Subsequent focusing by means of a short-focus quartz lens (f = 3 cm) made it possible to obtain a spot with a diameter of 17 μm in the focal plane. The diameter of the focused spot was determined by means of a microscope equipped with an ocular micrometer, on the basis of the dimension of the region burned out by this beam on the surface of an illuminated photographic plate. Under the action of UV radiation with a high power density, the molecules of the fluophors underwent photobreakdown. This was manifested in a decrease of their fluorescence intensity as registered at timed wavelengths, 395 nm for Py and 410 nm for DMA. The process of photobleaching lasted for a period \(\tau_{ob} = 45-50\) min.

The kinetics of the processes of photobleaching of Py molecules adsorbed on the silica surface are shown in Fig. 1, where a value of 100% is assigned to the intensity of fluorescence of the molecules before photobleaching. It should be noted that even after 40-min exposure, the intensity of fluorescence of the molecules on the illuminated section had not dropped to zero. This behavior is related to residual divergence of the laser beam, scattering of laser radiation on the aerosil particles, and so on; therefore, the most intense laser spot was surrounded by a halo with a considerably lower intensity. Fluorescence of these molecules that had fallen into this halo and were not subjected to photobreakdown was the specific reason why it was impossible to reduce the fluorescence intensity to zero. However, after \(\tau_{ob}\), there was essentially no further decrease of fluorescence intensity. This level of intensity was taken as 0%.

We were unable to detect experimentally any sort of influence of the fluophor concentration on the kinetics of the photobleaching process. Hence we can state that within the region of sorbent surface coverage from 0.03% to 20% of a monolayer [9], the photostability of the pyrene molecules is practically independent of the fluophor concentration.

According to estimates made in [7], the diffusion coefficient of pyrene molecules on an aerosil surface is \(10^{-7}\) cm²/sec. Therefore, when we take into account the specimen illumination time and the pulse type of illumination, we can say that the mean square shift of the molecules during this time (~2.2\(\cdot\)10^{-5} cm) is commensurate with the mean dimension of the aerosil