CHARACTERISTICS OF THE KINETICS OF EXCIPLEX FORMATION BETWEEN PYRENE AND N,N-DIMETHYLANILINE ON A POROUS SILICA SURFACE

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The bimolecular photochemical quenching of the fluorescence of pyrene by N,N-dimethylaniline on the surface of various porous silicas with low coverage of the surface (less than a monolayer) has been studied. The kinetics of this process on porous and nonporous silica have been compared.

Phototransfer of an electron is one of the most important types of elementary conversion of electronically excited organic molecules, and it plays an important role in photochemistry and photobiology. The characteristics of the kinetics of photochemical reactions which occur with the formation of donor-acceptor complexes in excited states have been successfully used recently for the diagnostics of the surfaces of various carriers, SiO₂ [1-3], Al₂O₃ [4], CaF₂ zeolites [5], TiO₂, and also heterogeneous systems – micelles of surfactants, biological cells [6], etc.

Both the properties of the adsorbent surface and the concentrations of the components forming exciplexes have an important effect on the kinetic and thermodynamic characteristics of photochemical reactions occurring on the surface layer of silicas with various surfaces.

The inhomogeneity of the adsorbent surface is apparent from the irregularity of the distribution of adsorption centers and the energetic variability of the hydroxyl groups.

The fractal nature is a very important characteristic of the carrier [7]. Investigation of the effect of the fractal nature of adsorbents on the formation of exciplexes from the pyrene-N,N-dimethylaniline pair was initiated by D. Avnir and M. Ottolonghi [8, 9] who used stationary fluorometry to study the conditions of formation of the exciplexes.

However, the conditions for the formation of exciplexes in porous carriers were not discovered, and there is no adequate description of this process at present. There is currently no explanation for different kinetics for the same reaction occurring in porous (silicagel, fractagel, porous glass) and nonporous (aerosil) carriers. In our opinion, impulse laser spectroscopy is a more informative way to investigate the nature of the formation of excited complexes. The objectives of the present investigation were to study the kinetics of the photochemical formation of the pyrene-N,N-dimethylaniline exciplex on the surface of porous carriers (fractosil, porous glass) by impulse laser spectroscopy and to compare the characteristics of the kinetics of the formation of the exciplex on the surfaces of porous and nonporous (aerosil) silicas.

EXPERIMENTAL

Chemically pure grade pyrene was used as the fluorophore, while N,N-dimethylaniline, purified by repeated low-pressure sublimation under nitrogen, was used as the quenching agent. Specially pure grade n-hexane, initially dehydrated and then distilled twice at atmospheric pressure, was used as the solvent. The porous silicas used as adsorbents were: fractosil-200 (Sₚ = 150 m²/g, dₚ₀ = 22.8 nm), fractosil-500 (Sₚ = 50 m²/g, dₚ₀ = 43.0 nm), and porous glass (Sₚ = 27 m²/g, dₚ₀ = 81.0 nm) while the nonporous silica was aerosil (type A-300, Sₚ = 280-300 m²/g). Both porous and nonporous silicas were
Fig. 1. Kinetic curves for the quenching of pyrene fluorescence at 395 nm in the presence of N,N-dimethylaniline on Fractosil-200 surfaces with a pyrene concentration of $10^{-7}$ mol/g and DMA concentrations of 0 (1), $10^{-7}$ (2), $10^{-6}$ (3), $10^{-5}$ (4), $10^{-4}$ (5) and $10^{-3}$ (6) mole/g.

Fig. 2. Fluorescence spectra of pyrene and N,N-dimethylaniline adsorbed on the surface of porous and nonporous silicas dehydrated at 473 K, [N,N-dimethylaniline] = $10^{-4}$ mole/g; 1) porous glass, [pyrene] = $10^{-7}$ mole/g; 2) fractosil-500, [pyrene] = $7.0 \times 10^{-8}$ mole/g; 3) fractosil-200, [pyrene] = $3.4 \times 10^{-7}$ mole/g; 4) aerosil A-300, [pyrene] $2.5 \times 10^{-7}$ mole/g.

Results and Discussion

It follows from the results, examples of which are shown in Fig. 1, that within the limits of a monolayer covering the lifetime of the fluorescence of pyrene decreases with increasing concentration of the quenching agent N,N-dimethylaniline, i.e., just as with the case of nonporous carriers a bimolecular photochemical reaction between pyrene and N,N-dimethylaniline occurs for all of the porous carriers studied at low coverage of the surface. Quenching of the luminescence is observed no matter what the size of the pores or the surface of the carrier. This experimental fact contradicts the conclusions of the previous authors [8] that quenching of the fluorescence of pyrene on porous carriers occurs only after there is more than a monolayer on the surface of the porous silica.

In Table 1 are cited lifetimes of the fluorophore, $\tau_p$, for porous carriers with different concentrations of N,N-dimethylaniline and also quenching constants, $k_q$, calculated using the Stern-Folmer equation. The data in the table show that, for the porous carriers studied, the lifetime of the fluorophore in the absence of quenching agent is shorter than for nonporous carriers at equal degree of covering of the surface, $\theta$. It should be noted that the dependence of the quenching constant on the concentration of quenching agent in the surface layer has the same character for both porous and nonporous carriers: the quenching constant $k_q$ decreases as the concentration of N,N-dimethylaniline increases.