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Abstract

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ABSORPTION SPECTRA AND E.P.R. SPECTRA OF POSITIVE ACENE IONS FORMED UPON VACUUM ADSORPTION

In works from our laboratory, spectra have been described for molecular positive ions of dimethylparaphenylenediamine, diphenylamine, benzidine, and also acenes, appearing upon adsorption of their vapors in vacuum on Al_2O_3–SiO_2 gels (^{1}-^{3}). Earlier, the spectra of acene radical ions had been detected in their solutions in acids and studied extensively (^{4}), in particular by the e.p.r. method (^{5}). The e.p.r. method was also applied in studying the formation of positive radical ions of aromatic amines and acenes upon their adsorption from solutions on an Al_2O_3–SiO_2 catalyst (^{6}). In contrast to these works, in our investigations adsorption of aromatic amines and acenes is carried out under vacuum conditions from the gas phase without the use of any solvent. The adsorbents used, in powder form, were Al_2O_3–SiO_2 gel (25% Al_2O_3/75% SiO_2), SiO_2 gel, Degussa aerosil, Al_2O_3 gel, γ-Al_2O_3 powder, and Al_2O_3 powder used for the manufacture of sapphire. The powder adsorbents were calcined in air for 5 h at 650–700° and conditioned for 3 h in a vacuum of 10^{-5} mm Hg at 475° in a glass cuvette connected to a vacuum apparatus. A weighed portion of the adsorbed acene was placed in a side arm separated from the adsorbent by a thin glass partition and was degassed for 1.5 h in high vacuum. Adsorption of acene vapors was carried out after breaking the partition with a striker at temperatures of 87, 124, and 122° C, respectively, for anthracene, perylene, and tetracene; the vapor pressure in this case was about 1 mm Hg. To check the influence of temperature, adsorption of anthracene was also carried out at 20° for a long time: the same results were obtained. In the course of the work, the influence on the spectra of adsorbed acenes of additional adsorption of H_2O and NH_3 vapors was studied. The water was previously conditioned in vacuum in order to remove gases dissolved in it, by repeated freezing followed by pumping and thawing. Gaseous NH_3 was obtained from aqueous ammonia and thoroughly dried.

For measuring the absorption spectra and e.p.r. spectra of adsorbed acenes,

Fig. 1 and Fig. 2: absorption spectra

Figure 1: Fig. 1 and Fig. 2: absorption spectra

glass cuvettes were used consisting of a spherical ultraviolet bulb for measuring absorption spectra and a volume-calibrated small-diameter glass tube for measuring e.p.r. spectra. After adsorption had been carried out, the cuvettes were sealed off from the vacuum apparatus. The absorption spectra were measured by the diffuse-reflection method on an SF-4 spectrophotometer with an attachment ([7]) allowing two identical powder samples of adsorbent to be compared, adsorption having been carried out on one of them. The e.p.r. spectra were measured on an RE1301 radiospectrograph. The results are presented in Figs. 1-4. Adsorption of anthracene vapors on $Al_2O_3{-}SiO_2$ gel, as we have shown previously ([2]), leads to the appearance of three new absorption bands with maxima at 460, 610, and 760 mμ (Fig. 1, 1), absent in the spectrum of anthracene dissolved in a neutral solvent or adsorbed on SiO_2 gel (Fig. 1, 2). It is known that proton-donor and electron-acceptor centers are present on the surface of $Al_2O_3{-}SiO_2$ gels (cracking catalysts). It was shown ([2]) that the addition of a proton to an anthracene molecule adsorbed on $Al_2O_3{-}SiO_2$ gel leads to the formation of the carbonium ion AH^+ ([8]) with an absorption band at 460 mμ. The presence on the surface of $Al_2O_3{-}SiO_2$ gel of electron-acceptor centers causes the appearance of the 760 mμ band, due in origin to the surface radical ion A^+ ([2]).

Indeed, under our conditions the EPR signal appeared upon adsorption of anthracene only on the $Al_2O_3{-}SiO_2$ gel (Fig. 4, 1). Upon adsorption of anthracene on SiO_2 gel, Degussa aerosil, and also on Al_2O_3 gel, powdered γ-Al_2O_3, and dispersed Al_2O_3 (powder), no EPR signal arose, although in the last case, in addition to the absorption bands of physically adsorbed anthracene molecules, the spectrum contains a band at 600 mμ (Fig. 1, 3). In our previous work ([2]), the absorption band at 600 mμ was tentatively assigned to a π-complex of anthracene molecules with surface Al atoms, which is consistent with the absence of an EPR signal.

Fig. 1 **Fig. 2**

When H_2O vapor or dry NH_3 was admitted to anthracene adsorbed on the Al_2O_3 $-SiO_2$ gel, the intensities of the absorption bands at 610 and 760 mμ decreased (Fig. 1, 4, 5), new bands appeared at 454, 482, 530, and 570 mμ ([3]), and the intensity of the EPR signal decreased. Upon pumping off the H_2O vapor, the spectrum assumed its original form (Fig. 1, 1) and the EPR signal was restored again. This reversible change indicates a purely surface interaction of anthracene molecules with the adsorbent. H_2O and NH_3 molecules, being more strongly bound, evidently disrupt the direct contact of anthracene molecules with electron-acceptor centers of the $Al_2O_3{-}SiO_2$ gel. The new bands, which appear and disappear reversibly upon adsorption of H_2O and NH_3 vapors, are

Fig. 3

Figure 2: Fig. 3

apparently due to dimers of radical ions devoid of paramagnetism.

Curve 1 in Fig. 2 represents the absorption of perylene adsorbed on the Al_2O_3–SiO_2 gel. The EPR signal has a well-pronounced hyperfine structure consisting of 9 lines (Fig. 4, 2). Such a structure was previously found for the perylene radical ion in concentrated H_2SO_4 (^{5}). Recently it has also been found for perylene adsorbed

from solution on an Al_2O_3–SiO_2 gel (^{6}). Adsorption of perylene on SiO_2 gel, as in the case of anthracene, did not give rise to an EPR signal, which is consistent with the absence of absorption bands corresponding to the perylene radical ion (Fig. 2, 2). When vapors of H_2O or NH_3 were admitted to perylene adsorbed on Al_2O_3–SiO_2 gel, the intensity of the absorption bands at 332, 534, 650, 685, 705, 730, 765, and 850 mμ decreased, new bands appeared at 645 and 750 mμ, and the EPR signal decreased markedly in intensity (Fig. 2, 3, 4).

Fig. 3

Similarly to perylene, tetracene adsorbed from the vapor phase on Al_2O_3–SiO_2 gel has a rich optical absorption spectrum (Fig. 3, 1). The EPR spectrum of adsorbed tetracene (Fig. 4, 3), unlike the EPR spectrum of adsorbed perylene, has a poorly resolved hyperfine structure and in this respect is similar to the EPR spectrum of adsorbed anthracene, where hyperfine structure is absent. EPR signals did not arise upon adsorption of tetracene on SiO_2 gel, which is consistent with the absorption spectrum, in which the absorption bands of the molecular ion are absent (Fig. 3, 2). Admission of H_2O or NH_3 vapors to tetracene adsorbed on Al_2O_3–SiO_2 gel decreased the intensity of the EPR signal. At the same time the intensity of the bands at 630, 680, 730, and 850 mμ decreased, and new ones appeared at 580 and 615 mμ (Fig. 3, 3, 4).

Thus, comparison of the absorption spectra of different acenes adsorbed on Al_2O_3–SiO_2 gel, SiO_2 gel, and Al_2O_3 gel with the EPR spectra makes it possible to unambiguously identify the absorption maxima of the acene radical ion. For adsorbed anthracene such an absorption band is the band at 760 mμ, since the maximum at 460 mμ, as we established earlier (^{2}), belongs to the carbonium ion AH^+, which gives no EPR signal (^{5}). The band at 600 mμ appears upon adsorption of anthracene on powdered γ-Al_2O_3. The absence of an EPR signal in this case as well makes it possible to assign it to a chemisorbed π-complex of anthracene molecules with surface Al atoms. The conclusion that the 760 mμ band belongs to the anthracene radical ion is confirmed by the results of studying the action of H_2O and NH_3 vapors on the absorption spectra and EPR spectra of adsorbed anthracene. The decrease in the intensity of the band at 760 mμ was accompanied by a decrease in the intensity of the EPR signal.

Fig. 4

Figure 3: Fig. 4

The spectrum of the molecular ion of perylene agrees with the data of other authors, who obtained the perylene ion by oxidation in concentrated H_2SO_4 (9). The reversible change in the intensity of the bands in the spectra of the molecular ions after admission and removal of H_2O or NH_3 vapors is accompanied by approximately the same reversible change in the magnitude of the EPR signal. The new bands that appear after admission of H_2O or NH_3 vapors, shifted toward shorter wavelengths, are due to nonparamagnetic species, apparently of the dimer type.

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Fig. 4

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