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SPECTRA OF MOLECULAR IONS OF ANTHRACENE FORMED DURING VACUUM ADSORPTION

In continuation of the work of our laboratory on the electronic absorption spectra of organic molecules adsorbed from vapors under vacuum conditions (1-3), a spectral study was carried out of those colorations that were observed when anthracene vapors came into contact with the surface of active oxides. Along with aromatic amines, which upon adsorption on aluminosilicate catalysts give visible spectra of their positive ions (1), in the course of these experiments A. I. Sidorova established that, when anthracene vapors also came into contact with aluminosilica gel subjected to preliminary vacuum treatment up to 100°, a green coloration appeared, the spectrum of which revealed distinct absorption maxima (minima in the diffuse-reflection spectrum) at 380, 480, 590, and 770 mμ.

Since this coloration appeared upon heating and could be explained by products of oxidation of anthracene by oxygen not completely removed from the adsorbent,* these experiments were repeated with silicate and oxide adsorbents permitting vacuum treatment at a higher temperature.

In the present work, after preliminary calcination in air (600°, 3 hours), to burn out organic impurities, the adsorbents were subjected to vacuum treatment (500°, 3 hours), and then brought into contact with saturated anthracene vapor at 100° (0.12 mm Hg). Anthracene, preliminarily distilled in vacuum, was placed in a sealed ampoule, which was broken after completion of the treatment of the adsorbent contained in a sealed-off spherical cell made of ordinary or uviol glass.**

As adsorbents there were used, in the form of powders: silica gel (manufactured in the GDR and distinguished by the smallest amount of impurities); Aerosil from Degussa (specific surface area 175 m^2/g); Al_2O_3 powder used for manufacturing sapphire (transparent and with an admixture of 3% Cr_2O_3); γ-Al_2O_3;

Fig. 1. Absorption spectra of adsorbed anthracene: 1 —on $BaSO_4$; 2 —on aerosil; 3 —on Al_2O_3 (powder); 4 —on Al—Si gel (11% Al_2O_3)

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alumogel; industrial and laboratory samples of aluminosilica gel with different contents of Al_2O_3 and SiO_2 (specific surface area 300-450 m^2/g); laboratory samples of aluminosilica gel with Na^+ and Li^+ cations (obtained as a result of ion exchange of H^+ for Na^+ and Li^+ in solutions of CH_3COONa and CH_3COOLi, specific surface area 300-450 m^2/g).***

Measurements of the absorption spectra of adsorbed molecules were carried out, as in previous work, with an attachment to an SF-4 spectrophotometer, by the method of comparing the diffuse reflection of the initial sample—

* Indeed, in our laboratory the appearance of a pink coloration was observed upon adsorption of naphthalene vapors on Al—Si gel during heating; however, it was not reproduced upon thorough degassing of the adsorbent.

** Adsorption of anthracene vapors was also carried out at 20°, which likewise led to the appearance of the same green coloration; however, the low vapor pressure (0.0003 mm Hg) prolonged the adsorption procedure, which was inconvenient. The production of coloration in this case also convincingly shows that the surface coloration is not due to an impurity of naphthalene or anthraquinone in the anthracene, which at 20° have vapor pressures incomparably lower than that of anthracene. In addition, this shows that the spectral pattern does not remain even at the smallest surface coverage, i.e., it is not due to association of several anthracene molecules.

*** For the kind provision of aluminosilica gels of various composition and treatment we are especially indebted to Professor K. V. Topchieva, I. F. Moskovskaya, and M. A. Kaliks. Alumogel was kindly provided by A. I. Kaganova and B. L. Moldavskii.

sample subjected only to vacuum pretreatment, in the same manner as was in contact with anthracene vapors ([2], [3]).

It should be emphasized that the selective absorption bands measured in the visible region, observed in this and in our preceding works, lie in the transparency region both of the adsorbents themselves and of anthracene molecules dissolved in inert solvents.

Fig. 1. Absorption spectra of adsorbed anthracene: 1 —on $BaSO_4$; 2 —on aerosil; 3 —on Al_2O_3 (powder); 4 —on Al—Si gel (11% Al_2O_3).

In Figs. 1—3 the spectral curves obtained are presented. The minima on them correspond to maxima of the absorption bands appearing as a result of adsorption of anthracene vapors. The observed structure in the UV region (400—300

Fig. 2

Figure 2: Fig. 2

mμ) (Fig. 1) is due to discrete absorption bands of physically adsorbed anthracene molecules (A), only slightly perturbed by the adsorbent, since they are close to the discrete bands 323, 339, 356, 375 mμ observed for a solution of A in isooctane. The accuracy of measurements of diffuse-reflection spectra is not so high that real significance could be attached to the difference in the positions of these bands (within 2–3 mμ) on $BaSO_4$ and on highly dispersed Al_2O_3 powders. However, the blurring of this structure observed for A on Al–Si gel, in contrast to SiO_2 and Al_2O_3 gels taken separately, of approximately the same degree of dispersion, is apparently a consequence of stronger interaction with the more acidic surface of the former. The main attention on this adsorbent is drawn not by the UV maxima, but by the new broad absorption maxima that appear, lying at 470, 610, 760 mμ ($±$10 mμ) (see Fig. 1).

On dispersed powders of γ-Al_2O_3 and Al_2O_3 (powder) there is only a hint of a band near 610 mμ (Fig. 1); on silica gel and aerosil it, like the other visible bands, is completely absent (see Fig. 1).

The green coloration imparted to aluminosilicate gel by anthracene does not disappear when the adsorbent is heated in vacuum, which indicates a strong chemical type of interaction. To clarify the nature of the chemisorption centers causing such profound changes in the spectrum of anthracene, experiments were carried out with samples of Al–Si gels, obtained from K. V. Topchieva and M. F. Moskovskaya, in which the accessible protons had been replaced by Na^+ or Li^+ cations ([4]). Comparison of the behavior of these "poisoned" samples of the aluminosilicate catalyst with the original one shows that the band at 470 mμ is sensitive to this change in the surface of the adsorbent and disappears first (Fig. 2, compare curves 1, 2, 3). The band at 610 mμ is only somewhat weakened, being retained even in a strongly "poisoned" sample. The most intense band at 760 mμ is retained, but on strongly "poisoned" samples–

also disappears (see Fig. 2). Thus, it may be assumed that the 470 mμ band arises as a result of interaction of A molecules with proton-donor centers of the surface, the existence of which on Al–Si gels has been proved ([3],[4]).

Indeed, A dissolved in H_2SO_4, HCl + $AlCl_3$, and other strongly protonating media, on adding a proton, is converted into the carbonium ion AH^+, with an absorption band in the region 420-440 mμ, in agreement with theoretical calculations for the meso-ion of A ([5]). To check this, we adsorbed A vapor on the ion-exchange resin KU-2, characterized by a high content of proton centers (H-form), and observed the appearance of a single broad band which, with time of standing in vacuum, shifted its maxima from 520 to 470 mμ. This confirms the assignment of the 470 mμ band to the carbonium ion AH^+*.

Fig. 2. Absorption spectra of adsorbed anthracene: **1**–on the initial Al–Si

Fig. 3. Absorption spectra of adsorbed anthracene: 1—on Al_2O_3/Cr_2O_3 (3% Cr_2O_3); 2—on powdered $AlCl_3$; 3—on KU-2; 4—on KU-2 after 70 h.

Figure 3: Fig. 3. Absorption spectra of adsorbed anthracene: 1—on Al_2O_3/Cr_2O_3 (3% Cr_2O_3); 2—on powdered $AlCl_3$; 3—on KU-2; 4—on KU-2 after 70 h.

catalyst (30% Al_2O_3/70% SiO_2); **2**—on the Al—Si catalyst poisoned with Na^+ No. 3 (30% Al_2O_3/70% SiO_2); **3**—on the Al—Si catalyst poisoned with Na^+ No. 4 (30% Al_2O_3/70% SiO_2); **4**—on the Al—Si catalyst poisoned with Na^+ (50% Al_2O_3/50% SiO_2).

Studies in our laboratory of the adsorption of aromatic amines on Al—Si gels have shown beyond doubt that, along with proton centers, there exist electron-acceptor centers (Lewis acid centers) capable of detaching an electron from an adsorbed amine molecule ([1-3]). The conclusion suggests itself that the bands at 610 and 760 mμ, less sensitive to the removal of protons from the surface, are due to interaction precisely with the latter centers. The spectrum of the positive molecular ion A^+ is not yet known, but according to theoretical estimates ([6]) it should be close to the spectrum of the negative ion A^-, which is well known and has an intense band at 720 mμ.

In this case the band observed by us at 760 mμ for A adsorbed on Al—Si gel must be assigned to the positive molecular ion A^+. The disappearance of this band at a high concentration of Na^+ cations replacing H^+ ions may be ascribed to the screening action of the large alkali-metal cations, which hinder access of A molecules to electron-acceptor centers that apparently are located in the immediate vicinity of proton centers on the surface of the aluminosilicate. The origin of the 610 mμ band of adsorbed A remains unclear (see Figs. 1, 3, 4). It may tentatively be assigned to a π-complex between A and surface aluminum atoms that are part of the structure of the Al—Si gel or Al_2O_3 and that have a tendency to fill a *p*-orbital with two electrons.

* Vacuum pretreatment of the KU-2 resin was carried out only at 100° in order to avoid its decomposition.

To test the hypothesis that electron-acceptor centers play a substantial role in the appearance of the 760 and 610 mμ bands, experiments were carried out with vacuum adsorption of A vapors on $AlCl_3$ powder.

From Fig. 3, 3 it is clear that, in contact with such a strong electron-acceptor agent, the spectrum of physically excited A molecules is shifted from 380 (for Al—Si gel) to 400 mμ, and broad bands appear with maxima at 430 and 700 mμ. In light of the interpretation given above, the presence of the 430 mμ band would indicate the presence of protonic action, for example traces of HCl formed as a result of hydrolysis of $AlCl_3$, while the bands at 700 mμ would indicate the presence of an electron-acceptor interaction.

Fig. 3. Absorption spectra of adsorbed anthracene: **1**—on Al_2O_3/Cr_2O_3 (3% Cr_2O_3); **2**—on powdered $AlCl_3$; **3**—on KU-2; **4**—on KU-2 after 70 h.

Recently a paper appeared ([7]) in which, upon adsorption of A from a decahydronaphthalene solution on Al–Si gel, strong bands at 420 and 750 mμ, similar to ours, and weak bands at 585 and 640 mμ, located in the region of the one maximum observed by us at 610 mμ, were found. The difference in wavelengths may have been caused by the presence of a liquid solvent. The authors assign all the bands to the carbonium ion AH^+, which, on the basis of our experiments, is valid only for the 420 mμ band.

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Note: Figure translations are in progress. See original paper for figures.