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CONCENTRATION EFFECT IN THE ABSORPTION AND E.P.R. SPECTRA OF ADSORBED MOLECULAR IONS OF ANTHRACENE

In the development of the spectral study of molecular ions of acenes formed during vacuum adsorption of their vapors on the surface of aluminosilicate gel (abbreviated ASG) ([1]), the present work has revealed a substantial influence of the surface concentration on the position and character of the absorption bands, as well as on the e.p.r. signals of molecular ions of anthracene (abbreviated A). In the previous work ([1]), the appearance in the absorption spectrum of A molecules adsorbed on ASG of three absorption bands was established: at 760, 610, and 480 mμ. Comparison of the absorption spectra of A molecules adsorbed on various adsorbents—ASG, silica gel (SG), alumina gel (AG), the acidic ion-exchange resin KU-2, and on $AlCl_3$—and comparison of them with known spectra of molecular ions of A in acid solutions led to the following interpretation of the observed absorption bands: the 760 mμ band appearing on ASG was assigned to the ion-radical A^+; the 480 mμ band, to the carbonium ion AH^+; and the 610 mμ band, to a π-complex of A molecules with surface Al atoms. This interpretation was supported by e.p.r. measurements. ([3])

In the course of further investigation it was noted that the coloration arising during adsorption of A vapors on the surface of ASG changes, depending on the residence time in the vapors, from light blue to dark green. Naturally, the assumption arose that these changes are due to different surface concentrations of adsorbed A molecules. Therefore the spectra of adsorbent samples that had remained in the vapors for different times were measured.

ASG samples were obtained, as before, by grinding catalyst beads of composition 25% $Al_2O_3 : 75\% SiO_2$, used for cracking. The powders were preliminarily calcined in air at 700° for 5-10 hr to burn off organic impurities. Conditioning of the adsorbents was carried out in a vacuum of 10^{-5} mm Hg at 500° for 3 hr, after which the beads containing them, together with the all-glass sealed system, were sealed off from the vacuum apparatus. Vapors of A, preliminarily sublimed into one of the side arms of the system and degassed for 1.5 hr in a

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

vacuum of 10^{-5} mm Hg, entered the adsorbent samples after the glass partition was broken with a striker. Adsorption of A vapors was carried out at a temperature of 90–95° simultaneously on 10 samples of powdered ASG placed in separate beads. At definite time intervals the beads were sealed off one after another. The construction of the beads with a side arm ([3]) made it possible to measure both the absorption spectra in diffusely reflected light on an SF-4 spectrophotometer with attachment ([4]), and the e.p.r. spectra.

The results obtained are presented in the form of spectra in Figs. 1–4. Adsorption of A vapors on ASG for 15 min leads to the appearance in the absorption spectrum of well-resolved bands at 720, 670, 570, 520, 425, 352, and 315 mμ (Fig. 1, 1). When the adsorption time is increased to 1 hr, the absorption bands of the adsorbed A molecules retain their positions, increasing in intensity (Fig. 1, 2). A further increase in the surface concentration of adsorbed molecules leads to a blurring of the entire observed—

of the spectrum, to the broadening of the 720 mμ band and to the appearance of a new band at 460-480 mμ (Fig. 1, 4–10). The appearance of the e.p.r. spectra changes correspondingly (Fig. 2). Upon adsorption of the first portions of A vapor, the e.p.r. signal has a distinct hyperfine structure (Fig. 2, 1), characteristic of the adsorbed anthracene ion-radical obtained upon adsorption from solutions ([5]). It should be noted that we were unable to reproduce the hyperfine structure of the e.p.r. signal observed previously in work ([5]) by carrying out adsorption of A from its vapors on ASG. However, the hyperfine structure is readily reproduced upon vacuum adsorption of A from vapors on specially prepared AG.

Fig. 1. Absorption spectra of anthracene molecules adsorbed from vapors on ASG (25% Al_2O_3 : 75% SiO_2) as a function of adsorption time: **1** –15 min.; **2** –30 min.; **3** –45 min.; **4** –1 hour; **5** –1 hour 15 min.; **6** –2 hours; **7** –3 hours; **8** –6 hours; **9** –21 hours; **10** –65 hours.

Fig. 2. E.p.r. spectra of anthracene adsorbed from vapors on ASG (25% Al_2O_3 : 75% SiO_2). The numbering of the curves corresponds to the designations in Fig. 1. The numbers on the right indicate the relative scale of the curves.

The use in the present work of ASG different from that in ([5]), as well as carrying out adsorption from vapors, which excludes the effect of the solvent, perhaps explains the discrepancy in the form of the e.p.r. spectra.

With an increase in the surface concentration of adsorbed A molecules, the intensity of the e.p.r. signal initially increases (Fig. 2, 2, 3), while retaining the hyper-

fine structure, and then decreases (Fig. 2, 4–10), with simultaneous disappear-

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

ance of the superhyperfine structure. The width of the EPR line decreases somewhat in this process. The disappearance of the superhyperfine structure is probably caused by the interaction of ion radicals A^+ with physically adsorbed molecules A (electron transfer) (7). Let us note that an analogous concentration effect in absorption and EPR spectra was observed by us earlier for naphthalene molecules adsorbed on ASG.

The absorption spectrum of A adsorbed on ASG at low surface concentrations (Fig. 1, 1-3) contains bands close to the absorption bands of the multiply charged ion radical A^+ and the carbonium ion AH^+, obtained in acid solutions (6). The band at 425 mμ is attributed by the authors of (6) to the carbonium ion AH^+. Indeed, comparison of the absorption spectra obtained as a result of adsorption of A on the original ASG and on ASG poisoned with Na^+ ions, composition 30% $Al_2O_3 : 70\%\ SiO_2$, indicates a certain decrease in the intensity of the band at 425 mμ in the latter case, although the intensity of the bands at 720 mμ is almost the same (Fig. 3, 1, 2). The corresponding EPR signals are comparable in magnitude (Fig. 4, 1, 2). The decrease in the intensity of the band at 425 mμ is accompanied by the appearance of a new band at 376 mμ, which, together with the band at 352 mμ, is close to the absorption bands of molecules A in the state of physical adsorption (376 and 356 mμ (1)). However, the first two bands differ sharply from the latter both in shape and in the ratio of intensities.

It is noteworthy that the 425 mμ band disappears with increasing time of adsorption of A vapors, and instead a new band appears in the region 460-480 mμ, which we observed earlier (Fig. 1, 3-10). Earlier (1) we showed that the intensity of the band at 480 mμ also decreases upon adsorption of A on ASG poisoned with Na^+ ions. In addition, it increases upon additional heating at 200° for 15 h of the previously obtained ASG sample with A adsorbed on it (Fig. 3, 3, 4). The increase in the intensity of the band at 480 mμ is accompanied by a decrease–

Fig. 3. Absorption spectra of anthracene molecules adsorbed from vapor on: 1 –ASG, original (30% $Al_2O_3 : 70\%\ SiO_2$); 2 –ASG poisoned with Na^+ ions (30% $Al_2O_3 : 70\%\ SiO_2$); 3 –ASG (25% $Al_2O_3 : 75\%\ SiO_2$), adsorption at 100° for 3 h; 4 –ASG (25% $Al_2O_3 : 75\%\ SiO_2$), after additional heating of sample (3) at 200° for 15 h in a sealed ampoule.

Fig. 4. EPR spectra of anthracene adsorbed on ASG. The numbering of the curves corresponds to the designations in Fig. 3. The numbers on the right

indicate the relative scale of the curves.

by absorption of physically adsorbed molecules A in the region of 390 mμ and by broadening and, possibly, a decrease in the intensity of the band at 720 mμ. The intensity of the EPR signal correspondingly decreases only slightly (Figs. 4, 3, 4), and a well-resolved hyperfine structure consisting of 12 components appears.

Thus, with an increase in the surface concentration of adsorbed molecules A, it follows directly from the spectra that part of the physically adsorbed molecules passes into the state of molecular ions AH^+. Further development of surface reactions involving the proton-donor and electron-acceptor centers of the catalyst and the molecular ions A^+ and AH^+ leads to a decrease in the intensity of the absorption bands and of the EPR signal, with a blurring of the structure of the latter.

In conclusion, we express our gratitude to E. I. Kotov for discussing the results of the work, and also to M. A. Kaliko, Prof. K. V. Topchieva, and I. F. Moskovskaya for kindly providing the ASG samples.

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