Doklady of the Academy of Sciences of the USSR

V. A. BARACHEVSKII, E. I. KOTOV, and Academician A. N. TERENIN

1962

SovietRxiv

Abstract

Full Text

Doklady of the Academy of Sciences of the USSR
1962. Volume 144, No. 2

PHYSICAL CHEMISTRY

V. A. BARACHEVSKII, E. I. KOTOV, and Academician A. N. TERENIN

SPECTRAL STUDY OF THE ACTION OF WATER VAPOR ON ADSORBED MOLECULAR IONS OF ANTHRACENE

In our preceding article ([1]), the spectrum was presented of the green coloration that appears upon vacuum adsorption of anthracene vapor on aluminosilicate. The observed absorption bands at 480 and 760 mμ were attributed to molecular positive ions AH^+ ($\lambda_{max} = 480$ mμ) and A^+ ($\lambda_{max} = 760$ mμ), while the band at 610 mμ was tentatively attributed to a π-complex between molecules A and surface Al atoms (A here and below denotes an anthracene molecule). In the present work the experimental procedure remained the same, but the adsorbent, colored as a result of adsorption of A vapor, was additionally brought into contact in vacuum with H_2O vapor at a pressure of 5 to 15 mm Hg. Distilled water was used; beforehand it had been evacuated with repeated freezing and thawing in order to remove dissolved oxygen and other atmospheric gases.

When H_2O vapor was admitted in vacuum, the color of the aluminosilicate changed abruptly from green to crimson. Evacuation of the crimson-colored aluminosilicate at 20° (3 hours) led to regeneration of the green coloration observed before admission of H_2O vapor. This regeneration was accelerated if evacuation was carried out at 100° (1 hour).

In Fig. 1 and the following figures, spectral curves of diffusely reflected light are given, in which the minima correspond to the maxima of the absorption bands of the various forms of adsorbed molecules A. Comparison in Fig. 1 of curves 1 and 2, corresponding to the state of the adsorbate on aluminosilicate of composition 11% Al_2O_3, 89% SiO_2 before and after admission of H_2O vapor, shows that a sharp change occurs in the absorption bands. The 780 mμ band is greatly weakened, and the 610 mμ band disappears completely, as does the broad band at 480 mμ. In the region of the latter, distinct, narrower bands appear at 575, 530, and 480 mμ, with weak additional bands at 450 and 430 mμ. A slight long-wavelength shift and narrowing of the band at 380 mμ are also observed, due to physically adsorbed molecules A that remain unchanged. When the pressure of H_2O vapor is brought to saturation and capillary condensation occurs in the pores of the adsorbent, the spectral pattern is generally retained, with small

Figure 1 and Figure 2: absorption spectra

Figure 1: Figure 1 and Figure 2: absorption spectra

shifts and broadening of the new bands in the 600-400 mμ region (Fig. 1, 3). Similar, but less clearly expressed, bands are given by adsorbate A on powdered natural aluminosilicate—bauxite (Fig. 1, 4, 5)—when H_2O vapor is admitted.

In the case of adsorbate A on aluminosilicate of composition 30% Al_2O_3 and 70% SiO_2, upon admission of H_2O vapor the same bands appear, the most intense of them at 570 mμ and weaker ones at 530 and 480 mμ (Fig. 2, 1, 2). An analogous picture is observed under the action of H_2O vapor on adsorbate A on aluminosilicate of the same composition "poisoned" with Na^+ cations (Fig. 2, 3, 4), which replace free protons*.

With a successive increase in the quantity of adsorbed H_2O vapor up to its capillary condensation, here too there occurs a broadening and

* We express our deep gratitude to Prof. K. V. Topchieva and I. F. Moskovskaya (Moscow State University) for kindly providing aluminosilicate cracking catalysts of various compositions and "poisoned" samples.

broadening of the bands (Fig. 2, 5), as also on the aluminosilicate of composition 11% Al_2O_3, 89% SiO_2, considered above (Fig. 1, 3). Some slight differences observed in the spectral pattern for these two adsorbent samples are apparently connected with subtle differences in the structure of their surface. In order to explain the causes producing the change in the spectrum of adsorbates A on

Fig. 1. Absorption spectra of adsorbed anthracene: 1 —on aluminosilicate of composition 11% Al_2O_3, 89% SiO_2; 2 —after admission of H_2O vapor; 3 —in the presence of capillary condensation of H_2O; 4 —on natural aluminosilicate—bauxite (11% Al_2O_3); 5 —after admission of H_2O vapor

Fig. 2. Absorption spectra of adsorbed anthracene: 1 —on aluminosilicate of composition 30% Al_2O_3, 70% SiO_2; 2 —after admission of H_2O vapor; 3 —on an aluminosilicate of the same composition, "poisoned" with Na^+ cations; 4 —after admission of H_2O vapor; 5 —on an aluminosilicate of the same composition in the presence of capillary condensation of H_2O vapor

aluminosilicate catalysts upon additional adsorption of H_2O vapor, we carried out analogous experiments for adsorbates A from its vapors on the surface of a strongly proton-acid adsorbent—KU-2 ion-exchange resin (H-form), and also on powders of γ-Al_2O_3 and MgO. The latter were subjected to preliminary vacuum treatment up to 320°, the ion-exchange resin up to 100°.

Under the action of water vapor on adsorbate A on KU-2, the absorption band at 480 mμ, assigned in the preceding paper ([1]) to the carbonium ion AH^+, weakens and completely disappears when capillary condensation of H_2O vapor occurs (Fig. 3, 1–3). At the same time, in contrast to aluminosilicate, the

Figure 3

Figure 2: Figure 3

Figure 4

Figure 3: Figure 4

product-carrier of the raspberry-red coloration is not formed. For adsorbate A on powdered γ-Al_2O_3, upon admission of water vapor, a weak absorption band-

of adsorbed A at 610 mμ, presumably assigned in the preceding paper (1) to the π-complex of A with surface Al atoms, completely disappears (Figs. 3, 4, 5). The crimson-colored product carrier, just as for A, is not formed on KU-2.

Vacuum adsorption of A vapors on MgO powder, carried out according to a procedure analogous to that for aluminosilicate catalysts, led to the appearance of a light-blue coloration, which rapidly disappeared when exposed to air. In the absorption spectrum, in addition to the band near 380 mμ, belonging to physically adsorbed molecules of A, there are new bands at 600, 730, and 845 mμ (Fig. 3, 6). The 600 and 730 mμ bands are close in position to the 610 and 760 mμ bands observed for the adsorbate A on aluminosilicate. The origin of the 845 mμ band is unclear.*

When H_2O vapor acts on adsorbate A on MgO, its color changes to a faint crimson coloration. This is caused by the disappearance in the absorption spectrum of adsorbate A of the bands at 845, 730, and 600 mμ and by the appearance of a new broad band in the 600-400 mμ region (Fig. 3, 7), i.e., in the absorption region of the carrier of the crimson coloration on aluminosilicate catalysts, but without structural bands.

Fig. 3. Absorption spectra of adsorbed anthracene: **1** —on cation exchanger KU-2; **2** —after introduction of H_2O vapor; **3** —in the presence of capillary condensation of H_2O vapor; **4** —on γ-Al_2O_3; **5** —after introduction of H_2O vapor; **6** —on MgO; **7** —after introduction of H_2O vapor.

Fig. 4. Absorption spectra of the crimson-colored product carrier, eluted from the surface of aluminosilicate: **1** —immediately after washing off; **2** —after one day.

* The MgO sample used by us, however, contained impurities of heavy metals. EPR measurements of this sample, carried out by V. E. Kholmogorov, revealed signals in it indicating the presence of an impurity of paramagnetic ions. Spectral analysis, kindly performed by A. V. Karyakin, showed the presence of Mn, Fe, Ti, etc. This makes it possible to explain the formation of molecular ions A^+ on MgO, which has no intrinsic electron-acceptor centers.

As indicated above, evacuation of the aluminosilica gel colored crimson led to regeneration of the original green coloration. Nevertheless, the carrier of the

crimson color, to which the new bands in the 600–400 mμ region belong, is a stable product that can be eluted from the surface of the aluminosilica gel upon repeated immersion in cyclohexane. The crimson-colored product that has passed into cyclohexane has a spectrum with well-defined absorption bands at 550, 510, 470, and 440 mμ (Fig. 4, *1*), which, allowing for the shift, fully corresponds to the spectrum of the adsorbed product. On standing in air, the color of the solution changes from crimson to yellow-green; moreover, the bands at 550 and 510 mμ disappear, while the bands at 470 and 440 mμ become stronger (Fig. 4, *2*).

It follows from the investigation described that the molecular ions A^+ on aluminosilica gel react with adsorbed molecules of H_2O, leading to the formation of an unstable intermediate product with characteristic absorption bands, which undergoes further transformation. This product should naturally be assigned to the semiquinone forms of hydroanthraquinone, formed as a result of hydration of A^+ ions on the surface of the aluminosilica gel. It should be emphasized that the experiment shows that H_2O molecules react mainly with the A^+ ions formed at the electron-acceptor centers of the adsorbent (band at 760 mμ), and not with the protonated ions AH^+ (band at 480 mμ), which for the most part remain unchanged.

Physical Institute
of Leningrad State University

Received
25 II 1962

CITED LITERATURE

1. V. A. Barachevskii, E. I. Kotov, A. N. Terenin, DAN, **143**, No. 2 (1962).

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