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Abstract

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PHYSICAL CHEMISTRY

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ABSORPTION SPECTRA AND E.P.R. OF QUINONES ADSORBED FROM THE GAS PHASE ON OXIDE SURFACES

Adsorption on the surface of oxide semiconductors of the *n*-type of molecules of electron-acceptor gases, for example O_2 , benzoquinone, etc., leads to changes in their photoconductivity and photoluminescence, explained by the capture of semiconductor electrons ⁽¹⁾ by adsorbed molecules with their conversion into negative ions.

For the spectral detection of a possible electron transfer from the semiconductor surface to an adsorbed molecule under pure vacuum conditions, we chose the well-known *n*-semiconductor ZnO. For comparison, the following oxides were taken as adsorbents: MgO, BaO, and silica gel.

ZnO, MgO, and BaO were obtained by pyrolysis of the basic carbonic-acid salts (carbonates) of zinc, magnesium, and barium, respectively. The temperature of the adsorbent under pumping was raised during one hour to 400° and maintained unchanged for two hours. After the adsorbent had cooled to 20°, adsorption of quinone vapors was carried out.

As adsorbates, *n*-benzoquinone and anthraquinone were taken, whose molecules possess a considerable electron affinity ^(2,3).

Benzoquinone was placed in a glass side arm of the vacuum system, from which its vapors entered the cell with the adsorbent. The vapor pressure of saturated *n*-benzoquinone vapors is, at 20°, 0.06 torr, and at 0°, 0.01 torr ⁽⁴⁾. Anthraquinone (chemically pure) was additionally purified by vacuum distillation with freezing of the vapors into glass ampoules, which were then sealed off. The ampoule was placed in the cell with the adsorbent, in a side arm that was not subjected to heating. After the usual conditioning and cooling of the adsorbent to 20°, the cell with the ampoule and adsorbent was sealed off, and the ampoule was broken inside the cell with a "striker." Adsorption of the vapors proceeded at 50° for anthraquinone. In the case of MgO, adsorption of anthraquinone vapors was carried out at 20° for three days.

Fig. 1. Absorption spectra of *n*-benzoquinone adsorbed on ZnO (from carbonate): I, II –vapor pressure ≤ 0.01 torr; III, IV –vapor pressure ≈ 0.06 torr; V –change in the spectrum at the first moment after admission of air

Figure 1: Fig. 1. Absorption spectra of *n*-benzoquinone adsorbed on ZnO (from carbonate): I, II –vapor pressure ≤ 0.01 torr; III, IV –vapor pressure ≈ 0.06 torr; V –change in the spectrum at the first moment after admission of air

The optical spectra of diffuse reflection were recorded on an SF-4 spectrophotometer with a special attachment ⁽⁵⁾.

On the ordinate axis (Fig. 1) is plotted the relative “transmission” T —the ratio of the intensity of light scattered from the adsorbent with the adsorbed substance to the intensity of light scattered only from the reference adsorbent. To record the e.p.r. signals (see Fig. 4a), part of the powder was transferred into a thin side arm, 4 mm in diameter, present on the cell. The e.p.r. signal was recorded on a standard RE-1301 instrument.

Upon adsorption of benzoquinone vapors on ZnO obtained by the method described above, after several seconds a bright bluish-green coloration appeared. The diffuse-reflection spectrum shown in Fig. 1 reveals absorption bands with broad maxima at 650–700 and 450–500 m μ . Simultaneously with the coloration there also arises an e.p.r. signal consisting of an intense line with half-width $\Delta H = 8$ oersted and $g = 2.005$. Excess surface concentration of adsorbed quinone diminished the e.p.r. signal.

On ZnO of grade M-1, obtained by burning Zn in a muffle furnace, benzoquinone gave no coloration, while an e.p.r. signal with $\Delta H = 2$ oersted and $g = 2.004$ was

approximately 30 times weaker in intensity than in the case of ZnO from carbonate. Benzoquinone vapors adsorbed on MgO also gave a green color and showed an intense EPR signal with a line width $\Delta H = 7$ Oe and $g = 2.005$. Upon adsorption of benzoquinone on BaO no coloration was observed, and the EPR signal was 100 times weaker than in the case of MgO. Adsorption of benzoquinone on silica gel gave neither coloration nor an EPR signal.

Fig. 1. Absorption spectra of *n*-benzoquinone adsorbed on ZnO (from carbonate): I, II –vapor pressure ≤ 0.01 torr; III, IV –vapor pressure ≈ 0.06 torr; V –change in the spectrum at the first moment after admission of air.

Anthraquinone vapors, upon adsorption on ZnO (from ZnCO_3) at 50°, gave a pink coloration and an intense, somewhat asymmetric EPR line with $\Delta H = 5$ Oe and $g = 2.005$. On MgO, anthraquinone vapors adsorbed at 20° gave, after three days, a pink coloration, the spectrum of which is shown in Fig. 3, curve 1. On ZnO (M-1), anthraquinone vapors give no noticeable coloration, and the EPR signal (Fig. 4b) is 30 times weaker than on ZnO (from ZnCO_3). Adsorption of anthraquinone vapors on BaO and silica gel caused neither coloration nor an

Fig. 2. Absorption spectrum of *p*-benzoquinone adsorbed on MgO (from carbonate): 1 –vapor pressure ≤ 0.01 torr; 2, 3 –vapor pressure ~ 0.06 torr

Figure 2: Fig. 2. Absorption spectrum of *p*-benzoquinone adsorbed on MgO (from carbonate): 1 –vapor pressure ≤ 0.01 torr; 2, 3 –vapor pressure ~ 0.06 torr

EPR signal.

Dry oxygen at a pressure above 100 torr destroys the coloration within several hours, turning it gray. Water vapor with a pressure of 14–18 torr destroys the coloration within a few seconds, turning it pale lilac.

If, by cooling the side arm with benzoquinone to 0° , its vapors are adsorbed at a lower vapor pressure and, after 10–15 min of absorption, the weakly bound, physically adsorbed benzoquinone is removed from the surface of the adsorbent by evacuation, then at such a lower surface concentration (small coverages) benzoquinone proves more sensitive to admission of air and oxygen. The absorption spectrum in this state reveals more detail (Fig. 2).

At small coverages of the ZnO surface (from carbonate) by benzoquinone molecules, two maxima at 438 and 480 $m\mu$ are observed in the absorption spectrum (Fig. 1). The maximum at 438 $m\mu$ coincides with the most intense maximum in the absorption spectrum of the *n*-benzoquinone anion obtained in solution during a chemical reaction in a stream ⁽⁶⁾. The second maximum in the absorption of the anion at 407 $m\mu$ is not observed on ZnO, since the edge of the intrinsic absorption of ZnO is superimposed on it. But on MgO both of these maxima are clearly visible (Fig. 2). The maximum at 480 $m\mu$ (Fig. 1, curves II, IV) may be compared with the maximum at 488 $m\mu$ observed upon hydroxylation of quinone in alkaline solution, and is assigned to such an anion ⁽⁶⁾. At large coverages, along with the maximum at 438 $m\mu$, maxima appear at 460 and 500 $m\mu$ (Fig. 1, curves I, III), which may be assigned to absorption by physically adsorbed benzoquinone molecules, since after evacuation of the excess quinone these maxima disappear (Fig. 1, curves II, IV). At small coverages, and espe—

especially at high values, in the region from 530 to 900 $m\mu$ a broad absorption band arises with a maximum at 650 $m\mu$. From the very beginning of the appearance of these bands, and, correspondingly, of the coloration, an EPR signal appears. The long-wavelength band may be attributed either to absorption by dimers of semiquinone-benzosemiquinone, which in principle can form on the surface and of which it is known that they give coloration ⁽⁷⁾ (a few percent of dimers are in equilibrium dissociated into monomers, which may be partly responsible for the appearance of the EPR signal), or to a complex of the quinone with the metal of the reduced oxide ⁽⁸⁾.

Fig. 2. Absorption spectrum of *p*-benzoquinone adsorbed on MgO (from carbonate): 1 –vapor pressure ≤ 0.01 torr; 2, 3 –vapor pressure ~ 0.06 torr

Let us note the difficulty of identifying the maxima of adsorbed benzoquinone in the region 400–500 $m\mu$ because of overlap with the absorption spectrum of physically adsorbed molecules. The double maximum observed upon adsorption of benzoquinone on MgO at 415 and 430 $m\mu$ corresponds to the double absorption maximum of the semiquinone anion observed in solution (6), and coincides exactly with the double maximum reported in (9) upon adsorption from solution on alumina. This maximum is also accompanied by an EPR signal.

The presence of a maximum at 480 $m\mu$ suggests that, upon adsorption of quinones on ZnO, hydroxylation takes place, which, generally speaking, is not usually observed on ZnO. However, the suppressing action of water vapor completely rules out the possibility of the reaction proceeding in an alkaline hydrate film on the surface of the adsorbent, as is assumed in (11).

In the case of the electronic semiconductor ZnO, one may suppose, as follows from measurements of conductivity, photo-emf (1), and infrared transmission (10) during adsorption of electron-acceptor molecules, that formation of the negative quinone ion occurs as a result of capture of an electron from the semiconductor.

For BaO and MgO the possibility of electron transfer also exists, if it is assumed that, as a result of thermal treatment in vacuum, lattice defects are formed—oxygen vacancies that have captured two electrons (12). These defects may act as electron donors. This is also indicated by the necessity of preliminary reduction of the oxides by heating in vacuum in order to obtain coloration and a significant EPR signal upon adsorption. Moreover, if O_2 is admitted onto previously trained and still hot ZnO, then the sample is cooled and again pumped off at 20°, the coloration upon adsorption of benzoquinone is slight. The coloration and EPR intensify with an increase in the training temperature up to 500°. A further increase in the training temperature leads to weakening of the coloration and EPR signal obtained upon adsorption of quinones.

The coloration of ZnO (from $ZnCO_3$) pink upon adsorption of anthraquinone is associated with the appearance of an absorption band with a maximum at 510 $m\mu$.

(Fig. 3). Such an absorption band is present for anthraquinone in alkaline solution and is associated with the appearance of the doubly charged negative ion of anthraquinone (¹³). This ion is diamagnetic and cannot be responsible for the appearance of the E.P.R. signal. On this same spectral curve there is an inflection at 480 $m\mu$. This inflection is reproduced on all spectral curves for anthraquinone on ZnO (from $ZnCO_3$). It should naturally be ascribed (¹⁴) to the semiquinone ion of anthraquinone, which is confirmed by the presence of an E.P.R. signal.

Fig. 3

Fig. 3. Absorption spectrum of adsorbed *p*-anthraquinone: **I** —on MgO at 20°; **II** —on ZnO at 50°; **III** —absorption spectrum of the doubly charged ion of

p-anthraquinone in solution ⁽¹⁷⁾

Fig. 4

Fig. 4. E.P.R. spectra of benzoquinone (*a*) and anthraquinone (*b*) adsorbed on ZnO

Thus, from the absorption spectra and the E.P.R. signal, transfer of an electron from the surface of the oxide adsorbent to the adsorbed electron-acceptor molecule has been detected, with the formation of ions and ion-radicals that are stabilized by the surface of the adsorbent under vacuum conditions.

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CITED LITERATURE

1. A. N. Terenin, in collection: *Photoelectric and Optical Properties of Semiconductors*, Kiev, 1959, p. 255.
2. L. E. Lyons, *Nature*, **196**, 573 (1962).
3. R. Gerani, *Ions in Solutions*, Moscow-Leningrad, 1938.
4. A. S. Coolidge, M. S. Coolidge, *J. Am. Chem. Soc.*, **49**, 100 (1927).
5. E. I. Kotov, *Optics and Spectroscopy*, **3**, issue 2, 115 (1957).
6. M. Eigen, P. Matthies, *Chem. Ber.*, **94**, 3309 (1961).
7. B. B. Golyubev, Yu. M. Boyarchuk, V. B. Evdokimov, *ZhFKh*, **34**, 696 (1960).
8. Goldschmidt, F. Crustman, *Ber.*, **57**, 714 (1924).
9. Takamura, J. Kashiwakura, *Bull. Chem. Soc. Japan*, **36**, 1538 (1963).
10. V. N. Filimonov, *Optics and Spectroscopy*, **5**, 709 (1958).
11. D. Bijl, H. Kainer, A. C. Rose-Innes, *Nature*, **174**, 830 (1954).
12. C. I. Revane, *Phys. Rev.*, **133**, No. 5A, 1431 (1964).
13. H. L. G. Bäckström, Beatty, *J. Phys. Chem.*, **35**, 2535 (1931).
14. N. K. Bridge, G. Porter, *Proc. Roy. Soc.*, **244**, 274 (1958).

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