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Figure 1

Figure 1: Figure 1

Abstract

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RADIOLYSIS OF HYDROCARBONS ON A SEMICONDUCTOR ADSORBENT*

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The study of the electrical properties of adsorbents during the radiolysis of adsorbed substances makes it possible to obtain additional information for understanding the role of intermediate particles formed at the solid—gas (liquid) interface.

During the radiolysis of chemical compounds, active fragments of molecules arise —atoms, radicals, ions—which, as investigations have shown ([1,2]), are capable, in comparison with molecules, of changing to a significantly greater extent the electrical properties of the near-surface layer of a solid. The accumulation of active particles on the surface of an adsorbent, and the charging of the surface (double electric layer), may be one of the main reasons determining the influence of adsorbents on the rate and direction of radiation-chemical heterogeneous processes.

Fig. 1. γ-effect in butane at $t = 20^\circ$ and different pressures.
1—$p_{\text{but}} = 572$ mm; 2—$p_{\text{but}} = 250$ mm; 3—verification of equation (4) for these experiments (curves 1, 2)

In the present work an attempt was made to identify some of these particles, arising during radiolysis on the surface of an adsorbent, and to investigate their interaction with adsorbed molecules and with the adsorbent. For this purpose it is convenient to use an adsorbent possessing semiconductor properties, i.e., an adsorbent that would simultaneously serve as a probe for active particles. Zinc oxide, prepared in the form of a thin film deposited on a quartz substrate, was chosen as such an adsorbent. Zinc oxide is a typical electronic semiconductor with well-studied physical properties. Under the influence of γ-radiation it does not decompose appreciably and changes its electrical conductivity only slightly in vacuum and in an atmosphere of inert gas. Hydrogen, butane, isobutylene, and neon were chosen as adsorbates.**

Results. In all cases, for all substances, during radiolysis we observed an in-

Fig. 2

Figure 2: Fig. 2

crease in electrical conductivity (see Figs. 1, 2, 3) to a considerably greater extent than occurred when the ZnO films were irradiated in vacuum or in an atmosphere of neon.*** Moreover, in vacuum or in neon (regardless of its pressure), the results obtained were the same also—an insignificant increase in conductivity, which is associated with a change in the concentration of defects. Increasing the pressure in the case of butane led to an increase in the radiolysis effect. The slope of the curves increases in proportion to the pressure (see Fig. 1, 1, 2). In liquid butane a considerable increase in the γ-effect is observed. Termination of irradiation led to the reverse process—a decrease in the electrical conductivity of the film. The higher the temperature, the faster the reverse process. In the case of isobutylene (see Fig. 2), increasing the pressure and changing the aggregate state (curves I, II, III) had little effect on the γ-effect. With increasing temperature the effect first increases and then decreases, passing through a maximum (see in Fig. 3 the slopes at the initial moments—curves I, II, III). At 300° the effect practically disappears. The extremal region in the case of isobutylene lies approximately within 160-170°.

Fig. 2. γ-effect in isobutylene at $t = 20°$, at different pressures and aggregate states of the substance. Curves: I—gas, $p = 710$ mm; II—gas in equilibrium with liquid gas; III—liquefied gas. 1, 2, 3—verification of equation (4) for experiments I, II, III, respectively.

In the case of butane and hydrogen there is also an extremal region; however, it lies considerably higher (for hydrogen, about 280°). At room temperature and below, the γ-effect decreases for all the substances studied to approximately the same extent.

Discussion of results. Analysis of the experimental data and their comparison with the results obtained by us in studies of the interaction of radicals with semiconductors and of the influence of chemisorption of these active particles on the electrical conductivity of semiconductors allowed us to suppose that the increase

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* A. P. Sysoeva took part in the experimental part of the work.

** The experiments were carried out in sealed glass ampoules, with thin films of zinc oxide on quartz substrates introduced inside.

*** Admission into the ampoules of butane and isobutylene before irradiation practically did not change the electrical conductivity of ZnO at +200°C and below. Neon at all temperatures does not change the electrical conductivity of ZnO.

Fig. 3

Figure 3: Fig. 3

in the electrical conductivity of ZnO films during radiolysis of hydrocarbons is associated not with chemisorption of butane and isobutylene and the formation of the corresponding hydrocarbon positive ions (^{3}) on the surface of the adsorbent, but with chemisorption of hydrogen atoms formed as a result of radiolysis of hydrocarbon molecules both in the adsorbed layer (mainly) and in the bulk. The H atoms and alkyl radicals arising under the influence of γ-radiation during adsorption on the semiconductor change its electrical conductivity in opposite directions (^{1}). This process, however, in the case of H atoms proceeds with an activation energy of about 2 kcal/mole, and in the case of alkyl radicals, 6-8 kcal/mole. The mobility of H atoms, moreover, considerably exceeds the mobility of alkyl radicals, and therefore the adsorption centers of the surface are attacked first of all by H atoms. As for the influence on electrical conductivity of ions formed in the radiation field, they, in all probability, recombine with wandering electrons and are converted into the corresponding neutral particles earlier than they interact with the surface of the adsor-

Fig. 3. γ-effect in isobutylene at different temperatures. I—$t = 270°$; II—$t = 140°$; III—$t = 20°$. 1, 2, 3—verification of equation (4) for experiments I, II, III, respectively. 4—for $t = 100°$.

bent. All this leads to the conclusion that the most effective active particles with respect to their influence on the electrical conductivity of the adsorbent are H atoms, arising mainly in the adsorption layer as a result of the radiolysis of hydrocarbons.

The concentration of H atoms on the surface of the adsorbent is determined by competition among four principal processes*:

$$\begin{gathered}\text{a) } \mathrm{M} \to \mathrm{M}_a \rightsquigarrow \mathrm{R}_a + \mathrm{H}_a; \quad \text{b) } \mathrm{H}_a + \mathrm{R}_a \to \mathrm{M}_a; \\ \text{c) } \mathrm{H}_a + \mathrm{H}_a \to (\mathrm{H}_2)_a \to \mathrm{H}_2; \quad \text{d) } \mathrm{H}_a + \mathrm{M}_a \to \mathrm{R}_a + \mathrm{HR} \text{ and } \mathrm{R}_a + \mathrm{M}_a \to \mathrm{R}'_a.\end{gathered} \tag{1}$$

where $\mathrm{M}_a, \mathrm{R}_a$ are adsorbed molecules and hydrocarbon radicals, and H_a are adsorbed H atoms. The principal processes leading to the loss of adsorbed atoms are apparently reactions c and d. The process directly responsible for the increase in the electrical conductivity of ZnO is associated with the chemisorption of adsorbed H atoms, which may be represented schematically as follows:

$$\mathrm{H}_a \rightleftarrows \mathrm{H}_a^+ + e^-. \tag{2}$$

Owing to the fact that the activation energy of adsorption of H atoms is close to zero, it may be assumed that the limiting stage in the increase of the electrical conductivity of ZnO upon irradiation of hydrocarbons is process (2)**.

It follows from what has been said that the concentration of adsorbed hydrogen atoms $[H_a]$ in the process of radiolysis and of the change in the electrical conductivity of the film, i.e., in the process of reaction (2), will remain constant and will be determined only by the rates of reactions (1). On the basis of the considerations given above, we assume that the increase in the electrical conductivity of the film is proportional to (H_a), and the decrease to the value (H_a^+) and to the electrical conductivity. The total rate of change of the film conductivity will obviously be determined by the expression

$$\frac{dT}{dt} = K_1[H_a] - K_2[H_a^+][e^-], \tag{3}$$

where K_1 and K_2 are kinetic constants dependent on temperature, and e is the concentration*** of conduction electrons.

Transformation and integration of equation (3) under the conditions: $[H_a] =$ const and $\sigma = \sigma_0$ at $t = 0$ leads to the expression (for the case where $A < X$) (4):

$$\frac{2}{X}\left[th^{-1}\left(\frac{A}{x}\right) - th^{-1}\left(\frac{1}{x}\right)\right] = K_2' t, \tag{4}$$

where $A = (2\Delta\sigma/\sigma_0 + 1)$; $x = \sqrt{1+4K}$; $K = K_1'/K_2'$; $\Delta\sigma = \sigma - \sigma_0$; $K_1' = K_1/[e^-]_0$; $K_2' = K_2[e^-]_0$, σ_0 and σ $(\sigma = [e^-]qu)$ are the electrical conductivity of the film before and after irradiation, q and u are the charge and mobility of the current carriers, and t is time.

It follows from equation (4) that the quantity K_1', characterizing the rate of the direct process, depends on the magnitude of adsorption and on the radiation intensity; the quantity K_2', characterizing the reverse process, depends only on temperature. To verify the validity of expression (4), the quantities K were calculated from the experimental data, and then graphs were plotted. From the slopes of the straight lines the values of K_2' were determined.

From the values of K and K_2', K_1' was calculated. Table 1 gives the values of these quantities for room temperature.

* A reaction of the type $M_a \rightsquigarrow R_a + R_a'$ is unlikely in comparison with reaction a), since in the adsorption layer, as in the radiolysis of liquids and solids, owing to the "cage" effect, the leading act of radiolysis is the detachment of an H atom.

** It should be noted that, as the surface is filled with particles (H_a^+), the activation energy will increase owing to the double electric layer (in accordance with Hauffe' s "edge layer" theory).

*** This refers to the concentration of conduction electrons in crystalline filaments that fuse crystallites together and determine the electrical conductivity of the film as a whole.

Figure 1 shows the applicability of equation (4) in the case of irradiation of butane at different pressures. It is evident from the figure that the experimental points from two experiments lie on one straight line, which means (in accordance with the requirement of the equation) equality of the quantities K_2'. The quantities K_1', however, are different and depend on the butane pressure (see curves 1 and 2 and Table 1). In the case of liquid butane, the quantity K_1' increases considerably. Figures 2 and 3 show the results of irradiation of isobutylene, from which it is evident that equation (4) is also fulfilled in this case. However, the quantities K_1' depend little on pressure and on the aggregate state (see Fig. 2, curves I, II, III).

Table 1

No.	Substance	Aggregate state	$K_1' \cdot 10^2$	$K_2' \cdot 10^2$	T, °C
1	Butane	Gas $p = 250$ mm	0.13	0.65	20
2	“	Gas $p = 572$ mm	0.32	0.65	20
3*	Isobutylene	Gas $p = 64$ mm	–	0.40	0
4	”	Gas $p = 710$ mm	0.80	0.35	20
5	”	Gas (in equilibrium with liquid)	0.93	0.76	20
6	”	Liquid	1.03	1.03	20
7	Hydrogen	Gas $p = 600$ mm	1.85	1.25	20
8	”	Adsorption layer	–	0.45	0

* The results were calculated from the experimental data of paper (^{3}).

This result is, in all probability, connected with the fact that in all these experiments the surface of the adsorbent was covered by at least a monolayer, which apparently in this case plays the chief role in delivering active particles to the surface. In the case of unsaturated hydrocarbons (acceptors of H atoms), the subsequent layers do not affect the radiation effect (with respect to electrical conductivity), because the H atoms formed there do not reach the surface.* In the case of saturated hydrocarbons, however, the subsequent adsorption layers also play a role.

If there is no filling of the surface, then in both cases the irradiated volume also affects the electrical conductivity of the adsorbent. It is also evident from Fig. 2 that the pressure and aggregate state in the case of isobutylene have little effect (see Table 1) on the slope of straight lines 1, 2, 3, i.e., on the values of the quantities K_2. This may be connected with the fact that the quantities σ_0 in the film samples differed somewhat from one another, and also with the fact that the adsorbed isobutylene (or products of its radiolysis) affects the rate of the reverse process. Figure 3 presents the results of experiments for isobutylene carried out at different temperatures. It is evident from the figure that, as the temperature rises, the quantities $K_1' \sim K_1[\mathrm{H}_a]$ (the slope of the curves at the initial points) first increase and then decrease, which is connected, on the one hand, with the increase of K_1 with temperature, and on the other hand with the decrease of the quantities $[\mathrm{M}_a]$ (desorption of isobutylene molecules) and of the quantities $[\mathrm{H}_a]$ (reactions 1c and 1d). These circumstances also explain the existence of the extremal regions discussed above. The lower-temperature position of the extremum for isobutylene is connected with its greater reactivity toward H atoms. As for the quantities $K_2' \sim K_2$, with increasing temperature their steady increase is observed, which corresponds to the requirement of (4). The quantity σ_0 changed insignificantly in the indicated temperature interval (the activation energy of electrical conductivity in vacuum or neon was 2 kcal/mole).

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* This result agrees well with the data obtained in paper (^{5}), and emphasizes the leading role of the active particles arising in the adsorption layer.

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

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