PHYSICAL CHEMISTRY

E. V. BARANOV, V. E. KHOLMOGOROV, Academician A. N. TERENIN

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. V. BARANOV, V. E. KHOLMOGOROV, Academician A. N. TERENIN

PHOTOINDUCED E.P.R. SIGNALS IN ZINC OXIDE

Recently, numerous works carried out by Soviet and foreign researchers have been devoted to the phenomena of photodesorption and photosorption of gases and vapors on zinc oxide ($^{1-7}$). Zinc oxide is a typical photocatalyst capable of carrying out the photosynthesis of hydrogen peroxide from water and oxygen, as well as other reactions (^{8}). Until now, no attention has been paid to the direct detection of surface free-radical formations arising in the course of the photoreaction. In the present work the method of electron paramagnetic resonance (e.p.r.) was applied to the investigation of the surface properties of zinc oxide under irradiation with ultraviolet and visible light.

Experimental procedure

E.p.r. measurements were carried out on an RE1301 radiospectrograph with high-frequency modulation of the magnetic field. The sensitivity of the apparatus was 10^{-11} mole of DPPH. Powdered zinc oxide samples of three grades were studied: 1) for phosphors, 2) "ch. d. a.," 3) muffle grade M-1. Most of the results were obtained with grade M-1 as the most photosensitive. The zinc oxide samples were placed in thin-walled quartz ampoules 6 mm in diameter, which could be evacuated. The samples were illuminated directly in the resonator of the radiospectrograph, and in some cases outside the resonator, with the light of an SVDSh-250 mercury quartz lamp or an incandescent lamp. The light was focused on the ampoule by means of mirrors and lenses so that the illumination of the ampoule in the spectral region 365 mμ, isolated by a UFS-1 light filter, was of the order of 10^{-4} W/cm^2. Low-temperature measurements were carried out in a special quartz Dewar vessel placed in the resonator of the radiospectrograph.

To prevent heating of the samples during illumination, a heat-protective water filter 100 mm thick was placed in the path of the light beam. In some cases (see below) a change in the dark conductivity of the zinc oxide samples under illumination could be observed from the change in the Q of the resonator.

Results and discussion

A summary of the results is given in Table 1. Zinc oxide samples, both before calcination and after calcination in air up to 500° C, do not give e.p.r. signals at 20° C either in the dark or under illumination in air (see the first line of the table). No changes in the conductivity of the samples under illumination were observed either. If the irradiation of the samples is carried out at 77° K, both in air and after evacuation, two narrow symmetric e.p.r. lines are detected, with $g = 1.964$, $\Delta H = 4.5$ Oe, and with $g = 2.018$, $\Delta H = 3.0$ Oe. (ΔH is the half-width of the line): Fig. 1a and Table 1*. At 77° K the e.p.r. lines remain after illumination is stopped, without change in intensity. When the samples are brought to 20° C these lines disappear in samples irradiated in air. Upon repeated illumination at 77° K they reappear. In vacuum samples, upon thawing, the line with $g = 2.018$ disappears and the line with $g = 1.964$ disappears incompletely. Such a reversible cycle of changes upon freezing, illumination, and thawing can be repeated many times. By irradiating the samples at 77° K with light filtered through various optical filters, it was established that the indicated EPR lines appear not only under the action of $\lambda = 365$ mμ, but also under the action of the visible region of the spectrum, with the intensity of the lines decreasing as the infrared region of the spectrum is approached.

Samples of zinc oxide that had been conditioned for two hours in vacuum (10^{-4} mm Hg) at 20° C without illumination do not give EPR signals. Under illumination at 20° C, with continuous pumping, an intense EPR line with $g = 1.964$, $\Delta H = 7.5$ oersted (Fig. 1), appears in the samples and does not change its intensity after illumination is stopped. At the same time, an increase in the conductivity of these samples is observed, as judged by the decrease in the resonator quality factor. However, if zinc oxide samples are illuminated in an ampoule evacuated to 10^{-4} mm Hg at 20°, but disconnected from the vacuum apparatus, two EPR lines arise, with $g = 1.964$, $\Delta H = 7.5$ oersted, and with $g = 2.004$, $\Delta H = 4.5$ oersted, which do not change their intensity after illumination is stopped (Fig. 1). The conductivity of these samples is high. In this case too, the EPR lines also arise under the action of the visible region of the spectrum. When zinc oxide samples with

Fig. 1. EPR spectra of zinc oxide samples. **A** –illuminated: **a** –in air at 77° K; –in vacuum under pumping at 20° C; –in vacuum without pumping at 20° C. –heated at 450° C: **a** –in vacuum under pumping; –in vacuum without pumping; –in vacuum under pumping, then cooled to 20° C and brought into contact with oxygen (10^{-3} mm Hg). –previously heated in vacuum at 450° C for 2 h, with adsorbed vapors: **a** –quinone (10^{-2} mm Hg), –iodine (10^{-1} mm Hg).

---

* In the figures, as usual, the derivatives of the e.p.r. absorption lines are shown.

Fig. 1. EPR spectra of zinc oxide samples. A —illuminated: a —in air at 77° K; —in vacuum under pumping at 20° C; —in vacuum without pumping at 20° C. —heated at 450° C: a —in vacuum under pumping; —in vacuum without pumping; —in vacuum under pumping, then cooled to 20° C and brought into contact with oxygen (10^{-3} mm Hg). —previously heated in vacuum at 450° C for 2 h, with adsorbed vapors: a —quinone (10^{-2} mm Hg), —iodine (10^{-1} mm Hg).

Figure 1: Fig. 1. EPR spectra of zinc oxide samples. A —illuminated: a —in air at 77° K; —in vacuum under pumping at 20° C; —in vacuum without pumping at 20° C. —heated at 450° C: a —in vacuum under pumping; —in vacuum without pumping; —in vacuum under pumping, then cooled to 20° C and brought into contact with oxygen (10^{-3} mm Hg). —previously heated in vacuum at 450° C for 2 h, with adsorbed vapors: a —quinone (10^{-2} mm Hg), —iodine (10^{-1} mm Hg).

photoinduced signals obtained at 20° C are cooled to 77° K, the intensity of the line with $g = 1.964$ increases anomalously, whereas the intensity of the line with $g = 2.004$ changes analogously to the change in the lines of free radicals in the crystalline phase upon cooling.

In interpreting the EPR signals obtained, attention is drawn to the appearance, under illumination, of the line with $g = 1.964$ in a zinc oxide sample that was certainly not freed from sorbed oxygen (Table 1), since the vacuum conditioning was carried out at 20° C. To clarify the role of sorbed oxygen, a series of experiments was carried out with conditioning of zinc oxide at 450° C in vacuum (lower half of Table 1). After such treatment, the samples give, without illumination, an intense symmetric signal with

$g = 1.964$, $\Delta H = 7.5$ oersted, while exhibiting increased conductivity (Fig. 2a). Such a sample is extremely sensitive to traces of oxygen: admission of dry oxygen at a pressure of 10^{-3} mm Hg sharply decreases the line with $g = 1.964$ and causes the appearance, in its place, of new lines associated with oxygen adsorption*. If oxygen comes into contact with heated (100—250°C) zinc oxide, a new intense symmetrical line with $g = 2.004$ appears (Fig. 2b). In the case where oxygen is adsorbed on a sample kept at 20°C, an asymmetric signal appears with $g_\perp = 2.003$ and $g_\parallel = 2.008$, having the form usually observed for peroxide radicals (Fig. 2c) ([9,10]). When the pressure of dry oxygen is raised from 10^{-3} to 100 mm Hg, the line with $g = 1.964$ disappears completely, while the newly appearing EPR line broadens and decreases in intensity; this explains the absence of EPR signals in zinc oxide exposed to air. These results lead to the conclusion that the light-induced signal with $g = 1.964$ is due to the release, i.e., the photodesorption, of oxygen from the surface of zinc oxide. The absence of photodesorption at high oxygen pressure is understandable, since adsorption equilibrium is rapidly reestablished. The centers released from oxygen during photodesorption and responsible for the EPR signal with $g = 1.964$ apparently represent unpaired electrons at donor levels, whose existence in zinc oxide is known ([11]).

The EPR signal with $g = 2.004$, which appears upon illumination of a vacuum sample of zinc oxide in an ampoule disconnected from the vacuum setup (Table 1), and which also arises without illumination when oxygen contacts heated zinc oxide, is possibly due to a chemisorbed form of atomic oxygen with one unpaired electron $]\text{—}\dot{\mathrm{O}}$.

Table 1

EPR signals in zinc oxide without illumination (t) and under illumination (c) (The plus sign denotes the presence of a signal, and the minus sign its absence)

Conditions of treatment of zinc oxide samples before EPR measurement	$g =$ 1.964, t	$g =$ 1.964, c	$g =$ 2.004, t	$g =$ 2.004, c	$g =$ 2.003, 2.008, t	$g =$ 2.003, 2.008, c	$g =$ 2.018, t	$g =$ 2.018, c
In air, 20°C	–	–	–	–	–	–	–	–
In air, 77°K	–	+	–	–	–	–	–	+
In vacuum, 77°K	–	+	–	–	–	–	–	+

Conditions of treatment of zinc oxide samples before EPR measurement	$g =$ 1.964, t	$g =$ 1.964, c	$g =$ 2.004, t	$g =$ 2.004, c	$g =$ 2.003, 2.008, t	$g =$ 2.003, 2.008, c	$g =$ 2.018, t	$g =$ 2.018, c
In vacuum under pumping at 20°C	–	+	–	–	–	–	–	–
In vacuum without pumping, 20°C	–	+	–	+	–	–	–	–
Heated 2 hours, 450°C, in air	–	–	–	–	–	–	–	–

Conditions of treatment of zinc oxide samples before EPR measurement	$g = 1.964$, t	$g = 1.964$, c	$g = 2.004$, t	$g = 2.004$, c	$g = 2.003$, t	$g = 2.003$, c	$g = 2.018$, t	$g = 2.018$, c
Heated 2 hours, 450°C, in vacuum under pumping	+		−		−		−	
Heated 2 hours, 450°C, in vacuum without pumping	+		+		−		−	

Conditions of treatment of zinc oxide samples before EPR measurement	$g = 1.964$, t	$g = 1.964$, c	$g = 2.004$, t	$g = 2.004$, c	$g = 2.003, 2.008$, t	$g = 2.003, 2.008$, c	$g = 2.018$, t	$g = 2.018$, c
Heated 2 hours, 450°C, in vacuum under pumping, admission of oxygen onto heated zinc oxide	–		+		–		–	

Conditions of treatment of zinc oxide samples before EPR measurement	$g = 1.964$, t	$g = 1.964$, c	$g = 2.004$, t	$g = 2.004$, c	$g = 2.003, 2.008$, t	$g = 2.003, 2.008$, c	$g = 2.018$, t	$g = 2.018$, c
Heated 2 hours, 450°C, in vacuum under pumping, admission of oxygen onto zinc oxide at 20°C	−		−		+		−	

Conditions of treatment of zinc oxide samples before EPR measurement	$g =$ 1.964, t	$g =$ 1.964, c	$g =$ 2.004, t	$g =$ 2.004, c	$g =$ 2.003, 2.008, t	$g =$ 2.003, 2.008, c	$g =$ 2.018, t	$g =$ 2.018, c
Heated 2 hours, 450°C, in vacuum under pumping, admission of quinone vapor	−		+		−		−	

Conditions of treatment of zinc oxide samples before EPR measurement	$g =$ 1.964, t	$g =$ 1.964, c	$g =$ 2.004, t	$g =$ 2.004, c	$g =$ 2.003, 2.008, t	$g =$ 2.003, 2.008, c	$g =$ 2.018, t	$g =$ 2.018, c
Heated 2 hours, 450°C, in vacuum under pumping, admission of iodine vapor	–		+		–		–	

Conditions of treatment of zinc oxide samples before EPR measurement	$g = 1.964$, t	$g = 1.964$, c	$g = 2.004$, t	$g = 2.004$, c	$g = 2.003, 2.008$, t	$g = 2.003, 2.008$, c	$g = 2.018$, t	$g = 2.018$, c
Heated 2 hours, 450°C, in vacuum under pumping, admission of water vapor	—		—		—		—	

The “peroxide” signal with $g_\perp = 2.003$ and $g_\parallel = 2.008$ in this case may be caused by a covalently bound, surface, uncharged radical]—O—$\dot{\mathrm{O}}$.

* At the same time the conductivity of the zinc oxide samples decreases.

The origin of the light-induced signal with $g = 2.018$, which appears only under illumination of zinc oxide at 77° K (Table 1), is unclear. It is possible that it is produced by electrons at shallow acceptor levels.

Adsorption of vapors of other electron-acceptor molecules (quinone, iodine) has a quenching effect on the light-induced or thermally produced EPR signal with $g = 1.964$, analogous to the action of oxygen (Fig. 3). Pumping out and freezing the vapors at 20° C do not regenerate the initial signals. Adsorption of water vapor (18 mm Hg) also quenches the signal with $g = 1.964$ and decreases the conductivity of the samples, without producing new EPR lines.

Preliminary experiments were also carried out to determine the possibility of the appearance of light-induced EPR signals in zinc oxide colored with organic dyes upon absorption of light by the latter. This question is of interest in connection with the photosensitization of the internal photoeffect of zinc oxide to visible light ([12]). Samples of powdered zinc oxide M-1 were colored from ethanolic solutions (conc. 10^{-5} mol/liter) of the following dyes: eosin, erythrosin, magnesium phthalocyanine, and carbocyanine photographic sensitizer No. 1543. Upon illumination of such samples with spectral regions isolated by light filters and coinciding with the absorption bands of the dyes, both in vacuum and in air at 77° K, two EPR signals arise, with $g = 1.964$ and $g = 2.018$, analogous to those described above for uncolored zinc oxide. Upon illumination of colored samples in vacuum at 20° C, signals with $g = 1.964$ and $g = 2.004$ arise, the behavior of which is also similar to that in uncolored samples. Consequently, EPR signals may be produced in zinc oxide, like the internal photoeffect, through the agency of an adsorbed dye that absorbs outside the absorption region of zinc oxide. Since the appearance of the EPR line with $g = 1.964$ was attributed to photodesorption of oxygen, the result obtained for colored samples indicates the possibility of photosensitization of oxygen desorption from zinc oxide.

An attempt was made to detect free-radical formations upon irradiation with ultraviolet light of powdered zinc oxide in contact with moist oxygen at 20° C, and also at 77° K. In the first case no EPR signals were detected; in the second case symmetric EPR signals with $g = 1.964$ and $g = 2.003$ appeared, which disappeared after the samples were warmed to room temperature. No EPR signal with $g = 2.018$ was detected. Work in this direction is continuing.

Received
20 IV 1962

CITED LITERATURE

1. I. A. Myasnikov, S. Ya. Pshezhetskii, DAN, **99**, 125 (1954).

2. F. Stöckmann, Zs. Phys., **146**, 407 (1956).

3. G. Heiland, Zs. Phys. **142**, 415 (1955).

4. D. A. Melnik, J. Chem. Phys., **26**, 1136 (1957).

5. D. B. Medved, J. Chem. Phys., **28**, 870 (1957).

6. Yu. P. Solonitsyn, ZhFKh, **23**, 2142 (1958); A. Terenin, Yu. Solonitzin, Disc. Farad. Soc., **28**, 28 (1959).

7. I. Fujita, T. Kwan, Bull. Chem. Soc. Japan, **31**, 379 (1958).

8. G. A. Korsunovskii, Yu. S. Lebedev, ZhFKh, **35**, 1078 (1961).

9. R. J. Abraham, D. H. Whiffen, Trans. Farad. Soc., **54**, 1291 (1958).

10. Yu. D. Tsvetkov, Ya. S. Lebedev, Yu. N. Molin, V. V. Voevodskii, Vysokomolek. soed., **1**, 1519, 1639, 1806 (1959).

11. G. Heiland, Zs. Phys., **132**, 354, 367 (1952).

12. E. K. Putseiko, A. N. Terenin, ZhFKh, **23**, 676 (1949); Usp. nauchn. fotograf., **3**, 101 (1952); DAN, **90**, 1005 (1953).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.