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1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ON THE NATURE OF THE LIGHT-INDUCED E.P.R. SIGNAL IN SILVER BROMIDE SENSITIZED WITH CYANINE DYES

(Presented by Academician A. N. Terenin, January 10, 1962)

In the works of Terenin, Putseiko, and Akimov ($^{1-10}$), devoted to elucidating the mechanism of spectral sensitization, arguments were given in favor of the process of transfer of excitation energy from the dye to the semiconductor, and the possibility of transfer of a dye electron to the semiconductor was criticized. Recently, Nidler, Griffith, and West (^{11}), in experiments designed to resolve this alternative, observed the appearance of an e.p.r. signal in AgBr powders colored with certain quinoline and thiacyanine dyes when illuminated in the absorption region of the sensitizer. The observed light-induced e.p.r. signal was attributed to free radicals arising from dye molecules as a result of the transition of electrons from the latter into the conduction band of AgBr in the act of optical sensitization. Such a result is regarded by the authors as evidence in favor of the second of the sensitization mechanisms indicated above. However, the same authors do not rule out the possibility of formation of free radicals as a result of the reaction of bromine atoms with adsorbed dye molecules.

It should be noted that the effect was observed on samples subjected to strong irradiation: the e.p.r. signal reached its maximum value after 4 min of irradiation with the light of a 500-watt incandescent lamp with light filters. Meanwhile, in a paper by one of the authors of the present article (^{10}) it was shown that even under weak exposure of colored AgBr powders with an energy of the order of 10^{-5} W$\cdot$cm^{-2}, the sensitized photoeffect in them, already after several seconds, falls to an insignificant value as a result of destruction of the sensitizer dye by bromine liberated during the photochemical decomposition of AgBr.

The purpose of the present work was to elucidate the nature of the light-induced e.p.r. signals arising upon illumination of AgBr powders colored with sensitizers. The measurements were carried out on an e.p.r. apparatus of the RE1301 type with high-frequency modulation of the magnetic field, with a transmission cylindrical resonator of the H_{01} type. The sensitivity of the apparatus, calibrated with the crystalline free radical diphenylpicrylhydrazyl, was $5 \cdot 10^{-12}$ mole.

The samples were irradiated directly in the resonator through an aperture 13 mm in diameter located in the lower cover of the resonator, with light from an incandescent lamp. To isolate the necessary region of the spectrum, in addition to a water filter absorbing infrared radiation, glass light filters of types OS, KS, and SS were used. The illumination of the samples, measured with a calibrated thermopile, in the spectral interval 600-700 mµ (the absorption region of the dye) was $4 \cdot 10^{-4}$ W • cm^{-2}, and in the spectral interval 350–500 mµ (the absorption region of AgBr) was 10^{-5} W • cm^{-2}. Low-temperature measurements were carried out at temperatures of 77°K and 90°K in a quartz Dewar vessel placed directly in the resonator. The investigation was carried out on microcrystalline AgBr powders (crystallite size 3-5 μ). The following cyanine dyes were used as sensitizers*:

1.

[structural formula]

2.

[structural formula]

3.

[structural formula]

4.

[structural formula]

5.

[structural formula]

6.

[structural formula]

7.

[structural formula]

Preparation of the powders and adsorption of dyes on them from alcoholic solutions of concentration 10^{-4} mol/l were carried out under nonactinic light. The powders under investigation (a 400 mg sample) were sealed in narrow quartz ampoules, allowing evacuation of air and cooling in the resonator.

The following results were obtained. Powders of undyed AgBr, neither in the dark nor under illumination in the intrinsic-absorption band, in air or in vacuum, gave any noticeable e.p.r. absorption. In AgBr powders colored with sensitizers 1–7, in the dark, either in air or in vacuum, at both room and low temperatures no e.p.r. signals were observed. An e.p.r. signal arose upon illumination of AgBr samples colored with dyes Nos. 3, 4, 5, and 7, in air at room temperature, and reached its maximum value within several minutes. Illumination

* The dyes were kindly provided by I. I. Levkoev, to whom the authors express their sincere gratitude.

Fig. 1. Light-induced EPR signal in AgBr powder dyed in an alcoholic solution of dye No. 5 of concentration 10^{-4} mol/l

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was carried out at wavelengths in the absorption band of the sensitizer. The EPR signal (Fig. 1) was a single symmetric line without hyperfine structure, with $g = 2.005$ and $\Delta H = 12$ Oe. (ΔH is the half-width of the absorption line, i.e., the distance between the points of maximum slope of the absorption line) and corresponded to 10^{13}–10^{14} unpaired electrons in the sample. The most intense EPR signals were observed in AgBr powders dyed with sensitizers Nos. 4 and 5. When analogous AgBr powders were illuminated under vacuum conditions (10^{-4} mm Hg), the intensity of the EPR signals was 1.5–2 times greater; admitting air to these samples did not change the magnitude of the effect. The EPR signal persisted after illumination was stopped, decreasing in intensity to 1/3 of its initial value over 10–15 h while the sample was kept in the dark. Cooling to 77°K samples that had been exposed at room temperature in air or in vacuum led to an increase in the intensity of the EPR signals by approximately 1.5–2 times. Irradiating samples previously exposed at room temperature with light of greater intensity than was usually used led to a decrease in the signal and, simultaneously, to bleaching of the adsorbed sensitizer.

Fig. 1. Light-induced EPR signal in AgBr powder dyed in an alcoholic solution of dye No. 5 of concentration 10^{-4} mol/l.

The dependence of the EPR signal intensity on the concentration of the adsorbed dye was investigated; for this purpose AgBr powders were dyed in alcoholic dye solutions of different concentrations. The experiments showed that, as the concentration of the dye solution increased up to the maximum, a monotonic increase in the EPR signal of the dyed AgBr powder under illumination was observed. It is known, however, that optimal sensitization of the photographic sensitivity of emulsions and of the internal photoeffect of semiconductors by dyes is observed when layers are dyed in solutions of concentration 10^{-5}–10^{-4} mol/l, whereas with a further increase in the dye concentration the sensitized effect decreases sharply. The observed effect cannot be attributed to an EPR signal in the dye itself, since it was shown earlier ([12]) that these dyes do not give EPR absorption.

The EPR signal arises upon illumination of dyed AgBr powders kept in vacuum at 77°K, reaching its maximum value in 4 min; the signal intensity does not change after illumination is stopped. If this sample is warmed in the dark to room temperature and again cooled to 77°K, the signal intensity decreases considerably. Upon repeated exposure of the sample at 77°K, the EPR signal again increases. Such a cycle can be repeated several times. An analogous effect was observed in the above-mentioned work ([11]) by American authors.

As is known, the internal photoeffect can be sensitized by dyes Nos. 1—7 not only in the case of AgBr, but also for silver and thallium iodides ($^{1-10}$). In the present work, exploratory experiments were carried out to detect a light-induced EPR signal in dyed TlJ powders under conditions analogous to those described above. Neither in the dark nor under illumination at room and low temperatures, in air or in vacuum, were these signals observed in TlJ powders dyed with dyes Nos. 1—7.

The results obtained made it possible to assume that the observed light-induced EPR signal in AgBr is due to free radicals that are an intermediate product of a chemical reaction of the adsorbed

colored dye molecules with bromine liberated as a result of photolysis of AgBr(10). In the case of TlJ, destruction of the adsorbed dye does not occur(10), and therefore in these powders we did not observe e.p.r. absorption.

To test this assumption, the following experiments were carried out. AgBr powder was dyed with dye No. 4, which has no absorption in the visible region of the spectrum below 530 mμ. The sample was illuminated in the region of the intrinsic absorption of AgBr through a glass filter SS-5, which does not transmit light in the absorption region of the dye (520–680 mμ). In this case the same e.p.r. signal appeared as upon irradiation of dyed AgBr powder in the absorption region of the dye.

In the next experiment, a small amount of bromine vapor was adsorbed in the dark on the dyed AgBr powder. As a result, an e.p.r. signal similar to that described above was detected in the unilluminated sample. After additional adsorption of bromine vapor on the sample under study, the e.p.r. signal disappeared. This was accompanied by decoloration of the AgBr powder, evidently as a result of complete destruction of the dye by bromine.

We set up an experiment to detect free-radical intermediate products of the reaction of the dye in an alcoholic solution with bromine molecules. When a very weak solution of bromine in alcohol was added to the dye solution at room temperature, a complex change in the color of the solution was observed: blue → yellow-green → dark blue → yellow. No e.p.r. signal was observed in this solution, probably because of the rapid course of the reaction. However, e.p.r. absorption is observed in dye solutions frozen immediately after the addition of bromine, i.e., under conditions of stabilization of the reaction at the first (yellow-green color of the solution) stages of the process.

The investigation carried out makes it possible to conclude that the light-induced e.p.r. signal in silver bromide sensitized with cyanine dyes is due to intermediate free-radical products of the interaction of adsorbed dye molecules with bromine molecules. The absence of e.p.r. signals in AgBr powders dyed with dyes Nos. 1, 2, and 6 can be explained by the instability of the intermediate products of the reaction of these dyes with bromine.

In conclusion, we express our deep gratitude to Academician A. N. Terenin for

advice and valuable discussion of this work.

Received
28 XII 1961

CITED LITERATURE

1. E. K. Putseiko, A. N. Terenin, ZhFKh, **23**, 676 (1949); DAN, **70**, 401 (1950); DAN, **90**, 1005 (1953).
2. E. K. Putseiko, DAN, **91**, 1071 (1953); **129**, 303 (1959).
3. I. A. Akimov, E. K. Putseiko, DAN, **102**, 481 (1955).
4. A. Terenin, E. Putzeiko, I. Akimov, Wiss. Phot. Intern. Konf., Köln, 1956, Darmst., 1958, S. 117; J. Chem. Phys., **54**, 717 (1957); Farad. Soc. Disc., No. 27, 83 (1959).
5. A. Terenin, E. Putzeiko, J. Chim. Phys., **55**, 681 (1958).
6. I. A. Akimov, E. K. Putseiko, in: *Collection: Photoelectric and Optical Phenomena in Semiconductors*, Kiev, 1959, p. 301.
7. I. A. Akimov, ZhFKh, **30**, 1007 (1956); DAN, **121**, 311 (1958); **128**, 691 (1959).
8. I. A. Akimov, A. N. Terenin, DAN, **135**, 109 (1960); *Journal of Scientific and Applied Photography and Cinematography*, **6**, 108 (1961).
9. A. Terenin, I. Akimov, Zs. Phys. Chem. (DDR), Leipzig, **217**, 307 (1961).
10. I. A. Akimov, DAN, **137**, 624 (1961).
11. W. C. Neadler, R. L. Griffith, W. West, Nature, **191**, 902 (1961).
12. V. E. Kholmogorov, D. N. Glebovskii, *Optics and Spectroscopy*, **12**, No. 6 (1962).

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