DARKENING OF SOLIDS IN ULTRAVIOLET LIGHT

THE DARKENING OF CADMIUM HALIDES AND OF ANTIMONY OXIDE BY ULTRAVIOLET LIGHT¹

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Received June 17, 1943

The photochemical processes in solid matter are little known except for the photochemistry of the alkali halides and the silver halides, which belong to the simplest types of solids. In the present paper the conditions are discussed under which more complicated and anisotropic lattices—cadmium iodide, cadmium bromide, and antimony oxide—have been found to be light sensitive. These observations may contribute in gaining information about the reasons for photochemical changes in solids.

THE DARKENING OF CADMIUM IODIDE (8)

Cadmium iodide crystallizes in a layer lattice. The ions within the layers are strongly bound, while the layers are held together by relatively weak forces. Cleavage occurs, therefore, between the layers. Cadmium iodide is usually obtained in plates the base faces of which are parallel to the layers. The prism faces contain the layer ends. When carefully dried single crystals of cadmium iodide (area of base plane, 7–8 mm.²; height of prism plane, 1–2 mm.) or pellets pressed from smaller crystals were irradiated with ultraviolet light the following changes were observed:

(1) A darkening occurred when the surrounding atmosphere contained a trace of moisture, and when no oxygen was present. In the presence of oxygen a faint yellow color was developed.

(2) The darkening started at corners or at accidental scratches of the crystals, and it spread from there over the entire prism faces. The final dark color was established within a few minutes. The base faces remained white even after several hours of irradiation. With the pressed pellets the darkening was more pronounced. By the pressing the thin plates of cadmium iodide had been packed together with the base planes so that the cylindrical surfaces of the pellets contained only prism faces and darkened strongly upon irradiation. The top and bottom surfaces of the pellets containing the base faces showed a net of dark lines formed by the darkened edges of the crystals in the pellet.

Evidently only the prism faces of cadmium iodide are able to adsorb water in such a fashion that photoproducts can be formed in the surface layer. The prism faces have probably stronger adsorption forces than the base faces, so that a

¹ Presented before the Division of Physical and Inorganic Chemistry at the 105th Meeting of the American Chemical Society, which was held in Detroit, Michigan, April, 1943. sufficiently polarized adsorption layer can only be established at the prism faces. This is supported by the observation that graphite adsorbs more strongly at the layer ends than on surfaces parallel to the layers (12).

(3) Annealing of the crystals for 3 days at 150° C. did not affect the darkening. The light sensitivity is, therefore, a property of the stable lattice and is not caused by the occurrence of unstable structures which seem to be possible in cadmium iodide (9).

(4) The darkening could be produced by irradiating with light of the wave length of 366 m μ . Strong absorption of solid cadmium iodide has been measured at 325 m μ (4), but the absorption band extends presumably to considerably longer wave lengths. Hence the darkening appears to set in at the threshold of absorption.

(5) The products of the photodecomposition could not be identified. Presumably elementary cadmium and iodine are formed and remain adsorbed at the surface in close neighborhood. Any detachment by an analytical operation will cause immediate recombination. A slow fading of the darkening did already occur after some days at ordinary temperature. The color disappeared immediately when the crystals were touched with water. Experiments were made in which the crystals were irradiated in the presence of a possible acceptor for iodine in the gas phase (ethylene, ethyl alcohol). This procedure failed, however, to enforce the darkening or to remove iodine from the solid phase.

(6) The darkening could be delayed or even entirely prevented by adsorbing in advance substances on the cadmium iodide which are more strongly adsorbed than water. The most effective inhibitor was pyridine.

THE DARKENING OF CADMIUM BROMIDE (8)

Cadmium bromide crystallizes like cadmium iodide in a layer lattice but with a somewhat different arrangement of the ions in the layers (cadmium chloride structure (10)). Cadmium bromide was found to be insensitive to ultraviolet light under the same conditions under which cadmium iodide had been light sensitive. Apparently no stable photoproducts can be formed after the electron transition, because the adsorptive binding of the reaction product is not strong enough to prevent the regression to the unexcited state. The energy required for the excitation is considerably greater in cadmium bromide than in cadmium iodide. Strong absorption of solid cadmium bromide occurs first at 235 m μ (4); presumably the absorption begins at longer wave lengths.

Cadmium bromide can exist as another "modification" which can be obtained by exerting pressure on the crystals. By the stressing of the lattice a displacement of atoms in the layers is produced, and a structure results which can be considered as alternating between the cadmium chloride and the cadmium iodide structures (1). Cadmium bromide returns to its normal state when heated to about 200°C. The second modification of cadmium bromide was found to be light sensitive in principally the same way as cadmium iodide. The prism faces darkened upon irradiation with ultraviolet light in the presence of water vapor and in the absence of oxygen. The base faces were not affected. The coloring was less pronounced than with cadmium iodide. Obviously cadmium bromide is able to yield stable photoproducts only in its unstable state.

THE DARKENING OF ANTIMONY OXIDE (5)

Antimony oxide exists in two forms. The stable form at room temperature is cubic and contains Sb_4O_6 molecules (2). The form which is unstable at room temperature but which can be easily prepared is orthorhombic and contains continuous chains of antimony and oxygen (3). Upon exposure of antimony oxide to ultraviolet light the following changes were observed:

(1) Of the two forms, only the unstable orthorhombic modification was light sensitive.

(2) This modification darkened if it contained some adsorbed water. The light sensitivity was dependent on the conditions of preparation of the orthorhombic form. It occurred only when the water had been incorporated by a suitable precipitation of the oxide. Dry crystals in contact with moisture were not light sensitive. The sensitivity of the antimony oxide was lost when the substance was heated to about 250°C. in a high vacuum. At this temperature the adsorbed water was given off rapidly. The light sensitivity was not restored by exposing the heated crystals to water vapor for a week or longer. The presence of oxygen had no influence on the darkening.

(3) The darkening did not fade at room temperature or when the crystals were kept over phosphorus pentoxide. The color disappeared instantaneously when the adsorbed water was removed by heating to 250° C. in a high vacuum.

(4) The threshold of photosensitivity coincided with that of absorption. The strong absorption of the orthorhombic form sets in at about 385 m μ , while the absorption of the stable cubic modification begins first at 300 m μ .

(5) Elementary antimony and oxygen could not be detected. Presumably the elements are formed in the photoreaction but remain adsorbed at the surface in neighboring positions. When they are detached by an analytical operation, recombination takes place.

 (θ) Antimony oxide underwent another entirely independent photoreaction in contact with reducing substances like glycerol, hydroxylamine, etc. Under these conditions both the cubic and the orthorhombic modifications were reduced, each modification having a threshold of sensitivity which coincided with the threshold of absorption. In these reactions the number of reactive centers at the surfaces was larger than in the darkening of the orthorhombic antimony oxide alone.

DISCUSSION

From the observed phenomena the significance of certain factors becomes evident which may also be of importance for the photodecomposition of other solid matters.

1. The light sensitivity was dependent on crystallographic factors. It occurred either at certain presumably especially strongly adsorbing crystal faces or it required the presence of an unstable modification of the crystals. An unstable crystallographic modification can be considered as the distorted form of the stable one having a greater energy content. By distorting a crystal lattice its chemical reactivity is increased and usually also its adsorptive power. The adsorptive binding after the electron transition which is necessary to yield photoproducts of finite life time might, therefore, be facilitated at the surfaces of the unstable modifications.

2. The darkening required the presence of a foreign substance which was in all cases water. Since the water had to be adsorbed specifically in the reactions studied in order to obtain a photosensitive system, it either partakes directly in the chemical part of the reaction, or it at least facilitates the photodecomposition by distorting the lattice and by stabilizing the new chemical arrangement.

3. If it is assumed that the water is involved chemically, a reaction mechanism might be formulated analogously to the scheme proposed by Weiss (11) for the darkening of zinc sulfide by ultraviolet light. For example, in the case of cadmium iodide:

$$I^{-}_{surface}HOH + nh\nu \longrightarrow I + H + OH^{-}$$
$$Cd^{++}_{surface} + H \longrightarrow Cd^{+} + H^{+}$$

respectively:

 $Cd_{surface}^{++} + 2H \longrightarrow Cd + 2H^{+}$ $H^{+} + OH^{-} \longrightarrow HOH$

In this scheme no statement is made regarding the primary process or the mechanism of the energy transfer from the absorbing to the reacting centers. The possibility that quanta may be lost in the transfer is indicated by writing $nh\nu$.

The water appears to be essentially involved in the process, and this might also be true in other photoreactions of solids in which the presence of water is necessary. The view that in the darkening of zinc sulfide the water acts merely as the solvent for a surface electrolysis (7) might, therefore, be inadequate.

Further support for a reaction mechanism which involves the direct chemical participation of the adsorbed foreign substance is given by the numerous observations of photosensitized reactions in adsorbed layers (for the literature see reference 6). In these reactions the light is likewise being absorbed by the solid, but in the subsequent steps use is made of the absorbed energy for a chemical change in the adsorbed layer. Hence it will merely depend on the nature of the two components whether the net result of a photoreaction will be a chemical change of the crystal or of the adsorbed molecule.

SUMMARY

The conditions for the darkening of cadmium iodide, cadmium bromide, and antimony oxide by ultraviolet light are briefly described. The following factors are significant for the darkening of these substances:

1. The photosensitivity is dependent on the crystallographic orientation of the surface, respectively on the presence of an unstable modification. 2. The water adsorbed by the crystal is essentially involved in the chemical process, indicating a relationship between photochemical changes of solids and reactions photosensitized by solids.

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SOME NEW COMPLEXES OF ZINC AND GLYCINE¹

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Received June 14, 1943

In 1882, Curtius (3) reported that solutions of zinc glycinate deposited part, but not all, of their zinc as zinc oxide on warming, and that the addition of sodium carbonate to solutions of zinc glycinate precipitated only part of the zinc. He suggested that a complex of zinc and glycine existed in solution.

Ley (16), in 1909, found that the conductivity of zinc glycinate solutions was very low and suggested that complex formation was responsible.

The zinc electrode was used by Fuseya, Murata, and Yumoto (10), who found that the addition of glycine to a zinc sulfate solution markedly reduced the activity of the zinc ion. They interpreted this as being due to the formation of a complex. Since electrophoresis experiments showed no migration of zinc to the anode, it was evident that the complex was not an anion. Their observations, made on only two mixtures of glycine and zinc sulfate, could give no additional information regarding the nature of the complex.

Apparently without knowledge of any of these observations, Joseph (14), in 1935, published the results of similar but more numerous experiments with the

¹ A preliminary report was read before the American Society of Biological Chemists, Boston, Massachusetts, April, 1942.