NOTES

The Phototropy of the Alkaline Earth Titanates[1]

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This note reports observations on the phenomenon of phototropy in alkaline earth titanates. Chalkley[3] reviewed the general subject of phototropy in 1929. Tanaka[4] has reported the development of a red color on exposure of calcium titanate to light and stated that both oxygen and moisture were necessary. He also found that temperature affected the speed of reversal. Weyl and Forland[5] concluded from a study of titanium dioxide that when light strikes an impurity ion, for example, Fe^{III} in a titanium dioxide lattice, an electron of the foreign ion is excited and the electron moves either into an oxygen vacancy of the defective rutile structure thus producing an Fe^{IV} ion or the electron attaches itself to a Ti^{IV} ion to give colored Ti^{III}. Weyl and Johnson[6] reached similar conclusions. Preliminary experiments showed that random samples of barium, calcium and strontium titanates exhibited the phenomenon strongly, while it did not appear at all in magnesium titanate. It was of interest therefore to consider possible reasons for this difference in response to light.

A spectrographic analysis of the barium, calcium and strontium titanates showed the presence of impurities of iron, silver, antimony and copper. In magnesium titanate, iron was the only impurity detected. An attempt was made to incorporate impurities of silver, antimony and copper into magnesium titanate by the method of Williamson,[7] which consists of evaporating a slurry of magnesium titanate containing soluble salts of the desired impurities equivalent to 0.25% of silver, antimony and copper. The dry mixtures were ground and ignited at 1000° for three hours. Upon exposure to ultraviolet light, no color development could be detected. Magnesium titanate also was prepared by the method of Tanaka[8] in the presence of each of these metals. No phototropy could be detected. These results indicate the probable basic dependence of the phenomenon upon the different specific crystal structures of barium, calcium and strontium titanates (octahedral) and the crystal structure of magnesium titanate (close-packed cubic) rather than primarily upon the presence of impurity metals.

The necessity for impurities for the phenomenon was further investigated by synthesizing barium and calcium titanates with the incorporation of impurities during preparation. Barium carbonate and calcium oxide were each ground in a ball mill with equivalent quantities of titanium dioxide, and ignited at 1200° for five hours. Barium titanate was a white powder. Calcium titanate was slightly violet on the surface when first examined in daylight. Impurities of salts of Fe^{III}, Zn^{II}, Sb^{III}, Sb^{V}, V^{V}, Ag^{I}, Cu^{II}, Sn^{IV}, Zr^{IV} and Co^{II} ranging from 0.02 to 0.5% of metal were dissolved in water or dilute hydrochloric acid. Slurries prepared with solutions of each impurity and samples of the synthesized barium and calcium titanates were evaporated to dryness, ground and ignited at 1000° for three hours. Impure and pure samples of the synthesized titanates were then exposed to ultraviolet light. Among the pure titanates only calcium showed a visible trace of violet color. Several of the impure titanates of barium and calcium exhibited phototropic change. Table I summarizes the observations. In general the effect is more intense with calcium than with barium titanate. The effects do tend to parallel in the two titanates. Iron (Fe^{III}), zinc (Zn^{II}), antimony (Sb^{V}) and vanadium (V^{V}) gave the most pronounced effects whereas silver (Ag^{I}), copper (Cu^{II}), antimony (Sb^{III}), tin (Sn^{IV}), zirconium (Zr^{IV}) and cobalt (Co^{II}) produced no detectable color in barium titanate and no detect-

Table I

Induction of Phototropy in Barium and Calcium Titanates by Impurities

Impurity, %		$BaTiO_3$	$CaTiO_3$
None added		None	None
Fe^{III}	0.02	None	None
	.06	None	Violet
	.08	Violet	Dark violet
	.16	Violet	Dark violet
Ag^{I}	.02	None	None
	1.0	None	None
Cu^{II}	0.02	None	None
	.22	None	None
Sb^{III}	.02	None	None
	.26	None	None
Sn^{IV}	.02	None	None
	.30	None	None
Zn^{II}	.02	None	Violet
	.20	Gray	Dark violet
	.30	Gray	Dark violet
Mg^{II}	.10	None	....
	.20	None	....
Sb^{V}	.10	Gray	Violet
	.20	Gray	Violet
V^{V}	.10	Gray	Dark violet
	.20	Gray	Dark violet
Zr^{IV}	.10	None	None
	.20	None	None
Co^{II}	.10	None	None
	.20	None	None

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[2] Research Fellow, 1951–1952.

[3] L. Chalkley, *Chem. Revs.*, **6**, 217 (1929).

[4] Y. Tanaka, *Bull. Chem. Soc. Japan*, **16**, 458 (1941).

[5] W. A. Weyl and T. Forland, *Ind. Eng. Chem.*, **42**, 257 (1950).

[6] W. A. Weyl and G. Johnson, *J. Am. Ceram. Soc.*, **32**, 398 (1949).

[7] W. O. Williamson, *Nature*, **143**, 279 (1939).

[8] Y. Tanaka, *Bull. Chem. Soc. Japan*, **16**, 428 (1941).

able increase in the slight coloration of the pure calcium titanate. These results indicate the necessity for impurities, for specific impurities and that the phototropic effect increases with the concentration of the impurity ion.

Reflectance spectra were obtained with dried slurries of the impure barium and calcium titanates evaporated on glass plates in darkness. Duplicate preparations of each were made and placed in the diffuse reflectance of attachment of the DU spectrophotometer. One plate was covered while the other was exposed at a distance of 4.5 inches from the ultraviolet radiation source. Figure 1 shows the reflectance spectra at 400 to 700 mμ for barium and calcium titanates after 5-minute exposures to ultraviolet.

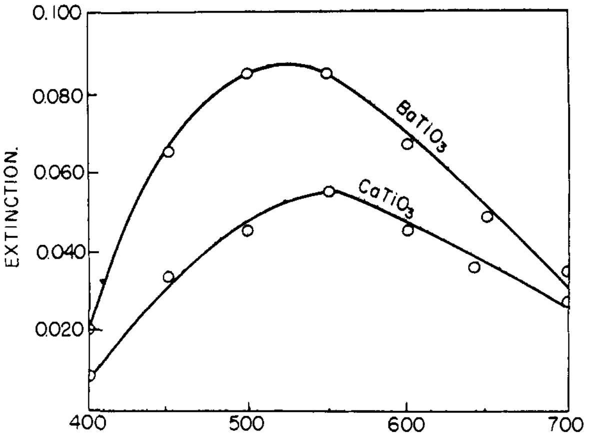

Fig. 1.—Reflectance spectra for barium and calcium titanates.

The effect of exposure time on the intensity of reflected light was determined by measurements of extinction at 550 mμ after different periods of exposure. Figure 2 shows that at least a one-half-hour exposure is needed for the extinction for calcium titanate to become constant.

Fading of the color produced on exposure to ultraviolet was also studied by measurement of the extinction curve for calcium titanate which had been exposed for 30 minutes and then stored in the dark at 25°.

The reversal temperature of 220° for the color change reported by Tanaka for calcium titanate was found to be somewhat higher with calcium titanate used in this work. The violet color, developed in calcium titanate on exposure to ultraviolet, was retained until a temperature between 360 and 400° was reached. With barium titanate the color disappeared between 220 and 270°. When the samples were heated during exposure to ultraviolet light, a temperature between 480 and 610° was needed to prevent entirely the development of color in both barium and calcium titanates. These experiments on the development and discharge of color were repeated 25 times with no apparent change in the response of the samples.

Samples of barium and calcium titanates were sealed in quartz tubes containing phosphorus pentoxide for 72 hours and then exposed to ultraviolet. Samples of barium and calcium titanates in equilibrium with atmospheric moisture were also exposed simultaneously and at various temperatures. Dry and moist samples responded in exactly the same way contrary to the report of Tanaka. Similar experiments in the presence and absence of oxygen showed no difference in color response due to oxygen.

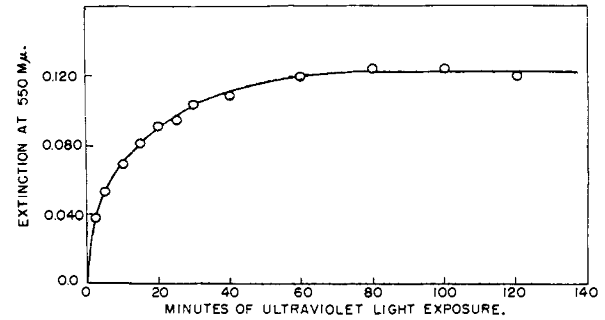

Fig. 2.—Calcium titanate extinction at 550 mμ with varying time of ultraviolet light exposure.

These results indicate that the occurrence of phototropy in barium and calcium titanate and not in magnesium titanate is basically dependent upon the existence of the proper crystal structure in barium and calcium titanates, which is different from that of magnesium titanate. They also indicate that an impurity must be present such as Fe^{III}, Zn^{II}, V^{V} or Sb^{V}, and that the phototropic effect increases with the amount of impurity.

Calcium titanate has a structure in which Ca^{II} and O^{II} ions together form a close-packed lattice. The small Ti^{IV} ion is surrounded octahedrally by six O^{II} ions. However, in magnesium titanate, only the O^{II} ions form a close packed configuration and the Mg^{II} and Ti^{IV} ions exist in the interstices. Ferrous titanate is isomorphous with Fe_2O_3 and magnesium is known to replace iron.[9] Thus an iron impurity added to $MgTiO_3$ can replace either the Mg^{II} or Ti^{IV} ion without producing an unsymmetrical field. $Zinc^{II}$, similar in size to Mg^{II} and Ti^{IV} may replace one or both ions without strain on the close packed O^{II} structure.

These results also indicate that effective impurities in inducing phototropy have ionic radii near that of Ti^{IV}. Ions larger than Ti^{IV}, for example Ag^{I} and Cu^{II} which cannot fit even a distorted lattice, do not induce phototropy. It is also apparent that in order for an impurity ion to induce phototropy, it must have a radius approximately that of Ti^{IV} but not exactly the same, otherwise no distortion would occur. The impurity ion must also have a valence other than 4 in order that electron transfer be possible.

The greater intensity of color development in calcium than in barium titanate may be due to slight reduction of Ti^{IV} to colored Ti^{III} during the preparation. Not only does the pure calcium titanate show a slight trace of color but upon exposure to ultraviolet, the color produced is more intense. This behavior suggests a "memory" factor which may be retained by the once reduced titanium ions

(9) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1945, p. 332.

as a force field associated with this state. Similar phenomena have been observed by Feitknecht and Haberle.[10]

(10) W. Feitknecht and E. Haberle, *Helv. Chim. Acta*, **33**, 922 (1950).

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Potassium, Rubidium and Cesium Borohydrides

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The relatively small ionic potentials (= charge/radius) of the potassium, rubidium and cesium ions and the consequent low coördinating power of the ions suggested that the borohydrides of these metals would not form hydrates. Interest in these compounds was prompted by this consideration, because of the instability of the borohydride ion toward water. Sodium borohydride forms a dihydrate under normal atmospheric conditions and consequently has a poor shelf-life after exposure.

Potassium borohydride has been prepared by the absorption of diborane by potassium tetramethoxyborohydride[1] but none of its properties were reported. This is a difficult preparative method because of the unusual nature of the chemicals and equipment necessary. This note describes a simple method for the preparation of potassium borohydride, and in addition the hitherto unknown rubidium and cesium borohydrides by metathetical reactions from sodium borohydride.[2] In aqueous or alcoholic media the products are easily obtained in a pure form, are non-hygroscopic, and as such have good storage stability. Investigation of some of the properties and reactions of the potassium compound show it to be similar to sodium borohydride in many respects.

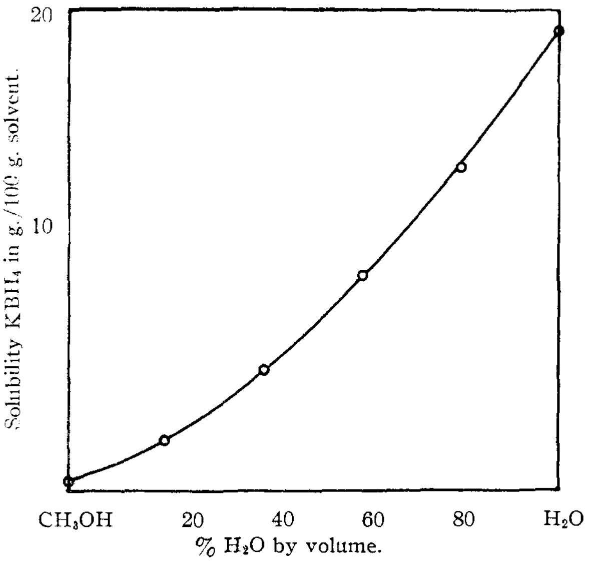

Fig. 1.—Solubility of potassium borohydride in methanol, water and methanol–water mixtures at 20°.

Experimental

Materials.—Commercial sodium borohydride from Metal Hydrides, Incorporated, was used for the preparation of potassium borohydride. For the preparation of the rubidium and cesium compounds, it was purified by the method of Davis, Mason and Stegeman.[3] Rubidium and cesium metals were obtained from the Fairmount Chemical Company. Organic compounds used in the reduction studies were obtained from the Eastman Kodak Company.

Preparation of Potassium Borohydride.—A solution of 74.2 g. of 94.7% sodium borohydride in 130 cc. of distilled water was added to a stirred solution of 133.2 g. of potassium hydroxide (85% assay) in 110 cc. of water. The resulting thick slurry was filtered through a medium-porosity, sintered glass disc under nitrogen pressure. The precipitate was washed with three 100-cc. portions of ice-cold, 95% ethanol. The product was then dried in a vacuum oven at 80° for three hours; 75.5 grams of potassium borohydride was obtained, representing a yield of 75.5%.

Anal. Calcd. for KBH_4: K, 72.48; B, 20.06; H, 7.47. Found: K, 73.3; B, 19.8; H, 7.25.

Preparation of Rubidium and Cesium Borohydrides.—10.8 grams of rubidium metal was dissolved in 750 cc. of absolute methanol to give a clear, water-white solution of rubidium methoxide. This solution was concentrated by distillation of the excess methanol to give a nearly saturated methoxide solution; 4.93 grams of 99.0% pure sodium borohydride dissolved in a minimum amount of methanol was added to the stirred methoxide solution. A white precipitate formed immediately, which was isolated by filtration on a medium-porosity, sintered glass disc, followed by two washes with methanol. The product was dried in a stream of nitrogen, then in a vacuum oven at 80° for two hours. The combined methanol washes were concentrated by evaporation to precipitate more product. This was filtered as before, and washed with 10–20 cc. of methanol and dried. A combined yield of 12.2 g., or 95.3% of theory, was obtained.

Anal. Calcd. for $RbBH_4$: Rb, 85.20; B, 10.78; H, 4.02. Found: Rb, 84.59; B, 10.74; H, 4.00.

Cesium borohydride was prepared by a similar procedure in 85% yield.

Anal. Calcd. for $CsBH_4$: Cs, 89.95; B, 7.32; H, 2.73. Found: Cs, 89.44; B, 7.37; H, 2.71.

Hygroscopicity of Potassium Borohydride.—A weighed sample of 99.0% potassium borohydride was placed in a hygrostat over a saturated, aqueous solution of ammonium chloride in contact with an excess of solid ammonium chloride. In this manner a constant humidity of 79.5% at 20° (13.8 mm.) was maintained. Exposure for 24 hours resulted in a weight gain of 0.85%. Further evidence of the good storage stability of potassium compound was found when exposure of a weighed sample to normal laboratory atmosphere for seven days resulted in no weight gain and no detectable change in purity.

Solubilities of Potassium Borohydride.—Solubility measurements were carried out by agitation of an excess of the solid with the solvent in a warm water-bath, followed by cooling of the mixture to the desired temperature. A portion of the solution was then removed with a pipet fitted with a glass wool plug to prevent entry of solids. The solution was weighed, the solvent vacuum evaporated, and the weight of the residue determined. Purity was checked in each case by chemical analysis. It was observed that heat was absorbed during solution in water and alcohols. Data for the solubility in aqueous methanol solutions are presented in Fig. 1. Potassium borohydride was observed to be very soluble in liquid ammonia, but no quantitative measurements were made. One hundred grams of 95% ethanol dissolved 0.25 g. of potassium borohydride at 25°. The compound is insoluble (<0.01%) in isopropylamine, benzene, hexane, ether, dioxane, tetrahydrofuran and acetonitrile.

Thermal Stability of Potassium Borohydride.—A small sample of 98.8% pure potassium borohydride was placed in

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(1) H. I. Schlesinger, H. C. Brown H. R. Hoekstra and L. R. Rapp, This Journal, **75**, 199 (1953).

(2) J. Kollonitsch, *Nature*, **173**, 125 (1954), has recently described an analogous procedure for the preparation of lithium, magnesium and calcium borohydrides, the latter two at −20 to −50°.

(3) W. D. Davis, L. S. Mason and G. Stegeman, This Journal, **71**, 2775 (1949).