cipitate was separated from the liquid and was added to the sulfuric acid solution obtained with the original bauxite sludge.

Sulfuric Acid Solution.—This solution to which metatitanic acid obtained from the solid residue was added was treated with the calculated quantity of zinc dust (about 6.4 g.). On heating, a clear solution was obtained first which with a rise of temperature gave a precipitate of $ZnSO_4 \cdot Ti(SO_4)_2$. It was separated and boiled with water to get metatitanic acid. This product was ignited and titania obtained from it was 99.12% pure with only traces of iron. The yield of titania obtained was 73.52%.

As the mixture of titania with certain metallic oxides are used as paint materials, the sulfuric acid solution referred to above may be treated with sulfates of zinc, copper, manganese or cobalt and titanium precipitated as the compound $RSO_4 \cdot Ti(SO_4)_2$ and finally decomposed thermally to give colored products containing titania and the metallic oxides.[1]

Before concluding, a modification of the procedure outlined above for the treatment of bauxite sludge may be mentioned. The finely powdered bauxite sludge may be mixed with zinc dust and then digested with concd. sulfuric acid so as to obtain a solid material containing most of the titania. This solid may then be separated from the liquid and treated with water so as to bring titanium, aluminum and iron into solution leaving only insoluble siliceous material. This liquid can then be treated in the same manner as already given before to obtain metatitanic acid.

In an actual experiment carried out according to the above procedure the percentage recovery of titania was found to be 76.47.

Summary

The recovery of titania from its sulfuric acid solution in the form of $RSO_4 \cdot Ti(SO_4)_2$ has been found to be about 100%.

When solutions of titania in sulfuric acid are heated in the presence of aluminum sulfate, substances which appear to be either titanyl sulfate with small amount of aluminum or aluminum sulfate with small amount of titanium are obtained.

By experimenting with artificial mixtures containing TiO_2, $Al_2(SO_4)_3 \cdot 18H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ approaching the proportion present in the bauxite sludge, it is shown that titania can be recovered quantitatively from its sulfuric acid solution in the form of $ZnSO_4 \cdot Ti(SO_4)_2$.

It is shown that from a sample of bauxite sludge titania can be recovered by taking advantage of the formation of $RSO_4 \cdot Ti(SO_4)_2$ which either can be hydrolyzed and then ignited to give pure titania or can be decomposed thermally into colored residues which may be useful as paint materials.

BOMBAY, INDIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE ROYAL INSTITUTE OF SCIENCE]

The Behavior of Solutions of Titanium Dioxide in Sulfuric Acid in the Presence of Certain Bivalent Metallic Sulfates

BY S. M. MEHTA AND R. P. PONCHA

Following the general procedure described in the previous paper[1] two more compounds, *viz.*, $NiSO_4 \cdot Ti(SO_4)_2$ and $CdSO_4 \cdot Ti(SO_4)_2$ were obtained when titanium dioxide (0.1 g.) and metallic bivalent sulfate (0.1 to 0.6 g.) were heated with sulfuric acid (sp. gr. 1.8, 50 cc.). Similarly when titanium dioxide (0.1 g.) and calcium sulfate (0.4 to 0.6 g.) were heated with sulfuric acid (sp. gr. 1.8, 50 cc.) a precipitate was obtained which agreed with the formula $CaSO_4 \cdot Ti(SO_4)_2$. Weinland and Kühl[2] have described the preparation of the latter compound by a slightly different method. These authors dissolved titanium dioxide (1.6 g.) and calcium sulfate (5 g.) each separately in concd. sulfuric acid, the former in 200 cc., the latter in 100 cc. On mixing these two solutions and concentrating the liquid the product containing calcium was isolated. It may be observed in this connection that if their method is followed the liquid requires prolonged boiling before the precipitate is obtained, while using the method described in this work the compound is more readily obtained. It is found that these compounds are deliquescent and readily soluble in dilute hydrochloric acid.

When attempts were made to prepare compounds containing strontium and barium, $TiOSO_4$ was invariably obtained instead. This appeared surprising since Weinland and Kühl[2] have described isolation of a compound $SrSO_4 \cdot Ti(SO_4)_2$ and $2BaSO_4 \cdot 3Ti(SO_4)_2$ by following a method similar to that used for the preparation of the compound containing calcium.

In order to ascertain if the compounds containing strontium and barium are ever possible, experiments were carried out using concd. sulfuric acid (40 cc.) and titanium dioxide (0.1 g.) with varying amounts of strontium sulfate and barium sulfate. The quantities of the former taken for this purpose were 0.2, 0.4, 0.8 and 1.0 g., while those of the latter were 0.1, 0.2 and 0.6 g. In all these experiments the product obtained was $TiOSO_4$. The $TiOSO_4$ which separated out from solutions containing strontium sulfate and barium sulfate dissolved readily on heating in dilute hydrochloric acid but was only partially soluble in concd. hydrochloric acid even on boiling. From the above facts the conclusion seems inevitable that the compounds containing strontium and barium described by Weinland and Kühl[2] do not appear to exist and they have probably handled $TiOSO_4$ contaminated with the mother liquor containing strontium sulfate and barium sulfate. Another interesting fact to be noted in this connection is that the theoretical values of titanium, barium and sulfate given by these authors do not correspond with the formula $2BaSO_4 \cdot 3Ti(SO_4)_2$. This is made clear in Table I.

TABLE I

	Titanium, %	Barium, %	Sulfate, %
Weinland and Kühl	9.89	23.69	66.19
Recalcd. values	12.1	23.1	64.8

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[1] Mehta and Patel, THIS JOURNAL, **73**, 224 (1951).

[2] Weinland and Kühl, *Z. anorg. Chem.*, **54**, 253 (1907).

It is curious that the values of titanium, barium and sulfate experimentally obtained by these authors should correspond not with the correct recalculated values but with the wrong ones given by them. Even assuming the formula $BaSO_4 \cdot Ti(SO_4)_2$ the figures obtained are titanium, 10.1%; barium, 29.1%; and sulfate, 61.0%, which do not agree with the experimental values given by Weinland and Kühl.

Summary

It is shown that while it is possible to prepare $CaSO_4 \cdot Ti(SO_4)_2$ described by Weinland and Kühl the strontium compound $SrSO_4 \cdot Ti(SO_4)_2$ and the barium compound $2BaSO_4 \cdot 3Ti(SO_4)_2$ described by these authors could not be obtained in spite of following the details given by these authors. It has been shown that the solid phase which separated out consisted of $TiOSO_4$.

Two more compounds of the type $RSO_4 \cdot Ti(SO_4)_2$ where R = nickel and cadmium have been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Absorption Spectra of Some Chloro-Substituted Tetracyclones

BY FLOYD J. THALLER,[1] DONALD E. TRUCKER AND ERNEST I. BECKER

Although tetracyclone[2,3,4] (tetraphenylcyclopentadienone) and a number of its substituted derivatives and analogs[5,6,7,8] have been prepared, no absorption data for any have been published. In view of the fact that these substances are all highly colored, it seemed desirable to synthesize several and measure their absorption spectra. Tetracyclones containing chlorine atoms were chosen in this report. The chlorine-containing tetracyclones were prepared employing the basic reaction of Dilthey and co-workers[4,6] in which benzil and dibenzyl ketone, or their appropriately substituted derivatives, in ethanol are condensed in the presence of potassium hydroxide. The appropriate pairs of compounds condensed readily to give the desired tetracyclones. The three new compounds—A-II, A-III and A-IV—are dark purple, dichroic, high-melting substances. Each was derivatized by conversion to its corresponding colorless tetraphenylphthalic anhydride by reaction with chloromaleic anhydride in bromobenzene, according to the elegant procedure of Synerholm.[9]

TABLE I

TETRACYCLONES (SERIES A) (FIG. 1) AND TETRAPHENYLPHTHALIC ANHYDRIDES (SERIES B)

			Analyses, %					
			Carbon		Hydrogen		Chlorine	
Compound	M. p., °C.	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found
A-I: $R_1 = R_2 = H$	219–220	91–96[a]						
A-II: $R_1 = H, R_2 = Cl$	239–240	92[b]	76.83	76.62 76.59	4.00	4.22 4.12	15.64	15.32
A-III: $R_1 = Cl, R_2 = H$	253–254	85[b]	76.83	76.89 76.76	4.00	4.30 4.33	15.64	15.40
A-IV: $R_1 = R_2 = Cl$	297–299	82[b]	66.69	66.81	3.09	2.96	27.16	27.09
B-I: $R_1 = R_2 = H$	288[c]	83[c]						
B-II: $R_1 = H, R_2 = Cl$	277–278	73[d]	73.71	73.77	3.48	3.53	13.60	13.70
B-III: $R_1 = Cl, R_2 = H$	299.5–300.5	27[d]	73.71	73.33	3.48	3.70	13.60	13.43
B-IV: $R_1 = R_2 = Cl$	373–374	31[d]	65.11	65.22	2.73	2.73	24.03	24.14

[a] Reference 12. [b] The yields are for the once recrystallized products. [c] Reference 9. [d] The yields are for the twice recrystallized products.

The absorption spectra were determined in a Beckman quartz spectrophotometer, Model DU, using 1-cm. quartz cells and a concentration of 1.5×10^{-4} molar in benzene (see Fig. 1 and Table II). It was found necessary to obtain the spectra soon after making up the solutions since the absorption characteristics changed on standing. It should be noted that the introduction of chlorine atoms into the tetracyclone molecule does not drastically alter its spectrum.

TABLE II

SPECTRAL CHARACTERISTICS OF THE TETRACYCLONES

	$\lambda(1)$	$a_m(1)$	$\lambda(2)$	$a_m(2)$
A-I	342	6760	512	1320
A-II	340	7880	514	1220
A-III	341	7080	512	1750
A-IV	341	8600	514	1580

Experimental

All melting points are corrected.

Starting Materials.—4-Chlorophenylacetic acid (m.p. 103.5–106°) was prepared through the nitrile from 4-chlorobenzyl chloride[10,11] [b.p. 109.5–111° (21–23 mm.)]. Dibenzyl ketone [b.p. 174–179° (15–17 mm.), 198–199° (24

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[1] Taken from a thesis by F. J. T. for the B.S. degree, Polytechnic Institute of Brooklyn, June, 1949.

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