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

Behavior of Solutions of Double Sulfates of Titanium and Bivalent Metal in the Presence of Hydrogen Peroxide

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Upon treating solutions of $RSO_4 \cdot Ti(SO_4)_2$ where R = a bivalent metal with a solution of hydrogen peroxide, unstable oily liquids are obtained which when heated to about 200–230° give solid residues agreeing with the formula $RSO_4 \cdot TiOSO_4$. It is inferred from the analytical data obtained that the unstable oily liquids contain $RSO_4 \cdot TiO_2SO_4$.

Salts of titanium peroxide of the type $M_2SO_4 \cdot TiO_2SO_4 \cdot xH_2O$ (where M = Na, K, NH_4 or Li) have been described by Mazzucchelli and Pantanelli[1] who found that they are readily soluble and practically non-crystallizable. These compounds are obtained by adding alcohol to a solution containing titanium sulfate, hydrogen peroxide and alkali sulfate in rather less amount than corresponding to the ratio $TiO_2 \cdot M_2SO_4$.

These authors isolated the potassium compound $K_2SO_4 \cdot TiO_2SO_4$ as an orange yellow powder and found it to be fairly stable. The same compound was prepared using the general procedure outlined in this investigation. It could be converted into a reddish oily liquid by treating it with a very small amount of water and from this behavior it appeared that the oily liquids obtained with the bivalent metals in this investigation are also mixtures of the compounds $RSO_4 \cdot TiO_2SO_4$ with small amounts of water. The difference between the compounds containing the bivalent metal sulfates and those which contain alkali sulfates lies in the fact that the former are unstable and cannot be isolated in the solid state although their existence can be inferred by quickly analyzing the oily liquids.

Schwarz and Geise[2] prepared compounds of the type $K_2[TiO_2(SO_4)_2] \cdot 3H_2O$ by the addition of acetone, previously treated with hydrogen peroxide, to a solution of titanic sulfate, potassium sulfate and hydrogen peroxide. The complex nature of the salt with Ti as the central atom was ascertained by the electrolysis of a solution of it in sulfuric acid. From the amount of titanium estimated in the cathode and anode compartments it was inferred that the titanium is combined with the active oxygen and sulfate, forming a complex ion.

A search of the literature showed that compounds with alkali sulfates in combination with $TiOSO_4$ have been described, but those with bivalent metals in similar combination have not been prepared. In an English Patent[3] the preparation of combinations of alkali sulfates with $TiOSO_4$ has been described and it is stated that they are obtained by concentration of sulfuric acid solutions containing titanium and the alkali sulfates.

Rosenheim and Schütte[4] obtained the salts $2K_2SO_4 \cdot 3TiOSO_4 \cdot 10H_2O$ and $(NH_4)_2SO_4 \cdot TiOSO_4 \cdot 2H_2O$ in the form of colorless needles by the action of a concentrated aqueous solution of alkali sulfate on a saturated solution of titanic acid in concentrated sulfuric acid.

Billy[5] obtained the compound $K_2SO_4 \cdot TiOSO_4$ by treating a solution of titanic acid in concentrated sulfuric acid with potassium carbonate required by the formula $K_2SO_4 \cdot Ti(SO_4)_2$ and twice this amount of hydrogen peroxide. On evaporating below 15° K_2SO_4 separated first and was removed. This was followed by the separation of a mixture of orange and pale yellow crystals which when washed with cold water gave an orange liquid and colorless crystals of $K_2SO_4 \cdot TiOSO_4$.

Experimental

A weighed quantity (0.1 to 0.5 g.) of the carbonate of the bivalent metal was taken in a clean dry wide tube placed in ice. This was treated with ice-cold hydrogen peroxide solution (1 cc. of 39% solution). Next a solution of ice-cold titanium sulfate (2.5 cc. of the solution prepared by heating 20 g. of titanium tetrachloride in 50 cc. of concd. sulfuric acid to fumes of sulfuric acid) was added gradually. The solution was set aside until it attained room temperature (about 28°). The clear liquid was treated with 5 cc. of ice-cold absolute alcohol and then with 10–15 cc. of ice-cold ether. On standing, after thorough shaking, a red or reddish-brown liquid separated which was removed by means of a small separating funnel. A portion of this was quickly transferred to a weighing bottle containing a known quantity of dilute sulfuric acid and titrated with standard $KMnO_4$ for available oxygen. Another portion was heated in an air-oven to about 200–300° and the loss in weight was determined. The residue left after heating was then dissolved in concentrated hydrochloric acid and analyzed for titanium, the bivalent metal and sulfate. From the analytical data obtained it was possible to determine the amount of water present in the oil as well as the available oxygen which was in combination with the residue left on heating.

In the case of the manganese compound the above procedure was modified a little since hydrogen peroxide was quickly decomposed by the manganese compound. The weighed quantity of manganese carbonate was first treated with the solution of titanium sulfate and the hydrogen peroxide added afterwards.

These oily liquids contained a certain amount of water which could not be removed by keeping them over dehydrating agents such as P_2O_5, NaOH, H_2SO_4 and $CaCl_2$. It was observed that during this process available oxygen was lost along with water and a sticky mass was left behind. Even when this procedure was followed at 4–10° the same observations were made. The use of anhydrous solvents such as absolute alcohol, ether, acetone, etc., was also unsuccessful.

The oily liquids are unstable and lose oxygen upon standing for some time; when diluted with water they formed orange-yellow solutions which on further dilution formed precipitates. These oily liquids swelled when heated probably due to loss of available oxygen and water. The residue obtained after heating to 200–230° was white in the case of the Cu, Cd, Zn and Mg compounds, yellow in the case of Mn, and light pink in the case of the cobalt compound. These residual solids are hygroscopic and soluble in dilute mineral acids. The data obtained with different starting quantities of the carbonate of the bivalent metal indicate

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[1] A. Mazzucchelli and E. Pantanelli, *Atti. reale accad. Lincei*, [V] **181**, 608 (1909).

[2] R. Schwarz and H.Geise, *Z. anorg. Chem.*, **176**, 209 (1928).

[3] F. M. Spence, D. D. Spence and H. Spence, British Patent 4183 (1899); *J. Soc. Chem. Ind.*, **19**, 246 (1900).

[4] A. Rosenheim and O. Schütte, *Z. anorg. Chem.*, **26**, 239 (1901).

[5] M. Billy, *Compt. rend.*, **172**, 1411 (1921).

that the products are $RSO_4 \cdot TiOSO_4$ where R = a bivalent metal ion.

The data obtained for the compounds $MgSO_4 \cdot TiO_2SO_4$ and $MgSO_4 \cdot TiOSO_4$ are given in Tables I and II for illustration.

TABLE I

Magnesium carbonate, g.	Total loss on heating, %	Loss due to available oxygen, %	Loss calculated due to water, %	Available oxygen in the oily liquid minus water, %	Available oxygen calculated for $MgSO_4 \cdot TiO_2SO_4$, %
0.2	55.38	2.38	53.0	5.1	5.4
.3	56.26	2.46	53.8	5.3	5.4
.4	55.35	2.45	52.9	5.2	5.4

TABLE II

$MgSO_4 \cdot TiOSO_4$ requires 17.08% Ti, 8.68% Mg, 68.52% SO_4.

Magnesium carbonate, g.	Wt. of oily liquid, g.	Wt. of residue after heating the oily liquid, g.	Mg, %	Ti, %	SO_4, %
0.2	0.278	0.124	8.5	16.5	69.2
.3	.290	.127	8.2	16.8	68.9
.4	.260	.116	8.7	16.2	69.2

The above data as well as the data of earlier publications indicate that three series of compounds appear to exist: (1) $RSO_4 \cdot Ti(SO_4)_2$; (2) $RSO_4 \cdot TiO_2SO_4$ and (3) $RSO_4 \cdot TiOSO_4$ in which R = a bivalent metal. It is suggested that in any continuation of this work efforts may be made to find conditions under which $Ti(SO_4)_2$ and the peroxide compound TiO_2SO_4 can be isolated; $TiOSO_4$ is already known.

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H-Ion Concentration of Aqueous Solutions Containing Boric Acid and Hydroxylic Substances

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Levulose has been found to be more effective in increasing the acidity of boric acid in concentrated solutions than either mannitol or sorbitol. The *p*H values obtained in this investigation in the case of levulose are in good agreement with those of Böeseken, Vermaas and Kuchlin but differ from those obtained by Krantz, Beck and Carr. By use of an expression derived by Böeseken, Vermaas and Kuchlin the values of "*n*" (the number of molecules of a polyhydric substance in combination with one mole of boric acid) have been calculated.

In this paper the H-ion concentration of solutions containing varying proportions of boric acid and hydroxylic substances, *viz.*, (1) mannitol, (2) sorbitol, (3) levulose, (4) glucose, (5) galactose and (6) mannose is reported. It was determined by the quinhydrone method using an electrode vessel of the Morton type and saturated KCl as the bridge liquid. An amplifying unit was used to measure the e.m.f. The apparatus was standardized with *M*/20 potassium hydrogen phthalate. From the observed e.m.f. the *p*H was obtained from the expression $pH = (0.455 - E)/0.06$.

The results obtained are given in the Table I in which the following symbols have been used: *R* = ratio boric acid:hydroxylic substance; *C* = molar concentration of boric acid in the solution.

TABLE I

BORIC ACID:MANNITOL

R *C*	1:3 *p*H	1:2 *p*H	2:3 *p*H	1:1 *p*H	2:1 *p*H	3:1 *p*H
0.200	2.683	2.899	3.083	3.207	3.525	3.692
.125	2.961	3.207	3.35	3.508	3.832	4.007
.100	3.099	3.341	3.482	3.642	3.975	4.159
.050	3.541	3.799	3.95	4.1	4.466	4.658
.025	3.999	4.287	4.424	4.633	4.923	5.116
.005	5.041	5.258	5.428	5.474	5.492	5.692
B. Boric acid:sorbitol						
0.200	2.906	3.042	3.108	3.445	3.517	3.642
.125	3.188	3.323	3.375	3.692	3.816	3.916
.100	3.325	3.475	3.523	3.850	4.058	4.142
.050	3.808	3.907	3.941	4.142	...	4.508
.025	4.249	4.333	4.441	4.474	4.681	4.775
C. Boric acid:levulose						
0.200	2.678	2.774		3.180	3.458	3.591
.125	3.011	3.191		3.466	3.716	3.991
.100	3.191	3.375		3.624	3.978	4.092
.050	3.709	3.824		4.007	4.271	...
.025	4.058	4.241		4.325	...	4.704
.005	4.708	4.725		4.808	4.907	5.058
D. Boric acid: glucose						
0.200	3.816	3.958	4.108	4.192	4.441	4.591
.125	4.142	4.175	4.391	4.508	4.742	4.825
.100	4.308	4.341	4.474	4.591	4.808	4.841
.050	4.633	4.541	4.874	4.708	4.857	4.891
.025	4.775	4.625	4.391	4.991	4.991	4.941
.005	4.991	4.742	5.041	5.041	5.024	5.024
E. Boric acid:galactose						
0.200	3.824	3.999	4.133	4.275	4.241	4.475
.125	4.100	4.241	4.441	4.525	4.591	4.633
.100	4.258	4.357	4.483	4.575	4.792	4.808
.05	4.575	4.591	4.708	...	4.857	4.891
.025	4.691	4.766	...	4.891	4.907	4.923
F. Boric acid:mannose						
0.200	3.741	3.891	3.991	4.168	4.291	4.451
.100	4.058	4.072	4.325	4.408	4.608	4.608
.050	4.180	4.325	4.474	4.523	4.725	4.742
.025	4.461	4.505	4.605	4.708	4.934	4.907
.005	4.651	4.951	4.920	...	5.308	5.208

Discussion.—When the *p*H values are plotted against dilution, curves are obtained which show that the *p*H of all the mixtures increases with dilution. These curves are nearly all of the same type except in the case of galactose and glucose