

The Action of Hydrogen Sulphide on Mercurous Chromate.

By. M. A. HAMID, V. S. BHATIA AND H. B. DUNNICLIFF.

The reduction of chromates by hydrogen sulphide has been investigated by Dunnicliff and co-workers (*J. Phys. Chem.*, 1929, **33**, 81; 1930, **35**, 3214; 1935, **39**, 1217; *J. Indian Chem. Soc.*, 1935, **12**, 595).

Dunnicliff and Prakash (*J. Indian Chem. Soc.*, 1935, **12**, 505,) have shown that silver chromate, when reduced with hydrogen sulphide, yields sulphite as one of the final products. It has been pointed out that silver chromate is one of those substances which are not hydrolysed to any extent by water. Further support of this view has been obtained in the action of hydrogen sulphide on mercurous chromate, a substance which is hydrolysed only at temperatures about 60°. The effect of temperature on the products formed is also emphasised.

For the purpose of this work, mercurous chromate was obtained by mixing approximately equivalent proportions of potassium chromate and mercurous nitrate. The basic mercurous chromate which separated was converted into the normal compound by boiling with a few drops of concentrated nitric acid and washing till free from acid.

The reaction was studied at three temperatures :

I. *At room temperature.* A known weight of the sample when subjected to the action of hydrogen sulphide at the room temperature (about 20°), gave an orange-red suspension which changed ultimately to dull black. After 8 hours, about 50% of the mercurous chromate had been attacked. Sulphite, thiosulphate and sulphate were absent from the filtrate. On extraction with potassium hydroxide, the precipitate was found to contain thiosulphate, sulphite and sulphate. The residue was chromium hydroxide, mercurous sulphide and free sulphur.

II. *At 80-85°.* A known weight was suspended in water and treated as before, the reaction being maintained at 80-85° in a water bath. The final reaction mixture was black in colour but there was no sulphite in the alkali extract. Other products were the same as before.

III. *At about 0°.* The vessel was placed in melting ice. The products were the same as at the room temperature, except that, for a

given weight of mercurous chromate, more of the sulphite was formed. This has an important bearing on the subject.

For purposes of quantitative relations, the following reactions are assumed :

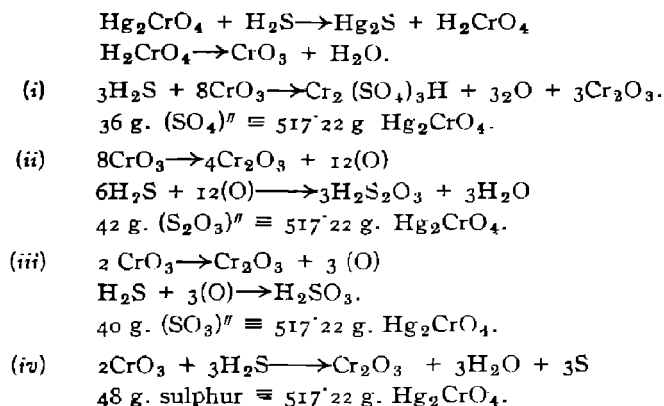


TABLE I.

The action of hydrogen sulphide on mercurous chromate in ice-cold solutions.

Analysis of the final greenish black precipitate.

	I.	II.	III.	Mean
1. Sulphite $(\text{SO}_3)''$				
(a) Actual wt. 100/x*	0.543 g.	0.482 g.	0.573 g.	0.533 g.
(b) In terms of 100 g. of Hg_2CrO_4 .				6.88%
2. Thiosulphate $(\text{S}_2\text{O}_3)''$				
(a) Actual wt. 100/x*	3.194	3.040	3.437	3.224
(b) In terms of 100 g. of Hg_2CrO_4 .				39.67%
3. Sulphate $(\text{SO}_4)''$				
(a) Actual wt. 100/x*	1.251	1.096	1.192	1.180
(b) In terms of 100 g. of Hg_2CrO_4 .				16.95%
4. Sulphur				
(a) Actual wt. 100/x*	3.27	3.70	3.96	3.64
(b) In terms of 100 g. of Hg_2CrO_4 .				39.22%

Total mercurous chromate accounted for = 102.72

* Where x is the percentage of mercurous chromate actually attacked.

TABLE II.

The action of hydrogen sulphide on mercurous chromate at 80-85°.

	I.	II.	III.	Mean.
1. Sulphite (SO_3)"	Absent
2. Thiosulphate (S_2O_3)				
(a) Actual wt. 100/ x *	3.129 g.	3.547 g.	3.276 g.	3.317 g.
(b) In terms of 100 g. of Hg_2CrO_4 .				40.85%
3. Sulphate (SO_4)"				
(a) Actual wt. 100/ x *	1.455	1.234	1.521	1.403
(b) In terms of 100 g. of Hg_2CrO_4 .				20.16%
4. Sulphur				
(a) Actual wt. 100/ x *	3.65	4.21	3.89	3.92
(b) In terms of 100 g. of Hg_2CrO_4 .				42.25%

Total mercurous chromate accounted for = 103.26

In view of the fact that the gas had to be passed for about 8 hours, the high values of sulphur are attributable to the adventitious oxidation of hydrogen sulphide.

The total oxidising power of the chromate has been accounted for in terms of the products formed.

The results show that, when the reaction is conducted in ice-cold solutions, the final precipitate contains chromium sulphate, thiosulphate, sulphite and hydroxide, mercurous sulphide and free sulphur. At temperatures above 60°, *i.e.*, when hydrolysis occurs, sulphite is absent and the analytical results show that it is quantitatively converted into sulphate, since the values for thiosulphate are practically the same as at the lower temperature. It appears, therefore, that in the event of hydrolysis, sulphite is converted quantitatively into sulphate. Thallous chromate is not hydrolysed by water and also gives sulphite among the reduction products.

Similar experiments with barium chromate and chromic acid have shown that at 80-85°, the products show an increase in the sulphate content and decrease in the value for thiosulphate, although no sulphite appears in the final products. High temperatures, therefore, favour the reaction $\text{SO}_3 + \text{O} \rightarrow \text{SO}_4$ in preference to $\text{SO}_3 + \text{S} \rightarrow \text{S}_2\text{O}_3$.

GOVERNMENT COLLEGE,
UNIVERSITY OF THE PUNJAB,
LAHORE.

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* Where x is the percentage of mercurous chromate actually attacked.