

THE OXIDATION OF HYDROGEN SULPHIDE BY POTASSIUM IODATE

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Received February 12, 1951

DEAN¹ studied the oxidation of sulphides with potassium iodate and found that the amount of sulphur oxidised to sulphuric acid depended on the concentration of the hydrochloric acid employed. Iodine monochloride appeared to be the actual oxidant and when the concentration of the acid was sufficient to prevent the hydrolysis of iodine monochloride, the sulphur was quantitatively oxidised to sulphate.

Our preliminary experiments showed that as in the case of chloramine-T² the products formed by the oxidation of hydrogen sulphide by potassium iodate were sulphur and sulphate, depending upon the pH of the system. The experiments were carried out in buffers having a pH sufficiently high as not to liberate iodine from iodate, on addition of potassium iodide. At lower pH values, the oxidation of hydrogen sulphide by iodate would be complicated by the reaction of hydrogen sulphide with the iodine liberated from iodate in an acid medium, in presence of iodide, formed by the reduction of iodate. The lowest pH employed was 7.0 at which there was no liberation of iodine by any reaction between iodate and iodide.

Iodate was always used in excess, and the oxidant left over after the complete removal of hydrogen sulphide, was estimated iodometrically.

The experimental technique of study of the oxidation of hydrogen sulphide was the same as that employed in the case of the reaction between the gas and chloramine-T².

0.1 N potassium iodate solution was prepared from A.R. potassium iodate.

* This investigation was conducted at Central College, Bangalore, and formed part of the thesis of A. R. Vasudeva Murthy accepted for the M.Sc. Degree of the Mysore University.

EXPERIMENTAL RESULTS

TABLE I

Reaction between Hydrogen Sulphide and Potassium Iodate

Sl. No.	pH solution	Buffer used*	Value of 'a'†	Value of 'b'‡	Ratio of b to a
1	7.0	Phosphate—borax	2.69	5.43	2.02
2	7.0	Phosphate—borax with 0.1 N potassium iodide	5.77	1.41	0.25
3	7.0	Phosphate—borax + osmic acid	5.16	1.88	0.36
4	7.0	Phosphate—borax + brucine	5.1	1.8	0.36
5	7.0	Phosphate—borax + 2 ml. of 5% sodium molybdate	5.61	1.62	0.33
6	9.2	Borax	4.4	3.9	0.88
7	11.7	Phosphate—Sodium hydroxide	5.44	1.86	0.33
8	11.7	Phosphate—Sodium hydroxide with 0.1 N potassium iodide	6.5	0.86	0.13

† *a* = Volume of hydrogen sulphide (at N.T.P.) oxidised to sulphur and water.

‡ *b* = Volume of hydrogen sulphide (at N.T.P.) oxidised to sulphuric acid.

* The composition of the buffers was as indicated in *Hydrogen ions*, by Britton, 3rd Edn., Vol. I, p. 300, 1942.

TABLE II

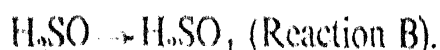
Redox Potentials of Potassium Iodate—Potassium Iodide Systems

Sl. No.	pH	Buffer	System	Electrode	Redox potential in volts.
1	7.0	Phosphate—borax	Potassium iodate—iodide	Platinum bright	0.557
2	7.0	do	do + osmic acid	do	0.557
3	7.0	do	do	Platinum black	0.557
4	7.0	do	Potassium iodate—iodide + a crystal of iodine	Platinum bright	0.557
5	7.0	do	Potassium iodide—iodine	do	0.557
6	9.2	Borax	Potassium iodate—iodide	Platinum bright	0.335
7	9.2	Borax	do	Platinum black	0.335
8	11.8	Phosphate—sodium hydroxide	do	Platinum bright	0.299
9	11.8	do	do + osmic acid	do	0.299

DISCUSSION

As stated in an earlier paper, dihydrogen sulphoxide appears to be the primary product of oxidation of hydrogen sulphide.² The sulphoxide can simultaneously undergo two reactions:

A decomposition (Reaction A) and an oxidation (Reaction B).



Examination of Table I indicates that the presence of potassium iodide considerably diminishes the production of sulphate both at pH 7.0 and pH 11.7. The oxidation potential of potassium iodate is greatly reduced by the presence of potassium iodide as shown in Table II. The rate of oxidation of the hydrogen sulphoxide to sulphate is thus diminished and the decomposition of the sulphoxide to sulphur therefore, takes place to a greater extent. Osmic acid and brucine, as in the case of chloramine-T, diminish sulphate formation. The molybdate also seems to diminish sulphate formation while in the case of chloramine-T, it considerably accelerates the production of sulphate. It is therefore to be concluded that catalysts have specific influence on the two simultaneous reactions undergone by dihydrogen sulphoxide.

Redox potentials were measured in the same way as in the case of chloramine-T. The results are given in Table II.

It is found that when 0.1 N potassium iodide and iodine are present in the solution along with iodate (0.1 N), the potential is the same as that of a solution having 0.1 potassium iodide and iodine only. It is also noticed that osmic acid does not affect the potential though it alters the relative proportions of sulphate and sulphur produced, during the oxidation of hydrogen sulphide by the iodate, at pH 7.0.

REFERENCES

1. S. Dean .. *J. Am. Chem. Soc.*, 1918, **40**, 619.
2. A. R. V. Murthy and B. Sanjiva Rao .. "Oxidation by Chloramine-T. Part I. Reaction between Hydrogen Sulphide and Chloramine-T," *Proc. Ind. Acad. Sci.*, 1952, **35A**, 7.