

OXIDATION BY CHLORAMINE - T

Part II. Redox Potential of Chloramine-T—Sulphonamide Systems

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IN connection with the study¹ of the oxidation of hydrogen sulphide by chloramine-T, it was deemed necessary to determine the effect of pH on the redox potential of chloramine-T—sulphonamide systems.

When chloramine-T was acidified, there was turbidity due to the separation of dichloramine-T. Whether the formation of this sparingly soluble substance had any effect on the potential was also determined. Dichloramine-T was prepared from chloramine-T by treatment with cold sodium hypochlorite. The purity of the dichloramine-T was determined by estimation of (a) available oxygen (iodometrically) and (b) Nitrogen (by Micro-Kjeldahl method). The purity of the substance was found to be 99.6% by the first method and 99.8% by the second.

The chloramine-T and the sulphonamide (M.P. 137° C.) employed were also of high purity. The potentials were determined in 0.2 N solutions of chloramine-T containing sulphonamide in excess. Various types of electrodes were tried. A saturated calomel electrode was used in combination with the redox half cell.

EXPERIMENTAL RESULTS

TABLE I

Effect of Dichloramine-T on the Redox Potential

1 Sl. No.	2 pH	3 Buffer used	4 System	5 Redox potential in volts
1	0.65	Sodium acetate-hydrochloric acid	(Chloramine-T saturated with sulphonamide)	1.139
2	0.65	do	do + dichloramine-T	1.139
3	7.0	Phosphate	(Chloramine-T saturated with sulphonamide)	0.778
4	7.0	do	do + dichloramine-T	0.778
5	9.2	Borax	(Chloramine-T saturated with sulphonamide)	0.614
6	9.2	do	do + dichloramide-T	0.615

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

TABLE II

Redox Potential with Various Types of Electrodes

1 Sl. No.	2 pH	3 Buffer	4 Electrode	5 Redox potential in volts
1	0.65	Sodium acetate-hydrochloric acid	Bright platinum	1.138
2	0.65	do	Platinum black	1.139
3	0.65	do	Tungsten	1.139
4	0.65	do	Silver	1.139
5	0.65	do	Gold	1.139
6	2.64	do	Platinum bright	0.946
7	2.64	do	Platinum black	0.945
8	4.76	do	Platinum bright	0.834
9	4.76	do	Platinum black	0.835
10	7.0	Phosphate	Platinum bright	0.778
11	7.0	do	Platinum black	0.778
12	7.0	do	Platinum bright + osmic acid	0.778
13	7.0	do	Platinum bright + 2 ml. sodium molybdate (5%)	0.777
14	7.0	do	Platinum bright + 2 ml. sodium tungstate (5%)	0.778
15	9.2	Borax	Platinum bright	0.615
16	9.2	do	Platinum black	0.614
17	12	Borax-sodium hydroxide	Platinum bright	0.500
18	12	do	Platinum black	0.499
19	12	do	Tungsten	0.499
20	12	do	Silver	0.499
21	12	do	Gold	0.499

Redox system: 0.2 N chloramine-T saturated with sulphonamide

TABLE III

Solubility of p-Toluene Sulphonamide at 25° C.

1 Sl. No.	2 pH	3 Buffer	4 g. per litre of the saturated soln.
1	0.65	Sodium acetate-hydrochloric acid	1.150
2	4.76	do	2.102
3	7.0	Phosphate	3.019
4	..	Water	3.15
5	9.2	Borax	4.266
6	12	Borax-sodium hydroxide	5.821

DISCUSSION

The results show that the redox potential of chloramine-T-sulphonamide system is influenced by the pH of the solution. The influence of pH on the potential may be attributed to the increase in solubility of the sulphonamide as the pH rises. The solubility of sulphonamide at various pH

values was determined by the estimation of nitrogen (Micro-Kjeldahl) in aliquots of the saturated solution.

The nature of the electrode seems to have no effect on the potential difference. From this, it may be concluded that the potential differences measured are real redox potentials.

In our paper on the oxidation of hydrogen sulphide by chloramine-T, it has been pointed out, that with an increase in pH, sulphate production diminishes, while oxidation of hydrogen sulphide to sulphur increases in magnitude. The decrease in redox potential with rise in pH would no doubt account for this. But the experimental results cannot be fully explained on the basis of redox potential. For, while the redox potential of chloramine-T is not affected by the presence of osmic acid, sodium molybdate or sodium tungstate, these reagents have a marked effect on the relative proportion of sulphate and sulphur formed during the oxidation of hydrogen sulphide by chloramine-T. The molybdate increases sulphate formation while the other two reagents depress it.

The specific influence of these reagents on the oxidation of hydrogen sulphide, while the redox potential is unaffected, can be accounted for on the basis of the catalytic effect of each of these reagents on dihydrogen sulphoxide, the primary product of oxidation of hydrogen sulphide. The reagents probably influence the decomposition of the sulphoxide to sulphur and water, as also the further oxidation of the sulphoxide to sulphate, by chloramine-T.

SUMMARY

Potentials of the chloramine-T—sulphonamide system have been found to be real redox potentials. With an increase in pH, the oxidation potential decreases. Depending on the pH of the solution, the oxidation of hydrogen sulphide by chloramine-T yields varying proportions of sulphur and sulphate. Reagents like osmic acid, sodium tungstate and sodium molybdate are also found to affect the ratio of sulphur to sulphate, formed by the oxidation of hydrogen sulphide.

A complete explanation for the observed results cannot be based on the effect of pH on the redox potential, as these reagents do not alter the potential. The specific effect of these reagents is probably due to their influence on dihydrogen sulphoxide, the primary product of oxidation of hydrogen sulphide.

REFERENCE

1. Vasudeva Murthy, A. R. and Sanjiva Rao, B. *Proc. Ind. Acad. Sci.*, 1952, **35**, 7.