USE OF SODIUM PERBORATE IN THE PREPARATION OF SODIUM CHLORITE

BY S. M. MEHTA, F.A.SC. AND D. J. MEHTA (Department of Chemistry, The Institute of Science, Bombay) Received August 16, 1956

1. INTRODUCTION

SODIUM CHLORITE which is present in the commercial product 'Textone' is generally prepared by the action of chlorine dioxide on hydroxides or peroxides of alkalis and alkaline earths. The only reference on the use of persalts appears to be a qualitative observation of Levi¹ that persulphates do not react with chlorine dioxide to give the corresponding chlorites but that percarbonates and perborates do so. In connection with the investigations started on the study of the reactions of perborates with both organic², ³ and inorganic substances, the quantitative data on the formation of sodium chlorite by the action of chlorine dioxide on sodium perborate under different conditions were obtained and are reported in this paper.

2. EXPERIMENTAL

In the experimental procedure, a convenient mol. fraction (varying from 0.005 to 0.05) of the reactants (either sodium perborate, hydrogen peroxide or any other reagent) was diluted to 100 c.c. and treated at 29–30° C. with chlorine dioxide prepared by oxalic acid method⁴ till the reaction was compplete. Excess of chlorine dioxide was then removed by aeration. The resulting colourless solution was estimated for its chlorite content from an aliquot portion using the method of White.⁵ The data obtained are given in Table I.

	Amount of NaBO ₃ .4H ₂ O Mol. fr.	Amount of NaClO ₂ in gm. formed in the mixture = Y	Yield of NaClO ₂ % of theory = P
· · · · · · · · · · · · · · · · · · ·	0.005	0.565	62.48
	0.010	1 · 130	62.49
	0.02	2.261	62.49
	0.05	5.517	60.99
	0.1	9.993	55.23
	0.2	16.550	45.73

TABLE I

The data in Table I show that the yield of sodium chlorite as per cent. of theory is practically constant in the beginning and then gradually diminishes. This behaviour appears to be due to the fact that sodium chlorite decomposes in higher concentrations since larger amount of sodium chlorite is produced with higher proportions of sodium perborate in the same total volume.

To note the effect of change of temperature experiments were carried out at 15°, 30° and 35° C. which revealed that there is practically no change in the yield of sodium chlorite when the temperature is changed from 15-35° C. This showed that the reaction between chlorine dioxide and sodium perborate could be conducted without any need for elaborate temperature control. All experiments, therefore, were carried out at the room temperature which was $29-30^{\circ}$ C.

Another series of experiments carried out in order to see if the yield could be increased by the addition of hydrogen peroxide, boric acid or borax to the reaction mixture following the same procedure gave data which are discussed below (Table II).

0.	005	0.01		
Y	Р	Y	Р	
0.565	41.64	1 • 13	41.66	
0.565	31.23	1.13	31.245	
0.546	24 · 14	1.062	23.49	
	• 0 • 0 • ¥ 0 • 565 0 • 565 0 • 546	Y P 0.565 41.64 0.565 31.23 0.546 24.14	Y P Y 0.565 41.64 1.13 0.565 31.23 1.13 0.546 24.14 1.062	

TABLE II

In the above Table II, the amount of sodium chlorite (Y) is unaffected by the presence of hydrogen peroxide but when considered on the basis of available oxygen in the mixture theoretically obtainable they are far lower as shown under P. In other words formation of sodium chlorite appears to depend on the sodium perborate present in the mixture and not on the available oxygen alone. The yield remained similarly unaffected when increasing amounts of boric acid were added.

Experiments on the action of chlorine dioxide on sodium perborate in the presence of borax revealed that the yield is greatly increased as given in Table III below:

Mol. fr. of NaBO ₃ .4 H	0.01		0.02		0.05			
Molecular ratio of NaBO ₃ : Na ₂ B ₄ O ₇	Y	Р	Y	Р	Y	Р	Y	Р
1:0.5	0.87	96 ·18	1.741	96-23	3.48	96 •23	8·107	89.62
1:1	0.87	96.18	1•741	96 •23	3.48	96.23	8 · 107	89.62
1:1.5]	0.87	96 •18	1.741	96 •23	3.48	96.23	8 • 107	89.62

TABLE	ш
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The addition of borax therefore increases the yield though no advantage is gained by adding increasing amounts of the same. The lower percentage in the case of 0.05 mol. fraction is attributed to the decomposition of sodium chlorite at higher concentrations. This means that the yield of sodium chlorite is dependent upon the alkalinity of the solution and not upon the available oxygen alone.

To verify this conclusion experiments were carried out in which sodium perborate was dissolved in sodium hydroxide of different normalities (N) making up the volume to 100 c.c. The data obtained are given below in Table IV.

IABLE IV					
0.005	0.01	0.02			
0.058	0.116	0.232			
0.870	1.741	3.48			
96.18	96.23	96.23			
	0.005 0.058 0.870 96.18	IABLE IV 0.005 0.01 0.058 0.116 0.870 1.741 96.18 96.23	IABLE IV 0.005 0.01 0.02 0.058 0.116 0.232 0.870 1.741 3.48 96.18 96.23 96.23		

From the data in Table IV it appears that by adding sodium hydroxide of suitable concentration, in place of borax, to the reaction mixture the same yield of sodium chlorite is possible. Experiments carried out by passing chlorine dioxide through solutions of sodium hydroxide of various normalities showed that the amount of chlorite formed is very small compared with that obtained when mixtures of sodium perborate and alkali are used.

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In the reaction of chlorine dioxide with sodium perborate alone the yield reaches a maximum of about 62.5% but the same can be augmented by increasing the alkalinity by the addition of borax or sodium hydroxide. No advantage is gained by the addition of hydrogen peroxide or boric acid alone nor is any appreciable amount of chlorite formed with sodium hydroxide alone. Thus it appears that it is the available oxygen as well as the alkalinity of the solution which taken together give nearly theoretical yield of sodium chlorite.

Chlorine dioxide gave no chlorous acid with hydrogen peroxide alone but if alkali or alkaline substance was also present along with hydrogen peroxide appreciable quantities of chlorite were detected as will be seen from Tables V and VI.

	TABLE V									
	Mol. fr	. of H ₂ O ₂	0.005		0.01			0.02		_
	N of N	laOH	0.	058	0·116 1·130			0·232 2·26		
	Y		0.	5652						
	P	<u></u>	62	•48		62.49		62 · 49		
	<u> </u>	····			TABLE V	Ï				- -
				······································	Molecu	ılar ratio	of H_2O_2	and		
Mol.	fr. of H	2O2	Na ₂ CO	3		NaHCO		Na	₂ B ₄ O ₇ .10	H₂O
	<u> </u>	1: 0·5	1:1	1:1.5	1:0.5	1:1	1:1.5	1:0.5	1:1	1:1.5
	Y	0.406	0.565	0.588	0· 2 16	0.452	0.678	0.407	0.825	0.880
0.005	Р	44.88	62.46	65·0	23.89	49 •9 9	74 ·9 9	44 · 99	91·20	97.45
	Y	0.814	1.153	1.176	0.452	0.905	1.357	0.846	1 · 6 50	1.760
0.01	Р	44 · 9 9	63.73	64·98	24.99	49 •9 9	74 ·9 8	46 ·76	91·20	97.45
	Y	1.628	2.306	2.351	0.905	1.831	2.714	1.673	3.323	3.527
0.02	Ρ	44 • 99	63.73	64 · 9 7	24·99	50.60	75·01	46.22	91.84	97.45
0.05	Ŷ	4.115	5.778	5.856	2.261	4.545	6.76	4.115	8.185	8.795
	Р	45.49	63·98	64·74	25.0	50.2	74.73	45·49	90·48	97·23

Results in Table V indicate that a solution of sodium perborate behaves in its reaction with chlorine dioxide in the same way as a solution containing equivalent amounts of sodium hydroxide and hydrogen peroxide. The particular advantage in preferring sodium perborate to hydrogen peroxide and sodium hydroxide mixture is that it is solid and stable and can be most easily and conveniently handled.

In Table VI the higher yield (nearly 75% for the ratio $1:1\cdot 5$) in the case of sodium bicarbonate than in case of sodium carbonate is probably due to the instability of hydrogen peroxide in the presence of alkali. The use of borax in place of sodium hydroxide, sodium carbonate or sodium bicarbonate gives an appreciable increase in the yield of sodium chlorite. When these values are compared with those in Table III where sodium perborate is used instead of hydrogen peroxide, the yield is found to be very nearly the same.

Hydrogen peroxide in the presence of boric acid gave no chlorous acid with chlorine dioxide.

Experiments to observe the yield of sodium chlorite by taking the combination: hydrogen peroxide, sodium perborate and borax gave results which are tabulated below:

Mol. fr. of H_2O_2		0.0)05	0	·01	0.02	
Molecular ratio of H_2O_2 : NaBO ₃ : Na ₂ B ₄ O ₇		Y	P	Y	Р	Y	Р
0.5:1:1		1.311	96.6	2.62	96.54	5.2	95.8
1:1:1	••	1.402	77 · 49	2.8	77.38	5.607	77 · 48
1.5:1:1		1.380	61.02	2.787	61 · 48	5.584	61.72

TABLE VII

It is seen from the above table that the yield of sodium chlorite is nearly the same as that obtained with sodium perborate and sodium hydroxide. Hence one might take hydrogen peroxide, sodium perborate and borax or sodium perborate and sodium hydroxide for the preparation of sodium chlorite. However, due to the instability of hydrogen peroxide in the presence of alkali the former is not suitable but a mixture of sodium perborate and sodium hydroxide is more convenient.

3. SUMMARY

Chlorine dioxide and sodium perborate give sodium chlorite and the yield is not affected by the addition of hydrogen peroxide or boric acid in different ratios but is greatly enhanced in the presence of borax, sodium hydroxide or sodium carbonate. The reaction between chlorine dioxide and hydrogen peroxide or alkali alone is negligible. The chlorite formation is determined by the available oxygen and the alkalinity of the solution. By proper adjustment of experimental conditions nearly theoretical yield of sodium chlorite is obtained.

4. **References**

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