HYPOCHLORITE OXIDATION OF STIBNITE

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Introduction

Although antimony trioxide has been extensively used in glasses and paints, its use in enamels has been substituted by alkali and alkaline earth antimonates because of the latter enamels being less toxic and more stable in acid medium.[1] In recent years more interesting uses of antimony pentoxide and antimonates have been suggested. These include their uses in the clarification of glass,[2] as a catalyst in the production of producer gas[3] and the activation of oxy-acid phosphors.[4] Alkali and alkaline earth antimonates are very resistant to high temperature and have thus been recommended for flame-proof paints. The oxides, Sb_2O_4 and Sb_2O_5, are also useful in the production of ceramics with high dielectric constant.[5] Metal antimonates have been found[6] to exert a profound influence on the electrical and thermal properties of refractory bodies, such as barium titanate.

Till recently,[7] there was a lot of confusion about the structure of antimonates and it was believed that compounds having different compositions were obtained from different wet methods. As a result, antimonates have so far been prepared by dry methods only. The potassium salt is the only soluble antimonate from which others are prepared. This is prepared by the fusion of antimony pentoxide with caustic potash or by the fusion of the trioxide (or tartar emetic) with potassium nitrate. A number of other reagents such as hydrogen peroxide, potassium dichromate, potassium ferrocyanide or potassium permanganate have been tried[8] for oxidation of Sb_2O_3, in hot soda lye, for preparation of sodium antimonate, but these do not appear to have been accepted for commercial production. As the trioxide itself is commercially prepared from stibnite, the present method of preparation of alkali antimonates requires at least two major steps. Some scanty information is available regarding attempts to prepare antimonates directly from Sb_2S_3. These are summarized below:

1. Sb_2S_3 (in alkali) $+ Na_2O_2$ (or H_2O_2) $\longrightarrow$ Sod. antimonate[9]

2. $Sb_2S_3 + KOH \xrightarrow[\text{with CuO}]{\text{boil}}$ Pot. antimonate[1]

3. $Sb_2S_3 + Br_2$ (in KOH) $\longrightarrow$ Pot. antimonate[11]

Nothing is known about the quantitative aspects of any of the above reactions. But use of any cheap oxidizing agents for direct oxidation of Sb_2S_3 to alkali antimonate and sulphate shows promise and considerable advantage over the available commercial methods.

No study has been made of the oxidation of stibnite by alkali hypochlorite although obviously this reagent would be cheap and readily available on a large scale. In the present investigation, therefore, we studied the reaction between alkali hypochlorite and stibnite and set forth conditions for preparation of potassium antimonate on a large scale.

Theoretical

A solution of Sb_2S_3 in alkali contains a mixture of antimonites and thio-antimonites.[12] Consideration of the redox potentials of the systems SbO_2^-/SbO_3^- and OCl^-/Cl^-[13] leads one to expect that antimonites can be readily oxidized to antimonates by hypochlorite, but no information is available regarding the oxidation of thio-antimonites by hypochlorite. As a working hypothesis, we may consider oxidation of thio-antimonites through either of the two following ways:

(i) $M_3SbS_3 + MOCl \longrightarrow MSbO_3 + S^=$

(ii) $M_3SbS_3 + MOCl \longrightarrow MSbO_3 + S^\circ$

Now, hypochlorites are known to react with both soluble sulphide[14] and elementary sulphur.[15] It was quite reasonable, therefore, to expect that alkali hypochlorite may be employed for the direct production of anti-monates, alkali sulphate would be obtained as a useful by-product.

Experimental

For a clearer understanding of the mechanism and the optimum conditions, it was convenient to work with a filtered extract of the Sb_2S_3 in alkali. In the preliminary experiments, filtered extracts of the sulphide in NaOH or KOH were treated with excess of NaOCl or KOCl solutions and the mixture warmed. In the case of NaOH solution a white crystalline precipitate immediately separated. This precipitate was filtered, washed free of adhering electrolytes with absolute alcohol and dried overnight in a vacuum desiccator over fused calcium chloride and analysed.

Calculated for $NaSbO_3.3H_2O$: Sb, 49.35%; Na, 9.32%; H_2O, 21.89%. Found: Sb, 49.30%; Na, 9.39%; H_2O, 22.1%.

In the case of KOH extracts, after addition of excess KOCl solution and warming, the whole mass was cooled and the potassium antimonate was crystallized by adding alcohol. It was similarly washed free of all adhering electrolytes with absolute alcohol, dried in a vacuum desiccator and analysed.

Calculated for $KSbO_3.3.5H_2O$: Sb, 44.78%; K, 14.38%; H_2O, 23.17%. Found Sb, 44.74%; K, 14.41%; H_2O, 23.01%.

The solutions left after separation of the antimonates were found to be free from sulphide sulphur and gave tests for sulphate and chloride. For studying the process variables, filtered extracts of the Sb_2S_3 in alkali were chlorinated in later experiments so that alkali hypochlorite was constantly formed in situ. In the final experiments, however, suspension of the ore in KOH was directly chlorinated.

It was observed that dissolution of the ore depends on factors such as alkali concentration, temperature of extraction and agitation and that the ratio of Sb:S in the extract did not conform to 2:3. In view of the above reasons it was necessary to employ a definite ratio of ore-alkali for the preparation of the extract. Concentration of alkali and the time allowed for agitation (extraction) and settling were kept identical. After filtration, the filtrate was made up to the volume of alkali taken and the final solutions were analyzed for the total antimony and sulphur. A measured volume of the extract was taken out for subsequent chlorination.

A slow, regulated stream of chlorine gas was bubbled through the alkali extract taken in a flask which was occasionally shaken. As appreciable heat was liberated, the flask needed cooling so as to maintain a definite temperature. With NaOH extracts, chlorination was continued till no more white precipitate separated and the solution turned yellow. This was taken to be the end point of reaction, as further chlorination tends to separate antimony sulphide. The solution was heated to dissolve the sulphur, cooled and filtered. The crystalline residue (sodium antimonate) was analyzed for pentavalent antimony by the iodometric method. An aliquot part of the filtrate was analyzed for sulphate according to the recommended method[16] after adding HCl.

With KOH extracts, the general procedure was similar, but analytical procedure had to be modified due to the solubility of potassium antimonate. At the end of the chlorination of the extract, the whole solution was boiled down to a small volume, (a third to a fifth of the original) and cooled. An equal volume of alcohol was added to crystallize the potassium antimonate. The solid was separated by filtration and washed free of sulphate, chloride and free alkali with alcohol and the washings collected with the filtrate. The solid was analyzed for pentavalent antimony and the filtrate for sulphate.

For oxidation of bulk quantities only potassium hypochlorite oxidation was studied. In

Table 1.—Chlorination of Alkali Extracts of Stibnite.

Effect of alkali concentration on the yield of antimonate and sulphate

Amount of ore treated = 10.0 gms.   Alkali solution used for dissolution = 200 ml.
Alkali extract taken for chlorination = 100 ml.   Temperature of chlorination = 24-28°C.

Rate of chlorine flow = 14.0-15.0 c.c./min.

Percentage Concentration of alkali.	Antimony content of solution (g. Sb.)	Sulphur content of solution (g. S.)	Period of chlorination (min.)	Yield of antimonate (g. Sb.)	%	Yield of sulphate (g. S.)	%
10 NaOH	1.6410	0.5884	66.0	1.1520	70.20	0.4728	80.34
10 KOH	1.1950	0.4574	63.5	0.4909	41.09	0.2576	56.31
15 NaOH	1.6000	0.5712	82.5	1.3960	87.26	0.5211	91.22
15 KOH	1.1480	0.4514	79.0	0.7129	62.09	0.2966	65.70
20 NaOH	1.5770	0.5891	97.5	1.4780	93.71	0.5801	98.47
20 KOH	1.0900	0.4462	105.3	0.8770	80.46	0.3802	85.21

these experiments, a suspension of the ore in KOH solution (mechanically agitated) was chlorinated till the solution was completely free from sulphide sulphur. The whole mass was then boiled and filtered. The filtrate was treated for separation of potassium antimonate.

Discussion

In order to make a comparative study of the effect of alkali, the same amount of the ore was treated with the same volume of alkali solution. The concentration of alkali used in the different experiments was different. Results obtained with NaOH and KOH are given in Table I.

It will be noted that although 200 c.c. of the alkali solution was employed for dissolution only half of it was used in the oxidation, the other half being used in determining the antimony and sulphur content of the solution. Contrary to expectation, variation of alkali concentration had no pronounced effect on the dissolution. With NaOH, 100 c.c. solutions contained on the average 1.60 gms. of antimony and 0.58 gms. of sulphur. This corresponded to a dissolution of only about 32% of the Sb_2S_3 content of the ore. According to a pre-

vious work in the laboratory, by boiling the ore with hot alkali an antimony concentration of about 3 gms. per 100 c.c. could be obtained. In the present case, however, this was not followed as the subsequent oxidation with hypochlorite was to be carried out at room temperature. It is important to point out that the dissolution does not increase to appreciable extent by increasing the alkali concentration.

With similar amounts (by weight) of KOH the dissolution of antimony and sulphur is less.

Chlorination of alkali extracts was continued till the stage at which precipitation of Sb_2S_3 tends to start. This point was taken to be the end point of chlorination. It is clear from Table I that with increasing concentration of alkali, oxidation could be continued for longer period and as such yields of antimonate and sulphate were higher. Yields as recorded are on the basis of the antimony and sulphur present in the solution taken (and not that present in the ore). Higher oxidation efficiency with increasing alkali concentration is attributed to the availability of more alkali for hypochlorite formation (which in fact is the oxidizing agent here) after thioantimonite and antimonite are formed. Oxidation

efficiency was found generally higher for NaOH. With 20% NaOH, oxidation could be carried nearly to completion and this took 97.5 minutes, whereas with 20% KOH solution, the antimonate formation proceeded to only 80.46% in 105 minutes. Sulphide precipitation started at this stage. Another interesting observation is that in all cases the yield of sulphate was somewhat higher than that of antimonate. This can be explained only by the fact that the thioantimonate is somewhat more readily oxidized than antimonite.

As the absorption of chlorine results in evolution of heat, it was considered worthwhile to study the effects of temperature. For this set of experiment, 20% alkali solutions were used throughout, as this was found most satisfactory for oxidation. It will be seen (in Table 2) that with NaOH, lower temperature favours the formation of antimonate. Higher temperatures would tend to form chlorates and consequently less of hypochlorite. If OCI—is the active (major) oxidant for thioantimonite and antimonite, the results are understood. Effect of temperature on the formation of sulphate is not very pronounced. Since the chief diffi-culty in separating oxidation products is offered by sulphide and allied products, a temperature of 30°C. was considered optimum—because the antimony oxidation is over 90% and sulphate formation quantitative.

With KOH solution, on the other hand, antimonate formation is maximum at 30°C., decreasing on either side by change of temperature. Sulphate formation follows the same trend as with NaOH solution. Interestingly enough, at a temperature of 30°C. and with 20% KOH concentration, the yield of antimonate is nearly the same as that with NaOH viz., slightly over 90%. Sulphate formation again is quantitative.

Progress of oxidation with time: It was also decided to study the course of oxidation under optimum conditions (alkali concentration 20%; temperature 30°C.). In order that a conveniently long time interval could be available for study, 200 c.c. of the alkali extracts were utilized in each of the present sets of experiments instead of 100 c.c. used previously.

TABLE 2.—CHLORINATION OF ALKALI EXTRACTS OF STIBNITE.

Effect of reaction temperature on the yield of antimonate and sulphate.

Amount of ore treated = 10.0 gms. Alkali solution used for dissolution = 200 ml.

Alkali extract taken for chlorination = 100 ml. Concentration of alkali = 20 %.

Rate of chlorine flow = 14.0-15.0 c.c./min.

Temperature of chlorination (C.)	Nature of alkali Solution	Antimony content of solution. (g. Sb.)	Sulphur content of solution. (g. S)	Period of chlorination. (min.)	Yield of antimonate (g. Sb) %		Yield of sulphate (g. S) %	
15	NaOH	1.5980	0.5890	120.5	1.5700	98.24	0.5727	97.23
,,	KOH	1.0920	0.4468	130.5	0.8574	78.52	0.3679	82.35
30	NaOH	1.6090	0.5897	96.3	1.5070	93.67	0.5843	99.08
,,	KOH	1.0920	0.4461	113.5	0.9972	91.33	0.4423	99.15
45	NaOH	1.6050	0.5889	84.6	1.4730	91.77	0.5888	99.97
,,	KOH	1.0950	0.4472	100.6	0.9802	89.52	0.4462	99.77

TABLE 3(a).—CHLORINATION OF NaOH EXTRACTS OF STIBNITE.

Progress of oxidation under optimum conditions.

Amount of ore treated = 20.0 gms.   Alkali solutions used for dissolution = 400 ml.

Alkali extracts taken for chlorination = 200 ml.   Concentration of NaOH and KOH = 20 %

Temperature of chlorination = 30°C.   Rate of chlorine flow = 14.0-15.0 c.c./min.

Period of chlorination (min.)	Antimony content of solution (g. Sb)	Sulphur content of solution (g. S)	Yield of antimonate (g. Sb)	%	Yield of sulphate (g. S)	%
60.0	3.2160	1.1790	1.1100	34.51	0.5450	46.23
120.0	3.2180	1.1794	2.1980	68.29	0.7364	62.46
180.0	3.2160	1.1789	2.9770	92.58	1.0060	85.33
215.0	3.2200	1.1799	2.9820	92.60	1.1740	99.49

TABLE 3(b).—CHLORINATION OF KOH EXTRACTS OF STIBNITE.

60.0	2.2040	0.8942	0.8876	40.27	0.4480	50.10
120.0	2.2040	0.8948	1.4788	67.10	0.6918	77.32
180.0	2.2180	0.8962	1.9136	86.30	0.8158	91.03
210.0	2.2100	0.8952	1.9958	90.33	0.8914	99.68

TABLE 4.—OXIDATION OF BULK QUANTITIES OF STIBNITE.

Vol. of KOH solution used = 400 ml. Temperature of chlorination = 30±5°C.

Analysis of ore (Sb : 48.5%; S : 18.7%; SiO$_2$: 32.0%)

Experiment No.	Amount of ore used. g.	KOH used g.	Period of chlorination (min.)	As KSbO$_3$.3½H$_2$O g.	Yield of antimonate (g. Sb)	%
1.	5.0	80.0	127.0	5.2	2.1920	90.38
2.	10.0	80.0	230.0	9.0	4.1150	84.82
3.	20.0	100.0	345.0	17.2	7.8940	81.37

Results in Table 3a indicate that in NaOH, oxidation of Sb^{III} to antimonates proceeds steadily upto about 150 minutes (found from actual plotting, not reproduced here) after which it slows down and approaches equilibrium at a point somewhat higher than 90%. Complete oxidation is impractical. Formation of sulphate is rapid in the first hour after which it slows down somewhat, but steadily proceeds to completion. The products of such reaction contains therefore (in addition to antimonate and sulphate) some amount of antimonite.

Parallel results (Table 3b) have been obtained with KOH extracts. Antimonate formation is rapid to begin with, but afterwards becomes slow and in 210 minutes 90.3% of Sb^{III} is converted to antimonate. By this time all the sulphides have been converted to sulphate. Obviously with further progress of reaction, the rest of the antimonite would be oxidized to antimonate.

Oxidation of bulk quantities of ore Suspensions

The above experiments were all carried out with filtered alkali extracts so as to enable a better understanding of the mechanism of reactions involved. From a practical point of view, however, oxidation of the suspension of the ore in alkali would eliminate the difficult step of filtration of the alkaline solution. As the ore contains silica as an impurity, the insoluble sodium antimonate could not be conveniently separated. Thus, bulk preparation of only potassium antimonate was undertaken.

The first experiment (Table 4) on the bulk oxidation of the suspension of 5.0 g. of the ore should be comparable with the series given in Table 3b, because although each experiment in Table 4 represented treatment of 10.0 g. of the ore, the dissolution was limited to only half of the antimony content. Oxidation of the suspended ore proceeds just as satisfactorily and 90% of the total antimony content of the ore is converted to antimonate in two hours' time. With larger quantities of the ore treated, the yield is somewhat less but could possibly be increased by further chlorination. It was experienced that during the reaction, simultaneously with the formation of the antimonate, the sulphide (or thioantimonite) was oxidized to sulphate through intermediate formation of sulphur. In order that the potassium antimonate could be satisfactorily crystallized out it must be ensured that no sulphur is present in the soluble sulphide (or thioantimonite) form. It was not necessary to continue the reaction for complete oxidation of sulphur (to sulphate) because any residual sulphur in the elementary form could be filtered off alongwith the silica.

The procedure thus offers a convenient method for direct preparation of potassium antimonate from stibnite ores. The only problem appears to be the consumption of relatively large proportions of KOH. The over-all reaction for complete oxidation, i.e.

$$Sb_2S_3 + 36KOH + 14Cl_2 \longrightarrow 2\,KSbO_3 + 3\,K_2SO_4 + 28\,KCl + 18H_2O$$
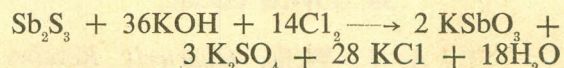
requires the KOH consumption equal to about nine times the amount of antimony present in the ore. In the third experiment, the proportion of KOH is only slightly higher than this. The main bulk of the caustic potash, however, is converted to potassium chloride which could possibly be re-used for production of caustic potash and chlorine. It would therefore require, in a commercial process, only that amount of caustic potash which is being converted to potassium sulphate.

Conclusion

Oxidation of stibnite with alkali hypochlorites yields the corresponding antimonates $(NaSbO_3.3H_2O; KSbO_3.3.5H_2O)$ and sulphates. The reaction can be carried out successfully through the action of gaseous chlorine on filtered extracts of the ore in alkali or (in the case of potassium antimonate) by passing chlorine through KOH suspension of the pulverised ore. The process is considered suitable for large scale production of pure potassium antimonate.

Acknowledgement

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