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Hydronium ion formation during the hydrometallurgical formation of valentinite (Sb_2O_3)

R. D. BERNETT
Independent Process Solutions Pty Ltd., Armidale, NSW, Australia

A. MITCHELL, T. C. BROWN*
Chemistry, School of Biological, Biomedical and Molecular Sciences, University of New England, Armidale, NSW 2351, Australia
E-mail: tbrown3@metz.une.edu.au

Cubic antimony trioxide or senarmontite (Sb_4O_6) is used as an additive to facilitate the flame retardancy of plastics and other commercial materials. This retardancy is due to the propensity of antimony trioxide to form gas-phase antimony trihalide under flame conditions, which is in turn able to stabilize the free radicals in the flame. Orthorhombic Sb_2O_3 or valentinite shows similar properties as senarmontite, but is not normally used because it oxidizes from a white to gray color when exposed to air and sunlight [1]. Such graying can impact on the coloring of plastics, paints and textiles, and so photo stable white senarmontite is the preferred choice.

Pyrometallurgical processes are most frequently used to prepare senarmontite, but recently more environmentally friendly hydrometallurgical [2, 3] and electrochemical methods [4, 5] have been examined. For both these aqueous methods the process conditions are sensitive to the yields of each dimorph [6–8]. An example is that at high pH valentinite dominates, while a 100% yield of senarmontite is observed at low pH in electrolytic antimony trioxide [6]. In this letter the observed formation of hydronium ions is used as an indicator for the mechanism for valentinite and senarmontite production.

Valentinite was prepared by flowing 13 ml of 5% w/w NaOH into 50 g of 10% w/w slurry of $Sb_4O_5Cl_2$ (antimony oxychloride) at ca. 25 °C. Antimony oxychloride was supplied by New England Antimony Mines and was purified by dissolving in concentrated HCl, filtering through a 0.44 μm membrane filter, adding excess deionized water, collecting the precipitate on Whatman No. 1 filter paper and drying at 80 °C. Sodium hydroxide addition rate was controlled by a motorized syringe pump (KD Scientific Model 200) and varied between 12 and 48 ml h^{-1}. The slurry was stirred with a magnetic stirrer and stirring bar, while pH was continuously monitored before and during the mixing. Fig. 1 shows the pH profiles associated with adding 5% w/w NaOH solution at flow rates of 12, 24, 30, 35 and 48 ml h^{-1} to the $Sb_4O_5Cl_2$ slurry. Each of the resultant substrates were filtered, dried, weighed and analyzed by powder X-ray diffraction. In all cases ca. 100% yields of valentinite were observed.

The first 2.5 ml of the 5% w/w NaOH titrations are plotted in Fig. 2 for 12, 24 and 48 ml h^{-1} flow rates. From these profiles it is clear that the initial 10% w/w slurry of $Sb_4O_5Cl_2$ has a low pH in the range 3–3.5. The pH then rapidly rises to 11–12 upon the addition of 5% w/w NaOH, but then falls to a pH in the range 9–10. This rise and fall is dependent on volume but independent of time as shown in Fig. 1. As a consequence these preliminary fluctuations reflect the mixing rate of the OH^- in the slurry. For all except the highest flow rate (48 ml hr^{-1}) the pH then drops sharply after a delay of 230 to 270 s, which is weakly dependent on flow rate, to a pH of 3–4. The minimum pH is similar in magnitude to the initial pH of the $Sb_4O_5Cl_2$ slurry.

The sharp decrease in pH indicates that hydronium ions are being produced at a rate faster than hydroxide ions are being added to the slurry. Fig. 1 shows that the duration of the low-pH plateau is strongly dependent on OH^- addition rate, and at a sufficiently high rate (48 ml min^{-1}) no hydronium ion formation is observed. Near completion of each titration hydroxide ions are in excess and so pH returns to 11–12. The major conclusion from the observations of low pH for the initial slurry and the sharp increase in acidity of the OH^- plus slurry mixture is that water molecules are key reactants in antimony trioxide production.

In order to elucidate the mechanism for valentinite formation a crucial assumption is that the final step is dehydration of aqueous $HSbO_2$ [5]

$$2HSbO_2(aq) \rightarrow Sb_2O_3(s) + H_2O$$

This reaction step is thermodynamically favored as indicated by $\Delta_r G^\circ_{298} = -167$ kJ/mole Sb_2O_3 [9, 10]. Alternative precursors to $HSbO_2$ at intermediate pH (2–11) is the metastable crystalline $Sb(OH)_3$, and at high pH is SbO_2^- [9]. Two competing pathways to $HSbO_2$ are apparent, with the first resulting in the production of hydronium ions:

$$\begin{aligned}&Sb_4O_5Cl_2(s)\\ &\quad + 2H_2O \rightleftharpoons Sb_4O_5Cl(OH)(s) + H_3O^+ + Cl^-\end{aligned}$$

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*Author to whom all correspondence should be addressed.

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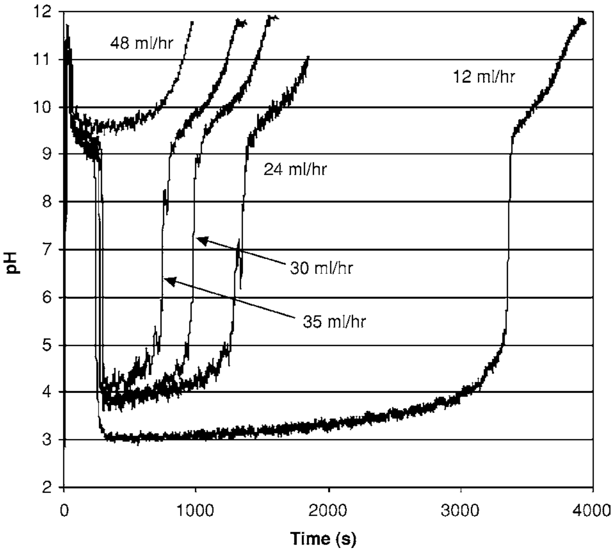

Figure 1 Time-dependent pH profiles when 5% w/w NaOH solution is added to a 10% w/w slurry of $Sb_4O_5Cl_2$ at 5 flow rates.

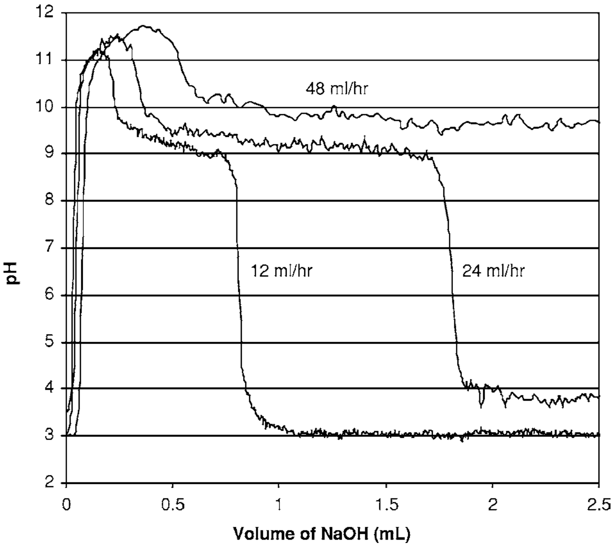

Figure 2 Initial volume-dependent pH profiles when 5% w/w NaOH solution is added to a 10% w/w slurry of $Sb_4O_5Cl_2$ at 3 flow rates.

where the driving force to the hydroxylated complex is neutralization of the hydronium with hydroxide ions. This complex has previously been reported by Lea and Wood [11], who undertook gravimetric experiments on crystalline hydrated $Sb_4O_5Cl_2$ and observed $Sb_4O_3(OH)_5Cl$ or $Sb_4O_5Cl(OH)\cdot 2H_2O$ [11]. The second pathway involves direct attack by OH^- and under these conditions hydronium ions are not formed.

$$Sb_4O_5Cl_2(s) + OH^- \rightleftharpoons Sb_4O_5Cl(OH)(s) + Cl^-$$

At sufficiently high pH the reaction may bypass the hydroxylated complex. For both pathways the resultant hydroxylated complex rearranges to eliminate the required aqueous precursor to valentinite.

$$Sb_4O_5Cl(OH)(s) \longrightarrow Sb_3O_4Cl(s) + HSbO_2(aq)$$

Although senarmontite did not form in any of the experiments it is reasonable to assume that water molecules are also key reactants. Indeed the analogous arsenolite (As_4O_6) can be prepared by the hydrolysis of $AsCl_3$ [12]. In the case of senarmontite simultaneous substitution of both chlorides with concomitant hydronium ion formation is required

$$Sb_4O_5Cl_2(s) + 3H_2O \rightleftharpoons Sb_4O_6(s) + 2H_3O^+ + 2Cl^-$$

where the driving force is again neutralization. The implication of this overall reaction step is that senarmontite formation involves a solid-state rearrangement, while valentinite forms via aqueous species ($HSbO_2$). In order to maximize senarmontite yield, the challenge is to ensure that an excess of water molecules is always in the vicinity of the $Sb_4O_5Cl_2$ substrate, but sufficient hydroxide ions are available to remove the forming hydronium ions. If the ratio of water molecules to chloride groups at the $Sb_4O_5Cl_2$ surface is less than 3:2 or if direct hydroxylation of the substrate is allowed to proceed then valentinite formation will occur. A detailed study of the optimum conditions for hydrometallurgical senarmontite formation is being undertaken.

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