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REACTION OF SODIUM BISMUTHATE WITH FLUORIDE IN AN AQUEOUS MEDIUM TO GIVE FLUORO COMPOUNDS OF BISMUTH(III)

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SUMMARY

Bismuth(V) as sodium bismuthate, $NaBiO_3$, is quantitatively reduced to bismuth(III) in aqueous hydrofluoric acid at the expense of water oxidation. $NaBiO_3$, with aqueous hydrofluoric acid and a solution of ammonium fluoride in aqueous hydrofluoric acid, gave trifluorobismuth(III) monohydrate, $BiF_3.H_2O$, and ammonium tetrafluorobismuthate(III), NH_4BiF_4, respectively. $BiF_3.H_2O$ undergoes dehydrofluoridation (-2HF) at 350-400°C in the presence of air to produce BiOF. The results of chemical analyses and infrared and laser Raman studies have been used to characterise the compounds.

INTRODUCTION

Bismuth(V) is generally unstable in an aqueous medium [1,2] and water is slowly oxidised to oxygen by bismuth(V), particularly in acid solution [2]. A chelated peroxide intermediate is implicated in the oxidation of water by Bi(V) [1,2].

We recently reported that a fluoroperoxo-iron(III) intermediate reacts with further fluoride to give a desired fluoroferrate(III) [3], that is very difficult to obtain otherwise. Thus unstable peroxo-metal intermediates, if formed, may constitute good synthetic precursors for the synthesis of fluoro-metal compounds from an aqueous medium.

In the present paper we provide a simple route to $BiF_3.H_2O$ and NH_4BiF_4 from pentavalent bismuth in an aqueous medium. BiOF, may be formed by pyrolytic decomposition of $BiF_3.H_2O$.

EXPERIMENTAL

Reagent-grade chemicals were used throughout (purity of $NaBiO_3$: 90%). Infrared and laser-Raman (LR) spectra were recorded on instruments already described [3,4]. All reactions and other manipulations were conducted in polyethylene apparatus.

Synthesis of Trifluorobismuth(III) Monohydrate, $BiF_3.H_2O$

Hydrofluoric acid (48%, 6cm^3, 144 mmol) was added to a suspension of sodium bismuthate, $NaBiO_3$ (2g, 7.14 mmol) in 15 cm^3 of water with continuous stirring. The stirring of the reaction mixture was continued for 5-6 hours and the mixture allowed to stand overnight. The yellow solid slowly turned white with simultaneous evolution of oxygen. The white solid obtained at this stage was isolated by filtration and again treated with a solution of 6 cm^3 of 48% HF in water (15 cm^3), by keeping in contact for a period of ca 7 days with occassional stirring, to ensure complete conversion of bismuth(V) to bismuth(III). The reaction was monitored by isolating small amounts of the product and testing for complete reduction by iodometry. The white microcrystalline solid was then separated by filtration. The product was dried *in vacuo* over conc. H_2SO_4. Yield 1.7g (85%). Found : Bi, 72.3; F, 20.7. Calc. for $BiF_3.H_2O$: Bi, 73.5; F, 20.0%.

Synthesis of Ammonium Tetrafluorobismuthate(III), NH_4BiF_4

Sodium bismuthate, $NaBiO_3$ (2.0g, 7.14mmol) was added to a solution of NH_4F (1.6g, 4.57mmol) in water (15cm^3). 6 cm^3 (144 mmol) of 48% HF was added to the reaction mixture with continuous stirring. The reaction mixture was left under stirring for 5-6 h and then allowed to stand overnight. The off-white solid thus obtained was isolated and again treated with a solution containing NH_4F (1.6g, 4.57 mmol) and 48% HF (6 cm^3, 144 mmol) and allowed to stand overnight. The process was repeated 5-6 times until complete reduction of Bi(V) to Bi(III) was achieved with the resultant product becoming clear white. The total reaction time was *ca*. 7 days. The reaction was monitored by iodometry. The white microcrystalline compound thus obtained was isolated by filtration and finally dried *in vacuo* over conc. H_2SO_4. Yield 1.8g (83%). Found : Bi, 68.1; F, 25.0; N, 4.3. Calc. for NH_4BiF_4 : Bi, 68.9; F, 25.08, N, 4.6%.

Synthesis of BiOF Through Pyrolysis of $BiF_3.H_2O$

A cleaned platinum crucible was heated at 400°C to constant weight. $BiF_3.H_2O$ (1g, 3.5 mmol) was placed in the platinum crucible and heated in the temperature range 350 - 400°C until the whole attained a constant weight. The calculated weight loss corresponding to expulsion of two molecules of HF per formula weight is 14.1%. The percent weight loss in the process was found to be 14%. Yield of BiOF : 0.86g. Found : Bi, 84.9; F, 8.3. Calc. for BiOF : Bi, 85.6; F, 7.78%.

Elemental Analyses

The fluoride, nitrogen and hydrogen contents were determined by the methods described earlier [5]. Bismuth was estimated gravimetrically as BiOI [6].

RESULTS AND DISCUSSION

Two principal types of fluorocomplexes of Bi(III), viz. BiF_3 and $[BiF_4]^-$ are documented in the literature [7-10]. The importance of BiF_3 and the oxo-fluoro species, BiOF, as catalytic and fluorinating agents in various reactions are also well established [7-10]. We have now shown that Bi(V) is quantitatively reduced to Bi(III) in aqueous hydrofluoric acid to afford fluoro complex of Bi(III), $BiF_3.H_2O$. The reaction when conducted in presence of excess NH_4F, yielded the complex, ammonium tetrafluorobismuthate(III), NH_4BiF_4. This is the first reported synthetic route to fluoro complexes of Bi(III) in which $NaBiO_3$ is used as the source of bismuth. The literature method generally used Bi_2O_3 as the starting point [11].

Efforts to reduce the reaction time by conducting the reaction at higher temperatures led to the formation of a brick red product containing bismuth in an oxidation state higher than +3. Therefore, it is emphasised that, in order to synthesise the compounds through the route described herein, the reactions have to be conducted at ambient temperature.

$BiF_3.H_2O$ on being heated at 350-400°C underwent dehydrofluoridation with the loss of two molecules of HF to produce BiOF. The literature methods of preparation of BiOF require (i) heating of BiOF.2HF with water at 200°C for a prolonged period in an autoclave [12a], (ii) a reaction of BiF_3 with Bi_2O_3 at 200°C [12b] or (iii) action of conc. HF on $Bi(NO_3)_3$ [12c].

The IR and Raman spectra of the compounds $BiF_3.H_2O$ and NH_4BiF_4 were similar except for the bands due to H_2O in $BiF_3.H_2O$ and NH_4^+ in NH_4BiF_4. The band at $450cm^{-1}$ in the IR spectra of the complexes has been assigned to ν(Bi-F) of co-ordinated fluoride ligand in conformity with reported spectrum of BiF_3 [13]. Another weak intensity, broad band appears in the IR as well as LR spectra at ca. $370cm^{-1}$ indicating the possible existence of a Bi-F-Bi bridge.

The bands at $3450cm^{-1}$ and $1630cm^{-1}$ in the spectrum of $BiF_3.H_2O$ were attributed to ν(O-H) and δ(H-O-H) modes of lattice water [14]. However, from the results of the pyrolysis studies of this compound it was evident that a much higher temperature (>200°C), than that usually required for the removal **of loosely held lattice water, was needed for the expulsion of** water molecule which implies that H_2O is strongly held in the lattice through hydrogen bonding. This has been further supported by comparing the NH_4^+ modes of NH_4BiF_4 with those of some other ammonium-fluorometallates reported in the literature [15] in which hydrogen bonding between the NH_4^+ cation and the complex anion is operative. In NH_4BiF_4 each bismuth atom was shown to have nine fluorine neighbours (as in BiF_3) with nets of BiF_4 co-ordination polyhedra being linked to nitrogen atoms by hydrogen bonds [16].

The IR spectrum of the pyrolytic product of $BiF_3.H_2O$, BiOF, exhibited two broad bands at 560m and 365m cm^{-1} which were assigned to ν(Bi-O) and ν(Bi-F) vibrations, respectively. The assignments are on the basis of the general trend that the ν(M-O) mode of oxyfluoride appears at higher frequency than ν(M-F) modes. ,

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