LIQUID HYDROGEN BROMIDE SOLVENT SYSTEM: REACTIONS OF SOME GROUP V DERIVATIVES

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(Received 21 June 1976)

Abstract—The properties and reactions of various group V derivatives, such as Ph_3M , M = N, P, As, Sb, Bi, in liquid anhydrous hydrogen bromide have been studied. In acid-base reactions, HCl showed no acidic properties and BBr₃ was used as a solvoacid. In oxidation reactions, Br_2 was an oxidizing agent and oxidized Br^- to Br_3^- , I^- to IBr_2^- and Ph_3MH^+ to Ph_3MBr^+ (M = P, As). Ph_3Sb , Ph_3Bi , Ph_3Ccl and PCl_3 were solvolysed. New compounds isolated included $Ph_3MH^+BBr_4^-$ (M = N, P), $Ph_3MBr^+BBr_4^-$ (M = P, As).

INTRODUCTION

While the solvent properties of liquid hydrogen fluoride[1] and chloride[2] have been relatively extensively studied, those of liquid hydrogen bromide and iodide have not been studied in as much detail[3]. The reactions previously reported in liquid hydrogen bromide and iodide have been restricted to base-acid reactions and solvolyses. In this paper, these have been extended to include redox reactions.

RESULTS AND DISCUSSION

This paper is concerned primarily with the reactions of the triphenyl derivatives of the group V elements, Ph_3M , M = N, P, As, Sb, Bi. The acid-base, solvolysis and some oxidation reactions of these compounds in liquid hydrogen chloride have been studied [4, 5]. The conductivities of the various solutions were measured. The preparative reactions studied can be divided into two categories, acid-base and redox reactions. In the acid-base reactions, boron tribromide was used as a solvoacid and in the redox reactions, bromine was employed as an oxidizing agent. Triphenylbismuthine was completely solvolysed and triphenylstibine partially solvolysed: analogous results were found in liquid hydrogen chloride [4].

$$Ph_3Bi + 3HBr \rightarrow BiBr_3 + 3C_6H_6$$
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The relative acidities of the hydrogen halides are HF < HCl < HBr < HI[6]. Liquid hydrogen bromide should be a somewhat more acidic solvent than liquid hydrogen chloride. A particular solvoacid in liquid hydrogen chloride would be expected to be somewhat weaker in liquid hydrogen bromide, and conversely a solvobase should be somewhat stronger. Comparison of acidic or basic strengths in the liquid hydrogen halide solvent systems is difficult due to the complex mode of ionization, including the formation of triple ions[7]. The conductivities will only give a rough idea of the relative strength of an acid or base in a particular solvent. The conductivities of the solvobases Ph_3M , M = N, P, As, in liquid hydrogen chloride and bromide (see table) are of similar magnitude and show the same trends.

Hydrogen bromide and iodide act as solvoacids in liquid hydrogen chloride and the HBrCl⁻ and HCll⁻ anions can be isolated from solution as their tetra-*n*-butylammonium salts [8].

$$n - Bu_4N^+HCl_2^- + HBr \rightarrow n - Bu_4N^+HClBr^- + HCl.$$

As expected, hydrogen chloride showed no acidic properties in liquid hydrogen bromide.

As hydrogen chloride would not interfere in any reaction, bromine can be generated in solution by the addition of chlorine.

$$Cl_2 + 2HBr \rightarrow Br_2 + 2HCl.$$

Chlorine is considerably easier to handle in a vacuum system than bromine, and has been used as a source of bromine in oxidation reactions.

In the solvolysis reactions of chlorine containing compounds observed, hydrogen chloride was formed in solution. The presence of ions in the reaction

$$Ph_3CCl + HBr \rightarrow Ph_3CBr + HCl$$

can be inferred from the relatively high specific conductivity of the saturated solution. Solvolysis of phosphorus pentachloride occurred forming the solvobase PBr₅, as PBr₄*Br⁻.

Triphenylamine dissolved in liquid hydrogen bromide to form a pale yellow brown solution. In liquid hydrogen chloride solution, the colour observed was either pale yellow or blue. The latter has been attributed to formation of the radical anion, Ph_3N^+ [6]. After removal of the solvent from solutions of Ph_3M (M = N, P, As), the free bases Ph_3N and Ph_3As and the protonated phosphine, $Ph_3PH^+Br^-$, were recovered at room temperature. Solutions of the bases Ph_3M were reacted with boron tribromide, and at room temperature $Ph_3NH^+BBr_4^-$, $Ph_3PH^+BBr_4^-$, and Ph_3AsBBr_3 were recovered.

$$Ph_3P + HBr \rightarrow Ph_3PH^+ + Br(HBr)_x^-$$

 $Ph_3PH^+ + Br(HBr)_x^- + BBr_3 \rightarrow Ph_3PH^+ + BBr_4^-$.

The salt $Ph_3AsH^+BBr_4^-$ may have been formed in solution and lost HBr on warming to room temperature. In similar reactions in liquid hydrogen chloride, using boron trichloride as a solvoacid, the analogous chlorine containing products were prepared [4].

Bromine is thermodynamically the strongest oxidizing agent that can exist in liquid hydrogen bromide, being a product of the oxidation of the solvent. In solutions of bases such as Ph₃P, two distinct oxidation reactions can

Compound	Conc'n (mole/%)	Specific conductance (µmho cm ⁻¹)	Molar conductance (cm ² mho mole ⁻¹)	Solvent
Ph	0.078	38,95	0.50	HBr
3	0.181	497	2.75	HBr
	0.22	1500	6.85	HCl [7]
Ph ₂ P	0.090	920	10.2	HBr
5	0.208	3051	14.7	HBr
	0.31	6510	21.1	HC1 [7]
			a (a	
Pn ₃ As	0.088	767	8.68	HBr
	0.204	5690	27.9	HBr
	0.20	7700	39.3	HCI [7]
ph ppr	0 1 2 2	1014	9 33	UB~
¹¹³ ¹ ² 2	0.122	1014	0.00	IID <u>r</u>
Ph_AsBr_	0.102	1281	12.5	HBr
3 2				
Ph ₃ CCl	0.15	5180	34.2	HC1 [7]
5				
Ph ₃ CBr	sat'd	1/8		HBr

Table 1. Conductivities in liquid hydrogen chloride and bromide

occur, oxidation of the cation, Ph₃PH⁺

$$Ph_3PH^+ + Br_2 \rightarrow Ph_3PBr^+ + HBr$$

or oxidation of the anion

$$Br^{-}(HBr)_{x} + Br_{2} \rightarrow Br_{3}^{-}$$

The oxidation of the cation occurred before oxidation of the anion as Ph₃PBr₂ rather than Ph₃PH⁺Br₃⁻ was the initial oxidation product isolated from solution. The salt Ph₃PBr⁺BBr₄⁻ was obtained either when a solution of Ph₃PBr⁺Br⁻ was treated with boron tribromide or from Ph₃P with bromine and boron tribromide. The analogous arsenic compounds Ph₃AsBr₂, Ph₃AsBr₄ and $Ph_3AsBr^+BBr_4^-$ were prepared similarly. The redox reactions in liquid hydrogen chloride of various phosphorus compounds such as Ph₃P with chlorine or bromine as oxidizing agents, has led to the isolation of Ph₂PCl₂, but in the bromine oxidation mixed products were obtained due to partial solvolysis [5].

The iodide ion can also act as a reductant, being oxidized by bromine

$$I^- + Br_2 \rightarrow IBr_2^-$$

The dibromoiodide ion was isolated as its tetra-*n*-butyl ammonium salt. The tetramethylammonium salt, $Me_4N^+IBr_2^-$, has been obtained from Me_4NI and Br_2 in liquid hydrogen chloride[9].

EXPERIMENTAL

Reagents were all available commercially and used as purchased except hydrogen bromide, which was purified by trap to trap distillation. The main preparative reactions were studied in sealed tubes, using about 1.5 mmole of reactant in approx. 4 ml of liquid hydrogen bromide. After allowing to equilibrate at room temperature, the cooled tube was opened, the excess solvent removed and the product isolated. Halide was analysed either gravimetrically or volumetrically by Volhard's method: the absence of mixed halides was inferred from the similarity of the results from both methods. High values for bromine in simple bromides may be due to the presence of small amounts of solvated bromide ions, Br(HBr)⁻. Boron was analysed volumetrically as its mannitol complex. Free halogen was determined from the amount of iodine liberated on addition to a potassium iodide solution and subsequent titration against thiosulfate. Conductivity measurements and conductometric titrations were examined as described previously[4]. IR spectra were recorded on a Perkin-Elmer 457 as mulls with Nujol and hexachlorobutadiene.

Triphenylamine dissolved readily in liquid hydrogen bromide, forming a pale brown solution, and was recovered on removal of the solvent (Found: m.p. 124°, lit. 126–8°[10]). Reaction of triphenylamine in solution with boron tribromide, allowed triphenylammonium tetrabromoborate, Ph₃NH⁺BBr₄⁻ to be isolated. Ph₃NH⁺BBr₄⁻, off-white; m.p. 129–130°; (Found: B, 2.0; Br, 56.3. Calc. for C₁₈H₁₆BBr₄N: B, 1.9; Br, 55.4%). The IR spectrum showed the presence of the BBr₄⁻ anion[11]. A yellow nonidentified solid which did not liberate bromide ion on hydrolysis was isolated after treatment of a triphenylamine solution with two moles bromine per mole Ph₃N.

Tetrabutylammonium chloride dissolved readily and Bu₄N⁺HBr₂⁻ was obtained after removal of the solvent. Bu₄N⁺HBr₂⁻: (Found: Br, 41.2 (Volhard), 41.1 (gravimetric): Calc. for C₁₆H₃₇Br₂N: Br, 39.6%). A conductometric titration of tetrabutylammonium bromide with hydrogen chloride showed no breaks and indicated that hydrogen chloride was not a solvoacid. Bu₄N⁺HBr₂⁻ was recovered: (Found: Br, 37.9; Calc. for $C_{1e}H_{37}Br_2N;\ Br,\ 39.6\%).$ In the bromine oxidation of tetrabutylammonium bromide and iodide, $Bu_4N^+Br_3^-$ and Bu₄N⁺IBr₂⁻ were formed. Bu₄N⁺Br₃⁻, yellow, m.p. 73-5°: (Found: moles free halogen/100 gm, 0.210: Calcd. for C16H36Br3N: moles free halogen/100 gm, 0.207). Bu₄N⁺IBr₂⁻, yellow, m.p. 66°: (Found: moles free halogen/100 gm., 0.183: Calcd. for $C_{16}H_{36}Br_2IN$: moles free halogen/100 gm., 0.189).

Triphenylphosphine formed a few pale brown solution from which triphenylphosphonium bromide was isolated after removal of the solvent. Ph₃PH⁺Br⁻, m.p. 195-6°, lit. 193°[12]: (Found: Br, 24.0. Calc. for C18H16BrP: Br, 23.3%). Hydrolysis gave triphenylphosphine. (Found: m.p. 76-8°, lit. 78-80°[10]). Triphenylphosphonium tetrabromoborate was obtained after reaction with boron tribromide. Ph₃PH⁺BBr₄⁻, white, m.p. 215°; (Found: B, 1.8; Br, 53.1. Calc. for C18H16BBr4P: B, 1.8; Br, 53.8%). Oxidation of triphenylphosphine with bromine mole ratio 1:1 or 1:2 (Ph₃P:Br₂) enabled slightly solvated Ph₃PBr₂ and Ph₃PBr₄ to be isolated. Ph₃PBr₂, yellow, m.p. 92-4°: (Found: Br, 39.2. Calc. for C₁₈H₁₅Br₂P: Br, 37.9%). Hydrolysis gave Ph₃PO: (Found: m.p. 156°, lit. 156-7°[10]). Ph₃PBr₄, orange, m.p. 103-5°, lit. 117°[13]: (Found: moles free halogen/100 gm, 0.165: Calc. for C18H15Br4P: moles free halogen/100 gm, 0.172). Bromotriphenylphosphonium tetrabromoborate, Ph₃PBr⁺BBr₄⁻, was obtained from either Ph₃PBr₂ and BBr₃ or Ph₃PBr₂ and BBr₃. Ph₃PBr⁺BBr₄⁻, pale yellow, m.p. 135-7°: (Found: B, 1.6; Br, 59.2: Calc. for $C_{18}H_{13}BBr_{5}P$: B, 1.6; Br, 59.4%).

Phosphorus pentachloride formed a bromine colored solution from which phosphorus pentabromide, identified as the only product from its infrared spectrum, was isolated.

Triphenylarsine was readily soluble, forming a colorless solution and was recovered on removal of the solvent. (Found: m.p. 57-60°, lit. 60.5-61.5°[10]). The boron tribromide adduct, Ph₃AsBBr₃, was isolated after reaction with boron tribromide Ph_3AsBBr_3 , was isolated after reaction with boron tribromide Ph_3AsBBr_3 , white, m.p. 175-6°: (Found: B, 2.0; Br, 42.5: Calc. for C₁₈H₁₅AsBBr₃: B, 1.9; Br, 43.1%). Oxidation with bromine, mole ratio Ph₃As:Br₂, 1:1 or 1:2, allowed Ph₃AsBr₂ and Ph₃AsBr₄ to be prepared. Ph₃AsBr₂, white, m.p. 229-230°, lit. 215°[14]. (Found: Br, 34.7: Calc. for C₁₈H₁₅AsBr₂: Br, 34.3%). Ph₃AsBr₄, orange, m.p. 91-2°, lit. 89°[14]. Bromotriphenylarsonium tetrabromoborate, Ph₃AsBr⁺BBr₄⁻, was isolated after the reaction of Ph₃As, Br₂ and BBr₃. Ph₃AsBr⁺BBr₄⁻, pale brown, m.p. 136-9°: (Found: B, 1.5; Br, 55.4; Calc. for C₁₈H₁₅AsBr₅: B, 1.5; Br, 55.8%). The IR spectrum showed the presence of the BBr₄⁻ ion[11].

Triphenylstibine was partially solvolysed forming $Ph_x SbBr_{3-x}$. The semi-solid product gave a positive test for halide after hydrolysis.

Triphenylbismuthine and triphenylmethyl chloride were completely solvolysed to BiBr₃ and Ph₃CBr respectively. BiBr₃, m.p. 218°, lit. 218°[10]. Ph₃CBr, m.p. 148-151°, lit. 152°[10].

Acknowledgement—The author wishes to thank the National Research Council of Canada for generous financial support.

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