690. *New Methods of preparing Polonium Metal.*

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Polonium metal has been prepared by the action of aqueous ammonia on polonium hydroxide and of anhydrous liquid ammonia on the hydroxide and some other polonium compounds. It can also be prepared by reducing polonium hydroxide with hydrazine, hydroxylamine, or sodium dithionite in alkaline solution and polonium tetrachloride with stannous chloride, titanous chloride, or sodium dithionite in hydrochloric acid.

THE usual methods of obtaining the metal from polonium compounds on the milligram scale have been by deposition on a supporting metal[1] or chemical precipitation,[2] followed by vacuum sublimation. Early trace-level work had indicated that reduction, presumably to the element, could be brought about by many reagents including hydrazine[3] (from alkaline solution) and stannous chloride[4] or titanous chloride[3] (from acid solution). These and other reducing agents have now been applied to polonium compounds on the milligram scale.

Quadrivalent polonium hydroxide in aqueous potassium hydroxide is reduced rapidly at laboratory temperatures by hydrazine, hydroxylamine, and the dithionite ion, and the black product is definitely the metal. On trace evidence sodium dithionite had been said[5] to give sodium polonide under a blanket of hydrogen at higher temperatures, but this would be difficult to confirm on the milligram scale owing to the intensely oxidising conditions associated with the α-bombardment from curie-level sources. By contrast, sulphite reduces alkaline quadrivalent polonium hydroxide only to the bivalent state, which rapidly reverts to the quadrivalent condition when the reagent is consumed.

In dilute hydrochloric acid, polonium tetrachloride is reduced by stannous chloride, titanous chloride, and sodium dithionite, in every instance to the metal, though in the last the product is contaminated with sulphur. Whether produced from acid or alkaline media, the metal is present in both the α- and the β-form, with the former predominating. This mixture of allotropes is consistent with recent findings[6] which indicate that the two forms co-exist over the temperature range 18—54°.

Strangely, and contrary to earlier reports[3] on the behaviour of trace polonium with formaldehyde in the presence of alkali, neither formic acid nor formaldehyde reduces quadrivalent polonium in either acids or alkalis.

A new route to the metal has been found as a result of our early observation that polonium hydroxide, left in contact with moderately concentrated aqueous ammonia, turns black. The product behaved like the metal in being converted into the quadrivalent hydroxide by prolonged treatment with aqueous potassium hydroxide. Analysis showed nitrogen to be absent and *X*-ray powder photography identified it as the mixture of the low- and the high-temperature form of the metal (70% of α-Po, 30% of β-Po) found previously. This reduction, however, took place only when the concentration of the ammonia was above 5N, and had an induction period which decreased as the concentration of the reagent increased. Furthermore, its inception was invariably at the centre of the particles of hydroxide, whereupon it spread outwards rapidly. With anhydrous liquid ammonia instead of the aqueous solution, the reaction appeared to be immediate.

Because of these interesting features this reaction was examined more closely. First it was shown that substituted ammonias also brought about the reduction and that the

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[1] Bagnall and D'Eye, *J.*, 1954, 4295.
[2] Bagnall and Robertson, *J.*, 1957, 1044.
[3] Guillot and Haissinsky, *Bull. Soc. chim. France*, 1935, **2**, 239.
[4] Marckwald, *Ber.*, 1902, **35**, 4239.
[5] Chlopin and Samartzewa, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 433.
[6] Goode, *J. Chem. Phys.*, 1957, **26**, 1269.

induction period progressively increased in the order $EtNH_2 < Et_2NH < Et_4N^+ < Et_4N{\cdot}OH$. The rate of reduction was always slower than with aqueous ammonia. The reaction went to completion with the first two, though it required 20 min. for liquid diethylamine, whereas the last two failed to reduce more than a small fraction of the polonium hydroxide even after 40 min. Secondly, it was shown that a previous irradiation of the aqueous ammonia by α-particles did not alter the characteristics of the reaction.

Neither aqueous ammonia nor a substituted ammonia behaves as reducing agent under the conditions of these experiments, and the phenomena must therefore be related to the α-radiation from the polonium. In evidence of this, tellurous acid, which is unaffected by aqueous ammonia, was rapidly reduced to tellurium when a suspension of polonium metal in aqueous ammonia was added to it.

It is not easy to decide on the reducing species produced by the α-irradiation, but the fact that 15M-ammonium hydroxide, which had been irradiated for 15 min. by α-particles from a curie source of polonium metal, failed to behave differently from the unirradiated reagent suggested that the reduction could not be ascribed to the radiolytic production of such stable compounds as hydrazine or hydroxylamine. Both of these reduce polonium compounds immediately in alkaline media. The nitrogen–hydrogen bond is not strong and hydrogen atoms may be expected from α-particle bombardment. Their life would be short in this medium but they seem to be the most probable reducing agent. They would be produced in decreasing proportions by a corresponding irradiation in passing from liquid ammonia to liquid diethylamine, in the order in which the rates of reduction fall. On these premises, reaction with triethylamine and tetraethylammonium hydroxide would not be expected and the slight slow reaction shown by these compounds may be due to adventitious, incompletely substituted ammonias, possibly formed by the α-bombardment. It is certainly significant that effective reduction takes place as long as the compound has a hydrogen bonded to a nitrogen atom.

Further experiments were carried out in which an aqueous suspension of polonium hydroxide was saturated with hydrogen, but no reduction was observed after 15 hr.: this may well be due to the low solubility of hydrogen in water and the consequent very low probability of a fruitful collision of an α-particle and a hydrogen molecule. It is also clear that the radiolysis of water and of the hydroxyl ion does not contribute to the reduction.

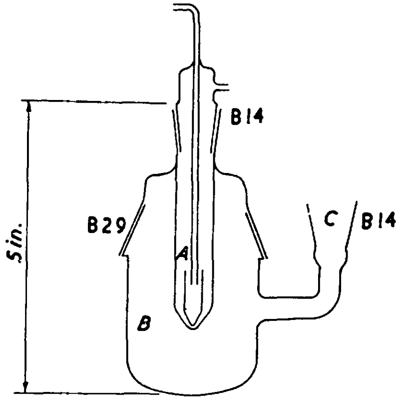
Atomic nitrogen was ruled out as an active agent since nitrogen atoms are more likely to combine with one another than with anything else.

The induction period is shorter, the greater the concentration of ammonia in the aqueous solution and is absent with liquid ammonia, which suggests that NH_3 is the species suffering disruption. It also suggests that before any reduction becomes noticeable a specific concentration of hydrogen atoms has to be reached which is first attained at the centre of the particle of hydroxide, where the α-particle radiation is greatest. Neither lead, the product of decay, nor polonium metal itself acts as a catalyst. There is, furthermore, no ground for supposing an intermediate step in the reduction, for bivalent polonium hydroxide is very much darker than the quadrivalent compound and the only colour change in the early stages of the reaction is in the other direction, owing presumably to dilution of the gel.

The state of the hydroxide or oxide also affects the rate of reduction; a specimen of the dioxide prepared by slow oxidation at room temperature gave the same induction period as the hydroxide, whereas another specimen consisting of larger crystals prepared at 450° gave a much longer induction period. The difference is probably due to the time required for the hydration of the high-temperature material. All this suggests that the induction period is simply a measure of the rate of penetration by the ammonia which will be faster when it is as discrete molecules than when it carries attached water molecules.

It seems fairly safe to assume that the reduction is due to α-particle radiolysis and that it will be much slower, if it takes place at all, with the longer-lived isotopes ^{208}Po and

^{209}Po. When these become available, the question will be readily answered. Nevertheless the present work provides two convenient methods of obtaining polonium metal on the milligram scale; they are (*a*) the spontaneous reduction of the hydroxide in concentrated aqueous ammonia, which is probably only applicable to ^{210}Po, and (*b*) the precipitation of the metal from 2N-hydrochloric acid by titanous chloride or stannous chloride, which is effective for all isotopes.



EXPERIMENTAL

All the work was carried out in glove-boxes.

Reagents.—Ammonia, from ammonium chloride and calcium hydroxide, was dried over soda lime. The amines were redistilled and the appropriate-boiling fractions collected.

Reactions with Liquid Ammonia.—The apparatus shown in the Figure was devised. The polonium compound was placed in a micro-cone in *A*, which was flushed out with dry ammonia gas, and then cooled in a liquid nitrogen bath. Dry ammonia gas was then passed into *A* until the tube was approximately one-quarter full of solid ammonia. The cooling bath was then removed and the section *A* fitted into the jacket *B* which was evacuated *via* the side-arm *C*, thus converting the apparatus into a transparent vacuum flask. The excess of ammonia was finally evaporated off after admission of air to the jacket (*B*), and the micro-cone transferred to a B14 socket drawn down to an *X*-ray capillary into which the contents of the micro-cone could be tapped out under vacuum.

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