726. *The Polonium Nitrates.*

By K. W. BAGNALL, D. S. ROBERTSON, and M. A. A. STEWART.

Polonium tetranitrate and two basic nitrates have been prepared and evidence for the existence of a nitrite has been obtained. The cation-exchange behaviour of polonium in nitric acid solution has been investigated.

THE only available data on the polonium–nitric acid system are Orban's solubility determinations [1] and some fragmentary information suggesting the probability of a basic nitrate from this laboratory.[2] Orban, who determined the concentration of polonium in the aqueous phase in contact with oxidised polonium on a platinum foil, found that the solubility of quadrivalent polonium in dilute nitric acid was extremely low, suggesting the formation of a basic salt. The higher solubilities at higher nitric acid concentrations indicate complex-ion formation. Some solubility determinations with carrier-free polonium made here were in fair agreement with Orban's, and it was of interest to attempt the analysis of the solid nitrate.

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[1] Orban, American report MLM-973, 1954.

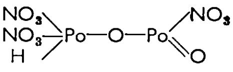
[2] Bagnall and D'Eye, *J.*, 1954, 4295; Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

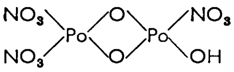
Preliminary experiments showed that solid polonium hydroxide or tetrachloride reacted immediately with dilute (0·1—2N) nitric acid to give a white, crystalline solid which readily decomposed to polonium dioxide under vacuum or on heating and was readily hydrolysed to the quadrivalent hydroxide. All attempts to analyse it failed and it is probably an unstable addition compound ($PoO_2,xHNO_3$). Both polonium hydroxide and tetrachloride, however, on long standing (12 hr.) in 0·5N-nitric acid, gave a white crystalline product which could be dried under vacuum at room temperature with only slight decomposition. In this compound, *A*, the ratio NO_3^- : Po = 1·5 : 1. The analyses of a similar yellowish-white product, *B*, formed by evaporating the solution obtained from polonium hydroxide and 2N-nitric acid to small volume and finally drying under vacuum, were less consistent, but indicated a ratio NO_3^- : Po = 0·5 : 1 analogous to the only known tellurium nitrate.[3]

The white product obtained by keeping polonium metal in air for 72 hr. or, more rapidly, in a mixture of nitrogen dioxide and oxygen, was found to have the same composition as *A*, the results being very consistent. The fixation of nitrogen by the α-bombardment supplied the nitrogen dioxide in the first method.

Compound *A* is readily decomposed by water, dilute aqueous potassium hydroxide, or dilute hydrochloric acid, giving the quadrivalent hydroxide or chloride. It decomposes to *B* below 100° and *B* decomposes to polonium dioxide at about 130°; attempts to determine the decomposition temperature accurately were frustrated by the slow spontaneous decomposition of the compound under the intense α-bombardment. Both *A* and *B* yield polonium metal by way of the dioxide on long standing in a stream of dry nitrogen or under vacuum. *X*-Ray powder photographs of these compounds have not yet had sufficient definition to provide any information about their structure. Indeed, by the nature of the materials, such evidence may always fall short of that required to justify an unequivocal statement. As further work is likely to be postponed, it may be useful to put forward some tentative conclusions.

Both compounds probably have a dimeric (or polymeric) oxygen-bridge structure, for, as a monomer, *A* could be represented as (I) or (II), in which one would expect a single nitrate ion to be eliminated as nitric acid on heating, rather than a pair of nitrate ions as nitrogen dioxide and oxygen. A more probable structural unit appears to be (III) or (IV) with the latter, which is symmetrical, as the most likely.


(I)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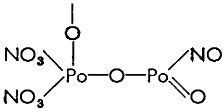
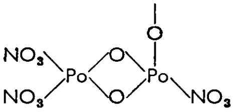

(III)


(IV)

White crystalline compounds were also obtained by the action of aqueous M-potassium nitrate or nitrite on solid polonium tetrachloride. These are presumably a polonium nitrate and a nitrite; they could not be analysed owing to the difficulty of removing the excess of reagent and because both were converted into the quadrivalent hydroxide on standing in contact with an excess of the aqueous reagent for a few hours.

The reactions of polonium dioxide and polonium tetrachloride with liquid dinitrogen tetroxide were then investigated. The white product thus formed was the tetranitrate, $Po(NO_3)_4$, with at least one molecule of dinitrogen tetroxide of crystallisation. The tetranitrate is almost insoluble in liquid dinitrogen tetroxide and is very easily hydrolysed. The N_2O_4 of crystallisation was partially lost when the preparation was freed from excess of dinitrogen tetroxide under vacuum and the remainder very soon on standing at room temperature in dry air. The tetranitrate slowly decomposes in air at room temperature giving the basic salt *A*, the conversion being complete in $1\frac{1}{2}$—2 hr. under vacuum (15 μ).

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[3] Norris, according to Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green & Co., London, 1931, p. 119.

It is noteworthy that polonium dioxide, after being heated above 250°, scarcely reacts with either gaseous or liquid dinitrogen tetroxide and the metal fails to react at all with either the liquid or its solution in ethyl acetate.

Ion-exchange Data.—The cation-exchange behaviour of polonium in dilute nitric acid showed a trend similar to that observed in the solubility curve.[1] The distribution ratio, K_r, defined as the concentration of polonium/g. of resin divided by the concentration of polonium/ml. of solution, decreases markedly as the acid concentration increases (see Table).

	$[HNO_3]$ (N)	0·1	0·2	0·4	0·6	0·8	0·9	1·0	2·0	8·0
Resin	Zeo-Karb 225 40/60 mesh (K_r)	366	126	42	28	9·9	7·0	6·5	3·2	$\sim$0
	Amberlite IR-120(H) 40/60 mesh (K_r)	—	—	16·1	10	—	6	—	5	—

The results were not very reproducible owing to radiation damage to both solvent and resin, and it is not possible to draw any definite conclusions concerning the nature of the ionic species in the solutions.

EXPERIMENTAL

All the experimental work was carried out in glove-boxes.[2]

Preparative.—Specimens made by the action of dilute nitric acid on the solid tetrachloride or hydroxide were allowed to stand in contact with the acid before being dried for analysis; the best results were obtained with amounts of polonium in the range 200—400 μg. of ^{210}Po; analyses of larger specimens were usually very much less consistent, probably owing to radiation damage. The most consistent analytical results were obtained with specimens prepared by the action of oxygen–nitrogen dioxide mixtures on the metal, but the method is very slow if thick layers of metal are used. The optimum is 100—150 μg. of ^{210}Po. The reaction of polonium dioxide or tetrachloride with liquid dinitrogen tetroxide is complete in about 4 hr.

Liquid dinitrogen tetroxide was prepared by heating lead nitrate, drying the evolved gases with phosphoric oxide, and condensing them in a cooling bath.[4]

Analytical.—The main problem in the analysis of sub-milligram amounts of the nitrates lay in the removal of the excess of nitric acid. A preparation carried out with 1 curie (222 μg.) of ^{210}Po would contain 4×10^{-6} g.-ions of nitrate if a tetranitrate were formed and it was therefore necessary to reduce the excess of nitrate-ion content to below 10^{-7} g.-ion, equivalent to 5×10^{-5} ml. of 2N-nitric acid, which was used for some preparations. It was soon found that insufficient of the excess of nitric acid could be eliminated by centrifugation through a number 3 porosity filter pad and that washing with dry acetone was ineffective, while washing with water led to hydrolysis.

The preparations were then dried for 25 min. at 130—150°c, but this yielded only the dioxide; in the course of these analyses it was found that the correction to be applied for the fixation of nitrogen by the α-bombardment of air in alkaline solution was quite small. Vacuum-drying at 50° also led to decomposition. It was finally found that little decomposition occurred if the preparation, together with its excess of nitric acid, was frozen and then dried under vacuum (15 μ) at room temperature for 20 min. Blank runs with nitric acid only showed that this procedure eliminated it all.

The dried polonium nitrate was then decomposed with 0·5N-potassium hydroxide (0·5 ml.); the low hydroxide concentration is necessary to avoid loss of the polonium into the aqueous solution as polonite.[5]

The insoluble polonium hydroxide was then filtered off on a number 3 porosity filter stick and dissolved in 2N-hydrochloric acid for assay by α-counting. The filtrate, containing the nitrate ion for analysis, was transferred to a Conway micro-diffusion cell for final acidimetric assay as ammonia.[6] An " Agla " micro-burette was used for the final titration with 0·02N-hydrochloric acid. All the analytical preparations were carried out in groups of three, together with a fourth " blank " preparation in which all the reactions were carried out without polonium.

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[4] Bagnall, Robinson, and Stewart, *J.*, 3426.

[5] Bagnall and Freeman, *J.*, 1957, 2161.

[6] Conway, "Microdiffusion Analysis and Volumetric Error," Crosby Lockwood and Son, Ltd., London, 1947, p. 85.

Qualitative experiments showed that a part of the nitrate ion was reduced to nitrite by the α-bombardment during the separation for analysis.

Ion Exchange.—A known quantity of the resin (50—100 mg.) was equilibrated with acid of the same concentration as that to be used in the exchange experiment. The excess of acid was then removed and the polonium solution (100—250 mc/5 ml. of acid) was added, and the solution and resin stirred by means of an air-pulsed agitator.[7] Sampling showed that equilibrium was attained in 1½—2 hr. The concentration of polonium in the resin was calculated from the decrease in concentration of polonium in the aqueous phase. It was not possible to determine the distribution ratio of the polonium between the resin and fresh batches of acid owing to the decomposition of the resin by radiation.

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[7] Bagnall and Miles, *J. Sci. Instr.*, 1953, **30**, 172.