

QUATERNARY ARSONIUM SALTS AND THEIR METALLIC CO-ORDINATION COMPOUNDS.

PART II. CADMIUM.

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Following on the investigation of the use of the quaternary arsonium iodides for the micro-detection of bismuth, reported in a previous communication, it was decided to examine the possibility of using them in a similar capacity for cadmium.

The micro reagents for the detection of cadmium depend either upon the formation of sparingly soluble complexes of the type R_2CdI_4 , for which allyl iodide hexammine (Evrard, 1929), β -naphthoquinoline (Berg and Wurm, 1927), phenyl trimethyl ammonium iodide (Pass and Ward, 1933) and ferrous 2, 2' dipyridyl (Feigl, 1943) have been suggested; the formation of coloured cadmium hydroxide lakes with diphenyl carbazide (Feigl and Neuber, 1923), its nitro derivative (Heller and Krumholtz, 1929), or p-nitrobenzenediazoaminoazobenzene (Dwyer, 1937); or finally the precipitation of the sparingly soluble salt of 3-nitro-4-hydroxy-phenyl arsonic acid (Pavelka and Kolmer, 1930). The iodide complexes will not in general detect less than 10 γ of Cd/ml., while some are less sensitive, and interference occurs with antimony, bismuth, lead, mercury, silver and copper, owing to the formation of similar complexes or the precipitation of the iodide of the metal. Among the cadmium hydroxide lakes, p-nitrobenzenediazoaminoazobenzene is by far the most sensitive, but does not lend itself to quantitative estimation, and may be regarded as too sensitive for normal analytical work.

The arsonium reagents described in this paper, whilst they also depend on the formation of complex iodides and hence suffer from the usual interference by the other metals, have the advantage of being extremely insoluble, in most cases, and in the best two reagents are twenty times as sensitive as those previously available.

As in the case of bismuth, two series of methyl aryl tetraiodo cadmium compounds have been prepared, and the effect of the substituent groups in the arsonium radical on the properties of the resultant compounds studied, with special reference to the sensitivity of the reaction.

The latter two members of both the phenyl and p-tolyl series are insoluble in water, while the first member of each series is sparingly soluble in cold water and readily soluble in hot. The compounds are soluble in hot acetone and alcohol and may be crystallised in white monoclinic plates.

In both series the melting points first fall, then rise, as the molecular weights increase.

The sensitivity of the reagents increased with the molecular weight, owing to the fact that it depended on one factor only, namely the solubility of the co-ordination compound, which decreased as the molecular weight increased.

During the examination of the sensitivity of the reaction, it was noted that cadmium could be estimated by turbidometric comparison with solutions of known cadmium concentrations in the presence of ten thousand times the amount of zinc.

The highest sensitivity obtained was 0.2 γ /ml. with p-tolyl₃ MeAsI, which is considerably higher than any reagent with the exception of p-nitrobenzene-diazoaminoazobenzene. Since the compounds contain less than 10% Cd, and since at concentrations of the order of 10 γ Cd/ml. the complexes are formed as very fine suspensions which coagulate very slowly, it is proposed to investigate the compounds for the gravimetric and nephelometric estimation of cadmium, for which suitable reagents are still required.

EXPERIMENTAL.

Bis triphenylmethylarsonium tetra-iodo cadmium. (C₆H₅)₃MeAsI (1 gm.), potassium iodide (1 gm.) and sulphuric acid (0.5 ml.) were dissolved in water (400 ml.) with warming. To this solution was added in a thin stream with stirring, a solution of cadmium sulphate (equivalent to 0.1 gm. of cadmium). The arsonium tetra-iodo compound separated as a fine white milky precipitate, which coagulated on continued stirring, leaving the supernatant liquid quite clear and colourless. The crystalline compound was filtered quite readily with suction, washed twice with 100 ml. of N/2 hydrochloric acid, then with distilled water, dried with suction and finally in the desiccator over calcium chloride.

The compound was not hydrolysed by boiling with water, but hot N/2 ammonium hydroxide decomposed it chiefly to diammine cadmium iodide.

The compound was analysed as follows: The iodine was estimated by the method of Dwyer and Nyholm (1942). Arsenic was estimated by fuming with sulphuric acid and potassium nitrate to remove organic matter. Traces of nitrous acid were removed with urea, and the arsenic acid, after reduction with sulphurous acid, estimated in the usual way with iodine. Cadmium was estimated by electrolysis from a cyanide solution after removing organic matter as before.

The other compounds (Table 1) were prepared and analysed similarly.

Found: As=10.8%; Cd=8.36%; I=39.5%. Calculated for ((C₆H₅)₃(CH₃)As)₂(CdI₄): As=11.1%; Cd=8.36%; I=40.2%.

Sensitivity. The cadmium solutions were prepared from purified 3CdSO₄ · 8H₂O prepared as a stock solution containing 1,000 γ Cd/ml. which was 1N with respect to H₂SO₄. This solution was diluted as required with distilled water.

TABLE 1.

Compound.	Melting Point.	Iodine Found.	Iodine Theoretical.	Sensitivity. γ Cd./ml.
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄) ¹	189° C.	49.5%	50.1%	200.0
((C ₆ H ₅) ₂ (CH ₃) ₂ As) ₂ (CdI ₄)	173° C.	44.4%	44.6%	0.7
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	179° C.	39.5%	40.2%	0.3
((C ₇ H ₇) ₃ (CH ₃)As) ₂ (CdI ₄)	188° C.	47.9%	48.7%	200.0
((C ₇ H ₇) ₂ (CH ₃) ₂ As) ₂ (CdI ₄)	128° C.	41.7%	42.5%	0.7
((C ₇ H ₇) ₃ (CH ₃)As) ₂ (CdI ₄)	203° C.	37.0%	37.8%	0.2

Where C₇H₇=the p-tolyl radical.
C₆H₅=the phenyl radical.

¹ Burrows and Turner (1921).

SUMMARY.

The use of quaternary arsonium iodides for the micro-detection of cadmium has been investigated, and it has been shown that these compounds can be used to detect cadmium in a concentration of less than 1 γ of cadmium per millilitre of solution, tri-p-tolylmethylarsonium iodide giving a reaction down to 0.2 γ

Cd/ml. The reaction may be used in the presence of large amounts of zinc, which does not interfere.

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