615. *The Preparation and Properties of Tungstoarsenic*(III) *Acid.*

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Arsenic(III) forms a heteropolyacid with tungsten(VI). This acid forms an ether-addition compound, which is unstable in aqueous solution but apparently stable in strong acid solutions. Analysis indicates that the complex anion is $(As_2O_3,6WO_3)_x$; the molecular weight is about 7000, in several solvents.

Arsenic(V) forms normal 12-heteropolytungstoarsenates with tungsten. Arsenic(III), however, does not. Rosenheim and Wolff[1] prepared potassium salts, $7K_2O(As_2O_3,18WO_3),24H_2O$, by the addition of arsenious oxide to a boiling solution of sodium tungstate in hydrochloric acid, concentrating the solution, and precipitating the salt with concentrated potassium chloride solution. Guanidine and ammonium salts were also prepared. Preliminary experiments showed that a variety of compounds could be prepared by Rosenheim and Wolff's method by varying the initial content of arsenious oxide and the acidity of the solution. However, extraction with ether and 12N-sulphuric acid gave an ether-addition compound which contained both arsenic(III) and tungsten(VI). The present investigation was to determine the nature of the heteropolyacid formed by analytical and molecular-weight determinations. Light-scattering measurements were used since the acid ionised in polar solvents and was insoluble in most non-polar solvents. Also this technique had been used [2-4] to determine the molecular weight of tungstosilicic acid and isopolytungstates with marked success.

Experimental

The tungstoarsenic(III) acid was prepared by dissolving arsenious oxide (15 g.) in boiling aqueous sodium tungstate (30 g./l.). The solution was cooled, saturated with ether, and slowly acidified with 12N-sulphuric acid, with stirring, until the ether-addition compound began to form. The mixture was then decanted and set aside for 12 hr. The addition compound was purified by filtration; solutions of the acid were prepared by adding the ether-addition compound to the required solvent and warming gently.

The tungstoarsenic(III) acid and its salts were analysed as follows: The compound was heated with sodium hydroxide solution and the pH then adjusted to 10 with sodium phosphate–phosphoric acid. Arsenic(III) was estimated by titration with standard iodine solution, with starch as indicator, or by titration with standard potassium permanganate solution, with potassium iodide as catalyst (in acid solution). The tungsten content was found by precipitation with cinchonine hydrochloride in acid solution and ignition to tungsten trioxide. Water was estimated by difference.

The light-scattering measurements were made with a SOFICA instrument, based on an original design due to Wippler and Scheibling.[5] The intensity of light at 5461 Å, scattered at right angles to the incident beam, was measured, for a series of solutions of decreasing concentration, with reference to that from a glass cylinder which had previously been calibrated against very pure benzene. Measurements at 45° and 135° to the incident beam were also made to check the absence of dust. Solutions and solvents were clarified by filtration through No. 5 sintered-glass filters directly into the measuring cells. The rate of change of refractive index with concentration (dn/dc) was measured with an Abbé refractometer for fairly concentrated solutions. The errors in this measurement are probably the limiting factors in the molecular-weight determinations. The theory of light scattering[6] leads to the expression

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[1] Rosenheim and Wolff, *Z. anorg. Chem.*, 1930, **193**, 66.

[2] Johnson, Kraus, and Scatchard, *J. Phys. Chem.*, 1960, **64**, 1867.

[3] Kronman and Timasheff, *J. Phys. Chem.*, 1959, **63**, 629.

[4] Bettinger and Tyree, *J. Amer. Chem. Soc.*, 1957, **79**, 3355.

[5] Wippler and Scheibling, *J. Chim. phys.*, 1954, **51**, 201.

[6] Zimm, *J. Chem. Phys.*, 1948, **16**, 1093.

$kc/I = (1/M) + (2Bc)$ for the molecular weight (M) of a solute in terms of the intensity of light scattered by solutions of the solute, where I is the intensity scattered by a solution, of concentration c (g./ml.), minus the intensity scattered by the solvent, B is the second virial coefficient and $k = [2\pi^2 n_1^2(\mathrm{d}n/\mathrm{d}c)^2 I_1]/(\lambda_0^4 N R_1)$ (R being the Rayleigh ratio and subscript 1 referring to benzene). The equation is rigorously correct for two-component systems [7] and can be extended. In most of the systems examined, mineral acid was added to suppress ionisation of the tungstoarsenic(III) acid. To a first approximation any change in light scattering due to the mixed solvent is allowed for by subtracting the scattering due to solvent from that due to solution, provided there is little preferential solvation of the solute by one component of the solvent.

RESULTS

In the preparation of the tungstoarsenate(III) ether-addition compounds, different quantities of arsenious oxide were added to sodium tungstate solution (30 g./l.) (see Table 1).

Immediate titration of a tungstoarsenate(III) solution in 2N-hydrochloric acid with standard potassium permanganate gave a value for arsenic(III) which was only 2% of that obtained after decomposition of the complex anion with sodium hydroxide, acidification, and titration. This suggested that the arsenic was almost completely complexed to the tungsten. The concentration of arsenic(V) was 1·5% of the total arsenic content, determined by estimating the amount of arsenic(V) before and after oxidation with potassium bromate solution.

TABLE 1.

As_2O_3 added (g.)	50	25	20	15	12½	10	9	8	7	6
As_2O_3 (% by wt.)	11·65	11·31	11·18	11·20	10·10	11·00	11·00	10·00	9·15	6·79
WO_3 (% by wt.)	75·11	77·25	77·00	77·86	77·48	77·53	76·84	75·25	74·70	74·60
WO_3/As_2O_3 (molar) ...	5·49	5·82	5·88	5·94	6·53	6·01	5·95	6·41	6·97	9·36

The tungstoarsenic(III) acid appeared to decompose slowly in aqueous solution. Titration with permanganate of samples which had been kept for more than 5 min. indicated a higher concentration of free arsenious acid.

Precipitation of the barium, guanidine, and pyridine salts of freshly prepared tungstoarsenic(III) acid, gave compounds or mixtures of compounds which had a lower arsenic to tungsten ratio (Table 2). These salts were precipitated from solutions whose pHs were around 2, 3, and 6. All the tungsten was precipitated, leaving free arsenious acid in solution. Attempts to purify the compounds by recrystallisation resulted in further hydrolysis of the tungstoarsenate(III) anion. The complex appeared to be more stable in strongly acid solution, but no salt other than of cinchonine could be precipitated (Table 2).

TABLE 2.

Ratio As : W.

Salt	2N	pH2	pH3	pH6
Cinchonine	1 : 3·0, 1 : 3·1, 1 : 3·0			
Barium		1 : 4·4	1 : 6·0	1 : 9·3
Guanidine		1 : 4·2	1 : 6·1	1 : 9·8
Pyridine		1 : 4·2	1 : 6·0	1 : 9·0

Since water obviously hydrolysed the complex, salts were prepared from ethanolic solutions. Four pyridine salts were precipitated. Their arsenic to tungsten ratios were found to be 1 : 3·4, 1 : 3·5, 1 : 3·5, 1 : 4·0, suggesting that a little decomposition had also occurred in ethanolic solution.

The anionic nature of the complex was confirmed by passing a freshly prepared solution of tungstoarsenic(III) acid through a cation-exchange resin; the arsenic and the tungsten content of the solution were not altered.

The addition of arsenious oxide altered the curve obtained for the potentiometric titration of sodium tungstate solution with hydrochloric acid (Fig. 1). The region of slow pH change, due to the formation of the paratungstate ion, was much shortened, indicating that even at pH 7 some complex formation was taking place.

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[7] Mazur, *Adv. Chem. Phys.*, 1958, **1**, 309.

The ether-addition compound of the tungstoarsenic(III) acid was analysed on the thermogravimetric balance. For every arsenic atom present, 5 moles of ether were lost between 60° and 150°, and two moles of water between 260° and 320°. This water could have been water of hydration or water produced in the decomposition of the oxide lattice.

The results of light-scattering measurements are recorded in Fig. 2 as plots of kc/I against concentration for various solvents. (I was the intensity scattered at 90°.) The units for k are so chosen that the reciprocal of kc/I at $c = 0$ gives the molecular weight directly. The curves obtained in the presence of added electrolyte all extrapolate linearly to molecular-weight values in the region of 7,000. The molecular weight obtained is an average value for all solute species present (in this case, the weight average molecular weight).

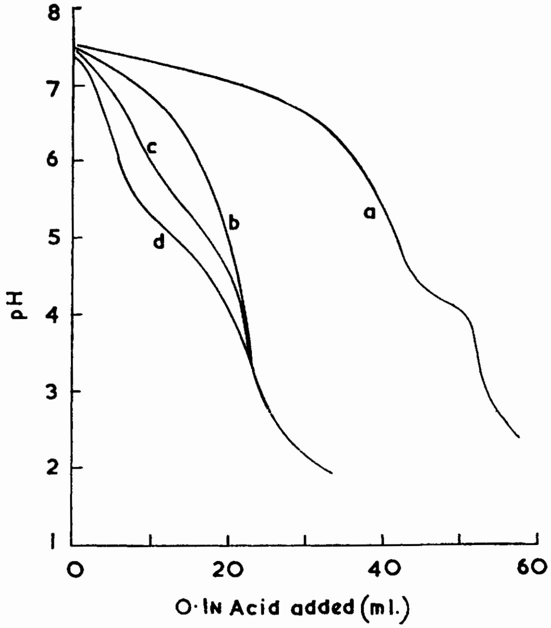

FIG. 1. Potentiometric titration with 0·1N-hydrochloric acid of (a) 0·1M-sodium tungstate; (b) 0·1M-sodium tungstate + 0·033M-arsenious oxide; (c) 0·1M-sodium tungstate + 0·1M-arsenious oxide; (d) 0·1M-sodium tungstate + 0·3M-arsenious oxide.

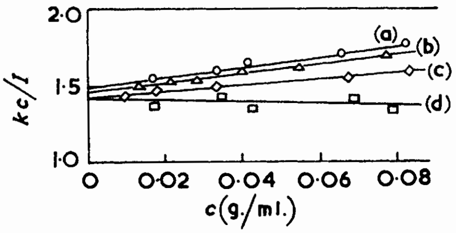

FIG. 2. Molecular-weight determinations of tungstoarsenic(III) acid in (a) n-propanol + 2N-sulphuric acid; (b) water + 2N-sulphuric acid; (c) ethanol + 2N-sulphuric acid; (d) dimethyl sulphoxide + 2N-sulphuric acid.

DISCUSSIONS

An As : W ratio of 1 : 3 in preparations formed from solutions initially of various As : W ratios suggests combination between one $As(OH)_3$ molecule and a trimeric tungstate group, for which evidence exists [3] as an intermediate in the formation of the hexatungstate ion. That the initial tungstate group is a lower polymer than the hexatungstate ion is also suggested in the method of preparation. After dissolution of the arsenious oxide in the sodium tungstate solution, the pH of the solution was around 8. This solution could then be acidified directly with 12N-sulphuric acid without further heating to form the ether-addition compound.

Little is known about the nature of arsenites in aqueous solution. However, the As(III)–O–As(III) link can apparently be hydrolysed easily as no polyanion in solution similar to the polyphosphates has been described. Thus, the tungstoarsenic(III) anion must be held together by –W–O–W– links with the arsenic atoms linked through oxygen to the tungsten or by –W–O–As–O–W– links. The compound is acidic and ionises in ethanol and in dimethyl sulphoxide, although with little apparent decomposition. In aqueous solution, however, ionisation appears to be accompanied by hydrolysis and the anion decomposes in weak acid solution. Light-scattering measurements suggest a molecular weight around 7000; if this represents an actual species the molecule could have the formula $(As_8W_{24}O_{100})H_{32},xH_2O$ giving a molecular weight of over 6650—the actual value depending on the number of associated water molecules. Although the molecular weights obtained in a wide variety of solvents were of the same order, this could have been due to the fact that the tungstoarsenate(III) was prepared in the same way. However, whatever the actual structure, the tungstoarsenic(III) acid is polymeric in aqueous acid solution and in this it differs from the 12-heteropolytungstates which, however, it resembles in its method of preparation through an ether-addition compound.

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