CXCII.—*Complex Acid Tungstates.*

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THE primary object of this research was to investigate the properties of that series of acid tungstates described by Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2027; *Chem. News*, 1924, **129**, 198, 207, 224, 257, 286) as 4 : 10 salts, *i.e.*, salts of composition $4R_2O,10WO_3,xH_2O$. The sodium salt, prepared by the method recommended by Smith, and the potassium and barium salts derived from it, did not give analytical results in accordance with the above formula, and from their appearance and behaviour they were suspected to be identical with the paratungstates.

Many types of acid tungstate have been described, but few have been accurately investigated; hitherto, the existence of the para-tungstates only, in which the ratio $R_2O : WO_3$ is 5 : 12 or 3 : 7, has been established, and the constitution of these and their relation to the normal tungstates still remain in doubt. Exact analysis of the salts is difficult owing to the ease with which they undergo partial dehydration in air and hydrolysis in presence of water; also, owing to the high atomic weight of tungsten, the differences in tungsten

content of salts designated as 3 : 7, 5 : 12, 4 : 10, 9 : 22, etc., are very small. In determining the composition of the hydrated salts, the value of the ratio WO_3/R_2O was found to be a more trustworthy guide than the actual percentage of tungsten.

Gibbs (*Amer. Chem. J.*, 1879, **1**, 217), by the action of acetic acid on normal sodium tungstate, obtained products which he described as 4 : 10, 9 : 22, and 5 : 12 salts. Smith (*loc. cit.*) considered the products to be mixtures of 4 : 10 and 5 : 12 salts, but by the use of formic acid claimed to produce the 4 : 10 salt only.

The solubility in water of sodium paratungstate has been little investigated. Forcher (*Sitzungsber. K. Akad. Wiss. Wien*, 1862, **44**, 164) stated that 1 part of the salt dissolves in 12·6 parts of water at 22°, whilst Marignac (*Compt. rend.*, 1862, **55**, 888) stated that 1 part dissolves in 12 parts of " cold " water. Smith (*loc. cit.*) gave the solubility of his 4 : 10 salt as 19 parts of salt in 100 parts of water at " room " temperature.

The solubility of the sodium salt obtained by the formic acid method has now been accurately determined between 0° and 102°. The results at lower temperatures are in accord with Forcher's and Marignac's statements, but much lower than Smith's value, and a salt of such solubility could not be obtained by the author.

EXPERIMENTAL.

Sodium Salt.—50 G. of A. R. sodium tungstate, $Na_2WO_4,2H_2O$, were dissolved in 55 c.c. of water at boiling point. Formic acid was run into the hot solution until the latter was just acid to litmus. Before the neutral point is reached the solution turns distinctly yellow. The total amount of formic acid added is slightly more than is theoretically required to form the 4 : 10 salt. Momentary precipitation of tungstic acid occurs only towards the end of the titration. The solution kept over-night deposits white, oblique, hexagonal crystals, which appear to be monoclinic. The product after being washed with cold water was recrystallised from hot water, and the crystals were drained on a porous tile and dried between absorbent paper at a pressure of 4 lb. per sq. in.

The tungstic oxide in the product was estimated by conversion into tungstic acid by evaporation with hydrochloric and nitric acids (2 : 1). After dilution and addition of cinchonine hydrochloride, the mixture was heated below boiling for ½ hour, filtered through filter-paper pulp, and washed free from alkali. The residue and pulp were gently ignited in a platinum crucible, and the resulting tungsten trioxide weighed. The colour of the ignited trioxide was regarded as an index of its purity, and when necessary, reprecipitation was resorted to. The total water content was obtained by

gentle ignition in a platinum crucible; the salt fuses to an orange-coloured liquid which sets to a pale yellow solid and finally becomes white on cooling. This residue is difficultly soluble in hot water. The sodium oxide was determined by difference.

	Found.		Calc. for	
	(a).	(b).	$4Na_2O,10WO_3,23H_2O.$	$5Na_2O,12WO_3,28H_2O.$
WO_3	77·42	77·50	77·79	77·37
H_2O	13·90	13·83	13·89	14·02
Na_2O	8·68	8·67	8·32	8·62
WO_3/Na_2O	8·919	8·939	9·354	8·986

The salt effloresced rapidly in dry air, as much as 8·9% of water being lost after 3 days.

According to Smith, only one acid tungstate is produced by this method. In order to test this and further to determine the WO_3/Na_2O ratio, the first crop of crystals obtained after a few hours was removed from the solution, a second crop was removed after a further 24 hours, and finally the mother-liquor was evaporated to dryness and the residue well washed with cold water. The three products were then recrystallised once, the total yield being about 60% of the sodium tungstate taken. In the analysis both tungsten and sodium were estimated, the latter as sulphate.

Crop.	WO_3, %.	Na_2O, %.	H_2O (by diff.), %.	WO_3/Na_2O.
1	77·89	8·69	13·42	8·963
1	77·49	8·56	13·95	9·051
2	77·65	8·75	13·60	8·873
3	77·52	8·97	13·51	8·638
3	79·27	8·83	11·90	8·985

The last sample was a specimen which had been kept for 8 months and was partially dehydrated. It is obvious that the products consist of the 5 : 12 salt. The fact that the water content is slightly below that required by $5Na_2O,12WO_3,28H_2O$ is due to the tendency to efflorescence.

Numerous dehydration experiments were performed in order to determine the loss under various conditions. Specimens of the salt, some of which had been recrystallised 5 times, were carefully dried without unnecessary exposure to air and then ignited to fusion. The following losses resulted : 13·96, 14·03, 13·94, 14·07, 13·96, 13·99; mean 13·99%. At 105° the losses were : 10·62, 10·37, 10·29, 10·45; mean 10·43% (corresponding to 17·14 out of 23 mols. or of 20·87 out of 28 mols.). These figures may equally well represent a loss of 17 out of 23 molecules, or of 21 out of 28 molecules. The conclusion that the expelled molecules are held in essentially different combination from the remaining molecules is scarcely justified, however, since similar experiments at 110° resulted in a loss of : 11·63, 11·45, 11·63% (corresponding to 19·02 out of 23 or of 23·15

out of 28 mols.), and at 160°, of 12·01% (corresponding to 19·73 out of 23 or of 24·03 out of 28 mols.).

In a vacuum desiccator after 6 days the loss was 8·77, 9·24, 9·15, 9·07 ; mean 9·06% (*i.e.*, 14·9 out of 23 or 18·1 out of 28 mols.), and it was possible completely to dehydrate the salt by this means. On addition of water to the anhydrous salt, considerable evolution of heat occurred.

Sodium paratungstate was next prepared by the addition of hydrochloric acid (1 : 1) to a solution of normal sodium tungstate heated to boiling, until the solution became permanently yellow but not quite neutral. After each addition of acid, it was necessary to agitate the liquid in order to redissolve the precipitated tungstic acid. On keeping, well-defined crystals were obtained, which on recrystallisation yielded hexagonal plates similar to those obtained with formic acid. First, second, and third crops of crystals were obtained as described for the previous salt, and after one recrystallisation were carefully dried and analysed.

Crop.	WO_3, %.	Na_2O, %.	H_2O (by diff.), %.	WO_3/Na_2O.
1	77·74	8·45	13·81	9·196
1	77·53	8·35	14·12	9·287
2	77·65	8·54	13·81	9·089
3	77·53	8·80	13·67	8·812

It will be observed that the WO_3/Na_2O ratio, although in accordance with the 5 : 12 ratio, is less accurately so than in the case of the salt prepared by means of formic acid.

The two salts behaved similarly on dehydration. A specimen of each after 5 recrystallisations was finely ground, dried for 24 hours between absorbent paper under 4 lb. pressure, and then heated to constant weight at (*a*) 105° and (*b*) 110°, about 7 hours being required in each case. The losses were as follows :

(*a*) 10·45%, (*b*) 11·50%, for the formic acid product,

(*a*) 10·47%, (*b*) 11·52%, for the hydrochloric acid product.

There was no evidence of any change in composition taking place during the recrystallisation, and the crystalline forms of the products appeared to be identical.

Potassium Salt.—The potassium salt was next prepared by fusing together anhydrous potassium carbonate and tungsten trioxide in molecular proportion to yield $4K_2O,10WO_3$, the residue being extracted with hot water and the solution made slightly acid with formic acid. After concentration, a poor yield of crystals was obtained of composition : WO_3, 80·58; H_2O, 5·81; K_2O, 13·61%; $WO_3/K_2O = 5·921$.

By addition of aqueous potassium chloride to a solution of the sodium salt (formic acid product), a copious white crystalline pre-

cipitate was immediately formed. This was separated, washed with cold water, dried, and analysed :

	K_2O, %.	WO_3, %.	H_2O, %.	WO_3/K_2O.
Found for Sample 1	13·63	80·50	5·87	5·906
,, ,, 2	13·35	80·62	6·03	6·048
Calc. for $4K_2O,10WO_3,8H_2O$ ...	13·26	81·67	5·07	6·160
,, $4K_2O,10WO_3,9H_2O$ ...	13·18	81·15	5·67	6·157
,, $4K_2O,10WO_3,10H_2O$ ...	13·10	80·64	6·26	6·154
,, $5K_2O,12WO_3,11H_2O$ ...	13·64	80·62	5·74	5·910

Thus, again, the product is the 5 : 12 salt, as also is that obtained by fusion above.

The potassium salt on heating turns pale yellow, deepens in colour, and melts to a pale yellow liquid, which on cooling sets to a yellow solid and becomes white when cold. The loss on gentle ignition was 5·70% (mean of 7 experiments). At 110°, 1·60% was lost, equivalent to 3 out of 11 mols. of water. At 120° the loss was 2·12% or 6 out of 11 molecules. Dehydration in a vacuum desiccator to constant weight gave losses 1·51, 1·63, 1·56%, corresponding to 3 out of 11 mols. The anhydrous salt exposed to air for 15 hours reabsorbed 55% of the original water content, i.e., 6 out of 11 molecules.

The potassium salt produced by precipitation from a solution of sodium paratungstate prepared by means of hydrochloric acid, behaved similarly to the above. The loss on ignition was 5·65% (mean of 3 expts.), and on exposure to air for 15 hours 52% of the water was reabsorbed.

Attempts were made to analyse the various salts by ignition of the anhydrous substance in a current of carbon tetrachloride vapour, whereby the tungsten vaporises as tungstyl chloride, WO_2Cl_2, and the alkali chloride remains. Many experiments were made, the substance being heated in a porcelain boat inside a silica tube. The tungstyl chloride condensed as a yellow solid on the walls of an adaptor and excess of carbon tetrachloride was condensed under water. The tungstyl chloride dissolved in aqueous sodium hydroxide. Results with the alkali salts were not consistent owing to volatilisation or mechanical carrying over, and a constant weight of the chloride was not obtained. In 50% of the estimations on the sodium salt the residue gave a value for Na_2O less than 8% (Calc. for 5 : 12-salt, 10·02 ; for 4 : 10-salt, 9·66%). When carbon tetrachloride was passed over fused sodium chloride there was a loss of 1% in ½ hour. The method, however, was successful with the barium salt.

Barium Salt.—The barium salt was obtained by addition of barium chloride to a solution of the sodium salt (formic acid product). A white flocculent precipitate was immediately formed, the tungstic acid being completely precipitated. When treated with a small

quantity of warm hydrochloric acid the barium passed into solution as chloride, leaving a residue of yellow tungstic acid ; with excess of concentrated hydrochloric acid, however, tungstic acid passed into solution and a residue of barium chloride remained. The salt was carefully dried and analysed (Found : BaO, 21·72, 21·60, 21·74. Calc. for $4BaO,10WO_3$: BaO, 20·91 ; for $5BaO,12WO_3$: BaO, 21·60 ; for $3BaO,7WO_3$: BaO, 22·08%).

Barium paratungstate prepared similarly from sodium paratungstate (hydrochloric acid product) contained in the anhydrous salt : 21·69, 21·47, 21·59% BaO. These results are important, not only in establishing the identity of the two salts, but also in defining the paratungstate as the 5 : 12-salt and not as the 3 : 7-salt (von Knorre, *Ber.*, 1885, **18**, 326, 2362).

When heated, the barium salt turned green, yellow, and finally brown, but did not melt ; on cooling, the anhydrous salt remained a pale lemon-yellow colour. The losses on ignition for the two salts were (*a*) formic acid product : 11·99, 11·94, 12·51 ; (*b*) hydrochloric acid product : 12·63, 11·94, 12·11. Calc. for $5BaO,12WO_3,27H_2O$: H_2O, 12·05 ; for $4BaO,10WO_3,22H_2O$: H_2O, 11·90%).

The foregoing results show that the salt obtained by titration of normal sodium tungstate with formic acid is the paratungstate, $5Na_2O,12WO_3,28H_2O$, and that the potassium and barium salts obtained by precipitation are respectively $5K_2O,12WO_3,11H_2O$, and $5BaO,12WO_3,27H_2O$. Physico-chemical methods are being employed to detect possible formation of compounds containing the 4 : 10 ratio, but this has not yet been observed. Smith (*loc. cit.*) claims to have synthesised the sodium 4 : 10-salt by crystallising a solution containing the normal and the metatungstate in the proportion represented by $6Na_2WO_4 + 6Na_2W_4O_{13}$, but his values of the ratio WO_3/Na_2O (*viz.*, 9·102, 8·996, 9·299, 9·497. Calc. for 4 : 10-salt, 9·354 ; for 5 : 12-salt, 8·986) cannot be accepted as conclusive. The binary systems Na_2WO_4–WO_3,K_2WO_4–WO_3 have been studied by van Liempt (*Z. anorg. Chem.*, 1925, **143**, 285) and the former also by Parravano (*Gazzetta*, 1909, **39**, ii, 55), but no evidence has been obtained of the formation of 4 : 10-salts. Jander, Majert, and Aden (*Z. anorg. Chem.*, 1929, **180**, 129) consider the paratungstates as derivatives of hexatungstic acid, $H_6W_6O_{21}$, the sodium salt being formulated $2Na_5H(W_6O_{21}),27H_2O$. Electrochemical examination gives direct evidence of complex formation, but the dehydration experiments do not suggest the retention of one molecule of water.

The Solubility of Sodium Paratungstate in Water at 0—102°.—The salt used was that prepared by the formic acid method and shown to have the composition $5Na_2O,12WO_3,28H_2O$. The method

adopted was that described in a previous paper (J., 1927, 1328). The salt was stirred with water for about 6 hours and allowed to settle; a portion of the solution was then drawn over through a sintered glass filter into a receiving tube. The whole apparatus was sufficiently immersed in a thermostat for the solution to remain under water during the transference, a constant temperature being carefully maintained. A suitable quantity of the filtered solution was weighed, evaporated to dryness in a platinum crucible, and the residue heated to fusion and weighed as the anhydrous salt. The results are in Table I, where S represents g. of anhydrous salt in 100 g. of solution. The values are plotted in Fig. 1.

FIG. 1.
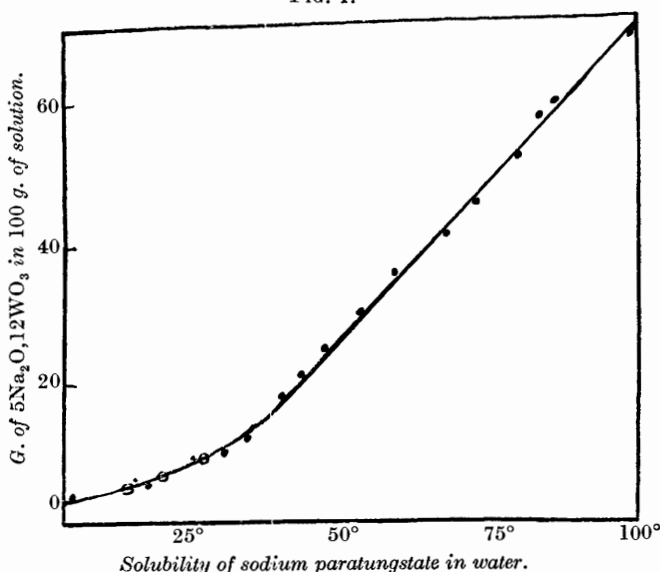
Solubility of sodium paratungstate in water.
⊙ Values obtained with sample prepared by hydrochloric acid method.

TABLE I.

Temp.	$S.$	Temp.	$S.$	Temp.	$S.$	Temp.	$S.$
0·5°	2·20	24·2°	9·17	47·0°	25·79	73·9°	46·27
0·7	2·87	24·4	9·21	53·4	30·48	81·8	53·59
12·4	5·62	28·6	10·25	53·5	29·83	85·9	59·28
14·7	5·93	32·9	12·73	59·4	36·01	87·8	60·51
16·6	6·24	39·6	17·94	68·7	40·19	101·8	70·60
16·9	6·28	42·8	21·02				

The solubility curve is seen to be continuous, but there is some variation at higher temperatures apparently owing to hydrolysis. Indeed, if the solution is kept near boiling point for some time, traces of precipitated tungstic oxide appear.

The boiling point of the saturated solution was found to be $101 \cdot 8°/745 \cdot 3$ mm. The sample for analysis at this temperature was taken after 15 minutes' boiling.

The density of the saturated solution at room temperatures was $D^{14 \cdot 8°}$ $1 \cdot 0536$; $D^{16 \cdot 8°}$ $1 \cdot 0541$.

The solubility of sodium paratungstate prepared by the hydrochloric acid method was found to be

Temp.	$11 \cdot 3°$	$17 \cdot 3°$	$25 \cdot 0°$
S	$4 \cdot 79$	$6 \cdot 71$	$9 \cdot 76$

It will be observed that these values fall on the curve given above.

Several lower hydrates of sodium paratungstate have been described but these could not be separated from the solution. Only on one or two occasions were octahedral crystals present where crystallisation had taken place above 70°, and recrystallisation at that temperature invariably produced the usual hexagonal crystals. One sample containing octahedral structures contained $13 \cdot 2\% H_2O$ (the 25-hydrate, monoclinic prisms, contains $12 \cdot 7\%$ H_2O; the 21-hydrate, octahedra, contains $10 \cdot 89\%$ H_2O. These were described by Marignac, *Ann. Chim. Phys.*, 1864, **3**, 5, 76). In order to observe whether any change in the solid phase was apparent, apart from that due to hydrolysis after prolonged contact at higher temperatures, a series of dilatometric experiments was undertaken over the range 20—75°, both for rise and fall of temperature. The bath was arranged so that the temperature rose about 1° every 5 minutes. It was found that the dilatometric readings fell on smooth curves in every case so that no abrupt change could be recorded.

Summary.

The product of the reaction between formic acid and aqueous sodium tungstate under such conditions that the solution becomes slightly acid is sodium paratungstate, $5Na_2O,12WO_3,28H_2O$, as proved by analysis and dehydration experiments.

The potassium and barium salts obtained by precipitation have the respective compositions $5K_2O,12WO_3,11H_2O$ and $5BaO,12WO_3,27H_2O$. The behaviour of these salts on dehydration has been examined.

No evidence of the existence of the salt $4Na_2O,10WO_3,23H_2O$ has been obtained.

The solubility of sodium paratungstate has been determined at temperatures from 0° to 102°.

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