347. *Sodium Paratungstate.*

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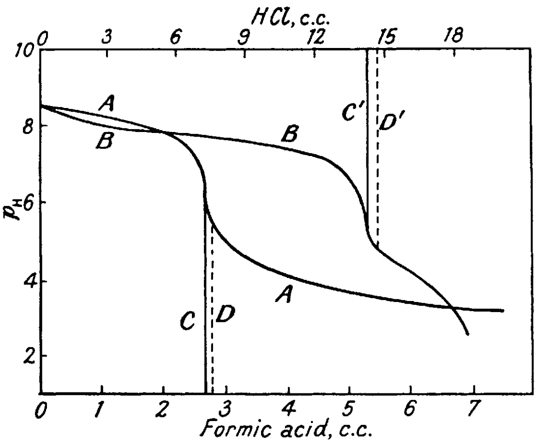
In a previous paper (Vallance, J., 1931, 1421) it was shown that analytical and dehydration experiments pointed to the identity of the so-called 4 : 10-tungstates (Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027) with the paratungstates, the composition of the sodium salt being $5Na_2O,12WO_3,28H_2O$. Physicochemical methods have now been employed to test this conclusion, and incidentally to throw light on the paratungstate molecule.

Experimental.

The titration of normal sodium tungstate with formic acid (26·235*N*) under the conditions employed in the preparation of the 4 : 10-salt, and with hydrochloric acid (4·93*N*), as in the usual preparation of paratungstate, was examined potentiometrically. In each case 20 g. of sodium tungstate, $Na_2WO_4,2H_2O$, dissolved in 25 c.c. of water, were titrated with the acid at 60—70°, the higher temperature being necessary to redissolve, with stirring, the precipitated tungstic acid, potentiometer readings then being taken at 60°. An electrometer-valve potentiometer was used with a Morton glass-electrode system. The glass electrode was first calibrated at 18° on 0·05*M*-solutions of potassium hydrogen phthalate and borax and the Prideaux–Ward universal buffer solution. The calibration was then repeated at 60°, slight changes in p_H of the solutions being detected by means of indicators. It was necessary to protect the electrode from sudden changes of temperature. The *E.M.F.*–p_H curve obtained was nearly parallel to that obtained at 18°, and approximate p_H values could thus be derived between p_H 3 and 9·5. During the titrations, consistent and reproducible results were obtained to a point well beyond the completion of tungstic acid precipitation.



AA. Na_2WO_4–*Formic acid titration curve, at* 60°.
BB. Na_2WO_4–HCl (1 : 1) *titration curve, at* 60°.
C,C′. *Amounts of acid required to form* 5 : 12-*salt.*
D,D′. *Amounts of acid required to form* 4 : 10-*salt.*

The results are shown graphically in the figure. With allowance for the difference in concentration of the acids, the similarity of the curves is obvious. In each case the main fall in p_H occurs when the proportion of acid added is very nearly equal to that required for the 5 : 12 salt, and certainly before that required for the 4 : 10 salt.

Samples of the two sodium salts were next prepared, the so-called 4 : 10-salt by addition of formic acid to a hot aqueous solution of normal sodium tungstate (50 g. in 55 c.c. of water) until the solution was just acid to litmus (Smith, *loc. cit.*), and the 5 : 12-salt, sodium paratungstate, by addition of hydrochloric acid (1 : 1) to a similar hot solution of sodium tungstate until the solution became permanently yellow and only faintly alkaline to litmus (Scheibler, *J. pr. Chem.*, 1860, **80**, 204; 1861, **83**, 273; Gonzalez, *ibid.*, 1887, **36**, 44). In both cases the crystals formed over-night were washed with cold water and purified by four successive recrystallisations from hot water, the products being finally dried between absorbent paper at a pressure of 4 lbs. per sq. in. After one recrystallisation, the mother-liquor from the formic acid product was neutral to litmus, whereas that from the hydrochloric acid product was alkaline in reaction, probably owing to adsorbed normal salt. The final products both gave neutral solutions. The p_H of a 0·1*N*-solution at 18° was in each case 6·58.

The equivalent conductivities of the two products were determined on the assumption that both were the pure paratungstate, 5 : 12 : 28, so that 0·1 g.-mol. per l. was considered to be a *N*-solution with respect to sodium. Owing to the readiness with which hydrolysis occurs, the electrical conductivity of solutions of these complex tungstates increases on keeping or warming, and the increase is particularly marked on boiling; *e.g.*, the following values were obtained : Λ_1 with fresh solutions of the formic acid product, Λ_2 with the same solutions after 1 week, and Λ_3 with solutions after boiling for ½ hour. In all cases steamed Jena flasks were used.

v (litres)	16	64	256
Λ_1	53·3	71·1	91·3
Λ_2	56·0	74·6	97·5

v	16	64
Λ_1	54·4	72·6
Λ_3	73·2	88·6

Changes of the same order were observed in solutions of the hydrochloric acid product (cf. Junius, *Diss.*, Berlin, 1905; Rosenheim and Wolff, *Z. anorg. Chem.*, 1930, **193**, 47). For comparable conductometric determinations, it was necessary, therefore, to dissolve equal weights of the two products simultaneously in equivalent amounts of water shaken at room temperature for about 3 hours and to carry out the measurements as rapidly as possible thereafter. The following table gives the equivalent conductivities so obtained at 25°.

v (litres)	16	32	64	128	256	512	1024
Λ_a (HCl product)	50·85	58·1	67·5	79·2	92·3	106·3	116·5
Λ_b ($H{\cdot}CO_2H$ product)	50·93	58·1	67·5	79·4	92·3	105·7	117·0

By extrapolation, Λ_∞, in both cases, approximates to 132. The conductivities of the two products are obviously identical.

The basicity of the parent acid, deduced from the above data, would appear to be 6. This does not agree, however, with any formula hitherto proposed except $3Na_2O,7WO_3$, aq., which is not in agreement with analytical results. Ostwald's basicity rule was based on data obtained with normal salts of comparatively simple constitution and is by no means of universal applicability. It is not to be expected that it should be valid with salts giving rise to large complex ions and subject to ready hydrolysis which would cause abnormal increase in conductivity. The formula based on analytical results is $Na_{10}W_{12}O_{41},28H_2O$, and by calculation the ionic conductivity at 25° of the ion $(W_{12}O_{41})^x$ is 80·8, which is probable for a large ion. The hexatungstate formula, $Na_5(HW_6O_{21})$, proposed by Copaux and favoured by Jander, postulates a pentabasic acid of which the ionic conductivity of the anion would also be 80·8. If the tungstate is considered as an acid salt, $Na_5H(W_6O_{21})$, aq., the ionic conductivity of the anion would be 8·5, which is very low. It has been already pointed out (Vallance, *loc. cit.*) that dehydration experiments do not justify the differentiation of 1 mol. of water to provide the constituent hydrogen necessary in the above formulæ. Rosenheim (*Z. anorg. Chem.*, 1930, **193**, 47) suggests the constitution $Na_{10}H_4[H_4(WO_4)_6(W_2O_7)_3],24H_2O$, the molecule being completely hydrolysed on heating in solution to $10Na^{\cdot} + 10H^{\cdot} + 2[H_2(WO_4)_6]^x$; such an acid salt would be expected to give much higher conductivity than is indicated in the results above.

It is of interest that the equivalent conductivity of $N/64$-sodium tungstate, Na_2WO_4, at 25° is 101·8 (Walden, *Z. physikal. Chem.*, 1887, **1**, 529); the corresponding figure for the paratungstate is 67·5, and although it increases on keeping or boiling, in no case has the value been found to reach 101·8. When such boiling takes place, however, a cloudiness generally occurs owing to separation of tungsten trioxide. This behaviour suggests that on hydrolysis sodium tungstate is formed, tungsten trioxide remaining in colloidal form and gradually separating.

The identity of the hydrochloric acid and the formic acid product was further established by a study of certain optical properties of their solutions. The refractive indices of solutions saturated at room temperature were identical, *viz.*, $n_D^{21\cdot2^\circ} = 1{\cdot}3431$. The solutions gave no absorption bands in the visible region.

It was observed by Rosenheim and Itzig (*Ber.*, 1900, **33**, 707) that the addition of sodium paratungstate to an aqueous solution of tartaric acid caused a considerable increase in the optical rotation, due apparently to the formation of a complex compound. The property is also shared by the normal tungstates. Attempts to use this effect in establishing the identity of the two samples of paratungstate were not at first successful, considerable variations in the polarimetric readings being obtained. The mechanism of the change was therefore investigated.

A $0{\cdot}2M$-solution of tartaric acid was employed, and 5 g. of sodium paratungstate added to 100 c.c. Polarimetric readings were taken at 22° immediately dissolution was complete and at intervals thereafter. A rapid rise in rotatory power was at once apparent, but after 30 minutes the increase was much less rapid. After 5 hours the solution had acquired a bluish tint, and when kept overnight it afforded a white gelatinous precipitate having a bluish tinge which deepened with age. This precipitate on drying in a steam-oven yielded the blue oxide of tungsten. The addition of hydrochloric acid to the colourless filtrate caused precipitation of tungstic acid

Increasing quantities of the paratungstate up to 35·985 g. (equivalent to 0·1 mol.) were added to 100 c.c. of the $0{\cdot}2M$-tartaric acid. Rapid increase in rotatory power was observed in all cases. In solutions containing up to 10% of paratungstate the increase continued until precipitation commenced, but with larger proportions no precipitation occurred and a constant rotation was attained after about 90 mins., the maximum effect being obtained with a solution containing 20% paratungstate, thus :—

Sodium paratungstate, g.		0	5·00	7·50	10·00	12·50	15·00
Polarimeter reading	2 hours	9·27°	104·10°	111·10°	111·59°	112·67°	113·95°
	24 hours	—	pptn.	pptn.	pptn.	113·92°	113·90°
Sodium paratungstate, g.		17·9925	20·00	21·591	22·49	25·00	35·985
Polarimeter reading	2 hours	114·35°	114·70°	114·57°	114·56°	114·14°	110·54°
	24 hours	113·75°	113·87°	113·67°	113·51°	113·59°	110·03°

The values after 24 hours were fairly uniform except in the last case, in which it remained practically unchanged. With further lapse of time, however, the solutions showed a continued decrease in rotation.

When examined in this way the products from formic acid and from hydrochloric acid gave identical results. The maximum effect is obtained when the molar ratio of tartaric acid to sodium paratungstate is 1 : 0·278. For this solution $[\alpha]_D^{22°} = 405·3°$ (= 27 times the specific rotation of the original tartaric acid solution). When the molar ratio was 2 : 1, $[\alpha]_D^{22°} = 336$. In this respect the action differs from that of normal sodium tungstate, which gives a maximum effect when an equimolar proportion is present.

The solutions after being kept for 24 hours were titrated with 0·1*N*-sodium hydroxide, which reacted only slowly. The results were somewhat inconsistent; the amount of alkali required for neutralisation was always more than that required by the tartaric acid alone, but the excess was less than that required to convert the paratungstate into the normal salt. When the solutions were concentrated over sulphuric acid, no crystalline product could be obtained, but on evaporation a colourless translucent glass remained, which gradually assumed a bluish tinge. Tartaric acid could not be extracted from this by alcohol or ether. With water it became sticky and then dissolved to form a colourless acid solution. When heated, the amorphous glass gave off a little water and inflammable vapour and after charring melted to a yellowish liquid which set to a white solid. It is concluded, therefore, that the addition of the paratungstate to tartaric acid results in the formation of colloidal aggregates of indefinite composition which remain on evaporation as a homogeneous glass. It appears probable that in such reactions as the above there is a gradual change from ionic complexes to micelles in accordance with the views of Dumanski and others (*Kolloid-Z.*, 1926, **38**, 208), and such a change would prevent simple quantitative relations between the reactants being attained.

SUMMARY.

The identity of the crystalline products obtained by titration of hot aqueous solutions of sodium tungstate with formic acid or with hydrochloric acid has been established by physicochemical methods, both being sodium paratungstate, $5Na_2O,12WO_3,28H_2O$.

The potentiometric curves for the two titrations are similar, and the equivalent conductivities and optical refractivities of the two products in solution are identical. The results obtained are in accord with the formula based on analytical results, *viz.*, $Na_{10}(W_{12}O_{41}),28H_2O$, and in conjunction with the dehydration results already published they discount the probability of the molecule's containing acidic or nuclear hydrogen.

The influence of the salt on the rotatory power of tartaric acid has been examined. Evidence of the formation of a simple addition compound is not forthcoming, and it is suggested that chemical combination between the reactants is accompanied by micelle formation.

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