

bis(p,αdihydroxy-m-methoxy-benzylamino)-4,4'-dihydroxy-arsenobenzene; *3,3'-bis[(hydroxymethyl) amino]-4,4'-dihydroxy-arsenobenzene dihydrochloride*; *3,3'-bis(α-hydroxy-m-nitrobenzylamino)-4,4'-dihydroxy-arsenobenzene*; *3,3'-bis(α-hydroxy-γ-phenylallylamino)-4,4'-dihydroxy-arsenobenzene*.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE SODIUM TUNGSTATES. I

BY EDGAR F. SMITH

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Wolcott Gibbs¹ wrote:

"The alkaline tungstates are numerous and unusually complex. Salts of essentially different formulas approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. . . . The analyses are hardly sufficiently close to decide the question upon purely analytical grounds."²

This comment was evoked on considering more particularly the various sodium tungstates; for, he added:

"As the general result of my own study of the salts themselves and of the work of Scheibler, Marignac, Lotz, Forcher, Laurent, Lefort, and others. . . . I have arrived at a new classification and arrangement: the normal and metatungstic series."³

Gibbs repeatedly obtained a sodium salt, the analysis of which agreed very closely with the formula, $9\text{Na}_2\text{O} \cdot 22\text{WO}_3 \cdot 51\text{H}_2\text{O}$, and thought it might be the representative of a new class or series. A glance at Dammer's *Handbuch*, picking out the recorded sodium salts, discloses at least eight ratios between basic oxide (Na_2O) and acid oxide (WO_3); and, of the $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ salt, containing sometimes less than $28\text{H}_2\text{O}$, depending upon the manner of its crystallization, he said its constitution, it was believed by some, was best expressed by the formula $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$.

In the Gibbs arrangement there are only three outstanding members claiming consideration: (a) normal sodium tungstate; (b) sodium paratungstate; and (c) sodium metatungstate. To these, through the studies of Gibbs, there should be added $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ and probably $9\text{Na}_2\text{O} \cdot 22\text{WO}_3 \cdot 51\text{H}_2\text{O}$.

In commencing the present study, the writer desired to prepare a series of derivatives of "complex inorganic acids," starting with ammonium paratungstate but, annoyed by its sparing solubility, he turned to its sodium analog, made by the method of Scheibler.⁴

¹ Wolcott Gibbs, *Am. Chem. J.*, **1**, 218 (1879).

² See also Dammer, "Handbuch der anorganischen Chemie," **3**, p. 639; and Abegg, "Haudwörterbuch der anorganischen Chemie," **4**, p. 791.

³ Gibbs, *Am. Chem. J.*, **1**, 2 (1879).

⁴ Scheibler, *J. prakt. Chem.*, **83**, 278 (1861).

Dammer⁵ states that this salt— $5\text{Na}_2\text{O}\cdot 12\text{WO}_3\cdot 28\text{H}_2\text{O}$ —is produced by adding carbon dioxide to the aqueous solution of the normal salt ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$), whereas Forcher⁶ got $4\text{Na}_2\text{O}\cdot 10\text{WO}_3\cdot 23\text{H}_2\text{O}$, by this procedure.⁷ Small, brilliant crystals separated and when they no longer increased appreciably in quantity, were filtered out and washed repeatedly with ice-cold water, until the wash-water did not effervesce on the addition of hydrochloric acid. They were recrystallized.

Forcher was, probably, the first person to observe this salt, to which he ascribed the formula, $2\text{Na}_2\text{O}\cdot 5\text{WO}_3\cdot 12\text{H}_2\text{O}$. Marignac obtained it, but was ignorant of the fact that Forcher had prepared and analyzed it. Marignac gave it the formula, $2\text{Na}_2\text{O}\cdot 5\text{WO}_3\cdot 11\text{H}_2\text{O}$. The literature contains very little relating to the salt.⁸

As the writer, at the beginning, had in mind using various sodium tungstates, namely, those in which the ratio of basic oxide and acid oxide varied, in the preparation of "complexes," this ratio, $4\text{Na}_2\text{O}\cdot 10\text{WO}_3\cdot 23\text{H}_2\text{O}$, arrested his attention, and caused him to devote more time to its preparation and to the study of its behavior, as well as to the properties of allied derivatives. Therefore, the following observations on the salt, $4\text{Na}_2\text{O}\cdot 10\text{WO}_3\cdot 23\text{H}_2\text{O}$, are offered, which for convenience, may be designated the 4:10-salt.

Historical

Despite the possibility of repetition, a brief historic sketch is submitted. Vincenz Forcher⁶ experimenting with the normal salt ($\text{Na}_2\text{O}\cdot \text{WO}_3\cdot 2\text{H}_2\text{O}$) followed a hint previously given by Riche,⁹ namely, passed carbon dioxide through an aqueous solution of the normal salt for several days, and obtained the 4:10-salt. He busied himself no further with it. Other chemists had it in hand but disregarded it, thinking no doubt that it was an accidental product. But Gibbs¹⁰ gave it study, analyzed it not only repeatedly, but also made the corresponding potassium, ammonium (also made by Marignac) and zinc salts thus establishing, as he believed, the 4:10-series.

Formation of the 4:10-Salt

The writer, in due course, succeeded in making the salt by the method of Gibbs' whose observations¹¹ tell the story quite well and may on that account be given here:

The general result of my own study of the action of acetic acid upon the neutral tungstate is that we obtain the 5:12, the 9:22, or the 4:10 salt, according to the cir-

⁵ Dammer, Ref. 2, p. 664.

⁶ Forcher, *J. prakt. Chem.*, **86**, 240 (1862).

⁷ See also Lefort, *Ann. chim. phys.*, [5] **9**, 97 (1876).

⁸ *Z. anorg. Chem.*, **96**, 139 (1916).

⁹ Riche, *Jahresber.*, **1857**, 189; *Ann. chim. phys.*, [3] **50**, 5; *Jahresber.*, **1856**, 372.

¹⁰ Ref. 1, p. 221.

¹¹ Ref. 1, p. 226.

circumstances of the case, the constitution of the salt formed depending mainly upon the degree of concentration of the acid and upon the duration of its action.

The indefiniteness confessed in this quotation indicates how easily one may be led astray in the preparation of the 4:10- salt.

In the experiments of the writer definite amounts of the constituent materials were used; 100 g. of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 140 cc. of water and 50 cc. of glacial acetic acid was gradually introduced into the solution; the flask was cooled under running water as it became heated. Beautiful white needles separated, but on recrystallization from water the 4:10- and 5:12- salts were the products. Were the white needles not recrystallized, but simply washed with cold water, and then analyzed, the result was: water, 13.62%; Na_2O , 8.17%; WO_3 , 78.08%; approximating closely the requirements of a formula $9\text{Na}_2\text{O} \cdot 22\text{WO}_3 \cdot 51\text{H}_2\text{O}$. Many similar trials gave like results, which would mean that the preceding conditions gave in reality two salts—4:10 and 5:12. Usually there was a preponderance of the first salt, the 4:10- salt, which Jules Lefort⁷ claims to have made by pouring a saturated solution of the normal salt into an excess of glacial acetic acid in the cold, when a white insoluble precipitate separated. This was collected, washed with alcohol, and then dissolved in boiling water. On cooling, it separated in very beautiful, transparent, oblique prisms, unalterable in the air. And yet this same chemist—Jules Lefort, p. 96 of the same Journal,⁷ advises that sodium bitungstate, $\text{Na}_2\text{O} \cdot 2\text{WO}_3 \cdot 6\text{H}_2\text{O}$, is produced when glacial acetic acid is added (to acid reaction), to a saturated solution of normal sodium tungstate. After a day or two the salt was said to separate in long, prismatic needles. At least fifty experiments were made by the writer in the hope of obtaining this bitungstate. The working conditions in one trial will suffice to indicate the manner of procedure.

One hundred and fifty g. of normal sodium tungstate was dissolved in 100 cc. of water. To this solution was added 15 cc. of crystallized (glacial) acetic acid in portions at a time of 0.5 cc. to 1 cc. The liquid warmed. When 13 cc. of acid had been added sodium acetate separated. After 72 hours the liquid was poured from the crystals adhering to the flask, and these were then washed four or five times with cold water, after which they were dissolved in warm water. In the course of a few hours crystals appeared. The water content of these was determined and found to be 14.10%, approximating 14.02%, the water content of the 5:12- salt. In the filtrate from these crystals a second salt appeared. Its analysis gave 12.86% of water, 8.45% of sodium oxide, and 77.67% of tungstic oxide, corresponding to the requirements of the 4:10- salt.

Thus it occurred in the many other experiments conducted with the greatest care. Gibbs, on following Lefort's suggestion, was "without success in any one instance, the results. . . . being in all cases very different in composition." G. von Knorre¹² says: "I have twice tried to pre-

¹² G. von Knorre, *J. prakt. Chem.*, N. F., 27, 84.

pare this salt exactly according to Lefort's direction, but both times obtained the compound $5\text{Na}_2\text{O}\cdot 12\text{WO}_3\cdot 28\text{H}_2\text{O}$;" and Gonzales¹³ adds his inability to confirm the work of Lefort.

Therefore, it would appear that Forcher's method and that of Gibbs were the best suited for the preparation of the 4:10- salt, although the writer found that if to 100 g. of normal sodium tungstate, dissolved in 100 cc. of water, there be gradually added *formic* acid to a distinct acid reaction there will appear, after 24 hours, an abundant yield of the 4:10- salt. His experience leads him to regard this procedure as superior to that in which acetic acid is employed. The 4:10- salt was the only product. The 5:12- and 9:22- salts were not observed, so that the 4:10- product could readily be obtained pure by one or more recrystallizations from water. It was also shown that Forcher's procedure was superior to that in which acetic acid, ordinary or glacial, was used.

It is interesting to note that Forcher⁶ alludes to the fact that once, when endeavoring to make sodium metatungstate by adding tungstic acid to a boiling solution of the normal salt, his work was interrupted and upon his return he found crystals which analyzed for the 4:10- salt. This was, too, the experience of the writer, who obtained a very abundant yield of 4:10 in this way. Indeed, the scheme offers a very simple method for the preparation of the latter salt.

The writer, on one occasion, added a calculated amount of tungstic acid (enough to yield the 5:12- salt) to a boiling solution of normal sodium tungstate. The liquid was filtered, and crystals separated. On analysis these showed 14.02% of water; 8.16% of Na_2O ; and 77.82% of WO_3 , in harmony with the requirements of the 5:12- salt.

In the determination of the tungstic trioxide in these various salts, Gibbs' modified Berzelius method was used. The sodium oxide was estimated both directly and by difference.¹⁴

Properties of the 4:10- Salt

These have received scant notice. The common opinion is that the crystals of the salt are monoclinic in form. They effloresce rapidly in dry air, and upon resolution in water considerable heat is evolved. Their solubility is, according to Forcher, one part in 12.6 parts of water at 22°; according to Lefort, 100 parts of water at 15° dissolve 16 parts of the salt; according to the writer, 100 parts of water at room temperature dissolve 19 parts of the salt.

The specific gravity of the salt was found to be 4.3, the mean of three determinations.

The melting points of normal sodium tungstate, the 5:12- salt, the

¹³ Gonzales, *J. prakt. Chem.*, N. F., **35**, 47.

¹⁴ Ref. 1, p. 219.

4:10- salt, the 9:22- salt, and the sodium metatungstate were repeatedly determined with these results.

1. $\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot 2\text{H}_2\text{O}$: 665° . The liquid fusion was colorless and transparent as water.

2. $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$: 705.8° . The liquid was very yellow in color. The cooled mass was crystalline and yellow in color for quite a while after congelation.

3. $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$: 680.8° . Again the liquid was yellow in color and retained this color until quite cold, when it was crystalline and white, with a faint blue tint.

4. $9\text{Na}_2\text{O} \cdot 22\text{WO}_3 \cdot 51\text{H}_2\text{O}$: 683.3° . The liquid was yellow in color, even after cooling.

5. $\text{Na}_2\text{O} \cdot 4\text{WO}_3 \cdot 10\text{H}_2\text{O}$: 706.6° . The meta salt melted with comparative ease. The deep yellow color of tungstic acid predominated both while it was liquid, and when the molten mass became solid.

If, for a moment, we arrange the salts referred to above as follows

(1)	(2)	(3)	(4)	(5)
$\text{Na}_2\text{O} \cdot \text{WO}_3$	$5\text{Na}_2\text{O} \cdot 12\text{WO}_3$	$4\text{Na}_2\text{O} \cdot 10\text{WO}_3$	$9\text{Na}_2\text{O} \cdot 22\text{WO}_3$	$\text{Na}_2\text{O} \cdot 4\text{WO}_3$
1:1	1:2.4	1:2.5	1:2.444	1:4
665°	705.8°	680.8°	683.3°	706°

interesting conclusions are apparent. Among these it is plain that (1) and (5) represent the two extremes, and it is disappointing that the ratios between basic oxide and acid oxide as they would exist in $\text{Na}_2\text{O} \cdot 2\text{WO}_3$ and $\text{Na}_2\text{O} \cdot 3\text{WO}_3$, and as Lefort thought he had made evident, appear not to exist. v. Knorre, it is true, made $\text{Na}_2\text{O} \cdot 2\text{WO}_3$, by fusing together calculated amounts of sodium hydroxide and tungsten trioxide, but when the anhydrous body was brought into solution, the latter yielded no crystalline deposit, even upon protracted standing.¹⁵ It is most regrettable that Lefort's experiences have not been confirmed by subsequent investigators. Probably all of these have overlooked some little step in the preparation process, though confident that they proceeded in accordance with the printed directions. Or, it may be that Lefort failed to note a step, to him trivial, but which if known might have aided later colleagues to confirm his observations, which are numerous and bear the imprint of careful work.

A further examination of the ratios of basic and acid oxides in the 5 salts, represented above, discloses that (4)—the 9:22- salt—has a ratio (base to acid) close to those of the second and third salts—the 5:12- salt and the 4:10- salt. The 9:22- salt we owe to Wolcott Gibbs.¹¹ It resembles in some points the suggestion he gave for the production of the 4:10- salt. Indeed, the writer's product prepared in the manner of Gibbs, analyzed as follows: H_2O , 13.75%; Na_2O , 8.08%; and WO_3 , 78.19%. These results would pass well for the requirements of a 4:10- sodium salt and, therefore, a doubt does come to mind as to whether the 9:22- salt is a distinct individual.

¹⁵ Ref. 12, p. 27.

When Gibbs described the preparation of the 5:12- salt, according to Scheibler,¹⁶ he cautiously added: "If the proportion of chlorhydric acid is just sufficient to give an onion-red reaction with litmus, crystals are obtained, which are either a combination or a mixture of equal molecules of the 4:10- and 5:12- salts. Their analyses agree closely with the formula $5\text{Na}_2\text{O}.12\text{WO}_3.4\text{Na}_2\text{O}.10\text{WO}_3.51\text{H}_2\text{O}$." Gibbs left this point undecided, although he did make a zinc salt by adding a cold solution of zinc sulfate to a cold solution of the 9:22- sodium salt. A precipitate formed at first and then redissolved, but when the zinc sulfate was in small excess white needles separated. These proved insoluble in water. They were dried for some time upon woolen paper. Their analysis led to the formula $9\text{ZnO}.22\text{WO}_3.66\text{Aq}$. Gibbs had found the zinc salt of the 4:10 series to have the formula $4\text{ZnO}.10\text{WO}_3.29\text{H}_2\text{O}$, while Gonzales¹⁷ speaks of zinc *para*-tungstate as having the formula, $5\text{ZnO}.12\text{WO}_3.37\text{H}_2\text{O}$.

It crystallized in white needles. These formulas added together would give the formula $9\text{ZnO}.22\text{WO}_3.63\text{H}_2\text{O}$, which differs from the 9:22 salt of Gibbs by only 3 molecules of assumed water of crystallization.

It must, however, be said that whenever the writer made Gibbs' 9:22-sodium salt, he found upon its recrystallization that the two salts, 5:12- and 4:10-, appeared, so that he is skeptical in regard to the individuality of the 9:22- salt.

In the extensive work, for so it was, made upon the action of acetic acid and normal tungstates, hoping that the bitungstate of Lefort would be found, it was noticed that the crystals which separated after solution in water and recrystallization left a mother liquor which grew alkaline upon concentration. These alkaline liquors separated from 4:10- and 5:12- salts with eventually not a little sodium acetate, but the liquid from the latter had a yellow color and gave the alkaline reaction to which reference has just been made. The thought was entertained that perhaps at the beginning, when acetic acid reacted with the normal tungstate, sodium bitungstate was really produced and that in its solution hydrolysis occurred with the production of 4:10- and 5:12- sodium salts. Patiently, all mother liquors were evaporated, the separating salts removed from time to time, then finally the liquid was allowed to evaporate spontaneously, when cauliflower-like white masses separated. These were dissolved in little water and permitted to separate spontaneously. Their analysis showed that these residues were nothing more than sodium hydrate mixed with sodium tungstate, which must be regarded as hydrolytic products of the several sodium tungstates formed on acting with acetic acid upon normal sodium tungstate. At present this seems the only reasonable explanation of what evidently occurred during the process of concentration.

¹⁶ Ref. 1, p. 225.

¹⁷ Ref. 13, p. 51.

Properties of the 4:10- Salt

On testing the 4:10- salt, in solution, with various metallic salt solutions these behaviors were noted.

The addition of a cold aqueous solution of zinc sulfate produced a white precipitate soluble in a slight excess of zinc sulfate. From this solution, on standing, white needles separated in stellar aggregations. These were the 4:10- zinc salt described by Wolcott Gibbs.

Cadmium sulfate occasioned a white voluminous precipitation, insoluble in an excess of cadmium sulfate as well as in cold and hot water, thus differing from the zinc salt.

With cobalt sulfate and nickel nitrate precipitates appeared soluble in an excess of the precipitants. That with cobalt was quite granular.

A solution of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) gave (in a solution of the 4:10- salt) a heavy, white and extremely gelatinous precipitate, insoluble in water and in an excess of the precipitant.

Lanthanum sulfate gave a white, insoluble gelatinous precipitate. This also occurred with praseodymium and neodymium nitrates. There was nothing remarkable about these products. They proved to be insoluble and were easily decomposed by nitric acid, even in the cold.

Uranyl nitrate gave a flocculent yellow colored precipitate (with the 4:10- salt). It redissolved in a slight excess of the uranyl salt. The solution was filtered, when a white granular powder separated.

Ferric ammonium sulfate gave a curdy, slightly yellow precipitate, insoluble in an excess of the precipitant.

Alum produced a copious, finely divided precipitate, which curdled on agitation. It proved perfectly insoluble.

Chromium potassium sulfate occasioned a precipitate. It was greenish-gray in color, gelatinous and insoluble in excess of the reagent and also in large volumes of water.

Lead nitrate produced a white, gelatinous precipitate, insoluble in an excess of the precipitant and also in hot water.

Hydroxylamine hydrochloride (in a solution of 4:10- salt) caused no precipitation.

With hydrazine sulfate a rather voluminous, somewhat flocculent, white precipitate appeared, insoluble in cold water, but dissolving rather freely in hot water, and was not soluble in an excess of hydrazine sulfate.

Benzidine hydrochloride produced a white, heavy precipitate not soluble in an excess of the precipitant or in boiling water.

Phenylhydrazine hydrochloride was without visible reaction.

Naphthylamine hydrochloride gave a flesh-colored precipitate, insoluble even in boiling water. Hydrochloric acid slowly decomposed it.

Aniline hydrochloride gave no precipitation.

That the ratio observed in the sodium salt (4:10) might be further confirmed, the subjoined salts were analyzed. They were made by adding an excess of the respective metallic chlorides to boiling aqueous solutions of the 4 : 10- sodium salt. They were washed thoroughly with boiling water.

Calcium Salt.—A white granular powder, which did not melt on heating to intense redness.

Calc. for $4CaO \cdot 10WO_3 \cdot 25H_2O$: CaO, 7.48; WO_3 , 77.38; H_2O , 15.14. Found: CaO, 7.55; WO_3 , 77.20; H_2O , 15.14.

The barium and strontium salts were also white insoluble granular

powders, giving results agreeing very closely with the requirements of the formulas, $4\text{BaO} \cdot 10\text{WO}_3 \cdot 22\text{H}_2\text{O}$ and $4\text{SrO} \cdot 10\text{WO}_3 \cdot 26\text{H}_2\text{O}$.

The **nickel** salt is a greenish-white powder. The **cobalt** salt is pink in color and very granular. Both are insoluble in hot water. Their analytical data conformed closely with the demands of the formulas, $4\text{NiO} \cdot 10\text{WO}_3 \cdot 34\text{H}_2\text{O}$, and $4\text{CoO} \cdot 10\text{WO}_3 \cdot 35\text{H}_2\text{O}$.

The **manganese** salt, white in color, resembled freshly precipitated calcium oxalate from a cold solution, and on standing became coarsely granular in character. The results from several analyses were concordant and pointed to the formula, $4\text{MnO} \cdot 10\text{WO}_3 \cdot 30\text{H}_2\text{O}$.

Sodium paratungstate, $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$.—On drying at 100° until its weight was constant this salt lost exactly 11% of its water content.¹⁸ This percentage was equivalent to 21 molecules of water which, deducted from the total water content, 28 molecules, left 7 molecules as fixed water or water of constitution. In short, this amount of water was probably combined in the form of tungstic acid (H_2WO_4), and the formula of paratungstate might well be written, $(5\text{Na}_2\text{O} \cdot 5\text{WO}_3 \cdot 7\text{H}_2\text{O} \cdot 7\text{WO}_3) \cdot 21\text{H}_2\text{O}$. Such a formulation would indicate that the paratungstate was an acid salt.

Upon casting about among the various sodium tungstates for a possible corroboration of the light which was thrown upon the constitution of the para salt it was discovered that sodium metatungstate, $\text{Na}_2\text{O} \cdot 4\text{WO}_3 \cdot 10\text{H}_2\text{O}$, when dried at 100° to constant weight, lost 11.7% of water,¹⁹ corresponding to 7 molecules of water, which, deducted from the total water content (10 molecules), left 3 molecules as water of constitution, so that the meta salt might be expressed thus: $\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot 3\text{H}_2\text{O} \cdot 3\text{WO}_3 \cdot 7\text{H}_2\text{O}$.

The well defined barium metatungstate, $\text{BaO} \cdot 4\text{WO}_3 \cdot 9\text{H}_2\text{O}$, similarly dried, lost 8.65% of water,²⁰ corresponding to 6 molecules, which therefore would justify the formula, $\text{BaO} \cdot \text{WO}_3 \cdot 3\text{H}_2\text{O} \cdot 3\text{WO}_3 \cdot 6\text{H}_2\text{O}$.

Scheibler mentioned²¹ that on exposing metatungstic acid to a red heat, its loss in weight was 15.85%, equivalent to 9 molecules of water; but, that on heating the acid to 100° until its weight was constant, the loss was 11.5%, corresponding to 6 molecules of water of crystallization, which would point to the following formula, $\text{H}_2\text{O} \cdot \text{WO}_3 \cdot 3\text{H}_2\text{O} \cdot 3\text{WO}_3 \cdot 6\text{H}_2\text{O}$.

Four portions of the 4:10- salt ($4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$) were strongly ignited and lost 13.80%, 13.79%, 13.81% and 13.73% of water, respectively, corresponding to 23 molecules of water. Again, 4 samples of the salt were dried at 100° to constant weight, when the loss was 10.23%,

¹⁸ Ref. 4, p. 287.

¹⁹ *ibid.*, 4, p. 301.

²⁰ *ibid.*, 4, p. 307.

²¹ *ibid.*, 4, p. 310.

10.27%, 9.94% and 9.80%, respectively, corresponding to 17 molecules (10.24%) of water of crystallization, so that if this quantity be subtracted from 23 molecules, 6 molecules would remain as water of constitution and the formula of the salt might be written: $4\text{Na}_2\text{O}\cdot 4\text{WO}_3\cdot 6\text{Na}_2\text{O}\cdot 6\text{WO}_3\cdot 7\text{H}_2\text{O}$, which would stamp it as a very definite acid salt.

The evidence that not only the 4:10- salt but the other sodium salts to which attention has been called, were in reality acid salts suggested that their acidity might be determined.²² This was done with a 0.1 *N* sodium carbonate solution, using methyl orange as an indicator. In every instance the acidity was the same as indicated in the preceding formulas. Further, conductance experiments were made, using barium hydroxide to neutralize the acid present, when the break in the conductivity curve corresponded with the work set forth in the preceding experiments. A series of experiments was plotted for the 5:12- salt, the 4:10- salt, and the 1:4- salt, with most satisfactory results, hence there is no reason why the particular salt (4:10), under discussion in this communication, should not be formulated $4(\text{Na}_2\text{O}\cdot\text{WO}_3)\cdot 6(\text{H}_2\text{O}\cdot\text{WO}_3)\cdot 17\text{H}_2\text{O}$. It could also be graphically set forth after the manner of Werner,²³ which is possible, too, for the other salts but as these are still under study, being exposed among others to X-ray analysis, further comments on their constitution will be withheld for the present, and the antiquated formulas²⁴ retained for comparison's sake and their use will therefore be excused.

Summary

Summarized, the preceding experiments demonstrate the following points.

1. The 4:10- salt represents a very definite series among sodium tungstates.
2. Forcher's procedure leads to the 4:10- salt and not to the 5:12- salt.
3. Formic acid, acting on normal sodium tungstate, produces only the 4:10- salt.
4. The 9:22- salt is a mixture of the 4:10- and 5:12- salts.
5. The 4:10- salt is an *acid* salt, as proved by the difference in its kind of water content, the ready neutralization of its acidity and by conductance experiments during its neutralization.
6. The analysis of a series of new salts confirms in every way the ratio 4:10 between the basic and acid oxides.

The writer has been graciously assisted in his experimental work by Messrs. E. P. Fenimore and Russell Davis, as well as by his associate,

²² Schmidt, *Am. Chem. J.*, **8**, 16 (1886).

²³ Werner, *J. prakt. Chem.*, [2] **77**, 439 (1908); *Z. anorg. Chem.*, **69**, 247, 261 (1910); **70**, 73 (1911).

²⁴ *Z. anorg. Chem.*, **70**, 300 (1911).

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PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY]

THE FORMATION OF BUTADIENE FROM ETHYLENE

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Introduction

The action of ethylene at high temperatures has been studied by several investigators.

Marchand¹ who was the first to make a careful study obtained carbon and hydrogen from ethylene at a "white heat."

Magnus² working at "red heat" obtained methane, hydrogen, carbon and naphthalene.

Berthelot³ in several investigations obtained acetylene, ethane, styrolene and naphthalene.

Norton and Noyes⁴ had observed that a certain hydrocarbon called crotonylene, C_4H_6 (butadiene) was among the products when ethylene was formed by the action of heat, and that its formation had not been observed where ethylene was absent. They, therefore, passed a current of ethylene through a "red-hot" tube and examined the products. They succeeded in identifying benzene, naphthalene, anthracene (?), propylene, butylene, divinyl (butadiene), methane, ethane and carbon. Only a trace of hydrocarbons of the acetylene series was reported.

Day⁵ was the first of the workers on this subject to get away from the use of such indefinite terms as "red heat" and "white heat" to denote the temperature at which he worked. His experiments were carried out at 400°, but he does not report the formation of butadiene.

Bone and Coward,⁶ starting with a known volume of ethylene, determined the changes in the partial pressures of the gases; ethylene, acetylene, ethane, methane and hydrogen, present at definite temperatures over certain time intervals. The object of their studies was to throw more light on the much mooted questions regarding the mechanism of the transformations which occur in pyrogenic reactions. The hydrocarbon divinyl (butadiene) is not mentioned by them.

A search of the literature fails to show any other work that has been done on the formation of butadiene by the pyrogenic reaction of ethylene.

Staudinger, Endie and Herold,⁷ in an investigation of the thermal decomposition

¹ Marchand, *J. prakt. chem.*, **26**, 478 (1842).

² Magnus, *Pogg. Ann.*, **90**, 1 (1853).

³ Berthelot, *Compt. rend.*, **50**, 805 (1860); **62**, 94 (1866); *Ann. chim. phys.*, [4] **16**, p. 144 (1869), etc.

⁴ Norton and Noyes, *THIS JOURNAL*, **8**, 362 (1886).

⁵ Day, *ibid.*, **8**, 66 (1886).

⁶ Bone and Coward, *J. Chem. Soc.*, **93**, 1216 (1908).

⁷ Staudinger, Endie and Herold, *Ber.*, **46**, 2467 (1913).