

## Complexes of tungsten (VI) with tartaric acid. Comparative study of the various schemes of formation

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**Abstract.** The complex formation occurring between tungstic acid and tartaric acid has been investigated in order to explain the optical activity of tartaric acid in the presence of constant amounts of tungstic acid. A new scheme of formation that includes three different complexes is presented, which explains the experimental results found in the literature.

**Keywords.** Tungstene compounds; tartaric acid; hydroxycarboxylic acids; oxo-anionic complexes.

### 1. Introduction

The tungsten (VI) species that occur in solution are able to form anionic complexes with a large number of polyhydroxy acids, one of them is tartaric acid (TH<sub>2</sub>).

Polarimetric studies on formation of tungstate and molybdate complexes with tartaric acid have been carried out by Britton and Jackson (1934), Biswas (1945), Ballie and Brown (1961) and Banerjee and Bhattacharya (1962), among others. All these authors conclude that if there is an excess of tartaric acid or equimolecular amounts of tartaric and tungstic acids, the only complexes formed are those whose stoichiometric ratio is  $W/TH_2 = 1$ . On the other hand, Raman and Vaishya (1934) have pointed out that a complex with a  $W/TH_2$  ratio equal to 1/2 could be formed in alkaline medium.

In a previous publication (Cervilla *et al* 1979) we have shown that the tungstate can form three different complex species with tartaric acid depending on the pH of the solution. The stable species at a higher pH has a W/T ratio of 1/2,  $(O_2W(OH)_2T_2)^{-4}$ , and is a monomer whose formation from tungstate and tartrate ions requires two H<sup>+</sup> moles per mole of W(VI). The other two species, stable at lower pH, are dimeric complexes of stoichiometry 1/1,  $(O_6W_2(OH)_2T_2)^{-4}$  and

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$(\text{HO}_5\text{W}_2(\text{OH})_2\text{T}_2)^{3-}$ . The former requires  $2\text{H}^+/\text{W}$  for its formation from  $\text{WO}_4^{2-}$  and neutral sodium tartrate whereas the last one requires  $2.5\text{H}^+/\text{W}$ .

In disagreement with this scheme of complex formation based on polarimetric measurements are the schemes due to Britton and Jackson, and Baillie and Brown. The present paper attempts to show that the above scheme of complexes formation explain in a more coherent way the polarimetric and potentiometric measurements on which the other two indicated schemes are based.

## 2. Experimental

A Perkin Elmer 141 digital reading photoelectronic polarimeter, accurate to  $\pm 0.002$  degrees, was employed.

The cell is set at  $30 \pm 0.05^\circ\text{C}$  and has a length of  $10 \pm 0.002$  cm. The measurement could be taken at five different wavelengths (589, 578, 564, 436, 365 nm). The results obtained for each one of these wavelengths were comparable in all cases. The pH was measured with a Radiometer pH meter 26 at  $30^\circ\text{C}$ . The accuracy of the measurements was  $\pm 0.005$ .

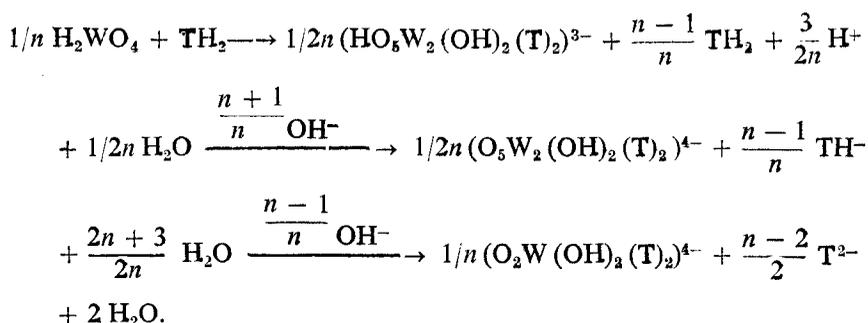
## 3. Results and Discussion

### 3.1. Excess of tartaric acid

Following polarimetrically the neutralisation with NaOH of a mixture of tartaric and tungstic acids in which the ratio  $\text{WO}_3/\text{TH}_2$  is constant and higher than one, Britton and Jackson observed the existence of two points of discontinuity that they ascribed to the formation and dissociation of a complex whose formula is  $\text{Na}_2(\text{WO}_3)\text{C}_4\text{H}_4\text{O}_6$ .

The neutralisation curves have an ascending section with a maximum or first discontinuity point. Independent of the amount of tungstic acid present, the curves show that maximum rotation is found for solutions containing two equivalents of alkali. This maximum value should indicate the complete formation of this complex. Further addition of alkali rapidly diminishes the rotatory power until the alkali concentration is sufficient to neutralise the tungstic acid as sodium tungstate, the rotation then becoming exactly equal to that of the parent sodium tartrate. Hence it is inferred that the complex formed whilst the solution is still incompletely neutralised, is completely broken down into normal sodium tartrate and sodium tungstate.

We are able to confirm observations of Britton and Jackson by doing a similar experiment. In figure 1, the rotatory power and the pH values are plotted against the equivalents of NaOH added. Each sample contained, in a total volume of 50 ml, 1 ml of *l*(+) tartaric acid (1M), 1 ml of tungstic acid (0.5M) and increasing volumes of NaOH (0.18M). All the samples were prepared in such a way as to result (1M) in  $\text{NaClO}_4$  to maintain the ionic strength of the medium constant. The scheme that we have deduced previously would describe the first section of the polarimetric curve, not as a single equilibrium but as a sequence, according to the following equations



These equations indicate consumption of two equivalents of alkali. Variations in the tungstic acid concentration did not affect the position of the maximum rotatory power and at this point (pH = 5.5) the only stable species is that of stoichiometry 1 : 2.

Further addition of alkali gives a regular drop of optical rotation until the alkali is sufficient to neutralise the  $(\text{O}_2\text{W}(\text{OH})_2(\text{T})_2)^{4-}$  species as sodium tungstate and  $l(+)$  sodium tartrate (pH = 7.5).

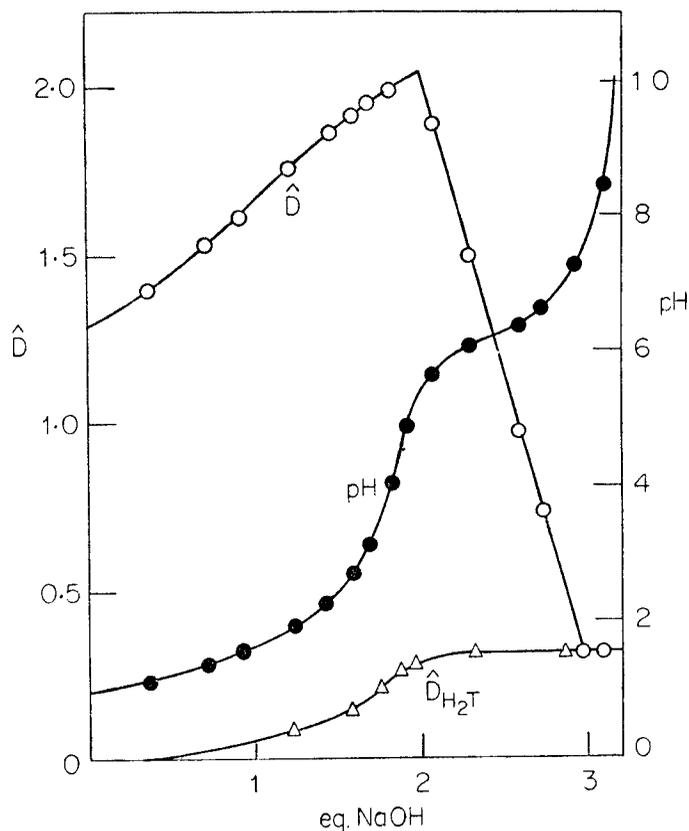
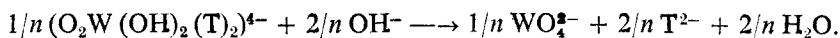


Figure 1. Plots of optical rotation and pH against equivalents of NaOH. (tartaric acid =  $2 \cdot 10^{-3}$  M, tungstic acid =  $10^{-3}$  M,  $\lambda = 365$  nm,  $\hat{D}$  = degrees).

As we can see our scheme as well as that of Britton and Jackson explains the experimental observations. This scheme also interprets more coherently the polarimetric measurements. Therefore, the initial high rotatory power of the solution of tartaric and tungstic acids indicates the formation of complexes at low pH values. The increase in the optical rotation when this solution is neutralised does not follow a linear course demonstrating the presence of more than one complex species at low pH values.

### 3.2. Equimolecular amounts of tartaric and tungstic acids

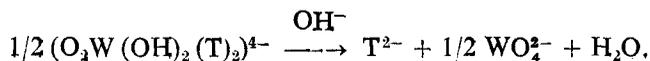
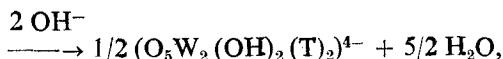
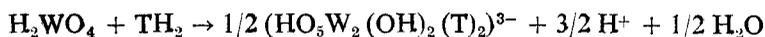
The scheme proposed by Baillie and Brown tries to be an improvement over that of Britton and Jackson but both suggest that complex species of 1:1 stoichiometry are only present. However, Baillie and Brown employed equimolecular solutions of the two acids to study the neutralisation polarimetrically and potentiometrically. According to them the polarimetric curve is different from that observed by Britton and Jackson for solutions containing excess of tartaric acid. A maximum rotation is also obtained for two equivalents of alkali (pH = 4.2) but now, instead of a regular decrease in the optical rotation with pH, three breaks in the curve were obtained at 7.0, 8.3 and 11.0 pH.

To explain these results, Baillie and Brown propose that the breaks in the curve correspond to the presence of three different complexes:  $(\text{WO}_4(\text{C}_4\text{H}_3\text{O}_6))^{2-}$ , pH 4.2;  $(\text{WO}_4(\text{C}_4\text{H}_3\text{O}_6))^{3-}$ , pH 7.0; and  $(\text{WO}_4(\text{C}_4\text{H}_4\text{O}_6))^{4-}$ , pH 8.2. The tetrabasic complex appears to be stable up to pH 11.0, above which dissociation to tartrate and tungstate occurs.

We have been able to verify most of Baillie and Brown's observations. A plot of optical rotation against pH is presented in figure 2. Each sample contained, in a total volume of 50 ml, 1 ml of *l*(+)-tartaric acid (1 M), 2 ml of tungstic acid (0.5 M), 12.5 of  $\text{NaClO}_4$  (4 M) and increasing volumes of NaOH (0.18 M).

Baillie and Brown's curve is similar to our own except that the latter is slightly displaced towards stronger acidity area and the first three discontinuities are found at pH 3.5, 5.5 and 7.2. However, after the maximum (pH 3.5) the variation of rotation with pH shows two breaks instead of three. At pH 7.2, in the present work, the optical rotation of the tartrate-tungstate solution was the same as that of *l*(+)-sodium tartrate solution of the equivalent concentration, whereas in the Baillie and Brown's curve it occurs at pH 11.0. Excepting this, we observe close similarity between the two curves.

We have plotted optical rotation and the pH values against the equivalents of added NaOH (figure 3). Three breaks are found at 2 (pH = 3.5), 2.4 (pH = 5.5) and 4.0 equivalents of NaOH. To explain these results, the following equilibria are suggested:



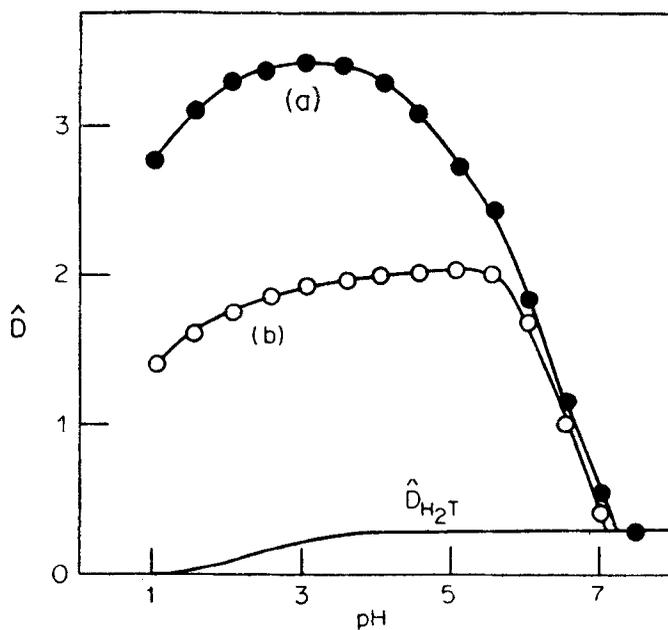


Figure 2. Plots of optical rotation against pH for : (a)  $H_2T/H_2WO_4 = 1$ , (b)  $H_2T/H_2WO_4 = 2$ ,  $\lambda = 365 \text{ nm}$ ,  $\hat{D} = \text{degrees}$ .

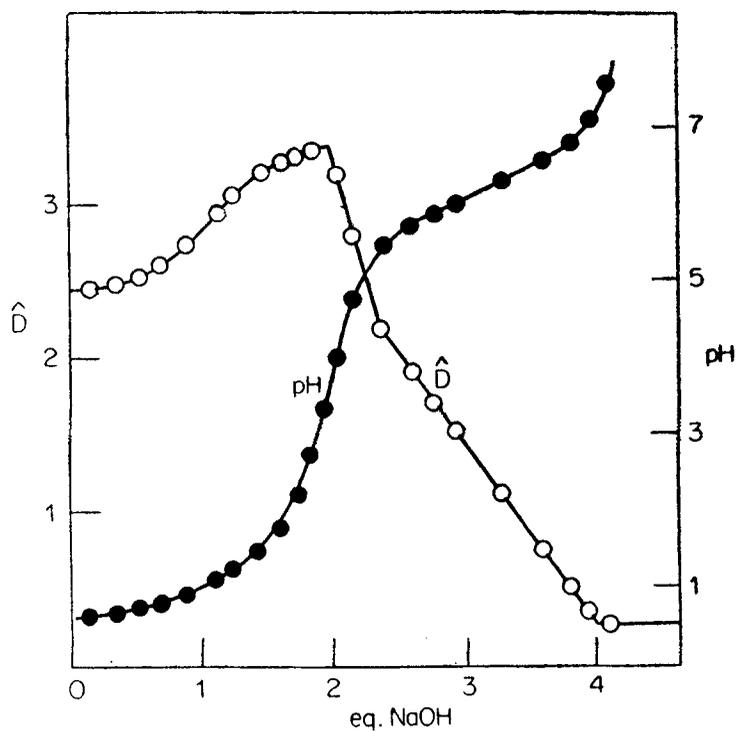
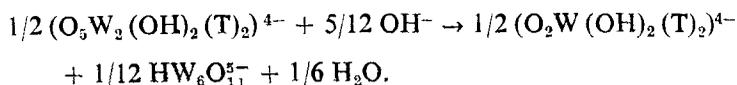


Figure 3. Plots of optical rotation and pH against equivalents of NaOH (tartaric acid =  $2 \cdot 10^{-2} \text{ M}$ , tungstic acid =  $2 \cdot 10^{-2} \text{ M}$ ,  $\lambda = 365 \text{ nm}$ ,  $\hat{D} = \text{degrees}$ ).

The equimolecular solution of tartaric and tungstic acids has a pH less than 1.0 before adding NaOH. Consistent with our scheme the only stable species present is  $(\text{HO}_5\text{W}_2(\text{OH})_2(\text{T})_2)^{4-}$ , and its existence is confirmed by the high optical rotation of the solution.

The increase in the optical rotation, as the neutralisation progresses, with the subsequent complex transformation, from  $(\text{HO}_5\text{W}_2(\text{OH})_2(\text{T})_2)^{3-}$  to  $(\text{O}_5\text{W}_2(\text{OH})_2(\text{T})_2)^{4-}$ , is easily understood because the specific molar rotation of the latter complex is higher than that of the former.

The second break may be interpreted as due to the complete formation of  $(\text{O}_2\text{W}(\text{OH})_2(\text{T})_2)^{4-}$ . According to the equations given above, it would appear that three equivalents of alkali are needed. However, in figure 3, it is noted that this discontinuity appears some time before the stoichiometric amount of NaOH had been added (2.4 equivalents). This is explained as follows: when the complex  $(\text{O}_5\text{W}_2(\text{OH})_2(\text{T})_2)^{4-}$  is converted to  $(\text{O}_2\text{W}(\text{OH})_2(\text{T})_2)^{4-}$ , the free tungstate ions are not stable in an acid medium. In this pH interval the condensation of tungstate yields mainly the paratungstate ions  $(\text{HW}_6\text{O}_{11})^{5-}$  and we can write the interconversion between these complexes as:



Further addition of alkali (1.6 equivalents) is consumed to neutralise the paratungstate and the complex of stoichiometry 1:2, into tungstate and tartrate ions. In this way the discontinuity at pH 7.2, is interpreted as in that of Britton and Jackson and it indicates complete decomposition of the complex.

It has not been possible for us to reproduce the interval from pH 8.2 to 11, in the curve of Baillie and Brown which was interpreted as due to  $(\text{WO}_4(\text{C}_4\text{H}_4\text{O}_6))^{4-}$  stability zone. However, it is difficult to admit the existence of complex species when the tungstic and tartaric acid have been completely neutralised and, even more to explain how the pH can influence its dissociation. On the other hand, Liska and Plsko (1961) have proved that the rotatory power of solution containing sodium tungstate and  $l(+)$  sodium tartrate is the one due to the tartrate anions that they contain.

To conclude, in figure 2, a plot of the rotatory power against pH for a ratio  $\text{WO}_3/\text{TH}_2$  equal to 1 (Baillie and Brown experiment) and for 1/2 (Britton and Jackson experiment) is given to provide further experimental support to our scheme. Before adding NaOH the pH is less than 1.0. When the ratio is 1/2, it is observed that the rotatory power of this solution is half of that reached when the ratio is equal to 1.0. At this pH the only stable complex is  $(\text{HO}_5\text{W}_2(\text{OH})_2(\text{T})_2)^{3-}$  and for a ratio equal to 1/2, the concentration of this species is half of that obtained when we start from equimolecular amounts, and the free remaining tartaric acid has a negligible rotatory power.

However, for pH values higher than 5.5, an equal concentration of  $(\text{O}_2\text{W}(\text{OH})_2(\text{T})_2)^{4-}$  is formed for both ratios, leading to identical variation of the rotatory power.

**References**

- Baillie J M and Brown D H 1961 *J. Chem. Soc.* 3961  
Banerjee S P and Bhattacharya A K 1962 *J. Indian Chem. Soc.* **39** 69  
Beltrán J, Cervilla A and Beltrán A 1979 *An. Quim.* **57** 773  
Biswas A B 1945 *J. Indian Chem. Soc.* **22** 351  
Britton H T S and Jackson P 1934 *J. Chem. Soc.* 998  
Cervilla A, Beltrán A and Beltrán J 1979 *Can. J. Chem.* **57** 773  
Liska M and Plsko E 1961 *Sb. Prac. Chem. Fak SVST* 73  
Raman R and Vaishya B L 1934 *J. Indian Chem. Soc.* **11** 179