

717. Tungstate and Molybdate Complexes with Tartaric, Malic, and Succinic Acid.

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Tungstate and molybdate ions form 1 : 1 complexes with tartaric, malic, and succinic acid over a limited range of pH. The complexes are weaker acids than the parent organic acids. The nature of the anions formed has been investigated by polarimetric, conductometric, and potentiometric methods. The salts obtained on precipitation at a fixed pH are related to the anions existing in solution at that pH. The possible structures of the complex anions are discussed.

NORMAL tungstate and molybdate ions form complexes with a number of carboxylic acids. Most of these complexes have been isolated in solid form but, apart from the stoichiometry, little has been elucidated about the ions present in solution. Tartaric acid and sodium tungstate, for example, form tartratotungstates¹ $[\text{WO}_3(\text{C}_4\text{H}_4\text{O}_6)]^{2-}$ and ditartratotungstates² $[\text{WO}_2(\text{C}_4\text{H}_4\text{O}_6)_2]^{2-}$, but, in solution, only the stoichiometry of the 1 : 1 complex anion has been found by Britton and Jackson.³ These authors modified Rosenheim and Itzig's method¹ by confining their optical rotation experiments to 0.1M-tartaric acid solutions so as to avoid effects due to alkali-metal ions.⁴ They confirmed the finding that the optical rotation was maximal when equimolar proportions of tungstate and tartrate were present in solution, *i.e.*, that a 1 : 1 complex was formed. Similarly, with molybdate a 1 : 1 complex was obtained. The object of the present investigation was to determine the nature of the complexes and to study also the complexes with succinic and malic acid.

We confirmed Britton and Jackson's finding of maximal optical rotation at a 1 : 1 ratio of tungstate or molybdate to tartrate. However, different results were found when the optical rotation was examined at different pH values: equal volumes (20 ml.) of 0.1M-sodium tungstate and tartaric acid were mixed, the pH was adjusted with *N*-sodium hydroxide or -hydrochloric acid, the volume made up to 50 ml., and the whole left for 24 hours. The numerical values of α (identical for *D*- and *L*-tartaric acid) are shown in curve A of Fig. 1. Instead of the regular drop of optical rotation with pH in alkaline solution described by Britton and Jackson, four breaks in the curve were obtained, at pH 4.2, 7, 8.3, and 11. At pH > 11.5, the optical rotation of the tartratotungstate solution was the same as that of sodium tartrate solution (curve E) of the same concentration at the same pH, suggesting that at pH 11.5 the complex breaks down to sodium tartrate and sodium tungstate. With *L*-malic acid, a similar curve (B) was obtained with a smaller optical rotation and with the breaks a little less well defined, probably because only one asymmetric centre is involved. The corresponding molybdate complexes appeared to be stable over a rather lower pH range and the curves (C, D) do not show any breaks.

Conductometric-titration curves (Fig. 2) for 10⁻³M-tartratotungstate with 0.1M-sodium hydroxide showed an end-point corresponding to two equivalents of alkali, the acidic groups being weaker in the complex than in the free acid. Similar results were given by malic acid and succinic acid. The same end-point (2 equivalents of alkali) was obtained with solutions containing an excess of the organic acid: curve (C) shows a titration of a solution containing a five-fold excess of malic acid.

¹ Rosenheim and Itzig, *Ber.*, 1900, **33**, 707.

² Barr and Henderson, *J.*, 1896, **69**, 1451.

³ Britton and Jackson, *J.*, 1934, 1055.

⁴ Britton and Jackson, *J.*, 1934, 998.

solution, the composition of the salts varied with pH, limiting values being obtained at pH 4 and 10 as given in Table 1. The barium salts were used, as the sodium salts were so soluble that they separated only on addition of ethanol to concentrated solutions. The formulæ given retain the initial number of oxygen atoms. Previous workers^{1,2} have written their formulæ to suggest breaking of W-O bonds. This seems unlikely, first, owing to the ease of reversibility of the reactions in solution and, secondly, because both tungsten and molybdenum commonly exist with six oxygen atoms co-ordinated for the polymerised forms. The possible structures of these complexes, discussed below, retain these oxygen atoms co-ordinated to the ions without loss of oxygen from the ligands.

TABLE 1. *Barium tartratotungstates.**

	C	H	WO ₄	Ba
At pH 4: Found (%)	9.7	1.2	46.15	25.35
Calc. for Ba[WO ₄ (C ₄ H ₄ O ₆)] (%)	9.0	1.1	46.5	25.7
At pH 10: Found (%)	6.4	0.6	37.3	41.9
Calc. for Ba ₂ [WO ₄ (C ₄ H ₄ O ₆)] (%)	7.2	0.5	36.8	42.9

* Ba, by dissolution in HCl and precipitation as BaSO₄. W, by removal of Ba, precipitation by cinchonine, and ignition to WO₃. Organic acid by combustion.

Infrared spectra (KCl discs) of the two barium tartratotungstates were compared with those of tartaric acid, disodium tartrate, and barium tartrate. The carboxyl peak at 1730 cm.⁻¹ in tartaric acid shifts to 1590 cm.⁻¹ in spectra of the salts. For salts of the complex, however, the peak is slightly broader, indicating that the carboxyl group is probably involved in complex-formation; however, complex- and salt-formation would involve similar shifts, so that this evidence does not alone confirm the state of ionisation of the carboxylic acid groups. The contrast between the breadth of the hydroxyl peaks at 3340 cm.⁻¹ in the spectra of the two complex barium salts indicates probably a decrease in hydrogen bonding in the salt precipitated at pH 10 since this salt gives a much narrower peak.

The relative thermal stabilities of the two barium salts were compared on a thermogravimetric balance. That prepared at pH 4 was stable up to 250°, the other started to decompose at 150°.

When equimolar solutions of sodium tungstate and tartaric acid, adjusted to the same pH, were mixed, the pH rose. This, along with the shapes of the conductivity graphs in Fig. 2, suggested that the complex was a weaker acid than tartaric acid. The complex appeared to be formed fairly completely in 0.1M-solution since, when varying amounts of sodium tungstate were added to a fixed concentration of tartaric acid and the pH adjusted to 9.5 in each case, the optical rotation reached a maximum when the ratio of tungstate to tartrate was 1 : 1 and did not increase, even with a large excess of sodium tungstate present. For the equilibria



and



the approximate dissociation constants can be calculated from the polarimetric data, by assuming that at pH 4.2 the dibasic, at pH 7.0 the tribasic, and at pH 8.2 the tetrabasic complex are present almost exclusively. Typical results obtained are given in Table 2. For malic acid, the mean K_1 and K_2 values were 6.9×10^{-7} and 3.0×10^{-8} respectively.

TABLE 2. *Approximate dissociation constants of sodium tartratotungstates.*

pH	4.6	5.0	5.4	6.0	7.2	7.4	7.8	8.0
10 ⁶ K ₁	3.5	3.3	3.5	3.4	—	—	—	—
10 ⁶ K ₂	—	—	—	—	3.0	3.0	2.9	3.2

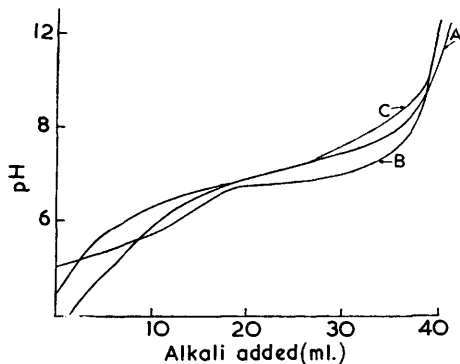
To confirm these K_1 and K_2 values, potentiometric titrations of equimolar solutions of sodium tungstate and malic, tartaric, and succinic acid respectively in 0.2M-potassium

chloride were carried out with alkali. The curves (Fig. 3) show only one point of inflection, in agreement with the relative proximity of the K_1 and K_2 values. These values were calculated by means of Britton's formula;⁵ the mean values are given in Table 3. Included

TABLE 3. *Dissociation constants.*

	K_1	K_2
Tartaric acid	1.32×10^{-3}	1.15×10^{-4}
Tartratotungstate complex	2.8×10^{-6}	3.4×10^{-8}
Malic acid	5.50×10^{-4}	2.09×10^{-5}
Malatotungstate complex	7.3×10^{-7}	3.0×10^{-8}
Succinic acid	8.51×10^{-5}	5.25×10^{-6}
Succinatotungstate complex	5.1×10^{-7}	1.3×10^{-7}

are K_1 and K_2 for the free acids given by Cannan and Kibrik.⁶ The potentiometric show close agreement with the polarimetric data for the tartaric and malic acid complexes. The K_1 values of the complex acids are similar to each other in the same way as those of the free acids. The K_2 values, however, of the malic and tartaric acid complexes are very close to each other whilst the K_2 value for the succinic acid complex is larger, thus reversing the order for the free acids. A possible explanation is discussed below.

FIG. 3. *Potentiometric titration of :*

- (A) 0.05M-tartratotungstate,
 (B) 0.05M-succinatotungstate, and
 (C) 0.05M-malatotungstate, each 40 ml., with 0.108N-sodium hydroxide.

The conductometric and potentiometric experiments described above were repeated with diethyl tartrate in place of tartaric acid. No complex-formation was apparent with either tungstate or molybdate ions.

Discussion.—Tartaric, malic, and succinic acid form 1:1 complexes with tungstate and molybdate ions. In the case of the tartratotungstate complex, which has been studied most fully, the considerable change in acid dissociation constants, the infrared spectra, and the fact that no complex is formed with diethyl tartrate indicate that both the carboxylic groups are involved. From scale models, it seems that the O—O distance between the two C=O groups of the carboxylic acid groups could be *ca.* 3.0 Å, corresponding to that in the octahedral WO_6 group in heteropolytungstates⁷ (2.6—3.2 Å). For both pairs of oxygen atoms in the carboxylic acid groups to be bonded directly to the central tungsten atom, the W—O distances involved would be too large. When the model was arranged with one oxygen atom from each carboxylic acid groups in the WO_6 octahedron, forming a seven-membered ring, the hydrogen atoms of both carboxylic groups were well within the limits for hydrogen bonding⁸ to another oxygen atom of the WO_6 octahedron. This would lead to the formation of two six-membered rings which are normally stable groups. The restriction placed on the ionising proton by inclusion in this ring would account for the fact that the complex is in each case a weaker acid than the corresponding

⁵ Britton, "Hydrogen Ions," Chapman and Hall Ltd., London, 1955, Vol. I, p. 217.

⁶ Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314.

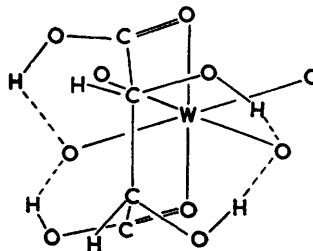
⁷ Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.

⁸ Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, New York, 1948, pp. 329 *et seq.*

free acid. The greater thermal stability of the un-ionised than of the ionised complex could also be due to the two extra ring systems formed.

When one proton ionises, in the case of all three complexes, a similar type of ring has to be broken; thus the order of the K_1 values remains the same as in the free acids. From qualitative evidence, *e.g.*, the very small change in the optical rotation on addition of succinic acid to a solution of D-tartratotungstate, it appears that the succinatotungstate is very much less stable than the tartratotungstate complex. Therefore, the α -hydroxy-groups are possibly involved through hydrogen bonding, in the complex, as shown in Fig. 4; these bonds will assist in stabilising the complex after the first proton is ionised. Thus, since there are no hydroxyl groups the succinatotungstate complex will have a greater tendency for hydrolysis after the first ionisation stage, so that K_1 and K_2 become approximately equal. As shown above, this was the case.

FIG. 4. Possible structure of the $[\text{WO}_4(\text{C}_4\text{H}_6\text{O}_6)]^{2-}$ ion.
The broken lines represent hydrogen bonds.



The molybdate complexes appear only to exist over a limited, more acid region. They are hydrolysed as ionisation occurs and the only stable species are formed by the un-ionised acids with the molybdate ion, giving bivalent complexes possibly similar to the bivalent tungstate complexes described above. This difference in stability is possibly due to the smaller ring of the molybdate ion which, to exist in solution, requires the stabilising effect of the two six-membered ring systems of the un-ionised carboxylic acid groups with the molybdenum and oxygen atoms.

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