# 934. *Tungstate and Molybdate Complexes with Glycollic and Mandelic Acid.*

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Tungstate and molybdate ions form 1 : 2 complexes with glycollic and mandelic acid over a limited range of pH. The stoicheiometry of the complexes is confirmed by conductometric and polarimetric methods. The possible structures of the complex ions in solution are discussed. The inability of tungstate or molybdate ions to form complexes with acetic and phenylacetic acid is also shown.

COMPLEXES of α-hydroxy-carboxylic acids with tungstate, molybdate, and other inorganic anions have been known for some time.[1] In particular, Richardson[2] examined the stoicheiometry of the mandelic acid–molybdic acid and mandelic acid–tungstic acid complexes by conductometric methods, in acid solution. He claimed a 2 : 1 ratio for the former and a 3 : 1 ratio for the latter. The purpose of the present investigation was to confirm the stoicheiometry and to determine the nature of the complexes formed in solution by tungstate and molybdate ions with mandelic and glycollic acid.

## EXPERIMENTAL AND RESULTS

Complexes of tungstate and molybdate with organic acids exist, in general, in weakly acid, neutral, and weakly alkaline solution, *i.e.*, at pH's where polymerisation of the simple anions normally occurs. Thus it can be difficult to determine whether complexes are formed and, if so, what is their nature, by conductometric or potentiometric methods involving a change in pH unless the species of tungstate or molybdate ion involved in the complex is known. Quantitative ultraviolet-absorption measurements are also confusing, as complex-formation and polymerisation cause similar shifts in the maxima.[2,3] In addition, the ultraviolet spectra of some of the 12-acids change with pH.[4] However, with some optically active organic compounds, a large increase in optical rotation is obtained when a complex is formed with tungstate or molybdate ion.[5] For L-mandelic acid, a plot of optical rotation against molar fraction of acid indicated a 2 : 1 mandelic acid : metal complex for both tungstate and molybdate (Fig. 1). Conductimetric measurements obtained on adding 10M-mandelic acid to $10^{-3}$M-sodium tungstate confirmed the stoicheiometry (Fig. 2). The pH of these solutions changed, during the conductimetric titrations, from ~7·5 to ~3·0. In this pH range polymerisation of the tungstate ion

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[1] Rimback and Ley, *Z. phys. Chem.*, 1922, **100**; Fairbrother and Taylor, *J.*, 1956, 4946.
[2] Richardson, *J. Inorg. Nuclear Chem.*, 1960, **13**, 84.
[3] Lindquist, *Acta Chem. Scand.*, 1951, **5**, 568; Cannon, *J. Inorg. Nuclear Chem.*, 1959, **9**, 252.
[4] Keller, Matigeric, and Kerker, *J. Phys. Chem.*, 1961, **65**, 56.
[5] Britton and Jackson, *J.*, 1934, 1055; Baillie and Brown, *J.*, 1961, 3691.

would certainly have competed with complex-formation unless the latter had been dominant. There was no break in the curves at $\frac{7}{6}$ equivalents of added hydrogen ion: this suggested that little paratungstate ion was formed. The reactions of the mandelatotungstate ion solutions also supported the relative absence of polymerisation; *e.g.*, at pH 5·3 barium paratungstate was precipitated rapidly when barium chloride solution was added to 0·001M-paratungstate whereas if an excess of mandelic acid was present the precipitate was that of the complex. This value for the tungstate–mandelic acid complex is different from that obtained by Richardson.[2] He, however, started with tungstic acid of unknown molecular weight, in solution at a pH <2, where, as judged from Fig. 3, polymerisation of the tungstate ions competes with complex-formation.

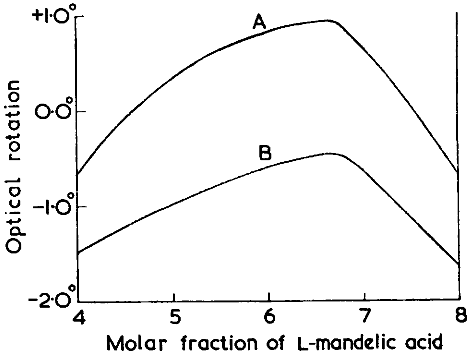

FIG. 1. Optical rotation plotted against molar fraction of L-mandelic acid.

(A) $2 \times 10^{-2}$M-Sodium molybdate and $2 \times 10^{-2}$M-L-mandelic acid. (B) $2 \times 10^{-2}$M-Sodium tungstate and $2 \times 10^{-2}$M-L-mandelic acid.

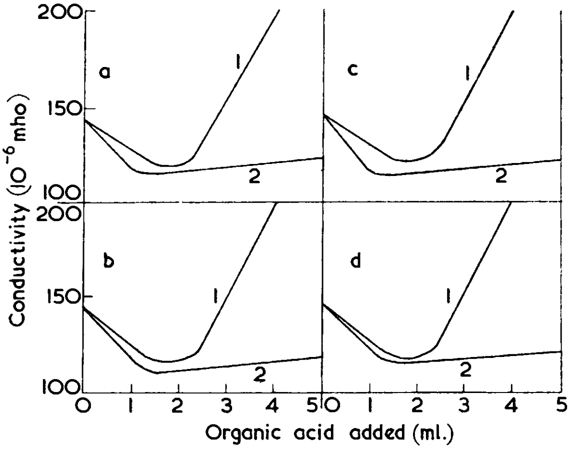

FIG. 2. Conductometric titrations. $10^{-1}$M-Organic acid added to $10^{-3}$M-inorganic salt solution (100 ml.).

a, (1) Mandelic acid–sodium tungstate. (2) Phenylacetic acid–sodium tungstate. b, (1) Glycollic acid–sodium tungstate. (2) Acetic acid–sodium tungstate. c, (1) Mandelic acid–sodium molybdate. (2) Phenylacetic acid–sodium molybdate. d, (1) Glycollic acid–sodium molybdate. (2) Acetic acid–sodium molybdate.

To determine the range of stability of the L-mandelato-tungstate and -molybdate complexes, the optical rotations for solutions of a fixed concentration at different pH values were found (Fig. 3) (20 cm. tube; sodium D light). They show that complex-formation on the alkaline side begins around pH 8·8 for the tungstate complex and around pH 7·6 for the molybdate complex. In both cases the region of maximum optical rotation occurs in the region of pH 3—5. Below this pH range, presumably, the competing reaction of tungstate or molybdate polymerisation had a greater effect, and above it the complexes are hydrolysed. The greater change in the optical rotation with the molybdate than with the tungsten complex is probably due to the smaller size of the molybdenum(VI) ion, causing a greater electron shift away from the asymmetric carbon atom towards the metal ion.

Potentiometric titration of solutions of mandelato-molybdate and -tungstate with sodium hydroxide solution show equivalence points around pH 7·6 and 8·6, respectively, after two equivalents of alkali have been added. These values correspond to those mentioned above for complete hydrolysis of the complexes. Thus complete neutralisation of the acid present appears to correspond to complete hydrolysis of the complexes. This will be the case if the acidic hydrogen in the carboxylic acid group is involved in the complex-formation. The initial steep rise in pH between 4·3 and 6 corresponds to part of the region of approximately constant optical rotation (Fig. 3) where the concentration of the complexes appears to be fairly constant. Thus addition of sodium hydroxide causes a rapid increase in pH until the hydroxyl ion concentration is sufficiently high to cause hydrolysis of the complexes with subsequent neutralisation of the liberated acids.

To determine if the α-hydroxy-group was involved in the complex, phenylacetic was used in place of mandelic acid, the dissociation constants 3·41 for mandelic acid[6] and 4·31 for phenylacetic acid[7] being sufficiently close to make comparisons reasonably valid. Conductometric titrations (Fig. 2) suggested that there was no complex-formation and that the turning points were due to polymerisation. The first stage in the polymerisation of the tungstate ion involves the formation of the paratungstate ion: $6WO_4^{2-} + 7H^+ \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O$. The turning points due to this reaction are observed in the phenylacetic and acetic acid graphs. Further acidification involves the taking up of two other hydrogen ions to give the anion $H_3W_6O_{21}^{3-}$. This stage, although characterised to some extent in titrations with hydrochloric acid, is masked when weaker organic acids are used, and a slow increase in conductivity due to the buffering action of the polytungstate ions results. This is in contrast to the rapid increase of conductivity after the turning point in the mandelic and glycollic acid graphs. Here, after all the tungstate has been converted into complex, the increase in conductivity is due to the addition of the organic acid. Similar conclusions can be drawn from the molybdate titrations. These results were confirmed by adding phenylacetic acid to a standard solution of D-tartratotungstate and comparing the optical rotation with that of a similar solution with dilute hydrochloric acid in place of the phenylacetic acid, both solutions being adjusted to pH 4. There was no change in the optical rotation even when a large excess of phenylacetic acid was used. Similar results were obtained on use of D-tartratomolybdate. Thus it seems that phenylacetic acid does not form a complex with tungstate or molybdate ions or, if it does, the complex formed is very weak and cannot compete with the normal polymerisation.

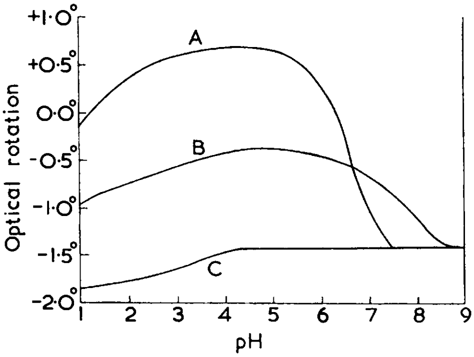

FIG. 3. Optical rotation plotted against pH.

A, 0·02M-L-Mandelatomolybdate. B, 0·02M-L-Mandelatotungstate. C, 0·02M-L-Mandelic acid.

To confirm this effect of the α-hydroxy-group acetic and glycollic acid were also compared. Again conductometric evidence (Fig. 2) suggested that glycollic acid formed a 2 : 1 complex with both molybdate and tungstate ions and that acetic acid did not. This was confirmed, as above, by measuring the effect on the optical rotation of D-tartrato-tungstate and -molybdate solutions at pH 4. Glycollic acid in both cases lowered the optical rotation whereas acetic

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[6] Banks and Davies, *J.*, 1938, 73.

[7] Lloyd, Wycherley, and Monk, *J.*, 1951, 1786.

acid had no effect. Since the optical rotation of D-tartratotungstate solution is proportional to its concentration, the use of known initial concentrations of D-tartratotungstate and glycollic acid and measurement of the resulting optical rotation of the solution permits the concentration of D-tartratotungstate and hence the equilibrium constant for the following equation to be calculated:

$$\text{D-Tartratotungstate} + C \times \text{Glycollic acid} \rightleftharpoons \text{Glycollatotungstate} + \text{D-Tartaric acid}$$

where $C$ is an integral constant. By using various concentrations of glycollic acid, a constant value for the equilibrium constant was found for $C = 2$. The values for $C = 1$ are given for comparison (Table; 20°; pH 4·0). A similar result was found for the glycollatomolybdate complex. These results confirm the 1 : 2 stoicheiometry.

| Glycollic acid, orig. concn. (M) | D-Tartratotungstate orig. concn. (M) | D-Tartratotungstate final concn. (M) | $K$ for $C = 1$ | $K$ for $C = 2$ |
|---|---|---|---|---|
| 0·050 | 0·040 | 0·028 | 0·135 | 7·63 |
| 0·060 | 0·040 | 0·026 | 0·168 | 7·42 |
| 0·070 | 0·040 | 0·024 | 0·197 | 7·41 |
| 0·080 | 0·040 | 0·022 | 0·238 | 7·64 |

The silver salts of the mandelato- and glycollato-tungstate complexes were prepared and the infrared spectra measured (potassium chloride discs). These salts were dibasic and had the general formula $Ag_2WO_4(\text{organic acid})_2$. Their spectra were compared with those of the corresponding free acids and normal silver salts. The carbonyl peak for the free acids, the normal salts, and tungstate complexes were at 1725, 1580, and 1630 cm.$^{-1}$, respectively. These figures suggested that the carbonyl group was involved in complex-formation. Similar results were obtained for the molybdate complexes. There was no apparent change in the wavelength of the hydroxyl peak at 3400 cm.$^{-1}$ though it appeared relatively much stronger in the complex than in the normal salts. Since the free acid showed hydrogen-bonded hydroxyl groups, this confirmed the view that those in the complex were also hydrogen-bonded.

The silver content of the salts described above was found by dissolving the salts in dilute nitric acid, precipitating silver with sodium chloride, and drying and weighing the precipitate. After the silver had been removed, cinchonine hydrochloride was added to precipitate the tungstate or molybdate complex which was then filtered off and ignited to $WO_3$ or $MoO_3$. The organic acid content was found by standard analysis. Typical results are:

| | Found (%) | | | | Required (%) | | |
|---|---|---|---|---|---|---|---|
| Ag salt | Ag | $MO_4$ | Org. acid | Formula | Ag | $MO_4$ | Org. acid |
| Mandelatotungstate ...... | 28·7 | 32·4 | 39·4 | $Ag_2WO_4(C_8H_8O_3)_2$ | 28·1 | 32·3 | 39·6 |
| Glycollatotungstate ...... | 35·3 | 40·5 | 24·5 | $Ag_2WO_4(C_2H_4O_3)_2$ | 35·1 | 40·3 | 24·7 |
| Mandelatomolybdate ... | 31·9 | 23·7 | 44·6 | $Ag_2MoO_4(C_8H_8O_3)_2$ | 31·8 | 23·5 | 44·7 |
| Glycollatomolybdate ... | 50·1 | 30·4 | 28·6 | $Ag_2MoO_4(C_2H_4O_3)_2$ | 40·9 | 30·3 | 28·8 |

The ethyl esters of the four organic acids were prepared. However, even when added in large excess to solutions of D-tartratotungstate (or molybdate), they did not alter the value of the optical rotation from that observed in a solution acidified to the same pH with hydrochloric acid, thus showing their inability to form complexes. This evidence also suggests that the hydroxy-group of the carboxylic acid is involved in the complex.

## DISCUSSION

Our evidence indicates that mandelic and glycollic acid form 2 : 1 complexes with molybdate and tungstate ions whereas phenylacetic and acetic acids do not. Also, since the carbonyl and two hydroxy-groups are involved in the complex, the un-ionised organic acid appears to be the complex-forming ligand. The state of the tungstate and molybdate ions is more difficult to confirm. Analyses of the solid salts of the complexes suggest that the complex-forming species are the normal molybdate and tungstate ions. Since no change in pH occurs on precipitation, there appears to be no depolymerisation of polytungstate or polymolybdate. Some qualitative evidence can also be obtained from the change in pH obtained on mixing solutions of sodium tungstate and mandelic acid, both being adjusted to the same initial pH (6·2) where the main species are paratungstate and mandelate: the pH of the resulting mixture was 6·9. After an initial pH of 2·2, the main species being the more acidic forms of the paratungstate ion and mandelic acid, the pH of the mixture was 1·8. In the first case, the increase in pH is probably due to uptake of hydrogen ion to give the un-ionised mandelic acid which is the complex-forming species. This is partly compensated by the hydrogen ions produced by depolymerisation of the polytungstate ions. In the second case, the decrease in pH can only be due to depolymerisation of polytungstate.

Optical-density measurements also gave some indication of the nature of the complex-forming metal anion. The optical densities of $10^{-4}$M-solutions of sodium tungstate, sodium paratungstate, sodium glycollatotungstate, and glycollic acid at 240 mμ were 0·05, 0·30, 0·11, and 0·04, respectively, which suggests that the complex-forming species was the normal tungstate and not the paratungstate ion.

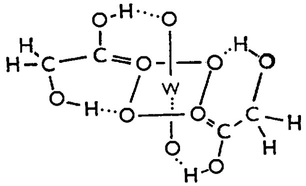

FIG. 4. Possible structure for the glycollatotungstate ion.

In most tungstate and molybdate structures so far confirmed, a central metal ion surrounded octahedrally by six oxygen ions is the basic building unit.[9] If we assume for the glycollatotungstate ion an octahedral structure around the central tungsten atom, then a possible structure might be that shown in Fig. 4. This includes a six- and a seven-membered ring, both involving relatively weak hydrogen bonding and both necessary for stability of the complex. A similar structure can be drawn for the glycollatomolybdate ion and for the corresponding mandelic acid complexes.

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[8] Souchay, *Ann. Chim.* (*France*), 1943, **18**, 169.

[9] Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75; Brown and Mair, *J.*, 1958, 2597; Waugh, Shoemaker, and Pauling, *Acta Cryst.*, 1954, **7**, 438.