

757. *Complexes between Polyhydroxy-compounds and Inorganic Oxyacids. Part IV.¹ Dimolybdate and Ditungstate Ions as Complexing Agents, and Paper Electrophoresis of Maltodextrinols and Isomaltodextrinols in Molybdate and Tungstate Solutions.*

By H. J. F. ANGUS and H. WEIGEL.

Dimolybdate and ditungstate ions have been shown to be agents complexing with polyhydroxy-compounds. The complexes contain either one or two polyol components. Equations for the paper-electrophoretic mobilities of maltodextrinols and isomaltodextrinols are presented.

MOLYBDATE and tungstate have been shown to form anionic complexes with certain polyhydroxy-compounds. In these the M/polyol ratio, where M represents a molybdenum or tungsten atom, is either one¹⁻³ or two.^{2,4} On the basis of evidence previously provided it was not possible to assign detailed structures to these complexes, although the technique of paper electrophoresis in molybdate^{2,5} or tungstate^{1,4} solutions (pH 5), where widely differing mobilities have been observed, has found much use in the separation and identification of polyhydroxy-compounds. In several instances the affinities of polyhydroxy-compounds for ions of inorganic oxy-acids, *i.e.*, borate, germanate, and stannate, have been related to the known structures of the anions existing in aqueous solutions of the particular pH employed.⁶ It was difficult to account for the M/polyol ratios of one

¹ Part III, Angus, Bourne, Searle, and Weigel, *Tetrahedron Letters*, 1964, 55.

² Bourne, Hutson, and Weigel, *J.*, 1961, 35.

³ Spence and Su-Chin Kiang, *J. Org. Chem.*, 1963, **28**, 244.

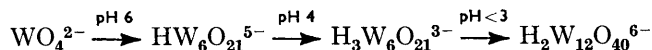
⁴ Angus, Bourne, and Weigel, unpublished results.

⁵ Bourne, Hutson, and Weigel, *J.*, 1960, 4252.

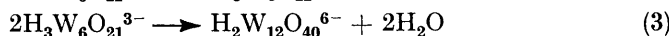
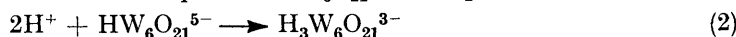
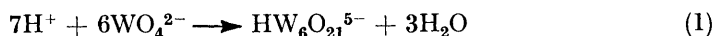
⁶ Weigel, *Adv. Carbohydrate Chem.*, 1963, **18**, 61.

[*e.g.*, D-mannose, D-ribose, and 3-*O*-glycopyranosyl-L-gulitols (4-*O*-glycopyranosyl-D-glucitols)] and two [*e.g.*, D-mannitol, D-glucitol, 2-deoxy-D-*arabino*-hexitol and 1-*O*-glycopyranosyl-L-gulitols (6-*O*-glycopyranosyl-D-glucitols)], if the normal ions, MoO_4^{2-} or WO_4^{2-} , or indeed the ions of the isopoly-acids derived therefrom and known to exist in aqueous solutions, were assumed to be the complexing agents. Thus, it was necessary to ascertain the nature of the inorganic complexing agents before any attempt could be made to interpret previous results in relation to the structures of the complexes.

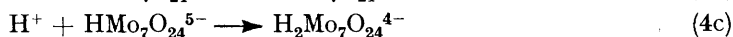
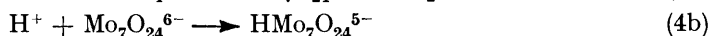
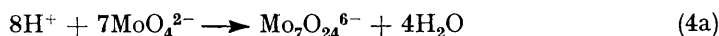
The steps involved in the formation of the ions of isopoly-acids, *e.g.*, isopolytungstates:



have already been deduced from physicochemical studies.⁷ We have essentially confirmed these findings. Thus, the potentiometric and conductimetric titrations of sodium tungstate solutions with dilute sulphuric acid gave the results shown in Figs. 1(A) and 2(A). The inflexion points occur at $\text{H}^+/\text{WO}_4^{2-}$ ratios (Fig. 1A, 1.17 and 1.45; Fig. 2A, 1.13 and 1.50) close to those expected for the formation of $\text{HW}_6\text{O}_{21}^{5-}$ (1.17) and $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ (1.50) (or $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$) according to equations (1—3).



The potentiometric titration of sodium molybdate with sulphuric acid gave a curve (Fig. 1B) with no distinct inflexion point. This is probably not surprising since it is claimed⁸ that the condensation gives, in the first instance, three coexisting polymolybdates according to equations (4a—c).



However, when the titrations were carried out in the presence of excess D-mannitol (*i.e.*, $\text{M}/\text{polyol} < 2$), inflexion points occurred at $\text{H}^+/\text{WO}_4^{2-}$ or $\text{H}^+/\text{MoO}_4^{2-}$ ratios of *ca.* 1.00 (Figs. 1C, 1D, 2B). In a similar manner sodium tungstate was titrated in the presence of other polyhydroxy-compounds. The results (Table 1) show that in all cases, except for

TABLE 1.

Potentiometric titration of tungstate in presence of polyols.

Added polyol	Inflexion points ($\text{H}^+/\text{WO}_4^{2-}$)		Added polyol	Inflexion points ($\text{H}^+/\text{WO}_4^{2-}$)
None	1.17	1.45	Erythritol	0.97
D-Glucose	1.17	1.49	Melibiitol	1.04
D-Mannitol	1.00		D-Mannose	1.00
D-Glucitol	0.98		L-Rhamnose	1.03
Galactitol	1.02		D-Fructose	0.99
			L-Sorbose	0.96

D-glucose, inflexion points occurred at $\text{H}^+/\text{WO}_4^{2-}$ *ca.* 1.0. It is interesting to note that all compounds examined, except D-glucose, migrate during paper electrophoresis in tungstate^{1,4} or molybdate solutions.^{2,5}

The molybdate and tungstate ions which might formally be produced from a $\text{H}^+/\text{MO}_4^{2-}$ ratio of 1, where M is a molybdenum or tungsten atom, are HMO_4^- , $\text{M}_2\text{O}_7^{2-}$, $\text{HM}_3\text{O}_{11}^{3-}$, $\text{M}_4\text{O}_{14}^{4-}$, $\text{HM}_5\text{O}_{18}^{5-}$, and $\text{M}_6\text{O}_{21}^{6-}$, or their hydrated forms. However, it is reasonable to

⁷ Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul, Ltd., London, 2nd edn., 1952, p. 206.

⁸ Sasaki, Lindquist, and Sillén, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93.

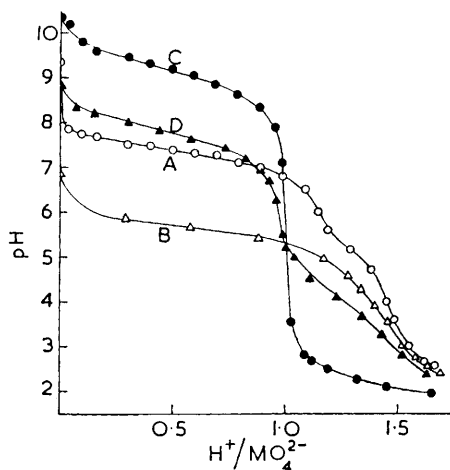


FIG. 1. Potentiometric titrations of tungstate and molybdate solutions. A, Sodium tungstate; B, sodium molybdate; C, D-mannitol and sodium tungstate (molar ratio = 0.2 : 1); D, D-mannitol and sodium molybdate (molar ratio = 1.15 : 1). M represents W or Mo.

FIG. 2. Conductimetric titration of tungstate solutions. A, Sodium tungstate; B, D-mannitol and sodium tungstate (molar ratio = 1.15 : 1).

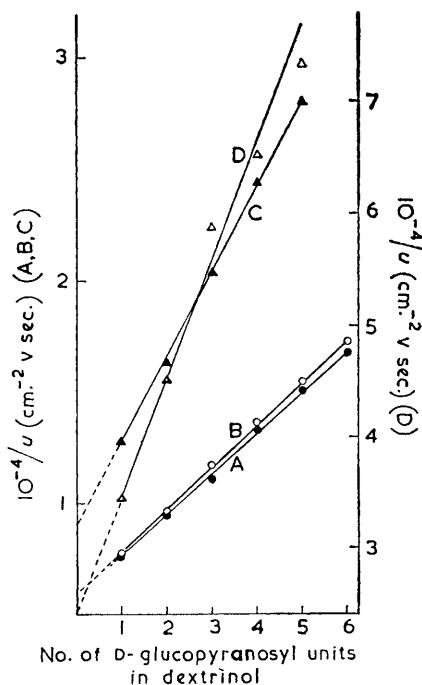
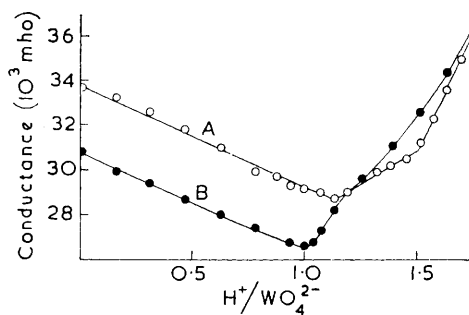


FIG. 3. Reciprocals of paper-electrophoretic mobilities of malto- and isomaltodextrins in molybdate and tungstate solutions. A, Isomaltodextrins in molybdate; B, isomaltodextrins in tungstate; C, maltodextrins in molybdate; D, maltodextrins in tungstate.

assume that the complexes of the various polyhydroxy-compounds shown in Table 1 are all produced from the same type of inorganic ions.

With the exception of the ions HMO_4^- and $\text{M}_2\text{O}_7^{2-}$, all can be eliminated as possible complexing species for the following reasons: the complexing ions are likely to contain either one or an even number of molybdenum or tungsten atoms since polarimetric measurements have shown that in some complexes the M/polyol ratio is 2.^{2,4} However, it is difficult to perceive why the ions containing four (or six) Mo or W atoms can also form complexes in which the M/polyol ratio is 1.¹⁻³ Examination of molecular models of the conceivable structures of an ion containing six molybdenum or tungsten atoms shows that it is impossible to arrange around it three molecules of a hexitol or pentitol known to give complexes in which the M/polyol ratio is 2.

The normal molybdate and tungstate ions (MO_4^{2-}), and presumably the ions corresponding to HMO_4^- , have a tetrahedral symmetry,^{9,10} whereas in their known poly-acids Mo and W are 6-co-ordinated.⁷ It is also reasonable to assume that the complexes are co-ordination compounds with 6-co-ordinated Mo or W. To complete the 6-co-ordination the ions HMO_4^- would require only two hydroxyl groups. However, no compound possessing fewer than three hydroxyl groups showed any tendency to complex with either molybdate² or tungstate.⁴

On the other hand, the M/polyol ratios in the complexes are related to structures of the polyhydroxy-compounds: (a) a ratio of 2 is found for complexes formed from acyclic polyhydroxy-compounds possessing at least four adjacent hydroxyl groups; (b) compounds possessing a triol system, which can assume a spatial disposition approximating to that of (I), give rise to complexes in which the M/polyol ratio is 1. It is thus likely that the complexing species are the dimolybdate, $\text{Mo}_2\text{O}_7^{2-}$, and ditungstate, $\text{W}_2\text{O}_7^{2-}$, ions, or their hydrated forms and that the complexes are formed by reaction between either one molecule (II; M/polyol = 2) or two molecules (III; M/polyol = 1) of a polyhydroxy-compound and one dimolybdate or ditungstate ion. In each case four hydroxyl groups, provided by either one (II) or two (III) molecules of a polyhydroxy-compound, have completed the 6-co-ordination of the two Mo or W atoms. However, in (III) a third hydroxyl group of each molecule of the polyhydroxy-compound has reacted by elimination of water.

In order to substantiate the above conclusions we have examined, by paper electrophoresis, the reduced oligosaccharides of the isomaltose series [isomaltodextrinols; *i.e.*, 1-*O*- α -glycopyranosyl-L-gulitols (6-*O*- α -glycopyranosyl-D-glucitols)] and the maltose series [maltodextrinols; *i.e.*, 3-*O*- α -glycopyranosyl-L-gulitols (4-*O*- α -glycopyranosyl-D-glucitols)] in molybdate and tungstate solutions. These were chosen because (a) in each the hexitol portion of the molecule acquires a negative charge by complexing, and (b) 1- and 3-*O*-glycopyranosyl-L-gulitols form, at least with molybdate, complexes in which the M/polyol ratios are 2 and 1, respectively.

The plot of the reciprocals of the electrophoretic mobilities ($1/u$) against the number of D-glucopyranosyl units, n , present in the dextrinols gives a straight line (Fig. 3). It is unlikely that the charge acquired by the hexitol portion is affected by the molecular size of the dextrinols. Thus, the frictional resistance to motion increases linearly with the number of D-glucopyranosyl units. Extrapolation to $n = 0$ gives the reciprocal of the paper-electrophoretic mobility of the unsubstituted hexitol portion (D-glucitol, $5.88 \times 10^3 \text{ cm.}^{-2} \text{ v sec.}$) only in the series of isomaltodextrinols (Fig. 3, plots A and B). Thus D-glucitol behaves as the first member in the isomaltodextrinol series, whereas maltitol behaves as the first maltodextrinol. For practical use (*e.g.*, determination of molecular size of dextrinols) the $M_s(\text{Mo}$ and $\text{W})$ values (M_s = mobility relative to D-glucitol; Mo and W refer to the electrolytes molybdate and tungstate, respectively) of isomaltodextrinols can be expressed by equations (5) and (6), respectively:

$$1/M_s(\text{Mo}) = 1 + 0.31n, \quad (5)$$

$$1/M_s(\text{W}) = 1 + 0.32n, \quad (6)$$

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whereas those of the maltodextrinols are given by equations (7) and (8), respectively:

$$1/M_s(Mo) = 1.52 + 0.65n, \quad (7)$$

$$1/M_s(W) = 4.07 + 1.81n. \quad (8)$$

It is interesting to note that the M_{BG} values (mobilities relative to *N*-benzyl-D-glucosyl ammonium ion) of the *N*-benzyl-glycosyl ammonium ions of maltose, maltotriose, maltotetraose, and maltopentaose ($n = 1, 2, 3$, and 4 , respectively) reported by Barker, Bourne, Grant, and Stacey,¹¹ obey a similar relation [equation (9)]:

$$1/M_{BG} = 1 + 0.34n. \quad (9)$$

These compounds, of course, migrate as cations.

The plots of $1/u$ against n (Fig. 3) can be affected by (a) the size of the complexing agents; (b) the number of dextrinol molecules, P , combining with the complexing agents; (c) the ionic charge, z , of the complexes; and (d) the stability of the complexes. It is reasonable to assume that the complexing agents are of the same type and, since the interatomic distances in MoO_4^{2-} and WO_4^{2-} (and presumably in the lower poly-anions) are comparable,^{9,10} it is not surprising that D-glucitol has the same mobility in both electrolytes. It has also been shown that, under the conditions of the electrophoresis, 1- and 3-*O*-glycopyranosyl-L-gulitols are completely converted into their molybdate complexes.^{2,4} Thus, variation of P and z for two series of complexes (S_1 and S_2) should give the relations between the plots of $1/u$ vs. n shown in Table 2. The results (Fig. 3)

TABLE 2.

Effect of variations of P and z on plots of $1/u$ against n of two series of complexes (S_1 and S_2).

P (in S_1 and S_2)	z (in S_1 and S_2)	Relation between plots Theor.*	Exp. (series)
Identical	Identical	$u_0(S_1)/u_0(S_2) = \Delta(S_2)/\Delta(S_1) = 1$	A, B
Identical	Not identical	$u_0(S_1)/u_0(S_2) = \Delta(S_2)/\Delta(S_1)$	(A, B); C, D
$P(S_2) > P(S_1)$	Identical	$\Delta(S_2)/\Delta(S_1) = 2, 3 \dots$	A, C; B, C
Not identical	Not identical	$u_0(S_1)/u_0(S_2) \neq \Delta(S_2)/\Delta(S_1)$	A, D; B, D

* u_0 = mobility when $n = 0$; Δ = slope of plot $1/u$ vs. n .

show that the complexes of series A (molybdate-isomaltodextrinols), B (tungstate-isomaltodextrinols), and C (molybdate-maltodextrinols) have identical charges, but those of C contain twice as many dextrinol molecules as are contained in the complexes of series A or B. Since the complexes of series C and D (tungstate-maltodextrinols) contain the same number of dextrinol molecules, it is concluded that those of D also contain twice as many dextrinol molecules as are contained in the complexes of series A or B, but are less stable. These results are in agreement with our conclusions drawn from potentiometric and conductimetric measurements.

It would now be expected that three distinct complexes are formed from mixtures of two maltodextrinols (M_1 and M_2) containing (a) only M_1 , (b) only M_2 , and (c) M_1 and M_2 . In order to test this hypothesis mixtures of two maltodextrinols (M_1 and M_2) were subjected to paper electrophoresis in molybdate solution. In all cases (Table 3) a third component ($M_{1,2}$), in addition to those corresponding to the added maltodextrinols (M_1 and M_2) was detected. The mobilities of the components $M_{1,2}$ are in good agreement with those calculated from equation (7) and $n = (n_{M_1} + n_{M_2})/2$.

Since 3-deoxy-D-ribo-hexitol, 3-deoxy-D-arabino-hexitol, and 2-deoxy-D-erythro-pentitol do not form complexes⁴ with molybdate or tungstate it now becomes clear that an acyclic compound, not possessing four adjacent hydroxyl groups, will form a complex only if it

⁹ Sillén and Nylander, *Arkiv Kemi, Min., Geol.*, 1943, **17**, A, No. 4.

¹⁰ Donohue and Shand, *J. Amer. Chem. Soc.*, 1947, **69**, 222.

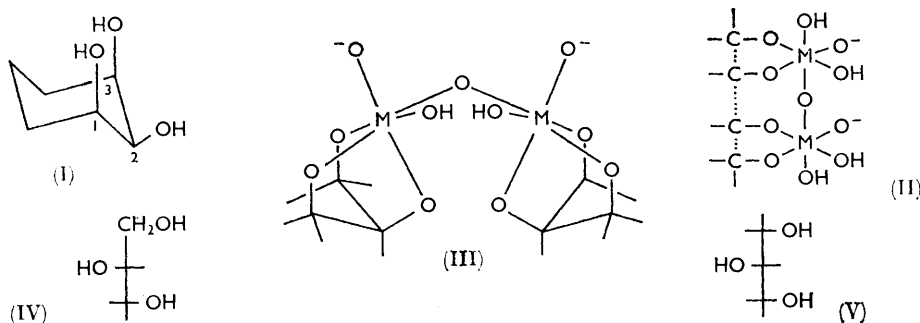
¹¹ Barker, Bourne, Grant, and Stacey, *J.*, 1957, 2067.

TABLE 3.

Electrophoresis of mixtures of two maltodextrinols (M_1 and M_2) in molybdate solution.

No. of glucopyranosyl units in maltodextrinol (n)		$M_s(Mo)$ of components of mixture			$M_s(Mo)$ of $M_{1,2}$ (calc.)
M_1	M_2	M_1	M_2	$M_{1,2}$	
1	4	0.46	0.24	0.33	0.32
1	5	0.46	0.21	0.29	0.29
3	4	0.29	0.24	0.27	0.26

contains a 1,2,3(α , α T)-triol system (IV) (Barker and Bourne's nomenclature¹²) or, presumably a 1,2,3(α T, α T)-triol system (V). The hydroxyl groups of (V), when the carbon chain is in the planar zig-zag conformation, are in the same relative disposition as those in (I), whereas those of (IV) can be brought, without distortion of the conformation of the carbon chain, into this spatial arrangement. Considerable distortion of the planar zig-zag conformation of the carbon chain would be required to bring other acyclic triol systems [e.g., 1,2,3(α , α C)-, in 3-deoxy-D-ribo-hexitol] into a spatial disposition approximating to that of (I).



If the M-O (M = Mo or W) distances in the co-ordination compounds do not differ greatly from those in Ag_2MoO_4 ¹⁰ and $BaWO_4$ ⁹ the O-O distances in octahedral molybdate and tungstate can be estimated to be 2.59 and 2.56 Å, respectively. These values are close to the O-O distances in (I) ($O_{(1)}-O_{(2)}$, 2.82 Å; $O_{(1)}-O_{(3)}$, 2.51 Å). Thus (III) is suggested as the structure (partial) of molybdate and tungstate complexes of five- or six-membered ring compounds possessing a *cis-cis*-1,2,3-triol system, and acyclic compounds which contain a 1,2,3(α , α T)- or 1,2,3(α T, α T)-triol system.

EXPERIMENTAL

Materials.—These were obtained from our Departmental Collection.

Potentiometric Titrations.—Several solutions containing sodium molybdate or sodium tungstate and the polyhydroxy-compound (*ca.* 1%) in the molar ratio of *ca.* 0.1:1—0.2:1 were titrated with 0.1N-sulphuric acid. The pH of the solutions was measured initially and after each addition of acid. The results are shown in Fig. 1 and Table 1. In control experiments, solutions containing only sodium molybdate or sodium tungstate were titrated with 0.1N-sulphuric acid.

Conductimetric Titrations.—A solution containing sodium tungstate and D-mannitol (1.2%) in the molar ratio of 1.15:1 was titrated with 0.1N-sulphuric acid. The conductance of the solution was measured initially and after each addition of acid. In a control experiment a solution containing sodium tungstate only was titrated with 0.1N-sulphuric acid. The results are shown in Fig. 2.

Paper Electrophoresis.—The apparatus used was capable of delivering up to 10,000 v at 100 mA. Electrophoresis was carried out on sheets of Whatman No. 3MM filter paper 10 cm.

¹² Barker and Bourne, *J.*, 1952, 905.

wide. The electrolytes consisted of 2% aqueous sodium molybdate or sodium tungstate solutions, adjusted to pH 5 with concentrated sulphuric acid. Electrophoretograms were prepared by applying a voltage of *ca.* 70 v/cm. for *ca.* 1 hr. Compounds were detected by spraying with acetone-silver nitrate-ethanolic sodium hydroxide.¹³ Under the conditions used D-glucitol had a mobility (u) of 1.7×10^{-4} cm.² v⁻¹ sec.⁻¹ in both electrolytes. Glycerol or hydroxymethylfurfural were used as non-migrating markers for correction of electro-osmosis. The results are shown in Fig. 3 and Table 3.

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¹³ Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.
