COMPLEXES BETWEEN POLYHYDROXY-COMPOUNDS AND INORGANIC OXY-ACIDS

VI. PAPER ELECTROPHORESIS IN STANNATE SOLUTION*

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Polyols are known to form complexes with the anions of several inorganic oxy-acids, *e.g.* borate[2,3], arsenite[3], germanate[4,5], antimonate[6], molybdate[7], and tungstate[7]. Such complexes form the basis for paper electrophoresis of carbohydrates and related compounds. In many cases their electrophoretic mobilities have been correlated with the structures of both the inorganic complexing agents and the polyols. We now report the paper electrophoretic behaviour of polyols in stannate solution.

EXPERIMENTAL

Electrophoresis was carried out on 10 cm wide sheets of Whatman No. 3MM filter paper. The electrolyte was a solution of sodium stannate in water (2 %, pH 11.5). Compounds were detected with acetone–silver nitrate–ethanolic sodium hydroxide[8]. D-Glucitol was used as a standard for comparison of rates of migration, and hydroxymethylfurfural as a non-migrating marker for correction of electro-osmosis. Migration rates in stannate solution are thus expressed as $M_s(Sn)$ values. Under the conditions used, D-glucitol had a mobility (u) of 14.3×10^{-5} cm^2 V^{-1} sec^{-1}.

RESULTS AND DISCUSSION

In all cases examined the mobilities (u) of polyols in stannate solution are appreciably higher than in 0.1 *N* sodium hydroxide[3]. Moreover, the sequence of mobilities of the polyols in stannate solution is markedly different from that in 0.1 *N* sodium hydroxide. Thus, migration in stannate solution of the compounds examined is due primarily to complex formation rather than ionisation of hydroxyl groups, and the method can be regarded as complementary to those in other electrolytes[7].

Table I shows that only two hydroxyl groups are required for complex formation. It is interesting that the mobility of *erythro*-2,3-butanediol is about half that of the *threo*-isomer. On the other hand, the mobility of *erythro*-2,3-butanediol in borate[3], arsenite[3], and sulpho-benzeneboronic acid[9] is *ca.* 25, 18, and 0 %, respectively, of that of *threo*-2,3-butanediol. Neither of these isomers migrates in germanate solution[10]. From the Sn–O distances[11] in sodium stannate, $Na_2Sn(OH)_6$, and potassium stannate,

* For Part V see ref. 1.

TABLE I

$M_8(Sn)$ VALUES OF POLYHYDROXY COMPOUNDS

Polyhydroxy compounds	$M_8(Sn) \times 10^2$
Acyclic compounds	
1,2-Ethanediol	1
1,2-Propanediol	1
erythro-2,3-Butanediol	2
threo-2,3-Butanediol	4
Glycerol	23
Erythritol	57
L-Threitol	62
D-Arabinitol	95
1-deoxy-	58
D-Lyxitol, 1-deoxy-	78
Ribitol	72
Xylitol	100
1-deoxy-D-	88
Allitol	88
D-Altritol	95
1-deoxy-	80
1,6-dideoxy-	45
Galactitol	99
1-deoxy-L-	87
1,6-dideoxy-	72
D-Glucitol	100
1-deoxy-	89
3-O-methyl-	30
L-Gulitol	
1-deoxy-	94
3-O-methyl-	85
D-*arabino*-Hexitol	
2-deoxy-	48
3-deoxy-	24
D-*ribo*-Hexitol, 3-deoxy-	24
D-Mannitol	93
1-deoxy-	94
1,2-di-O-methyl-	66
2-O-methyl-	88
L-Mannitol, 1,6-dideoxy-	67
Cyclitols	
*Allo*inositol	100
(+)-Inositol	55
*Epi*inositol	101
*Muco*inositol	67
*Myo*inositol	42
*Scyllo*inositol	50
Aldoses and derivatives	
DL-Glyceraldehyde	94
D-Erythrose	107
L-Threose	103
D-Arabinose	84
methyl α-pyranoside	48
D-Lyxose	115
methyl α-pyranoside	53
D-Ribose	104
methyl β-pyranoside	104

(continued on p. 362)

TABLE I (*continued*)

Polyhydroxy compounds	$M_s(Sn) \times 10^2$
D-*erythro*-Pentose	
2-deoxy-	24
1,2-dideoxy-	19
D-Xylose	81
methyl α-furanoside	3
D-Altrose, 1,6-anhydro-β-pyranose	80
D-Galactose	78
1,6-anhydro-β-pyranose	81
methyl β-pyranoside	43
L-Galactose, 6-deoxy- (L-fucose)	69
D-Glucose	63
1,6-anhydro-β-pyranose	0
6-deoxy-	63
3-O-methyl-	78
4-O-methyl-	44
methyl α-pyranoside	28
D-Gulose	107
1,6-anhydro-β-pyranose	77
6-deoxy-	105
D-*arabino*-Hexose, 2-deoxy-	31
D-*lyxo*-Hexose, 2-deoxy-	23
D-*ribo*-Hexose, 2-deoxy-	52
D-Mannose	100
1,6-anhydro-β-pyranose	96
3,4-di-O-methyl-	71
methyl α-pyranoside	41
L-Mannose, 6-deoxy- (L-rhamnose)	100
Ketoses and derivatives	
D-Fructose	91
1-O-methyl-	80
D-*erythro*-Hexulose, 3-deoxy-	60
L-Sorbose	94
Disaccharides	
α,α-Trehalose	11
Sophorose	57
Nigerose	57
Laminaribiose	75
Maltose	65
Cellobiose	62
Isomaltose	58
Gentiobiose	65

$K_2Sn(OH)_6$, an average O–O distance in $Sn(OH)_6^{2-}$ ions of 2.77 Å can be calculated. This is probably great enough to allow the formation of a non-planar 5-membered ring (I, from *threo*-2,3-butanediol). In this event, the complex of *erythro*-2,3-butanediol (II) will be more stable (relative to that of the *threo*-isomer) than those formed from the other oxy-acid anions.

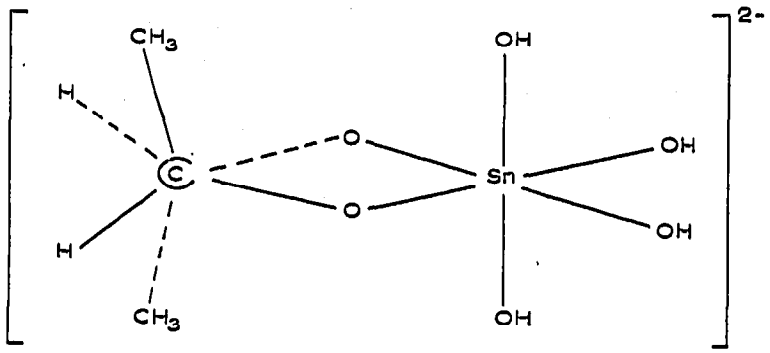
The order of mobility of acyclic polyols of identical molecular size is, with the exception of 1-deoxy-D-mannitol, related to the number of *threo*-1,2-diol groupings in each. This is not unexpected as, in the planar zig-zag conformation of these compounds, the O–O distance in *threo*-1,2-diol groups (2.82 Å) is close to that in the

$Sn(OH)_6^{2-}$ ion. Thus, the contribution to mobility arising from *threo*-disposed adjacent hydroxyl groups is larger than that from *erythro*-1,2-diol groupings.

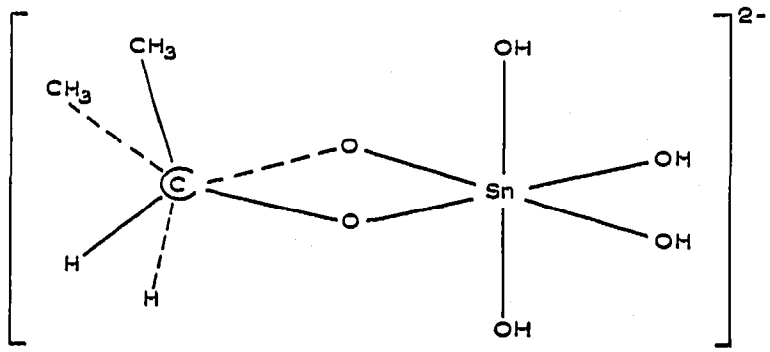
In the series of aldopentoses and -hexoses the largest contribution to mobility seems to arise from *cis*-1,2-diol groupings of their pyranose forms, although the O–O distances in the chair conformation of *cis*- and *trans*-1,2-diols of six-membered ring compounds are identical (2.82 Å). This is in agreement with the differences in reactivity of 1,2-cyclohexanediols observed in other cyclisation reactions[12]. Substitution in or of one of the *cis*-disposed adjacent hydroxyl groups reduces the mobility (*e.g.* D-mannose, 2-deoxy-D-*arabino*-hexose, D-ribose; 2-deoxy-D-*erythro*-pentose). By virtue of the α,β-equilibrium all pyranoses can possess a *cis*-1,2-diol grouping. Thus, in all cases examined, except D-ribose, glycoside formation also reduces the mobility. It is noteworthy that D-ribose is thought to exist, in aqueous solution, almost entirely in its β-pyranose form[13], which possesses the same number of *cis*-1,2-diol groupings as its methyl pyranoside.

The complex-forming 1,6-anhydro-β-pyranoses have higher $M_s(Sn)$ values than expected (*cf.* 1,6-anhydro-β-D-galactopyranose, methyl β-D-galactopyranoside; 1,6-anhydro-β-D-mannopyranose, methyl α-D-mannopyranoside). It is probable that, owing to the formation of the 1,6-anhydro-ring, their *cis*-related, adjacent hydroxyl groups have moved into a spatial disposition even more favourable for complex formation.

Of the 1,6-anhydro-β-pyranoses examined the glucose derivative is the only compound which did not migrate during electrophoresis in stannate solution. Its pyranose ring can, theoretically, adopt the 1C and 3B conformations (REEVES' nomenclature[14]), possessing, respectively, axially and equatorially disposed hydroxyl



(I)



(II)

Fig. 1.

groups. The fact that a 1(*eq*),2(*eq*)-diol grouping can complex with stannate (*cf.* methyl α-D-glucopyranoside, D-glucose, 6-deoxy-D-glucose) suggests that the pyranose ring in 1,6-anhydro-β-D-glucopyranose exists in the 1C conformation.

The cyclitols possessing four *cis*-1,2-diol groupings (*epi*inositol and *allo*inositol) have higher mobilities than those possessing only two (*muco*-, *dextro*-, and *myo*inositol). However, *scyllo*inositol, which possesses only *trans*-arranged hydroxyl groups, migrates faster than *myo*inositol. A tridentate structure, as proposed for borate complexes of certain cyclitols[15], would not account for this effect unless two stannate ions could combine with *scyllo*inositol, when all hydroxyl groups are axially disposed.

Tin and germanium are members of the same group in the periodic table of elements and form the same type of anion, *i.e.* $Sn(OH)_6^{2-}$ and $Ge(OH)_6^{2-}$. The sequences of electrophoretic mobilities of polyols in stannate and germanate[4] solutions show certain similarities, *e.g.* in the series of aldohexoses, methyl pyranosides of aldohexoses, and cyclitols. However, the same similarities are not observed in the series of aldopentoses and acyclic polyols. The investigation has also shown that stannate forms complexes with a greater range of polyols than do molybdate and tungstate[7], which require, for complex formation, very specific structural features.

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SUMMARY

Paper electrophoresis in stannate solution has shown that stannate forms complexes with several acyclic and cyclic polyols. *Threo*-1,2-diol groups in acyclic compounds complex more strongly than the corresponding *erythro* groupings. With six-membered ring compounds the largest contribution to mobility arises from *cis*-1,2-diol groups, although *trans*-1,2-diol groups can complex. The paper electrophoretic mobilities of the polyols are discussed from the view-point of the conformations of the polyols and the structure of the stannate ion.

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