[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

The Polyol–Tellurate Complex Formation Reaction. I. Thermodynamics of Telluric Acid Ionization and of Complex Formation[1]

BY HERBERT R. ELLISON, JOHN O. EDWARDS AND E. A. HEALY

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The first and second ionization constants for telluric acid have been measured over a range of temperatures and the thermodynamic quantities have been calculated. Equilibrium constants for the formation of polyol-tellurate ion complexes have been evaluated. Only a 1:1 complex is present in significant concentrations. The constants and derived thermodynamic quantities are discussed for the three classes of polyols (1,2-diols, 1,3-diols, and sugars) studied.

Introduction

Complexes are formed between various oxyanions and polyhydroxylic compounds (hereafter polyols). In 1842, Biot[2] reported that a solution of boric acid becomes acid to litmus when sugars are added. Recent studies[3,4] indicate that the borate ion rapidly forms a cyclic diester with the polyol and that it can complex with either one or two polyol molecules. Similar polyol complexes have been reported for the benzeneboronate ion,[5] $C_6H_5B(OH)_3^-$, and for the hydroxyanions of arsenic,[3] germanium,[6,7] iodine[8,9] and molybdenum,[10] to mention a few.

Rosenheim and Weinheber[11] observed that glycerol could be used to make telluric acid a stronger acid so that it could be titrated with base. Fouasson[12] measured the increase of the first ionization constant of the acid in the presence of various sugars but made no attempt to evaluate equilibrium constants for the formation of the complexes. Antikainen[13] using cryoscopic and potentiometric methods and Roy, Laferriere and Edwards[3] using a *p*H method found that the constants are large and that only a 1:1 complex is present. Comparative formation constants showed that the ability of five anions to bind a simple 1,2-diol such as propylene glycol is in the order: periodate > tellurate > phenylboronate > borate > arsenite.

Good linear free-energy plots were found with the last three anions, but the formation constants for tellurate complexes did not correlate well. Therefore it was decided to reinvestigate the tellurate values that were reported earlier and to extend this work further in two ways. The first was an investigation of the thermodynamics of complexing, which is presented in this paper. The second is the kinetics of complex formation which will be presented in the following paper. Since both approaches require better knowledge of the thermodynamics of ionization of telluric acid, it was necessary first to obtain these values.

Experimental

Reagents.—Telluric acid was prepared and purified as described earlier.[14] Stock solutions of approximately 0.1 *M* H_6TeO_6 were standardized by *p*H titrations in the presence of glycols.[15] All polyols were either from Distillation Products or from Aldrich Chemical Co.; they were used without further purification except for three butanediols which were further purified by vacuum distillation. Potassium nitrate, used to maintain constant ionic strength, and KOH were reagent grade.

Equipment.—All *p*H measurements were made using a Beckman Model GS meter, which has a reproducibility of ± 0.003 *p*H unit, and glass and calomel electrodes. The meter was standardized with commercial certified buffers at *p*H 4, 7 and 10. Titrations were carried out in an atmosphere of CO_2-free N_2; temperature was controlled to within $\pm 0.01°$.

Procedure.—Determination of the first two ionization constants of H_6TeO_6 was done by titrating solutions of the acid with carbonate-free KOH. Small increments of 2.5 *M* KOH were added from a microburet and the *p*H was measured. This procedure was continued until the *p*H had risen to ~11.

The formation constants were measured by filling seven beakers with a telluric acid–tellurate buffer (prepared by exactly half-neutralizing a solution of H_6TeO_6 with KOH), distilled water, KNO_3 solution and polyol. The initial concentration of tellurate ion was usually about 2×10^{-3} *M* in these solutions. The concentration of the polyol was varied from zero to about 1 *M* in most cases. These solutions were thermostatted for 1 day at the desired temperature and then *p*H measurements were made; equilibrium was found to be attained in this length of time.

Units.—All concentrations are given in moles per liter, free energies and enthalpy values are in kilocalories per mole and entropy values are in calories per mole-degree.

Results and Discussion

Thermodynamics of Ionization of Telluric Acid.—Recent work[14] demonstrated that at concentrations of H_6TeO_6 employed in these measurements polymerization is negligible. Therefore when $[H_6TeO_6] = [H_5TeO_6^-]$ (brackets denote concentrations), *p*H is equal to pK_1.

In a solution of H_6TeO_6 exactly neutralized by KOH, Earley, *et al.*,[14] have shown that $[H_6TeO_6] = [OH^-] + [H_4TeO_6^=]$. By multiplying by $[H^+]^2/[H_6TeO_6]$ and inserting K_W, K_1 and K_2, one obtains

$$[H^+]^2 = \frac{K_1K_W}{[H_5TeO_6^-]} + K_1K_2$$

For the concentration region of the present measurements ($[H_6TeO_6]_0 \sim 10^{-3}\,M$)

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[1] Ph.D. Thesis of H. R. E. at Brown University (1960).

[2] M. Biot, *Compt. rend.*, **14**, 49 (1842).

[3] G. L. Roy, A. L. Laferriere and J. O. Edwards, *J. Inorg. Nuclear Chem.*, **4**, 106 (1957).

[4] P. J. Antikainen, *Suomen Kemistilehti*, (a) **B30**, 185 (1957); (b) **B31**, 255 (1958).

[5] J. P. Lorand and J. O. Edwards, *J. Org. Chem.*, **24**, 769 (1959).

[6] D. A. Everest and J. C. Harrison, *J. Chem. Soc.*, 4319 (1957).

[7] P. J. Antikainen, (a) *Suomen Kemistilehti*, **B30**, 147 (1947), (b) *Acta Chem. Scand.*, **13**, 312 (1959).

[8] F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1947).

[9] G. J. Buist, C. A. Bunton and J. H. Miles, *J. Chem. Soc.*, 4567 (1957).

[10] H. Buchwald and E. Richardson, *Chem. and Ind.* (London), 753 (1959).

[11] A. Rosenheim and M. Weinheber, *Z. anorg. Chem.*, **69**, 266 (1910).

[12] F. Fouasson, *Ann. Chim.*, [12], **3**, 594 (1948).

[13] P. J. Antikainen, *Suomen Kemistilehti*, **B29**, 14 (1956).

[14] J. E. Earley, D. H. Fortnum, A. Wojcicki and J. O. Edwards, *J. Am. Chem. Soc.*, **81**, 1295 (1959).

[15] J. O. Edwards and A. L. Laferriere, *Chemist–Analyst*, **45**, 12 (1956).

$$K_1K_2 > \frac{K_1K_W}{[H_5TeO_6^-]}$$

and so $[H^+]^2 = K_1K_2$. Thus, at the neutralization point, $pH_n = \frac{1}{2}(pK_1 + pK_2)$.

Therefore by measuring the pH values at the half-neutralization and neutralization points, both pK_1 and pK_2 can be calculated. By determining the two constants at several ionic strengths and then extrapolating to infinite dilution, the thermodynamic ionization constants can be obtained. From the straight lines found it can be shown that for ionic strength $\mu \leq 1$

$$pK_{\text{thermo}} = pK_{\text{obsd}} - m\sqrt{\mu}$$

Values of the thermodynamic constants and of m at the four temperatures investigated are shown in Table I. Also listed in this Table are the Debye–Hückel values of m and constants reported by Earley, *et al.*,[14] and Antikainen.[13] Other values of K_1 and K_2 that can be found in the literature[12,16] are not included here for comparison since none are thermodynamic equilibrium constants but are merely values reported for specific conditions of concentration and ionic strength. The constants listed in Table I were determined at $[H_6TeO_6]_0 = 5.22 \times 10^{-3}$ M. However several measurements at lower concentrations gave similar results while measurements at higher concentrations gave significantly different results; presumably this is a result of polymerization.[14]

TABLE I

IONIZATION CONSTANTS OF TELLURIC ACID[a]

Temp. (°C.)	pK_1	m_1 (obsd.)	m_1[b]	pK_2	m_2 (obsd.)	m_2[b]
5	8.03 ± 0.02	0.51	0.49	11.45 ± 0.03	1.58	0.98
25	7.70 ± .01	.54	.51	10.95 ± .02	1.18	1.02
25[c]	7.70	.53	.51	11.04	0.98	1.02
25[d]	7.61	..	.51	...	..	1.02
35	7.59 ± .01	.52	.52	10.80 ± .02	.96	1.04
61	7.28 ± .02	.39	.55	10.27 ± .03	.69	1.10

[a] $[H_6TeO_6]_0 = 5.22 \times 10^{-3}$ M. [b] Debye–Hückel value. [c] Earley, *et al.*[14] [d] Antikainen.[13]

At 25° the agreement in pK_1 and pK_2 with the values reported by Earley, *et al.*,[14] is good. Agreement between the observed and calculated values of the slope of pK *vs.* $\sqrt{\mu}$ are in general very good for pK_1 but only fair for pK_2. The principal deviations are for the measurements at 61° where polymerization may be significant.[14]

The heats, ΔH_i^0, free energies, ΔF_i^0 and entropies, ΔS_i^0, of ionization are presented in Table II. The only other known thermodynamic quantities reported for telluric acid are those given by Antikainen.[13] It can be seen that for the first ionization of the acid the agreement is good for ΔF_i^0 and poor for ΔH_i^0 and ΔS_i^0. Pitzer[17] has estimated that the entropy of ionization of a weak acid should be about −22. For large ions, it would be expected that the entropy would be less negative than this estimate. Examination of a series of acids, both organic and inorganic, shows that this is a fairly good approximation. Thus it appears that the value of −15.9 is more consistent with theoretical and experimentally measured entropies of ionization than the value of −2.7.

TABLE II

THERMODYNAMICS OF TELLURIC ACID IONIZATION AT 298°K.

Reaction	ΔH_i^0	ΔF_i^0	ΔS_i^0
$H_6TeO_6 \leftrightarrows H^+ + H_5TeO_6^-$	5.8 ± 0.2	10.5 ± 0.1	−15.9 ± 1.0
$H_6TeO_6 \leftrightarrows H^+ + H_5TeO_6^-$	9.6[a]	10.4[a]	− 2.7[a]
$H_5TeO_6^- \leftrightarrows H^+ + H_4TeO_6^=$	9.4 ± 0.4	15.0 ± 0.1	−18.6 ± 2.0

[a] Antikainen.[13]

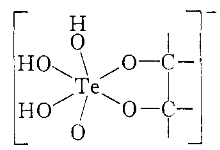
The positive values of ΔH_i^0 have generally been considered unusual for acids. However, if Pitzer's theory about the value of ΔS_i^0 is correct, then it can be readily shown that for any acid with a $pK_a > 5$, ΔH_i^0 must be positive. Water, hydrogen cyanide, boric, carbonic and sulfurous acids and others agree with this theory.

For the second ionization of an acid it is usually found that ΔS_i^0 is more negative than for the first ionization.[17,18] Such is the case here, however strong conclusions from the present data are unwarranted since it is possible that the thermodynamics of the polymerization and the dehydration reactions, even if present to only a small extent, are included in the measured values.

Thermodynamics of Complex Formation.—Previous measurements have shown that the complexing of a polyol molecule with a tellurate ion has the stoichiometry

$$H_5TeO_6^- + G \rightleftarrows HTeO_4G^- + 2H_2O,\ K_{C_1}$$

where G stands for the polyol and $HTeO_4G^-$ represents the complex ion which presumably has the structure



The mass-action expression for K_{C_1} can be rearranged and simplified by making certain assumptions which have been shown to be valid under the conditions employed here. They are: (1) no H_2TeO_4G is formed, *i.e.*, the acid does not form a complex; (2) $[H_5TeO_6^-] = [H_5TeO_6^-]_0 - [HTeO_4G^-]$, where zero subscript indicates initial amount; and (3) the concentrations of acid and polyol do not change significantly during the reaction. The result obtained by rearranging the equilibrium expression is

$$K_{C_1} = \frac{\alpha[H^+] - K_1}{K_1\,[G]_0}$$

where α is the initial acid buffer ratio defined by $\alpha = [H_5TeO_6^-]_0/[H_6TeO_6]_0$.

Calculation of K_{C_1} thus depends upon the knowledge of K_1 of the tellurate buffer at the ionic strength of the measurement as well as on the knowledge of the pH of the solution at equilibrium. A medium effect on the ionization constant of the acid is to be expected along with the complexing since addition of polyol slightly reduces the dielectric constant of the solution. This effect predicts a decrease in K_{C_1} as the concentration of the polyol is increased.

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(16) (a) A. Rosenheim and G. Jander, *J. Chem. Soc.*, **114**, II, 194 (1918); (b) E. Blanc, *J. Chim. Phys.*, **18**, 28 (1920); (c) H. T. S. Britton, R. A. Robinson, *Trans. Faraday Soc.*, **28**, 531 (1923).

(17) K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

(18) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959).

In most cases plots of K_{c_1} *vs.* [G] were linear with negative slopes indicative of 1:1 complexes. However with glucose, galactose, arabinose and one or two others positive slopes were found. The cause of this result is not known. Values of the formation constants from these static measurements extrapolated to zero polyol concentration and at various temperatures are shown in Table III. Also listed in Table III are the slopes of the plots of K_{c_1} *vs.* [G] and the constants previously

TABLE III

POLYOL-TELLURATE COMPLEX FORMATION CONSTANTS AT [G] = 0.0

Polyol	Temp. (°C.)	Sets	K_{c_1} (This work)	Slope	K_{c_1} (Ref. 3)
1. Ethylene glycol	20.5	5	18.2 ± 0.2[a]	− 3.70 ± 0.24[a]	
	25.0	7	15.0 ± .5	− 2.68 ± .23	16.0
	30.0	5	14.5 ± .3	− 2.83 ± .46	
	40.0	5	11.1 ± .5	− 2.44 ± .23	
2. Propylene glycol	20.5	5	37.2 ± .5	−14.1 ± .4	
	25.0	6	33.0 ± 1.0	−14.1 ± .7	30.0
	30.0	5	28.3 ± 0.1	−12.4 ± .5	
	40.0	5	21.9 ± .9	− 9.8 ± 1.0	
3. (*meso*)-2,3-Butanediol	25.0	2	16.5 ± .1	−10.9 ± 0.1	14.5
	35.0	1	14.1	− 4.5	
	45.0	1	11.8	− 5.1	
4. 3-Methoxy-1,2-propanediol	20.5	5	35.9 ± .5	− 7.6 ± 0.4	
	25.0	2	30.2 ± .7	0.0 ± 0.1	25.0
	29.8	5	29.8 ± .5	− 7.4 ± 1.5	
	40.0	5	23.6 ± .9	− 6.3 ± 0.4	
5. Phenyl-1,2-ethanediol	20.5	3	46.6 ± .5	21.6 ± 1.5	
	25.0	1	42.0	76.0	45.6
	30.0	5	37.9 ± .8	8.8 ± 0.8	
6. Pinacol	19.8	2	4.0 ± .1	7.8 ± 0.6	
	25.0	2	3.7 ± .2	12.4 ± 1.0	
	34.2	2	3.2 ± .2	23.7 ± 1.7	
	44.6	2	2.7 ± .2	21.0 ± 0.1	
7. *trans*-1,2-Cyclohexanediol	19.8	2	16.3 ± .1	0	
	25.0	2	14.7 ± .2	0	
	34.2	2	12.5 ± .2	0	
	45.2	2	10.6 ± .3	0	
8. Glycerol	19.0	1	96.9	−33.2	
	25.0	4	79.6 ± 3.7	−34.6 ± 2.7	73.0
	35.5	1	66.5	−20.9	
	45.0	1	53.5	−11.8	
9. 1,2,4-Butanetriol	25.0	1	42.5	−24.0	
10 1,3-Propanediol	19.8	2	3.57 ± 0.07	2.04 ± 0.11	
	25.1	2	3.20 ± .07	1.57 ± .09	1.75
	34.2	2	2.47 ± .03	1.97 ± .01	
	44.6	2	1.90 ± .06	1.90 ± .06	
11. 2,2-Diethyl-1,3-propanediol	19.8	2	1.93 ± .03	1.43 ± .10	
	25.2	2	1.70 ± .05	6.64 ± .45	
	34.2	2	1.39 ± .03	3.90 ± .10	
	44.6	2	1.00 ± .06	6.25 ± 1.00	
12. 2-Hydroxymethyl-2-methyl-1,3-propanediol	19.8	2	0.70 ± .02	0.41 ± 0.03	
	25.0	2	.62 ± .02	.35 ± .02	
	34.2	2	.52 ± .01	.30 ± .02	
	45.2	2	.44 ± .04	.35 ± .01	
13. Pentaerythritol	19.8	2	3.50 ± .17	1.05 ± .41	
	25.0	3	3.09 ± .04	1.47 ± .26	
	34.2	4	2.50 ± .06	0.71 ± .10	
	44.6	4	1.99 ± .07	0.0	
14. Polyvinyl alcohol	25.0	1	2.19	0	1.00
15. L-(+)-Arabinose	19.8	2	48.8 ± .08	95.2 ± .8	
	25.0	2	46.9 ± .6	69.8 ± 4.7	
	34.2	2	43.1 ± .4	134 ± 8	
	45.2	2	41.1 ± .4	115 ± 2	
16. Fructose	19.8	4	311 ± 20	−91 ± 4	
	25.0	4	289 ± 10	−80 ± 10	278
	34.2	4	256 ± 6	−66 ± 6	
	44.8	4	218 ± 4	−65 ± 25	

17. D-Galactose	20.5	3	48.5 ± 1.2	63.9 ± 2.7	
	25.0	2	46.0 ± 0.0	60.0 ± 0.1	39.2
	30.0	2	44.1 ± 2.2	36.9 ± 1.5	
	40.0	3	41.2 ± 0.6	27.6 ± 2.4	
18. D-Glucose	20.5	3	15.1 ± 0.3	7.40 ± 0.09	
	25.0	4	12.7 ± 1.0	0.10 ± .05	14.6
	30.0	3	14.7 ± 0.6	5.18 ± .18	
	40.0	3	13.9 ± 0.1	3.20 ± .30	
19. D-Mannose	25.0	2	1680	– Curve	
20. Mannitol	25.0	2	106	– Curve	

[a] Average deviations.

reported.[3] It was found that there is no apparent reaction with the 3-methyl- or 2-methyl-2,4-pentanediols, 2,2-dimethyl-1,3-propanediol, 1,3- and 1,4-butanediols and diethylene glycol. Addition of these compounds to the tellurate solution led to an increase rather than a decrease of the pH.

Most of the constants listed in Table III and all of those reported earlier[3] were made with a buffer ratio of $\alpha = 1.00$. However several sets of measurements made at other ratios showed that the dependence of Kc_1 on α is indeed correct.

In most cases plots of log Kc_1 *vs.* $1/T$, where T is the absolute temperature, yielded good lines as can be seen by plotting of the results in Table III. Values of the heats, free energies and entropies of reaction at ionic strength 0.10 are shown in Table IV.

TABLE IV

VALUES OF THE THERMODYNAMIC FUNCTIONS FOR FORMATION OF POLYOL–TELLURATE COMPLEXES AT 298°K.

Polyol	ΔH_c	ΔF_c	ΔS_c
Ethylene glycol	−4.6	−1.60	−10
Propylene glycol	−5.0	−2.08	−10
(*meso*)-2,3-Butanediol	−3.2	−1.66	− 5
3-Methoxy-1,2-propanediol	−3.8	−2.02	− 6
Phenyl-1,2-ethanediol	−3.6	−2.22	− 5
Pinacol	−2.9	−0.8	− 7
trans-1,2-Cyclohexanediol	−3.2	−1.59	− 5
Glycerol	−3.8	−2.59[a]	− 4[a]
1,3-Propanediol	−4.8	−0.69	−14
2,2-Diethyl-1,3-propanediol	−4.7	−0.31	−15
2-Hydroxymethyl-2-methyl-1,3-propanediol	−3.4	+0.28[b]	−12[b]
Pentaerythritol	−4.3	−0.67[c]	−12[c]
L-(+)-Arabinose	−1.3	−2.28	+ 3
Fructose	−2.7	−3.36	+ 2
Glucose	−0.7	−1.51	+ 3
Galactose	−1.4	−2.27	+ 3

[a] After correction for statistical factor of two, values of ΔF_c and ΔS_c are −2.18 and −5, respectively. [b] After correction for statistical factor of three, values of ΔF_c and ΔS_o are +0.93 and −15, respectively. [c] After correction for statistical factor of six, values of ΔF_c and ΔS_c are +0.39 and −16, respectively.

As mentioned above, good linear free-energy relations are found between the borate, arsenite and phenylboronate systems, but the tellurate values do not correlate well. Using the polyol–tellurate formation constants of Table III and polyol–borate formation constants previously reported[3,5] (it was necessary to measure a few which were lacking), it was possible to make the plot shown in Fig. 1 of log Kc_1–tellurate *vs.* log Kc_1–borate. In this plot statistical corrections for the number of ways a polyol can react have been made with glycerol, pentaerythritol and 2-hydroxymethyl-2-methyl-1,3-propanediol.

Several conclusions can be drawn from this plot. The observed 1,2-diols appear to form a line with a slope of 0.7; the largest deviation of the simple 1,2-diols is produced by propylene glycerol which is about 0.20 log units off. The large deviations from this line shown by pinacol and by the sugars are most likely due to steric factors.

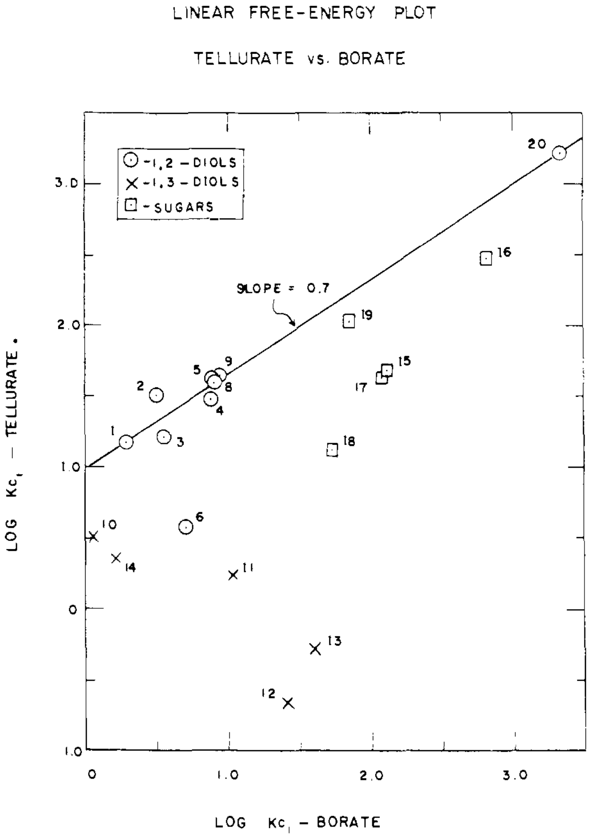

Fig. 1.—Linear free-energy plot of tellurate *vs.* borate polyol formation constants. See Table III for key to numbers.

Using Fisher–Hirschfelder–Taylor models one can show that when sugars complex with an octahedral tellurate ion one of the OH groups attached to tellurium pushes against the ring of the sugar. Such a hindrance (which is not observed in models of the borate, phenylboronate or arsenite complex ions) can be expected to lower the stability of the complex, and this is observed. Pinacol, which is a highly methyl-substituted 2,3-diol, shows a marked decrease in Kc_1 for the tellurate system which is due almost entirely to the inability of the two OH groups to approach the tellurate ion without interference by the methyl groups.

It is interesting to observe that the values for four of the five 1,3-diols fall on a line with a negative slope. The formation constants with tellurate ion do not vary over a wide range, but those with borate are spread out over two orders of magnitude. Again, molecular models show that the 1,3-diols can complex with borate with less strain than they can with tellurate ion. Also the O–Te–O angle is 90° which should favor a five-membered ring; thus complexes of a 1,2-diol should be more stable than those from a 1,3-diol for conformational reasons. There should be little conformational preference in the boron complexes as the O–B–O angle is tetrahedral.

That the steric properties of a polyol influence the stability of the complex also can be seen from the thermodynamic quantities listed in Table IV. The free energies of complex formation do not vary greatly. However inspection of the entropy values shows that these constants fall into three distinct groups; the sugars with $\Delta S_c = 3 \pm 1$, the 1,2-diols with $\Delta S_c = -7 \pm 2$ and the 1,3-diols (corrected for statistical factors) with $\Delta S_c = -15 \pm 1$. This variation in values correlates well with the number of degrees of freedom being lost on complexing. A compound which already has a fixed ring system and not many internal degrees of freedom would not be expected to lose much entropy upon forming a cyclic complex with another compound; this is exactly what is observed with the sugars. The small increase in entropy that is found may be ascribed to the motion gained by the two molecules of water that are released.

A compound such as a 1,2-diol has internal rotations and bending vibrations; thus it would be predicted that some of this motion would be lost on formation of a complex involving a ring and so the entropy would measurably decrease. If now a methylene group is placed between the two OH-bearing carbons to form a 1,3-diol, the number of active modes will be increased in the free polyol. The formation of a six-membered ring would be expected to freeze out most of this motion with the result that more entropy would be lost than in either of the other two cases (sugars and 1,2-diols). Not surprisingly, the decrease in entropy in the order 1,3-diol > 1,2-diol > sugar is related to the general order of stability observed with these glycols. It is apparent that the equilibrium constant variations are "entropy dominated" in the cases of 1,2-diols and 1,3-diols.

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The Polyol–Tellurate Complex Formation Reaction. II. Kinetics[1]

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The kinetics of the reaction of polyols with $H_5TeO_6^-$ have been studied by a spectrophotometric method. The rate law for the forward reaction is $R_f = k_f[H_5TeO_6^-][\text{polyol}]/[H^+]$ at ionic strength 0.10 and at 21–45°. For different polyols, little variation in k_f is observed; the variations in equilibrium constant values are reflected in rate constants for hydrolysis of the complex. Activation parameters were measured for six polyols. A mechanism involving $TeO_4^{=}$ as an intermediate is presented and discussed.

Introduction

In the preceding paper[2] the results of determinations of equilibrium formation constants for certain polyol–tellurate complexes were presented. It was shown that their stabilities are influenced by the geometry of the polyol. Previous investigations[3–5] had shown that the complexes form at measureable rates at ambient temperatures, in contrast to the polyol complexes of the borate, phenylboronate and arsenite ions which appear to form very rapidly.[5,6]

Because of rapid protonic equilibria, it was possible to follow the rate of formation of a glycol–tellurate complex by measuring the change in *p*H with time.[7] The measurements indicated that the forward reaction rate depended on the first power each of the polyol concentration and of the tellurate ion concentration, and the rate increased as the hydroxide ion concentration was increased. However the observed rate dependence on base concentration did not appear to give a simple kinetic order. Since small amounts of acidic or basic impurities could greatly influence the measured *p*H and thus affect the observed rate constants it was decided to investigate the reaction in buffered solutions by using a spectrophotometric technique. The results of this investigation will now be described.

Experimental

Equipment and Reagents.—A Beckman DK-1 spectrophotometer, fitted with a thermostatted cell holder by means of which it was possible to control the temperature to ±

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(1) Ph.D. Thesis of H.R.E. at Brown University (1960).

(2) H. R. Ellison, J. O. Edwards and E. A. Healy, *J. Am. Chem. Soc.*, **84**, 1820 (1962).

(3) P. J. Antikainen, *Suomen Kemistilehti*, **B29**, 14 (1956).

(4) J. O. Edwards and A. L. Laferriere, *Chemist-Analyst*, **45**, 12 (1956).

(5) G. L. Roy, A. L. Laferriere and J. O. Edwards, *J. Inorg. and Nuclear Chem.*, **4**, 106 (1957).

(6) J. P. Lorand and J. O. Edwards, *J. Org. Chem.*, **24**, 769 (1959).

(7) J. O. Edwards, J. R. Abbott, H. R. Ellison and J. Nyberg, *J. Phys. Chem.*, **63**, 359 (1959).