a highly methyl-substituted 2,3-diol, shows a marked decrease in K_{C_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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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

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 pH 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 pH 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).

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(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).

0.1°, was used with glass-stoppered quartz cells. Other equipment and reagents were the same as described previously.[2]

Procedure.—The kinetic runs were carried out at four different temperatures and at ionic strengths of ~0.1. The procedure followed was to place water, the polyol and the phosphate buffer (to control ionic strength as well as *p*H) of the appropriate *p*H in a 50-ml. volumetric flask. This was then placed in the constant-temperature bath until thermal equilibrium was attained. At this point exactly 0.5 ml. of 0.10 *M* H_6TeO_6 was added, the solution was mixed and a portion was quickly transferred to the quartz cell. The time between the addition of the acid to the reaction mixture and the first absorbancy readings was ~35 sec. Changes in absorbancy were recorded for from 20–30 min., sometimes longer.

Units.—All concentrations are given in moles per liter, times are in seconds, activation energies, enthalpies and free energies are in kilocalories per mole, and entropies of activation are in calories per mole-degree.

Results

Treatment of Rate Data.—It is known that H_6TeO_6, $H_5TeO_6^-$ and $H_4TeO_6^=$ absorb light in the ultraviolet near 230 mμ.[8] When a small amount of polyol is added to a solution containing the telluric acid-tellurate ion buffer, the absorbancy increases with time, indicating that some species is being formed which absorbs light more strongly than any of the other substances present in the *p*H range of the buffer. At any time *t* the only species present in solutions of *p*H 6–8 are H_6TeO_6, $H_5TeO_6^-$, G (the polyol), $HTeO_4G^-$ (the polyol-tellurate complex) and the phosphate buffer constituents. The concentrations of $H_4TeO_6^=$, $TeO_4G^=$ and H_2TeO_4G are small in comparison to those of the others and can be neglected without appreciable error.

At 230 mμ the total absorbancy of a 1 cm. thickness of solution can be given by the following expression, assuming Beer's law where ϵ is the molar

$$A = \epsilon_{HT}[HT] + \epsilon_{T^-}[T^-] + \epsilon_{HTG^-}[HTG^-] + \epsilon_G[G] + A_0$$

absorbancy index, or extinction coefficient, and HT represents H_6TeO_6, $T^- \equiv H_5TeO_6^-$, $HTG^- \equiv HTeO_4G^-$ and A_0 is the background absorbancy due to the phosphate buffer and the cell. This background never amounted to more than 10% of the total absorbancy. In several experiments it was found that the polyol is essentially transparent in this region, thus the term $\epsilon_G[G]$ may be dropped out or merely considered as part of A_0.

Measurements showed that the *p*H of the buffered reaction mixtures remained essentially constant throughout a run, thus $[H^+] = [H^+]_0$. Also $[HTG^-] = [Te]_{total} - [Te]_{unc.}$ where $[Te]_{total}$ is the total concentration of tellurium present and $[Te]_{unc.}$ is the total amount of uncomplexed tellurium, in any form, present at time *t*. Thus $[HTG^-] = [HT]_0 + [T^-]_0 - [HT] - [T^-]$. Using the expression for K_1 it is possible to derive the relationship

$$A = [T^-]\left\{\frac{[H^+]}{K_1}(\epsilon_{HT} - \epsilon_{HTG^-}) + \epsilon_{T^-} - \epsilon_{HTG^-}\right\} + \epsilon_{HTG^-}[Te]_0 + A_0$$

which is of the general form $A = B\,[T^-] + C$, where *B* and *C* are constants for any one run. From this expression we can relate the rate of change of $[T^-]$ with time to the rate of change of absorbancy by

$$\frac{d[T^-]}{dt} = \frac{1}{B}\frac{dA}{dt}$$

On the basis of the previous work[7] it seemed probable that

$$\text{Rate} = -\frac{d[T^-]}{dt} = \frac{k_f{}^1[G][T^-]}{[H^+]^n} - \frac{k_r{}^1[HTG^-]}{[H^+]^n}$$

Since $[H^+]$ is a constant for any particular run, this rate expression can be rewritten in the following fashion

$$-\frac{d[T^-]}{dt} = k_f(\text{obsd.})[G][T^-] - k_r(\text{obsd.})[HTG^-]$$

Substituting in the expression for HTG^- and the results from the absorbancies yields

$$\frac{dA}{dt} = -\left\{k_f(\text{obsd.})[G] + k_r(\text{obsd.})\left(\frac{[H^+]}{K_1} + 1\right)\right\}A + \left\{k_f(\text{obsd.})[G] + k_r(\text{obsd.})\left(\frac{[H^+]}{K_1} + 1\right)\right\}C + k_r(\text{obsd.})[Te]_0B$$

This expression predicts that a plot of $\Delta A/\Delta t$ against the appropriate value of *A* should be a straight line with negative slope. Numerous runs at 230 mμ under conditions of varied temperature, concentration and *p*H all yielded data which gave fairly straight lines for the first 5–15 min., *i.e.*, to ~80% reaction; an example is shown in Fig. 1.

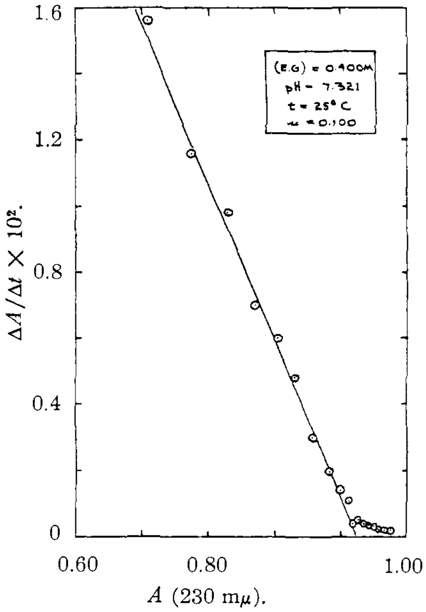

Fig. 1.—Rate plot of spectrophotometric data.

Moreover, examination of the above equation shows that the slope should be independent of the total amount of tellurium present at any particular polyol concentration. Several runs verified this. Nearly identical values were found for the slope on using different choices of Δt, from 0.5 to 0.1 min.

In order to obtain rate constants from the absorbancy data, it would appear that a knowledge of the extinction coefficients that appear in the B and C terms is necessary. However, the potentiometric measurements had shown that the ratio of the observed rate constants, $k_f(\text{obsd.})/k_r(\text{obsd.})$,

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[8] (a) C. Stüber, A. Braida and G. Jander, *Z. physik. Chem.*, **A171**, 320 (1934); (b) G. W. Leonard and R. W. Henry, *Anal. Chem.*, **28**, 1079 (1956); (c) J. E. Earley, Ph.D. Thesis, Brown University (1957).

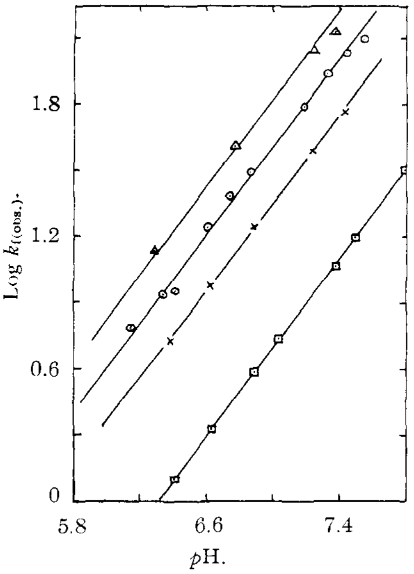

Fig. 2.—Sample inverse first order in hydrogen ion concentration plots: data are for 25° and μ = 0.10: ⊙, ethylene glycol; X, propylene glycol; ⊡, (*meso*)-2,3-butanediol, Δ, D-glucose.

which is equal to the formation constant, remained essentially constant over a wide range of pH.[1] Thus it is possible to replace k_r(obsd.) in the rate expression by the term k_f(obsd.)/Kc_1; placing this in the expression for the slope gives

$$k_f(\text{obsd.}) = \frac{\text{slope}\cdot Kc_1}{(Kc_1\cdot[\text{G}]) + ([\text{H}^+]/K_1) + 1}$$

from which k_f(obsd.) can be calculated using the slope, the pH of the reaction mixture and the value of Kc_1 at the polyol concentration used in the kinetic run. These latter values were measured in conjunction with the determination of the formation constants which were presented in the previous paper.[2]

Kinetics.—In Table I is shown an example of the steps involved in calculating k_f(obsd.); also the constancy of the rate constant at various polyol concentrations is demonstrated. From these data it is concluded that the previous observation[7] that the rate is first order each in [polyol] and [$H_5TeO_6^-$] is correct. These orders were checked with every polyol.

TABLE I

SAMPLE KINETIC DATA AND RESULTS WITH ETHYLENE GLYCOL[a]

[Glycol]$_0$	Kc_1	[H$^+$] × 10^8	−Slope × 10^3	k_f(obsd.) × 10^2
0.150	14.60	4.70	4.68	1.43
.200	14.47	4.73	5.33	1.40
.250	14.33	4.78	6.17	1.43
.320	14.14	4.70	7.22	1.43
.400	13.93	4.78	8.33	1.42
.500	13.65	4.73	9.67	1.40

[a] Average pH = 7.324, μ = 0.10, 25°. Average k_f (obsd.) = 1.42 ± 0.01 × 10^{-2} l. mole^{-1}sec.$^{-1}$.

As may be seen in Fig. 2, a plot of log k_f(obsd.) against pH is linear with a slope of 1.0. For every polyol studied, plots of this type were linear and the calculated values of the product k_f(obsd.)-[H$^+$] were fairly constant over a wide range of acidities. Kinetic data were obtained in the pH range from 6.04 to 7.82 with no evidence for deviation from 1/[H$^+$] dependence; thus it is apparent that the previous difficulties[7] with the pH dependence came (as suspected) from the analytical method used therein.

TABLE II

RATE CONSTANTS FROM THE SPECTROPHOTOMETRIC DATA[a]

Temp. (°C.)	Kc_1	k_f(obsd.)[H$^+$] × 10^{10}	k_f × 10^{-1}	k_r(obsd.)[H$^+$] × 10^{11}
Ethylene glycol				
21	17.8	4.47 ± 0.07	2.23 ± 0.03	2.52 ± 0.03
25	15.0	6.66 ± .35	2.48 ± .13	4.45 ± .23
35	12.5	13.30 ± .92	4.19 ± .29	10.61 ± .73
45	9.9	29.5 ± .23	6.45 ± .05	29.8 ± .25
Propylene glycol				
21	36.5	2.38 ± .01	1.19 ± 0.05	0.653 ± 0.028
25	33.0	3.71 ± .05	1.38 ± .02	1.12 ± .020
35	25.0	8.15 ± .35	2.58 ± .11	3.27 ± .13
45	19.3	18.8 ± .45	4.10 ± .10	10.1 ± .30
Glycerol				
25	79.6	8.32 ± 0.20	3.08 ± 0.07	1.05 ± 0.03
35	66.5	17.7 ± 1.2	6.07 ± .38	2.88 ± .18
45	53.5	43.3 ± 2.0	9.48 ± .43	8.10 ± .37
(*meso*)-2,3-Butanediol				
21	17.8	0.578 ± 0.005	0.290 ± 0.003	0.317 ± 0.003
25	16.5	0.830 ± .005	.308 ± .002	0.503 ± .003
35	14.0	2.90 ± .07	.918 ± .022	2.07 ± .07
45	11.8	6.10 ± .38	1.34 ± .083	5.17 ± .33
3-Methoxy-1,2-propanediol				
21	35.5	2.25 ± 0.02	1.13 ± 0.01	0.633 ± 0.002
25	30.2	3.43 ± .13	1.28 ± .05	1.14 ± .04
35	26.1	8.75 ± .30	2.78 ± .10	3.37 ± .12
45	21.2	20.3 ± .5	4.45 ± .10	9.59 ± .25
D-Glucose				
21	15.1	6.72 ± 0.40	3.37 ± 0.20	4.45 ± 0.27
25	13.4	10.6 ± .8	3.93 ± .28	7.90 ± .58
35	14.3	19.0 ± .8	6.00 ± .23	13.3 ± .8
45	13.6	41.7 ± .7	9.12 ± .13	30.5 ± .5
1,2,4-Butanetriol				
25	42.5	4.56 ± 0.10	1.70 ± 0.03	1.08 ± 0.03
L-(+)-Arabinose				
25	46.9	6.55 ± 0.43	2.43 ± 0.15	1.40 ± 0.18
Fructose				
25	289	11.4 ± 0.4	4.23 ± 0.10	0.395 ± 0.030
D-Galactose				
25	46.0	11.9 ± 0.1	4.42 ± 0.02	2.58 ± 0.02
D-Mannose				
25	106	8.85 ± 0.55	3.28 ± 0.20	0.835 ± 0.052
Pentaerythritol				
25	3.09	8.05 ± 0.12	3.00 ± 0.05	26.2 ± 0.3
2-Hydroxymethyl-2-methyl-1,3-propanediol				
25	0.624	1.66 ± 0.13	0.612 ± 0.048	26.5 ± 0.3

[a] All runs made at μ = 0.10 and [Te]$_0$ = 1 × 10^{-3} *M*. Values of Kc_1 are those at [G] = 0. The units of k_f(obsd.) are liter mole^{-1}sec.$^{-1}$, those of k_f(obsd.) [H$^+$] are sec.$^{-1}$ and those of k_r(obsd.)[H$^+$] are mole l.$^{-1}$sec.$^{-1}$. Standard deviations of the rate constants are also listed.

Rate data for thirteen polyols are given in Table II, which summarizes the results of over 500 kinetic runs. From our results, we feel certain that under the conditions of this study the rate law may be expressed as

$$-\frac{\text{d}[\text{T}^-]}{\text{d}t} = \frac{k_f'[\text{G}][\text{T}^-]}{[\text{H}^+]} - \frac{k_r'[\text{HTG}^-]}{[\text{H}^+]}$$

The most probable interpretation of this is that the reactive tellurate ion is $H_4TeO_6^=$ (or a dehydrated form of $H_4TeO_6^=$), *i.e.*

$$-\frac{\text{d}[\text{T}^-]}{\text{d}t} = \frac{k_f'}{K_2}[\text{G}][\text{H}_4\text{TeO}_6^=] - \frac{k_r'}{Ka_{c_2}}[\text{TeO}_4\text{G}^=]$$

TABLE III

THERMODYNAMIC ACTIVATION QUANTITIES AT 298°K.

Polyol	Forward reaction[a]				Reverse reaction[a,d]			
	Ea	ΔH^*	ΔF^*	ΔS^*	Ea	ΔH^*	ΔF^*	ΔS^*
Ethylene glycol[b]	8.1	7.5	15.6	−27	18.5	17.9	31.6	−46
Propylene glycol[b]	9.9	9.3	15.9	−22	20.4	19.8	32.4	−42
Glycerol	10.6	10.0	15.4[c]	−18[c]	19.5	18.9	32.5	−45
(*meso*)-2,3-Butanediol	11.9	11.3	16.6	−18	21.2	20.6	32.9	−41
3-Methoxy-1,2-propanediol	10.6	10.0	15.9	−20	20.7	20.1	32.4	−41
D-Glucose	7.2	6.6	15.3	−29	14.9	14.3	31.3	−57

[a] Ave. limits of error for both forward and reverse reactions are: Ea, 4%; ΔH^*, 4%; ΔF^*, 1%; and ΔS^*, 5%. [b] Values of k_f at 298°K. taken from plots of log k_f *vs.* $1/T$. [c] If corrected for statistical factor of two, values of ΔF^* and ΔS^* are 15.8 and −19.5, respectively. [d] These quantities contain the thermodynamics of the reaction $HTeO_4G^- \rightleftarrows H^+ + TeO_4G^=$.

where Kac_2 is the second acid dissociation constant of the complex

$$Kac_2 = [H^+][TeO_4G^=]/[HTeO_4G^-]$$

and K_2 is the acid dissociation constant of $H_5TeO_6^-$. Thus the rate constant for the combination of a tellurate ion and a polyol molecule is

$$k_f = \frac{k_f'}{K_2} = \frac{k_f(\text{obsd.})[H^+]}{K_2}$$

and similarly for the reverse reaction

$$k_r = \frac{k_r'}{Kac_2} = \frac{k_r(\text{obsd.})[H^+]}{Kac_2}$$

Since K_2 is known, k_f can be calculated from the observed rate constant. However Kac_2 is not known with certainty; it can be estimated from titration curves of telluric acid with added polyol as for the calculation of K_2.[2] Samples of such curves have been reported by Edwards and Laferriere,[4] but no calculations of Kac_2 were made. Rough determinations showed that with propylene glycol, Kac_2 is slightly larger than K_2, however determination of Kac_2 with other polyols and as a function of temperature was not done. Because Kc_1 is defined as $k_f(\text{obsd.})/k_r(\text{obsd.})$, k_f/k_r is not equal to the formation constant but is equal to Kc_1K_2/Kac_2. Since $Kac_2 > K_2$, $k_f/k_r < Kc_1$. The values of k_f that were determined for each polyol and at various temperatures are also shown in Table II. The values of K_1 and K_2 used in these calculations at ionic strength 0.1 and at various temperatures were presented in the preceding paper. Since Kac_2 is not known it has been impossible to evaluate k_r.

Plots of log k_f against $1/T$ produced straight lines. The Arrhenius activation energy Ea and the activation enthalpy, free energy and entropy are presented in Table III. Although values of k_r could not be obtained, it is possible to see the effect of different polyols on the thermodynamic activation quantities for the reverse reaction by using the values of k'_r. These results are also shown in Table III and are discussed below.

Discussion

In general the results of this study agree with the data obtained by the pH method.[7] Although the rate constants from the pH method are slightly higher (by from 1.14 to 3.03)[9] than those from the spectrophotometric method, both procedures indicated that the rate is first order each in tellurate ion and in polyol concentration. These facts allow the postulation of many mechanisms. In order to make a choice among them it is first necessary to consider some other pertinent facts.

(a) The stoichiometry of the reaction

$$H_5TeO_6^- + G \rightleftarrows HTeO_4G^- + 2H_2O$$

indicates that two moles of water are given off for every mole of complex formed. Because of the known slow rate of C–O bond fission, we assume that the oxygens in the water molecules are coming from the tellurate ion rather than from the polyol molecule.

(b) The reaction is base-catalyzed. This fact is somewhat surprising because almost all oxyanion reactions are acid-catalyzed.[10,11]

(c) The forward rate constants depend little on the nature of the polyol. For example, the five different mono-substituted ethylene glycols have k_f values which are identical within 15% of the mean. The large differences in equilibrium constant values must be reflected in the reverse rate constants.

(d) The entropies of activation in both directions are quite negative even after correction for the entropy of ionization of a second proton.

The observations that the forward rate constants are almost independent of the nature of the polyol and that the reverse rate constants reflect the variations in Kc_1 allow the reasonable conclusion that the polyol and tellurium atom are fairly far apart in the activated complex. Also, the fact that the entropies of activation are negative in both directions leads to the inference that the ring structure of the product is at least partially formed in the activated complex.

An explanation for these conclusions can be found if the tellurate ion could form a reactive intermediate of lower coordination number than six. The observation of base catalysis is, in this case of $H_5TeO_6^-$, strongly suggestive of $TeO_4^=$ as

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(9) Part of this difference could arise from use of the equation $[H^+] = \text{antilog}\,(-pH)$ for evaluation of $[H^+]$ and the neglect of activity coefficients. Examination of the derivation of the equations used to calculate the rate constants by the two methods shows that the pH data are too large by a factor $1/\gamma H^+$ and the spectrophotometric rate constants are too small by the factor γ_{H^+}, where γ_{H^+} is the activity coefficient of H^+. Using the Debye–Hückel theory, we estimate that γ_{H^+} is about 0.69, so that the rate constants should differ by a factor of ~2. The observed direction and size of the difference are the same then as predicted for an activity coefficient effect. The rate constants from the spectrophotometric method have a much lower variability and the plots using this method show less curvature than the pH method. We feel therefore that the rate data presented here (uncorrected for activity coefficients) are more reliable than those presented earlier.[7]

(10) (a) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952); (b) J. O. Edwards, *J. Chem. Educ.*, **31**, 270 (1954).

(11) H. Taube, *Rec. Chem. Prog.*, **17**, 25 (1956).

an intermediate. The stoichiometry of its formation is

$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^= \pm H_2O$$

$$H_4TeO_6^= \rightleftharpoons TeO_4^= + 2H_2O$$

and the reason for base catalysis is apparent therein. The postulation of $TeO_4^=$ as an intermediate also satisfies the assumption that the oxygen atoms in product water are derived from the tellurate ion.

Although at this time there is no evidence for the existence of $TeO_4^=$,[12] it is possible that this substance is present in such small concentrations that it cannot be detected by the usual physical or chemical methods. Consideration of the periodic chart and the nearest neighbors above and beside tellurium leads one to believe that a coördination number of four is possible. Selenium, in the same family, can exist as $SeO_4^=$ as does sulfur in $SO_4^=$. Iodine is known to exist as an oxyanion in two stable forms, $H_4IO_6^-$ and IO_4^-; the equilibrium constant for the dehydration reaction

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O$$

has been measured by Crouthamel, Hayes and Martin[13] and found to be 40 at 25° and 7.4 at 0°. Further consideration suggests that the dehydration equilibrium constant should be smaller for tellurate than for periodate. The small fraction of the tellurium which is present as $TeO_4^=$ should therefore be reactive. It is generally found in chemical reactions that intermediates are structurally similar to known stable compounds,[11] and so it might be expected that the intermediate in the present case should also be similar to other stable oxyanions.

Thus it is proposed that the following mechanism can suitably explain the experimental data.

$$H_5TeO_6^- \overset{K_2}{\rightleftharpoons} H^+ + H_4TeO_6^=$$

$$H_4TeO_6^= \overset{K_D}{\rightleftharpoons} TeO_4^= + 2H_2O$$

$$TeO_4^= + G \overset{k_{fc}}{\rightleftharpoons} [\neq] \underset{k_r}{\rightleftharpoons} TeO_4G^=$$

$$H^+ + TeO_4G^= \underset{Kac_2}{\rightleftharpoons} HTeO_4G^-$$

If it is assumed that the only slow steps in this mechanism are those involving formation and dissociation of the complex then the rate law can be written as

$$\text{Rate} = k_{fc}[TeO_4^=][G] - k_r[TeO_4G^=]$$

Defining the rate of reaction as the rate of disappearance of $H_5TeO_6^-$ and inserting the definitions of K_2, K_D and Kac_2 results in the expression

$$-\frac{d[H_5TeO_6^-]}{dt} = \frac{k_{fc}K_DK_2[G][H_5TeO_6^-]}{[H^+]} - \frac{k_rKac_2[HTeO_4G^-]}{[H^+]}$$

which is identical in form with the observed rate expression

$$-\frac{d[H_5TeO_6^-]}{dt} = \frac{k_f'[G][H_4TeO_6^-]}{[H^+]} - \frac{k_r'[HTeO_4G^-]}{[H^+]}$$

Comparison of these expressions with those in the section on results shows that k_r is the same in both cases but that k_{fc} is equal to k_f/K_D.

The fact that the forward rate constants (also the reverse rate constants—see Table II) do not vary over a very wide range can be viewed as being in part, the consequence of a linear relationship between the enthalpies and entropies of activation so that one nearly cancels the effect of the other. Thus the free energies of activation remain essentially unchanged. Such relationships have been observed by many workers and were recently discussed by Leffler.[14]

The thermodynamic activation quantities shed some light on the configuration of the activated complex. Inspection of Table III shows that there is a large change in the entropy of approximately −20 to −30 in going from the reactants, $H_4TeO_6^=$ and polyol, to the transition state. The values for the rate determining step would become even more negative than this if the entropy of the dehydration step were also taken into account. This is because the entropy change associated with the dehydration step is positive (for the similar reaction with the periodate ion it was found that ΔS_D^0 at 25° is 44[13]) and must be subtracted from the observed entropy of activation since $\Delta S_{fc}^{\neq} = \Delta S_f^{\neq} - \Delta S_D^0$. Using semi-empirical equations developed by Powell,[15] it is possible to calculate that for the dehydration of $H_4TeO_6^=$ (and similarly for $H_4IO_6^-$) ΔS_D^0 should be about 60.

The observed values of $\Delta S_f^{\neq}$ for all of the 1,2-diols except ethylene glycol are close to −20. Using the estimated values of ΔS_D^0, it would be predicted that $\Delta S_{fc}^{\neq}$ would be about −80 if $TeO_4^=$ were the reactive tellurate species. It is interesting to note that in the periodate oxidation of various polyols (which presumably involves IO_4^- and the formation of a cyclic complex as an intermediate) Bulgrin and co-workers[16,17] have found entropies of activation ranging from −40 to −90. This similarity in values of $\Delta S^{\neq}$ suggests that the reactions are alike and involve similar reactive anions.

Consideration of the thermodynamic activation quantities of the reverse reaction (in Table III) shows that for the five 1,2-diols the values of $\Delta S_r'^{\neq}$ are all close to −43. The relative constancy of these quantities indicates that the size and position of groups on the polyol molecule has little influence on the rate of decomposition of the mononegative complex. To get the correct values of $\Delta S_r^{\neq}$, it is necessary to subtract the entropy for the second ionization of the complex since $\Delta S_r^{\neq} = \Delta S_r'^{\neq} - \Delta S_{Kac_2}$. If it is assumed that ΔS_{Kac_2} has about the same value as ΔS for the second ionization of telluric acid (at $\mu = 0.1$ this is roughly -28^2), then to a good approximation $\Delta S_r^{\neq}$ is about −15. As mentioned earlier such a negative change in entropy indicates that there is insig-

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

[13] C. E. Crouthamel, A. M. Hayes and D. S. Martin, *ibid.*, **73**, 82 (1951).

[14] J. E. Leffler, *J. Org. Chem.*, **20**, 1201 (1955).

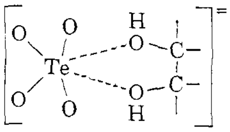
[15] R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).

[16] F. R. Duke and V. C. Bulgrin, *J. Am. Chem. Soc.*, **76**, 3802 (1954).

[17] V. C. Bulgrin and G. Dahlgren, *ibid.*, **80**, 3883 (1958).

nificant ring opening in going from the polyol-tellurate complex to the transition state, thus the activated complex should be structurally related to the cyclic diester. The large negative entropies in the formation of the activated complex from the reactants support this conclusion. A more positive $\Delta S_r^{\ddagger}$ would be expected if a non-cyclic intermediate were formed since fewer degrees of freedom would be lost in going over to the activated complex from the reactants. This does not conclusively rule out the possibility of forming a linear intermediate from $TeO_4^{=}$ and a polyol molecule (or from $H_2TeO_5^{=}$ and a polyol), but it does make it seem unlikely.

The decrease in entropies in going to the transition state from both directions is consistent with an unusual distribution of protons or solvent molecules or both in the activated complex. This complex presumably has characteristics of both the $TeO_4^{=}$ ion and the polyol molecule and the cyclic polyol-tellurate complex, *i.e.*



The transfer of the protons from the polyol to the tellurate portion of the complex, or *vice versa*, could take place in either of two ways, through internal hydrogen bonds or through the formation of hydrogen bonds with solvent water molecules. However, proton transfer need not take place in the transition state, indeed it is more likely to occur in the change of the activated complex to the dinegative complex.

Further information about the transition state may be obtained by comparing the values of k_f and k_r' with the formation constants, K_{C_1}. A plot of log K_{C_1} against log k_f shows no significant correlation between these two sets of constants. However a similar plot with the reverse rate constants yields a straight line with a slope of -1.4. From this it may be concluded that about 70% of the value of the formation constant is reflected in the rate at which the dinegative complex decomposes back to the reactants, while K_{C_1} has only a slight influence on the rate at which the polyol and tellurate ion come together. Since the complex is readily detected while $TeO_4^{=}$ is not, the former is in a lower free energy state, *i.e.*, is more stable, than the latter. Thus it appears reasonable that the breaking of two stable Te–O bonds and the necessary rearrangement of protons in going from the complex to the transition state must involve considerably more energy than the combination of the reactive $TeO_4^{=}$ with a polyol molecule. Hence the formation constant will be reflected in the reverse reaction more strongly than in the forward reaction.

The fact that the most stable products are not necessarily produced most rapidly has been put on a postulatory basis by Hammond.[18] Following his ideas, the highly reactive intermediate $TeO_4^{=}$ reacts with a polyol to form a transition state which should be structurally similar to the reactants (polyol and $TeO_4^{=}$ here) and quite different from the products; therefore there should be no regular tendency for the most stable complexes to be produced the most rapidly. The discussion which follows in the next few paragraphs should help to clarify this conclusion.

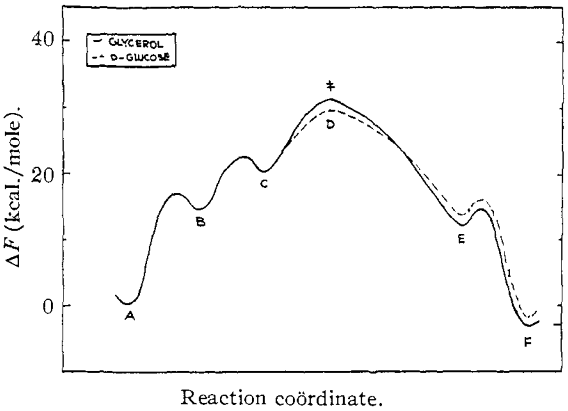


Fig. 3.—Reaction coördinate plot: for explanation of letters, etc., see text.

Much of what has been discussed above concerning the values of k_f and k_r and the postulated existence of $TeO_4^{=}$ can be visualized more easily from a diagram of the free energy of the system along the reaction coördinate as shown in Fig. 3. The initial state A consists of unreacted $H_5TeO_6^-$ and the polyol. State B, consisting of $H_4TeO_6^{=}$ and unreacted polyol, is at a higher free energy because of the small amount of this particular tellurate ion that is present in an equilibrium mixture of telluric acid and tellurate ion. The difference in energies between states A and B is the value of ΔF for the second ionization of telluric acid appropriate to the conditions. The height of the maximum between A and B is only an estimate, but the extreme rapidity of acid ionizations indicates that this barrier is not too high. State C consists of the still more reactive $TeO_4^{=}$ ion and unreacted polyol. Both the height of the maximum between B and C and the position of the minimum at C are estimated values, but the small concentration of $TeO_4^{=}$, at least less than 10% or it would have been detected,[12] argues that C should be at least 2 kcal. higher than B. State D is the transition state. The height of D above A is given by the experimentally measured free energy of activation (Table III) plus the ΔF for the second ionization of telluric acid. This is because $\Delta F_f^{\ddagger}$ was calculated on the basis of $H_4TeO_6^{=}$ being the reactive ion, and so it only gives the difference of B to D.

As the polyol and tellurate ion come closer together (past the transition state) to form Te–O bonds, there is a rearrangement of protons and the energy decreases until state E is reached. This is the dinegative complex which has thermodynamic properties of ionization similar to those of $H_4TeO_6^{=}$. Because of this similarity, the plot from E to F, the mononegative complex, should be roughly symmetrical with the shape of the curve from A to B and also of the same height. The posi-

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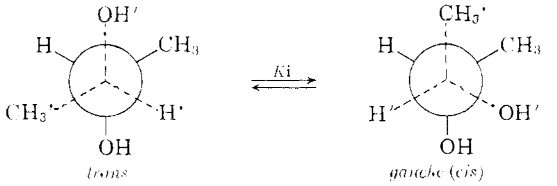
[18] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

tion of F has been determined in two ways; going from F to D prepresents $\Delta F_r{}'^{\ddagger}$ (Table III) and the net of going from A to F is the equilibrium free energy that was determined from the formation constants.[2]

The data from only two polyols, glycerol and D-glucose, are shown in this diagram; the values of the others lie near these two. The important point that this reaction coördinate plot illustrates is the high reactivity of $TeO_4^{=}$. At position C it has two paths which it may follow, neither of which requires a great deal of energy. It has the choice of either going back to $H_4TeO_6^{=}$ or it may climb the short height to the transition state. The relative closeness of states C and D shows why the rate constants in the forward directions are so similar even though there is considerable variety in the structures of the polyols.

Although the values of k_1 are remarkably similar, close examination of Table II reveals that there are systematic variations from the fast sugars to the slow (*meso*)-2,3-butanediol. This trend can be explained quite simply as being the result of having different fractions of the total polyol concentration present with *cis* hydroxyl groups. The tetrahedral tellurate is a highly reactive anion, and thus it is not unreasonable to assume that it reacts with all *cis* hydroxyl groups at roughly the same rate. From this it follows that the compounds present with higher proportions of *cis* hydroxyl groups will form complexes at faster rates. This statement can be placed on a somewhat more quantitative basis by considering the internal rotation equilibrium between the *trans* and *gauche* forms of a polyol. The *gauche* isomer is used here rather than the *cis* since $TeO_4^{=}$ can complex with both configurations with about the same arrangement of bond lengths and angles and since little is known about the true *cis* configuration. Using (*meso*)-2,3-butanediol as an example this rotational equilibrium is represented as



In this polyol the two hydroxyl groups will be pushed *trans* to one another because of steric crowding by the methyl and hydroxyl groups, therefore the equilibrium will lie to the left. If one of the methyl groups is replaced by a hydrogen atom to give propylene glycol, there will be less interaction between the various groups and thus K_i for this polyol should be larger than the value of K_i for (meso)-2,3-butanediol. Similarly, replacement of both methyl groups by hydrogens (resulting in ethylene glycol) will yield an even higher value of K_i. In the sugars the cyclic nature of these compounds prevents internal rotation, so that if two hydroxyl groups are *cis* to one another, they will be locked in that position and will not be able to become *trans* to each other.

Quantitative values of K_i are not available for these polyols, however it is possible to make rough estimates using a value of the energy difference between the *trans* and *gauche* rotational isomers of *n*-butane reported by Kreevoy and Mason.[19] These estimates are shown in Table IV along with the values of k_f for comparison. From this table it can be seen that there is a definite trend for the rate constants to parallel the changes in K_i. The similarity in k_f values found with propylene glycol, glycerol, 3-methoxy-1,2-propanediol and 1,2,4-butanetriol indicates that the groups CH_3, CH_2OH, CH_2OCH_3 and CH_2CH_2OH all have roughly the same effect on the *trans*, *gauche*, equilibria.

Kreevoy and Mason[19] also found that the barrier to internal rotation for many simple compounds fell in the range 3–5 kcal./mole. These values are much lower than the observed activation energies of complex formation, and so these rotational equilibria are attained at a great deal faster rate than the complexing equilibria. Thus it is not the height of the barrier, but rather the difference in energy levels of the rotational isomers which determines the amount of a polyol present in a favorable configuration for complexing.

Table IV

Comparison of K_i Values with Forward Rate Constants

Polyo	$K_i{}^a$	$k_f{}^b$
L-Arabinose	All *cis*	24.3
Fructose	All *cis*	42.3
D-Galactose	All *cis*	44.2
D-Glucose	All *cis*	39.3
D-Mannose	All *cis*	32.8
Ethylene glycol	1	24.8
Propylene glycol	0.5	13.8
Glycerol	.5	15.3[c]
3-Methoxy-1,2-propanediol	.5	12.8
1,2,4-Butanetriol	.5	17.0
(*meso*)-2,3-Butanediol	.1	3.0

[a] Estimated using data from ref. 19. [b] At 25°. Units of k_f are liter mole^{-1}sec.$^{-1}$. [c] Statistical correction made.

The much smaller values of k_i shown by the 1,3-diols (after correcting for statistical factors) are again what one would predict for these polyols. Because of the greater separation of the hydroxyl groups, it is less probable that the glycol will be in a favorable position to form two bonds with a $TeO_4^{=}$ than it is for a 1,2-diol. Also since six- rather than five-membered rings are being formed and because this involves somewhat more strain on bond lengths and angles, the complex will decompose much more rapidly than in the cases with the 1,2-diols, and so the values of k_r will be quite large.

Although the present data appear to offer good evidence for the existence of $TeO_4^{=}$, there is also indirect information which further substantiates this postulate. Recently, Buist, Bunton and Miles[20] reported rate constants for the formation of the cyclic intermediate in the periodate oxidation of glycols. Three of the six polyols that they studied, ethylene glycol, propylene glycol and

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(19) M. M. Kreevoy and E. A. Mason, Technical Report, IMP-ONR, Contract Nonr-595 (02), 1957.

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

(*meso*)-2,3-butanediol, were the same as used in this study. In order to be able to compare rate constants between the two systems, it was first necessary to correct the periodate values (which were measured at 0° and at a *p*H value of about 9.1) for the presence of $H_3IO_6^{=}$ so that they would fit the rate equation

$$\text{Rate} = k_f[IO_4^-][G] - k_r[IO_4G^-]$$

Comparison of the resultant rate constants with the tellurate values (see Table V) shows a remarkable correlation of the constants for the systems with ethylene glycol and propylene glycol but some divergence with (*meso*)-2,3-butanediol. If it is assumed that K_D for the tellurate system is about 0.01 and recalling that $k_{fc} = k_r/K_D$, it turns out that the forward rate constants for the two anions are of the same order of magnitude. This similarity in order of magnitude and the fact that several workers[16,17,20–22] have shown that the periodate oxidation of glycols probably involves the tetrahedral IO_4^- ion, makes it seem logical to assume that a similar species is involved in the formation of the polyol tellurate complexes, namely the isoelectronic $TeO_4^{=}$. However, it should be emphasized that this correlation between tellurate and periodate data is based on limited information; the agreement that there is could be coincidental. Runs with several other polyols including pinacol and some cyclic diols should be done in both systems before any further conclusions are made.

TABLE V

COMPARISON OF PERIODATE[a] AND TELLURATE[b] RATE AND EQUILIBRIUM CONSTANTS

Constant and system	Eth. gly.	Prop. gly.	*m*-2,3-But.
k_f(periodate)[c]	4300	2100	1300
k_f(tellurate)[c]	24.8	13.8	3.08
k_r(periodate)[d]	23	4.2	19
k_r(tellurate)[d]	2.66	0.676	0.302
Kc_1(periodate)	189	500	68
Kc_1(tellurate)	15.0	33.0	16.5

[a] Periodate rate constants at 0° from ref. 20; see text. [b] Tellurate constants at 25°. [c] k_f in units of M^{-1} sec.$^{-1}$. [d] k_r in units of sec.$^{-1}$.

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[21] F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1957).

[22] V. C. Bulgrin, *J. Phys. Chem.*, **61**, 702 (1957).

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

The Preparation of Boron Triisothiocyanate and Some Molecular Addition Compounds

BY D. B. SOWERBY[1]

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Boron trichloride reacts with either sodium or potassium thiocyanate in liquid sulfur dioxide to give boron triisothiocyanate. This compound, analogous to the boron trihalides, has Lewis acid characteristics and forms molecular addition compounds with nitrogen donor molecules such as tertiary amines and nitriles. The addition compounds with acetonitrile, benzonitrile and phenylacetonitrile can be prepared from the corresponding boron trichloride adducts and potassium thiocyanate in liquid sulfur dioxide. The infrared spectra of the addition compounds are presented.

Introduction

The boron trihalides and the tendency for these compounds to form molecular addition compounds with electron-pair donor molecules are well known. On the other hand, the pseudo-halogen derivatives of boron are less well characterized and no reactions have been reported which lead to similar Lewis acid-base adducts. The known boron pseudohalides have been listed by Lappert and Pyszora.[2] Although substituted boron isothiocyanates are known, the existence of the parent compound, boron triisothiocyanate is in doubt. The substance was reported to result from treatment of boron tribromide with silver thiocyanate in benzene suspension,[3a] but this could not be confirmed.[3b] The successful use of soluble ionic thiocyanates in acetonitrile or liquid sulfur dioxide as a means of preparing non-metallic isothiocyanates from the corresponding chlorides[4] led to an examination of similar reactions with boron trichloride and some of its molecular addition compounds.

Experimental

Boron triisothiocyanate.—Anhydrous sodium thiocyanate (26 g., 0.32 mole), or an equivalent amount of potassium thiocyanate, was added portionwise to a stirred solution of 13.0 g. (0.11 mole) of boron trichloride in 200 ml. of liquid sulfur dioxide, cooled to −30°. After a few minutes, a white precipitate began to form and the mixture was stirred vigorously for approximately 4 hr. The solution then was cooled to −60° and filtered in the absence of moisture. During removal of the sulfur dioxide from the filtrate under aspirator vacuum, the solution progressively darkened and finally yielded an orange semi-solid mass, which was immediately transferred to a vacuum distillation apparatus. Heating this material gave a pale brown liquid, which on redistillation gave 7.5 g. (38% yield) of a colorless liquid with a boiling point of 92° at 0.1 mm.

Anal. Calcd. for $B(NCS)_3$: C, 19.44; N, 22.69. Found: C, 19.55; N, 22.92.

The compound is miscible with benzene, and on cooling the solution, a white solid, rapidly turning yellow resulted.

Anal. Calcd. for $B(NCS)_3$: NCS^-; 94.17. Found: C, 19.20; N, 22.48; NCS^-, 93.9.

The solid decomposed on heating at $\sim$115°. Although the empirical formula was that of the boron triisothiocyanate, this solid no longer dissolved completely in benzene. Similar solids resulted when the liquid boron isothiocyanate was added to either chloroform or *n*-heptane.

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[1] Presently an ICI Fellow, Department of Chemistry, University College, London.

[2] M. F. Lappert and H. Pyszora, *Proc. Chem. Soc.*, 350 (1960).

[3] (a) H. E. Cocksedge, *J. Chem. Soc.*, **93**, 2177 (1908). (b) E. Pohland, *Z. anorg. u. allgem. Chem.*, **201**, 282 (1931).

[4] D. B. Sowerby, *J. Inorg. & Nuclear Chem.*, in press.