Making these substitutions into Equation 1, one can obtain Equation 2 from which k_i can be calculated at point i on the titration curve (up to the equivalence point).

$$k_i = \frac{10^{-x_i}\left\{\frac{V_iN}{V_o + V_i} + 10^{-x_i}\right\}}{\frac{(V_f - V_i)N}{V_o + V_i} - 10^{-x_i}} \quad (2)$$

While Equation 2 corrects for the ionization of the untitrated acid and the volume change at each point on the titration curve, it does not correct for ionic strength. Accordingly, a correction term was then derived from the limiting equation of Debye and Huckel for the mean activity coefficients of strong electrolytes. The use of this limiting equation was considered valid since the ionic strengths involved were all in the vicinity of 0.01.

The correction which should be applied to any experimental pK_i is equal to $-2 \log f_i$ where f_i is the mean activity coefficient at point i. At 25° this correction is equal to $1.011 (u_i)^{\frac{1}{2}}$, where u_i is the ionic strength at that point and is given by the equation

$$u_i = \frac{1}{2}\{[H^+]_i + [A^-]_i + [Na^+]_i\}$$

Using the symbols introduced above, u_i can be expressed by Equation 3.

$$u_i = \left\{10^{-x_i} + \frac{V_iN}{V_o + V_i}\right\} \quad (3)$$

Thus by use of Equations 2 and 3 it is possible to calculate a corrected pK_a for each point on the titration curve (up to the equivalence point) and hence a mean corrected pK_a for each titration.

Calculation by computer was deemed necessary since the denominator of Equation 1 may become very small because the solubilities of the sulfinic acids are limited and their extends of ionization are appreciable. With the aid of the computer, the pK_a's were conveniently calculated from a sufficient number of points to permit statistical treatment.

It should further be pointed out that near the equivalence point the first term in the denominator of Equation 2 becomes very small. Experimental data on the steeply rising portion of the titration curve close to the end point were generally found to be less reliable than those on the more horizontal portion. Accordingly, experimental points in this region were not analyzed by the computer. The number of experimental points analyzed in each titration averaged 22, but ranged from a low of 12 to a high of 58 depending on the sample size and the experimentor.

Manhattan, Kan.

[Contribution from the Metcalf Chemical Laboratories of Brown University]

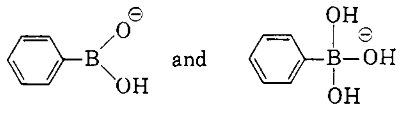
Polyol Complexes and Structure of the Benzeneboronate Ion

JOHN P. LORAND[1] and JOHN O. EDWARDS

Received September 11, 1958

The complexing equilibria of aqueous benzeneboronate ion with several polyols have been studied and the measured constants compared with those of borate. The results indicate that the anion has the formula $C_6H_5B(OH)_3^-$ with tetrahedral coordination about boron; this is consistent with a steric effect, previously cited, on the acid-base equilibria of *ortho* substituted benzeneboronic acids. Examination of the data on complexing equilibria requires modification of an earlier assumption that only anionic complexes are formed.

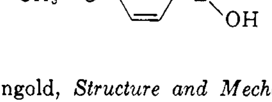
Following the recent elucidation of the structure of the borate ion in aqueous medium,[2] a study of the structure of aqueous benzeneboronate has been made, using quite different methods. Borate was previously thought to be either a trigonal Brönsted base form, $H_2BO_3^-$, or a tetrahedral Lewis acid-base adduct, $B(OH)_4^-$. The present case, likewise, offered a choice between



for the anion of benzeneboronic acid, $C_6H_5B(OH)_2$. The borate ion was studied by infrared and Raman spectroscopy, its behavior being found analogous to fluoborate, BF_4^-, because of the symmetry about boron. Such evidence was believed inapplicable to benzeneboronate because of the loss of symmetry and larger number of spectral bands.

Three different methods of attack were, however, available. The first two will be mentioned briefly, since the first proved inconclusive and the second has been previously cited. It was the third method for which complexing equilibria were experimentally studied.

Method A consisted of comparing *meta* and *para* substituted benzeneboronic acids[3] with benzoic acids[4] through their acid dissociation constants, using a plot of pK_a for $X\text{-}C_6H_4B(OH)_2$ *vs.* Hammett's σ values. It was thought that, if the tetrahedral form prdeominated, a curvature might be observed at negative values because of the presence of a resonance form,



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(1) Taken from the Sc.B. thesis of John P. Lorand at Brown University (1958).

(2) J. O. Edwards, G. C. Morrison, V. Ross, and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 266 (1955).

(3) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, N. Y. (1953), Chapter XIII, pp. 738, 741, 750.

(4) J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York (1956), pp. 72.

possible for a triangular boron but not for the tetrahedral anion. Although a straight line is, in fact, obtained, suggesting the trigonal form, the reasoning involved is admittedly tenuous and the conclusions conflicts with those of the other methods.

Method B depends upon detection of a rather strong steric effect on the acidity of *ortho* substituted benzeneboronic acids. McDaniel and Brown[5] have shown that *ortho* substituents inhibit the acidity of benzeneboronic acids, by comparison with substituted pyridines. Interpretation of the result as a steric effect leads to postulation of the tetrahedral structure; the trigonal form does not adequately account for the observed inhibition of the acidic function by substituents. Comparison of *ortho* substituted benzeneboronic acids with the corresponding benzoic acids yields the same result. Table I[6] lists the ratio, "o/p", of K_a for *ortho* substituted isomers in both series. Although the trigonal form would require that "o/p" be roughly the same for a given substituent in both series, the ratio is invariably smaller in the benzeneboronic acids. A steric effect is again implied, supporting the bulky tetrahedral structure for the benzeneboronate anion.

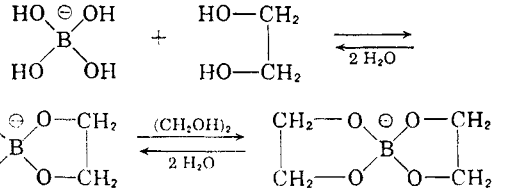
TABLE I

IONIZATION CONSTANTS OF SUBSTITUTED ACIDS

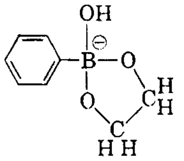
Acid	Substituent	K_a (*para*)	K_a (*ortho*)	"*o/p*"
Benzoic[a]	OCH_3	3.38×10^{-5}	8.06×10^{-5}	2.38
	CH_3	4.24	12.3	2.90
	H	6.27	6.27	8
	Cl	10.5	114.	10.8
	NO_2	37.0	671.	18.
Benzeneboronic[b]	OC_2H_5	0.608×10^{-10}	0.91×10^{-10}	1.50
	CH_3	1.0	0.261	0.26
	H	1.97	1.97	8
	Cl	6.30	14.0	2.22
	NO_2	98.	5.6	0.057

[a] In water at 25°. [b] In 25% ethanol at 25°.

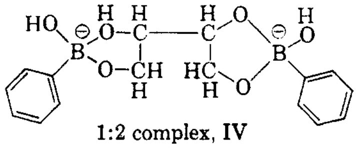
Method C involved measurements of equilibrium constants for formation of complexes between benzeneboronate ions and several organic polyhydroxy compounds, constants which had been measured for borate. Examples of such complexes are shown by the equations and structures I and II for the borates and III and IV for the phenylboronates. Formation of such complexes is well established, several having been isolated;[7,8] it is known that, at least in dilute solution, only anionic complexes are formed to a detectable extent;[9] and a simple method is available for measuring their formation constants.



1:1 complex, I   2:1 complex, II



III



1:2 complex, IV

Clearly, only the tetrahedral form of benzeneboronate ion has enough hydroxyl groups to form a complex. If, then, the tetrahedral form predominates, formation constants should be of the same order of magnitude as those of borate. If the constants were considerably smaller, it could be argued that the measured constants represent the product of the real constant for the tetrahedral form and a hydration constant for the trigonal form, which would then be seen as predominating.

For fourteen polyols (including 1,2- and 1,3-glycols and several sugars and derivatives), complex formation constants were calculated using the method of *p*H depression. The *p*H of a benzeneboronate–benzeneboronic acid buffer changes when a polyol is added, *i.e.*, the acid-base equilibrium shifts when some of the anion is removed by complex formation. This *p*H change, ΔpH, is related, as shown in the appendix, to the formation constant, K_c, and equilibrium polyol concentration, $[P]_f$, by the Expression 1 which is more compact and

$$K_c = \frac{10^{-\Delta pH} - 1}{[P]_f} \qquad (1)$$

direct than that previously employed.[9] It is subject to the condition that the acid and base forms are in equal concentrations initially, and to the assumption that the concentration of acid form remains constant.

In addition to the measurement of formation constants in benzeneboronate systems, certain experiments in the borate series which gave data either anomalous or inconclusive were repeated; two polyols are introduced which had not been measured. Symbols, definitions, assumptions, and derivations are all presented in the Appendix.

EXPERIMENTAL

Reagents. Polyols, with the following exceptions, were Eastman White Label grade and were used without further

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[5] D. H. McDaniel and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 3756 (1955).

[6] Compiled from the data of Branch and Dippy; see ref. 3.

[7] H. G. Kuivila, A. H. Keough, and E. J. Soboczenki, *J. Org. Chem.*, **19**, 780 (1954).

[8] J. M. Sugihara and C. M. Bowman, *J. Am. Chem. Soc.*, **80**, 2443 (1958).

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

purification: Phenyl-1,2-ethanediol, Eastman practical, recrystallized from benzene and hexane; polyvinyl alcohol, Du Pont Elvanol grade 70-05, not further purified[9]; D-glucose, Matheson reagent; D-mannose, Pfanstiehl C.P.; 1,3-propanediol, Eastman practical, redistilled. Weighed amounts of each were dissolved in 0.5*M* KNO_3 (B&A reagent) solution to provide stock solutions, usually one molar. From these were prepared replicates for measurement.

Benzeneboronic acid was prepared in yields up to 50% by the method of Bean and Johnson,[10] and recrystallized from benzene. Since the anhydride, $C_6H_5B{=}O$, is more stable and its purity more readily established than the acid, all samples were dehydrated by heating overnight at 105°. The neutralization equivalent (by alkali titration to the phenolphthalein end point in the presence of a tenfold excess of mannitol) was within 0.5 of the theoretical value of 103.93 g./mol. The acid melted at 225° on a heated bar; melting point was not, however, utilized as a criterion of purity because of well known complications attributable to dehydration.[11] Finally, three infrared bands reported recently for a number of benzeneboronic acids[12] were found for a sample of anhydride in CCl_4, using the Perkin Elmer Infracord instrument.

Benzeneboronic anhydride was made up as a buffer solution about 0.1*M* benzeneboronate by half neutralizing with potassium hydroxide (B&A reagent) the solution of a weighed sample. Borax, $Na_2B_4O_7 \cdot 10H_2O$ (B&A reagent), yields a solution in which the acid and base forms already have equal concentrations. The stock buffer solution was about 0.2*M* in borate.

Procedure. Differences in *p*H between polyol-free (blank) and polyol-containing benzeneboronate buffer solutions (rather than absolute *p*H) were measured. The expanded scale of a Beckman Model GS *p*H meter with standard calomel and glass electrodes was used, affording sensitivity better than ±0.003 *p*H unit and reproducibility about ±0.005 *p*H unit. Solutions, always 50 ml. in volume, were placed in a jacketed flask in 25.00 ± 0.01° and stirred at a constant rate.

In general, for a given polyol, five buffer solutions were prepared for measurement from the stock solutions: one blank and four replicates varying in polyol over a fourfold concentration range. In certain cases replicates needed to be very dilute in polyol or to include more than four concentrations. Equilibrium in the complexing reaction was ostensibly reached immediately upon mixing polyol and buffer, as was previously found with borate systems.

Results. A fairly extensive series of complex formation constants was obtained from *p*H depression data; values of the constants, treated as explained in the Appendix, are listed in Table II, along with the corresponding values for borate equilibria. For purposes of the original problem, discussion of these constants is straightforward. A number of problems have arisen, however, in the interpretation of these data, and have been carried over from the borate studies which will be dealt with afterward.

All measured constants except that for 1,3-propanediol ranged, within experimental error, from slightly larger than the borate constant to twice as large. The correlation of pairs of values is illustrated by Fig. 1; this plot of log K_c for benzeneboronate *vs.* log K_1 for borate is linear and shows a slope slightly greater than unity. The conclusion is inescapable that the benzeneboronate ion has the tetrahedral structure, the high degree of complex formation being unaccountable otherwise.

TABLE II

FORMATION CONSTANTS FOR POLYOL COMPLEXES

Polyol	No.	Benzene-boronate K	Borate K_1	K_{21}	K_1/K_2'
Ethylene glycol	1	2.76	1.85	0.07	50
Propylene glycol	2	3.80	3.10	1.60	6.0
2,3-Butanediol^a	3	$(3.6)^b$	3.45	4.85	2.5
3-Methoxy-1,2-propanediol	4	8.45	7.50	5.55	10.1
Phenyl-1,2-ethanediol	5	9.90	7.45	7.16	7.8
Catechol	6	17500	7800	14200	4300
Polyvinyl alcohol	7	$(1.9)^b$	1.8	4.3	0.75
Pentaerythritol^c	8	650	240	1110	52
1,3-Propanediol	9	0.88	1.15	—	—
Glycerol	10	19.7	16.0	41.2	6.2
D-(+)-galactose	11	276	127	298	54
Fructose	12	4370	650	98500	4.3
L-(+)-arabinose	13	391	130	675	25
D-glucose^d	14	110	80	770	8.3
D-mannose	15	172	50	49	51
Mannitol^e	16	2275^f	2100	88500	50

^{a} Probably a mixture of *dl* and meso forms. ^{b} Estimate from the log-log plot (Fig. 1). ^{c} K_{12} = 980,000 and K_1/K_{12}' = 0.31. ^{d} K_{12} = 39,500 and K_1/K_{12}' = 0.30. ^{e} K_{12} = 6,900,000 and K_1/K_{12}' = 0.75. ^{f} Average of two values (2450 and 2100) from different plots.

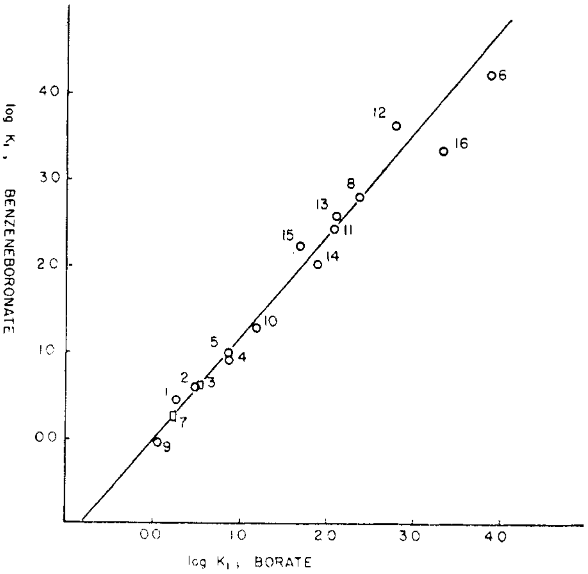

Fig. 1. Linear free energy plot of equilibrium constants forglycol-phenyl-boronates against glycol-borate. Numbers refer to glycols listed in Table II. Two points (3 and 7) shown as squares are not experimental points

The reasoning on which this conclusion is based is as follows: If the benzeneboronate ion were mainly trigonal, then the hydration equilibrium 2

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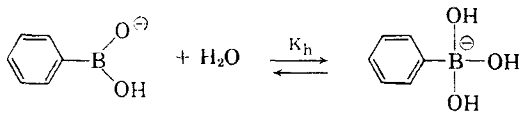
(10) F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, 54, 4415 (1932).

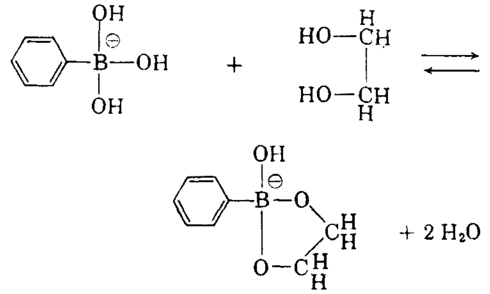
(11) L. M. Dennis and R. S. Shelton, *J. Am. Chem. Soc.*, 52, 3128 (1930).

(12) L. Santucci and H. Gilman, *J. Am. Chem. Soc.*, 80, 193 (1958).



(2)

would have a constant less than one. The over-all reaction of anion and glycol to form complex would have an equilibrium constant K_c which would be the product of K_h times K_{C4}, where K_{C4} is the Reaction 3 of glycol with tetrahedral anion to form



(3)

complex. Now the values with borate ion are K_{C4} values since the aqueous borate ion is tetrahedral.[2] Making the reasonable assumption that the replacement of hydroxyl by phenyl does not greatly influence the electronic picture about a four-coordinated boron, then one predicts that the K_{C4} for phenylboronate should be the same size as for borate. Indeed the observed complexing constants are just slightly larger with phenylboronate than with borate, thus we feel that the anion is primarily tetrahedral. The alternative explanation (that K_h is less than one and K_{C4} for phenylboronate is much larger than K_{C4} for borate) is unreasonable since no new types of bonds are formed or broken in the complexing reaction. In order to satisfy the quantitative aspects of these data, one must conclude that the phenylboronate ion is tetrahedral when uncomplexed as well as when complexed.

After submission of this paper, the recent article by Torssell[13] was called to our attention. From measurements on the fructose and benzeneboronate system, he draws a conclusion similar to the one presented here.

It might be argued that comparison of two such series of equilibria, in one of which a double complex is consistently observed, is not justified. To the extent, however, that extrapolation of all sets of values to zero polyol concentration eliminates the effect of the second equilibrium in the borate series, and introduces a standard concentration, the procedure is valid.

The first new problem in the interpretation of formation constants arose with the mannitol-benzeneboronate system as may be seen in Table III. In two series of measurements K_c leveled off, and $\Delta p\text{H}$ ceased to be a function of polyol concentration, with increasing $[P]$ although the $K_c - [P]_f$ plot is linear, with negative slope, at low concentrations. Such behavior has not been observed with other polyols, linear plots throughout being the rule. The usual significance of large variations in K_c with concentration is given in the Appendix. The leveling off of $\Delta p\text{H}$ is an indication of the formation of neutral complexes in competition with anionic complexes. Complexing of the acid form is a pH-increasing force, while that of the anion is a pH-decreasing one. This fact explains the observation that $\Delta p\text{H}$ becomes virtually constant, within experimental error, if the concentrations of anionic and neutral complexes are conceived to increase at comparable rates. On this basis, one can derive the Equation 4 where K_h is the formation constant for the neutral complex and $[\text{H}^+]_c$ is the value of hydrogen ion concentration when the pH has become constant. Using the values of $K_1 = 2275$ and $-\Delta p\text{H} = 2.80$, it is estimated the K_h is about 3.6 for the mannitol-benzeneboronic acid complex.

$$K_h = \frac{K_a K_1}{[\text{H}^+]_c} \tag{4}$$

TABLE III

Effect of Mannitol Concentration on pH Change

$[\text{Mannitol}]_f$	Series[a]	$-p$H	K_c[b]
0.183M	A	2.505	1750
0.338	B	2.630	1260
0.383	A	2.705	1330
0.499	B	2.730	1083
0.583	A	2.786	1050
0.597	B	2.760	955
0.697	B	2.795	881
0.783	A	2.830	865
0.797	B	2.795	771
0.897	B	2.825	747
0.977	B	2.805	655

[a] Series A; [benzeneboronate] = 0.0174M and Series B; [benzeneboronate] = 0.00174M. [b] Calculated assuming only a "1:1 complex."

Another conclusion that seems quite certain is that the neutral complexes of benzeneboronic acid must be more strongly acidic than the free acid itself. Such a conclusion can be drawn directly from a thermodynamic cycle involving the possible species and the known constants. The reason for this is possibly linked up with the oxygen-boron-oxygen angle which is roughly 120° in the neutral species and about 109° in the anionic species. In this connection, it should be pointed out that the observation here that anionic complexes are favored is in no way contradictory to the discovery of neutral complexes elsewhere,[7,8] since gross differences in conditions prevail.

It is notable that polyvinyl alcohol gave a pH increase with benzeneboronate. Although precipitation from these systems occurred, the highest pH increase was observed in the solution containing the smallest amount of precipitate. Polyvinyl alcohol in borate buffers gave a small measurable pH

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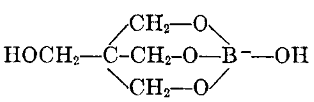
[13] K. Torssell, *Arkiv Kemi*, **10**, 541 (1957).

decrease[9] (see Table II for constants). The most concentrated replicate in the pentaerythritol-benzeneboronate series gave a precipitate; whether this contained a neutral or anionic complex, or pentaerythritol itself, has not been ascertained. When more accurate measurement of the catechol-borate system was attempted in the range 0.2 to 0.8*M*, precipitation occurred in all replicates. Since precipitation was not observed in the previous borate work,[9] and since no potassium ion was then present it was concluded that the precipitate contained the potassium salt of the anionic "2:1 complex." Since, however, this precipitate appeared to contain two crystalline phases, the conclusion is tentative. It may be that the other precipitates noted contained potassium salts of complexes, and further work along these lines is needed.

The great difference between constants for 1,3-propanediol and pentaerythritol is intriguing, since both have apparently simple 1,3-diol systems. Statistical reasoning would suggest that K_c for the former should be one sixth that for the latter: pentaerythritol can accommodate the first benzeneboronate (or borate) ion in six ways, 1,3-propanediol only one. Such things as statistical factors can not explain the orders of magnitude difference, however. Professor J. F. Bunnett has pointed out that pentaerythritol could form complexes of the type and this may well be the correct



reason for the high formation constants for this polyol as compared to 1,3-propanediol.

Mannitol, pentaerythritol, and glucose are the only polyols for which a value for the second formation constant K_{12} has been estimated in the benzeneboronate system. This suggests an explanation for the notable deviation of mannitol on the log-log plot. If there are mannitol-borate complexes of the 1:2 type (in dilute mannitol solutions) the observed constant K_1 with borate will be slightly large. The result of any correction would be to lower the K_1 value and thereby to bring the point on the plot closer to the line.

Other borate values redetermined here included 3-methoxy-1,2-propanediol (K_1 lower than reported in ref. 9), and fructose, previous data for which contained too much scatter for either a precise extrapolation or slope determination.[14]

A second major problem was encountered in the relationship of K_1 and K_{21}. That K_{21} is frequently far larger than K_1 is puzzling until it is realized that K_{21} describes the formation of a "2:1 complex" not from the "1:1 complex," but from the borate (or benzeneboronate ion if one is referring to K_{12}). The Appendix gives a derivation of the relationship among K_1, K_{21}, and the constant for the former process, K_2'.

$$K_2' = K_{21}/K_1$$

By simple statistical reasoning, K_1 and K_2' should be related by

$$K_1/K_2' = 4$$

if addition of the first glycol does not alter the binding capacity for the second glycol. It is this relationship which has significance, not that between K_1 and K_{21}. Values of K_2' and K_1/K_2' are presented in Table II. Departure from the ideal value for the ratio is widespread, approaching four only with simple 1,2-diols and fructose and glucose. There is little basis for speculation on this problem, but a few observations can be made; (1) Values may be accurate only within 50%. (2) Catechol gives an extremely large value and several sugars give values in the range 25–60. (3) Pentaerythritol, mannitol, and glucose with benzeneboronate are in the range 0.3 to 0.7 (reasoning for "1:2 complexes" of this type is analogous to that for 2:1 complexes of borate). (4) K_{21} for 1,3-propanediol was not measurable because the medium effect predominated.

Appendix. Origin of formulas. Symbols used:

K_c = measured equilibrium constant
$[P]_0$, $[P]_f$ = polyol concentration—initial and final, respectively
$[BH]$ = boric or benzeneboronic acid concentration
$[B^-]$ = borate or benzeneboronate concentration
$[BP^-]$ = "1:1 complex" concentration
$[BP_2^-]$ and $[B_2P^{--}]$ = "2:1 complex" and "1:2 complex" concentrations
$[BP_h^-]$ = $[BP^-] + [BP_2^-] + \ldots$ = total complex concentration

Equilibria and constants: acid-base—

$$BH + H_2O = B^- + H_3O^+ \qquad K_a = \frac{[B^-][H^+]}{[BH]} \tag{5}$$

complex-formation—

$$B^- + P = BP^- + 2H_2O \qquad K_1 = \frac{[BP^-]}{[B^-]_f{}^2} \tag{6}$$

$$B^- + 2P = BP_2^- + 4H_2O \qquad K_{21} = \frac{[BP_2]}{[B^-][P]_f{}^2} \tag{7}$$

$$2B^- + P = B_2P^{--} + 4H_2O \qquad K_{12} = \frac{[B_2P^{--}]}{[B^-]^2[P]_f} \tag{8}$$

$$K_c = \frac{[BP_n^-]}{[B^-][P]_f} \text{ or } \frac{[B_nP^{-n}]}{[B^-][P]_f} \tag{9}$$

Conservation of mass:

$$[B^-]_0 = [B^-]_f + [BP_n^-] \tag{10}$$

$$[P]_0 = [P]_f + [BP_m^-] \tag{11}$$

$$[BH]_0 = [BH]_f \tag{12}$$

Equation 12 is based on two assumptions, both of which are reasonable. The first is that only the anion forms complexes appreciably; its validity is based on the fact that the change in *p*H with glycol

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[14] G. L. Roy, Sc.M. thesis, Brown University (1956).

concentration cannot be explained if the acid form complexes (see text for the exceptional case of mannitol). The second assumption is that the change in concentration of acid form due to ionization (Equation 5) is negligible; such must be the case since the concentration of hydrogen ion never exceeded $10^{-6}M$.

From (5) $\log [H^+] = \log K_a + \log [BH] - \log [B^-]$

with polyol present,

$$-pH_f = -pK_a + \log [BH]_f - \log [B^-]_f$$

w/o polyol,

$$\underline{-pH_0 = -pK_a + \log [BH]_f - \log [B^-]_0}$$

and by addition,

$$pH_f - pH_0 = \Delta pH = \log [B^-]_f - \log [B^-]_0$$

Then $\Delta pH = \log \frac{[B^-]_f}{[B^-]_0}$ or

$$10^{\Delta pH} = \frac{[B^-]_f}{[B^-]_0} = \frac{[B^-]_0 - [BP_n^-]}{[B^-]_0} \quad (13)$$

by equation (9), and, $10^{\Delta pH} = 1 - \frac{[BP_n^-]}{[B^-]_n}$

by equation (6), $[BP_n^-] = K_c[B^-]_f[P]_f$

and $10^{\Delta pH} = 1 - K_c[P]_f \frac{[B^-]_f}{[B^-]_0} = 1 - K_c[P]_f \, 10^{\Delta pH}$

division by $10^{\Delta pH}$ gives $K_c = \frac{10^{-\Delta pH} - 1}{[P]_f}$

Measurements yield ΔpH; $[P]_f$ is found by correcting $[P]_0$ with the use of equations (10), (11), and (13).

Treatment of constants. $K_c = K_1$ if only "1:1 complex" is formed. K_c is then usually found to decrease slightly with polyol concentration increase, owing to decline in the dielectric constant; a standard value is obtained by extrapolation to $[P]_f = 0$.

When 2:1 complex (from two polyol molecules) is present,

$$K_c = \frac{[BP^-] + [BP_2^-]}{[B^-]_f[P]_f} = K_1 + K_{21}[P]_f, \text{ from (7) and} \quad (9)$$

K_1 and K_{21} ore obtained by plotting K_c, extrapolating to $[P]_f = 0$, and measuring the slope.

For a complex formed from two anions and one polyol molecule, reasoning is similar, and K_1 and K_{12} are obtained as above:

$$K_c = K_1 + 2K_{12}[B^-]_f$$

Relationship of K_2', K_2 and K_1. The formation constant for "2:1 complex" from "1:1 complex" is

$$K_2' = \frac{[BP_2^-]}{[BP^-][P]_f}$$

since $[BP^-] = K_1[B^-][P]_f$, it follows from (6) and (7) that

$$K_2' \cdot K_1 = \frac{[BP_2^-]}{[B^-][P]^2_f} = K_{21}$$

Acknowledgment. One of the authors (J.P.L.) expresses his gratitude to the Corporation of Brown University for a research assistantship.

PROVIDENCE 12, R. I.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Thermal Decomposition of Mixed Carboxylic-Carbonic Anhydrides; Factors Affecting Ester Formation

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Received November 12, 1958

A number of new mixed benzoic (and mesitoic)-carbonic anhydrides ($C_6H_5COOCOOR$) have been prepared and characterized. They are stable at room temperature, but decompose around 150-170° with carbon dioxide evolution. It has been shown that the thermal decomposition of these anhydrides proceeds by two different paths: A, formation of an ester by loss of carbon dioxide and B, disproportionation to the symmetrical anhydride, alkyl carbonate, and carbon dioxide. Path A is favored when the point of attachment of the alkyl group is a secondary carbon or a primary carbon, with heavy substitution on the β-carbon. Both paths A and B occur about equally when the alkyl group is primary, as ethyl or butyl. Although tertiary amines lower the temperature of decomposition of the anhydrides, they do not alter the course of the decomposition. Rearrangement of the mixed anhydride from (−)-2-octanol proceeds with complete retention of configuration. *N*-Methylpiperidine is a much more effective catalyst than triethylamine in forming the mixed anhydride from a highly branched chlorocarbonate.

It was shown in an earlier paper[2] that mixed carboxylic-carbonic anhydrides, RCOOCOOR,′ were, in general, reasonably stable compounds which could be obtained in pure form. It has been considered[2-4] that the mixed anhydrides decom-

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[1] National Science Foundation Fellow, 1958-59.

[2] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, 23, 1149 (1958). This paper contains leading references to the literature describing the usefulness of the mixed anhydrides as acylating agents.

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