The Reaction between Hydrogen Spiro-Borates and Carbinol Form of Crystal Violet in Toluene with Applications to Reagent Selection in Extraction-Spectrophotometry of Boron

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Synopsis. A study on equilibrium and kinetics of the reactions of boron complexes of a judiciously chosen series of hydroxy and dicarboxy acids (benzilic acid, mandelic acid, 3-chloro- and 4-hydroxy mandelic acid, salicylic acid, and phenylmalonic acid) as well as of the free acids with carbinol form of crystal violet in toluene demonstrated the distinct superiority of mandelic acid over the others, as a reagent for extraction-photometry of boron.

A popular method for the determination of boron is extraction-spectrophotometry of $(dye)^+(spiroborate)^-$ ion pair in a low dielectric constant aprotic solvent. Boron as boric acid is well-known to complex with a diol, hydroxy acid or gem-dicarboxy acid (H_2R) to form hydrogen spiro-borate, HBR_2. A spiroborate anion (BR_2^-), if sufficiently hydrophobic, can be extracted even into a toluene-like solvent in pairing with a triphenylmethae dye cation. Spectrophotometry of the ion pair $(dye^+BR_2^-)_{org}$ is used to determine boron. In fact, combinations of various H_2Rs such as α-hydroxy acids, *o*-hydroxy benzoic acids, catechols or naphthols, dye cations, and solvents were tried to get the best possible reagent system.[1-5] These extraction processes are considered to follow the mechanism.[2]

$$H_2R \rightleftarrows (H_2R)_{org} \quad (1a)$$

$$dye^+ + (H_2R)_{org} \rightleftarrows (dye^+)(HR^-)_{org} + H^+ \quad (1b)$$

$$H_3BO_3 + 2(H_2R)_{org} + dye^+ \rightleftarrows (dye^+)(BR_2^-)_{org} + 3H_2O + H^+ \quad (1c)$$

$$(dye^+HR^-)_{org} + H_2O \longrightarrow (dye\text{-}OH)_{org} + (H_2R)_{org} \quad (1d)$$

$$(dye^+\ BR_2^-)_{org} + H_2O \longrightarrow (dye\text{-}OH)_{org} + (HBR_2)_{org} \quad (1e)$$

In such extraction systems, color fading based on hydrolysis of a cationic dye to the colorless carbinol, dye-OH has been skillfully used to diminish the absorbance of a reagent blank. To develop a sensitive method, the overall rate of Eq. 1d must be sufficiently larger than that of Eq. 1e. Further, the equilibrium of Eq. 1b can be considered as equivalent to the sequences,

$$dye^+ + H_2O \rightleftarrows (dye\text{-}OH)_{org} + H^+ \quad (1b')$$

$$(H_2R)_{org} + (dye\text{-}OH)_{org} \rightleftarrows (dye^+\ HR^-)_{org} + H_2O \quad (1b'')$$

and that of Eq. 1c can be to 1b′ and

$$H_3BO_3 + 2(H_2R)_{org} \rightleftarrows (HBR_2)_{org} + 3H_2O \quad (1c')$$

$$(HBR_2)_{org} + (dye\text{-}OH)_{org} \rightleftarrows (dye^+\ BR_2^-)_{org} + H_2O \quad (1c'')$$

So, determinations of rate constants of Eqs. 1d and 1e and of equilibrium constants of Eqs. 1b″, 1c″ and of 1b′, 1c′ would allow complete evaluation and prediction of such extraction systems. It can be shown that given a dye, solvent and pH for the suitability of a H_2R in boron determination, both the equilibrium constant and the rate constant of the reverse step of Eq. 1b″ must be sufficiently larger than those of Eq. 1c″. The case has been critically examined for a selected set of H_2Rs (salicylic acid, mandelic acid, 3-chloro- and 4-hydroxy mandelic acid, benzilic acid, and phenylmalonic acid) in reference to Crystal Violet dye for toluene as extractant. Herein, are reported the results.

Experimental

Reagents: Reagents used were either of analytical reagent grade or highly purified by standard procedures. Carbinol form of Crystal Violet was prepared by basification of the aqueous dye solution (10^{-5} M) by 2 M NaOH (M=mol dm^{-3}) and subsequent extraction into toluene.[7] HBR_2 was prepared by reacting a definite quantity of a H_2R with aqueous boric acid, followed by extraction into toluene cxcept for 3-chloro- and 4-hydroxy mandelic acid. Its toluene solution was obtained by careful evaporation of chloroform extract and dissolution in toluene.

Choice of Reagents: The medium chosen was toluene due to its relatively low toxicity.[2] The choice of the dye fell on Crystal Violet because its carbinol form is enough basic to undergo slow reaction with acids of widely different strengths in benzene and the like media.[7-9] Any hydroxy carboxy or dicarboxy acid (H_2R) reagent chosen should form a boric acid complex (HBR_2) having sufficient solubility and stability in toluene. Accordingly, the choice fell on H_2Rs having aromatic moiety: phenylmalonic acid, salicylic acid, benzilic acid, mandelic acid, and 3-chloro- and 4-hydroxy mandelic acid.

Procedure: Kinetics as well as equilibrium of the reaction of the carbinol form of Crystal Violet (1.12×10^{-5} M) with both a HBR_2 and the corresponding H_2R (10^{-4} to 10^{-3} M) in toluene were followed by measurements of absorbance at 610 nm in a Shimadzu 160A spectrophotometer as well as in a Systronics 103 spectrocolorimeter at 25±0.5 °C.

Results and Discussion

The carbinol form of Crystal Violet (tris-4-(dimethylamino) phenyl methanol) is an example of an aquo-base.[6] Its reaction with an acid is written in a general form as

$$D + HA \rightleftarrows DH^+A^- \quad (2)$$

Where, D stands for the colorless carbinol form and DH^+A^- is the colored ion pair. The equilibrium constant is defined as:

$$K = \frac{[DH^+A^-]}{[D][HA]^n}. \quad (3)$$

Where, the acid exponent, n, is greater than unity but nonintegral and significantly dependent on the spe-

cific acid (HA), solvent and temperature as well.[7,10,11] The equilibrium 2 should thus be writlen as

$$D + fHA \rightleftarrows DH^+A^- + rHA \quad (4)$$

where, f and r stand for acid exponents of the forward and the reverse steps, respectively. Symbolizing the rate constant for forward and reverse reaction as k_1 and k_{-1} respectively, the following relations follow:

$$n \text{ (overall acid exponent)} = f - r, \quad (5)$$

$$K = k_1/k_{-1}. \quad (6)$$

When [HA]≫[D] the kinetic data[7-9] fitted the formula

$$k = \frac{2.303}{t} \log \frac{x_e}{x_e - x}, \quad (7)$$

where, x_e and x stand for $[DH^+A^-]$ at equilibrium and at the time interval t, respectively, in terms of absorbance. The rate constant, k, can be expressed as

$$k = k_1[HA]^f + k_{-1}[HA]^r. \quad (8)$$

Combining the relations 5, 6, and 8, the following equation can be derived

$$\log\left(\frac{k}{K+[HA]^{-n}}\right) = \log k_{-1} + f \log[HA]. \quad (9)$$

A plot of the left hand side of the Eq. 9 vs. log[HA] was linear for many acids.[7-9] Using the above relations one can obtain K (Eq. 3), k (Eq. 7), k_1 (Eq. 6), k_{-1} (Eq. 9), n (Eq. 3), f (Eq. 9), and r (Eq. 5).

Under the present conditions, where [HA]/[D] is in general 10—500, it was observed that for the reaction of the carbinol form of Crystal Violet with the HBR_2 as well as the H_2R chosen in wet toluene the equilibrium and the kinetic data fitted well the relations 3, 7, and 9. The results and the parameters (obtained by least square analysis) were given in Tables 1, 2, 3, and 4.

Implications of the Results in Boron Determination: On the basis of the mechanism (Eqs. 1a—1e) the extraction-photometry of boron would be more sensitive, larger the overall rate of hydrolysis of a ($dye^+ HR^-$) compared to that of the corresponding ($dye^+ BR_2^-$). The relative rate of hydrolysis, for a given dye, extractant and pH, depends on the differences in the intrinsic quantities k_{-1} and K (Eqs. 1b″ and 1c″) as also on the difference between $[H_2R]_{org}$ and $[HBR_2]_{org}$. Use of $[H_2R] \gg [HBR_2]$, a general condition in the boron determination, is thus of advantage to the method's sensitivity. Results on k_{-1} and K (Tables 3 and 4) lead clearly to the prediction that except salicylic acid, all the other acids should be potential reagents and that among these, mandelic acid or phenylmalonic acid should be preferred over benzilic acid and 3-chloro- and 4-hydroxy mandelic acid. However, the last one would be a poor choice owing to very low extractability of its BR_2^- into toluene. Further, between mandelic acid and phenylmalonic acid, the magnitudes of k_{-1} and K cause the rate of hydrolysis of dye^+HR^- very high for both the acids but that of $dye^+BR_2^-$ distinctly less for the former acid.

Thus, evaluation of the physicochemical results distinguishes mandelic acid as the most potential one

Table 1. Results at Fixed [D] (1.12×10^{-5} M)[a] at Different $[HBR_2]$ at 25±0.5 °C

HBR_2	$[HA]\times10^3$ / M	x_e	$\log\frac{[DH^+A^-]}{[D]}$[b]	k / min^{-1}	$\log\frac{k}{K+[HA]^{-n}}$
Hydrogen bis(salicylato)borate	0.10	0.14	−0.30	0.247	−6.95
	0.20	0.20	−0.04	0.790	−6.19
	0.30	0.27	0.26	1.036	−5.97
	0.40	0.32	0.51	1.458	−5.76
	0.50	0.36	0.78	1.612	−5.69
Hydogen bis(benzilato)borate	0.07	0.12	−0.40	0.433	−7.22
	0.14	0.22	0.04	0.766	−6.68
	0.21	0.27	0.26	1.013	−6.56
	0.24	0.31	0.45	1.051	−6.40
	0.28	0.34	0.63	1.471	−6.23
Hydrogen bis(mandelato)borate	3.00	0.17	−0.17	0.029	−7.59
	3.60	0.19	−0.08	0.037	−7.38
	4.20	0.24	0.13	0.042	−7.25
	5.10	0.26	0.21	0.051	−7.09
	6.00	0.33	0.56	0.054	−7.03
Hydrogen bis(3-chloro- and 4-hydroxy mandelato)borate	1.54	0.19	−0.08	0.037	−8.93
	2.16	0.22	0.04	0.043	−8.67
	3.08	0.35	0.70	0.045	−8.54
	4.32	0.38	0.98	0.057	−8.39
Hydrogen bis(phenylmalonato)borate	1.50	0.10	−0.51	1.448	−5.94
	2.50	0.20	−0.04	1.773	−5.54
	3.00	0.24	0.13	1.812	−5.45
	4.00	0.29	0.35	1.858	−5.35
	5.00	0.34	0.63	2.086	−5.25

a) Total concentration of the carbinol form of Crystal Violet in terms of absorbance=b=0.42.
b) $[DH^+A^-]/[D] = x_e/(b - x_e)$.

Table 2. Results at Fixed [D] (1.12×10^{-5} M)[a] at Different [H_2R] at 25±0.5 °C

H_2R	$\frac{[HA]\times10^3}{M}$	x_e	$\log\frac{[DH^+A^-]}{[D]}$[b]	$\frac{k}{min^{-1}}$	$\log\frac{k}{K+[HA]^{-n}}$
Salicylic acid	1.01	0.17	−0.18	0.550	−7.16
	1.51	0.22	0.04	0.691	−6.89
	2.01	0.25	0.18	1.184	−6.58
	3.02	0.32	0.51	1.555	−6.28
	4.02	0.37	0.87	1.935	−6.24
Benzilic acid	0.60	0.17	−0.18	0.230	−9.89
	0.69	0.21	0.00	0.385	−9.69
	0.90	0.27	0.26	0.509	−9.46
	1.00	0.29	0.35	0.710	−9.29
	1.50	0.35	0.70	0.762	−9.17
Mandelic acid	1.05	0.20	−0.04	0.185	−9.12
	1.58	0.26	0.21	0.237	−8.85
	2.10	0.32	0.51	0.402	−8.55
	2.63	0.36	0.78	0.944	−8.14
3-Chloro- and	0.30	0.42	∞	0.064	−∞
4-hydroxy mandelic	0.50	0.42	∞	0.115	−∞
acid	0.60	0.42	∞	0.160	−∞
Phenylmalonic acid	0.20	0.42	∞	—[c]	—

a) Total concentration of the carbinol form of Crystal Violet in terms of absorbance=b=0.42. b) $[DH^+A^-]/[D]=x_e/(b-x_e)$. c) Very large (too fast for ordinary spectrophotometry).

Table 3. Association Constant (K), Individual Rate Constants (k_1, k_{-1}), and Acid Exponents (n, f, r) for Hydrogen Spiro-Borate-Carbinol Form of Crystal Violet Reaction in Toluene at 25±0.5 °C

Hydrogen spiro-borate	$\log K$	$\log k_1$	$\log k_{-1}$	n	f	r
Hydrogen bis(salicylato)borate	5.81	6.35	0.54	1.56	1.86	0.30
Hydrogen bis(benzilato)borate	6.29	5.43	−0.86	1.61	1.52	−0.09
Hydrogen bis(mandelato)borate	5.63	2.80	−2.83	2.32	1.87	−0.45
Hydrogen bis(3-chloro- and 4-hydroxy mandelato)borate	7.10	1.50	−5.60	2.57	1.17	−1.40
Hydrogen bis(phenylmalonato)borate	5.46	3.24	−2.22	2.12	1.30	−0.82

Table 4. Association Constant (K), Individual Rate Constants (k_1, k_{-1}), and Acid Exponents (n, f, r) for H_2R-Carbinol Form of Crystal Violet Reaction in Toluene at 25±0.5 °C

H_2R	$\log K$	$\log k_1$	$\log k_{-1}$	n	f	r
Salicylic acid	6.46	5.54	−0.92	1.67	1.55	−0.12
Benzilic acid	8.96	6.87	−2.09	2.16	1.83	−0.33
Mandelic acid	8.04	8.12	0.08	2.04	2.36	0.32
3-Chloro- and 4-hydroxy mandelic acid	—[a]	—[b]	—[b]	—	—	—
Phenylmalonic acid	—[a]	—[c]	—[c]	—	—	—

a) K, very large (virtually complete reaction, Table 2). b) k_1, large and k_{-1} very small (*vide* k from Table 2 and very large K). c) k_1, very large and k_{-1}, moderate (*vide* very large k from Table 2, and very large K).

among the reagents considered and justifies its wider use in boron determination.[1,2,5,12,13]

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