Stability Constants for Hypochloritoborate and Hypobromitoborate Complex Ions in Aqueous Solution

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The formation of previously unreported hypohalitoborate complex ions in aqueous solution is described. The stability constant for the hypochloritoborate complex, $\beta' = \{B(OH)_3OCl^-\}/\{HOCl\}\{B(OH)_3\}$ (braces denote activity of the species), was found to be $\log \beta' = 2.25 \pm 0.01$ at 25 °C from a combination of spectrophotometric measurements at equilibrium and kinetic studies of the oxidation of the bromide ion. The corresponding constant (from equilibrium studies only) for the hypobromitoborate complex, $B(OH)_3OBr^-$, was $\log \beta' = 1.83 \pm 0.04$.

The use of chlorine for disinfecting drinking and cooling waters has led to extensive examination of its aqueous chemistry. Because of the very high, pH-dependent reactivity of dissolved chlorine, studies are often made in buffered synthetic solutions rather than natural waters.

In borate buffers we observed smaller u.v. absorbances for hypochlorite and hypobromite than in borate-free solutions. Moreover, the rate of bromide oxidation by hypochlorous acid was reduced when borate was present. These inconsistencies are attributed to the formation of previously unreported hypohalitoborate complex ions, $B(OH)_3OX^-$, with X = Cl or Br.

Theory

Hypochlorous acid,[1] hypobromous acid,[2] and boric acid[3] participate in acid–base equilibria according to equations (1)—(3).

$$HOCl + H_2O \longrightarrow H_3O^+ + OCl^-; \quad K_a = 2.9 \times 10^{-8}\ \text{mol dm}^{-3} \qquad (1)$$

$$HOBr + H_2O \longrightarrow H_3O^+ + OBr^-; \quad K_a = 2.19 \times 10^{-9}\ \text{mol dm}^{-3} \qquad (2)$$

$$B(OH)_3 + 2H_2O \longrightarrow H_3O^+ + B(OH)_4^-; \quad K_b = 5.8 \times 10^{-10}\ \text{mol dm}^{-3} \qquad (3)$$

The formation of the hypohalitoborate complex may be represented by the equilibria (4) and (5), where X = Cl or Br and braces denote the activity of the species.

$$B(OH)_3 + OX^- \longrightarrow B(OH)_3OX^-; \quad \beta = \{B(OH)_3OX^-\}/\{B(OH)_3\}\{OX^-\} \qquad (4)$$

$$B(OH)_4^- + HOX \longrightarrow B(OH)_3OX^- + H_2O; \quad \beta' = \{B(OH)_3OX^-\}/\{B(OH)_4^-\}\{HOX\} \qquad (5)$$

Maximal hypohalitoborate formation would be expected, from the dissociation constants in equations (1)—(3), to occur at pH 8—9, *i.e.* where boric acid and hypohalite are the predominant forms of total boron and total halogen, respectively. This suggests reaction (4) as the more appropriate representation, but in kinetic studies the hypohalous acid is usually the active species and for this reason β' was used in these calculations. The two stability constants are related by equation (6), where K_a and K_b are defined in equations (7) and (8). The

$$\beta = \beta'(K_b/K_a) \qquad (6)$$

$$K_a = \{H^+\}\{OX^-\}/\{HOX\} \qquad (7)$$

$$K_b = \{H^+\}\{B(OH)_4^-\}/\{B(OH)_3\} \qquad (8)$$

mass-balance equations are (9) and (10), where T_B = total borate and T_X = total hypohalite.

$$T_B = [B(OH)_3] + [B(OH)_4^-] + [B(OH)_3OX^-] \qquad (9)$$

$$T_X = [HOX] + [OX^-] + [B(OH)_3OX^-] \qquad (10)$$

(*i*) *Equilibrium Studies.*—The stability constant β' was calculated from the change in absorbance for hypohalite–borate mixtures at $\lambda_{max.}$ for the hypohalite ion. The complexes were assumed not to absorb significantly at these wavelengths, because only absorbance reductions, and not spectral changes, could be observed and attempts at allowing for absorbance of the complex were unsuccessful (see below). In the absence of borate, the absorbance is given by equation (11), where ε_{OX^-}

$$A_0 = T_X\left(\frac{K_a}{K_a + \{H^+\}\gamma}\right)\left(\varepsilon_{OX^-} + \varepsilon_{HOX}\frac{\{H^+\}\gamma}{K_a}\right) \qquad (11)$$

and ε_{HOX} are absorption coefficients for the hypohalite ion and hypohalous acid, respectively, and γ is the univalent ion activity coefficient calculated by the extended Debye-Hückel equation.[4] In the presence of borate at concentration T_B, the absorbance A_B is given by equation (12). By working with the function in equation (13), where A_0 is the absorbance in the absence of

$$A_B = T_X\left[\frac{K_a}{K_a + \{H^+\}\gamma + \beta' K_b\{H^+\}\gamma(T_B - [B(OH)_3OX^-])/(K_b + \{H^+\}\gamma)}\right]\left(\varepsilon_{OX^-} + \varepsilon_{HOX}\frac{\{H^+\}\gamma}{K_a}\right) \qquad (12)$$

$$\frac{A_0 - A_B}{A_0} = \frac{[B(OH)_3OX^-]}{T_X} \qquad (13)$$

borate, the absorption coefficients can be eliminated and after rearrangement the stability constant is obtained from equation (14).

$$\beta' = \frac{(A_0/A_B - 1)(\{H^+\}\gamma + K_a)(\{H^+\}\gamma + K_b)}{K_b\{H^+\}\gamma(T_B - [B(OH)_3OX^-])} \qquad (14)$$

At the concentrations used, the total borate concentration was greatly in excess of the total hypohalite concentration and the term ($T_B - [B(OH)_3OX^-]$) in equation (14) could be equated to T_B. The total borate concentration was not so large, however, that polyborate species needed to be considered.

(*ii*) *Kinetic Studies.*—The data obtained from measuring the effect of borate on the rate of the reaction between hypochlorite and bromide enabled the stability constant β' to be calculated for the hypochloritoborate complex. For reaction (15) the rate

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \qquad (15)$$

at constant pH and temperature, but variable borate concentrations, can be expressed through equations (16) and (17),

$$R_0 = k'T_{Cl}[Br^-] \qquad (16)$$

$$R_B = k'(T_{Cl} - [B(OH)_3OCl^-])[Br^-] \qquad (17)$$

incorporating the apparent rate constant, k', where R_0 and R_B represent the rates, $-dT_{Cl}/dt$, in the absence and presence of borate, respectively. It is assumed that the hypochloritoborate complex does not itself oxidise the bromide ion, in accordance with work showing that hypochlorous acid and not the charged hypochlorite ion is the active form of chlorine in this reaction.[5]

Equations (18) and (19) follow from those above; here also the total borate and total chlorine concentrations were chosen such that in equation (19) the term ($T_B - [B(OH)_3OCl^-]$) could be equated to T_B without significant error.

$$\frac{R_0 - R_B}{R_0} = \frac{[B(OH)_3OCl^-]}{T_{Cl}} \qquad (18)$$

$$\beta' = \frac{R_0 - R_B}{R_B} \cdot \frac{(\{H^+\}\gamma + K_a)(\{H^+\}\gamma + K_b)}{K_b\{H^+\}\gamma(T_B - [B(OH)_3OCl^-])} \qquad (19)$$

Experimental

The absorbances of mixtures of borate and hypohalite solutions were measured with a Perkin-Elmer 124 spectrophotometer at 292 nm ($\lambda_{max.}$ for the hypochlorite ion) or at 329 nm ($\lambda_{max.}$ for the hypobromite ion) in a 4-cm silica cell. The solutions contained 0.5 mol dm^{-3} sodium chloride as background electrolyte. The pH of the solutions was adjusted by adding sodium hydroxide or hydrochloric acid. The temperature was kept at 25 ± 0.1 °C.

The effect of borate on the total chlorine concentration was studied by titration with sodium arsenite, $NaAsO_2$, with bromocresol purple indicator (0.1% w/v).[6]

Commercial sodium hypochlorite solution (low in bromine) was standardised by titration with potassium iodide. Bromide-free sodium hypobromite was prepared by a procedure based on the methods of Pollack and Doktor[7] and Galal-Gorchev and Morris.[8] Liquid bromine (*ca.* 0.5 cm^3) was shaken with silver nitrate solution (20 cm^3 of 0.6 mol dm^{-3}) and the resulting hypobromous acid was separated from the solution by vacuum distillation at 25 °C. The distillate (collected at *ca.* 0 °C) contained *ca.* 0.15 mol dm^{-3} hypobromous acid. An excess of sodium hydroxide was added to a portion of the distillate before it was diluted to the desired (approximate) concentration, which was then determined by u.v. spectrophotometry. Other chemicals were of analytical reagent grade.

(*i*) *Thermodynamic Studies.*—The absorbances of mixtures of boric acid, H_3BO_3, and sodium hypochlorite solutions whose concentrations were varied in the ranges 0—1.0 mol dm^{-3} and 0—2.78 × 10^{-3} mol dm^{-3}, respectively, were measured at pH 9.50.

The absorbances of mixtures of 0.05 mol dm^{-3} boric acid and 1.28 × 10^{-3} mol dm^{-3} sodium hypochlorite solutions were measured at pH values between 7.6 and 9.8. Similarly, the absorbances of mixtures of 0.05 mol dm^{-3} boric acid and 1.01 × 10^{-3} mol dm^{-3} sodium hypobromite solutions were measured at pH values between 8.2 and 9.2.

(*ii*) *Kinetic Studies.*—Solutions at pH 9.54 containing 3.47 × 10^{-4} mol dm^{-3} sodium hypochlorite, 2.64 × 10^{-3} mol dm^{-3} sodium bromide, and 0—0.2 mol dm^{-3} boric acid were prepared. The change in the absorbance at 292 nm was recorded against time (half-lives were of the order of 10 s).

Results

(*i*) *Borate–Hypochlorite Solutions.*—The absorbance at 292 nm for a given hypochlorite concentration decreased linearly with increase in the borate concentration. In addition, the fraction by which the absorbance at 292 nm decreased, for a given borate concentration, was the same for all hypochlorite concentrations. This implied that the absorbance change could not be attributed to reaction of the hypochlorite with impurities in the boric acid. Spectra in the presence and absence of borate differed only in absorbance, *i.e.* no new peak appeared and the absorption maximum was not shifted.

Titration with sodium arsenite at pH 9.2 showed that the total oxidant concentration was not altered by the boric acid. Therefore, the formation of species such as chlorate did not occur, because this does not react with arsenite under these conditions. From absorbance measurements at five concentrations of hypochlorite and five concentrations of borate we obtained log β' = 2.19 ± 0.07.

The effect of the pH on hypochloritoborate complex formation is shown in Figure 1. This plot of $(A_0 - A_B)/A_0$ from equation (13) against pH reaches a maximum at pH 8.3, *i.e.* midway between the p*K* values for boric acid (9.23)[3] and hypochlorous acid (7.54).[1] The differences in absorbance were attributed to the formation of a non-absorbing complex, $B(OH)_3OCl^-$. The stability constant log β', from ten points over the range pH 7.8—9.6, had a mean value of 2.26 ± 0.05 (standard deviation for a single result). The solid line in Figure 1 shows the variation with the pH of the hypochloritoborate fraction, $[B(OH)_3OCl^-]/T_{Cl}$, calculated with this value for the stability constant, and its agreement with the observed relative difference in absorbance. An attempt was made to determine an absorption coefficient for $B(OH)_3OCl^-$ simultaneously with β' by the method of Gimblett and Monk[9] (suitably adapted for the different equilibria involved). The scatter did not justify assigning a value to the absorption coefficient and the simpler calculation of β', described above, was used.

The effect of hypochloritoborate complex formation on the rate of reaction between hypochlorite and bromide also enabled the stability constant β' to be calculated. As stated earlier, the oxidation of the bromide ion occurs *via* hypochlorous acid formation. The formation of the charged hypochloritoborate complex should reduce the apparent rate constant, since less hypochlorous acid should be available and the complex ion would not be expected to react with the bromide ion. Figure 2 shows that the rate (R_B) changes with borate concentration at constant pH, bromide concentration, and total hypochlorite

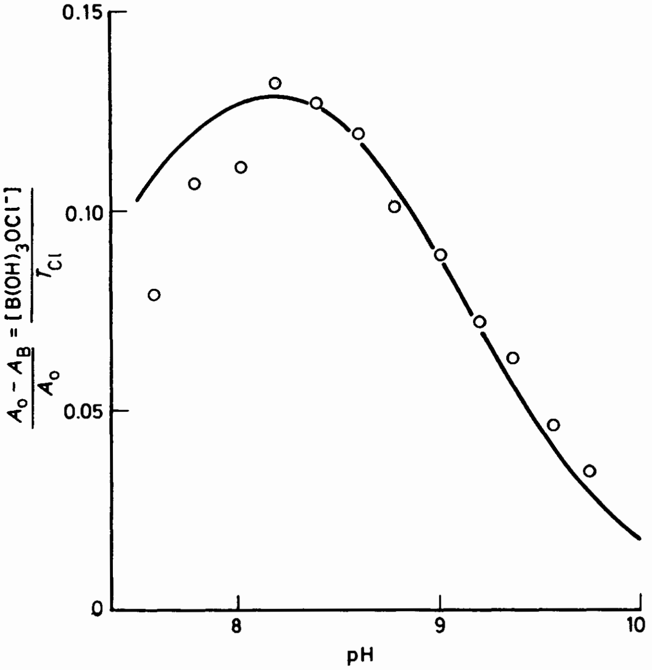

Figure 1. Relative difference in absorbance, $(A_0 - A_B)/A_0$ from equation (13), for hypochlorite solutions with (A_B) and without (A_0) borate (0.05 mol dm^{-3}) as a function of pH. Points show experimental values and line shows ratio $[B(OH)_3OCl^-]/T_{Cl}$ calculated with overall mean $\beta' = 178$ dm^3 mol^{-1}

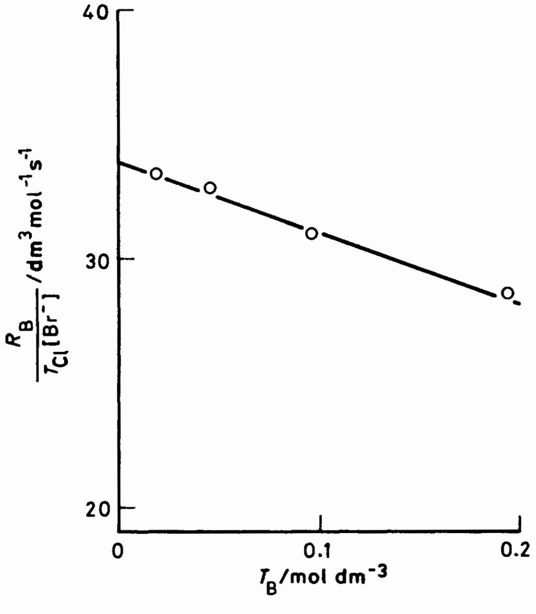

Figure 2. Effect of borate on the rate of reaction between hypochlorite and bromide at pH 9.54 [see equation (19)]

concentration. The value of R_0 was obtained by extrapolating to zero borate concentration and β' obtained by plotting $(R_0 - R_B)/R_B$ against T_B [equation (19)]. The plot was linear (correlation coefficient 0.998) and the stability constant was calculated from the gradient, equation (20). The value of log β' was 2.27 ± 0.02, which shows excellent agreement with that obtained from spectrophotometric measurements of equilibrium mixtures.

The weighted mean value for the stability constant from the three series of measurements gave log β' as 2.25 ± 0.01 and the corresponding value of log β as 0.56 ± 0.01 (errors representing one standard deviation of the mean).

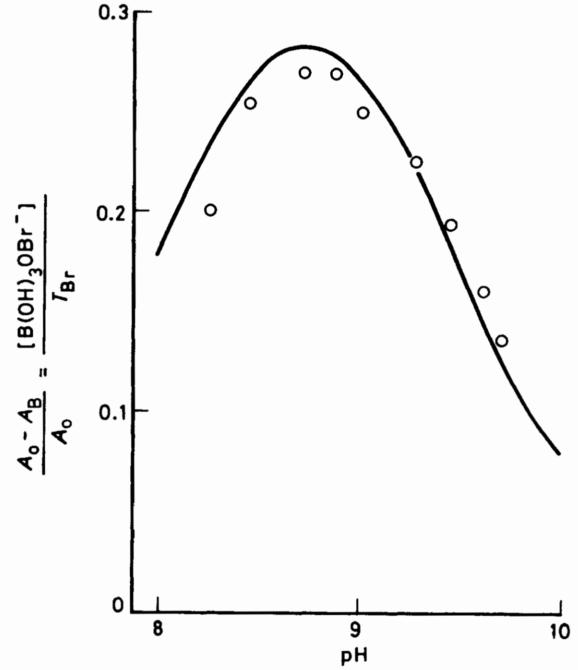

Figure 3. Relative difference in absorbance, $(A_0 - A_B)/A_0$ from equation (13), for hypobromite solutions with (A_B) and without (A_0) borate (0.05 mol dm^{-3}) as a function of pH. Points show experimental values and line shows values of $[B(OH)_3OBr^-]/T_{Br}$ calculated with $\beta' = 68$ dm^{-3} mol^{-1}

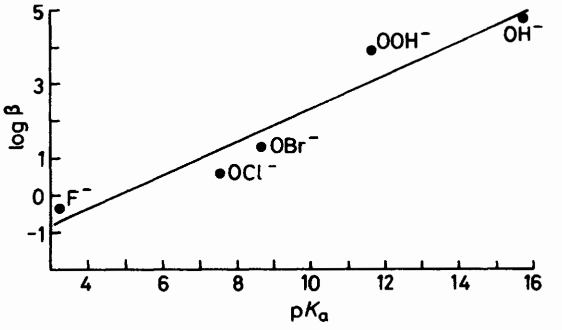

Figure 4. Linear free energy relationship between the stability constants (log β) of boric acid complexes and the protonation constants (pK_a) of the unidentate ligands. The line shows the least-squares fit log $\beta = -2.2(\pm 0.8) + 0.45(\pm 0.07)pK_a$ over the five points

$$\text{Gradient} = \frac{\beta' K_b\{H^+\}\gamma}{(\{H^+\}\gamma + K_a)(\{H^+\}\gamma + K_b)} \qquad (20)$$

(*ii*) *Borate–Hypobromite Solutions.*—The same considerations apply as for the borate–hypochlorite solutions, except that the absorbances were measured at 329 nm. Figure 3 shows the effect of the pH upon the formation of the hypobromitoborate complex. This plot of $(A_0 - A_B)/A_0$ against pH shows that complex formation reached a maximum approximately midway between the pK values for boric acid (9.23)[3] and hypobromous acid (8.66).[2] The stability constant was calculated for nine points, over the range pH 8.2—9.7, and gave log $\beta' = 1.83 \pm 0.04$ (standard deviation for a single result) and the corresponding value for log β as 1.26 ± 0.04. Figure 3 also shows the variation of the hypobromitoborate complex fraction, $[B(OH)_3OBr^-]/T_{Br}$, with the pH, calculated with this value for the stability constant, and its agreement with the observed relative difference in absorbance.

Discussion

The literature[10] yields three other unidentate ligands for $B(OH)_3$: fluoride, hydroxide, and hydrogenperoxide (OOH^-) ions. Figure 4 shows the linear relationship of log β with the protonation constants (pK_a) of the five ligands. The correlation coefficient of 0.96 indicates satisfactory linearity. The changes in standard enthalpy and entropy for protonation of the ligands[10] show that the $T\Delta S^{\circ}$ contribution to the free energy change is similar for all the ligands (19—36 kJ mol^{-1}) and that most of the variation between ligands comes from the enthalpy term (+13 to −56 kJ mol^{-1}). The same trends would be expected for the boric acid complexes, although the absolute magnitudes of both terms would be smaller because there is no neutralisation of charge to favour the enthalpy change and less water of hydration to be released with a consequent increase in entropy.

These results are good evidence for the formation of the hypochloritoborate and hypobromitoborate complexes, $B(OH)_3$-OCl^- and $B(OH)_3OBr^-$. The very close agreement between the stability constants calculated from thermodynamic and kinetic data confirms the assumption that these complexes do not themselves participate directly in oxidation reactions with anions (or do so at an insignificant rate compared with hypohalous acids). Perturbations to the hypohalous acid–hypohalite equilibrium can, however, be large enough to affect the results of studies carried out with a borate buffer for pH control and such buffers are not recommended for use in studies of hypohalous acid reactions.

An example of this effect can be shown by the results of Lewin and Avrahami[11] for the rates of hypochlorite–hypobromite decomposition in a 0.1 mol dm^{-3} borate (or borax) buffer. The rates of hypochlorite and hypobromite decomposition, over the range pH 7—10, increased with the hydrogen ion concentration and were best explained by two oxidation reactions involving hypochlorous acid and hypobromous acid. Calculation of the rate constants for these reactions did not take hypohalitoborate complex formation into account. Recalculating the rate constants in Table IV of ref. 11 (using our stability constants to allow for complex formation) increased the second-order rate constant for hypochlorous acid oxidation by hypobromous acid from 6.5×10^{-2} to 8.6 or 17.7×10^{-2} dm^3 mol^{-1} s^{-1} and that for hypobromous acid oxidation by hypochlorous acid from 2.6×10^{-2} to 3.2 or 5.4×10^{-2} dm^3 mol^{-1} s^{-1}. (The lower recalculated values apply to borate buffer and the higher ones to borax: the original text[11] is ambiguous as to which buffer was used.) The linearity of the plots was essentially the same in all cases, with correlation coefficients of 0.99, although increases in the third decimal place were obtained with the corrected results. Even with these increased rates, however, no significant error would occur in kinetic studies of oxidation by halogens in aqueous solution, *e.g.* the oxidation of bromide by hypochlorous acid to form hypobromite.[12]

Chlorine is added to industrial cooling waters to control fouling by bacterial slimes and, in marine waters, by molluscs such as the mussel, *Mytilus edulis.* The chemistry of chlorinated sea water has been extensively studied in recent years to provide information on the effectiveness of different forms of treatment and their environmental consequences. Gaseous chlorine rapidly hydrolyses in water to form hypochlorous acid, which in sea water reacts with the natural bromide present to form hypobromous acid. The hypochlorous and hypobromous acids react multifariously with dissolved and suspended inorganic and organic compounds, including living tissue. In borate solutions typical of many laboratory studies, the complexes we have described will bias rate and equilibrium constants unless appropriate allowances are made. In natural waters the concentration of borate is usually too low, *e.g. ca.* 4.3×10^{-4} mol dm^{-3} in sea water,[13] for complex formation to affect significantly the reactivity of the dissolved halogen. Complex ions could, however, account for a significant proportion of the total borate $B(OH)_3$ and $B(OH)_4^-$, especially near dosing points, where high halogen concentrations occur. In discharges of chlorinated cooling water into the environment, the concentration of active halogen would be too low ($< 3 \times 10^{-6}$ mol dm^{-3}) for complex formation to be significant.

The methods described for measuring the formation constants for the hypohalitoborate complexes, although successful, do not allow the complexes to be detected directly. It is believed that these complexes can be detected directly by laser-excited Raman spectroscopy. In aqueous solution, the hypochlorite ion ($\nu_{max.} = 713$ cm^{-1}),[14] the hypobromite ion ($\nu_{max.} = 620$ cm^{-1}),[15] boric acid ($\nu_{max.} = 495$, 872 cm^{-1}),[16] and the borate ion ($\nu_{max.} = 375$, 522, 745 cm^{-1})[16] all have reported absorption bands. Changes in peak heights would provide further indirect evidence of complex formation and the similarity in the symmetry of boric acid and hypohalitoborate complexes suggests that these complexes should be detectable.

Acknowledgements

A. B. thanks the Central Electricity Generating Board (C.E.G.B.) for financial support. This paper is published with the permission of the C.E.G.B.

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Received 3rd July 1986; *Paper* 6/1336