Inorganica Chimica Acta, 14 (1975) 227–236

Kinetics and Mechanism of the 1/1 Boron-2-Hydroxy-4-Methoxy-4'-Chlorobenzophenone Complex Formation in Concentrated Sulfuric Acid Media

M. MARCANTONATOS and C. MENZINGER

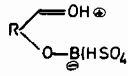
Department of Inorganic and Analytical Chemistry, University of Geneva, Geneva, Switzerland

Received December 10, 1974

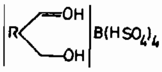
Results from kinetic and equilibrium studies for the formation of the 1/1 luminescent "boron-2-hydroxy-4-methoxy-4'-chlorobenzophenone" complex in 94.2% to 97.5% sulfuric acid, are reported.

It can be shown that the reaction takes place in at least two stages, involving successive formation of:

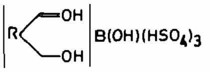
a)



intermediate, probably through

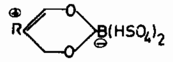


and



encounters, and

b)



chelate, by HSO_4^- *and* H^+ *expulsion from the intermediate and ring closure.*

There is kinetic evidence (although $B(HSO_4)_4^-$ *is the predominant form of boric acid in dilute solution in 100%* H_2SO_4*) for the formation, in less concentrated* H_2SO_4*, of a* $B(OH)(HSO_4)_3^-$ *species being in equilibrium with* $B(HSO_4)_4^-$*.*

Introduction

While a great number of coloured[1a–4a] and some luminescent[4b–10] reactions of boric acid with aromatic compounds, in conc. H_2SO_4, have been reported, very little is known about the structures and the mechanism of formation of the absorbing or emitting complexes in these media.

Most of the "BO_3H_3–R–H_2SO_4" systems (where R is the organic ligand) have been studied at equilibrium and thus only composition and apparent formation constants of the complexes could be obtained. Systems investigated in this way are those of boric acid with diaminochrysazin[12a], carminic acid[12b], quinalizarin[13–14], 1,1'-dianthrimide[15–17] and hydroxy-2-methoxy-4-chloro-4'-benzophenone (HMCB)[18].

With all these organic compounds, except with 1,1'-dianthrimide and HMCB, the formation of single 1/1 complexes has been reported. In the case of 1,1'-dianthrimide a 2/2 complex has been isolated[19], but previously a 1/1 was found in solution[16]. On the other hand, results from a fluorimetric study of the BO_3H_3–HMCB system in H_2SO_4 96% were found to be consistent with the formation of three 1/1, 2/1, 2/2 (HMCB/B) luminescent complexes[18].

To our knowledge, only the formation of the 1/1 boron-1,1'-dianthrimide complex has been investigated kinetically[16]. However, no sufficient information regarding the mechanism of the reaction could be obtained.

In this work, the kinetics of the 1/1 boron–HMCB complex, in 94% to 97.5% H_2SO_4, is investigated fluorometrically. Results from investigations of the formation of the 2/1 and 2/2 complexes will be published later.

Experimental

Reagents

Boric acid, sulfuric acid (d = 1.84) and oleum (30% SO_3) were of analytical grade quality (Merck). Hydroxy-2-methoxy-4-chloro-4'-benzophenone (HMCB) was purified by double recrystallization in water (tridistilled)/ethanol (analytical grade) 15/85 V/V. Sulfuric acids at different percentages (W/W) were prepared from H_2SO_4 (d = 1.84)–tridistilled H_2O and H_2SO_4–oleum and controlled conductometrically as described by Gillespie *et al.*[20–21]

Apparatus

A Zeiss (ZFM4C) fluorometer was used for fluorescence intensity determinations. Calibrations, regularily carried out during kinetic runs and equilibrium determinations, were made with a Zeiss fluorescent standard. Conductance measurements were made with a WIW conductimeter (Model LRR) 50 and 3000 Hz, 0.1 to 1*M* and with an LDT type cell, K = 1 and 100, volume 12 ml.

Fluorescence Measurements

Fluorescence measurements at 25 ± 1 ° C, were carried out at 490 nm (maximum of the B-HMCB emission) with an excitation wavelength of 366 nm. Reactions were carried out at 40 ± 0.5 ° C in a specially designed 250 ml capacity air-tight glassware from which aliquots of solutions can be cooled rapidly down to 25 ° C.

In all cases, emissions of the blanks (HMCB/H_2SO_4) were low. However, in all kinetic runs and equilibrium studies, sample solution emissions were corrected for the low blank contribution.

Special care was taken in choosing the initial reactant's concentrations in order to avoid any uncontrollable lowering of fluorescence intensity due to phenomena such as inner filter effects or concentration quenching.

Before each experiment, glassware were treated with hot HMCB sulfutic acid solutions, rinsed with tridistilled water and dried. No correction for boron contribution from H_2SO_4 was necessary, since it was shown[22] that the boron amount present in Merck (G.R.) sulfuric acids is less than 1 ppb.

Treatment of Data

Stability constant

In 94.2, 95.2, 96.0, 96.4 and 97.5% H_2SO_4, values of the apparent stability constant:

$\beta_1 = X/AR$,

where $X = [(OH)_m(HSO_4)_{2-m}BL]$, $A = \sum_j \sum_i [B(OH)_j (HSO_4)_i^{(i+j-3)-}] + \sum_j [B(OH)_j(HSO_4)_{4-j}H]$,

(with $j \leqq 3$, $i \leqq 4-j$), $R = [H_2L^+]$, L = HMCB and where, most probably, $X = [(HSO_4)_2BL]$, and $A = [B(HSO_4)_4^-] + [B(OH)(HSO_4)_3^-]$ (see ref. 24 and under proposal of mechanism), were obtained using the following method. As it was shown that 1/1 boron complexes in conc. H_2SO_4 are predominantly formed under conditions where boric acid is in excess over the organic ligand, and bearing in mind the moderate stability[12a–18] of these complexes, we worked with $A_o \gg R_o$, keeping R_o constant, and assumed the validity of the following expression:

$$\beta_1 = X/A_o\text{–}X)\,(R_o\text{–}X) \qquad (1)$$

where A_o and R_o stand for total concentrations of boric acid and HMCB.

Values of β_1 were extracted from the linear plots:

$$1/A_o \simeq \varphi_1\beta_1\Phi^{-1}\text{–}\beta_1 \qquad (2)$$

where φ_1 = apparent fluorescence efficiency of the complex, $\Phi = F_e/R_o$, $F_e = \varphi_1 Xl$ = fluorescence intensity at equilibrium, l = thickness of the solution (1 cm).

More consistent β_1 values were then obtained from the rigourous expression:

$$\beta_1 = F_e/(A_o\varphi_1\text{–}F_e)(R_o\varphi_1\text{–}F_e) \qquad (3)$$

in the following manner.

Values close to the extracted one from the expression (2), were attributed to φ_1 and consistent β_1 was obtained for the value of φ_1 which gave a minimum relative variability to β_1, judged by the statistical criterium:

$$E_{s(\bar\beta_1)}\,\% = 100 \cdot t \cdot S_{\bar\beta_1}/\bar\beta_1, \; (S_{\bar\beta_1} = S_{\beta_1}/\sqrt{N}$$
$$S_{\beta_1} \text{ standard deviation, N = number of } \beta_1 \text{ values}) \qquad (4)$$

For instance, in 96% H_2SO_4 and A_o/R_o: 26 to 90, $R_o = 4 \times 10^{-7} M$, N = 25.

$1/A_o = 1.10 \times 10^{13}\Phi^{-1}\text{–}2.23 \times 10^4$, with a linear regression coefficient of 0.9993 (see Figure 1), giving $\varphi_1 = 4.94 \times 10^8 M^{-1}\ cm^{-1}$.

Consistent φ_1 and β_1 values are (see Table I) $\varphi_1 = 4.90 \cdot 10^8 M^{-1}\ cm^{-1}$, $\beta_1 = 2.28 \times 10^4 M^{-1}$.

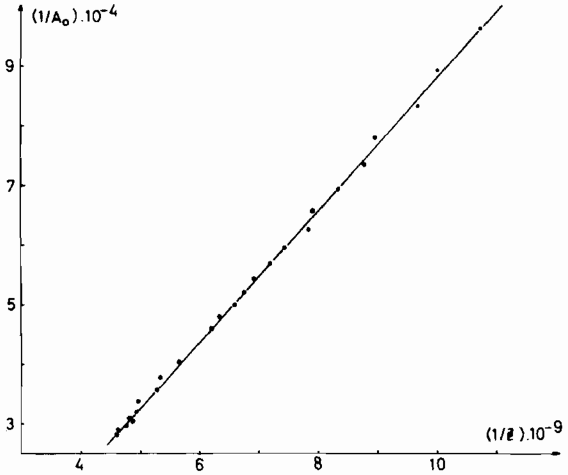


Figure 1. Graphical determination of φ_1 and β_1 according to (2) (96% H_2SO_4).

TABLE I. β_1 (M^{-1}) according to (3) and (4) for Different Values of φ_1 (M^{-1} cm^{-1}).

$\varphi_1 \times 10^{-8}$	5.5	5	4.95
$\beta_1(\pm E_{s(\beta 1)})$	1.92×10^4 (1.08)	2.21×10^4 (0.73)	2.24×10^4 (0.72)
$\varphi_1 \times 10^{-8}$	*4.9*	4.85	4.5
$\beta_1(\pm E_{s(\beta 1)})$	*2.28×10^4 (0.71)*	2.31×10^4 (0.72)	2.60 (1.00)

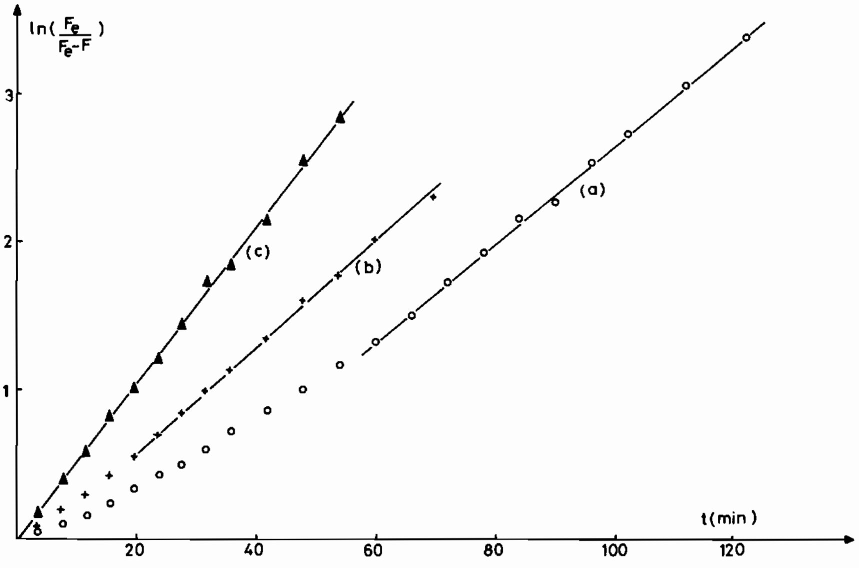


Figure 2. Reversible first order reaction logarithmic plots (96% H_2SO_4). A_o/R_o: $3.2 \times 10^{-5}/4 \times 10^{-7}$ (a), $8 \times 10^{-5}/2 \times 10^{-7}$ (b), $1.8 \times 10^{-4}/2 \times 10^{-7}$ (c).

Kinetics

Kinetics of formation of the complex were performed at 40 ± 0.5° C and monitored by fluorimetry at 490 nm (exc. 366 nm) after rapid cooling of the solutions to 25 ± 1° C. In all kinetic runs boric acid was in excess over HMCB (A_o/R_o: 20 to 1400) in order to have pseudo-zero-order reaction with respect to BO_3H_3. Thus for each run pseudo-first-order reversible formation of the complex was generally observed in accordance with the overall reaction scheme:

$$a + r \underset{k}{\overset{\vec{k}}{\rightleftharpoons}} x \qquad (5)$$

Observed rate constants k_{obs} were then extracted from the linear plots of

$$\ln(F_e/F_e–F) = k_{obs} \cdot t \qquad (6)$$

and the dependence of k_{obs} on boric acid initial concentration A_o was examined.

For $A_o/R_o < 400$ (see for example Figure 2), initial deviations from the reaction scheme (5) and expression (6) were observed, suggesting an at least two-stage reaction. Analysis of these kinetics was performed after evaluating parameters (see later) under A_o boundary conditions.

In all cases F, t values were averages of at least two, usually more, determinations, and variations seldom exceeded ± 10%. Regression coefficients for linear parts of the $\ln(F_e/F_e–F)$ *vs.* t plots were seldom inferior and most often superior to 0.999.

Results and Discussion

Probable Structure of the 1/1 B–HMCB Complex

There is limited information concerning the structures of boric acid chelates with organic compounds in conc. sulfuric acid media and discrepancies about, especially, the form of the central group (boron) moiety.

If consideration is taken of the fact that values of apparent stability constants of the various 1/1 complexes[12a–18] were determined under somewhat different solvent composition and temperature conditions, it can be seen that the value of β_1 of the B–HMCB 1/1 chelate (see Table II) and that found previously ($5 \times 10^4 M^{-1}$, 96% H_2SO_4, T = 70° C)[18] fall quite close to those reported (10^4 to 10^5)[12a–17] for the other complexes.

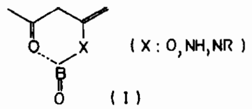
This suggests, since in the case of 1-hydroxy-anthraquinon derivatives the coordinating sites are similar and in that of 1,1-dianthrimide of closed properties, to those of HMCB, that in all of these chelates the environment of the boron atom must be similar.

Previous to Gillespie *et al.*[23–24] results on the nature of boron species in 100% H_2SO_4, the general tendency

TABLE II. Apparent Stability Constants β_1 of the B–HMCB Complex in 94.2% to 97.5% H_2SO_4.

% H_2SO_4	94.2	95.2	96	96.4	97.5
$\beta_1 \times 10^{-4} (M^{-1})$	3.19	2.97	2.28	2.14	2.46

was to assign structures (I) to the 1/1 chelates in which the environment of the boron atom is that of the metaborate ion (see for example ref. 1b and 3).

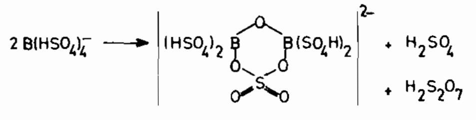


(I)

Presently, such structures have to be considered as improbable. In fact, there is now a good deal of evidence[23–24] that boric acid, in dilute solutions in 100% H_2SO_4, is in the form of tetra(hydrogensulfato)borate anion (II):

$$BO_3H_3 + 6H_2SO_4 \rightarrow \underset{(II)}{B(HSO_4)_4^-} + 3H_3O^+ + 2HSO_4^- \quad (7)$$

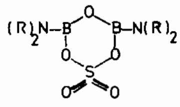
which, in more concentrated solutions, leads to the dimeric anion (III):



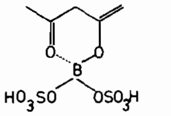
(III)

(8)

Moreover, the structures:



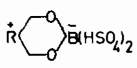
(IV)



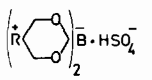
(V)

attributed to the boron 1,1′-dianthrimide 2/2 complex (IV) (which has been isolated[19]) and to the alizarin and quinalizarin 1/1 chelates[13–14] (V), are consistent with Gillespie's *et al.* results[23–24].

In addition, from a more recent fluorometric investigation of the BO_3H_3–HMCB system, the formation of three chelates 1/1, 2/2, 2/1 (HMCB/B) was reported[18]. Elemental analysis of the 2/2 chelate[25], suggested a structure analogous to (IV) but with boron being in its tetrahedral state. Structures



and

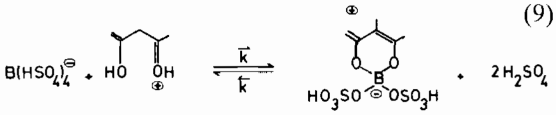


proposed for the 1/1 and 2/1 HMCB complexes are in agreement with other boron complexes of the same compositions[26–27], as well as, with the 1/1 boron benzoylacetonide and dibenzoylmethide luminescent complexes isolated in ether/H_2SO_4 (96%) (96/8 V/V)[11c, 28].

It may therefore be concluded that possible metaborate configuration of the central group in boron chelates is rather improbable in concentrated sulfuric acid media.

Mechanism of the B–HMCB 1/1 Complex Formation

In the sulfuric acids used, the simplest assumption as to the mechanism of formation of 1/1 chelate, is the rate determining reversible reaction between the tetra(hydrogensulfato)borate anion and the protonated HMCB:



(9)

If assumption is made that boric acid is predominantly in the form of $B(HSO_4)_4^-$, it appears at first sight that the results are not in disagreement with such a reaction scheme, since the integrated expression (6), of

$$\frac{dF}{dt} = \varphi_1 \vec{k} A_o (R_o - F\varphi_1^{-1}) - \overleftarrow{k}_s F\varphi_1^{-1}$$
$$= \varphi_1 \vec{k} A_o (R_o - F\varphi_1^{-1}) - [\vec{k} A_o (R_o - F_e\varphi_1^{-1})F]/F_e \quad (10)$$

where A_o and R_o: initial concentrations of boric acid and HMCB, F and F_e: fluorescence intensity of the chelate at time t and at equilibrium, $\overleftarrow{k}_s = \overleftarrow{k}[H_2SO_4]^2$, is applicable for A_o/R_o: 700–900–1000–1100–1400, $R_o = 2 \times 10^{-7}$, 96% H_2SO_4 (see for example Figure 2(c)).

For these initial concentrations, however, $k_{obs}F_e/R_o$ is not a linear function of A_o (see Figure 3(A)(c)), as expected from:

$$k_{obs} = \vec{k} A_o R_o \varphi_1 / F_e = \vec{k} A_o + \overleftarrow{k}_s \quad (11)$$

Moreover, for $A_o/R_o < 700$, ln(Fe/Fe–F) *vs.* t (see (6)) is linear only after some reaction period (*e.g.* Figure 2(a), (b)).

Values of $k_{obs}F_e/R_o$ extracted from these linear parts satisfy expression (11) up to $k_{obs}F_e/R_o = 6.7 \times 10^7 M^{-1}$ min^{-1} ($A_o = 3.2 \times 10^{-5}$, Figure 3(B)) and give for 96% H_2SO_4:

$$\vec{k} = 433 M^{-1} \text{min}^{-1}, \overleftarrow{k}_s = 0.0178 \text{min}^{-1}, \beta_1 = 2.43 \times 10^4 M^{-1} \quad (12)$$

which are in good agreement with the value of $\beta_1 = 2.28 \times 10^4 M^{-1}$, calculated from equilibrium data.

However, $k_{obs}F_e/R_o$ becomes nearly independent of A_o before the non linear part (c) (Figure 3(A)) and the peculiar dependence of $k_{obs}F_e/R_o$ upon A_o clearly indicate a modification in the k_{obs} expression.

On the other hand, if for a given initial concentration of boric acid and ligand, the concentration of sulfuric acid is decreased, kinetics become simpler (Figure 4) with a four-fold increase in $\vec{k}$ value (Table III). Also an approximately six-fold rise in $\overleftarrow{k}_s$ occurs, which, according to the scheme (9), is an opposite variation to that expected.

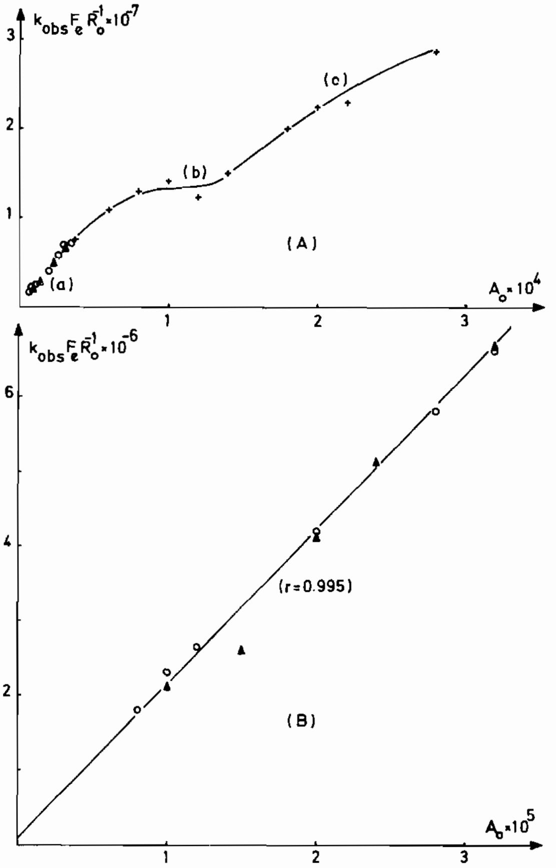


Figure 3. Dependence of $k_{obs}F_e/R_o$ upon initial boric acid concentration A_o (96% H_2SO_4). R_o: 4×10^{-7} ○, 5×10^{-7} ▲, 2×10^{-7} x.

TABLE III. k_{obs}(min^{-1}), $\overrightarrow{k}$* ($M^{-1}min^{-1}$), $\overleftarrow{k_s}$* (min^{-1}) and β_1 (M^{-1}) for H_2SO_4 94.2 to 97.5% ($A_o = 4\times10^{-5}$, $R_o = 2\times10^{-7}$ *M*).

% H_2SO_4	94.2	95.2	96	96.4	97.5
$k_{obs}\times10^2$	3.89	3.22	2.91	1.98	0.94
$\overrightarrow{k}\times10^{-2}$	5.11	4.54	3.93	3.18	1.29
$\overleftarrow{k_s}\times10^2$	1.84	1.4	1.34	0.71	0.42
$\beta_1\times10^{-4}$	2.8	3.2	2.94	4.5	3.07

* Calculated from (11).

Obviously, all these basic results indicate that the reaction scheme (9) is oversimplified and one has to consider a more involved mechanism.

Proposal of mechanism

In the interaction of the tetra(hydrogensulfato)borate anion with protonated ligand, one may assume the more detailed mechanism (Figure 5), according to which a two-step rate-determining reversible reaction takes place, following probably an encounter *W* formation rapid pre-equilibrium 4′ and involving two successive displacements 2 , 3 of one sulfuric acid molecule to give a non-chelate tetrahedral intermediate y and the final complex x. ·

Although there is no doubt that in the sulfuric acids used, the ligand is completely in the protonated form, boric acid may not be in the single tetra(hydrogensulfato)borate form, but also in the $B(OH)(HSO_4)_3^-$ reactive form.

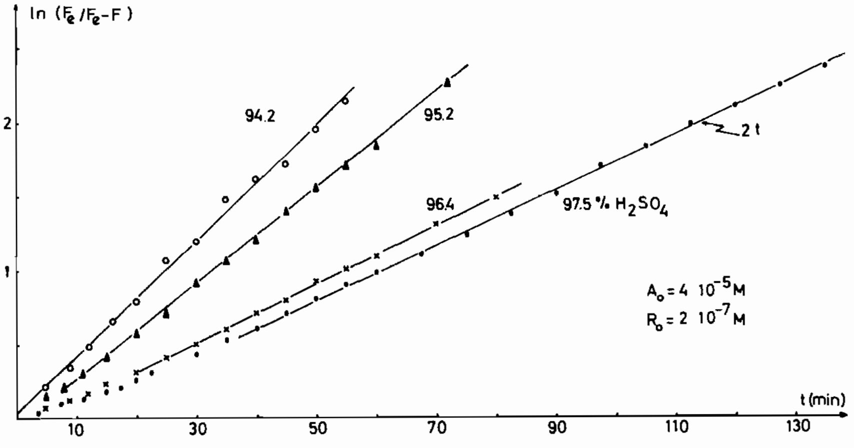


Figure 4. Logarithmic plots for different sulfuric acid concentrations.

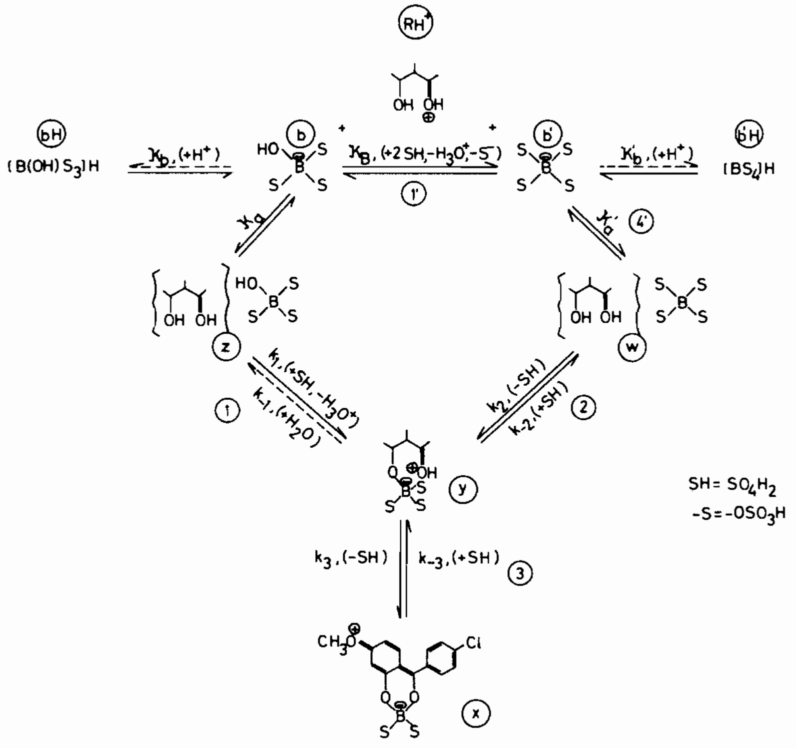


Figure 5. Proposed mechanism for the B–HMCB 1/1 chelate formation.

There is no direct evidence for the formation of this species, but this assumption may account for the marked increase (with slightly lowering sulfuric acid concentration) in the overall $\overleftarrow{k}$ rate constant, since forward reaction in step 1 involves a highly favoured water displacement and a decrease in H_2SO_4 will displace equilibrium 1' towards $B(OH)(HSO_4)_3^-$ species. From the proposed reaction scheme, the following expressions:

$$\frac{dX}{dt} = k_3Y - k_{-3}'X \tag{13}$$

$$\begin{aligned}\frac{dY}{dt} &= k_1^aBR + k_2^aB'R + k_{-3}'X - (k_{-2}' + k_3)Y \\ &= (k_1^aB + k_2^aB')R_o - (k_1^aB + k_2^aB' + k_{-2}' + k_3)Y + (k_{-3}' - k_1^aB - k_2^aB')X\end{aligned} \tag{14}$$

$$Y = k_3^{-1}\left(\frac{dX}{dt} + k_{-3}'X\right) \tag{15}$$

$$\frac{d^2X}{dt^2} = k_3\frac{dY}{dt} - k_{-3}'\frac{dX}{dt} \tag{16}$$

can be manipulated to give the complete expression:

$$\begin{aligned}\frac{d^2X}{dt^2} &= k_3R_o[k_1^a(A_oG^{-1}-Y-X) + k_2^a(A_oK_B^*G^{-1}-Y-X)] - [k_1^a(A_oG^{-1}-Y-X) + k_2^a(A_oK_B^*G^{-1} \\ &\quad -Y-X) + k_{-2}' + k_3 + k_{-3}']\frac{dX}{dt} - \\ &\quad [k_{-3}'[k_1^a(A_oG^{-1}-Y-X) + k_2^a(A_oK_B^*G^{-1}-Y-X) + k_{-2}'] + k_3k_1^a(A_oG^{-1}-Y-X) + k_3k_2^a(A_oK_B^*G^{-1} \\ &\quad -Y-X)]X\end{aligned} \tag{17}$$

where:

$$\begin{aligned} A_o &= [BO_3H_3]_o \\ R_o &= [RH^+]_o \\ k_1^a &= k_1K_a \\ k_2^a &= k_2K_a' \\ k_{-2}' &= k_{-2}[SH] \\ k_{-3}' &= k_{-3}[SH] \\ K_B^* &= K_B[SH]^2/[H_3O^+][S^-] = B_o'/B_o \\ B_o' &= [b']_o;\ B_o = [b]_o \\ G &= 1 + K_b[H^+] + (1 + K_b'[H^+])K_B^* \\ B_o &= A_o/G \\ B_o' &= A_oK_B^*/G \\ X &= [X];\ Y = [Y] \end{aligned} \tag{18}$$

If, by analogy to the strong acid $[B(HSO_4)_4]H$[29], it is assumed that $[B(OH)(HSO_4)_3^-]/[B(OH)(HSO_4)_3H] \geqq 100$,

$$G \simeq 1 + K_B^* \tag{18a}$$

Also for the ratios A_o/R_o used:

$$(A_oG^{-1}-Y-X) \simeq A_oG^{-1};\ (A_oK_B^*G^{-1}-Y-X) \simeq A_oK_B^*G^{-1} \tag{18b}$$

and equation (17) simplifies to:

$$\begin{aligned}\frac{d^2X}{dt^2} &= k_3R_oA_oG^{-1}(k_1^a + k_2^aK_B^*) - [A_oG^{-1}(k_1^a + k_2^aK_B^*) + k_{-3}']\frac{dX}{dt} - [k_{-3}'A_oG^{-1}(k_1^a + k_2^aK_B^*) \\ &\quad + k_{-3}'k_{-2}' + k_3A_oG^{-1}(k_1^a + k_2^aK_B^*)]X\end{aligned} \tag{19}$$

If, for some series of A_o/R_o, the condition $dY/dt \sim 0$ is, after some reaction time, satisfied, expression (19) reduces to:

$$\frac{dX}{dt} = \frac{k_3(k_1{}^a + k_2{}^2K_B{}^*)G^{-1}A_o}{k_{-2}' + k_3}(R_o - X) - \frac{k_{-2}'k_{-3}'}{k_{-2}' + k_3}X = \overrightarrow{k}A_o(R_o - X) - \overleftarrow{k}_sX \qquad (20)$$

It should be noted that the integrated expression of (20) is similar to that of equation (10), so this can explain: (i) the linear variation of $\ln(F_e/F_e - F)$ with t only after some reaction period (*e.g.* Figure 2(a), (b)); (ii) the linear dependance of $k_{obs}F_e/R_o$ upon A_o (Figure 3(B)) for $A_o/R_o \leqq 80$; (iii) the consistent value of β_1 obtained from kinetic data (see ref. 12).

For higher excesses of boric acid over ligand, *i.e.* for $A_o/R_o \geqq 700$, the condition $dY/dt \sim 0$ is readily satisfied, but on the other hand the concentration Y of the intermediate may not be rigourously negligible compared to R_o.

If this assumption is correct, (iv) Y will be given by:

$$Y = \frac{(k_1{}^a + k_2{}^aK_B{}^*)G^{-1}A_o(R_o - X) + k_{-3}'X}{(k_1{}^a + k_2{}^aK_B{}^*)G^{-1}A_o + k_{-2}' + k_3} = \frac{k_{12}A_o(R_o - X) + k_{-3}'X}{k_{12}A_o + k_{-2}' + k_3} \qquad (21)$$

(where $k_{12} = (k_1{}^a + k_2{}^aK_B{}^*)/G$), (v) the rate of formation of the chelate, if $k_{-3}'/k_3 \ll 1$, must be:

$$\frac{dX}{dt} = \frac{k_3k_{12}A_o}{k_{12}A_o + k_{-2}' + k_3}(R_o - X) - \frac{k_{-2}'k_{-3}'}{k_{-2}A_o + k_{-2}' + k_3}X = \overrightarrow{k}'(R_o - X) - \overleftarrow{k}'X, \qquad (22)$$

in which case:

$$\ln(F_e/F_e - F) = k_{obs}'t = (\overrightarrow{k}' + \overleftarrow{k}')t = \frac{k_{12}A_oR_o\varphi_1}{(k_{12}A_o + k_{-2}' + k_3)F_e}t, \qquad (23)$$

and (vi) the equations (24) and (25), obtained by the rearrangement of the k′ and k_{obs}' expressions, must be satisfied:

$$1/A_o = k_{12}k_3/(k_{-2}' + k_3)\overrightarrow{k}' - k_{12}/(k_{-2}' + k_3) \qquad (24)$$

$$1/A_o - (k_{12}k_3)/(k_{-2}' + k_3)k_{obs}' = k_2'k_{-3}/(k_{-2}' + k_3)k_{obs}'A_o - k_{12}/(k_{-2}' + k_3) \qquad (25)$$

For all kinetic runs (96% H_2SO_4) with $A_o/R_o \geqq 700$, linear plots for $\ln(F_e/F_e - F)$ *vs.* t were obtained and this from the beginning of the reaction.

For these initial conditions, equation (23) shows that $k_{obs}'F_e/R_o$ cannot depend linearly on A_o and this is indeed the case (see Figure 3(A) (c) and 6).

Also Figure 6(I) and 6(II) show that expressions (24) and (25) are obeyed well.

Values of $\overrightarrow{k} = k_{12}k_3/(k_{-2}' + k_3)$ and $\overleftarrow{k} = k_{-2}'k_{-3}'/(k_{-2}' + k_3)$ (see the slopes in Figure 6(I) and 6(II)) are lower than those obtained under $A_o/R_o \leqq 80$ conditions, but $\beta_1 = k_{12}k_3/k_{-2}'k_{-3}' = 2.2 \times 10^4 M^{-1}$ is in good agreement with the value from equilibrium (see Table I) and the previous kinetic ($A_o/R_o \leqq 80$) data (see (12)).

Figure 6(III) shows, according to equation (24), the variation of $1/A_o$ with adjusted k′ values. These were obtained by curvefitting using the expression (26):

$$F = \varphi_1R_o\left(1 - \frac{\overleftarrow{k}'}{\overrightarrow{k}' + \overleftarrow{k}'} - \frac{\overrightarrow{k}'}{\overrightarrow{k}' + \overleftarrow{k}'}e^{-(\overrightarrow{k}' + \overleftarrow{k}')t}\right) \qquad (26)$$

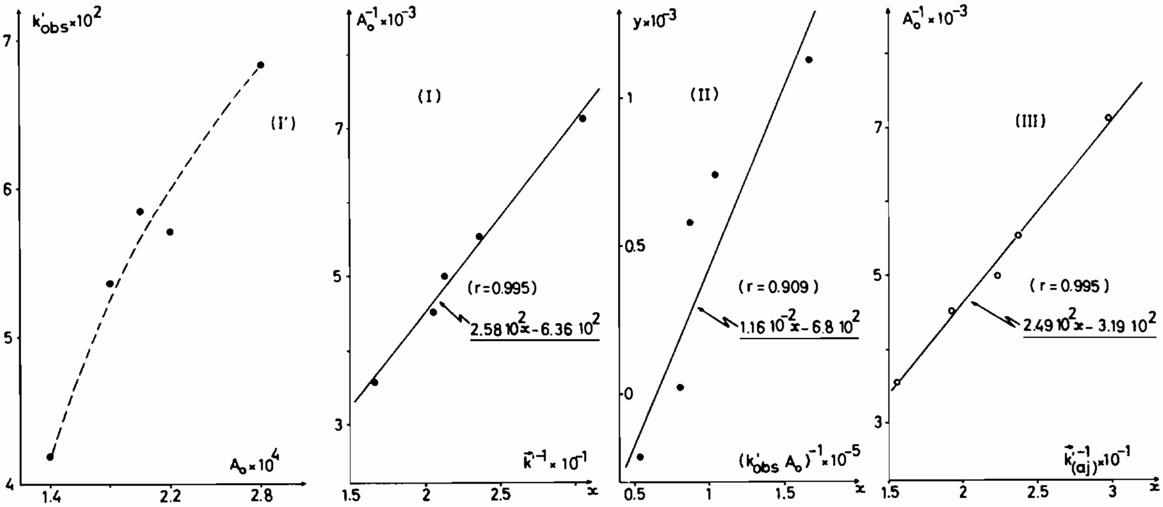


Figure 6. Dependence of k_{obs}' upon initial boric acid concentration A_o for $A_o/R_o \geqq 700$ (96% H_2SO_4) (I′) and graphical representation of equation (24) (I) and (III), and (25) (II). $y = 1/A_o - (k_{12}k_3)/(k_{-2}' + k_3)k_{obs}'$.

Variations between adjusted $\overrightarrow{k}'$ and $\overleftarrow{k}'$ values and those extracted from the linear plots (23) were in all cases inferior to ± 10%.

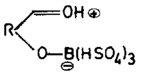
From the slope and intersection of the linear expression (24), the value $k_3 = 0.78$ min (Figure 6(III)) is obtained and from the condition $k_{-3}'/k_3 \ll 1$ (see (v) under proposal of mechanism) $k_{-3}' \sim 0.02$; $k_3 \sim 0.016$ min^{-1}.

Also from the expression of the slope of the straight line (Figure 6(II)), $k_{-2}' \sim 1.9$ min^{-1} and from $\beta_1 = k_{12}k_3/k_{-2}'k_{-3}' = 2.3 \times 10^4 M^{-1}$, $k_{12} \sim 840 M^{-1}$ min^{-1}. These values of k_{12} $(= (k_1^a + k_2^a K_B^*)G^{-1})$, k_3, k_{-2}' and k_{-3}' were then introduced into the solution of the differential equation (19) in order to check its validity.

Figure 7 shows – where solid curves are the calculated F *vs.* t variations with $k_{12} = 880 M^{-1}$ min^{-1}, $k_3 = 0.78$ min^{-1}, $k_{-2}' = 1.78$ min^{-1}, $k_{-3}' = 0.017$ min^{-1} and where open circles are the F, t values after which applicability of expression (20) is observed – that results are in agreement with the proposed reaction scheme.

The non-chelate intermediate formation

The basic kinetic evidence for the formation of the



(y) intermediate comes from the applicability of the equation (19) (*e.g.* Figure 7). Steady-state conditions

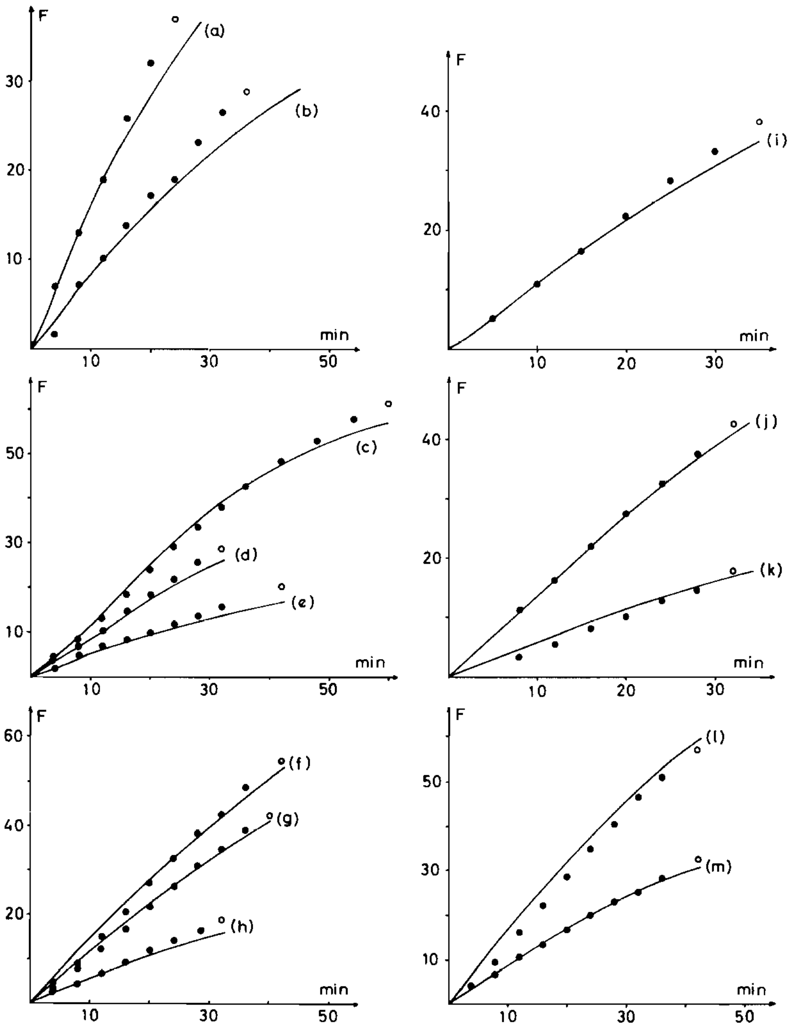


Figure 7. Experimental points ● and calculated kinetic curves —— (96% H_2SO_4) according to the complete rate expression (19). A_o/R_o: 400(a), 200(b), $R_o = 2 \times 10^{-7}$; 80(c), 50(d), 25(e), 90(f), 70(g), 30(h), $R_o = 4 \times 10^{-7}$; 40(i), 48(j), 20(k), 64(l), 30(m), $R_o = 5 \times 10^{-7}$.

for y may also account for its formation and have therefore to be checked.

An example of computation is given in Figure 8(a), where cross (x) and open circle points correspond to concentrations Y of the intermediate, calculated from the following steady-state (SS) approximation equation (see (14) and (18b)):

$$Y = \frac{(k_1^a + k_2^a K_B^*)G^{-1}A_0(R_0-X) + k_{-3}'X}{k_{-2}' + k_3} = \frac{k_{12}A_0(R_0-X) + k_{-3}'X}{k_{-2}' + k_3} \qquad (27)$$

and where full circle and triangle points are values obtained from the rigourous expression (15), taking $\Delta X/\Delta t$ (●) and dX/dt (▲).

Abscisses of open circle points are times after which, in the treatment of the F, t data, the SS assumption was made and the simplification of equation (19) to (20) was observed leading to a linear logarithmic plot (8(b)).

A comparison of Figure 8(a) with the logarithmic plot (8(b)) shows clearly intermediate's SS conditions after about 55 min.

Ring closure

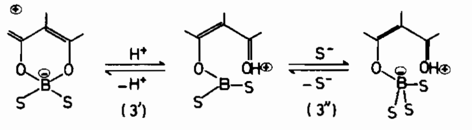
On the basis of our results, proposal of a detailed mechanism for the formation of the chelate from the intermediate is not justified, but some assumptions can be made as to the mode of ring closure and opening (step 3 , Figure 5).

The simplest, but quite plausible supposition as to the ringopening, is a rate-determining proton attack on the negative polar site of the chelate to give a compound in which boron is in the trigonal state, followed by rapid coordination of a hydrogensulfato anion to boron.

If it is assumed that proton reacts in its hydrated form, from the value of k_{-3}' (0.017 min^{-1}) in 96% H_2SO_4 and from approximate value of H_3O^+ taken from Kaandorp's *et al.*[30] data, k_{-3} is estimated to be $0.0062 M^{-1} min^{-1}$.

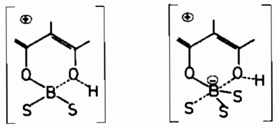
Comparison of this value with k_3 (0.78 min^{-1}) indicates a rather difficult six-membered ring opening, in agreement with the well-known chelate stabilisation of boron compounds in which the B atom is in the tetrahedral state.

On the other hand, it is not impossible that ring closure involves hydrogen-sulfate displacement, followed by proton expulsion, so that for ring opening and closure:



(28)

where:



may represent transition states in 3′ and 3″.

Effect of H_2SO_4 concentration

The most striking effect of sulfuric acid concentration is the unexpected decrease of the overall reverse rate constant $\overleftarrow{k_s}$ (see Table III) and the insensitivity of the stability constant β_1 (see Table II and III) with increasing sulfuric acid.

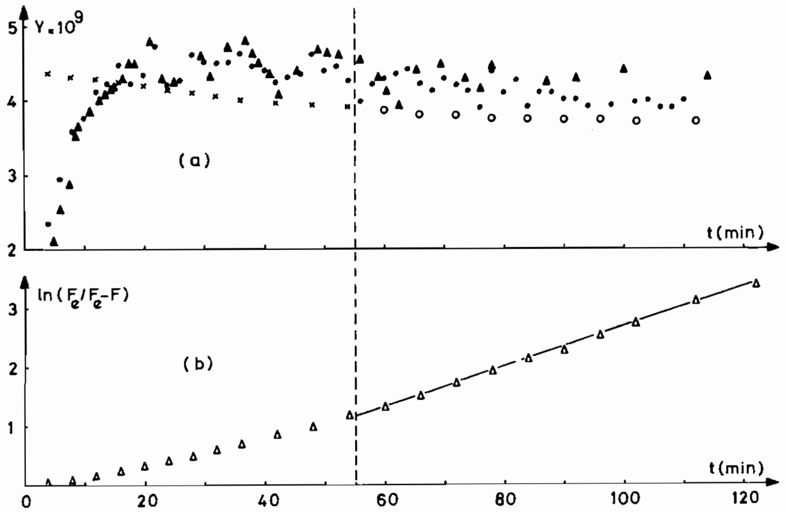


Figure 8. Concentration of the intermediate *vs.* time (a) and reversible first orfer reaction logarithmic plot for A_0/R_0: $3.2 \times 10^{-5}/4 \times 10^{-7}$ (b) (96% H_2SO_4).

From the proposed mechanism, expressions for these constants and for $\overrightarrow{k}$ are (see (20) and (18a)):

$$\overrightarrow{k} = \frac{k_3(k_1{}^a + k_2{}^a K_B{}^*)}{(k_{-2}[H_2SO_4] + k_3)(1 + K_B{}^*)} \tag{29}$$

$$\overleftarrow{k}_s = \frac{k_{-2}k_{-3}[H_2SO_4]^2}{k_{-2}[H_2SO_4] + k_3} \tag{30}$$

$$\beta_1 = \frac{k_3(k_1{}^a + k_2{}^a K_B{}^*)}{k_{-2}k_{-3}[H_2SO_4]^2(1 + K_B{}^*)}\,, \tag{31}$$

so that, with increasing sulfuric acid concentration, a lowering of $\overrightarrow{k}$ and β_1 and an increase of $\overleftarrow{k}_s$ is expected.

However, if the assumption that ring-opening occurs by a rate-determining proton attack is plausible, $\overleftarrow{k}_s$ must have the following expression:

$$\overleftarrow{k}_s = \frac{k_{-2}[H_2SO_4]k_{-3}[H^+]}{k_{-2}[H_2SO_4] + k_3}\,, \tag{32}$$

and considering the fact that, with increasing total sulfuric acid concentration $[H_2SO_4]_t$, the concentration of the hydrated proton decreases more rapidly than the free sulfuric acid concentration increases[30], one can explain by (32) the observed lowering of $\overleftarrow{k}_s$.

Moreover, β_1 must be given by:

$$\beta_1 = \frac{k_3(k_1{}^a + k_2{}^a K_B{}^*)}{k_{-2}[H_2SO_4]k_{-3}[H^+](1 + K_B{}^*)}\,, \tag{33}$$

so that, if no other boron reacting species, like $B(OH)(HSO_4)_3^-$, is present in equilibrium with $B(HSO_4)^-_4$, β_1 had to decrease with $[H_2SO_4]_t$ and $1/\overrightarrow{k}$ (see (29)):

$$1/\overrightarrow{k} = \frac{k_{-2}[H_2SO_4](1 + K_B{}^*) + k_3(1 + K_B{}^*)}{k_3(k_1{}^a + k_2{}^a K_B{}^*)} \tag{34}$$

would depend linearly on free sulfuric acid concentration $[H_2SO_4]$.

The fact, however, that β_1 is independent of $[H_2SO_4]_t$ could indicate the presence of this species, since $K_B{}^* = [B(HSO_4)_4^-]_o/[B(OH)(HSO_4)_3^-]_o$ increases with $[H_2SO_4]_t$.

Also approximate values of $[H_2SO_4]$ taken from Kaandorp's *et al.*[30] data, do not at all verify the $1/\overrightarrow{k}$ *vs.* $[H_2SO_4]$ linearity, but lead to a continuous increase in the $1/\overrightarrow{k}$ *vs.* $[H_2SO_4]$ slope as one could expect from (34), since $K_B{}^*$ increases with $[H_2SO_4]_t$ and hence with $[H_2SO_4]$.

These results could be considered as consistent with the formation of another boron reacting species together with $B(HSO_4)_4^-$, most probably $B(OH)(HSO_4)_3^-$, but unfortunately no quantitative checking of the relations (29) to (34) was possible, since Kaandorp's *et al.* distribution of H_2O–H_2SO_4 particles as a function of $[H_2SO_4]_t$ was determined at 25° C and our kinetic and equilibrium date were obtained at 40° C.

It is nevertheless interesting to note that, with other organic ligands such as Carmine and Dianthrinide[1(b)], an analogous variation in the rate of formation of the coloured boron complexes has been observed for about the same $[H_2SO_4]_t$ used in this work, indicating that the effect of sulfuric acid concentration lies on the relative concentrations of "BO_3H_3–H_2SO_4" species of different structure.

References

1 A. A. Nemodruk and Z. K. Karalova. Analytical Chemistry of Boron, Israel Program for Scientific Translations, Jerusalem (1965). (a) p. 19 and 39; (b) p. 41–47.
2 F. Vláčil and K. Drbal, *Chem. Listy, 62,* 1371 (1968).
3 K. Hiiro and J. Muraki, Report of the Governement Industrial Research Institute, Osaka, No. 321 (1964), p. 14–20.
4 F. Umland, Theorie und Praktische Anwendung von Komplexbildnern, Frankfurt am Main (1971). (a) p. 368; (b) p. 601.
5 G. H. Ellis, E. G. Zook and O. Baudisch, *Anal. Chem., 21,* 1345 (1949).
6 R. Ruggieri, *Anal. Chim. Acta, 25,* 145 (1961).
7 A. Holme, *Acta Chem. Scand., 21,* 1679 (1967).
8 M. Marcantonatos, D. Monnier and A. Marcantonatos, *Helv. Chim. Acta, 47,* 705 (1964).
9 D. Monnier, A. Marcantonatos and M. Marcantonatos. *Helv. Chim. Acta, 47,* 1980 (1964).
10 M. Marcantonatos, A. Marcantonatos and D. Monnier, *Helv. Chim. Acta, 48,* 194 (1965).
11 M. Marcantonatos, G. Gamba and D. Monnier. *Helv. Chim. Acta,* (a) *52,* 538 (1969), (b) *52,* 2183 (1969), (c) *Anal. Chim. Acta 67,* 220 (1973).
12 R.S. Brown, (a) *Can. J. Chem., 42,* 2635 (1964); (b) *Anal. Chim. Acta, 50,* 157 (1970).
13 F.J. Langmyhr and A. Holme, *Anal. Chim. Acta, 35,* 220 (1966).
14 A. Holme and F.J. Langmyhr, *Anal. Chim. Acta, 36,* 389 (1966).
15 L. Danielson, *Talanta, 3,* 138 (1959–60).
16 F.J. Langmyhr and O.B. Skaar, *Acta Chem. Scand., 13,* 2107 (1959).
17 O.B. Skaar and F.J. Langmyhr, *Acta Chem. Scand., 14,* 550 (1960).
18 M. Marcantonatos and B. Liebich, *Chimia, 24,* 447 (1970).
19 F.J. Langmyhr and R.T. Arnesent, *Anal. Chim. Acta, 29,* 419 (1963).
20 R.J. Gillespie and S. Wasif, *J. Chem. Soc.,* 204 (1953).
21 R.J. Gillespie, J.V. Oubridge and C. Solomons, *J. Chem. Soc.,* 1804 (1957).
22 M. Quizano-Rico, *Colloques Nationaux du CNRS,* No. *923,* 367 (1970).
23 R.J. Gillespie and E.A. Robinson, *Can. J. Chem., 40,* 1009 (1962).
24 R.H. Flowers, R.J. Gillespie and J.V. Oubridge, *J. Chem. Soc.,* 1925 (1956).
25 B. Liebich, *Thèse No. 1556,* Université de Genève (1971).
26 A.T. Balaban, A. Arsene, I. Bally, A. Barabás, M. Paraschi and E. Romas, *Tetrahedron Letters,* 3917 (1965).
27 A. Barabás, *J. Coord. Chem., 3,* 91 (1973).
28 M. Marcantonatos and G. Gamba. Results to be published.
29 T.C. Waddington, "Non-aqueous solvent systems", Academic Press, London 1965, p. 164–5.
30 A.W. Kaandorp, H. Cerfontain and F.L. Sixma, *Rec. Trav. Chim., 81,* 969 (1962).