ACTA CHEMICA SCANDINAVICA 13 (1959) 2107–2113

Spectrophotometric Determination of Formula, Rate of Formation and Stability Constant of the Boron 1,1′-Dianthrimide Complex

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The reaction between boron and 1,1′dianthrimide has been investigated spectrophotometrically. By means of the method of continuous variation the mole ratio between the reactants was found to be 1:1. The velocity constant for the formation of the complex in 93.8 % sulphuric acid at 71°C was determined to be $k = 1\,600$ $M^{-1} \cdot h^{-1}$. The stability constant in 93.8 % sulphuric acid and at 70°C was found to be $K = 1.4 \times 10^5$ M^{-1}.

A survey of the literature on the determination of boron with 1,1'-dianthrimide shows that neither the formula nor the stability constant of the complex has been determined previously. Mr. Danielsson [1] of Metallografiska Institutet, Stockholm, has informed the authors that his investigations on the composition of the complex indicate the mole ratio 1:1.

In the present investigation the formula, the rate of formation and the stability constant of the complex have been determined spectrophotometrically.

EXPERIMENTAL

Instruments. Extinction measurements were made with a Zeiss spectrophotometer PMQ II, a matched set of 1.000 cm glass cells being used.

Reagents. Boric acid of reagent grade quality was used for the preparation of standard solutions.

The 1,1′-dianthrimide (E. Merck) was recrystallized twice from nitrobenzene before use.

Sulphuric acid, 95–97 %, and other chemicals were of reagent grade quality. The strength of the sulphuric acid was found to be 96.8 %. Precautions were taken to prevent the acid from absorbing water vapour, and to avoid discoloration by contamination with dust.

Ordinary distilled water from an all metal still was employed.

Standard solutions. 0.5715 g of boric acid (H_3BO_3) were weighed out, dissolved in concentrated sulphuric acid and diluted to 1 000 ml with concentrated sulphuric acid. From this standard solution (containing 100 μg B per ml) 50 ml were pipetted into another

1 000 ml volumetric flask and diluted to the mark with concentrated sulphuric acid. From this latter solution (containing 5 μg B per ml) known amounts of boron were taken.

0.0794 g of 1,1′-dianthrimide were dissolved in concentrated sulphuric acid and diluted to 1 000 ml with the same acid.

Glassware. The different solutions were prepared and heat-treated in 50 ml bottles (*Jena Geräteglas*) with ground-in glass stoppers.

Heat treatment. The heat treatment was given in a thermostatically controlled drying oven of standard construction.

ABSORPTION CURVES

Absorption curves were plotted of solutions of the boron 1,1'-dianthrimide complex and of solutions of 1,1'-dianthrimide.

The solutions measured spectrophotometrically were prepared in the following way. 1 ml of boron standard solution (containing 5 μg boron), 1 ml of distilled water, 11 ml of concentrated sulphuric acid and 5 ml of 1,1'-dianthrimide standard solution were pipetted into a 50 ml bottle *. The concentration of sulphuric acid in the final solution was 93.8 %. After mixing the solution was heated for 16 h at 70° ± 2°C. The corresponding blank solution contained 1 ml of distilled water, 12 ml of concentrated sulphuric acid and 5 ml of 1,1'-dianthrimide standard solution. Heating time and temperature were as described for the sample solution.

Fig. 1, Curve 1 gives the absorption curve of the boron 1,1'-dianthrimide complex measured against the blank solution. Curve 2 shows the absorption curve of the 1,1'-dianthrimide blank solution measured against concentrated sulphuric acid.

The boron 1,1'-dianthrimide complex has a distinct maximum at 630 mμ. At lower wavelengths there are other, smaller maxima. The maximum at 630 mμ is suitable for the spectrophotometric determination of boron. At 630 mμ the Beer—Lambert law is followed up to at least 7 μg B per 17.6 ml, the molar extinction coefficient for the system being $\varepsilon = 1.97 \times 10^4$.

DETERMINATION OF FORMULA

Job's [2] method of continuous variation, as modified by Vosburgh and Cooper [3], was employed for elucidating the composition of the complex.

According to Job's method the extinctions are measured for series of solutions in which the sum of the concentrations of boron and 1,1'-dianthrimide is kept constant, while the ratio between the reactants is varied.

The series of solutions needed for the determination of the formula were prepared from the standard solutions of boron and 1,1'-dianthrimide (*vide supra*). Each sample solution was finally measured against a corresponding blank containing the same amount of 1,1'-dianthrimide. The concentration of sulphuric acid in the final solutions was again 93.8 %.

In the amounts of boron taken are included boron present as impurity in the reagents. The constant concentration of boron in the 17.6 ml reagent solutions was found to be 0.19×10^{-5} mole. The sample solutions were heated for 16 h at 70° ± 2°C. On the other hand, the blanks were not heated. By this

* Due to contraction the final volume is not 18.0, but 17.6 ml.

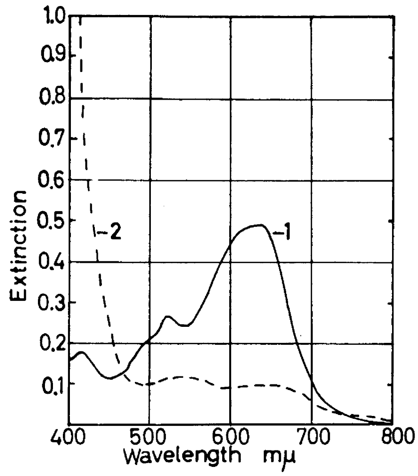


Fig. 1. Curve 1, Absorption curve of the boron 1,1'-dianthrimide complex in 93.8 % sulphuric acid. Curve 2, Absorption curve of 1,1'-dianthrimide in 93.8 % sulphuric acid.

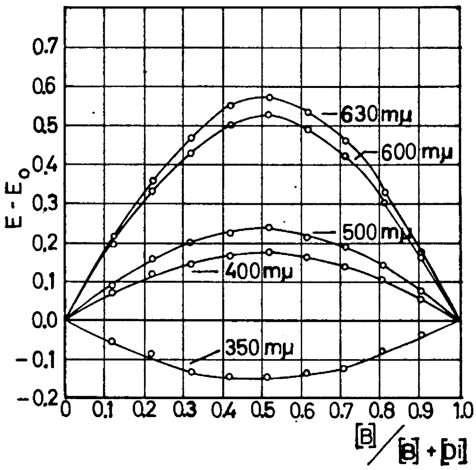


Fig. 2. Curves of continuous variation for mixtures of boron and 1,1'-dianthrimide.

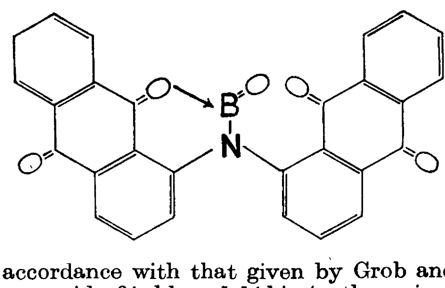
procedure the colour originating from the boron present in the blanks was not developed.

The extinctions were measured at five different wavelengths to guard against the possibility that more than one complex is present. Measurements, in which the sum of concentrations of boron an 1,1'-dianthrimide is varied, have not been carried out.

In Fig. 2 the curves of continuous variation are plotted. It is seen that negative extinction values were obtained for the curve plotted at 350 mμ. At this wavelength the blank solutions absorb more than the corresponding sample solutions.

From Fig. 2 it can be concluded that the mole ratio of boron to 1,1'-dianthrimide is 1:1.

Structure of the complex. Having determined the mole ratio of the complex, it is possible to suggest the following structure of the boron 1,1'-dianthrimide complex in solution.



The structure is in accordance with that given by Grob and Yoe [4] for the complex between boron and 5-benzamido-6'-chloro-1,1'-bis (anthraquinonyl) amine.

DETERMINATION OF RATE OF REACTION

In concentrated sulphuric acid boron (assumed to be present as metaboric acid, HBO_2) and 1,1'-dianthrimide react at a very slow rate. The rate of reaction increases with the temperature, but even at 70°C the colour is developed relatively slowly.

In the present investigation the progress of the reaction between boron and 1,1'-dianthrimide was followed spectrophotometrically. On the basis of these kinetic studies the reaction velocity for the formation of the complex was determined.

The experimental details were as follows: 12 sample solutions were prepared, each consisting of 1 ml of distilled water, 10 ml of concentrated sulphuric acid, 2 ml of boric acid standard solution (corresponding to 10 μg B) and 5 ml of 1,1'-dianthrimide standard solution. In addition a blank solution was prepared, in which the volume of boric acid solution was replaced by 2 ml of concentrated sulphuric acid. All sample solutions were placed in the drying oven at 71° $\pm$0.5°C and heated for different periods of time. After the prefixed time of heating, 2 sample solutions were removed, cooled in the air to room temperature and the extinction was measured against the unheated blank. In the extinctions given in Table 1 for the sample solutions are also included the contribution from the constant amount of boron present as impurity, *viz.* 0.19×10^{-5} mole B per 17.6 ml reagent solution. Corrections were further made for the different amount of free 1,1'-dianthrimide present in sample and blank solutions. The corrected extinction data are given in Table 1.

Table 1. Formation of boron 1,1'-dianthrimide complex in 93.8 % sulphuric acid at 71°C. Extinction (1 000 $\times$ E) for solutions heated for the specified number of hours after the removal of the first pair of sample solutions from drying oven.

Heating time, h	0	2	4	6	18	43
Average E of 2 samples (1)	104	231	326	369	594	720
Blank (not heated) (2)	10	9	8	7	5	3
Increase of E (1−2)	94	222	318	362	589	717

The following, rate-determining mechanism of reaction between metaboric acid (HBO_2) and 1,1'-dianthrimide ($(Anthra)_2NH$) is suggested:

	$(Anthra)_2NH$ +	HOBO $\rightleftharpoons$	$(Anthra)_2NBO$ +	H_2O
Concentrations at the time $t = 0$	a	b	0	y
Concentrations at the time t	$a - x$	$b - x$	x	y
Concentrations at the time $t = \infty$	$a - z$	$b - z$	z	y

The reaction takes place in concentrated sulphuric acid, and the water formed is taken up by the acid. The concentration of water (y) can then be considered constant.

The following kinetic equation is obtained for the formation of the complex:

$$\frac{dx}{dt} = k(a-x)(b-x)-k''xy \tag{1}$$

where k and k'' are the velocity constants of the forward and the reverse reaction, respectively.

Further $k''y = k'$ and $K'/y = K$, where K' is the stability constant of the complex. In this investigation y was considered constant at a constant concentration of sulphuric acid, and K was introduced as apparent stability constant. By introducing these values in eqn. 1 and integrating between x_1, t_1 and x_2, t_2 the following expression is obtained for k:

$$k = \frac{2.303 \cdot \log\left[\frac{a+b+1/K+\sqrt{\ }-2x_2}{a+b+1/K-\sqrt{\ }-2x_2} \cdot \frac{a+b+1/K-\sqrt{\ }-2x_1}{a+b+1/K+\sqrt{\ }-2x_1}\right]}{[t_2-t_1]\sqrt{\ }} \tag{2}$$

The square root sign $\sqrt{\ }$ stands for $\sqrt{(a+b+1/K)^2-4ab}$.

To calculate k from eqn. 2, it is necessary to know K (the apparent stability constant) and the constant impurity of boron originating from the reagents. By means of methods described below approximative data for K and the constant impurity of boron were obtained experimentally, and these data gave a preliminary value of k. This first value of k was employed to adjust the data for K and the constant impurity of boron, and these improved data were again used to correct k. The approximations were carried out until constant values were obtained. The final values were:

$$K = 1.4 \times 10^5 \ \mathrm{M}^{-1}$$
$$k = 1\ 600 \ \mathrm{M}^{-1} \cdot \mathrm{h}^{-1}$$

These data are valid in 93.8 % sulphuric acid and at 70° and 71°C, respectively.

The constant impurity of boron was found to be 0.19×10^{-5} mole B per 17.6 ml of reagent solution.

The experimental data (Table 1) gave a constant value of k, thus confirming the validity of eqn. 1.

DETERMINATION OF APPARENT STABILITY CONSTANT

The following expression is obtained for the apparent stability constant K of the boron 1,1'-dianthrimide complex:

$$K = \frac{z}{(a-z)(b-z)}$$

For experimental determination of K, the two concentrations in the denominator should preferably be of approximately the same magnitude, and should not differ too much from that of the numerator. These conditions are obtained by choosing small and nearly equal concentrations of the reactants.

The usual equilibrium measurements were not suitable for the determination of the apparent stability constant of the present system. Prolonged heating of solutions of 1,1'-dianthrimide resulted in destruction of considerable amounts of reagent. The following, special procedure was therefore introduced.

A series of sample solutions were prepared according to the formula:

1 ml of distilled water $+ (17-v_1-v_2)$ ml of concentrated sulphuric acid $+v_1$ ml of boron standard solution $+ v_2$ ml of 1,1'-dianthrimide standard solution.

In one series of experiments v_1 was 1.2 ml while v_2 was 2, 3.5 and 5 ml. In another series v_1 was 2 and v_2 was 1.5, 2 and 3 ml. Blank solutions were not prepared, but the extinctions due to the amount of 1,1'-dianthrimide not taking part in the reaction were calculated (Specified as Blank in Table 2).

The sample solutions were then heated for 40 h at 70° $\pm$ 2°C. By this procedure the solutions were brought near equilibrium without destructing appreciable amounts of 1,1'-dianthrimide. After cooling, the extinctions (E_{40}) were measured against concentrated sulphuric acid. These extinction data gave an approximative value of K (applied for the preliminary determination of k). The final, equilibrium extinction values ($E\infty$) were determined by calculating the difference ($E\infty - E_{40}$). This relatively small correction to the E_{40} data was found by approximation as described above. From the data for $E\infty$ the equilibrium concentration of complex was found with the application of the molar extinction coefficient ($\varepsilon = 1.97 \times 10^4$). Equilibrium concentrations of boron and 1,1'-dianthrimide could then be calculated.

Table 2. Spectrophotometric determination of apparent stability constant of the boron 1,1'-dianthrimide complex. (70°C and 93.8 % sulphuric acid.)

	Extinctions (1 000 × E_{40}) at the concentrations specified					
Concentration of boron/1.05 × 10^{-5} M	3.18	3.18	3.18	5.18	5.18	5.18
Conc. of 1,1'-dianthrimide/1.05 × 10^{-5} M	2.00	3.50	5.00	1.50	2.00	3.00
Average E_{40} for 2 samples (1)	272	406	503	252	330	468
Blank (2) (calculated)	1	3	6	1	1	1
Corrected, average E_{40} values (1−2)	271	403	497	251	329	267
$E\infty - E_{40}$	32	36	27	10	15	26
$E\infty$	303	439	524	261	344	493
Calculated apparent stability constant $K/10^5$ M^{-1}	1.54	1.39	1.53	1.35	1.39	1.38

From the data in Table 2 the average value of 1.4 × 10^5 M^{-1} was obtained for the apparent stability constant of the complex in 93.8 % sulphuric acid.

An approximative value for the constant impurity of boron present in the reagents was found spectrophotometrically. Two identical blank solutions were prepared, and one of the solutions was heated for 40 h at 70°C. The extinction of this solution was measured against the solution not heated and the content of boron was calculated to be 0.16×10^{-5} mole B per 17.6 ml reagent solution. This value was employed for the preliminary calculation of k.

REFERENCES

1. Danielsson, L. *Private communication.*
2. Job, P. *Ann. Chim.* **9** (1928) 113.
3. Vosburgh, W. C. and Cooper, G. R. *J. Am. Chem. Soc.* **63** (1941) 437.
4. Grob, R. L. and Yoe, J. H. *Anal. Chim. Acta* **14** (1956) 253.

Received June 25, 1959.