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Effect of Temperature and Concentration of Sulphuric Acid on the Rate of Formation of the Boron 1,1′-Dianthrimide Complex

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The effect of temperature and concentration of sulphuric acid on the rate of formation of the boron-1,1′-dianthrimide complex has been investigated spectrophotometrically. Series of solutions containing boron, 1,1′-dianthrimide and varying amounts of water were prepared and heated at four different temperatures. At intervals solutions were removed and measured photometrically. On the basis of the extinction data velocity constants were calculated. An empirical equation was derived for the influence of temperature and concentration of sulphuric acid on the velocity constant. The velocity constant is redoubled either by an 8°C increase of temperature, or by a decrease of concentration of sulphuric acid corresponding to the difference between 100.6 % sulphuric acid and the strength of the initial acid.

In the literature qualitative indications are given on the effect of temperature and concentration of sulphuric acid on the development of the colour of the boron 1,1'-dianthrimide complex. Ellis, Zook and Baudisch[1] state that 3 h heating at 90°C or 5 h heating at 80°C is necessary to develop the colour. According to Otting[2] the rate of colour formation increases with increasing water content. In a previous paper the authors[3] have described the determinations of formula, rate of reaction and stability constant of the boron 1,1'-dianthrimide complex. The solvent applied in these investigations was 93.8 % sulphuric acid, and the rate of reaction and the stability constant were determined for solutions heated at 71° and 70°C, respectively.

The present paper describes the effect of temperature and concentration of sulphuric acid upon the rate of reaction of the complex.

EXPERIMENTAL

Instruments. Extinction measurements were made with a Klett-Summerson spectrophotometer equipped with a B 650 filter. (In the authors previous publication[3] the absorption maximum of the boron 1,1′-dianthrimide complex was found at 630 mμ.)

Reagents. The 1,1'-dianthrimide (E. Merck) was recrystallized twice from nitrobenzene before use. Boric acid, sulphuric acid (95—97 %), and other chemicals were of reagent grade quality. The strength of sulphuric acid was found to be 96.8 %. The acid was protected against absorption of water vapour and contamination with dust.

Glassware. Reagent solutions were prepared in 50 ml bottles (Jena *Geräteglas*) with ground-in glass stoppers. The solutions were heated in specially made photometric cells, prepared from ordinary soda glass tube (14 mm outer, 12 mm inner diameter). The length of these cells was about 20 cm. The cells were marked to keep them in the same position during photometric measurement.

Heat treatment. This was given in a thermostatically controlled water bath. The temperature of the bath varied regularly about the prefixed temperature, the maximum deviations being ± 2°C.

Standard solutions. 0.5715 g of boric acid were weighed out, dissolved in concentrated sulphuric acid and diluted to 1 000 ml with the same 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 volume 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.

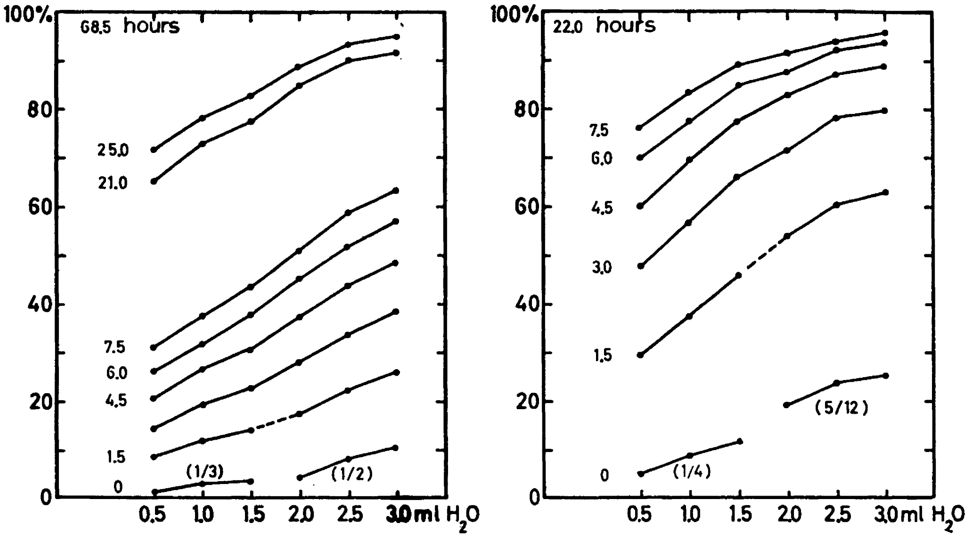
Preparation of reacting solutions. Reaction mixtures of boron and 1,1'-dianthrimide were prepared according to the formula: X ml of distilled water + (14—X) ml of concentrated sulphuric acid + 1 ml of boron standard solution + 5 ml of 1,1'-dianthrimide standard solution. The following values of X were chosen: 0.5—1.0—1.5—2.0—2.5 and 3.0. In a series of corresponding blank solutions the volume of boron standard solution was replaced by concentrated sulphuric acid. The solutions were pipetted into 50 ml bottles and were thoroughly mixed. Suitable amounts were then transferred to the photometric cells. To prevent uptake of water vapour during the heating period the cells were fitted with rubber stoppers. Four different series of solutions were prepared according to the formula given above, each series being heated at one of the following mean temperatures: 49.5—67.0—71.0 and 79.8° C.

PHOTOMETRIC MEASUREMENTS

The six reacting solutions and their corresponding blanks (all belonging to one temperature series) were placed in the water bath. At 1 to 1.5 h intervals a solution and its corresponding blank were removed and the extinction of both was measured against distilled water. A constant time of 10 min was employed for photometric measurement. The reacting solutions were finally brought near equilibrium by heating them for an extended period of time varying with the temperature applied. (Excessive heating resulted in destruction of considerable amounts of 1,1'-dianthrimide). The extinction data obtained were corrected for the absorption of the cells (filled with distilled water) and for the absorption of the blanks. The final, corrected extinction values are given in Figs. 1a, b, c and d. The data are given in per cent of the final extinction value obtained after the heating time specified in the figures. The values in Fig. 1 given in parenthesis for zero time indicate time of preheating period.

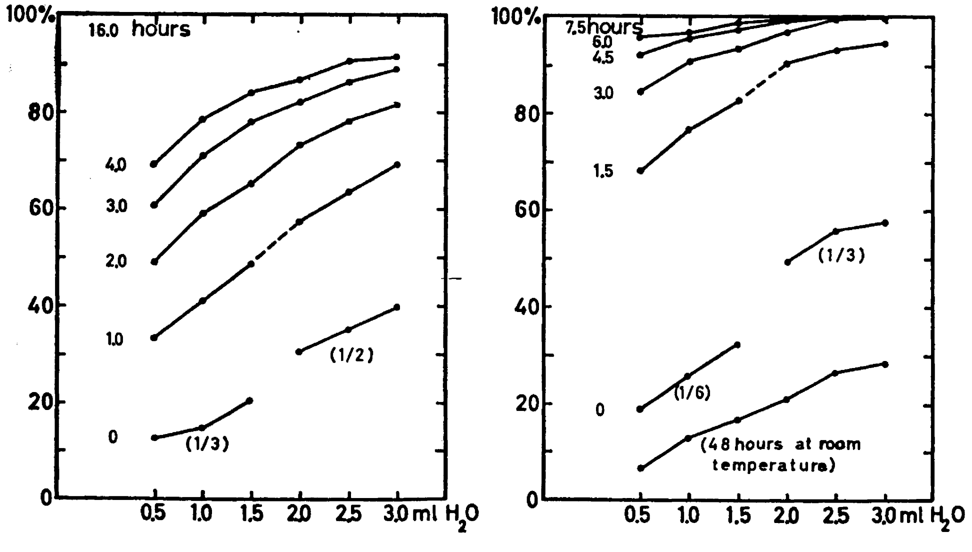
DISCUSSION

Figs. 1a, b, c and d show that the rate of complex formation increases with the temperature and the content of water. In order to develop an approximate expression for the influence of these factors on the rate of reaction the



a. (49.5°C)

b. (67.0°C)



c. (71.0°C)

d. (79.8°C)

Fig. 1a, b, c and d. The effect at different temperatures and heating times of concentration of sulphuric acid on the formation of the boron 1,1′-dianthrimide complex.

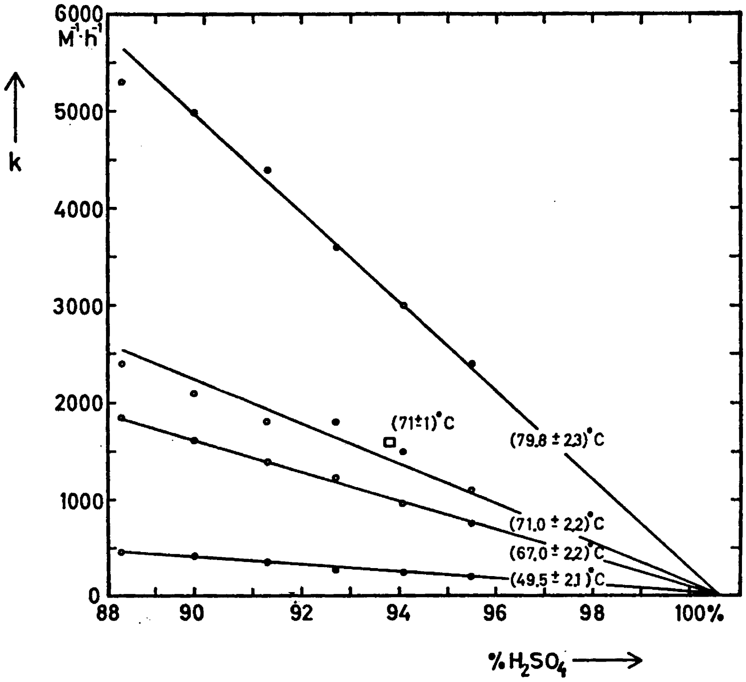


Fig. 2. The effect at different temperatures of concentration of sulphuric acid on the velocity constant of the boron 1,1'-dianthrimide complex.

following assumptions were made. The time of heating *t* employed in the calculations is the observed time of standing in the water bath. It was assumed that the reduced rate of reaction during photometric measurement corresponds approximately to the lowered rate of complex formation during reheating in the water bath. The assumptions were further made that equilibrium is attained at the final extinction measurements, and that the contamination of boron originating from the reagents is compensated for by subtracting the extinction of the blanks. The stability constant [3] $K = 1.4 \times 10^5$ M^{-1} was applied, and this value was considered constant within the temperature range 50°—80°C and concentration range 88.3—95.5 % sulphuric acid. All concentrations were calculated on the basis of a volume of 19.6 ml (19 ml of concentrated sulphuric acid plus 1 ml of water). In cases where the starting volume differed from 19.6 ml, corrections were made by multiplication with $19.6/V$, where V (in ml) was the volume in question. The original concentrations of boron and 1,1'-dianthrimide were 2.36×10^{-5} M and 29.7×10^{-5} M, respectively. The amount of boron not complexed at equilibrium was $2.3 \times 10^{-5} / (1.4 \times 10^5 \times 27.4 \times 10^{-5}) = 0.06 \times 10^{-5}$ M. The molar concentration of the boron 1,1'-dianthrimide complex (X) determined spectrophotometrically was $X = p\ (2.36 - 0.06) \times 10^{-5}/100$ where p is the percentage of maximum extinction. In the authors earlier publication[3] an expression for the velocity constant k was developed. Taking into consideration the assumptions made above, the original equation is transformed to:

$$k = \frac{2.303 \times V}{(t_2 - t_1) \times 19.6 \times 28.16 \times 10^{-5}\ \mathrm{M}} \log \frac{13.1 - p_2/100}{13.1 - p_1/100} \cdot \frac{100 - p_1}{100 - p_2}$$

This equation was then applied to calculate the velocity constants given in Table 1.

Due to the simplifications made, the values based on first and second extinction measurement are considered to be more reliable than those based on second and third. The values for k based on first and second measurement are also shown in Fig. 2 (the room temperature values are not included in this figure).

Table 1. Velocity constants at different temperatures and concentrations of sulphuric acid.

Temperature °C	Time interval in hours	Velocity constants in $M^{-1} \cdot h^{-1}$ at the following concentrations of sulphuric acid (%):					
		95.5	94.1	92.7	91.3	89.8	88.3
Room temperature	0 –48.0	5	10	13	16	21	23
49.5	0 – 1.5	190	240	270	360	410	460
49.5	1.5– 3.0	170	220	250	330	400	440
67.0	0 – 1.5	750	950	1 220	1 400	1 620	1 740
67.0	1.5– 3.0	760	960	1 210	1 240	1 510	1 550
71.0	0 – 1.0	1 100	1 500	1 800	1 800	2 100	2 400
71.0	1.0– 2.0	1 000	1 400	1 500	1 800	2 000	2 000
79.8	0 – 1.5	2 400	3 000	3 600	4 400	5 000	5 300
79.8	1.5– 3.0	2 000	2 500	2 600	3 100	(7 900)	(6 100)

It is seen from Fig. 2 that the k values at a constant temperature lie approximately on straight lines converging at at point corresponding to 100.6 % sulphuric acid. (The square seen in Fig. 2 indicates the value of k (1 600 $M^{-1}\ h^{-1}$) determined previously by the authors[3].)

The following empirical equation was finally derived for the influence of temperature and concentration of sulphuric acid on the velocity constant:

$$k_{t,c} = 235(100.6 - c)10^{0.038(t-71)}$$

The indexes t and c indicate the temperature and the concentration of sulphuric acid, respectively, for which the velocity constant is calculated. The formula was developed on the basis of the previously determined value for k, *viz.* $k_{71;\,93.8} = 1\ 600\ M^{-1}\ h^{-1}$. In view of the approximations made, the expression for the velocity constant is assumed to be valid within the ranges $50° < t < 80°C$ and $88.3\ \% < c < 95.5\ \%$ sulphuric acid. It is seen, that the velocity constant is redoubled by an 8°C increase of temperature, or by a decrease of concentration of sulphuric acid corresponding to the difference between 100.6 % sulphuric acid and the strength of the initial acid.

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