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Original Scientific Paper

## An X-ray and Proton Magnetic Resonance Study of the Dehydration and Deuteration of Borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8 \text{H}_2\text{O}$

A. Bezjak\*, I. Jelenić\*, S. Maričić, and Z. Meić

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

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A quantitative powder-x-ray analysis was developed for this case by which it was shown that carefully prepared borax dehydrates directly into an anhydrous amorphous phase. Eight molecules of water are quantitatively lost on complete dehydration (below 50°C) as required by the structural formula. The proton magnetic resonance results agree with these findings showing also that the spectrum due to OH-groups changes considerably on dehydration. This was used in following deuteration (solid/gas) of dehydrated borax. The p.m.r. spectra, the x-ray diagrams, and the measured regain indicate a reconstitution of the borax-lattice towards the formula  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{D}_2\text{O}$ .

### INTRODUCTION

Menzel<sup>1</sup> found that borax loses about seven molecules of water of crystallization on one-year desiccation at room temperature. He also showed that this dehydration may proceed in two ways: either by formation of an amorphous phase, or *via* an intermediate — the pentahydrate. Menzel used the tensiometric method and other means of dehydration and, in a qualitative way, the X-ray powder technique. The crystal structure of borax was not known at that time, and it was regarded as deca hydrate of sodium tetraborate.

Recently, Morimoto<sup>2</sup> solved the crystal structure with the result that borax is in fact an octa hydrate of sodium tetrahydroxotetraborate. On the other hand borax turned out to be a protonic semiconductor whose properties strongly depend on its crystalline water<sup>3,4</sup>. Thus, we thought it was time now to study the actual mechanism of the dehydration of this compound.

Our first approach was a kinetic one<sup>5</sup>, but it met with little success, partly because of the inherent difficulty of the method in which curve fitting of the kinetic data does not necessarily prove a particular dehydration mechanism, as pointed out by Jacobs and Tompkins<sup>6</sup>. We therefore applied the quantitative X-ray analysis in tackling the following problems.

The initial crystal lattice may be retained until achieving a certain dehydration stage which then causes final collapse into an amorphous state. Or, the two phases (original + amorphous) could be present from the very beginning till the end of dehydration, in which case differences within the water

\* Present address: Research Dept. Assoc. of the Yugoslav Cement Producers, Zagreb, P. O. B. 566

of crystallization may exist, such that the amorphous phase ought not to be completely anhydrous.

In addition, the proton magnetic resonance method was used in a complementary way, and particularly for: a) characterizing the amorphous state; b) following a partial deuteration experiment in an attempt to get resolved spectra, thus avoiding the difficulties in interpretation met with before<sup>7</sup>.

#### EXPERIMENTAL

##### Sample preparation

It has been experienced<sup>5</sup> that commercial analytical grade borax forms pentahydrate on dehydration even at room temperature, and that a double recrystallization with cooling from somewhat below 50° C to 0° C is also not satisfactory. Further, it was impossible to obtain by grinding and subsequent sieving (< 53 μ) a sample that would secure good reproducibility of X-ray measurements. Besides, any grinding before dehydration ought to be avoided. The samples which proved to be good for use in this work were eventually obtained in the following way: a saturated solution of borax in redistilled water was prepared at 40° C. It was then rapidly cooled under vigorous stirring to -10° C. The precipitated borax was quickly filtered and left over a saturated solution of sodium chloride and saccharose. After it attained constant weight the loss on dehydration over P<sub>2</sub>O<sub>5</sub> under vacuum (approx. 10<sup>-1</sup> mmHg) at 45° C was determined and it corresponded to a loss of eight moles of water. The result of ignition at 600° C was in good agreement with a loss of 8 H<sub>2</sub>O + 4 OH (equivalent to 10 H<sub>2</sub>O) from a formula unit of borax.

Partially dehydrated samples were obtained by desiccating the original borax over P<sub>2</sub>O<sub>5</sub> at room temperature under normal pressure.

Deuteration was done by leaving at room temperature a completely dehydrated borax (loss of 8 M H<sub>2</sub>O) over a NaCl-saccharose saturated D<sub>2</sub>O-solution. The regain was determined by subsequent dehydration at 45° C under vacuum, and the results calculated by assuming that in all these operations the OH-content remained intact.

##### X-ray measurements

A »Philips« diffractometer and counter were used with CuK radiation.

The internal standard (MgCO<sub>3</sub>) was used for determining the composition of dehydrated samples.

The coefficient  $\alpha$  in the relation

$$\frac{I_b}{I_s} = \alpha X_b \quad (1)$$

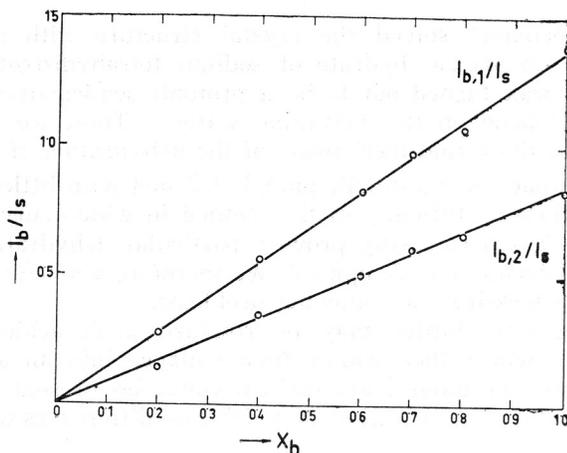


Fig. 1. The calibration-diagram for the quantitative X-ray analysis of borax + amorphous phase mixtures

was determined by preparing a series of artificial mixtures. The amount of the original borax was varied by mixing with MgO, and then adding 30% of MgCO<sub>3</sub>. The ratio of the borax line intensity ( $I_b$ ) to the intensity of the standard ( $I_s$ ) is plotted in Fig. 1. vs.  $X_b$ , the relative amount of borax in the mixtures. The lines  $d_1 = 2.83 \text{ \AA}$  and  $d_2 = 2.65 \text{ \AA}$  for borax, and  $d = 2.71 \text{ \AA}$  of MgCO<sub>3</sub> were chosen for this purpose. A least squares fit of the straight lines in Fig. 1 yields  $\alpha_1 = 1.186$  and  $\alpha_2 = 0.726$  for the respective borax lines.

In order to have a check on the homogeneity of the mixtures of partially dehydrated borax samples with 30% MgCO<sub>3</sub>, two independent ones were prepared in each case. With two intensity measurements the final value of  $X_b$  is a mean of four determinations.

#### Proton magnetic resonance measurements

A conventional bridge type apparatus was used as before<sup>7</sup>, but care was taken in handling the dehydrated and deuterated samples under anhydrous conditions like on another occasion<sup>8</sup>.

#### RESULTS

It was necessary in the X-ray work to establish first which, if any, reflections in the original pattern of borax change the intensities on dehydration. Indexing of the powder photographs was therefore done using Morimoto's<sup>2</sup> data with subsequent calculation of the contribution of all atoms for any particular reflection-intensity.

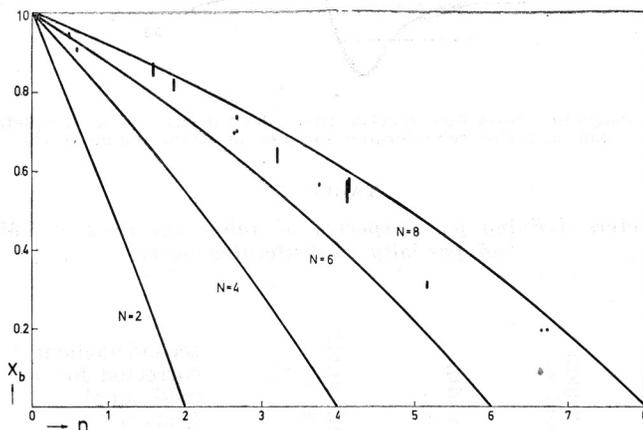


Fig. 2. Graphical presentation of eq. 2 with the experimentally determined points by independent measurements of:

- $n$ , number of moles of H<sub>2</sub>O lost from the original borax, and
- $X_b$ , the relative amount of borax in partially dehydrated samples.

It was found that oxygen atoms of the molecules of water of crystallization are most important for the contribution to the intensities of these reflections: 021, 022, 221, 400, 132, 421, 332, and 422. It was also established that their mutual intensity-ratios do not change on dehydration. This enabled the use of the internal standard method in determining the amount ( $X_b$ ) of original borax in any dehydrated sample in the presence of the amorphous phase.  $X_b$ 's and the corresponding values of  $n$  (= number of moles of water lost from the original sample of borax) are two independent sets of

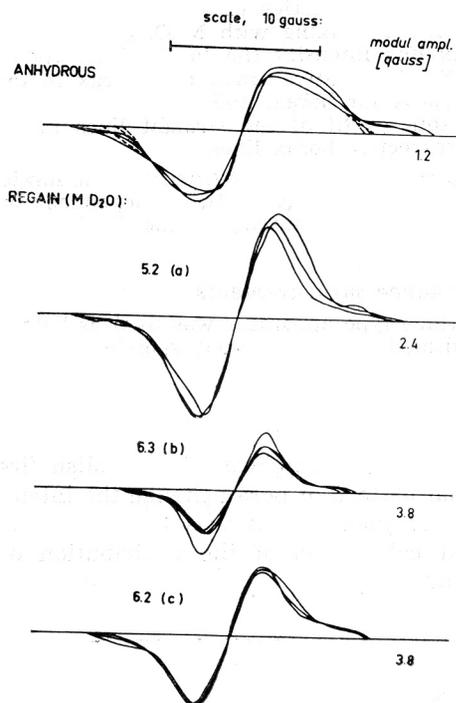


Fig. 3. Proton magnetic resonance spectra (first derivatives) of a completely dehydrated and partially re-deuterated samples at room temperature.

TABLE I

Parameters defining p.m.r. spectra of anhydrous (loss of 8 M H<sub>2</sub>O) and partially re-deuterated borax

sample	time of exposure to D <sub>2</sub> -vapours (months)	D <sub>2</sub> O-regain (in moles)	line-width (gauss)	modul. amplit. (gauss)	second moment, corrected for mod. ampl. (gauss <sup>2</sup> )
anhydrous			6.0 ± 0.5	1.2	10.9 ± 0.9 (total) 8.0 ± 0.8 (without wings; see Fig. 3)
a	3	5.2	4.5 ± 0.2	0.7	6.8 ± 0.9
a	5	5.7	3.3 ± 0.2	1.2	5.6 ± 0.7
b	7	6.3	4.0 ± 0.1	3.7	1.6 ± 0.2
c	13	6.2	4.2 ± 0.2	3.7	1.5 ± 0.6

experimentally determined parameters (see Figure 2) which are later used in the discussion of the dehydration mechanism.

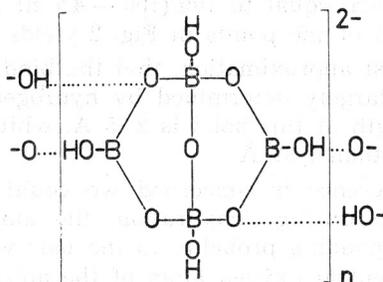
First derivative proton magnetic resonance spectra were also recorded (at room temperature) for samples which lost 1.0, 1.5, and 4.4 moles H<sub>2</sub>O.

Their shapes were practically identical with the corresponding line-shape of original borax<sup>7</sup>. The ratios of the peak-heights of the narrow to the broad component were (1.8 for original borax) 1.5, 2.2, and 2.4 in the order of increased dehydration. The probable error in these values is about 10%.

Proton magnetic resonance spectra of a completely anhydrous (amorphous) sample and of subsequently deuterated ones are given in Fig. 3. The characteristic parameters obtained from these spectra are collected in Table I. The deuterated samples were checked by x-rays and well developed borax patterns were found. In some cases small amount of tinalconite (the pentahydrate phase) seemed to be present too. Complete rehydration was not achieved: samples exposed to D<sub>2</sub>O vapours for about a year had a regain of some 6 moles of water. However, Fig. 3 shows that the line sharpens with rehydration. In Table I second moment values corrected for modulation broadening are given. The anhydrous spectrum shows wings, which are observable in the deuterated spectra too. We quote two second moments for the anhydrous spectrum: a) corresponding to the total line (including wings) and b) the other obtained by neglecting wings (see Fig. 3). All the other second moment values are due to total lines. These data confirm that, the closer the rehydration is to the state of original borax the narrower the proton magnetic resonance line. The important fact is, that this proton magnetic resonance line is present in spite of ample time for a D-H exchange.

#### DISCUSSION

In the dehydration of borax by Menzel<sup>1</sup> there was no constant-weight attainment after one year of desiccation. The final value obtained corresponded to a loss of 7 moles of water. The present experiments on complete dehydration (loss of 8 H<sub>2</sub>O) are in excellent agreement with Morimoto's<sup>2</sup> formula of borax. It is not surprising that two »molecules of water« are retained, as these are actually OH-groups used in hydrogen bonding of the anionic units of borax into infinite chains:



Loss of them would imply a disruption of these chains requiring substantially greater energies than the thermal energy available at the applied dehydration conditions. Differential thermal analysis<sup>9</sup> indicates maxima at higher temperatures (up to 202° C), which are possibly associated with the removal of OH-groups.

The fact that the intensity-ratios in X-ray diagrams did not change on partial dehydration of borax confirmed that the method of preparation of original borax secured the direct transformation of the crystal lattice of borax into an amorphous state. Thus, at any given stage of dehydration we have only two phases: one is crystalline (original borax) and the other is amorphous. As for the latter one, it may contain a certain number of water molecules, or it may be an anhydrous phase (loss of 8 moles of  $H_2O$ ).

The distinction between the two mechanisms can be made by a quantitative discussion of the X-ray results. In order to do this the following equation was derived (see Appendix):

$$X_b = \frac{100(N - n)}{N \cdot (100 - 4.7n)} \quad (2)$$

which relates the relative amount of original borax ( $X_b$ ) in the partially dehydrated mixture as determined by the internal standard method, to the number of moles of water ( $n$ ) lost (calcd. on the original-sample basis) as obtained by weighing.  $N$  in this equation is the number of moles of water lost per one mole of the dehydrated part of the sample, which we want to determine.

Now, in principle,  $N \leq n$ .  $N = n$  means that the whole specimen is amorphous. The complete-dehydration result (loss of 8  $H_2O$ ) sets the upper limit,  $N = 8$ . The symmetry of the crystal structure of borax<sup>2</sup> requires that these 8 molecules of water of crystallization are grouped in pairs. Thus,  $N$  may assume only even numbers up to 8. In Fig. 2 the relationship of eq. (2) is shown graphically for (assumed) constant values of  $N = 2, 4, 6,$  and  $8$ . The experimental points in the same figure lie between the theoretical curves corresponding to an amorphous state that has lost 6 or 8 moles of water. By rearranging equation (2) and with subsequent least-square minimization we obtain:

$$N = \frac{\sum f_1^2(n)}{\sum f_1(n) f_2(n) - \sum X_b \cdot f_2(n)} \quad (3)$$

where  $f_1(n)$  and  $f_2(n)$  are equal to  $100/(100 - 4.7n)$  and  $100n/(100 - 4.7n)$  respectively. The best fit of the points in Fig. 2 yields  $N = 7.4$ .

We assume, to a first approximation, that the binding of water molecules in the borax lattice is largely determined by hydrogen bonding. For one of the water pairs the length of this bond is 2.75 Å, while the other three have hydrogen bonds longer than 2.82 Å.

As far as this difference is concerned we could expect  $N$  to equal 6, which would mean that during dehydration, the amorphous phase retains 2 moles of water corresponding probably to the pair which has the strongest hydrogen bond to the central oxygen atom of the anionic ring. However, the best fit indicates  $N$  larger than seven. In fact, the more complete the dehydration the closer are the experimental points to the theoretical curve for an anhydrous amorphous phase. The deviation from the ideal ( $N = 8$ ) curve is possibly due to high rehydration ability of the amorphous phase during intermediate stages. Thus, although the bulk of the amorphous phase is completely anhydrous, small, but finite distribution of amorphous »lattices« with  $N < 8$  cannot be excluded.

Molecules of water of crystallization in borax are arranged octahedrally around sodium ions, forming infinite channels along the c-direction<sup>2</sup>. Thus, the dehydration-mechanism which satisfies formation of an anhydrous phase in the presence of the original crystal structure of borax would be the penetration of the dehydration-zone along the »water-channels«.

A linear kinetics is predicted for dehydration along a preferred crystallographic orientation within each grain (in a powdered sample)<sup>10</sup>. Such was the case in the kinetics-experiments<sup>5</sup> though the dehydration proceeded in a combination of the two possible ways. (The energy of activation was found to be  $18.2 \text{ Kcal/M} \pm 10\%$ ). The data collected in preparing the present samples for the X-ray work also lie on a straight line. The geometry of the dehydrated samples varied greatly, which would exclude a different interpretation of the linear kinetics<sup>11</sup>.

The proton magnetic resonance results obtained on partially dehydrated samples are in agreement with the conclusions reached by the x-ray study. However, if the narrow line, which the present results prove to be due to the OH-protons, were the same in the amorphous phase, then the peak-height ratio (narrow to broad) ought to double at 50% dehydration. This was not observed. This ratio remained practically unchanged, while the line shape resembled closely the borax-spectrum. That the latter shape is so dominant may only be explained by a different shape of the »amorphous« OH-line. According to Fig. 3. it is about three times as broad as in the original borax. Its contribution to the total line at 50% dehydration is only 6 per cent. Hence a seemingly unchanged borax-line.

The removal of water of crystallization must necessarily leave behind a disordered (x-ray amorphous) phase, because the anionic chains are interconnected to the cationic »water-channels« through several hydrogen bonds. However, there is no special reason to expect breaking of the hydrogen bonds which connect the anionic units within the chains. The largest contribution to the OH-line in proton magnetic resonance spectra is from the two closest hydrogens in these pairs of hydrogen bonds. Thus, in spite of a X-ray bulk disorder, we would rather not expect a change in the OH-line shape of the anhydrous amorphous state as compared to the OH-line in original borax.

This comparison is not easily made due to overlapping of the broad and the narrow part of the p. m. r. line at room temperature, to which other difficulties add if low temperature spectra of borax are to be considered<sup>7</sup>. Dharmatti *et al.*<sup>12</sup> claim an intensity ratio of 4 : 1 for the broad to the narrow component as required by Morimoto's formula, but we have not been able to obtain any meaningful result in this respect. We also disagree with the latter authors about the width of the OH-line. While they quote a value of as much as 6 gauss, we obtained<sup>7</sup> 2.2 gauss. Unless the sample is equilibrated before measurement as described, the peak-height of this line may vary with preparation, but in no case (including several commercial samples) had we observed any deviation in the width of the OH-line.

The width of the »anhydrous amorphous« OH-line of 6 gauss (see Fig. 3 and Table I) is in good agreement with the result in ref. 12. There, a sample with a loss of 7 moles of water was prepared by heating (obviously via the pentahydrate phase), but the line width of its proton magnetic resonance spectrum is also 6 gauss, and the line-shapes compare favourably. Another evidence that this line-width is much broader than the corresponding one of the original borax is its narrowing on rehydration (see Fig. 3 and Table I). We

obtained only 75% - reconstituted borax lattice, but with appropriate modification of the experimental conditions a complete rehydration may be possible, as suggested by Menzel<sup>1</sup>. However, the OH-line of such a deuterated sample should not be exactly the same as in the ordinary borax because of different magnetic environment (deuterium). Nevertheless, the evidence obtained so far strongly suggests that the »amorphous« OH-line is much broader than the »crystalline« one. We cannot explain this observation, because it was found before<sup>7</sup> that OH-groups undergo some kind of motion in crystalline borax. The broadening of the OH-line in the amorphous phase may be due to restriction in motion, which would be quite unexpected. On the other hand, if the cause of broadening is to be sought in a particular structural change, it is not at all obvious in which way the local magnetic fields at proton sites of the OH-groups in the amorphous phase could increase. Besides, as discussed above, no substantial rearrangement is likely within the infinite anionic chains.

Both this problem, and the mechanism of motion of the water molecules and OH-groups in borax, require further systematic study, in particular with changing temperature. The present results are encouraging, in that preparations of  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_1] \cdot 8 \text{D}_2\text{O}$  and  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OD})_4] \cdot 8 \text{H}_2\text{O}$  seem to be quite feasible. These partially deuterated compounds could yield further information separately on the  $\text{H}_2\text{O}$  and OH-line of the proton magnetic resonance spectrum of borax.

#### APPENDIX

At any given dehydration-stage the weight-percentage of the amorphous phase calculated on the initial-substance basis is given by:

$$A = (100 - \text{CH}_2\text{O}) (1 - \text{X}_b) \quad (2)$$

where:

$\text{CH}_2\text{O}$  = the weight percentage of water lost on the initial-substance basis;

$\text{X}_b$  = the relative amount of borax in the dehydration-mixture = borax/(borax + amorphous phase).

The relative amount of the lost water in the dehydrated part of the sample is

$$\frac{\text{CH}_2\text{O}}{A + \text{CH}_2\text{O}} \quad (3)$$

while the number of moles lost during dehydration per 1 mole of the dehydrated phase ( $A + \text{CH}_2\text{O}$ ):

$$\frac{100 \cdot \text{CH}_2\text{O}}{4.7 (A + \text{CH}_2\text{O})} = N \quad (4)$$

because 1 mole of  $\text{H}_2\text{O}$  is 4.7% of weight of the original borax. In order to express A as a function of N we rearrange Eq. (4), so that

$$A = \frac{100 \cdot \text{CH}_2\text{O} - 4.7 N \cdot \text{CH}_2\text{O}}{4.7 N} \quad (5)$$

On substituting the latter relation into equation (2) it follows

$$1 - \text{X}_b = \frac{(100 - 4.7 N) \cdot \text{CH}_2\text{O}/4.7 N}{100 - \text{CH}_2\text{O}} \quad (6)$$

or,

$$X_b = \frac{470 N - 100 \cdot C_{H_2O}}{4.7 N (100 - C_{H_2O})} \quad (7)$$

If by  $n$  we denote the number of moles  $H_2O$  lost from the total (initial) substance, then

$$C_{H_2O} = 4.7 n \quad (8)$$

which, introduced in equation (7) yields

$$X_b = \frac{100 (N - n)}{N (100 - 4.7 n)}$$

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#### IZVOD

**Istraživanje dehidratacije i deuteriranja boraksa,  $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ , rendgenografski i metodom protonске magnetske rezonancije**

A. Bezjak, I. Jelenić, S. Maričić i Z. Meić

Razrađena je metoda kvantitativne rendgenske analize kojom je ustanovljeno da boraks dehidracijom prelazi direktno u jednu bezvodnu amorfnu fazu. Potpuna dehidratacija (ispod  $50^\circ C$ ) prema strukturalnoj formuli odgovara kvantitativnom gubitku od 8 molekula vode. Rezultati protonске magnetske rezonancije slažu se s ovim nalazima i pokazuju da se spektar koji potiče od OH-grupa bitno mijenja dehidracijom. Ova je pojava iskorištena za praćenje deuteriranja (čvrsto/plin) dehidratiziranog boraksa. Spektri protonске magnetske rezonancije, rendgenogrami i porast težine pokazuju da dolazi do rekonstitucije kristalne strukture boraksa prema formuli  $Na_2[B_4O_5(OH)_4] \cdot 8D_2O$ .

INSTITUT »RUĐER BOŠKOVIĆ«  
ZAGREB

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