*J. Phys. Chem. Solids* Pergamon Press 1962. Vol. 23, pp. 1651–1659. Printed in Great Britain.

# PROTON CONDUCTIVITY IN BORAX, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

**S. MARIČIĆ, V. PRAVDIĆ and Z. VEKSLI**
"Rudjer Bošković" Institute, Zagreb, Yugoslavia

(*Received* 24 *April* 1962)

**Abstract**—Proton conductivity is established by solid state electrolysis experiments on borax powder. There is marked anisotropy in electrical conductivity, the *b*-axis-direction of a single crystal being the most favourable one for protonic conduction. A minimum temperature (~ 21°C) is observed, below which proton conduction ceases. This effect is discussed in relation to the competition between the reorientation rate of protons and their concentration.

## INTRODUCTION

A PROTON transfer mechanism through hydrogen bonds was invoked during the 1940's in order to explain high d.c. conductivity in several solids.(1) It was not until 1951 that KAKIUCHI *et al.*(2) proved this by spectroscopic evidence of hydrogen evolution in electrolysis of solid cetyl alcohol.

Ice has been the almost exclusively studied substance in this respect owing to its ideal three-dimensional continuous hydrogen-bond network. Coulometric measurements(3) on ice (evolution of gas on the cathode) have been regarded as proof of protonic conduction. Ice is nowadays generally accepted as a protonic semiconductor. (The term was independently introduced by RIEHL(4) and BRADLEY(5) and later discussed at length by EIGEN and DE MAEYER.(6)) A breakthrough in the elucidation of the mechanism of proton conductivity in ice was achieved by the latter authors(7) in measuring directly the concentration of the ionic species. In addition to the comprehensive discussion of the problem in Ref. 6, the reader is referred to other general articles which were published quite recently(8) by the Zürich school.

A search of the literature showed, firstly, that solid state electrolysis experiments could be used in a more extensive way than so far, and secondly, that a systematic study of a large number of solid protonic semiconductors with differences in their hydrogen bond networks may prove useful in gaining a more generalized picture of this mechanism.

Our preliminary electrical measurements(9) suggested borax as a potential protonic semiconductor with the *b*-axis-direction of its crystal structure(10) as the most possible path for proton transfer.(11) The present report is part of a study as outlined above.

## EXPERIMENTAL

### I. *Conductivity measurements*

1. *The Cell.* The cell for conductivity measurements was a Perspex holder with silver plated brass piston electrodes. The sample of borax, either a pellet, or a single crystal was held air-tight between the electrodes by means of a spring acting on the upper electrode. The Perspex cell was placed in a glass tube serving as a jacket through which distilled ethanol circulated from a thermostating bath. The temperature was kept constant to ± 0·1°C. For measurements on powder under pressure a press of simple design was used(12) with minor alterations (see Ref. 11 for details).

2. *Circuitry.* For most measurements of d.c. conductivity (resistances of $10^8$ to $10^{11}$ Ω), the current vs. voltage at low fields was measured. Voltages of up to 150 V were applied from a constant voltage source measured by a substandard precision voltmeter. The current was calculated from Ohm's law, taking readings on a vibrating reed electrometer (Vibron 33B, EIL, Richmond) for the potential drop over a series $10^6$ or $10^8$ Ω precision resistor. The output of the electrometer was fed to a recorder, and short term stable values were taken into calculations.

For lower resistances, measured with the powder samples in the press, an a.c. (50 c/s) conductivity bridge was used.

### II. *Electrolysis experiments*

The glass cell was described in detail in an earlier paper.(13) The samples were cemented to the cell by a polyester resin cement (Araldite). Bi-distilled mercury was used as contact to the pellet. The motion of the mercury meniscus in the 1 mm diameter precision bore capillary tube (Veridia) was followed by a cathetometer, or, in case of large displacements, by an attached milimeter scale. The cell had to be thermostated to ± 0·05°C of the desired temperature. This was achieved by circulating water from a 20 l. constant temperature bath through the jacket of the cell. The electric field was applied by a constant voltage power source, and measured by a light spot microammeter. In the first series of experiments the current was recorded on a potentiometric recorder measuring the voltage drop over a precision resistor, and afterwards integrated graphically. Later, an electronic integrator with digital read-out was used. The overall error of the current integration was estimated to be about one per cent.

The evolved gas was introduced into $PdCl_2$ solution. The precipitation of elemental palladium was taken as proof of hydrogen evolution. The gas formed very frequently on both the cathodic and anodic side, but was always hydrogen. It is supposed that this effect is due to diffusion through larger voids in the pellets which are difficult to prepare perfectly.

### III. *Samples*

The samples of ordinary borax were prepared from recrystallized Merck p.a. borax. Rapid cooling of a saturated solution was applied to obtain fine grain borax needed for the preparation of pellets. Deuterated borax was prepared from a dehydrated sample of ordinary borax (loss of 8 $H_2O$) by dissolving it into 99·76 per cent $D_2O$ at 50°C and crystalizing at −10°C. The loss on dehydration under vacuo at 45°C of the deuterated sample corresponded to 8 $D_2O$, while the loss on ignition at 600°C (49·78 per cent) was close to the theoretical amount for 10 $D_2O$ (49·84 per cent). The direct $D_2O$ analysis (falling-drop method) suggested a composition of 9 $D_2O + 1$ $H_2O$.

The pellets were prepared in a hydraulic press of a standard diameter of 13 mm. The pressure had to be applied slowly up to some 300 kg/cm$^2$ in order to avoid creep cracking of pellets. As already described(13) "sandwich" pellets of borax between two layers of graphite powder proved useful.

Single crystals of ordinary borax were grown from saturated solution by slow evaporation at 23°C. The orientation of each single crystal specimen was checked by X-ray back reflection photographs. Appropriate pieces of single crystals (3–5 mm lengths) were cut in the desired direction by a wet Nylon string, ground with fine emery paper, polished with fine alumina in Nujol and rinsed in chloroform before mounting into the cell. Every such specimen was used in a single run and then discarded.

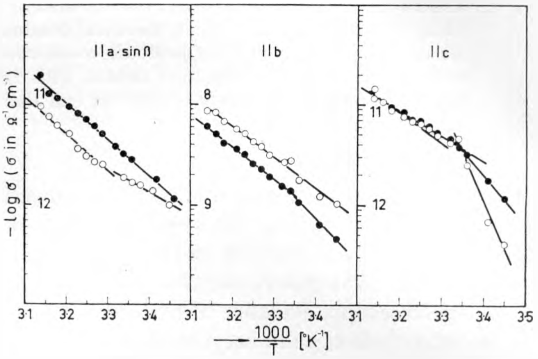

FIG. 1. Specific d.c. conductivity of borax single crystals vs. $1/T$, for three directions of the electrical field (250 V/cm).

## RESULTS

### I. *Conductivity measurements*

1. *Single crystals.* All the measurements of electrical conductivity of borax single crystals were performed at constant fields of 25, 50, 100, 250, and 500 V/cm. No deviations from Ohm's

*Table* 1. *Energies of activation (in eV) for electrical conductivity at different single crystal directions of borax*

| Temperature range | Measurement | Field of 250 V/cm parallel to | | |
|---|---|---|---|---|
| | | $a \sin \beta$ | $b$ | $c$ |
| higher | 1. | 0·72 ± 0·02 | 0·61 ± 0·02 | 0·60 ± 0·10 |
| | 2. | 0·73 ± 0·04 | 0·64 ± 0·01 | 0·49 ± 0·02 |
| lower | 1. | (0·72 ± 0·02) | (0·61 ± 0·02) | 1·92 ± 0·17 |
| | 2. | 0·47 ± 0·04 | 0·85 ± 0·05 | 0·95 ± 0·03 |

law were observed within the above range of fields. The results obtained at 250 V/cm were chosen for representation in Fig. 1, where the notations correspond to the direction of the electric field with respect to the three crystallographic axes. Each set of measurements was carried out with different single crystals. The straight lines were calculated by the least squares method.

The absolute value of the conductivity along the *b*-axis is by three orders of magnitude larger than for the other two orientations. The usual kink$^{(9)}$ in this plot is not reproducible though its presence is clearly indicated. Table 1 contains activation energies calculated from Fig. 1. It follows from these data, that best reproducibility is obtained at higher temperatures and especially for the *b*-direction.

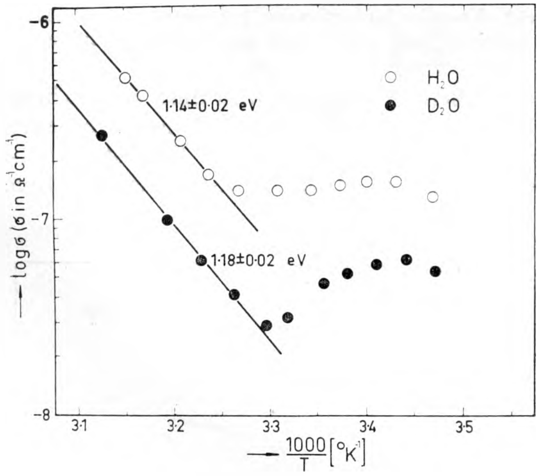

FIG. 2. Specific electrical conductivity (at 50 c/s) of ordinary (open circles) and deuterated (points) borax powder vs. $1/T$, at 6000 atm.

2. *Powder samples* In completing a series of measurements already briefly reported,$^{(9)}$ we found that the particle size greatly influences the results. This was particularly important in view of having to compare conductivities of the ordinary and deuterated borax. A narrow range of particle sizes was therefore sieved (0·105–0·088 mm size) for both of these samples. The results are shown in Fig. 2. The activation energies for both samples were found to be the same within the experimental error. However, the ratio of conductivities $(\sigma_H/\sigma_D)$ is of interest in further discussion, and for the "straight line" temperature range it is about 3·0. Two different temperature regions for the conductivity mechanism in borax$^{(9)}$ are again evident. The characteristic temperature is in the vicinity of 30°C. These measurements were done as the earlier ones at low electric fields (about 20 V/cm).

The validity of Ohm's law was checked by increasing gradually the d.c. voltage applied to either a bare or a sandwich-pellet of borax in contact with mercury in the electrolysis cell. The actual field distribution was unknown and the values of abscissa in Fig. 3 are estimated from the geometry of the experimental arrangement. One may note from this figure that Ohm's law appears to be satisfied at 15°C. Further, an approximate linearity is found at 35°C before and after electrolysis up to some $1{\cdot}5\times10^3$ V/cm. However, at higher field strengths there is a deviation from Ohm's law towards higher conductivities.

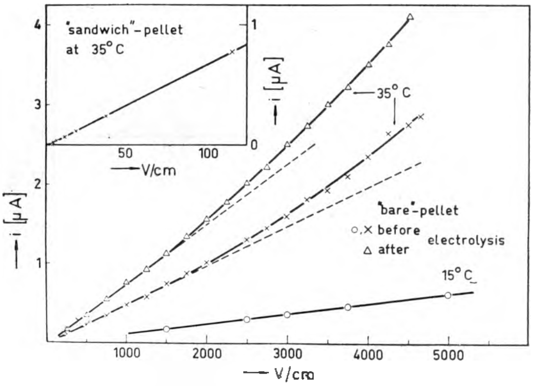

FIG. 3. Test of validity of Ohm's law for borax powder.

## II. *Solid state electrolysis*

All the experiments were done on graphite-borax sandwich pellets to avoid effects of bad contact experienced in similar measurements on lithium sulfate monohydrate.$^{(13)}$

Figure 4 illustrates the general behaviour of the rate of hydrogen evolution. The minimum in this curve is ascribed to the competition between the electro-osmotic penetration of mercury into the graphite layer and the build-up of the hydrogen pressure. If such an experiment is disrupted after steady state conditions have been attained, and afterwards repeated at the same or higher temperatures, no minimum is observed.

It is established from 31 electrolysis experiments, of which 13 were done on fresh pellets, that the current increases (in some cases to a constant value) with time at temperatures above 28°C. There is a decrease or constancy of the current with time for lower temperatures. The observed difference for the two temperature regions is a clear-cut effect for fresh pellets only, but even in experiments with already used pellets no case of rising current was found for temperatures below 32°C. In view of this finding a distinction will be made in further evaluation of the results obtained with "fresh" and "used" pellets.

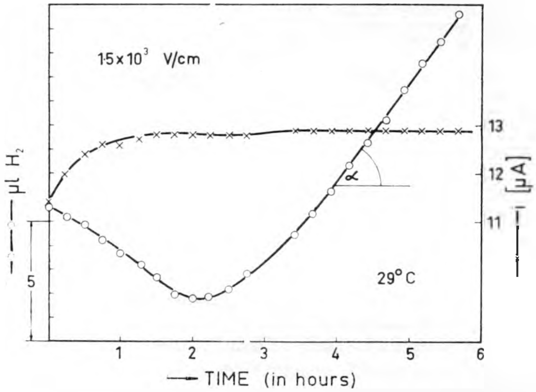

FIG. 4. Solid state electrolysis of borax powder ("sandwich"-pellet). *tg*α taken as measure of the rate of hydrogen evolution.

We choose as a measure of the rate of hydrogen evolution the slope of the straight line portion of the curves such as in Fig. 4 after steady state conditions had been attained. On plotting the logarithm of these slopes for different temperatures vs. 1/T one obtains Fig. 5, which also contains the relevant data of currents measured in the same experiments.

As all the results indicate two different temperature regions of the electrical conductivity of borax, it was of interest to see to what extent this difference is characterized by protonic (i.e. ionic) conduction. Having proved that the evolved gas is hydrogen (see Experimental Section) it was sufficient to analyse the current efficiency. In order to do this we calculated after Faraday's law the volume of gas that would correspond to the current for one hour period in the straight line portions in graphs like Fig. 4. It was found that an increase in protonic conduction resulted in experiments with used pellets as compared with fresh ones. Therefore, only the experiments with the fresh pellets were taken into consideration. The ratio of the evolved volume of gas to that calculated from current is drawn against temperature in Fig. 6. The points near 40°C in Figs. 5 and 6 are uncertain for the following reasons. The rate of hydrogen evolution became very large. There was hardly any straight line portions as in Fig. 4, the slope of the curve rising sharply, while the increase of the current at the same time indicated approach to

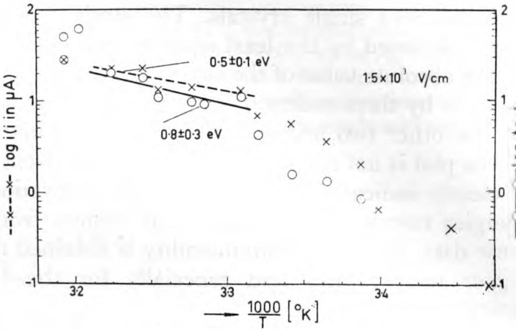

FIG. 5. Arrhenius plots of electrolysis rates at constant field. Energies of activation calculated from current (crosses), and rate of hydrogen evolution (circles).

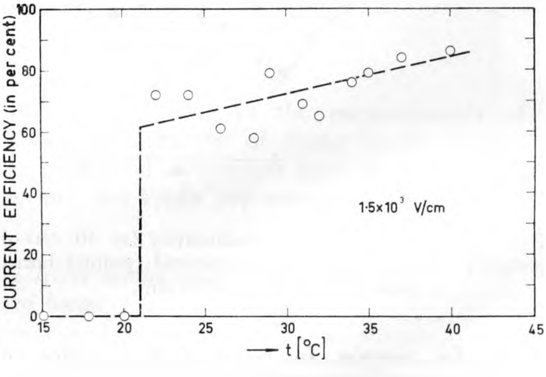

FIG. 6. Current efficiency for borax powder ("sandwich"-pellets) electrolysisat constan tfield.

breakdown. The applied voltage (which is at the limit of the Ohmic range) seems to be rather high for these temperatures. These results are not included in the least squares analysis. It should be pointed out that in case of zero results (15, 18, 20°C) the circuit was switched on for 36, 29 and 26 hr respectively, but no evolution of gas was observed. It therefore seems established with great certainty that the protonic conduction in borax is not operative below 20°C.

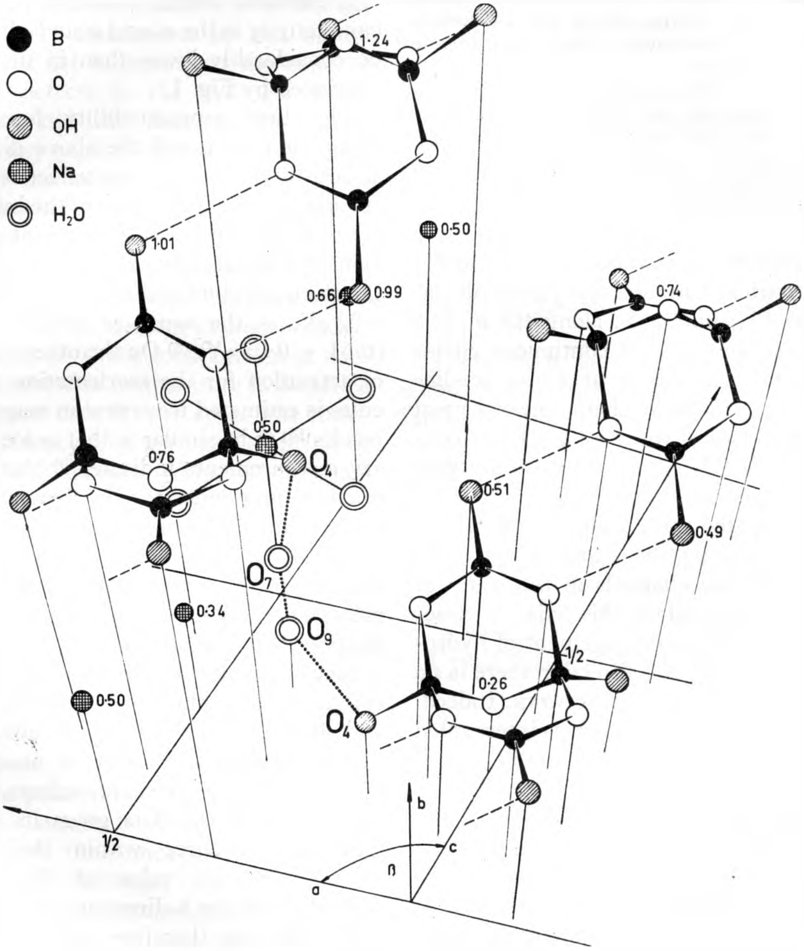

FIG. 7. A section of the crystal structure of borax after MORIMOTO.[10] Only one octahedron of water molecules around a $Na^+$-ion is shown in the cationic channel. Numbers indicate the positions in the $b$-direction (as ratios of the $b$-unit-cell dimension). Broken lines: supposed hydrogen bonds in the anionic chains. Dotted line: the proposed path for proton conduction.

## DISCUSSION

The difference in electrical conductivity by three orders of magnitude between that of $b$, and those of $a \sin \beta$ and $c$ directions in a single crystal of borax (Fig. 1) indicate considerable conduction anisotropy.

These are the main characteristics of the crystal structure[10] (consult Fig. 7). Two OH-groups of the anion $[B_4O_5(OH)_4]^{2-}$ make hydrogen bonds with adjacent $B_4O_5$-rings. In this way continuous chains are formed running parallel to the *c*-direction. For the sake of simplicity we call the described OH-groups "intra OH-groups".

Each of these chains is neighboured by four channels of $Na^+$-ions surrounded octahedrally with water molecules: two of these channels are "above and below" in the *b*-direction and the other two on either side along the *a*-direction. Thus, viewing along the *c*-direction there is a chess-table arrangement of alternating anionic chains and cationic channels.

The remaining two OH-groups connect the anion through hydrogen bonds to the water molecules of the cationic channels. We call them "inter OH-groups". There are also hydrogen bonds along the *b*-direction between the anionic part of the structure and the water of crystallization in the cationic channels.

Assuming protonic conduction, one would expect least electrical conductivity perpendicular to the chains and channels, i.e. along the $a \sin \beta$ direction, because there are no continuous chains of hydrogen bonds (in the sense of an ice-like structure). In fact the anionic chains present great resistance to such a mechanism of electrical conductivity. The intra OH–groups may hardly play a role in a proton transfer process.

It may be anticipated that of the remaining two directions the one along the *c*-axis is the most favourable, because the channels of the water of crystallization run parallel to this axis. A closer examination of the relative arrangement of hydrogen bonds reveals that in this direction there is no continuity in the hydrogen bond network. Indeed, there are sequences of hydrogen bonds interrupted by too large distances and unfavourable orientations.

However, regarding the conductivity along the *b*-axis, one may propose, taking into account the mutual orientations of the hydrogen bonds, the following path of protonic conduction. From the $O_4$-oxygen (notations after MORIMOTO(10) i.e. from one inter-OH group a proton may be passed over along the hydrogen bond to the $O_9$-oxygen of a water molecule in the cationic channel (2·86 Å). After some reorientation a further transfer of proton is possible to the $O_7$-water molecule (3·0 Å), though in a stationary model there is no hydrogen bond between the two oxygen atoms. There is a hydrogen bond (2·92 Å) between the last oxygen ($O_7$) and the next $O_4$ (inter OH-group) related to the starting one by a gliding plane. The sequence is thus completed and a continuous arrangement of hydrogen bonds along the *b*-axis is obtained. A zig-zag line is realized between the inter-OH groups ($O_4$) of two different anionic chains and two water molecules ($O_9$) of two different cationic channels (see dotted line in Fig. 7).

It therefore seems plausible, that the electrical conductivity in the *c*- and $a \sin \beta$-directions should be considerably lower than in the *b*-direction as suggested by Fig. 1.

The best reproducibility for measurements along the *b*-axis, and the above discussion of the anisotropy in the absolute values of conductivities suggest that the major part of the bulk conductivity in a powder sample is due to protonic conduction along the *b*-direction. The energy of activation for the electrical conductivity in this direction, 0·62 ± 0·02 eV, is the same as obtained on pure ice (0·61 ± 0·05 eV).(8) On the other hand, the energy of activation for the reorientation of water molecules is estimated from proton magnetic resonance results(14) to be similar to that in ice. Our preliminary measurements indicated(9) that protonic conduction preponderates in borax above certain temperatures. The present direct confirmation that the evolved gas is hydrogen (see Experimental Section) together with detailed electrolysis experiments (Fig. 6) leaves no doubt that proton conduction is indeed operative in borax.

Measurements of activation energy for proton conductivity in the polycrystalline borax (Fig. 2 and Ref. 9) yield values of about 1 eV. This higher result may be due to uncontrolled grain boundaries—and pressure—effects. Other values, obtained from the data given in Fig. 5 are less reliable, but agree within their experimental errors with the value of 0·62 ± 0·02 eV as measured for the *b*-direction of a single crystal of borax. We are therefore inclined to accept this last value as the true energy of activation for proton conduction in borax. GRÄNICHER(15) pointed out, and it is implicit in similar treatments by other authors, that both the generation and diffusion of ions proceed by translational motions of protons from one molecule to its neighbour, which is accomplished by quantum mechanical tunneling. CONWAY(16) showed by careful measurements of d.c. electrical conductivity of ordinary and heavy ice (at −10°C), that the ratio of the two values (2·4) yields a satisfactory ratio of mobilities, when compared with the one calculated on the basis of a tunnel effect. Our measurements (Fig. 2) at 50 c/s give a ratio of about 3·0. Thus, the energy of activation and the specific conductivity of borax together with the isotopic conductance ratio seem to allow a similar approach as in the case of ice. The present discussion is to be limited in scope and definite conclusions by lack of the following experimental information: the concentration of ionic defects in the hydrogen bond system of borax and the dielectric loss data. Neither is there any explicit relation between proton conductivity and temperature in the theories published so far, and borax is in this respect a special case.

For one thing, there is an upper limit at 50°C set up by dehydration of borax. There is also a lower limit at 20°C. The results in Fig. 6 clearly indicate that below 20°C the total current is non-protonic while above this temperature it is carried by protons at more than 50 per cent. The maximum current efficiency (100 per cent) seems to be attained in a linear increase from 20° to about 45°C.

Two temperature regions in electrical conductivity have also been observed with polyamides(17) in which, though not directly proved, protonic conduction is likely to be operative.(1a, b, 18, 17) The dielectric relaxation of whole chains is invoked as the rate controlling mechanism in order to explain the transition in electrical conductivity at about 100°C.(17)

No such transition temperature is detected in ice, though some possibility in this respect can be found in Riehl's results.(4) However, the basic requirement for a time independent protonic current is that the reorientation time is short compared with the proton concentration.(15) This amounts to

$$\frac{l}{v} > \tau_r \tag{2}$$

where $l$ is a measure of the free path of a "travelling" proton, and $v$ its linear velocity, with $\tau_r$ denoting the dielectric relaxation time. $l$ is related to the proton concentration ($N$) by

$$l = KN^{-1/3} \tag{3}$$

There seems to exist appreciable agreement in that the activation energy of electrical d.c. conductivity ($E_{dc}$) in pure ice corresponds actually to the half of the heat of dissociation for producing an ion pair from two water molecules in the hydrogen bond network (Refs. 6, p. 527, and 8, p. 120). We therefore may write:

$$N = N_0 \exp(-E_{dc}/kT), \tag{4}$$

and, of course

$$\tau_r = \tau_0 \exp(E_r/kT) \tag{5}$$

If one is justified in assuming that $v$ in (2) is practically independent of temperature (owing to the tunneling character of the proton mobility), then (2) can be rewritten as

$$K_1 \exp(E_{dc}/3kT) > K_2 \exp(E_r/kT) \tag{6}$$

There are in general three cases in the competition between the temperature dependence of ion-pair formation and the reorientation rate. It follows from (6):

| | |
|---|---|
| Case 1. $E_{dc}/3 < E_r$. | Unhindered protonic conduction is possible *above* a certain temperature, $T_p$, which depends on $K_1$ and $K_2$ as well. |
| Case 2. $E_{dc}/3 = E_r$. | Protonic conduction is either possible or not, which is decided by $K_1$ and $K_2$. |
| Case 3. $E_{dc}/3 > E_r$. | Unhindered protonic conduction is possible *below* a certain temperature $T_p$, depending on $K$ and $K_2$ too. |

$E_{dc}$ is 0·62 eV for ice and borax and $E_r$ is 0·575 eV for ice and possibly not lower than 0·3 eV(14) for borax, so that according to case 1 in both these substances there should be a minimum temperature, $T_p$, below which protonic conduction is hindered, and eventually stopped, because the reorientation time becomes too large according to (6). The former conclusion is also in agreement with the discussion on polyamides,(17) because there $E_{dc}$ = 1·1 eV, and $E_r$ is at least 0·9 eV.(19) The minimum $T_p$ has been determined with certainty for borax in the present study; there is reasonable possibility that the transition temperature for electrical conductivity in polyamides(17) is actually $T_{p,\min}$, while for ice it remains to be seen.*

The transition like character of the results given in Fig. 6 may also pose the possibility of a crystal structure transformation between 20° and 30°C. We checked on this point by careful differential thermal analysis from 0°C upwards. No sign of any thermal effect at all was observed up to 54°C. This is in full agreement with earlier findings of MENZEL:(20) a sample of borax free of crystallization centres of a pentahydrate phase, such as one used in the present work, is very stable under normal pressure at room temperature. Even with the substance that would dehydrate at 50°C via the pentahydrate, there is a continuous pressure-temperature relation from 15° to 25°C.

We are not aware of any other source of information that would support a crystal structure transformation in the critical temperature range. The present data strongly suggest that the observed effects are due to certain changes in the proton system of the hydrogen bond network in borax. The onset of measurable protonic conductivity above 20°C is most probably due to the sufficient increase in the reorientation rate so as to satisfy condition (6). At present one can estimate from proton magnetic resonance measurements(14) that above 20°C $\tau_r < 5 \times 10^{-5}$ sec. These latter measurements may well become sensitive to an energy state of the protons at a slightly higher temperature (36°C, see Ref. 14) at which an additional delocalization of the protons in the hydrogen bond network is coupled to the abrupt change of the hindering potential as the higher oscillational levels become more occupied on raising the temperature.

Finally, we should like to mention two unusual observations with borax: (a) the deviation from Ohm's law above some $10^3$ V/cm to higher values; (b) the current increase with time for the proton conductivity range (above 28°C). The first effect has been reported for polyamides too,(17) while the second one is also common to lithium sulphate monohydrate(13) and cetyl alcohol.(2) Solid state electrolysis with single crystals should show whether these two effects in powder samples may be accounted for by a sintering process taking place at grain boundaries.†

*Acknowledgement*—Thanks are offered to M. TOPIĆ for single crystal growing and to Mrs. A. DOBUD-SMILEK for measurements of single crystal d.c. conductivities. The design of the electrical integrator was kindly done by T. RABUZIN and made by D. GUDLIN. Several of our colleagues contributed to the analytical part of the work and also made suggestions during the experimentation. We are thankful in this respect in particular to Z. ŠTENBERG, Z. DESPOTOVIĆ and M. PINTAR. It is a pleasure to express our gratitude to Dr. P. GOSAR for his kindness and much helpful criticism concerning the interpretation of the present results.

## REFERENCES

1. FUOSS R. M., *J. Amer. chem. Soc.* **63** 378 (1941); BAKER W. O. and YAGER W. A., *Ibid.* **64** 2171 (1942); HOFFMAN J. D. and SMYTH C. P., *Ibid.* **71** 431 (1949).
2. KAKIUCHI Y., KOMATSU H. and HYOYA S., *J. phys. Soc. Japan* **6** 321 (1951).
3. WORKMAN E. J., TRUBY F. K. and DROST HANSEN W., *Phys. Rev.* **94** 1073 (1954); DECROLY J. C., GRÄNICHER H. and JACCARD C., *Helv. phys. acta* **30**, 465 (1957).
4. RIEHL N., *Zh. fiz. khim.* **29**, 1372 (1955).
5. BRADLEY E. S., *Trans. Faraday Soc.* **53**, 687 (1957).
6. EIGEN M. and DE MAEYER L., *Proc. Roy. Soc.* **247A**, 505 (1958).
7. EIGEN M. and DE MAEYER L., *Z. Elektrochem.* **59**, 986 (1955); *Ibid.* **60**, 1037 (1956).
8. GRÄNICHER H., *Z. Kristallogr.* **110**, 432 (1958); JACCARD C., *Helv. phys. acta* **32**, 89 (1959); GRÄNICHER H. and JONA F., *Helv. phys. acta, Suppl.* **5**, 50 (1960).
9. JELENIĆ I., LOVREČEK B., MARIČIĆ S., and VEKSLI Z. *Croat. chem. acta* **32**, 111 (1960); MARIČIĆ S. and PRAVDIĆ V., *Croat. chem. acta* **32**, 231 (1960).
10. MORIMOTO N., *Miner J.* **2**, 1 (1956).
11. VEKSLI Z., Thesis, University of Zagreb (1960).
12. KAMENAR B., BAN Z. and DADIĆ M., *Croat. chem. acta* **31**, 159 (1959).
13. MARIČIĆ S., PRAVDIĆ V. and VEKSLI Z., *Croat. chem. acta* **33**, 187 (1961).

---

* Some doubt may be cast as to the validity of these arguments. Namely, by taking the relevant data for ice at −10°C from Ref. 8 one obtains $l/v = 6{\cdot}5 \times 10^{-6}$ sec, while $\tau_r$ is $5 \times 10^{-5}$ sec. The proportionality constant in (3) has been taken as unity, and it seems unlikely that it be ten times larger, which is at least required to satisfy condition (2).

† We are indebted for this suggestion to Dr. R. SIZMANN of the Physical Institute, Technical High School, Munich.

14. Maričić S., Pintar M. and Veksli Z., *J. Phys. Chem. Solids* **23,** 743 (1962).
15. Gränicher H., *Proc. Roy. Soc.* **247A,** 453 (1958). (see p. 458).
16. Conway B. E., *Canad. chem. J.* **37,** 178 (1959).
17. Eley D. D. and Spivey D. I., *Trans. Faraday Soc.* **57,** 2280 (1961).
18. McCall D. W. and Anderson E. W., *J. chem. Phys.* **32,** 237 (1960).
19. Jones D. W., *Polymer* **2,** 203 (1961).
20. Menzel H., *Z. anorg. Chem.* **224,** 1 (1935).