

The Electrical Conductivity of Solid Alkali Hydroxides*

K.-H. HAAS AND U. SCHINDEWOLF

*Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe,
West Germany*

Received March 21, 1984

Measurements of the electrical conductivity of RbOH and NaOH confirm the proposed proton conduction mechanism previously reported for KOH and CsOH. The cubic high-temperature phases of Na-, K-, Rb-, and CsOH ("rotator phases") with free-rotating OH⁻-ions have an enhanced electrical conductivity caused by a Grotthus-type conduction mechanism. © 1984 Academic Press, Inc.

Introduction

According to X-ray and neutron-scattering experiments (1-3) the solid hydroxides of the alkali metals Na, K, Rb, and Cs undergo between 490 and 570 K a transition from a monoclinic (NaOH, KOH, RbOH) or orthorhombic (CsOH) to a cubic structure. In the cubic phase ("rotator phase") the OH⁻-ions are free to rotate whereas in the other phases the rotation is hindered. The hindered and the free rotation are reflected in the temperature dependence of the electrical conductivity as has been shown for solid KOH (4) and CsOH (5) (transition temperatures 493 and 521 K, resp.). Compared to normal solid alkali salts, already the low-temperature phases have a high conductivity with a relatively small temperature dependence (activation energy). At the rotator phase transition temperature the conductivity jumps up by a factor of 5 to 10 and then increases with a slightly smaller activation energy. At higher temperatures where no other phase transi-

tions are known, the conductivities of both hydroxides again increase steeply by several powers of 10 up to the melting point, above which the normal conductivity of a molten salt with low activation energy is observed (5, 6). In the following we report on the conductivities of solid NaOH and RbOH which qualitatively show the same conductivity behavior as KOH and CsOH.

The experimental procedure including treatment of the hydroxides has been described before (5). Commercial high-purity NaOH (C. Roth, Karlsruhe; maximal impurity 0.4 mol% Na₂CO₃) and RbOH (CERAC, Milwaukee, maximal impurity 3 mol% Rb₂CO₃) were used with unavoidable traces of water (<1 mol%) which could not be completely removed by bubbling high-purity argon (>99.999 vol%) through the molten hydroxides and which could not be determined by conventional analysis.

The experimental results are displayed in Fig. 1. Below 500 K RbOH has a conductivity of 10⁻⁶ to 10⁻⁵ Ω⁻¹ cm⁻¹, the activation energy is $E_a = 64 \pm 8$ kJ/mol. At the rotator-phase transition temperature (508 K the conductivity increases to 10⁻⁴ Ω⁻¹ cm⁻¹

* Dedicated to Dr. M. J. Sienko.

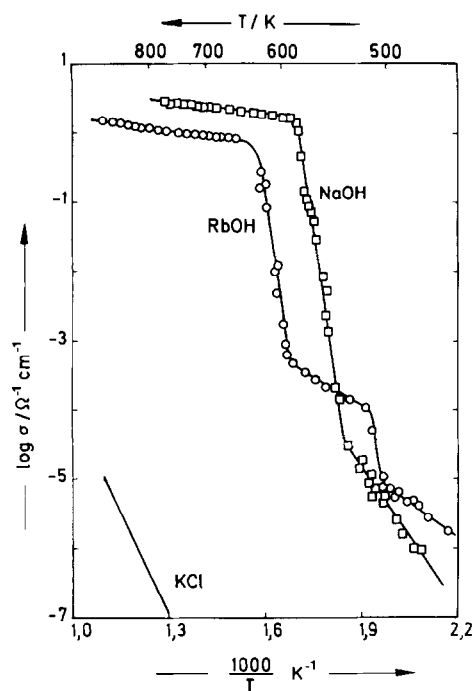


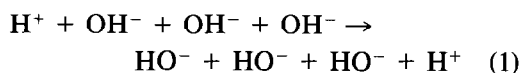
FIG. 1. Specific conductivity of solid and molten sodium- and rubidium hydroxide in dependence of temperature ($\log \sigma$ vs $1/T$; for comparison the conductivity of solid potassium chloride is given (9)).

and then has a slightly smaller activation energy $E_a = 55 \pm 5$ kJ/mol. From 608 to the melting point 655 K the conductivity rises steeply (but not discontinuously) up to $10^{-1} \Omega^{-1} \text{cm}^{-1}$ corresponding to $E_a \approx 600$ kJ/mol. Above the melting point the normal conductivity of a molten salt is obtained ($E_a = 12.7 \pm 1.5$ kJ/mol). NaOH shows the same behavior, but the discontinuity at the rotator-phase transition temperature (572 K) is hidden in the steep conductivity increase which with the other hydroxides starts far above their transition temperatures. At lower temperatures (518 K) NaOH has another phase transition (orthorhombic to monoclinic (7)) which we could not recognize by a change in conductivity.

The conductivity change of the four hydroxides by 3 to 5 powers of 10 below the

melting point cannot be related to any known structural changes. But the temperature where this steep increase starts coincides within a few degrees with the eutectic temperature of the respective hydroxide-carbonate mixtures (8) as already pointed out for CsOH and KOH (4, 5). Therefore we think the small carbonate contaminations to be responsible for this drastic effect in the conductivity. At the eutectic temperatures the liquid eutectic carbonate-hydroxide mixtures are formed in the framework of the solid hydroxides and thus lead to the conductivity increase. With further temperature increase more and more hydroxide is dissolved (following the solidus curve), i.e., the volume fraction of the liquid mixture phase and therefore the conductivity are increased until at the normal melting point of the hydroxides their porous structure collapses. Thus the steep conductivity increase between the eutectic point and the melting point should not be described by a special conductivity mechanism with an extremely high activation energy.

The relatively high conductivity and low activation energy of the low-temperature phases of the hydroxides cannot be due to an ion-hopping mechanism as in normal ion crystals (9) (compare data for, e.g., solid KCl in Fig. 1 (9)). Because of the discontinuity of the conductivity at the temperature of the rotator-phase transition point the conductivity somehow should depend on the rotation of OH^- -ions. Stephen (4) suggested that it is based on a proton conductivity process comparable to a Grotthustype mechanism



Further proton transport from left to right is possible only after a rotation of the OH^- -ions into the original orientation. Above the rotator-phase transition point of course the

reorientation will occur faster than in the low-temperature phase with hindered rotation and therefore the conductivity of the hydroxides sharply increases. The small difference in the activation energies of the conductivity in the two phases thus should reflect the activation energy of rotation in the low-temperature phase (around 10 kJ/mol for RbOH).

The proton donators might be the OH^- -ions themselves ($\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}^+$) or water formed in an equilibrium reaction ($2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^{2-}$) or more likely water which as a contamination is present in all hydroxides (the above hydroxide-water equilibrium is known in lithium and alkali earth hydroxides (10) which have no rotator phases; it is very unfavorable in the other alkali hydroxides (11)).

The explanation of the conductivity behavior of the alkali hydroxides is based on the coincidences of phase transition and eutectic temperatures on the one hand and the temperatures of steep conductivity increases. A proof would be possible by experiments with hydroxides of utmost purity which we could not prepare although a method for this has been described (3). With these high-purity hydroxides we would expect a lower conductivity because of the absence of a proton donator (unless water is intrinsically formed as described above) and only the sharp discontinuity at the normal melting points. The unwanted water decontamination enabled us to confirm by conduction experiments the concept of the rotator phases in the solid hydroxides.

However, one additional experiment confirms the concept of increased proton mobility above the rotator-phase transition temperature. The ^1H NMR relaxation rate $1/T_1$ of CsOH distinctly exhibits an increase at the transition temperature 493 K (Fig. 2; measured by the $180^\circ\text{-}\tau\text{-}90^\circ$ inversion recovery method with the Bruker instrument CPX 200; unfortunately the temperature

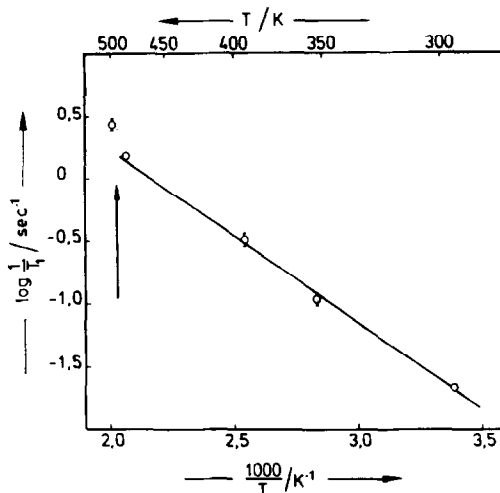


FIG. 2. ^1H NMR relaxation time T_1 of solid cesium hydroxide in dependence of temperature ($\log(1/T_1)$ vs $1/T$); the arrow indicates the rotator-phase transition temperature.

range could not be extended beyond 500 K because of limitations of the sample holder). Below this temperature the $\log(1/T_1)$ vs $1/T$ slope corresponds to an activation energy of 25 ± 5 kJ/mol. This is in agreement with the activation energy of hindered OH^- -ion rotation in the low-temperature phase $E_a = 20 \pm 8$ kJ/mol which we estimated from the temperature dependence of the conductivity of CsOH below and above the transition temperature (5). Thus we may conclude that OH^- -ion rotation is the predominant factor determining the proton relaxation rate and that this is indeed increased above the transition temperature.

Acknowledgments

We are grateful to Bruker Physik, Karlsruhe, for carrying out the NMR experiments. We are indebted to the Deutsche Forschungsgemeinschaft und to the Fonds der chemischen Industrie for valuable financial support.

References

1. TH. TACKE, thesis, Technische Hochschule Aachen, 1982.

2. R. G. SNYDER AND J. KUNAMOTO, J. A. IBERS, *J. Chem. Phys.* **33**, 1171 (1960).
3. H. JACOBS AND B. HARBRECHT, *Z. Naturforsch. B* **36**, 270 (1981).
4. M. S. STEPHEN AND A. T. HOWE, *Solid State Ionics* 461 (1980).
5. K. H. HAAS AND U. SCHINDEWOLF, *Ber. Bunsenges. Phys. Chem.* **87**, 346 (1983).
6. G. J. JANZ, "Molten Salt Handbook," Academic Press, New York (1967).
7. H. J. BLEIF, thesis, University of Tübingen (1978).
8. R. COHEN-ADAD, M. MICHAUD, J. SAID, AND A. P. ROLLET, *Bull. Soc. Chim. Fr.* 356 (1961).
9. R. J. FRIAF, in "Physics of Electrolytes," (J. Hladik, Ed.), Vol. 2, Academic Press, New York (1972).
10. F. FREUND AND H. WENGLER, *Ber. Bunsenges. Phys. Chem.* **84**, 866 (1980).
11. B. TREMILLON AND R. G. DOISNENN, *J. Chim. Phys.* **71**, 1379 (1974).