Protonic Conduction in Potassium Dihydrogen Arsenate

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The conductivity of potassium dihydrogen arsenate has been measured as a function of temperature between -20 and $190°$. Single-crystal cubes of the pure and sulfate-doped material were heated in a chamber which provided the water vapor pressure required to maintain a single phase. The activation energy of migration and the energy of formation of defects required for conduction have been determined and compared with conductivity parameters previously found for potassium dihydrogen phosphate. The conductivity of KH_2AsO_4 is given by $\log \sigma = 0.5 - 15.2 \text{ kcal}/2.3RT$ at $T < 110°$ and $\log \sigma = 4.0 - 22.2$ $\text{kcal}/2.3RT$ at $T > 110°$, where σ is in units of $\text{ohm}^{-1} \text{ cm}^{-1}$. Substitution of $KHSO_4$ in the lattice of KH_2AsO_4 resulted in an increase in conductivity. A comparison of these data with a conductivity study on KH_2PO_4 is made.

Introduction

Potassium dihydrogen arsenate, KH_2AsO_4, is a hydrogen-bonded crystal whose study we thought would complement previous work on ice,[1,2] borax,[3] ammonium dihydrogen phosphate,[4] potassium dihydrogen phosphate,[5] and potassium dideuterium phosphate.[6] A substantial amount of work has been done on ice and the potassium phosphates and these have been shown to be protonic conductors in which defects in the hydrogen-bonded network offer a mechanism for ionic conduction. A study of potassium dihydrogen phosphate (KHP)[5] has revealed a mechanism involving two definite types of jumps along the protonic network: an intrabond jump of a proton between oxygens on different tetrahedra and an interbond jump between oxygens on the same tetrahedron. A paper[6] on the effect of the conductivity when deuterium is substituted for hydrogen in the crystal related a connection between the ferroelectric phase transition and the temperature at which the conductivity curve shows a break or "knee." Thus, protonic motion is responsible not only for the ferroelectric properties[7] of the crystal but also for the conductivity. Much less work has been done in the case of ammonium dihydrogen phosphate (AHP) although similar conclusions have been reached.[4] Recently a paper by Kröger[8] reported investigations on protonic conduction in NH_4Cl.

It was the purpose of this study to determine whether the conductivity parameters for potassium dihydrogen arsenate (KHA) support and enhance the ideas of protonic conduction accepted in solid-state chemistry to date and to make a comparison between KHP and KHA. The full details of the mechanism of conduction in these crystals are reported in the paper on KHP[5] and will not be reproduced here. KHA is isomorphous[9] with KHP and therefore similar conductivity behavior is expected.

Experimental Section

Determination of the Phase Diagram.—Since KHA loses water as it is heated according to the reaction $KH_2AsO_4 \rightarrow KAsO_3 + H_2O(g)$, it was necessary to determine a partial phase dia-

gram in order to preserve single-phase KHA as the crystal is heated. This was obtained by measuring the water vapor pressure for the univariant three-phase equilibria: KH_2AsO_4e $KAsO_3-H_2O(g)$. We first determined the dissociation pressure for pure KH_2AsO_4 and then the water vapor pressure in equilibrium with a saturated solution of KHA in water. A differential mercury manometer was used to measure the water vapor pressure.

Conductivity Measurements.—Single crystals of pure and doped KHA were placed between two platinum electrodes, with a gold interface to reduce contact resistance. A platinum resistance thermometer was placed nearby and this unit was inserted into a cell which could be evacuated and also provide the proper water vapor pressure. A resistance heater was used to heat the crystal above room temperature and slush baths in dewar flasks were used to lower the temperature. A Keithley Model 610 B electrometer was used to measure the current and the voltage was supplied by a Keithley power supply, variable from 1 to 1000 V.

Results

Phase Diagram.—The partial phase diagram is shown in Figure 1. There is a wide region of stability of KHA and a variety of temperatures and pressures can be employed. The crystals did not show any discoloration or cracking even after extended heating at temperatures close to $160°$. This might have been predicted from the data of earlier workers, who reported that the dehydration reaction was reversible[9] to a greater extent than for KHP. Thus the phase diagram provides the temperature–pressure range in which the experiment is conducted. The dotted lines (Figure 1) indicate extrapolation rather than measured data.

Conductivity.—The conductivity, σ, of KHA at $25°$ was found to be $1.0 \times 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$ and varied exponentially with temperature according to the equations $\log \sigma = 0.5 - 15.2 \text{ kcal}/2.3RT$ at low temperatures and $\log \sigma = 4.0 - 22.2 \text{ kcal}/2.3RT$ at temperatures above $110°$, where σ is in units of $\text{ohm}^{-1} \text{ cm}^{-1}$. As is shown in Figure 2 the circles represent data points used to construct the low-temperature solid lines for two pure KHA crystals and the squares represent the high-temperature data for one crystal. The curve marked D refers to a crystal doped with 0.01 mol % $KHSO_4$. The conductivity of the doped crystal increased by a factor of 100 over the pure crystals. The slopes of the lines are reported in Table I (under T) as 15.2 kcal/mol for the pure crystal at low temperatures and 22.2 for temperatures greater than $110°$. The slope for the doped crystal is 13.0 kcal/mol. The standard deviation is less than ± 0.1 kcal/mol for each slope as calculated from a least-squares fit to the data.

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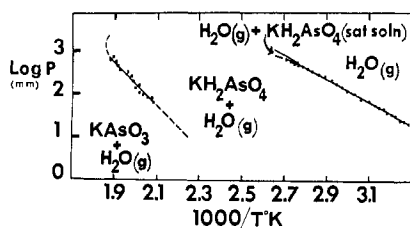(9) D. H. Dickson and A. R. Ubbelhode, *Acta Crystallogr.*, **3**, 6 (1950).

Figure 1.—Temperature–pressure projection of the KH_2AsO_4 field in the $KAsO_3$–H_2O system; $P = P_{H_2O(g)}$. The KH_2AsO_4-(satd soln) area is very narrow and at low temperatures its curve is nearly superimposed on the vaporization line for water.

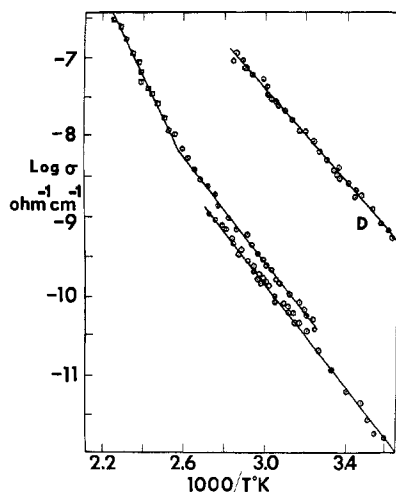Figure 2.—The conductivity of pure and sulfate-doped KH_2AsO_4 as a function of temperature: ○, low-temperature data; ☐, data above 110°; D indicates the doped crystal.

TABLE I[a]
DEFECT ENERGIES (KCAL/MOL)

		D, L		Ion		
	Temp	M	F	F	M	T
KH_2PO_4	Low	12.0	0.6	...	0	12.6
	High	12.0	0.6	5.4	0	18.0
KH_2AsO_4	Low	13.0	2.2	...	0	15.2
	High	13.0	2.2	7.0	0	22.2

[a] Key: M, activation energy of migration for the proposed defects; F, energy of formation of defects; T, total energy required for conduction.

Discussion

For crystals in which protonic conduction has been proven (ice, KHP, AHP), the conductivity at low temperatures is attributed to migration of the proton *via* interbond and intrabond jumps. Figure 3 represents
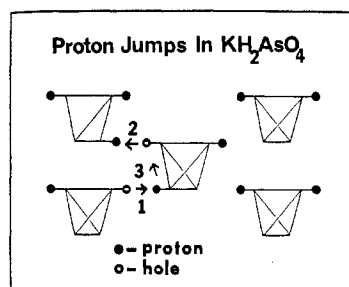

Figure 3.—A schematic diagram of proton jumps in KH_2AsO_4: 1 and 2, intrabond jumps; 3, interbond jump.

a section of KHA with H_2AsO_4 units and shows, schematically, three jumps which are suggested as the mechanism of conduction in KHP[5] and KHA. The arrows numbered 1 and 2 represent intrabond jumps causing the formation and migration of the ions, $HAsO_4^-$ and $H_3AsO_4^+$. We use the convention that the defects are effectively charged relative to the normal H_2AsO_4 ion. Thus we have a mechanism for charge formation and migration in the crystal. Arrow number 3 in Figure 3 illustrates interbond motion which results in placing two and zero protons between two oxygens on neighboring tetrahedra. These geometric defects have previously been referred to as D and L defects, respectively. Additional interbond jumps of the proton cause migration of the D and L defects. The existence of the interbond and intrabond jumps and their relationship to conduction in this class of crystals is indicated by magnetic resonance studies on potassium dideuterium phosphate[10] as well as by the conductivity studies previously mentioned.[5] The magnetic resonance experiments found the activation energy for deuteron interbond jumps and conduction, attributed to migration of geometric defects,[5] to be the same.

It is the interbond jump which has been shown to be the rate-controlling process at low temperatures in KHP[5] and potassium dideuterium phosphate.[10] The last column (T) in Table I gives the slope of the log (conductivity) *vs.* reciprocal temperature for KHA and KHP.[5] We find a low-temperature activation energy higher by 2.6 kcal/mol for the arsenate crystal. If we take the As–O and P–O internuclear distances to be 1.75 and 1.56 Å, respectively, the difference in the interbond jump distance, taken as the edge of the tetrahedron, is calculated to be 0.32 Å (2.85 − 2.53 Å). Assuming that the conductivity is due to interbond proton jumps, the larger jump distance in KHA accounts for the higher activation energy of migration.

The other distinctive feature of the pure KHA crystal is the break in the conductivity curve at 110° to a higher slope of 22.2 kcal/mol. Such a transition has been reported for other protonic conductors, AHP[4] and KHP[5]. This transition has been shown to be intimately connected to proton jumps by the spectroscopic work of Imry, Pelah, and Weiner[11] and O'Keeffe and Perrino.[6] The increase in energy required for conduction of 7.0 kcal/mol above 110° is attributed[5] to the energy of formation of ionic defects since thermal energy is available to produce them. Below 110° the crystal has a constant number of ionic defects incorporated into the crystal during preparation. As in ice and KHP, we take the energy of migration of ionic defects to be zero. This is because the proton may tunnel between two equivalent positions at temperatures above the Curie point and this motion requires no activation energy. The value of 7.0 kcal/mol should be compared to the 5.4 kcal/mol found for ion formation in KHP.[5] Both of these values are listed in Table I. There does not appear to be any literature data which would help us explain the slightly larger value we found for the arsenate crystal.

In other hydrogen-bonded crystals previously mentioned,[4,5] substitution of an ion with one less proton into a lattice position has resulted in an increase in the

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conductivity. For example ice has been doped with HF and KHP and AHP doped with $KHSO_4$. Doping the solution from which the crystal of KHA is growing with $KHSO_4$ should result in a number of hydrogen sulfate ions replacing dihydrogen arsenate ions in the lattice. A number of L defects should be built into the proton network since the hydrogen sulfate ion has one less proton and a corresponding increase in the conductivity realized. Such an effect has been found here and allows the calculation of the mobility of the L defect from the equation $\sigma = n_L e \mu_L$ provided we make the assumption that the L defects are not bound to the HSO_4 ions.[5] Using our dopant level for n_L and 1.6×10^{-19} C for e, we find $\mu_L = 2.40 \times 10^{-10}$ cm^2 V^{-1} sec^{-1}. This is very much in agreement with the proton mobility in KHP where μ_L was found to be 6.0×10^{-10} cm^2 V^{-1} sec^{-1} at 25°. The low-temperature slopes of the pure and doped crystals differ slightly. The probable explanation is that in the pure crystal the overall energy of conduction requires formation and migration of L defects, whereas in the doped crystal they are already present. For the purpose of discussion we have separated these energy terms in Table I. Table I shows that the energy of formation of L defects is found to be greater for KHA (2.2 kcal/mol) than for KHP (0.6 kcal/mol). We cannot explain this difference.

Conclusion

We submit that from the conductivity data and the effect of doping on KHA and from comparisons with results obtained for KHP, protonic conduction is indicated in potassium dihydrogen arsenate.

Spectroscopic Studies of Halosulfinate Ions

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In liquid sulfur dioxide solution, halide ions are specifically solvated so as to form halosulfinate ions. The halosulfinate ions also exist in other aprotic solvents and can be found in the well-known "solvates" which are isolated from liquid SO_2 solutions. The chloro-, bromo-, and iodosulfinate ions are highly colored due to an internal charge-transfer transition. Vibrational spectra of the XSO_2^- ions are consistent with the expected pyramidal (C_s) geometry. The results of an approximate normal-coordinate analysis as well as the relative intensities of the electronic transitions suggest the magnitude of the X^-–SO_2 interaction to be in the order $FSO_2^- > ClSO_2^- < BrSO_2^- < ISO_2^-$. It is apparent that the nature of the halide–sulfur dioxide interaction is obscured by solvation effects in solvents such as acetonitrile and dimethyl sulfoxide. The formation of halosulfinate ions probably plays a significant role in the chemistry of ionogenic halides in liquid SO_2.

Introduction

The existence of halosulfinate (XSO_2^-) ions in liquid sulfur dioxide solutions has been indicated by the work of several investigators[1-3] but there has been little systematic effort to demonstrate their existence or to define their structures. The ionogenic[4] character of the triarylchloromethanes in liquid SO_2 has been attributed to the formation of a complex between the chloride ion and the solvent molecules.[3] The presence of X^-–SO_2 complexes has been inferred from several unusually small rate constants for reaction in liquid SO_2.[5] Ultraviolet[3,6-8] and infrared[8] spectra of mixtures of halide ions and sulfur dioxide in various solvents have been interpreted in terms of $X^-\cdots SO_2$ complexes. The colors of solvates[1,2] of the type $MX \cdot nSO_2$ ($n = 1-4$) may be attributed to electronic transitions in complex anions, probably halosulfinates. The fluorosulfinate ion has been isolated and characterized;[9] the infrared spectrum of $KFSO_2$ has been interpreted in terms of the FSO_2^- ion of pyramidal (C_s) structure.[10] Recently, Woodhouse and Norris[11] and Salama, et al.,[12] have utilized ultraviolet spectroscopy to demonstrate the existence of Cl^-, Br^-, and I^- complexes with SO_2 in acetonitrile, dimethyl sulfoxide, and water. The formation constants reported in these studies strongly reflect the influence of the solvent on the stability of the halosulfinate ions.

This paper reports the results of a study of the halide ion–sulfur dioxide interaction in liquid sulfur dioxide

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