hedra of H_2O molecules in the structure seems to be well stabilized. The extremely perfect (010) cleavage of vivianite and symplesite may presumably take place across these H_2O–H_2O bonds. Interatomic distances calculated are given in Table 3.

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The Hydrogen Bond in Crystals. VIII. The Isotope Effect in KH_2AsO_4

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The axial lengths of tetragonal KH_2AsO_4 are found to be $a = 7{\cdot}609 \pm 0{\cdot}001$, $c = 7{\cdot}148 \pm 0{\cdot}001$ kX. at 18° C. X-ray measurements on KH_2AsO_4 show that the isotope effect when deuterium is substituted for hydrogen involves a lattice expansion in the direction of the short hydrogen bonds. On the basis of certain assumptions, the isotope effect (D for H) involves an expansion of 0·0080 kX. in KH_2AsO_4 which compares with 0·0097 kX. in KH_2PO_4 and 0·0100 kX. in $(NH_4)H_2PO_4$.

Various evidence indicates that the protons are less strongly bonded to the AsO_4 complex than to the PO_4 complex. Experiments are described which show (*a*) that, unlike KD_2PO_4, KD_2AsO_4 shows no evidence of a tendency to crystallize spontaneously in a monoclinic form; and (*b*) that, when heated, KH_2AsO_4 loses water fairly readily to form $KAsO_3$. When $KAsO_3$ is dissolved in water it undergoes the reaction $KAsO_3 + H_2O \rightarrow KH_2AsO_4$ practically instantaneously. On the other hand, KH_2PO_4 is much more resistant to heat. When the KPO_3 is dissolved in water, the PO_3' is at first largely polymerized and hydrates only with difficulty.

The free energies of transfer and heats of transfer of the proton in the reactions

$$2H_2PO_4' \rightleftharpoons H_3PO_4 + HPO_4'', \quad \Delta G = 6{\cdot}5, \quad \Delta H = 3{\cdot}8 \text{ Cal. mole}^{-1},$$

$$2H_2AsO_4' \rightleftharpoons H_3AsO_4 + HAsO_4'', \quad \Delta G = 5{\cdot}2, \quad \Delta H = 2{\cdot}2 \text{ Cal. mole}^{-1},$$

are briefly discussed in relation to the theory of the hydrogen bond in these crystals.

Introduction

From the isomorphism and from recent determinations of crystal structure (Helmholz & Levine, 1942), it may be inferred that KH_2AsO_4 contains short hydrogen bonds similar to those in KH_2PO_4 and in a number of other crystals. KH_2AsO_4 also shows a continuous transition to the ferro-electric state, analogous to that in KH_2PO_4, but at 95·6° K. instead of at 122° K. (Stephenson & Zettlemoyer, 1944). It was of particular interest to study the isotope effect in KH_2AsO_4 in view of these similarities, and also in view of the fact that KD_2PO_4 crystallizes spontaneously in a structure distinct from KH_2PO_4 (Ubbelohde, 1939*b*). In the course of experiments on the isotope effect, significant differences between H_2AsO_4' and H_2PO_4' were observed, which were further investigated because of their bearing on the behaviour of hydrogen bonds in crystals.

So far as the evidence goes, the hydrogen bonds in crystals of KH_2AsO_4 appear to be somewhat weaker than in KH_2PO_4. The origin of this difference may be tentatively related with the ionic sizes of the H_2AsO_4' and H_2PO_4' complexes.

Experimental procedure

Preparation of KH_2AsO_4

KH_2AsO_4 was prepared by neutralizing ignited K_2CO_3 ('Analar' grade) with the equivalent amount of As_2O_5 in hot distilled water according to the equation

$$K_2CO_3 + As_2O_5 + 2H_2O \rightarrow 2KH_2AsO_4 + CO_2 \qquad \text{(i)}$$

Owing to impurities of silicate in the As_2O_5 the solution had to be filtered; the amounts of As_2O_5 corresponding to the weight of insoluble residue were then added in a second neutralization. The KH_2AsO_4 was recrystallized three times. In the final sample, analysis of the arsenic content by precipitation as $Mg(NH_4)AsO_4 . 6H_2O$ and ignition to $Mg_2As_2O_7$ gave 41·48 % as the mean of four observations (theory 41·61 %). When the crystals were dehydrated at 400° C. according to the reaction

$$KH_2AsO_4 \rightarrow KAsO_3 + H_2O, \qquad \text{(ii)}$$

the yield of potassium metarsenate was 99·7 % of theory, which gave a further check on the purity.

Preparation of KD_2AsO_4

As is detailed below, special tests showed that the reaction

$$AsO_3' + D_2O \rightarrow D_2AsO_4' \qquad \text{(iii)}$$

is practically instantaneous. KD_2AsO_4 was therefore prepared by dissolving the appropriate amount of $KAsO_3$ in hot 99·6 % D_2O in a closed vessel to exclude air and water vapour, and allowing the solution to cool slowly by surrounding it with warm water in a vacuum vessel. Well-developed crystals of KD_2AsO_4 were obtained, most of which were needle-shaped with the needle axis the *c* axis.

Examination showed that, unlike KD_2PO_4, the KD_2AsO_4 crystals were produced only with the normal tetragonal structure, similar to that of KH_2AsO_4 and isomorphous with KH_2PO_4.

Measurement of the lattice parameters and isotope effect

(*a*) *Axial lengths in* KH_2AsO_4

Tetragonal crystals approx. 0·2 mm. thick of KH_2AsO_4 were rotated about the *b* and *c* axes in a beam of unfiltered Cu *K* radiation, and the reflexions on the zero-layer line were located, with reference to lines from platinum as standard, on a multiple-exposure spectrometer (Ubbelohde, 1939*a*). The use of this spectrometer eliminated some of the usual errors which hinder the evaluation of precise axial lengths.

With the *c* axis vertical, possible reflexions for the evaluation of precise axial lengths were:

Plane	Bragg angle
10,4,0	79° 29·26′
10,0,0	65° 50·64′
840	64° 50·81′ (α_2) 64° 32·43′ (α_1)

Only the 10,4,0 plane was in a region of sufficiently high dispersion and low absorption to give reasonably accurate axial lengths. On the basis of thirty independent observations the value computed was

$$a = 7{\cdot}609 \pm 0{\cdot}001\,\text{kX.} \quad \text{at} \quad 18^\circ\,\text{C.}$$

With the *b* axis vertical, data which could be used for precision evaluation of the axial lengths included

Plane	Bragg angle
0,10,4	82° 49·83′
093	75° 20·52′ (α_2) 74° 49·14′ (α_1)
048	72° 35·20′ (α_2) 72° 9·05′ (α_1)

The number of reflexions was too small for linear extrapolation by the method of Bradley & Jay (1932).

On the basis of standard formulae for tetragonal crystals, using the data from (0,10,4), $c = 7{\cdot}149 \pm 0{\cdot}0003$ kX. (the mean of eighteen observations). The value uncorrected for absorption, etc., from (048) was $c = 7{\cdot}136 \pm 0{\cdot}001$ kX. (the mean of eleven independent observations). Correction for absorption due to the finite size of the crystal gave $c(048) = 7{\cdot}147 \pm 0{\cdot}001$ kX. In spite of the bigger absorption correction this value was included in the definitive evaluation of the *c* axis, since it depends more on the *c* axis than the 0,10,4 plane. The mean of the two values was taken to give the best value of *c*, namely,

$$c = 7{\cdot}148 \pm 0{\cdot}001\,\text{kX.} \quad \text{at} \quad 18^\circ\,\text{C.}$$

The 093 plane had a large absorption correction with the shapes of crystal available and was not used in obtaining a definitive value for the *c* axis.

(*b*) *The isotope effect in* KH_2AsO_4

Rotation photographs about the *b* and *c* axes were taken with KH_2AsO_4 and KD_2AsO_4 on the multiple-exposure spectrometer. Experimental data are recorded in Table 1.

Comparisons were made between crystals produced in successive batches from the same solution, to verify that no change in lattice spacing arose from possible small changes in stoichiometric composition. Comparisons were also made between freshly isolated KD_2AsO_4 crystals protected from atmospheric moisture by a cellulose–amyl acetate envelope, and crystals of KD_2AsO_4 exposed for 11 days in an atmosphere of relative humidity 60 %, to verify that no rapid exchange occurred between D_2O in the crystals and H_2O in the outer atmosphere.

With one exception no significant discrepancy was observed in crystals from successive batches. Since this exceptional crystal also had an abnormally large dispersion of lattice spacings in different observations it was not included in the final calculations of lattice spacings and isotope effects. Variations observed in measurements made on the crystal exposed for a prolonged period to excess moisture were just outside the acceptable range. This indicated that any D_2O–H_2O exchange during the X-ray photography could be neglected under less extreme conditions.

Table 1. *Isotope effects in* KH_2AsO_4

Index	No. of independent observations	$\theta_H - \theta_D$ (°)	$\alpha \times 10^3$
	Rotation about the *c* axis		
10,4,0	30	0·67	2·237
10,0,0	18	0·30	2·419
840 α_2	15	0·26	2·188
α_1	15	0·26	2·124
	Rotation about the *b* axis		
0,10,4	18	0·759	1·756
093 α_2	12	0·380	1·817
α_1	12	0·378	1·759
048 α_2	11	0·087	0·480
α_1	11	0·068	0·383
084 α_2	12	0·191	1·453
α_1	11	0·196	1·593

The expansion α' per unit length along a plane whose normal makes an angle ψ with the *b* axis is given by an equation

$$\alpha' = A + B\cos 2\psi. \qquad \text{(iv)}$$

Using the data for rotation about the b and c axes, the method of least squares gives

$$A = 1{\cdot}052 \times 10^{-3}, \quad B = 1{\cdot}037 \times 10^{-3},$$

from which

$$\alpha_{11} = \alpha_{22} = 2{\cdot}090 \times 10^{-3} = A + B,$$

$$\alpha_{33} = 0{\cdot}015 \times 10^{-3} = A - B.$$

Errors may be estimated from the comparison between experimental points and the smoothed equation (iv) plotted in Fig. 1.

From Table 1 the main conclusion is that substitution of D for H causes an expansion $\alpha_{11} = 2{\cdot}090 \times 10^{-3}$ along the a and b axes, i.e. in the direction of the H bonds, and that the relative change in the length of the c axis is not greater than $0{\cdot}015 \times 10^{-3}$.

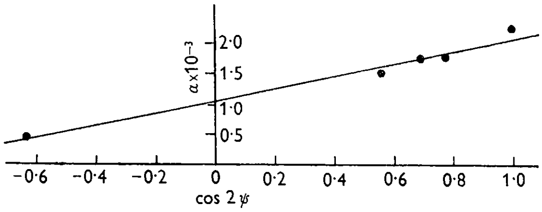


Fig. 1. The isotope effect in KH_2AsO_4. The points indicate experimental data; the straight line corresponds to equation (iv).

(c) *Rate of reaction of* H_2O *with* AsO_3' *and* PO_3'

In view of the rather unsatisfactory data on phosphates and arsenates in the literature, the following experiments were carried out:

(i) *Rate of loss of water from* KH_2AsO_4 *and* KH_2PO_4. By heating KH_2AsO_4 to various temperatures, cooling at intervals in a desiccator, and weighing, it was verified that the reaction

$$KH_2AsO_4 \rightarrow KAsO_3 + H_2O \qquad \text{(v)}$$

was complete within several hours at 400° C. On the other hand, the loss of water in the reaction

$$KH_2PO_4 \rightarrow KPO_3 + H_2O \qquad \text{(vi)}$$

was notably slower and required a higher temperature for the completion.

(ii) *Rate of hydration of* $KAsO_3$ *and* KPO_3. When $KAsO_3$ prepared according to (v) was dissolved in water, pH measurements at intervals on the solution showed that the reaction (for H_2O or D_2O)

$$AsO_3' + H_2O \rightarrow H_2AsO_4' \qquad \text{(iii)}$$

was practically instantaneous. This was further verified by precipitation tests with $AgNO_3$ which showed no change with the time of standing after dissolving the $KAsO_3$, indicating that the ionic equilibrium must be very rapid. Conductivity data (Walden, 1888) support this conclusion.

Though no precision measurements were made on the rate of reaction

$$KPO_3 + H_2O \rightarrow KH_2PO_4, \qquad \text{(vii)}$$

the rate of hydration of PO_3' was evidently much slower. Molten KPO_3 was poured into crushed ice, and the melt was filtered and analysed. Freezing-point data combined with analytical results showed that under these conditions the PO_3' was partly present as polymeric ions $(P_nO_m)^{n-}$, where n is approximately 2. At room temperature there was no increase in pH > 0·6 in a period of 48 hr., at a concentration of 21·5 g.l.$^{-1}$. Complete conversion to KH_2PO_4 would have caused a change of pH of 1·0.

Although these observations indicate qualitatively that the rate of hydration of PO_3' to H_2PO_4' is slower than for the hydration of AsO_3' to H_2AsO_4', no satisfactory quantitative comparisons are feasible on account of the polymerization of the metaphosphate (cf. Davies & Monk, 1949).

Changes in heat content and free energy for proton transfers in H_2AsO_4' and H_2PO_4'

Thermodynamic data in Table 2 have been calculated from various published values, and are of considerable interest but not all of equal reliability. Values for the successive stages of dissociation of H_3PO_4 have been taken from Bjerrum & Unmack (1929) and refer to accurate measurements of activity coefficients. Remaining data have been collected from the *International Critical Tables* and from *Landolt Bornstein Tabellen*, and involve larger uncertainties. ΔH values for the phosphates are derived from the temperature coefficients of the dissociation constants (Bjerrum & Unmack, 1929). Corresponding data for the arsenates are not available; calorimetric evaluations in dilute solutions (M/200) are given as the nearest corresponding results.

Table 2. *Thermodynamic data*

Molecule	Dissociation constant K (18° C.)	ΔH (Cal. mole^{-1})
H_3AsO_4	$4{\cdot}83 \times 10^{-3}$ (calc.)	$-1{\cdot}0$
H_3PO_4	$1{\cdot}32 \times 10^{-2}$	$-2{\cdot}43 \pm 0{\cdot}4$
H_2AsO_4'	$4{\cdot}21 \times 10^{-5}$	$+1{\cdot}2$
H_2PO_4'	$1{\cdot}69 \times 10^{-7}$	$+1{\cdot}35 \pm 0{\cdot}2$
$HAsO_4''$	$6{\cdot}97 \times 10^{-10}$	$+5{\cdot}5$
HPO_4''	$2{\cdot}92 \times 10^{-13}$	$+6{\cdot}20 \pm 0{\cdot}9$

These data indicate that the proton is less firmly held by H_2AsO_4' than by H_2PO_4'. For proton transfer in the crystals the free energy and heat changes in the following reactions are also significant. (The values are derived from those in Table 2 and are given in Cal. mole^{-1}.)

$$2H_2AsO_4' \rightarrow H_3AsO_4 + HAsO_4'', \quad \Delta G = 5{\cdot}2, \quad \Delta H = 2{\cdot}2, \qquad \text{(viii)}$$

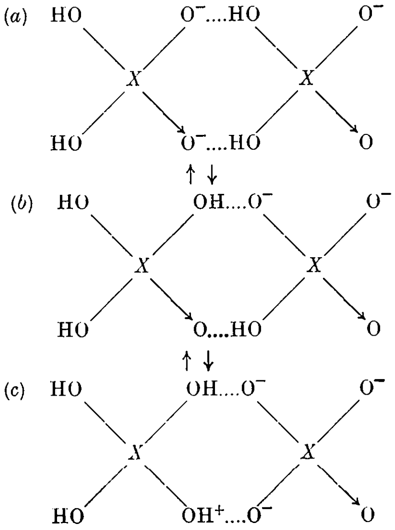
$$2H_2PO_4' \rightarrow H_3PO_4 + HPO_4'', \quad \Delta G = 6{\cdot}5, \quad \Delta H = 3{\cdot}8. \qquad \text{(ix)}$$

Discussion

Relation of the isotope effect to the crystal structure of KH_2AsO_4

When the value of α in relation to the direction in the crystal is plotted in a polar diagram it is found that the hydrogen bonds practically coincide with the direction of maximum expansion, as in the isomorphous salts KH_2PO_4 and $(NH_4)H_2PO_4$. The interpretation of this expansion as indicating a resonance contribution to the hydrogen bond in these crystals has been previously discussed (Robertson & Ubbelohde, 1939; Ubbelohde, 1949).

So far as this interpretation applies, possible distributions of protons in the crystal may be illustrated for four contiguous O atoms as follows:



The basicities of H_3PO_4 and H_3AsO_4 are so low that (*c*) is unlikely to be of any importance in the crystal. On the other hand, so far as the data for proton transfer in solution can be applied to the crystals, (*b*) may be of some importance. Any appreciable overlap of the energy states of (*a*) and (*b*) will contribute a resonance term to the total lattice energy, which will be sensitive to the exact separation of the O atoms, as in the previously discussed examples of hydrogen bonds in crystals.

Comparative properties of the hydrogen bonds in $(NH_4)H_2PO_4$, KH_2PO_4 *and* KH_2AsO_4

The present results permit a fairly precise comparison of isotope effects in crystals with similar structures.

If it is assumed that the whole of the lattice expansion on substituting D for H can be attributed to the H bonds, these bonds expand rather less in KH_2AsO_4 than in either KH_2PO_4 or $(NH_4)H_2PO_4$. Data in Table 3 have been calculated on this assumption from the data given above and in the previous publications (Ubbelohde, 1939; Ubbelohde & Woodward, 1942). The larger expansion in $(NH_4)H_2PO_4$ is accompanied by a small Poisson contraction at right angles.

Table 3. *Comparative expansions of* H *bonds on substituting* D *for* H

Crystal	Expansion of H bond (kX.)
KH_2AsO_4	0·0080
KH_2PO_4	0·0097
$(NH_4)H_2PO_4$	0·0100

The close similarity between these values indicates that the general nature of the isotope effect is the same in these three crystals.

On the other hand, the quantitative differences between the dissociation constants show that the proton is more firmly bound in H_2PO_4' than in H_2AsO_4'. The more rapid hydrolysis in reaction (iii) is probably due to the same fact.

A weaker proton bond between neighbouring groups, compared with H_2PO_4' groups, is suggested by the smaller isotope effect. Again, the hydrogen bridge in KH_2PO_4 (2·52 A.) is also shorter than that in KH_2AsO_4 (2·54 A.), indicating more overlap of energy states. Too much weight cannot be placed on this, however, since experimental error in the detailed analysis of the two crystal structures is of the order of 0·01–0·04 kX.

A somewhat stronger proton bond in the arsenate crystal might have been anticipated from the closer overlap of the heats and free energies in the proton transfer (viii) than in reaction (ix). However, these values of ΔG and ΔH refer to transfer in aqueous solution. In the crystal, the larger volume of the unit cell for the arsenate than for the phosphate,

$$KH_2AsO_4: 414{\cdot}1\,\text{kX.}^3, \quad KH_2PO_4: 384{\cdot}1\,\text{kX.}^3,$$

points to the greater influence of repulsion forces in the arsenate, which may outweigh the factors discussed above. These larger repulsion forces are probably due to the larger size of the central atom in the arsenate ion.

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