



difference between a.c. and d.c. conductivities, and at 75° for example, the 30-cycle conductance of 13-30 is 16.04  $\times$  10<sup>-9</sup> while the d.c. value is 15.86  $\times$ 10<sup>-9</sup>. These figures are cited in order to emphasize the need for precision in work at low frequencies; obviously an error of only 0.5% in either  $\kappa_{20}$  or  $\kappa_0$ would change  $\epsilon''$  by  $\pm 50\%$  in the above example.

Our frequency range was not wide enough to determine the complete a.c. properties of the conducting plastics, but enough information was obtained to show that a distribution of relaxation times<sup>14</sup> is needed to describe the response to a periodic electrical field. In Fig. 8, the a.c. loss factor (calculated from the excess of a.c. conductance over the observed d.c. conductance) is plotted against dielectric constant for several of the samples at  $75^{\circ}$  (except 27-0, whose curve refers to 25°). Most of the Cole plots can be approximated by circular arcs with centers below the  $\epsilon$ '-axis, and hence a single relaxation time does not suffice to describe the a.c. response. It will also be noted that guite long time constants are necessary, because even at 30 cycles, the static dielectric constant is still quite far away. Furthermore, another unknown mechanism for energy dissipation must appear at frequencies beyond our upper limit, because the apparent high frequency limits in Fig. 8 are considerably larger than the square of the index of refraction. Similar results also have been obtained in other polymeric systems which did not contain electrolyte.<sup>15</sup>

(14) R. M. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc., 63, 385 (1941).

(15) D. J. Mead and R. M. Fuoss, *ibid.*, **63**, 2832 (1941).

# POLYMERIZATION AND DEPOLYMERIZATION PHENOMENA IN PHOSPHATE-METAPHOSPHATE SYSTEMS AT HIGHER TEMPERATURES. II. THE THERMAL BEHAVIOR OF ALKALI METAL MONOHYDROGEN SULFATE-MONOHYDROGEN PHOSPHATE MIXTURES

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When equimolar mixtures of sodium monohydrogen sulfate and sodium monohydrogen phosphate are heated an initial exothermic acid-base reaction occurs below 200° resulting in the formation of sodium sulfate and the dihydrogen phosphate. The latter substance then undergoes stepwise dehydration-condensation resulting in the eventual formation at temperatures above 600° of the glassy metaphosphate. No evidence for a sulfatophosphate could be adduced from differential thermal analysis and X-ray diffraction studies, chemical analysis or weight loss experiments. Equimolar mixtures of potassium hydrogen sulfate and potassium dihydrogen phosphate behave in an analogous fashion. The initial highly exothermic proton transfer reaction takes place at about 200° whereupon conversion of the dihydrogen phosphate to the metaphosphate occurs, representing the only further detectable chemical change as the temperature is raised.

## Introduction

Recognition of the fact that the fundamental structural unit which characterizes all phosphates, polyphosphates and polymetaphosphates is the  $PO_4$  tetrahedron has made it possible to interpret more

(1) Abstracted in part from the doctoral dissertation presented to the Graduate College of the University of Illinois, 1952.

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precisely the many interesting aggregation reactions which the various hydrogen phosphates undergo at higher temperatures. Conversion of orthophosphate into pyrophosphate, triphosphate, and the high molecular weight polyphosphates involves the linking together of such PO<sub>4</sub> tetrahedra through oxygen atoms. The same structural unit also characterizes the cyclic metaphosphates in which stable structures consisting of three and four  $PO_4$  tetrahedra are built up which may be regarded as six- and eight-member ring ions containing alternate phosphorus and oxygen atoms.

Other neighboring acid forming elements, specifically silicon, chromium, sulfur and arsenic, each in their higher valence states, form similar structural XO<sub>4</sub> units which may be condensed to form polystructures resembling those specified for the polyand metaphosphates. It is interesting to note that the X–O bond lengths in each of these units differ only slightly, even though the charge on the oxo complex will vary depending upon the formal charge on the central atom. Recognition of the fact that these structural units are approximately of the same size leads to the interesting possibility that simple mixed poly-acids, in which a PO<sub>4</sub> tetrahedron is replaced by any one of the other tetrahedra, may be capable of existence. There is already some evidence in the literature that such acids or their salts have been synthesized. Thus, for instance, the well-known hydrocarbon cracking catalyst material called silicophosphoric acid may conceivably be a polysilicic acid in which the  $SiO_4$ tetrahedra are replaced in part by PO<sub>4</sub> structures. It also has been shown that if sodium dihydrogen phosphate is fused with a relatively small amount of sodium dihydrogen arsenate, a product is obtained in which  $AsO_4$  tetrahedra replace PO<sub>4</sub> groups in the lattice of the resulting insoluble metaphosphate.<sup>3</sup>

Poni and Cernatescu<sup>4</sup> claim to have prepared a compound by fusion of sodium monohydrogen sulfate and sodium monohydrogen phosphate which may be regarded as a sulfatophosphate, i.e., a pyrophosphate in which one of the  $\hat{PO}_4$  tetrahedra is replaced by an SO<sub>4</sub> structural unit. Such a compound would represent one of the simplest heteropoly acids capable of existence. However, application of Pauling's rules<sup>5</sup> governing the linking of coördination polyhedra indicates that such compound formation is improbable even though the P-O and S-O bond distances in the respective tetrahedra are quite similar (P-O, 1.55 Å. and S-O, 1.51 Å.). The formation of a sulfatophosphate in which both central atoms have a high formal charge and a relatively low coördination number would thus appear improbable on the basis of Pauling's generalizations. A more thorough investigation of the validity of the claims of Poni and Cernatescu was therefore considered advisable.

The investigation of the reaction between sodium hydrogen sulfate and sodium monohydrogen phosphate has revealed that no compound formation occurs. Instead a preliminary exothermic, acid-base type reaction takes place involving transfer of the proton from the hydrogen sulfate to the monohydrogen phosphate ion to yield sodium sulfate and sodium dihydrogen phosphate. The resulting sodium dihydrogen phosphate undergoes further dehydration and condensation upon heating to form disodium dihydrogen pyrophosphate, then

(3) E. Thilo and G. Schulz, Z. anorg. allgem. Chem., 266, 34 (1951).

(4) M. Poni and R. Cernatescu, Ann. Sci. Univ. Jassy, 28, Sec. I, 3 (1942).

(5) L. Pauling, J. Am. Chem. Soc., 51, 1010 (1929).

the metaphosphates and finally the metaphosphate glass as the temperature is raised.

Considerable evidence has, however, been presented by various investigators to demonstrate that the size of the cation has an appreciable influence on the stability of oxygen bridges in polyanionic aggregates consisting of linked coordination tetrahedra such as the  $PO_4$  and  $SO_4$  groups. In general, the larger the cation the more stable thermally is the condensed anion. The reaction of potassium monohydrogen sulfate with potassium monohydrogen orthophosphate was therefore studied in the hope that the larger potassium ion might possibly favor the formation of such a sulfatophosphate. Again, a strongly exothermic process oc-curs first, and is followed by a series of changes which are characteristic for mixtures of potassium sulfate and potassium dihydrogen phosphate as the temperature is raised.

**Experimental Procedures.**—The method of differential thermal analysis was used to gain some preliminary insight concerning the nature of the reactions which occur when composite samples of the reactants were heated at a controlled rate of approximately eight to ten degrees per minute. Weights of samples subjected to differential thermal analysis were standardized at ten grams. Check runs were also carried out subsequently using the newer Brown Electronik differential thermal analysis equipment now available for the study of reactions at higher temperatures and in the solid state. The identity of the intermediate and the final products was verified by chemical methods and X-ray diffraction studies. In general, procedures were similar to those which have been described previously by Osterheld and Audrieth.<sup>6</sup>

# Thermal Changes in the System NaHSO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>

The differential thermal analysis curves for the system NaHSO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub> and related mixtures and for various pure components are depicted schematically in Fig. 1. Reference to A (Fig. 1) shows that a strong exothermic reaction, commencing at approximately 150° and reaching its peak at 180°, is the first process which is evident when equi-molecular quantities of the two materials are heated after having been ground together to form an intimate mixture. The thermal changes which characterize this mixture most certainly do not correspond to those which are observed when either of the pure components (B and C) is heated. On the other hand, except for the initial exothermic reaction, the thermal behavior of the system under investigation is completely analogous to that which characterizes a mixture consisting of equimolar quantities of sodium sulfate and monosodium dihydrogen phosphate (D). The thermal changes which occur when pure samples of sodium sulfate and of the monosodium dihydrogen phosphate are heated are depicted by E and F in Fig. 1.

These findings lead to the conclusion that an exothermic acid-base reaction occurs initially involving proton transfer from the  $HSO_4^-$  to the  $HPO_4^-$  ion in accordance with the equation

# $NaHSO_4 + Na_2HPO_4 \rightarrow Na_2SO_4 + NaH_2PO_4$

after which each of the resulting components undergoes those high temperature changes characteristic of each. It is interesting to point out (a) that the

(6) R. K. Osterheld and L. F. Audrieth, THIS JOURNAL, 56, 38 (1952).



Fig. 1.—Schematic presentation of thermal changes which occur for components and products in the system NaHSO<sub>4</sub>-NaHPO<sub>4</sub>: A, NaHSO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> in equimolar quantities; B, NaHSO<sub>4</sub>; C, Na<sub>2</sub>HPO<sub>4</sub>; D, Na<sub>2</sub>SO<sub>4</sub>-NaH<sub>2</sub>-PO<sub>4</sub> in equimolar quantities; E, Na<sub>2</sub>SO<sub>4</sub>; F, NaH<sub>2</sub>PO<sub>4</sub>; G, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (in 2:1 mole ratio); H, (NaPO<sub>8</sub>)<sub>x</sub>; I, fusion product from equimolar quantities of NaHSO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

initial exothermic heat effect is of sufficient magnitude to cancel out the considerable endothermic effect which accompanies the melting and concomitant decomposition of the sodium hydrogen sulfate, and (b) that the proton transfer reaction occurs in that temperature range over which the phase change, *i.e.*, melting of sodium hydrogen sulfate, takes place (m.p. of NaHSO<sub>4</sub> is listed at 186° in the literature). The system thus becomes more labile and more susceptible to chemical change.

A continuing series of endothermic changes then takes place beginning at approximately 200°. These changes may be looked upon as involving first the conversion of the dihydrogen phosphate into the dihydrogen pyrophosphate which has been shown to take place rapidly at 220° (see Fig. 1(D)) followed by the endothermic solid phase transition of sodium sulfate from the low temperature orthorhombic form to the high temperature hexagonal lattice (transition temp.234°) and then by the further dehydration-condensation of the dihydrogen pyrophosphate into the insoluble sodium metaphosphate which normally takes place between 310 to 375°.<sup>7</sup> That the above interpretation of the process is correct is verified by thermal analysis of a mixture consisting of a 2:1 mole ratio of sodium sulfate-disodium dihydrogen pyrophosphate (see Fig. 1 (G)).

That the second process beginning at 200° results in formation of the dihydrogen pyrophosphate has been verified by carrying out weight loss experiments to determine quantitatively the amount of water eliminated when equimolar mixtures of NaHSO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> are heated at this temperature for an extended period of time. The data are depicted graphically in Fig. 2, and show that approximately one-half mole of water is lost per mole of mixture.

$$\frac{2Na_2SO_4 + 2NaH_2PO_4}{2Na_2SO_4 + Na_2H_2P_2O_7 + H_2O_7}$$

The product obtained by heating this mixture for 17 hours at 200° was found to give an X-ray pattern showing excellent agreement with that corresponding to a mixture of sodium sulfate and disodium dihydrogen pyrophosphate. Chemical analysis of the product was found to give values of 25.1 and 24.9%  $P_2O_5$  as pyrophosphate; these results agree fairly well with the theoretical value of 28.1% demanded by the above equation.



Fig. 2.—Weight loss curves for equimolar mixtures of: A, NaHSO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub> at 200°; B, KHSO<sub>4</sub>-K<sub>2</sub>HPO<sub>4</sub> at 210°; C, KHSO<sub>4</sub>-K<sub>2</sub>HPO<sub>4</sub> at 350°.

Although specific conditions are not disclosed by Poni and Cernatescu, it was their claim that an alleged phosphatosulfate is obtained when sodium monohydrogen phosphate dihydrate and sodium hydrogen sulfate are fused. It was still conceivable, although considered unlikely, that such compound formation might occur at temperatures above 600°. A sample of these components in

(7) Exact reproducibility with respect to temperatures at which these changes occur is not possible due to the rapid heating rate which is employed in studying the thermal changes by the method of differential thermal analysis. Sufficient time is not available to effect completion of a reaction at the temperature at which the reaction begins to take place. equimolar amounts and intimately mixed, was therefore heated gradually to 800° over a period of one hour and maintained at this temperature for ten minutes. The sample was found to have undergone a weight loss corresponding to three moles of water per mole of reactants. An X-ray diffraction pattern of the product formed by rapid cooling of the melt was found to reveal only the pattern of the high temperature form of sodium sulfate, leading to the assumption that the glassy metaphosphate had been formed as the other product.

The presence of the glassy metaphosphate was verified by subjecting the fusion product to differential thermal analysis. A strong exothermic reaction occurs when an authentic sample of the glassy metaphosphate is heated to approximately 320-400° (curve H in Fig. 1). This reaction is due to devitrification and conversion of the glassy polymer into the stable crystalline trimetaphosphate.<sup>8</sup>

The thermal analysis curve for the fusion product (curve I, Fig. 1) discloses an identical exothermic break with a maximum at about  $400^{\circ}$ —leading to the conclusion that the product formed by melting together NaHSO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> is not a sulfatophosphate, but a mixture of sodium sulfate and glassy sodium metaphosphate.<sup>9</sup>

# The System KHSO<sub>4</sub>-K<sub>2</sub>HPO<sub>4</sub>

The thermal changes which occur when equimolar mixtures of KHSO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub> are heated are represented schematically by (A) in Fig. 3. For comparison the curves for potassium hydrogen sulfate (B), potassium monohydrogen phosphate (C), potassium dihydrogen phosphate (D) and potassium sulfate (E) are also given.

The marked endothermic change which begins at about 200° when potassium hydrogen sulfate is heated corresponds to melting (reported variously in the literature as 200 to 210°) followed by dehydration and decomposition to form the pyrosulfate, thus accounting for continuation of the endothermic break beyond the melting point. The further endothermic break at approximately 420° corresponds to the melting point of the pyrosulfate.

The thermal changes which occur when potas-

(8) Reference should also be made to the fact that two small endothermic breaks occur above 600°, the second corresponding to the melting of the trimetaphosphate which takes place at approximately  $625^\circ$ . The cause for the first of these endothermic breaks has not been definitely established. Both of these endothermic breaks occur at somewhat lower temperatures when NaH<sub>2</sub>PO<sub>4</sub> and the 1:1 mixture of NaHSO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> are heated. These breaks are also evident in the thermal analysis curve for the fusion product.

(9) Further proof for this conclusion was sought by undertaking a study of phase relationships for the system  $Na_2SO_4$ -(NaPO<sub>8</sub>)<sub>x</sub> varying from 0 to 60 mole per cent. metaphosphate. The method of differential analysis is not well adapted for this purpose even when samples were originally heated to fusion, cooled to 300°, and then reheated at a controlled rate to determine thermal changes occurring at higher temperatures. Endothermic breaks corresponding to initial melting and complete melting were interpreted as corresponding, (a) to the eutectic temperature (approximately 595°) and the melting points of the various mixtures which decreased continuously from 885° to 725° for a mixture containing 60 mole per cent. metaphosphate. No compound formation appears to be indicated for mixtures containing 50 mole per cent. of each constituent. Consistent results could not be obtained for mixtures containing high percentages of the glassy metaphosphate and weight losses varying from 1 to 4% were also observed. These may be ascribed to a high temperature acidbase reaction between poly-metaphosphate and sulfate resulting in elimination of sulfur trioxide.

sium monohydrogen orthophosphate and potassium dihydrogen orthophosphate are heated have been studied in detail by Osterheld and Audrieth.<sup>6</sup> Dipotassium hydrogen phosphate is converted to potassium pyrophosphate whereas monopotassium dihydrogen phosphate changes at a temperature somewhat over 200° into the insoluble potassium metaphosphate. The final break at about 800° corresponds to the melting point of the waterinsoluble potassium metaphosphate. Reference is also made to the fact that potassium sulfate undergoes an endothermic change just below 600° corresponding to a solid phase transition from the rhombic to hexagonal lattice. The reported value in the literature for this transition is 588°.



Fig. 3.—Schematic presentation of thermal changes which occur for components and products in the system  $KHSO_4-K_2HPO_4$ : A,  $KHSO_4$  and  $K_2HPO_4$  in equimolar quantities; B,  $KHSO_4$ ; C,  $K_2HPO_4$ ; D,  $KH_2PO_4$ ; E,  $K_2$ -SO<sub>4</sub>.

If the heating curves for the various pure substances are compared with the differential curve characteristic of equimolar mixtures of potassium hydrogen sulfate and dipotassium hydrogen phosphate, it becomes immediately apparent that the initial strong exothermic reaction may be accounted for by assuming that an acid-base type of reaction takes place which leads to formation of potassium sulfate and potassium dihydrogen phosphate. This exothermic reaction is indeed much more marked in the potassium system than observed in the corresponding sodium system. It occurs at a somewhat higher temperature but again just a few degrees below the temperature at which the acid hydrogen sulfate begins to melt and undergo further dehydration.

The dihydrogen orthophosphate then undergoes dehydration to the insoluble metaphosphate whereas potassium sulfate undergoes no further change until a temperature just below 600° is reached where an endothermic reaction occurs corresponding to a change from the orthorhombic to the hexagonal form. The final break at 800° is due to the melting of potassium metaphosphate.

Weight loss experiments for equimolar samples heated at 210 and at 350° are presented in Fig. 2 and demonstrate that the reaction occurring slowly at the lower temperature and more rapidly at the higher one can be represented by the equation

$$KHSO_4 + K_2HPO_4 \longrightarrow K_2SO_4 + KPO_3 + H_2O_4$$

Chemical and X-ray diffraction analyses were performed on products obtained upon cooling melts produced by heating equimolar mixtures. The X-ray diffraction patterns were found to correspond with those consisting of intimately ground equimolar mixtures of potassium metaphosphate and potassium sulfate and composite patterns of each of the pure components. The insoluble potassium metaphosphate was determined by leaching thoroughly with water and weighing the insoluble residues. The soluble metaphosphate in the filtrate also was determined. Typical samples were found to contain 36.2 and 36.1% insoluble KPO<sub>3</sub>, 5.09% soluble KPO<sub>3</sub> giving a total of 41.3% metaphosphate (required by theory, 40.4%).

It is again apparent that no sulfatophosphate is formed when potassium hydrogen sulfate and dipotassium hydrogen phosphate are heated even up to the fusion point, but that instead an initial acidbase reaction occurs resulting in the formation of potassium sulfate and potassium dihydrogen phosphate, both of which subsequently undergo those thermal changes which characterize each of them as pure components.

# NOTE ON PROPERTIES OF AQUEOUS SUSPENSIONS OF TIC AND TIN

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An investigation of cataphoresis, pH and conductimetric titrations, and viscosity indicates that TiC, TiN and ZrN form stable electrocratic suspensions in an acid medium. Hydrogen ions adsorbed on the particle surfaces, together with a diffuse layer of anions, lead to positively-charged particles.

## Introduction

There have been no previous investigations reported on the properties of nitride-water or carbide-water systems. The properties of suspensions of these materials are of general interest in the preparation of stable suspensions, and in particular for the fabrication of various test suspensions and crucibles by casting in plaster molds. In the present study, experiments have been mainly concerned with TiN and TiC. A few experiments with ZrN were undertaken, but in a finely-ground form its reaction with water is fairly rapid.

There have been quite extensive investigations of the properties of various clay-water suspensions.<sup>2</sup>



Fig. 1.—Particle size distribution of TiC, TiN and ZrN.

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F. H. Norton and A. L. Johnson, J. Am. Ceram. Soc., 24, 189 (1941).

In these systems, the clay particles are negatively charged, the charge and suspension stability being largely determined by the nature of a diffuse layer of exchangeable cations. Investigations of oxidewater systems have shown that stable suspensions of finely-ground materials like aluminum oxide can be formed.<sup>8,4</sup> In an acidic suspension, hydrogen ions are preferentially adsorbed, while in alkaline suspensions hydroxyl ions are preferentially adsorbed.

## Experimental

Samples of TiN and ZrN (Metal Hydrides Company, 300 mesh) and TiC (Kennametal Company, 200 mesh) were ground for 24 hours in steel ball mills using ethanol as a grinding medium. After grinding, tramp iron was removed with a magnetic separator and repeated leaching with hydrochloric acid. The particle size distribution was determined by a hydrometer-sedimentation method,<sup>5</sup> and is given in Fig. 1.

Cataphoresis measurements were made with a U-tube having platinum electrodes in each arm connected through a series rheostat (to prevent overheating) to 110 volts d.c. The concentration of solids was 20 g./l.

A quantitative measure of hydrogen ion adsorption was determined by pH and conductivity titrations with dilute hydrochloric acid. Prior to testing, the solids were repeatedly washed with distilled water.

Measurements of viscosity at various supensions specific gravities and pH values were made with a modified Mac-Michael viscosimeter.

# Results

Cataphoresis experiments in acid medium gave deposits of TiC, TiN and ZrN at the negative electrode only, indicating that the particles in all cases

- (3) W. E. Hauth, Jr., THIS JOURNAL, 54, 150 (1950).
- (4) W. E. Hauth, Jr., J. Am. Ceram. Soc., 32, 394 (1949).
- (5) F. H. Norton and S. Spiel, ibid., 21, 89 (1938).