TABLE I

COMBUSTION DATA

Mass of sample, g.	Total energy cor. to 30°, cal.	Cor. for fuse, Elt. and HNO_3, cal.	Net energy, cal.	$-\Delta U_B$, cal./g.
		NbC		
1.99869	5437.12	8.17	5428.95	2716.3
1.99918	5438.46	8.24	5430.22	2716.2
1.99896	5440.45	8.33	5432.12	2717.5
2.00062	5439.36	8.41	5430.95	2714.6
1.50086	4080.99	7.39	4073.60	2714.2
1.51236	4113.67	8.33	4105.34	2714.5
1.51224	4116.26	8.14	4108.12	2716.6
1.50986	4109.41	8.27	4101.14	2716.2
			Mean	2715.8 ± 0.8
			Cor. for imp.	7.4
				2723.2
		ZrC		
1.11036	3264.50	12.08	3252.42	2929.2
1.11014	3264.49	12.46	3252.03	2929.4
1.11022	3264.77	14.26	3250.51	2927.8
1.11021	3264.06	12.71	3251.35	2928.6
			Mean	2928.8 ± 0.8
			Cor. for imp.	82.4
				3011.2

Heats of Formation.—The corrected mean result for niobium carbide corresponds to $\Delta E_{303.16} = -283.89$ kcal./mole of $NbC_{0.9445}$, the energy evolution under bomb conditions. Correction to unit fugacity of oxygen (−37 cal.), to a constant pressure process (−753 cal.), and to 25° (−2 cal. leads to $\Delta H_{298.16} = -284.69$ kcal./mole as the standard heat of combustion of $NbC_{0.9445}$. Employing Humphrey's[1] value of the heat of formation of niobium pentoxide and the N. B. S. value[4] for carbon dioxide, there is obtained $\Delta H_{298.16} = -31.75 \pm 0.8$ kcal./mole as the heat of formation of niobium carbide ($NbC_{0.9445}$) from the elements. Assuming zero heat of solution of niobium metal in carbide of stoichiometric composition, there is obtained $\Delta H_{298.16} = -33.6 \pm 0.8$ kcal./mole as the heat of formation of $NbC_{1.000}$ from the elements.

Similarly, the corrected mean value for zirconium carbide corresponds to $\Delta E_{303.16} = -310.85$ kcal./mole as the energy evolution under bomb conditions. Correction to unit fugacity of oxygen (−15 cal.), to a constant pressure process (−602 cal.), and to 25° (2 cal.) gives $\Delta H_{298.16} = -311.5$ kcal./mole as the standard heat of combustion of zirconium carbide. Applying Humphrey's[1] heat of formation of zirconium dioxide and the N. B. S. value[4] for carbon dioxide, there is obtained $\Delta H_{298.16} = -44.1 \pm 1.5$ kcal./mole as the heat of formation from the elements.

It is believed that the uncertainties assigned to the heat of formation values are large enough to account for errors in the corrections to exact stoichiometric composition. All other errors are minor in comparison to those associated with the impurity contents of the samples.

It is of interest to compare the present heat of formation values with those of tantalum carbide,[5] $\Delta H_{298.16} = -38.5$ kcal./mole, and titanium carbide,[5] $\Delta H_{298.16} = -43.85$ kcal./mole. As the entropies of formation should not differ greatly, it is evident that zirconium and titanium carbides have about the same thermodynamic stability, while niobium carbide is somewhat less stable than tantalum carbide.

(4) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Stands. Circ. 500, 1952.

(5) G. L. Humphrey, THIS JOURNAL, **73**, 2261 (1951).

MINERALS THERMODYNAMICS EXPERIMENT STATION
REGION II, BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR
BERKELEY 4, CALIFORNIA

Some Phosphates of Aliphatic Diamines[1]

BY ROY C. MAST[2] AND RALPH E. OESPER

RECEIVED AUGUST 19, 1955

Although both aliphatic diamines and the phosphoric acids are common chemicals, the salts which form during the reaction between solutions of these substances have not been described.[3] The primary objective of this investigation was the preparation of some of these salts. Diamines are diprotic bases which always react with two equivalents of acid in salt formation; therefore the various series of salts which could be isolated were due to changes in the phosphate ion with varying *p*H.

Experimental

Reagents.—Ethylenediamine was obtained from the Eastman Kodak Company, 1,2-diaminopropane from the Union Carbide and Carbon Company, and 1,3-diaminopropane and 1,3-diaminobutane from the Sharples Company. All were distilled shortly before use and were water white. Merck "Reagent Grade" orthophosphoric acid was used without further treatment. Lumpy pyrophosphoric acid was obtained from City Chemical Company, New York City. The material was stored under refrigeration, and only the required amount dissolved immediately before use. Such solutions of pyrophosphoric acid were kept cool (under 30°), and were not allowed to remain below *p*H 4 any longer than necessary. These precautions prevented any significant hydrolysis to orthophosphate during the reactions.

General Procedure.—All systems investigated were taken through the following systematic steps.

1. Approximately 6 *N* aqueous solutions were prepared. Solutions of this strength made it possible to obtain an appreciable amount of solid product from a relatively small volume of reaction mixture.

2. The changes in *p*H resulting from the slow addition of diamine solution to the acid were followed with a *p*H meter. The resulting curves of both ortho- and pyrophosphoric acids with all of the diamines studied have the same general form.[4] An inflection point near *p*H 4 (the dihydro-

---

(1) From the M.S. thesis submitted by Roy C. Mast to the Graduate School of the University of Cincinnati.

(2) Address all communications to this author: The Procter & Gamble Company, Miami Valley Laboratories, Box 175, Cincinnati 31, Ohio.

(3) J. P. Ebel and J. Colas, *Compt. rend.*, **239**, 173 (1954), have combined solutions of some diamines (including ethylenediamine) and condensed phosphates (including pyrophosphate) in an attempt to get precipitates of analytical value. They did not isolate and characterize any of the products to be described here.

(4) An accompanying figure showing the *p*H titrations and the tables of X-ray powder patterns have been deposited as Document number 4663 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

gen end-point) occurs at a molar ratio of 1:2 of diamine to orthophosphoric acid, and at 1:1 of diamine to pyrophosphoric acid. No product was obtained in which the diamine was only monoprotic in the crystals.

3. Acid and base were mixed until the *p*H reached the desired value at which a particular salt was expected to be present.

4. Crystallization was attempted. The usual procedure was to cool the reaction mixture and then add a solvent in which the diamine phosphate was insoluble. Since the optimum conditions for crystallization varied from product to product, it was usually necessary to try many variations before crystals could be successfully isolated.

5. When a solid product was obtained, its identity was established by chemical analysis. Nitrogen was determined first by a semi-micro Kjeldahl procedure (Winkler modification), using selenium as the catalyst. If the results of this determination did not indicate the presence of an anhydrous salt whose composition could then be deduced directly, the phosphorus content was determined by the alkalimetric phosphomolybdate method. Since hydrates were frequently obtained, dehydration was attempted.

6. The thermal behavior of the products was observed. They all melt with decomposition, losing diamine, and forming various condensed phosphates. None crystallize again when cooled. The decomposition products were established by well-known qualitative phosphate reactions; *viz.*, the formation of a yellow precipitate when orthophosphate reacts with silver ions, a white precipitate when zinc ions react with pyrophosphate at *p*H 3.8 and, finally, the instantaneous formation of a white precipitate when high-molecular weight polyphosphates react with barium ions in a strong acid solution.

The compounds isolated show a thermal decomposition behavior which is characteristic of the phosphates. The dihydrogen orthophosphates decompose to form glassy polyphosphates; the monohydrogen orthophosphates form pyrophosphates, and the pyrophosphates yield polyphosphates. Decomposition residues from monohydrogen orthophosphate give a positive test for both polyphosphate and pyrophosphate.

7. The solids were further characterized by their X-ray diffraction patterns.[4] These powder patterns were obtained on a North American Phillips X-ray unit equipped with a 114.6 mm. diameter cylindrical powder camera and nickel filtered Cu K_α radiation. Exposure times were approximately 2 hours. Samples were mounted in finely drawn Pyrex capillaries. The accuracy of the entire procedure was checked by running a pattern on pure sodium chloride.

Ethylenediamine[5] Preparations

Ethylenediammonium Dihydrogen Orthophosphate, $(enH_2)(H_2PO_4)_2$.—Aqueous ethylenediamine was added to orthophosphoric acid until the *p*H reached 3.5 (methyl orange end-point). The solution was cooled in ice and ethyl alcohol added slowly and with vigorous stirring. Two layers separated. Growth of acicular crystals started in the lower viscous layer after standing for approximately 20 minutes in the ice-bath. The product was recrystallized twice from water by the same non-solvent procedure, and then dried over a mixture of calcium chloride and sodium hydroxide.

Anal. Calcd. for $enH_2(H_2PO_4)_2$: N, 10.94. Found: N, 10.89; decomposition point, 177°.[6]

Ethylenediammonium Monohydrogen Orthophosphate, $(enH_2)(HPO_4)$.—This compound precipitates when ethylenediamine is added to orthophosphoric acid and *p*H 8–9 is reached. The reaction is carried out at room temperature. Cooling in an ice-bath produces a more abundant product. The salt was recrystallized twice from water by heating the solution to boiling, cooling and filtering. If the concentrated solution is cooled slowly, large (1 cm. or more), prismatic crystals are obtained.

Anal. Calcd. for $enH_2(HPO_4)$: N, 17.73. Found: N, 17.52; decomposition point, yellowing apparent at 220°; vigorous decomposition at 246°.

Ethylenediammonium Dihydrogen Pyrophosphate, $(enH_2)(H_2P_2O_7)$.—The break in the *p*H curve and the molar ratio of ethylenediamine and pyrophosphoric acid indicate that the ions necessary to form this compound are present in solution at *p*H 3.8. However, it cannot be crystallized from a solution at this *p*H. This substance was isolated by adding ethylenediamine to pyrophosphoric acid until the *p*H reached 2.7. The solution was cooled in ice, and acetone added until two layers appeared. After freezing the system in an acetone–Dry Ice bath, it was stored at 0° for three days. There was still no solid material present, so the freezing and refrigerating process was repeated, and this time crystals appeared. The product was recrystallized once from water by dissolving, adding acetone, cooling and seeding.

Anal. Calcd. for $enH_2(H_2P_2O_7)$: N, 11.77. Found: N, 11.69; decomposition point, 170°.

Ethyleneammonium Monohydrogen Pyrophosphate, $(enH_2)_3(HP_2O_7)_2 \cdot 2H_2O$.—Ethylenediamine was added to a solution of pyrophosphoric acid until a *p*H of 6.5 was reached. Minute prisms were obtained readily when cold alcohol was added to the solution. The compound was easily recrystallized twice from water by dissolving, and adding cold alcohol.

Anal. Calcd. for $(enH_2)_3(HP_2O_7)_2 \cdot 2H_2O$: N, 14.69; P, 21.66. Found: N, 14.62; P, 21.61.

A solid having the same nitrogen content is obtained whenever the foregoing procedure is stopped at *p*H values 5, 6, 6.5, 7 and 8. The crystals show no definite melting point. Vitrification was detected at about 150°. At 210°, the melt was translucent; carbonization and ethylenediamine evolution were apparent at 220°.

Ethylenediammonium Pyrophosphate, $(enH_2)_2P_2O_7$.—The order of addition was reversed, *i.e.*, a solution of pyrophosphoric acid was added to the ethylenediamine until the *p*H went down to 10.5. When cold alcohol was added to the cooled solution, the latter turned milky white. Acicular crystals appeared after overnight storage at 0°. The product was difficultly soluble in distilled water at room temperature, but dissolved readily when a small amount of ethylenediamine was added. The product was recrystallized twice before being analyzed.

Anal. Calcd. for N, 18.80. Found: N, 18.68; decomposition point, approximately 245°.

Diaminopropane Preparations

1,2-Propanediammonium Monohydrogen Orthophosphate, $(pnH_2)(HPO_4) \cdot H_2O$.—Propanediamine was added to orthophosphoric acid until the *p*H reached 9. After the reaction mixture was cooled in ice, addition of cold alcohol accompanied by vigorous stirring produced crystals. They were purified by recrystallizing twice from water.

Anal. Calcd. for $(pnH_2)HPO_4 \cdot H_2O$: N, 14.73; P, 16.37; H_2O, 9.50. Found: N, 14.61; P, 16.46; H_2O, 9.45.

The compound was easily dehydrated, losing all its water after heating at 110° for 30 minutes. The nitrogen content of the dehydrated product was 16.11%; calculated for $(pnH_2)HPO_4$ 16.28%; decomposition point, 216°.

1,2-Propanediammonium Pyrophosphate, $2(pnH_2)_2P_2O_7 \cdot H_2O$.—A solid having this composition was obtained over a broad *p*H range, from 5 to 11. When either cold alcohol or acetone was added to a solution containing pyrophosphoric acid and 1,2-diaminopropane anywhere in this *p*H range, the solution turned milky. If this turbid system was then vigorously stirred, it suddenly set to a semi-solid with the consistency of cold-cream. The liquid phase could be slowly drained away using a filter, leaving a product which, under the microscope, proved to consist of minute needles. The product was recrystallized twice from water.

Anal. Calcd. for $2(pnH_2)_2P_2O_7 \cdot H_2O$: N, 16.72; P, 18.55; H_2O, 2.49. Found: N, 16.61; P, 18.66; H_2O, 2.35. (Water content was determined by vacuum dehydration at room temperature over P_2O_5 for one week.) Decomposition point, discoloration at 205°, melts with vigorous decomposition at 215°.

1,3-Propanediammonium Dihydrogen Orthophosphate, $(tmdH_2)(H_2PO_4)_2$.—The diamine was added to orthophosphoric acid until *p*H 3.5 was reached. When the cold solution was treated with cold acetone, two layers formed. The upper layer was decanted, more cold acetone added,

---

(5) The following abbreviations are employed: en = ethylenediamine, pn = 1,2-diaminopropane (propylenediamine), tmd = 1,3-diaminopropane (trimethylenediamine), and db = 1,3-diaminobutane.

(6) Since there is frequently a temperature range over which the products decompose, all decomposition points are uncorrected.

and the system was repeatedly frozen in an acetone–Dry Ice bath, then thawed. It was finally stored overnight at 0°. This treatment produced crystals which were recrystallized by dissolving in water, cooling, adding cold acetone with vigorous stirring until an oily layer separated. When seeded, and kept at 0° for two hours, crystals appeared.

Anal. Calcd. for $(tmdH_2)(H_2PO_4)_2$: N, 10.36. Found: N, 10.40; decomposition point, 163°.

1,3-Propanediammonium Monohydrogen Orthophosphate, $(tmdH_2)(HPO_4)\cdot H_2O$.—This was a simple and straightforward preparation. The diamine was added to orthophosphoric acid until *p*H 8 was reached. Gradual addition of cold alcohol to the solution accompanied by vigorous stirring produced crystals. They were purified by recrystallizing twice from water.

Anal. Calcd. for $(tmdH_2)HPO_4\cdot H_2O$: N, 14.73; P, 16.37; H_2O, 9.51. Found: N, 14.73; P, 16.44; H_2O, 9.32 (constant weight at 125°); decomposition point, 225°.

1,3-Propanediammonium Pyrophosphate, $(tmdH_2)_2P_2O_7\cdot 3H_2O$.—This compound was more difficult to crystallize than were previous products which resulted in the alkaline *p*H range. The following procedure was found best. Pyrophosphoric acid was added to the diamine until the *p*H reached 10. Alcohol was added carefully to the resulting solution still at room temperature until an incipient cloudiness just appeared. After cooling this saturated solution in ice for one hour, small acicular crystals appeared. The same technique was followed in the two purifying recrystallizations.

Anal. Calcd. for $(tmdH_2)_2P_2O_7\cdot 3H_2O$: N, 14.72; P, 16.30. Found: N, 14.81; P, 16.14. Attempts to dehydrate the compound in an oven at 105° failed, as it decomposed after losing 82% of its weight; discoloration occurred and the odor of diamine was obvious.

Decomposition point, discoloration evident at 185°, melting and rapid decomposition at 225°.

Diaminobutane Preparations

1,3-Butanediammonium Monohydrogen Orthophosphate, $(dbH_2)(HPO_4)$.—The diamine was added to orthophosphoric acid solution until the *p*H reached 9. While the solution was still at room temperature, alcohol was added slowly and with vigorous stirring until an opaque, fluid, white emulsion formed. The preparation yielded crystals after standing in an ice-bath for 30 minutes. The product was recrystallized twice from water.

Anal. Calcd. for $(dbH_2)HPO_4$: N, 15.05. Found: N, 15.20; decomposition point, discoloration evident at 220°; vigorous decomposition at 232°.

1,3-Butanediammonium Pyrophosphate, $(dbH_2)_2P_2O_7$.—Pyrophosphoric acid was added to the diamine solution until the *p*H had fallen to 10.5. This solution was placed in a vacuum desiccator over ascarite. The preparation was tested daily with silver nitrate to be certain that no significant hydrolysis to orthophosphate had occurred. The system became increasingly viscous, and after one week, a few crystals appeared in the oil. When this thick suspension was stirred, it immediately set to a cold-cream consistency. The material was transferred to a filter and washed thoroughly with alcohol to remove the excess diamine. Purification was accomplished by dissolving the preparation in water, cooling, and adding alcohol until two layers separated. The upper layer was removed and the viscous lower layer seeded with some of the crude product previously obtained. Vigorous stirring induced crystallization.

Anal. Calcd. for $(dbH_2)_2P_2O_7$: N, 15.81. Found: 15.94; decomposition; discoloration evident at 200°, vigorous decomposition and melting at 230°.

Discussion.—During this investigation, extensive efforts were also made to prepare crystalline dihydrogen orthophosphates of 1,2-diaminopropane and 1,3-diaminobutane. The inflection point in the *p*H curve of each of these diamines with orthophosphoric acid indicates that the necessary ions are present in the solution. However all attempts at crystallization led to viscous oils or glasses. Since the corresponding orthophosphates of ethylenediamine and 1,3-diaminopropane do crystallize, it seems very probable that the failure of the former compounds to solidify may be attributed to steric hindrance of the methyl group beyond the amino group.

Similar efforts succeeded in producing only one crystalline dihydrogen pyrophosphate, namely, that of ethylenediamine described above. All the other diacid pyrophosphates of this series were obtained as viscous oils or glasses. Steric factors again offer the most likely explanation for this lack of crystallinity. Support for this view comes from the increasing difficulty of obtaining crystalline tetra-substituted pyrophosphates as the chain length of the diamine increases.

Exhaustive attempts were also made to prepare the tertiary orthophosphates, particularly of ethylenediamine. Even protracted refluxing of (enH_2)-HPO_4 with undiluted ethylenediamine produced no reaction. The most logical reason for this lack of reaction probably resides in the weakness of the third dissociation constant of the acid, and the energy necessary to arrange a stable lattice consisting of the ions in question.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

The Molar Refractions of Some Complex Ions in Solution

BY MAX T. ROGERS AND JIM G. MALIK

RECEIVED AUGUST 12, 1955

The molar refractions of ionic compounds in aqueous solution have been studied[1,2] and ionic refractions have been derived from such data. Complex ions have not been extensively investigated, however. We have measured the refractive indices of aqueous solutions of several compounds containing complex fluoride ions by use of an interferometer. The molar refractions of the salts have been found and ionic refractions estimated.

The refractive indices at 20° of solutions of the various electrolytes studied are shown in Table I for several concentrations. The molar refraction of the solute was found by the method of Halverstadt and Kumler[3] and values are included in Table I. The squares of the refractive indices of the solutions and the specific volumes of the solutions were each plotted *versus* the weight fraction of solute, w_2. From the slopes a and b of the resulting straight lines, along with the intercepts n_1^2 and v_1 at infinite dilution, the molar refraction MR was calculated by use of the equation

$$MR = M_2\left\{\frac{3av_1}{(n_1^2 + 2)^2} + (v_1 + b)\,\frac{n_1^2 - 1}{n_1^2 + 2}\right\}$$

where M_2 is the molecular weight of the solute. Although our values of MR are for λ = 5461 A., and so are not strictly comparable with the more common values of MR_D in tables, the differences are only about 1% which is less than the probable error of measurement.

---

[1] K. Fajans and G. Joos, *Z. Physik*, **23**, 46 (1924), *et seq.*

[2] A. Heydweiller, *Physik. Z.*, **26**, 526 (1925).

[3] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).