Long-chain Phosphates. I. Reactions of Solid Potassium Kurrol Salt with Solutions of Various Metal Salts

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Long-chain potassium metaphosphate,$(KPO_3)_n$, which is called potassium Kurrol salt, can be readily prepared by dehydrating potassium dihydrogen orthophosphate. It is a well-known fact[1] that potassium Kurrol salt is not easily soluble in pure water, but dissolution takes place in dilute solutions of salts of alkali metals other than potassium to give a highly viscous solution which is characteristic of a linear polymer of a high molecular weight. Thilo et al.[2,3], investigated the reactions between solutions of potassium Kurrol salt and those of various metal ions. It is the purpose of this paper to present some information on the behavior of potassium Kurrol salt in a solid state toward solutions of various metal ions. Solid potassium Kurrol salt reacts with solutions of certain multivalent cations to give gummy substances. The authors investigated particularly in details a reaction of potassium Kurrol salt with nickel ion, since the colored substance produced allowed easy observation upon the process of the reaction. The results indicated that the potassium ion in solid potassium Kurrol salt can be replaced by the nickel ion in a solution through a cation-exchange process. In the course of this investigation Weiss and Michel[4] found that reactions of solid potassium Kurrol salt with solutions of various alkylammonium ions can be regarded as a cation-exchange process.

Experimental

Preparation of Potassium Kurrol Salt.—Potassium Kurrol salt is usually prepared by dehydrating potassium dihydrogen orthophosphate. Pfanstiel and Iler[5] investigated the effect of minute variations in the original K/P ratio on the viscosity of the solution of potassium Kurrol salt and indicated that when there is a deficiency of potassium in a starting material, cross-linking occurs between phosphate polymer chains in the resulting potassium Kurrol salt crystal. An excess of potassium in a starting material forms potassium tripolyphosphate as a separate phase. Pfanstiel and Iler[5] gave the relationship between pH of a 0.1 M solution of potassium dihydrogen orthophosphate and its K/P ratio.

A 0.1 M solution of potassium dihydrogen orthophosphate of Wako special grade (lot 1335) was prepared in carbon dioxide-free distilled water. The pH of the solution was 4.50. According to Pfanstiel and Iler's data the K/P ratio of the potassium dihydrogen orthophosphate was calculated to be 0.9998 ± 0.0008. This value means that no further adjustment of the K/P ratio is necessary for the present purpose.

In a platinum dish 156.4 g. of the potassium dihydrogen orthophosphate was dehydrated at a lower temperature than the melting point, 807°C, of potassium Kurrol salt. Then it was melted in an electric furnace at 870°C. After being kept at this temperature for 30 min., it was gradually cooled to 775°C in 3 hr. After being kept at 775°C for 25 hr., the sample was removed from the furnace and chilled by holding the lower part of the dish in water. A transparent crystalline product was prepared. According to Malmgren and Lamm's study[6,7] the molecular weight of the potassium Kurrol salt prepared in this work was presumed to be about 10^6.

X-ray Diffractometry.—X-ray patterns of the potassium Kurrol salt as well as hydrated metaphosphate containing potassium and nickel and its dehydrated products were taken with Copper K_α radiation and a nickel filter by means of an automatic recording X-ray diffractometer, "Geigerflex", of Rigaku Denki Co., Ltd. For the potassium Kurrol salt a rotating mount was used to avoid the preferred Crientation.

Paper Chromatography.—Two-dimensional paper chromatography was carried out according to Karl-Kroupa's procedure[8]. Acid solvent was made by mixing 735 ml. of isopropyl alcohol, a solution of 50 g. of trichloroacetic acid in 265 ml. of water, and 2.5 ml. of concentrated aqueous ammonia. Basic solvent was made by mixing 387 ml. of isopropyl alcohol, 200 ml. of isobutyl alcohol, 408 ml. of water, and 5 ml. of concentrated aqueous ammonia. Filter papers used in this work were Toyo No. 53.

Analytical Methods for the Determination of Phosphate, Potassium, Nickel and Other Metal Ions.—For the determenation of phosphate, potassium, and nickel ions in a solid and an aqueous

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[1] J. R. Van Wazer, "Phosphorus and its Compounds", Vol. I, Interscience Publishers, New York (1958), p. 665.

[2] E. Thilo, G. Schulz and E. M. Wickmann, *Z. anorg. allgem. Chem.*, **272**, 182 (1953).

[3] E. Thilo and A. Winkler, *J. prakt. Chem.*, **7**, 46 (1958).

[4] A. Weiss and E. Michel, *Z. anorg. allgem. Chem.*, **296**, 313 (1958).

[5] R. Pfanstiel and R. K. Iler, *J. Am. Chem. Soc.*, **74**, 6059 (1952).

[6] H. Malmgren and O. Lamm, *Z. anorg. allgem. Chem.*, **252**, 256 (1944).

[7] H. Malmgren, *Acta Chem. Scand.*, **6**, 1 (1952).

[8] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956) and her private publication.

phase obtained by the reaction of the potassium Kurrol salt with an aqueous solution of nickel sulfate, the following method was used. An aliquot of the solution was charged into an ion-exchange column of Dowex 1-X4 of chloride form and the column was washed with water. From the solution which passed through the column, the nickel ion was precipitated with dimethylglyoxime and aqueous ammonia and determined gravimetrically. After the separation of nickel the filtrate containing the potassium ion was evaporated to dryness in a platinum dish and the residue was heated at a temperature 300~320°C. Ammonium chloride and the excess of dimethylglyoxime were sublimed and the potassium was determined gravimetrically as potassium chloride. The phosphate absorbed on the column was eluted with 3N hydrochloric acid, hydrolyzed to orthophosphate by boiling, precipitated with a magnesia mixture, and determined gravimetrically as magnesium pyrophosphate. The solid phase was dissolved in 1N hydrochloric acid, evaporated to dryness, dissolved in water, and neutralized with a dilute solution of sodium hydroxide. The solution thus obtained was treated using the same procedure as in the case of the aqueous phase.

In the process of the reaction with the potassium Kurrol salt, variation of nickel ion concentration was followed by a direct colorimetric method for the nickel ion with a filter of 390 mμ. Various metal ions in aqueous phases were determined as follows: the cobalt(II) ion was determined by the tricarbonato cobalt(III) method[9], the calcium, the magnesium, and the zinc ion were by the chelatometric titration with ethylenediaminetetraacetate, the iron(II) ion was by the permanganometric titration, and copper ion by the iodometric titration. The manganese(II) ion was oxidized with silver nitrate and ammonium persulfate to permanganate, a solution of ammonium iron(II) sulfate, of a known concentration was added, and the excess of iron(II) was titrated with a standard solution of permanganate. The iron(III) ion was reduced with zinc amalgam to iron(II) and determined by the permanganometric titration. A minute amount of condensed phosphate dissolved in the aqueous solution was determined by the colorimetry[10], after being hydolyzed to orthophosphate.

Results and Discussion

1. X-ray Diffraction Data of the Potassium Kurrol Salt.—Klement and Schmid[11] took the X-ray powder diffraction photographs of potassium Kurrol salt used in his study. Both results in Klement and Schmid's and the present work indicated a good coincidence as shown in Table I. The X-ray pattern of potassium Kurrol salt was not changed by any of the following treatments: Drying at 100° to 110°C for 1 hr., washing with ethanol and ether, and drying in air after being immersed in water for 50 hr.

TABLE I. X-RAY DIFFRACTION DATA OF POTASSIUM KURROL SALT

This work		Klement and Schmid[11]	
Spacing Å	Intensity	Spacing Å	Intensity
6.28	100	6.40	3
5.24	15	5.18	2
5.06	28		
4.50	30	4.54	2
3.75	18	3.92	2
3.45	60	3.42	5
3.35	21		
3.29	30	—	—
3.14	79	3.13	3
3.08	15		
2.83	14	2.82	2
2.74	9	2.74	2
2.68	37	2.64	2
2.58	6	2.55	1
2.26	35	2.25	4
2.21	12	2.20	3
2.10	5	—	—
2.05	3	2.02	2
2.03	3		
1.89	6	1.88	3
1.88	6		
1.80	3	—	—
1.74	5	1.72	2
1.69	3	—	—
1.67	5	—	—
1.64	3	—	—
1.61	3	1.61	2
1.57	5	1.57	2
1.50	4	—	—

2. Non-existence of Tripolyphosphate in the Potassium Kurrol Salt.—About 0.9 g. of the pulverized potassium Kurrol salt was further ground in 100 ml. of ice-water and the suspension was filtered. By this treatment potassium tripolyphosphate, if present, can be washed out of the sample and at the same time the hydrolysis of condensed phosphate may be reduced to a negligible extent. After the filtrate was dried by the use of a freeze-drying machine, the residue was brought into a solution with 0.5 ml. of water. In a two-dimensional paper chromatogram of this solution, there was only a non-moving spot at the original point. This means that the potassium Kurrol salt did not contain any tripolyphosphate or any other shorter chain or ring phosphates and that a minute amount of the potassium Kurrol salt was brought into the solution without intense hydrolysis.

3. Solubility of the Potassium Kurrol Salt.—About 1 g. of the potassium Kurrol salt was

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[9] M. Mori and M. Shibata, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **75**, 1044 (1954).

[10] M. Nakamura, *J. Agr. Chem. Soc. Japan* (*Nippon Nogei Kagaku Kai-shi*), **24**, 1 (1950).

[11] R. Klement and J. Schmid, *Z. anorg. allgem. Chem.*, **290**, 113 (1957).

put into 1 l. of water and stirred at room temperature (20~23°C). After 1, 2, 3, and 25 hr. the phosphorus content of the phosphate in the solution were determined to be 19, 17, 20, and 23 γ P per ml., respectively. From these values the solubility was calculated to be 0.007 ~0.009 per cent.

4. Qualitative Observation on the Behavior of the Potassium Kurrol Salt toward Aqueous Solutions of Various Metal Ions.—As mentioned previously, potassium Kurrol salt is dissolved in aqueous solutions of sodium salts. To 0.1 g. of the potassium Kurrol salt 10 ml. of a 0.1 M solution of each of the following sodium salts was added; acetate, bromide, carbonate, chloride, cyanate, dihydrogen orthophosphate, monohydrogen carbonate, monohydrogen orthophosphate, nitrate, orthophosphate (normal), oxalate, pyrophosphate, sulfate, and tripolyphosphate. In every case a greater part of the potassium Kurrol salt was dissolved. However, it appeared that the potassium Kurrol salt was more rapidly dissolved in the solutions of ortho-, pyro- and tripolyphosphate in comparison with the other salts.

To 0.1 g. of the potassium Kurrol salt, 10 ml. of 1, 0.5, 0.1, or 0.01 M solution of sodium chloride was added, respectively, where the ratio Na/K was 10, 5, 1, or 0.1. When the ratio was 5, the sample was most easily dissolved. When the ratio was 10, a part of the sample was converted into a gelatinous substance. Probably it was due to salting-out effect.

The results of the qualitative observation on the behavior of the potassium Kurrol salt toward solutions of various metal ions are summarized in Table II. These results were obtained when 0.1 g. of the potassium Kurrol salt was added to 10 ml. of a 0.1 M solution of the metal ion.

TABLE II. REACTIONS OF POTASSIUM KURROL SALT WITH SOLUTIONS OF METAL IONS

Metal ion	Reaction
Na^+, NH_4^+	Potassium Kurrol salt is gradually dissolved.
Ca^{2+}, Cr^{3+}, Ag^+	Potassium Kurrol salt forms a lump which has not plasticity.
Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Sn^{2+}	Potassium Kurrol salt forms a gummy substance.
Al^{3+}, Fe^{3+}, Ce^{3+}, Hg^{2+}, Bi^{3+}, Pb^{2+}	Potassium Kurol salt reacts with them very slowly.

5. Reaction between the Potassium Kurrol Salt and Solutions of Nickel Sulfate.—When the potassium Kurrol salt was added to a solution of nickel sulfate, the white crystalline potassium Kurrol salt was gradually converted into a green gummy substance. The absorption of nickel ion was investigated as follows. At a bottom of an Erlenmeyer flask of 300 ml., 1 g. of the ground potassium Kurrol salt was flatly placed and 200 ml. of a 0.0984 M solution of nickel sulfate was added to it. The mixture was kept at 20°C without agitation. The variation of the amounts of the nickel ion absorbed with time was determined by measuring the decrease of the nickel ion concentration in the solution. As shown by the curve A in Fig. 1, after about 8 hr. the reaction reached the equilibrium. When a 0.0366 M solution of nickel sulfate was used, the curve B in Fig. 1 was obtained by a similar experiment. In this case the reaction reached the equilibrium after about 11 hr. After the reaction was equilibrated, the solid phase was removed from the solution, washed quickly with water, and analyzed for potassium, nickel and phosphorus. The amounts of sulfate ion absorbed by the solid phase were negligibly small. The phosphorus contents in the solid phases were 8.50 mg. atom in both cases in comparison with 8.47 mg. atom which was the calculated value of phosphorus content in the initial potassium Kurrol salt. Therefore, all of the phosphorus in the initial sample were assumed to remain in the solid phase in the process of the reaction. As shown in Table III the quantity of the potassium ion which came out of the solid phase was equivalent to the quantity of the nickel ion which went into the solid phase. It was concluded that the reaction mentioned above is a kind of cation-exchange reaction. In the systems of 1 g. of the potassium Kurrol salt and 200 ml. of the 0.0984 M and 0.0366 M solution of nickel sulfate 91 and 74 per cent of potassium ion was exchanged with nickel

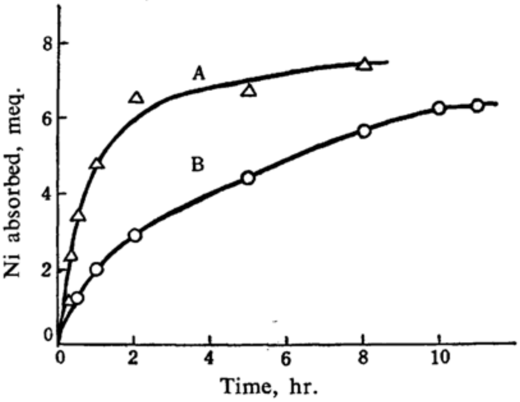

Fig. 1. The variation of the amounts of ion absorbed with time. The initial concentrations of nickel sulfate are 0.0984 M in Curve A and 0.0366 M in Curve B.

TABLE III. CATION-EXCHANGE REACTION BETWEEN POTASSIUM KURROL SALT AND SOLUTIONS OF NICKEL SULFATE

No.	Initial quantity of K^+ ion in the solid phase meq.	Final quantity of K^+ ion in the solid phase meq.	Quantity of K^+ ion which came out of the solid phase meq.	% exchange	Quantity of Ni^{2+} ion which went into the solid phase meq.	% exchange
A*	8.47	0.81	7.66	90.4	7.68	90.8
B**	8.47	2.16	6.31	74.5	6.24	73.7

*A A reaction between 1 g. of potassium Kurrol salt and 200 ml. of a 0.0984 M solution of $NiSO_4$ for 8 hr. at 20°C.

**B A reaction between 1 g. of potassium Kurrol salt and 200 ml. of a 0.0366 M solution of $NiSO_4$ for 11 hr. at at 20°C.

TABLE IV. PROPERTIES OF THE NICKEL-SUBSTITUTED PRODUCTS HEATED AT VARIOUS TEMPERATURES

Product	Heated at, °C	Appearance	For X-rays	Two-dimensional paper chromatographic information
A	100~110	green, transparent	amorphous	—
B	300	dark brown, powder	amorphous slightly crystalline	—
C	600	light yellow, powder	crystalline	non-moving spot indicating long-chain phosphate
D	1000	yellowish green, powder	crystalline	chain series containing ortho-, pyro-, tripolyphosphate, etc., ring series containing trimeta-, tetra-meta,, pentametaphosphate, etc. and non-moving spot
E	1200	dark yellow, powder	crystalline	chain series containing ortho-, pyro-, tripolyphosphate, etc. and non-moving spot

ions in 8 and 11 hr., respectively.

In order to confirm the reversibility of the cation-exchange reaction, a green product obtained by the reaction between 1 g. of the potassium Kurrol salt and 200 ml. of a 0.1052 M solution of nickel sulfate for 8 hr. at 20°C was subjected to react with 50 ml. of a 0.2 M solution of potassium chloride for 40 hr. at 20°C. Before and after the reverse reaction, the solid phase was analyzed for potassium, nickel and phosphorus. Phosphate was not dissolved in the process of this reaction. The quantity of the potassium ion which went into the solid phase was 1.48 meq. and the quantity of the nickel ion which came out of the solid phase was 1.47 meq. This fact indicates that the reaction is reversible. The rate of the reverse reaction was slower than that of the ordinary reaction, since the surface area of the primary product was smaller than that of the initial potassium Kurrol salt. The equilibration of the reverse reactoin was attained after about 40 hr.

6. Properties of the Nickel-substituted Product.—The nickel-substituted product in which about 90 per cent of the initial amount of the potassium ion is replaced by the nickel ion is green-colored and gummy. It is quite similar to chewed chewing-gum. The green product is gradually dissolved into a large amount of water. A similar product can be made in a short time by dissolving potassium Kurrol salt in a dilute solution of sodium chloride or sodium tripolyphosphate and adding a concentrated solution of nickel sulfate. This fact may be due to salting-out effect.

The variation in the properties of the green product by heating was investigated and the results are summarized in Tablle IV. The green primary product and the product A were completely amorphous for X-rays. The product B was practically amorphous for X-rays, but it contained a small amount of crystalline substance. The products C, D and E were all crystalline for X-rays and their X-ray patterns were different from one another. The products A and B were soluble in mineral acids, but the products C, D, and E were soluble in mineral acids only with difficulty. The product E was not dissolved even by heating it with 6 N hydrochloric acid, 6 N nitric acid, aqua regia, or 3 N sodium hydroxide. Each 0.1 g. of the products C, D and E was well mixed with 1 g. of Amberlite IR-120 resin in sodium form (100~200 mesh) in 8 ml. of water. After centrifugation the supernatant was concentrated

TABLE V. CATION-EXCHANGE REACTION BETWEEN POTASSIUM KURROL SALT AND SOLUTIONS OF VARIOUS METAL IONS

Metal salt	Concn.	pH, initial	Quantity of metal ion exchanged	Exchange capacity at the end of the reaction	% exchange
	M		meq.	meq.	
$MgCl_2$	0.0946	5.6	7.08	8.45	83.8
$CaCl_2$	0.0981	3.9	6.95	8.43	82.4
$MnCl_2$	0.1300	3.0	7.84	8.32	94.2
$FeSO_4$	0.0928	1.3	7.59	8.39	90.5
$Fe_2(SO_4)_3$	0.1568	0.8	3.80	7.35	51.7
$CoCl_2$	0.0987	4.7	7.39	8.46	87.3
$NiSO_4$	0.0984	5.6	7.68	8.47	90.8
$CuSO_4$	0.1006	4.3	5.03	5.77	87.2
$ZnCl_2$	0.0910	2.1	7.92	8.46	93.7

at room temperature. Two-dimensional paper chromatography for the solution was carried out. The results are shown in Table IV. Although only minute parts of the products C, D and E were brought into the solutions, the paper chromatographic data suggested the difference of the chemical compositions of these products.

7. Exchange-reactions of Various Metal Ions.—In conformity to the procedure used for the nickel ion, 1 g. of the potassium Kurrol salt was subjected to react with 200 ml. of about 0.09~0.16 M solution of each of the following metal ions for 8 hr. at 20°C: magnesium, calcium, manganese(II), iron(II), iron(III), cobalt(II), copper(II) and zinc. After the exchange reactions, the amounts of phosphate dissolved in the solution and the decreases in the metal ion concentrations were measured. With the aid of these measurements, percentages of exchange based on millieqivalent of cations were calculated as shown in Table V. Only in the case of copper(II) sulfate a large amount of the initial potassium Kurrol salt was dissolved in the course of the reaction. Except for iron(III), percentages of exchange for all cations investigated in the present work were in the range 82 to 94.

Summary

Pure crystalline potassium Kurrol salt was prepared and its X-ray pattern was compared with that obtained by Klement et al. The solubility of the potassium Kurrol salt in water was 0.007~0.009 per cent at room temperature. Qualitative observation was made for the reactions of the potassium Kurrol salt with various metal ions. Therefore was an optimum concentration of sodium chloride to dissolve the potassium Kurrol salt. The investigation of reactions of the potassium Kurrol salt in a solid state with solutions of nickel sulfate indicated that the reaction is a cation-exchange reaction between potassium and nickel ions. It was also found that the reaction is reverssible. The nickel-substituted product is green-colored and gummy. Some properties of the substances obtained by heating the above green product were studied. Exchange reactions of potassium Kurrol salt with various metal ions were investigated. Percentages of exchange for magnesium, calcium, manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc were all in the range 82 to 94 under the conditions used in the present work.

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