[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Observations upon the Ignition of Magnesium Ammonium Phosphate. VIII

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There are two interesting phenomena associated with the ignition of magnesium ammonium phosphate which have been noted in the procedure for the quantitative determination of either phosphorus or magnesium. The one phenomenon is the flash which passes through the substance in the crucible during the process of ignition. The other is the dark instead of the white residue so often obtained after the ignition has been performed.

The statements in the literature as to the cause of the "flash" in the ignition of $MgNH_4PO_4$ differ widely. Possibly the one most commonly mentioned is exemplified by Karaoglanow and Dimitrow,[1] who claim that the flash is due to the presence of organic matter. They state that the flash never occurs if all organic matter is absent; they also state that incandescence will not occur if the salt is precipitated at boiling temperature, and will if precipitated at lower temperatures. They claim that the properties of $Mg_2P_2O_7$ depend upon occurrence of incandescence. Their "flashed" variety is hard, lava-like, gray to black in color, while the unflashed is amorphous, loose and quite white. Balareff[2] also obtained the two varieties but claims that moist $MgNH_4PO_4 \cdot 6H_2O$ always gives the white variety, while drying over phosphorus pentoxide for several weeks before igniting always gives black residues. He does not believe, therefore, that the gray color results from impurities, and obtains gray residues even when the precipitate has been filtered through asbestos. But in the same report he says that the gray salt examined with the microscope was seen to consist of white material containing black spots. Balareff[2] believes that the properties of the pyrophosphate obtained depend upon the degree of hydration before ignition. Popp[3] in 1870 stated that the flash was likely due to an intra-molecular change within the pyrophosphate molecule. He even accepted the theory that a change from the crystalline to the amorphous form might account for the luminescence. After reviewing and rejecting all foregoing explanations, Wöhler[4] in 1926 advanced the hypothesis that luminescence is due to a type of surface fusion or sintering. Gmelin[5] long ago believed the phenomenon to be a change from the amorphous to the crystalline form.

Since magnesium pyrophosphate is so important in quantitative analysis and in view of the many conflicting statements and opinions which have

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(1) Karaoglanow and Dimitrow, *Z. anal. Chem.*, **57**, 353 and 497 (1918).

(2) Balareff, *Z. anorg. allgem. Chem.*, **97**, 149 (1916).

(3) Popp, *Z. anorg. Chem.*, **13**, 306 (1870).

(4) Wöhler, *Kolloid Z.*, **38**, 97–111 (1926).

(5) Gmelin, "Handbuch," Vol. I, 1848, p. 107 (English Ed.).

appeared in the literature, a study of some of the properties of $MgNH_4PO_4 \cdot 6H_2O$ based upon simple experiments would be highly desirable.

Preparation of Materials.—The preparation of all salts and materials used in this investigation has been described by us previously.[6]

Apparatus.—For determining the temperature of luminescence of the salts, the apparatus shown in Fig. 1 was used. F was a long-necked, round-bottomed 100-cc. Pyrex flask which served as an air-bath. B was a bulb about 15 millimeters inside diameter, on a Pyrex tube of about 7 millimeters inside diameter. The bulb held from 0.1 to 0.2 g. when about half filled. The junction of the platinum–platinum-rhodium thermocouple, T, was in the center of the sample. The thermocouple was connected to potentiometer K, previously described by us.[6]

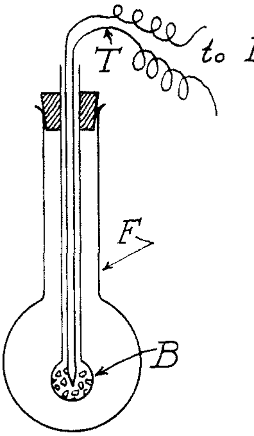

Fig. 1.

For heating the salts *in vacuo*, a thick-walled Pyrex tube 40 centimeters in length and 5 centimeters in diameter, with a ground-glass cap fitted with a stopcock, was employed. The lower third was placed in an electric furnace and the upper part was protected from the heat of the furnace by two tightly fitting asbestos sheets, so that when evacuated the lower part could be heated to above 450° while the upper end remained at room temperature. A platinum crucible containing the salt was lowered into the tube by means of a glass rod bent at the bottom into the form of a ring.

The ignitions were made in uncovered porcelain Gooch crucibles by means of either the Meker burner or an electric muffle furnace capable of maintaining a temperature of 1100°.

Experimental

TABLE I

LUMINESCENCE UPON IGNITION

	Salt	Relative intensity of flash	Temp. of flash, °C.	Nature of product
1	$MgNH_4PO_4 \cdot 6H_2O$ pptd. cold	Very strong	550–600	Snow-white, insoluble in water, volume less than half of original
2	$MgNH_4PO_4 \cdot 6H_2O$ pptd. at boiling temp.	Strong	600–615	Same as 1
3	$MgNH_4PO_4 \cdot H_2O$	Weak	600–625	Snow-white, sintered, insoluble, slightly less in vol. than original
4	$Mg_2P_2O_7$ by previously igniting $MgNH_4PO_4 \cdot 6H_2O$ at 480° in muffle	Very strong	550–600	Same as 1
5	$Mg_2P_2O_7$ by evacuating $MgNH_4PO_4 \cdot 6H_2O$ at 300°, 8 hrs.	Very strong	550–600	Same as 1
6	$MgHPO_4 \cdot 3H_2O$	Weak	550–650	Same as 3
7	$MgHPO_4 \cdot 7H_2O$	Weak	550–650	Same as 3

The $Mg_2P_2O_7$ in No. 5 above was prepared by evacuating a tube built for the purpose (described under "apparatus"), in which was placed a platinum crucible con-

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(6) Kiehl and Hardt, THIS JOURNAL, **55**, 605 (1933).

taining about 5 or 6 g. of the salt. The large samples could be successively weighed, evacuated, weighed, ignited and weighed. Thus one sample of 5.9736 g. after three hours of evacuation at 300°, weighed 2.7179 g. It was ignited to constant weight over a Meker burner. The weight was then 2.7073 g. A bright flash occurred during the process. The loss in weight during the ignition over the Meker was 4 parts per 1000, and the flash was only slightly, if at all, less intense than when $MgNH_4PO_4 \cdot 6H_2O$ is ordinarily ignited.

Consequently, experiments were performed with small samples to ascertain if the material could be changed stoichiometrically to pyrophosphate before the flash occurred. The following procedure was used and the results are recorded in Table II.

A stock solution was made by placing the carefully prepared crystals of $MgNH_4PO_4 \cdot 6H_2O$ in distilled water and dissolving them by adding dilute hydrochloric acid. The concentration was determined so that 45 cc. of the solution yielded approximately 0.15 g. of magnesium pyrophosphate. For the quantitative experiments, 45 cc. of this solution was measured by a buret into a 250-cc. beaker; 50 cc. of water and six drops of magnesia mixture were then added, and precipitation effected by the addition of very dilute ammonium hydroxide at 90–100° until alkaline. After eight hours or more the precipitate was transferred to the prepared Gooch crucible and dried in an oven at 110°. This preliminary procedure was followed in all analytical experiments. Seven different samples, after the above treatment, were weighed following each successive heating in a manner indicated by captions of Table II and then flashed and finally weighed.

TABLE II

THE EFFECT OF THE FLASH ON THE WEIGHT OF $Mg_2P_2O_7$

After heating one hour at 480°, g.	After 8 hours more at 480°, g.	After the flash, g.	After heating 1.5 hours at 925°, g.
0.1481	0.1480	0.1478	0.1478
.1476	.1473	.1471	.1473
.1478	.1480	.1478	.1479
.1480	.1481	.1478	.1479
.1482	.1482	.1480	.1480
.1474	.1474	.1474	.1473
.1479	.1479	.1478	.1478

The data in Table II indicate that conversion to the pyrophosphate was complete before the flash occurred.

Another interesting fact was learned in the flash. Our system rose in temperature at least fifty degrees during the change with samples of one-tenth of a gram. Heat was evolved. A substance of greater stability was without doubt formed. The substance also before the flash was quite soluble in acids while the final residue after the flash, as is commonly known, was difficultly soluble.

Moreover, when any of the hydrates of $MgNH_4PO_4$ or $MgHPO_4$ were converted to the pyrophosphate by heating below 500° and the residues examined with the microscope, it was found that the shapes of the original crystals had been retained. They were, however, always opaque. During the flash this shape disappeared entirely. But it was suspected, however, that the opaque crystal-shaped particles were amorphous because they were opaque and that since a large amount of energy was liberated in the transformation, the final amorphous-looking material might be crystalline.

In attempting to answer the questions thus raised, x-ray diffraction pattern photographs of samples of the salts in question were made. These photographs show in Fig. 2 very definite crystal patterns for 1, $MgNH_4PO_4 \cdot 6H_2O$; 2, $MgNH_4PO_4 \cdot H_2O$; and 4, the residue ($Mg_2P_2O_7$) after the flash from either $MgNH_4PO_4 \cdot 6H_2O$ or $MgNH_4PO_4 \cdot H_2O$. But 3, the unflashed pyrophosphate from either $MgNH_4PO_4 \cdot 6H_2O$ or $MgNH_4PO_4 \cdot H_2O$, shows no pattern and is therefore not crystalline. Samples of $Mg_2P_2O_7$ fused in an oxy-gas flame or heated in a muffle at 1000° for ten hours gave patterns identical with 4. The form thus obtained is no doubt the stable form.

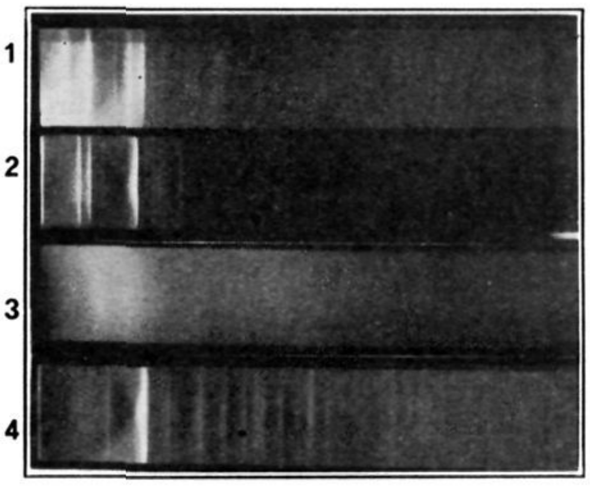

Fig. 2.

The Dark Residue.—$MgNH_4PO_4 \cdot 6H_2O$ possesses the very striking and interesting property of attaching firmly certain types of organic compounds while it is losing water of hydration and ammonia. When $MgNH_4PO_4 \cdot 6H_2O$ was heated in an open platinum crucible without contact with organic materials, it invariably gave a white residue, but in an atmosphere of certain gaseous organic compounds a black residue always resulted. Stearic acid wetting the end of a stirring rod which was held in the crucible above the salt—not touching it—while it was gently heated produced a black residue. Glycerin and paraffin treated similarly gave the black residue. A bit of filter paper placed upon the bottom of the platinum crucible with the salt on the other side out of contact produced gaseous products when it was gently heated and caused the formation of a black residue. A gentle stream of unignited commercial gas used as fuel in our laboratory—an ordinary commercial water gas enriched with illuminants—was directed upon the salt during the gentle heating. A black residue was left. In preparing the furnace for a long period of service at 250°, a clean strip of asbestos paper was placed in the bottom. The salt upon a clean watch glass which was covered with a larger one held by glass supports was placed in the furnace set for 250°. After one hour the salt was a dirty brown from the vapors given off, probably by the binder used in the asbestos paper. This material even after heating at 250° for days and final ignition over the Meker burner could not be freed from this coloration. A strip of the same asbestos paper 6.3 mm. wide and 5.1 cm. long placed across the top of the uncovered crucible invariably caused a brown-black residue to be formed when it was gently heated. The following liquids left the residue white when employed as above: benzene, carbon tetrachloride and chloroform. None of the following gases produced a coloration of the residue: hydrogen, acetylene, carbon dioxide, carbon monoxide, or air. On the other hand, the same treatment was applied to the magnesium ammonium phosphate monohydrate and the residue was white or under the severest test but a very light gray. When the $MgNH_4PO_4 \cdot 6H_2O$ was boiled with absolute alcohol, five molecules of alcohol substituted for five molecules of water. Ether also will displace some of the water.

It seems therefore that the hexahydrate during the process of losing water of hydration possesses an extraordinary capacity for firmly attaching certain types of carbon compounds, which decompose upon heating to higher temperatures and leave graphitic carbon.

Discussion

The x-ray photographs furnish the evidence that the two original salts are crystalline substances, that the unflashed but converted pyrophosphate from both sources is amorphous, and that the flashed pyrophosphates from both sources are identical in crystalline form.

The flash is therefore caused by the sudden heating of the material to incandescence when the energy is released upon crystallization of an amorphous substance. J. Böhm[7] has reported a similar behavior for other substances. The melting point of the substance, 1383°, together with its optical properties have been reported by Olaf Anderson.[8]

An amorphous substance is a supercooled liquid and is metastable. It should, upon crystallization, liberate energy. It should be more soluble. That the crystallization should occur rapidly between 500 and 650° for these substances is not strange. The melting point is 1383°, and below this the velocity of transition would gradually increase and reach a maximum which might be somewhere between 500 and 650°, then recede as is the case with many other substances. In this case a very rapid evolution of heat raises the temperature of the substance to incandescence. In fact, by holding the materials for a considerable time at a little over 500°, the crystalline form has been prepared from the amorphous less quickly and without the flash.

The dark colored residue from our experiments is caused by the adsorption of gaseous carbon compounds such as would result from the destructive distillation of cellulose. With carefully purified materials and in an atmosphere free from such compounds, a snow-white residue results. With gentle ignition of the hexahydrate in an atmosphere charged with gaseous products from charring filter paper, stearic acid, glycerin and some other substances, the black residue forms.

(7) Böhm, *Z. anorg. allgem. Chem.*, **149**, 217 (1925).

(8) Olaf Anderson, *J. Wash. Acad. Sci.*, **4**, 318 (1914).

The monohydrate does not possess this property to any degree comparable to the hexahydrate. But very light gray colored residues were produced under circumstances which produced the black residues with the hexahydrate.

It seems reasonable, therefore, that a substitution of these gaseous carbon compounds might be made for the water in the structure of complex hexahydrate. Higher temperatures would cause the firmly bound carbon compound to decompose and leave graphitic carbon which, upon further ignition, is extremely difficult to oxidize.

The authors wish to acknowledge their indebtedness to Professor Paul F. Kerr of the Department of Geology, Columbia University, for the x-ray work which appears in this paper.

Summary

1. The luminescence or flash during the ignition of magnesium ammonium phosphate hexahydrate and of magnesium ammonium phosphate monohydrate is due to the rise of temperature caused by the large quantity of heat liberated when the amorphous form of $Mg_2P_2O_7$ crystallizes.

2. The magnesium ammonium phosphate hexahydrate during the process of losing water of hydration in the early stages of ignition possesses the property of attaching firmly within its complex structure certain gaseous organic compounds, if present, which later break down and leave graphitic carbon.

NEW YORK CITY

RECEIVED APRIL 24, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Sorption of Organic Vapors by Resinous and Cellulosic Materials

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The objects of a recent sorption balance study of the behavior of glyceryl phthalate resins in the presence of acetone and methyl alcohol vapors were stated to be five-fold: (1) to determine the form of the sorption isotherms at several temperatures and to interpret the curves in terms of the porous structure of the resin; (2) to determine the heat of the sorption processes by the comparison of two isotherms; (3) to make an estimate of the average pore size from the sorption behavior in the neighborhood of saturation; (4) to study the changes in structure produced by variations in the curing process to which the resin has been subjected; (5) to study the reversibility of the sorption process. The results of this study[1] were so interesting that it was decided to extend the work to other artificial resins, to several

[1] Winning and Williams, *J. Phys. Chem.*, **36**, 2915 (1932).