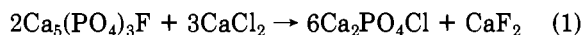


Production of Magnesium Phosphate Compounds via $\text{Ca}_2\text{PO}_4\text{Cl}$ from Fluorapatite and Chlorides

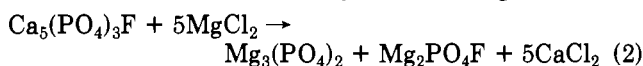
The reaction between $\text{Ca}_2\text{PO}_4\text{Cl}$ and MgCl_2 and between a mixture of $\text{Ca}_2\text{PO}_4\text{Cl}$ and CaF_2 and MgCl_2 was studied at the temperature range of 650–800 °C and at reaction times of up to an hour. The reaction between $\text{Ca}_2\text{PO}_4\text{Cl}$ and MgCl_2 produced soluble $\text{Mg}_2\text{PO}_4\text{Cl}$ and was completed after 5 min at 700 °C. When CaF_2 was present, insoluble $\text{Mg}_2\text{PO}_4\text{F}$ was also produced. Relatively high phosphate availability (81%) was observed in the latter reaction which might be related to partial defluorination of $\text{Mg}_2\text{PO}_4\text{F}$.

The most important source of phosphate fertilizer is rock phosphate, which is composed mainly of francolite. Francolite is a stable compound which has to be decomposed in order to make its phosphate content available to plants. The apatite structure can be destroyed by reacting it with chlorides, i.e., CaCl_2 or MgCl_2 .

The reaction between fluorapatite (FA) and CaCl_2 was studied (Kanazawa and Monma, 1970; Monma and Kanazawa, 1975a,b; Faibis, 1979). The reaction at 700 °C can be summarized as



The phosphate availability of the product, as measured by the amount of P_2O_5 soluble in 2% citric acid, is 60%. The reaction between FA and MgCl_2 was studied (Ando and Hongo, 1972; Baniel et al., 1965; Bar-On and Pelly, 1979; Pelly and Bar-On, 1979; Stawski, 1970). The reaction at 600 °C can be described by the following:



The maximum phosphate availability of the above reaction products is 67% and is related to $\text{Mg}_3(\text{PO}_4)_2$ which is completely soluble in citric acid, while $\text{Mg}_2\text{PO}_4\text{F}$ is insoluble.

Since direct reaction between FA and CaCl_2 or MgCl_2 produces phosphate compounds which are only partially soluble in citric acid, a different approach was tried in the present work, namely first reacting the FA with CaCl_2 and then reacting the reaction products with MgCl_2 . In order to clarify the results obtained, we first studied the reaction between $\text{Ca}_2\text{PO}_4\text{Cl}$ and MgCl_2 and then the reaction between the mixture of $\text{Ca}_2\text{PO}_4\text{Cl}$ and CaF_2 and MgCl_2 .

EXPERIMENTAL SECTION

Materials. $\beta\text{-Ca}_3(\text{PO}_4)_2$. Prepared by calcination (Simpson, 1969) of calcium orthophosphate, B.D.H.

$\text{Ca}_5(\text{PO}_4)_3\text{F}$ (FA). Synthesized from $\beta\text{-Ca}_3(\text{PO}_4)_2$ and CaF_2 .

$\text{Ca}_2\text{PO}_4\text{Cl}$ (CSp). Synthesized (Greenblatt et al., 1967) from $\beta\text{-Ca}_3(\text{PO}_4)_2$ and CaCl_2 , anhydrous, Baker analyzed.

$\text{Mg}_2\text{PO}_4\text{Cl}$. Synthesized (Rea and Kostiner, 1972) from $\text{Mg}_3(\text{PO}_4)_2$ and MgCl_2 , anhydrous. Electron microprobe chemical analysis gave 28.3% Mg, 38.2% P_2O_5 , 19.7% Cl.

CF. CF is the reaction product between FA and CaCl_2 . It was obtained by reacting FA and CaCl_2 in a molar ratio $\text{CaCl}_2/\text{FA} = 10$ by heating at 700 °C for 30 min. The product was washed to remove excess chlorides. X-ray diffraction analysis showed it to consist of CSp and CaF_2 . Chemical analysis has shown 38.5% Ca, 31.2% P_2O_5 , 15.7% Cl, 2.4% F, which corresponds to a 95:5 weight ratio of CSp: CaF_2 .

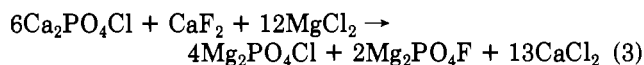
Methods and Instrumentation. The starting materials for the reactions studied were CSp or CF. The raw material (270–400 mesh) was mixed with MgCl_2 , anhydrous, by grinding them together in an agate mortar. The molar ratios of the reactants were $\text{MgCl}_2:\text{CSp} = 3, 5, 10$.

The reactants were put in a platinum crucible and calcined at different temperatures and times up to an hour. The products were removed and washed in water to remove excess chlorides. The dried products were examined by the powder X-ray diffraction method. Some samples were chemically analyzed. The phosphate solubility in 2% citric acid was also determined.

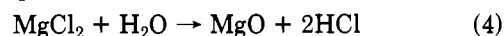
RESULTS AND DISCUSSION

The reaction between CSp and MgCl_2 was studied in the temperature range of 650–800 °C. The reaction products, as identified by X-ray diffraction, were $\text{Mg}_2\text{PO}_4\text{Cl}$ and MgO . The $\text{Mg}_2\text{PO}_4\text{Cl}$ phase was identified by comparing the X-ray diffraction pattern of the reaction product to the X-ray diffraction pattern of synthetic $\text{Mg}_2\text{PO}_4\text{Cl}$. The reaction was completed after 15 min at 650 °C (solid MgCl_2) and after 5 min at 700 °C (MgCl_2 in the molten state). $\text{Mg}_2\text{PO}_4\text{Cl}$ is completely soluble in 2% citric acid.

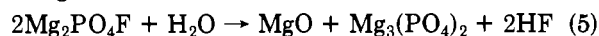
The reaction between CF (which contains 6 mol of CSp and 1 mol of CaF_2) and MgCl_2 was studied under the same conditions as the reaction between CSp and Ap, of temperature, time, and molar ratio. The reaction was completed after 15 min at 650 °C and after 5 min at 700 °C. The reaction between CF and MgCl_2 can be described as follows:



However, the X-ray diffraction pattern of the reaction products has shown the presence of MgO in addition to $\text{Mg}_2\text{PO}_4\text{Cl}$ and $\text{Mg}_2\text{PO}_4\text{F}$. The amount of MgO in the reaction products increased with the reaction temperature, time, and molar ratio MgCl_2/CSp . This suggests that, paralleling reaction 3, the hydrolytic decomposition of MgCl_2 takes place as follows:



The solubility of the products has been found to be 81%. $\text{Mg}_2\text{PO}_4\text{Cl}$ is soluble, while $\text{Mg}_2\text{PO}_4\text{F}$ is insoluble, and therefore the maximum theoretical phosphate solubility calculated should be only 67%. The higher solubility found seems to be in correspondence with the small amount of F found in the chemical analysis of the reaction products. The F/ P_2O_5 ratio found is 0.036 in the products compared to a ratio of 0.076 in the reactants. This means that less $\text{Mg}_2\text{PO}_4\text{F}$ forms than required by the chemical reaction in eq 3 and consequently higher solubility is obtained. Defluorination and the formation of volatile HF and MgO might be the reason for the fluorine loss in the products and the high solubility obtained resulting in the following reaction:



Such a defluorination reaction has been already reported (Faibis and Schieber, 1973).

As a conclusion of the above findings, it can be stated that the chemical reaction between CF and MgCl_2 as de-

scribed in eq 3 is accompanied by two competitive reactions: (a) the formation of MgO and the loss of citrate-soluble Mg_2PO_4Cl ; (b) the formation of volatile HF and the loss of citrate-insoluble Mg_2PO_4F . Further studies will be necessary to find the optimum conditions leading to a phosphate fertilizer with maximum phosphate availability.

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Mutagenicity of 1,5(or 7)-Dimethyl-2,3,6,7-tetrahydro-1*H*,5*H*-biscyclopentapyrazine Obtained from a Cyclotene/ NH_3 Browning Model System

1,5(or 7)-Dimethyl-2,3,6,7-tetrahydro-1*H*,5*H*-biscyclopentapyrazine (I), which was obtained from the browning reaction of 2-hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene) and ammonia under simulated cooking conditions, was tested for mutagenicity by using *Salmonella typhimurium* strain TA 1535, TA 100, TA 1537, TA 1538, and TA 98. I showed mutagenic activity with the frameshift mutation strains TA 98 and TA 1538.

Many nitrogen- and sulfur-containing heterocyclic compounds have been identified as the products of nonenzymatic browning model systems (Rizzi, 1972; Wilson and Katz, 1972; Shibamoto and Russell, 1977; Shibamoto and Bernhard, 1978). These chemicals include thiophenes, furans, oxazoles, thiazoles, pyrazines, pyrroles, and imidazoles. Mihara and Shibamoto (1980) observed mutagenicity of some fractions obtained from a D-glucose/cysteamine browning reaction mixture on Ames *S. typhimurium* strains TA 98 and TA 100. They also found that *N*-nitrosothiazolidine derivatives, which can be formed in a browning model system (Sakaguchi and Shibamoto, 1979), showed strong mutagenicity on *Salmonella typhimurium* strain TA 100 (base-pair substitution strain).

Recently, Bjeldanes and Chew (1979) reported that 1,2-dicarbonyl compounds (maltol, kojic acid, diacetyl, etc.) gave positive responses to the *Salmonella*/microsome mutagenicity assay. These dicarbonyls, which may be derived from degradation or caramelization of carbohydrates in foods (Hodge, 1967), have been shown to be precursors of pyrazines in browning reactions (Rizzi, 1972). Nishimura et al. (1980) obtained a polycyclic pyrazine (I) from a cyclotene (2-hydroxy-3-methyl-2-cyclopenten-1-one)/ NH_3 browning model system. Cyclotene is known as a product of sugar degradation, as is maltol (Hodge, 1972). In the present study, the mutagenicity of the product of cyclotene and ammonia is investigated.

EXPERIMENTAL SECTION

Sample Preparation. 2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene, 0.1 mol) was dissolved in 50 mL of deionized water in a 100-mL Kjeldahl flask. Thirty

milliliters of 30% ammonium hydroxide solution (0.5 mol as NH_3) was then added. The neck of the flask was flame-sealed, and the flask was placed in an oven at 90 °C for 2 h. The reaction mixture was extracted with 200 mL of methylene chloride, using a liquid-liquid continuous extractor for 16 h. The extract was dried over anhydrous magnesium sulfate. A brown oily liquid (ca. 0.5 g) was obtained after the solvent was removed. This brown material was dissolved in 10 mL of petroleum ether, and undissolved materials were filtered off. The petroleum ether filtrate was evaporated and the material obtained was purified by TLC [Merck silica gel; solvent, *n*-hexane/ethyl acetate 3:1; R_f = ca. 0.3]. The purified material (0.1 g) was identified as the mixture of four stereoisomers: *cis*-1,5-dimethyl- (*meso*), *trans*-1,5-dimethyl- (*meso*), *cis*-1,7-dimethyl- (*meso*), and *trans*-1,7-dimethyl-2,3,6,7-tetrahydro-1*H*,5*H*-biscyclopentapyrazine (*dl*). The structures of these isomers were confirmed by NMR, IR, and MS, using the methods described by Nishimura et al. (1980). Their possible structures are shown in Figure 1.

Mutagenicity Test. Mutagenicity tests were conducted as described by Umezawa et al. (1978), a modification of the method reported by Ames et al. (1975). Histidine-requiring *Salmonella typhimurium* strains TA 1535, TA 100, TA 1537, TA 1538, and TA 98 were used as indicator organisms for mutagenic activity.

RESULTS AND DISCUSSION

The results obtained from the mutagenicity tests are shown in Figure 2. In high concentration, I exhibited considerable antibacterial activity. It was difficult, therefore, to find the optimum concentration for investi-