TRIMETHYL PHOSPHATE INDUCED DECOMPOSITION OF KAOLINITE

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Abstract—The decomposition of kaolinite by treatment with trimethyl phosphate (TMP) and the composition of the new crystalline phase formed were studied. On hot treatment with TMP, kaolinite forms a crystalline white compound that is soluble in hot water. The X-ray diffraction pattern of the kaolinite treated shows both the typical reflections of kaolinite and, furthermore, a very strong reflection at 8.84 Å. After 30 days of treatment with TMP, the silicate structure of kaolinite is completely destroyed and a crystalline phase identical with that resulting from treatment of aluminium oxide (Al_2O_3) with TMP is formed. The results show that the compound in question is formed by hydrolysis of TMP, catalyzed by the hydration water of exchange cations of kaolinite, followed by removal of Al from the silicate structure by incompletely hydrolyzed TMP. The new crystalline phase thus formed is an aluminium alkyl phosphate of formula $Al(CH_3)_6(PO_4)_3$.

Key Words—Aluminium alkyl phosphate, Hydrolysis, Kaolinite, Kaolinite decomposition, Trimethyl phosphate.

INTRODUCTION

Some phyllosilicates form interlayer complexes with alkyl phosphates. Their formation is determined, among others, by such factors as the strength of interlayer bonds in the mineral, which in turn depends on the mineral structure. Thus, these organic compounds can readily penetrate into the interlayer spacing of smectites to form adsorption complexes of well-defined $d(001)$ basal spacings (González-García *et al.,* 1972; Sánchez-Camazano *et al.,* 1972). The vermiculite with high laminar charge density is less prone to undergo interlayer expansion (González-García *et al.,* 1970). Kaolinite, which possesses a high interlayer cohesion arising from strong hydrogen bonds between the hydroxyl groups in the octahedral layers and the oxygen atoms in the tetrahedral layers, forms no complexes with alkyl phosphates. However, treatment of this silicate with trimethyl phosphate in nonaqueous medium gives rise to a new crystalline phase (as revealed by X-ray patterns), prolonged treatment of which leads to complete decomposition of the silicate structure. Therefore, the interaction between kaolinite and alkyl phosphates gives rise to rather different results from those arising from interaction of these organic compounds with 2:1 layered silicates. In the light of this evidence and in search for new data on the interaction between kaolinite and organic compounds, we believed it of interest to study the mineral decomposition induced by trimethyl phosphate as well as the composition of the resulting crystalline phase.

We were unable to locate any literature references to the alteration of kaolinite by alkyl phosphates. However, phosphate fixation by soils has been widely studied in relation to the adsorption of inorganic phosphates by soils and their mineral components (Beek

and Riemsdijk, 1979; Goldberg and Sposito, 1985). Several authors have shown the structure of kaolinite (Low and Black, 1948; Haseman *et al.,* 1950), aluminium oxides (Van Riemsdijk *et al.,* 1975; Veith, 1978), and iron oxides (Jonasson *et al.,* 1988; Martín *et al.,* 1988) to be altered by lengthy treatment with dissolved potassium or sodium phosphates, which give rise to crystalline or amorphous aluminium or iron mixed phosphates. By using X-ray diffraction and electron microscopy, Kittrick and Jackson (1954) observed that kaolinite was completely decomposed on treatment with 1 M NaH_2PO_4 for 31 days.

MATERIALS AND METHODS

The study was carried out by using the <2 μm fraction of kaolin from Cuenca (Spain), which contains highly pure kaolinite and sparse quartz impurities (González-García *et al.,* 1965).

Aluminium oxide (Al_2O_3, primarily α phase) of 99.99% purity was supplied by Aldrich-Chemie (Steimheim, Germany). Trimethyl, triethyl, tripropyl, and tributyl phosphate were purchased from Fluka Chemie AG (Buchs, Switzerland).

Kaolinite samples air dried of 1 g were treated with 10 ml of TMP for various lengths of time, and the treatment was performed by refluxing in a water bath at 100°C.

Samples were disaggregated for chemical analysis by using *aqua regia* (2:1 HCl–HNO_3), followed by a boron-lithium solution ($LiCO_3$, HCl, H_3BO_3), as reported by García and Saavedra (1983). Si was determined colorimetrically as silicomolybdate complex (Pruden and King, 1969). Al was quantified by atomic absorption spectroscopy using a Varian AA1475 instrument. P was analyzed colorimetrically with the Lucena-Prat

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reagent (Lucena and Prat, 1957) after destroying organic matter with a 10:1:1 v/v mixture of HNO_3, H_2SO_4 and $HClO_4$. CH_3O groups were determined qualitatively by the Zeisel method (Fieser and Fieser, 1962), while CH_3 groups were analyzed quantitatively from the carbon content of the samples, which was in turn determined on a carbon autoanalyser.

X-ray diffraction patterns were recorded on a Philips PW 1710 instrument using CuK_α radiation. Finally, electron micrographs were obtained on a Philips 500 scanning electron microscope.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of natural kaolinite and after treatment with TMP for different lengths of time. The treated samples show both the typical peaks of kaolinite and a new reflection at 8.84 Å, the intensity of which increased relative to that of the $d(001)$ reflection of kaolinite at 7.13 Å with increasing treatment time. The patterns for kaolinite treated for 60 and 150 hr also show other new, weaker reflections at 9.30, 8.33 and 3.13 Å, in addition to several small peaks in the 5.21–4.48 Å region.

Initially, since TMP can form interlayer complexes with other laminar clay minerals such as montmorillonite and vermiculite (Sánchez-Camazano et al., 1972; González-García et al., 1970), the new reflection at 8.84 Å was tentatively assigned to the $d(001)$ spacing of an interlayer complex potentially formed between kaolinite and TMP. Some authors (Weiss, 1961; Sánchez-Camazano and González-García, 1966) have observed the formation of interlayer complexes of this mineral with organic substances possessing electron-releasing groups. However, visual careful examination of the kaolinite samples treated with TMP revealed the presence of crystalline white compounds. In order to separate kaolinite from the new crystalline phase, the solubility of the latter in water was assayed. In fact, it was not soluble in cold water, but was in hot water. Various solvents were also assayed to remove excess TMP from the kaolinite-crystalline phase system. Acetone was finally chosen since evaporation to dryness of the washing portions left no solid residue; hence, no crystalline phase was dissolved. The following procedure was then applied, the treated samples were washed with acetone and subsequently several times with hot water until complete disappearance of the reflection at 8.84 Å from the diffraction patterns. The waters of washings were evaporated to dryness, and the crystalline compound thus isolated was again dissolved in water for recrystallization. The diffraction pattern of the resulting compound (Figure 1E) showed a very strong reflection at 8.84 Å in addition to other, weaker reflections at 9.30, 8.33, 4.44, 3.57 and 3.13 Å, plus a few other, very weak diffractions. All these reflections except those at 4.44 and 3.57 Å, which coincide with
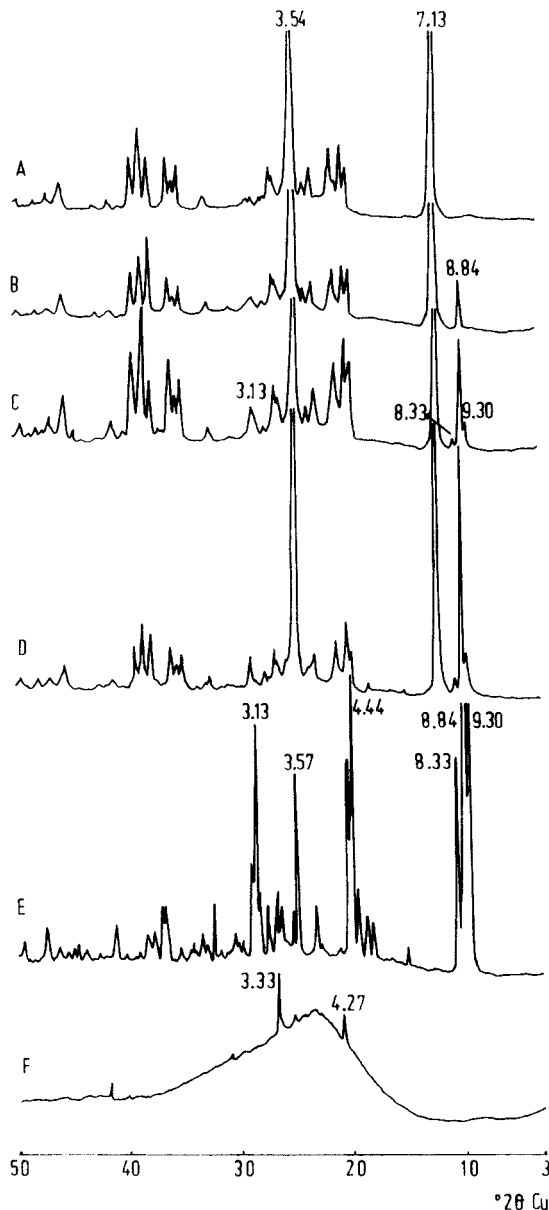

Figure 1. X-ray diffraction patterns of A) natural kaolinite; B–D) kaolinite treated with TMP for 30, 60, and 150 hr, respectively; E) the new crystalline phase; and F) kaolinite treated with TMP for 30 days and washed with hot water.

others of natural kaolinite, are normally observed in the diffraction patterns of TMP-treated kaolinite.

As can be seen in Figure 1F, which was obtained from a kaolinite sample that was treated with TMP for 30 days and subsequently washed with acetone and hot water to extract the crystalline phase formed, the original silicate structure was completely destroyed after that treatment time. The X-ray diffraction pattern shows none of the typical reflections of kaolinite. On the other hand, it includes some weak reflections at 4.27 and
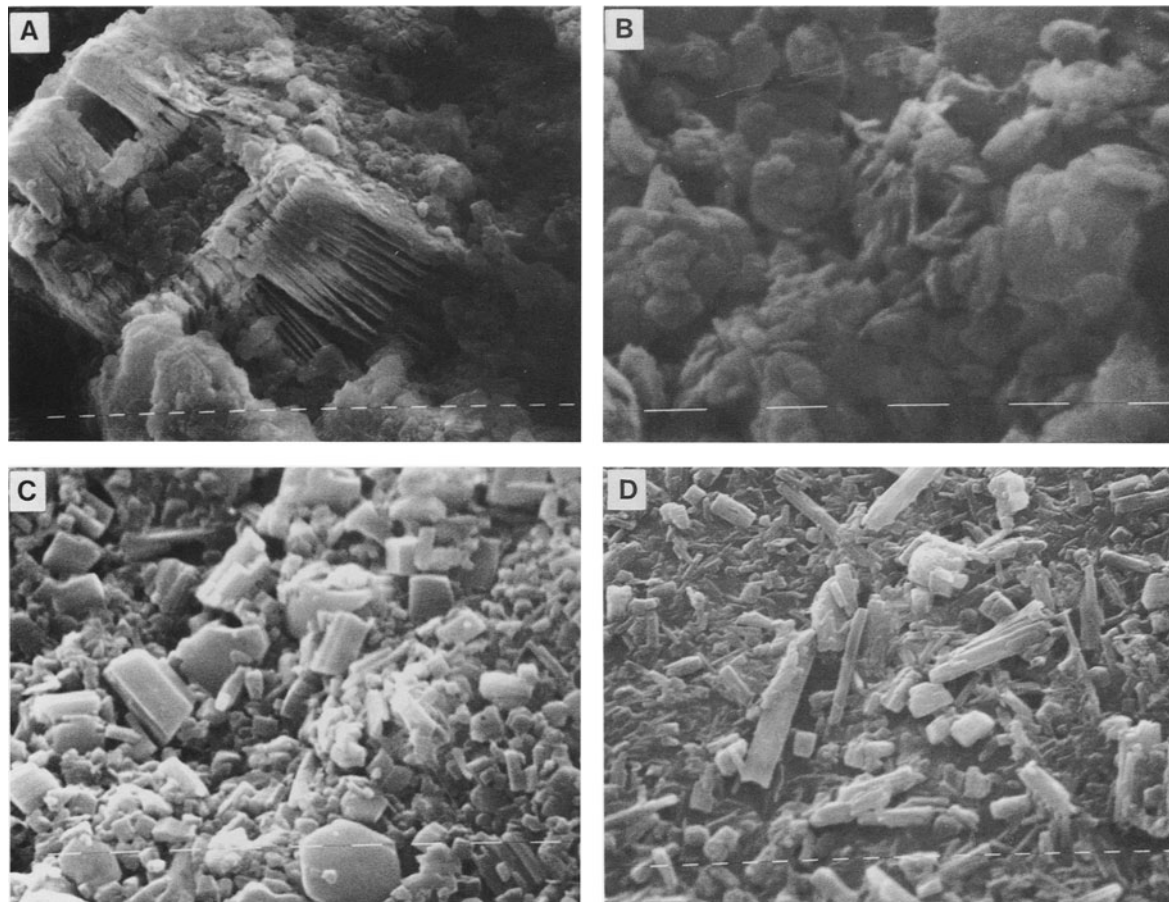
Figure 2. Scanning electron micrographs of A) natural kaolinite; B, C) kaolinite treated with TMP for 30 and 150 hr, respectively; and D) the new crystalline phase. Scale bars = 1 μm.

3.33 Å, yielded by the small amount of quartz present as an impurity in the mineral used in this work.

The scanning electron micrographs obtained also reflect the gradual destruction of the layers of natural kaolinite, concomitantly with the formation of the new crystalline phase. The micrograph of natural kaolinite (Figure 2A) shows the mineral to have a vermiform structure consisting of books of hexagonal plates. On the other hand, the micrograph of the kaolinite treated with TMP for 30 hr (Figure 2B) shows hexagonal outlines of kaolinite plates together with broken plates. The micrograph of the sample treated for 150 hr (Figure 2C) shows isolated hexagonal plates, most of which are severely damaged, in addition to elongated, rectangular crystals of the new phase. Finally, the micrograph of Figure 4D, which corresponds to the new crystalline phase, shows more or less elongated, rectangular crystals frequently piled.

In order to determine whether Al was extracted from the kaolinite lattice, accurately weighed amounts of kaolinite were treated with TMP for different lengths of time. The samples were washed with acetone and then with hot water until complete disappearance of the reflection at 8.84 Å from the diffraction patterns. This was followed by the determination of the distribution of Si and Al between the residue and water of washings (Table 1). As can be seen, the longer the TMP treatment of kaolinite was, the lower was the Al content in the residue and the higher that in the washings.

Aluminium oxide (Al_2O_3) samples were also treated under the same conditions as kaolinite for different lengths of time. The X-ray diffraction patterns obtained are shown in Figure 3. They reflect the formation of the same crystalline phase observed in the TMP treatment of kaolinite, with a very strong reflection at 8.84 Å and a few other, smaller peaks. The patterns also show some reflections of the crystalline phase (e.g., at 4.44 and 3.57 Å) not seen in those of treated kaolinite because they coincided with typical reflections of the starting mineral. These results confirm that Al is in fact the element extracted from the kaolinite structure, so it should precipitate with phosphate anion.

On the other hand, treating kaolinite with triethyl, tripropyl, and tributyl phosphate under the same con-

Table 1. Si and Al contents of natural kaolinite and their distribution between the residue and washings obtained from kaolinite treated with TMP for different lengths of time.

Oxide	Kaolinite	30 hr		60 hr		150 hr	
		Residue	Washings	Residue	Washings	Residue	Washings
SiO$_2$ (wt. %)	45.00	44.78	—	44.67	—	45.20	—
Al$_2$O$_3$ (wt. %)	37.77	34.01	3.57	28.50	8.65	16.86	20.15

ditions as with TMP also resulted in the formation of new crystalline phases, as reflected in the corresponding X-ray diffraction patterns (Figure 4). As can be seen, the spacing corresponding to the strongest peak increased with increasing size of the alkyl radical. This suggests that the new crystal phase must be a aluminium alkyl phosphate resulting from hydrolysis of one or two alkyl radicals in the original phosphate.

The chemical composition of the crystalline phase formed by treating kaolinite with TMP is given in Table 2, together with the theoretical P, Al, and CH$_3$ contents of mono- and disubstituted aluminium alkyl phosphates. Based on the results, the new compound must be an aluminium methyl phosphate of formula Al(CH$_3$)$_6$(PO$_4$)$_3$.

Inasmuch as it takes place in the absence of water, the hydrolysis of TMP by kaolinite must involve the hydration water of the exchange cations of the silicate.

Saltzman *et al.* (1974, 1976) and Mingelgrin *et al.* (1977) showed kaolinite to catalyze the hydrolysis of some organophosphorus pesticides and the catalytic activity of the mineral to depend on the nature and extent of hydration of the exchange cations. They found increasing moisture contents within the range of bound water to result in increasing catalytic activity of kaolinite on parathion. On the other hand, any amount of water outside this range hindered the effect. Sodium and calcium kaolinite dried at 105°C have a catalytic effect on the hydrolysis of parathion, so the effect must
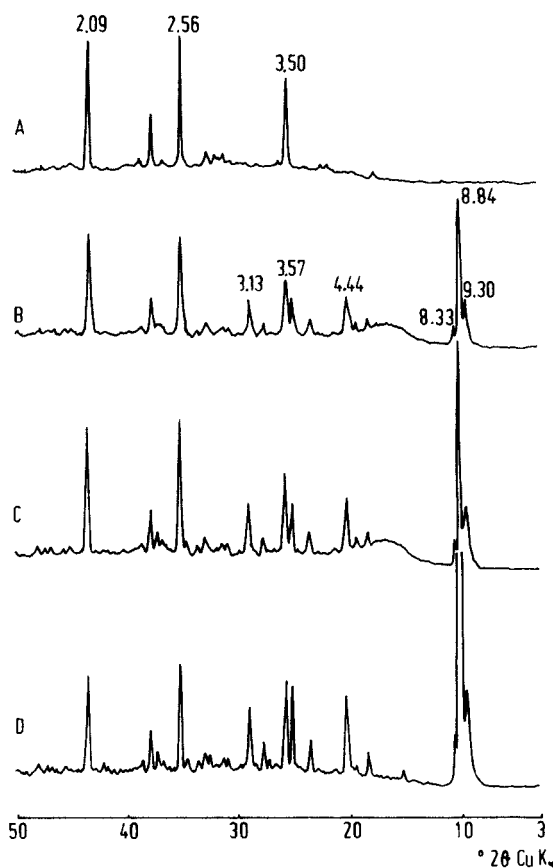

Figure 3. X-ray diffraction patterns of A) natural Al$_2$O$_3$; and B–D) Al$_2$O$_3$ treated with TMP for 30, 60 and 150 hr, respectively.
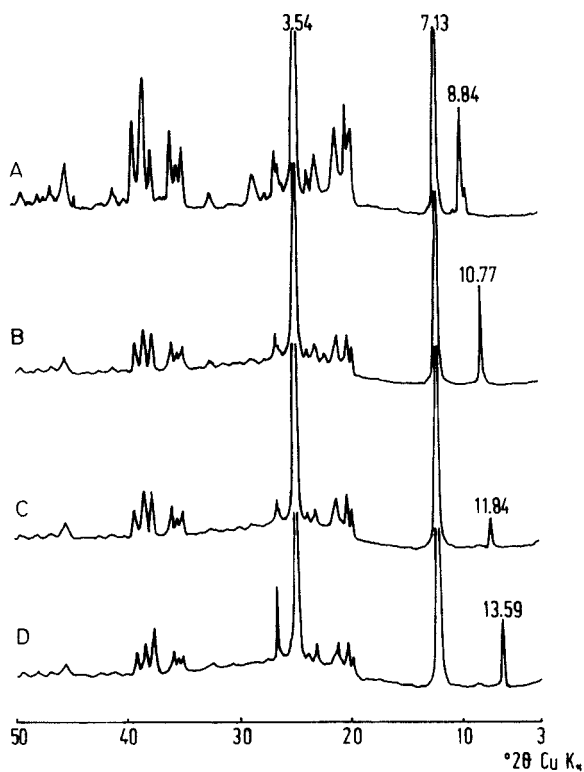

Figure 4. X-ray diffraction patterns of kaolinite treated with A) trimethyl phosphate; B) triethyl phosphate; C) tripropyl phosphate; and D) tributyl phosphate.

Table 2. Experimental chemical composition of the crystalline phosphate obtained by TMP treatment of kaolinite and theoretical chemical composition of the mono- and disubstituted aluminium methyl mixed phosphates.

Component	Phosphate (Kaolinite + TMP)	Monosubstituted phosphate	Disubstituted phosphate
Al (wt. %)	7.4	6.7	14.0
CH$_3$ (wt. %)	21.9	22.5	11.7
PO$_4$ (wt. %)	70.1	70.8	74.3

arise from hydration water remaining at the dry surface. The authors conclude that direct attack of the ligand water molecules on the P–O bond of parathion to hydrolyze the compound is enhanced by the cation-ligand interactions that polarize the water and weaken its OH–H bond. The presence of excess water dramatically reduces parathion adsorption and delays its hydrolysis, catalyzed by the kaolinite surface.

Based on the above findings, we believed it of interest to treat kaolinite samples previously dried at 105°C or equilibrated with ambient moisture or at a relative humidity (RH) of 35% or 100% with TMP for 40 hr. The X-ray diffraction patterns of the treated samples showed the formation of aluminium methyl phosphate from the samples equilibrated at ambient moisture and RH = 35%, as well as that heated at 105°C; on the other hand, no phosphate was formed by the sample that was equilibrated at RH = 100%. These results are similar to those reported by Saltzman et al. (1974, 1976) and Mingelgrin et al. (1977) for the interaction between parathion and kaolinite. Therefore, in treating kaolinite with TMP, water molecules directly bonded to the exchange cations must also be involved in the phosphate hydrolysis via a mechanism similar to that reported by the above-mentioned authors for parathion.

CONCLUSIONS

The results obtained in this work show that the interaction of kaolinite with TMP leads to a gradual decomposition of the silicate structure, which reaches completion after 30 days of treatment. In principle, one should bear in mind the hydrolysis of trimethyl phosphate catalyzed by the kaolinite surface, which must involve water molecules directly bonded to the exchange cations. Then, Al is removed from the kaolinite lattice by incompletely hydrolyzed TMP to form an aluminium methyl phosphate of formula Al(CH$_3$)$_6$(PO$_4$)$_3$.

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