NOTES

INTERACTIONS OF MONTMORILLONITE WITH
p-NITRO- AND p-METHOXYANILINES

Clay minerals are known to interact with a wide variety of organic molecules by adsorption, intercalation, cation exchange, and catalysis. In soil science and environmental engineering these interactions should be better known in order to describe and predict the transport of organic compounds through soil. Studies on the binding and transformation of well-defined organic compounds on pure clay minerals can provide models for interpreting the behavior of organic materials in soil. However, additional variables must be considered when dealing with the natural environment in soil. Among the clay minerals, montmorillonite (smectite) is an important component of many soils and shows interesting behavior in clay-organic interactions because it has unusual intercalation properties that afford opportunities to catalyze a wide variety of organic reactions (Ortego *et al.,* 1991).

Aniline and its substituted derivatives are components of numerous herbicides and many pesticides. They can be readily liberated by partial degradation to free aromatic amines in soil environments. In particular, nitroanilines are residues of herbicides bound as butralin (Helling and Krivonak, 1978), trifluralin (Seiber *et al.,* 1975; Golab *et al.,* 1979), and benefin (Golab *et al.,* 1970).

Interactions of organic compounds with montmorillonite depend on the composition and the structure of the organic molecules and the kinds of metal cations located on exchange sites of clay. Therefore, it seemed interesting for us to study the interactions of p-nitroaniline and p-methoxyaniline with montmorillonite as a function of different exchangeable cations.

EXPERIMENTAL

The organic reagents (p-nitroaniline and p-methoxyaniline) were analytical-grade chemicals from Aldrich and were used without further purification. The solvents (n-hexane and methanol) were HPLC-grade from Aldrich.

Cu^{2+}-, Fe^{3+}- and Al^{3+}-montmorillonites were prepared by suspending 10g of K-10 montmorillonite (from Aldrich) in 300 ml of freshly-prepared aqueous solutions of the metal chlorides (2×10^{-2} mol liter^{-1}) and stirring for 24 hours. The particular ion-exchanged montmorillonite was separated by filtration in a Buchner funnel, washed with distilled water until chloride-free, and finally dried in air at 110°C. The resulting powder was stored at this temperature until used.

A 0.05 g sample of p-methoxyaniline (or p-nitroaniline) was dissolved in 80 ml of n-hexane. One g of ion-exchanged montmorillonite was added to this solution. The suspension was stirred magnetically and heated to keep hexane boiling (69°C). After 6 hours the reaction vessel was cooled and the suspension filtered. The hexane filtrate was analyzed directly by gas chromatograph mass spectroscopy (GC/MS). The clay was dried in air and then treated with 40 ml of methanol. The suspension of clay in methanol was also stirred and heated in a reflux column for 15–20 minutes. After cooling, the suspension was filtered and the methanol extract analyzed by the GC/MS method. This procedure was conducted for each combination of organic compound and clay.

Analyses of the reaction products were performed on a Varian gas chromatograph coupled directly to a Finnigan MAT SSQ-70 quadrupole mass spectrometer system. Separations were performed on a DB5 fused silica capillary column (30 m × 0.25 mm, i.d.) manufactured by J & W Scientific, Inc. The conditions for GC were as follows: injector temperature, 250°C; transfer line temperature, 250°C. The capillary column temperature was programmed as follows: 120°C for 2 min; from 120° to 250°C at 12°/min; hold at 250°C for 10 min. Helium was used as a carrier gas. The mass spectrometer conditions were: ion source 150°C and ionization energy 70 eV. Mass spectra data were stored and processed with a Finnigan ICIS data system.

RESULTS AND DISCUSSION

Since several authors (e.g., Boyd and Mortland, 1986; Soma and Soma, 1989; Isaacson and Sawhney, 1983; Govindaraj *et al.,* 1987) have shown that aromatic molecules give rise to oligomeric or polymeric compounds on the clay surface, it was reasonable to assume that substituted anilines behave similarly. It can be seen from a mass chromatogram of a methanol extract (Figure 1) that p-methoxyaniline in contact with Cu^{2+}-montmorillonite gives rise to a higher molecular weight
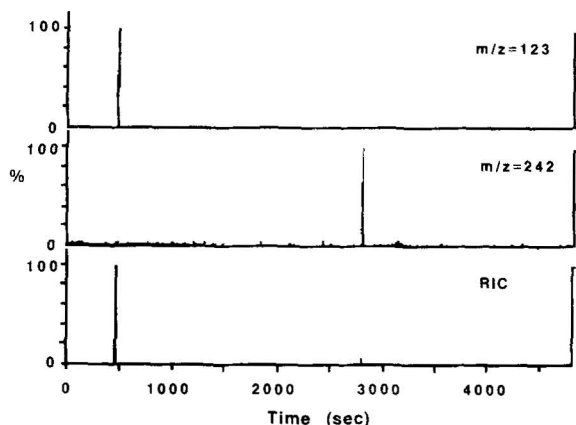
237

Figure 1. Mass chromatograms of the hexane filtrate of p-methoxyaniline over Cu^{2+}-montmorillonite. RIC is the reconstructed ion current.

Figure 2. Mass spectrum for the p-methoxyaniline and Cu^{2+}-montmorillonite reaction product.

product. A mass spectrum of this product is shown in Figure 2. The formation of a dimer is clearly evidenced by the mass at m/e 242 (molecular ion) and masses at 135 and 107, in accordance with patterns of fragmentation of azocompounds by electron bombardment that takes place in the ion source of the mass spectrometer. This product has been identified as 4,4'-dimethoxy-azobenzene. The same product can also be identified in methanol extracts over Fe^{3+}- and Al^{3+}-montmorillonite but the extracts should be three times more concentrated. No reaction product was found when p-methoxyaniline was heated over K-10 montmorillonite. The p-nitroaniline did not give rise to any reaction product over K-10 or the other ion-exchanged montmorillonites.

The different behavior of p-methoxyaniline and p-nitroaniline over montmorillonite may be explained by an influence of the substituant group on the property of the particular molecule. The nitro-group has a strong resonance effect with the electronic displacement towards this group, and p-nitroaniline is therefore more resonance-stabilized than aniline itself (Finar, 1973). This resonance effect tends to draw the lone pair on the nitrogen atom into the ring of the amino-group and makes the molecule nonreactive in the interlayer environment of the montmorillonites. In contrast, when an electron-releasing group such as methoxy is in the *para*-position, this reduces the resonance of the amino group with the ring, and makes this molecule reactive. However, the behavior of p-methoxyaniline over montmorillonite depends on the kind of exchangeable cations present in the interlamellar spaces.

The differential behavior of aniline over Fe^{3+}- and Cu^{2+}-montmorillonites has been described by Moreale *et al.* (1985) and Soma and Soma (1988). It was concluded from the spectroscopic characteristics of the organo-clay complexes formed that the Fe^{3+} cation interacts with the π-electrons of the aromatic ring to give
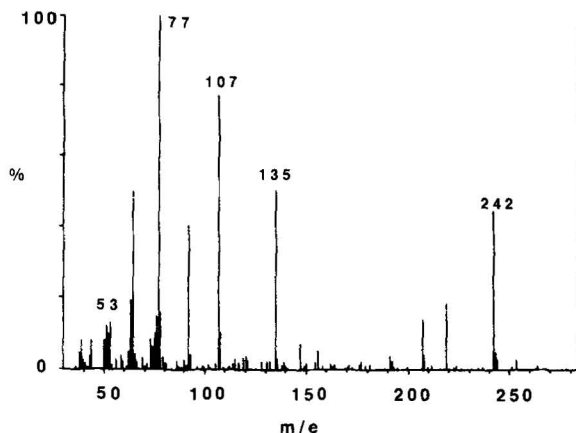
rise to radical cations or so-called type-II complexes. Direct coordination of the amine group to the exchangeable cation, followed by free-radical formation at the amine group, takes place for the Cu^{2+} cation. Al^{3+}-montmorillonite shows adsorptive and spectral features resembling those of Fe^{3+}-saturated clay and gives rise to type-II complexes of aniline and p-chloroaniline (Cloos *et al.*, 1979). It has been concluded

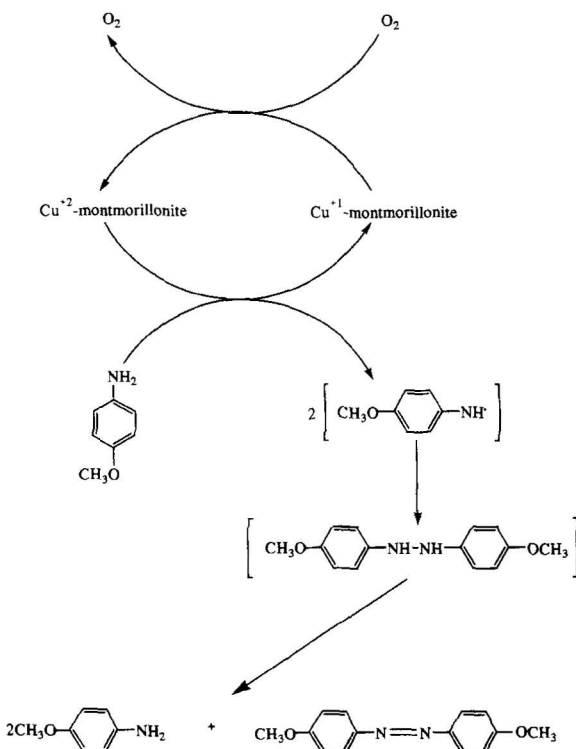Figure 3. Proposed scheme for the transformation of p-methoxyaniline over Cu^{2+}-montmorillonite.

from adsorption isotherms (Moreale and Van Bladel, 1979) and infrared data (Cloos *et al.*, 1979) that p-chloroaniline is adsorbed by montmorillonite through the same mechanisms as aniline. Because a halogen atom in the ring has the same resonance effect as the methoxy group, though weaker, it seems reasonable to assume that p-methoxyaniline is also adsorbed by montmorillonite in a similar manner as is aniline. Therefore, on Fe^{3+}- and Al^{3+}-montmorillonites p-methoxyaniline should also give rise to type-II complexes. Since type-II complexes have been shown to be able to polymerize (Pinnavaia *et al.*, 1974; Mortland and Halloran, 1976; Pinnavaia, 1982) the appearance of some reaction products of p-methoxyaniline over Fe^{3+}- and Al^{3+}-montmorillonites were expected.

For Cu^{2+}-montmorillonite the following interpretation is proposed for the transformation of p-methoxyaniline. As a consequence of the direct coordination of p-methoxyaniline by its amine group to the Cu^{2+} cation, the oxidation of amine to a free radical takes place, possibly by removal of a hydrogen atom from the amine group, and the reduction of Cu^{2+} to Cu^+ can occur. A condensation of the p-methoxyaniline free radical generated by the intercalated cation produces 4,4'-dimethoxyazobenzene, probably through 4,4'-dimethoxyhydrazobenzene as an intermediate (Figure 3).

The formation of 4,4'-dimethoxybiphenyl from anisole over Cu^{2+}-hectorite was reported by Fenn *et al.* (1973). One of the proposed mechanisms proceeds through a radical-cation intermediate with the redox participation of the copper cation. This pathway is similar to our mechanism for transformation of p-methoxyaniline over Cu^{2+}-montmorillonite.

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