

NOTES

ADSORPTION AND DEGRADATION OF FENARIMOL
ON MONTMORILLONITE

Key Words—Adsorption, Carbonium ion, Fenarimol, Fungicide, Infrared spectroscopy, Montmorillonite.

The importance of the non-biochemical reactions in decomposing organic molecules adsorbed on clay surfaces has been emphasized in recent years (Mortland, 1970; Theng, 1974; Crosby, 1976). The nature of the interlayer exchangeable cation is one of the most important factors in the adsorption and transformation of the organic molecules on the clay surface. The higher the charge, the greater is the polarizing effect of the cation on coordinated water molecules which promotes their dissociation and leads to an increase in surface acidity. Moreover, on heating, as the water content decreases, polarization forces become more concentrated on the fewer remaining water molecules causing an increase in hydrolysis and in their proton donating abilities (Farmer and Mortland, 1966; Mortland and Raman, 1968).

The formation of carbonium ions has been demonstrated when triphenylcarbinol is adsorbed on montmorillonite surface. These ions result from the acidity present in the interlayers of the montmorillonite (Fripiat *et al.*, 1964; Helsen, 1970; Helsen *et al.*, 1975). Once adsorbed, this compound transforms into its respective carbonium ions ($\text{Ph}_3\text{-C}^+$) by heating at 100°C as a consequence of the reaction with proton from the solvation water of the exchange cations. Rehydration results in the formation of the triphenylcarbinol.

The transformation of the fungicide Fenarimol adsorbed on montmorillonite saturated with different cations was investigated to ascertain whether the substitution of a pyrimidine for a benzene ring affects the nature of the reaction products.

EXPERIMENTAL

Materials

Homoionic montmorillonites were prepared from <2- μm equivalent spherical diameter fraction of a bentonite from Upton, Wyoming, by treatment with 1 N solutions of AlCl_3 , CaCl_2 , BaCl_2 , MgCl_2 , CuCl_2 , KCl , and NaCl . The excess salt was eliminated by repeated washings until a test for Cl^- was negative.

The Fenarimol [α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol] was supplied by Elanco (Italy). The melting point of the pure compound (99.8%) was 118°–119°C.

Infrared (IR) analysis

The IR spectrum of the Fenarimol was recorded in a KBr disk. The adsorption of the product on the clay surface was achieved by immersing self-supporting films of the clay in a saturated solution of Fenarimol in CCl_4 . These films were washed with CCl_4 and air dried. IR spectra of the Fenarimol-clay systems were recorded at room temperature on a Model 283B Perkin-Elmer spectrophotometer from: (1) the original sample, (2) the sample after heating at 100°C for 8 hr, (3) sample (2) after equilibration at 100% RH for 5 hr, (4) sample (3) after heating at 100°C for 30 hr, and (5) sample (4) after equilibration at 100% RH for 5 hr.

Ultraviolet (UV) analysis

Ultraviolet spectra of the films of the Fenarimol-clay complexes were recorded on a Model DB-GT Beckman spectrophotometer by placing a pure clay film in the reference beam and wetting the sample with Nujol to avoid scattering.

Thin-layer chromatography

Fixed amounts of the Fenarimol-clay complexes (original, heated, and humidified) were extracted with acetone. The solution was then transferred to 0.2-mm, silica-gel 60 F_{254} plastic sheets (Merck) and eluted with a 96:4 benzene-methanol solution (Stahl, 1969).

The well-defined spots of the components were revealed by UV light. The R_f values of the Fenarimol and of its decomposition product were 0.6 and 0.9, respectively. To obtain the product with $R_f = 0.9$ in sufficient amount for analytical purposes, several grams of the complex were used. The spots were scraped off and extracted in CCl_4 . A quantitative estimation of the isolated compounds was obtained by UV spectrophotometry (Fenarimol at 246 nm and the reaction product with $R_f = 0.9$ at 310 nm). To identify the nature and to obtain the formula of the yellow-colored decomposition product ($R_f = 0.9$), this compound was analyzed by IR and nuclear magnetic resonance (NMR) and subjected to elemental analysis.

RESULTS AND DISCUSSION

The Fenarimol molecule heated at 100°C (below its normal melting point of 118°–119°C) for several days in the absence of clay remained unaltered. The amount of adsorbed Fenarimol that decomposed when heated at 100°C for 38 hr increased from about 30% in the K-clay to a maximum of 70% in the Al-clay, according to the increasing polarizing power of the exchangeable cations. Because the reaction products obtained were always the same, regardless of the nature of the cation saturating the clay, this report and discussion is therefore limited to the spectra of the Fenarimol-Ca-montmorillonite complex (Figure 1).

Fenarimol-clay complexes at room temperature

The IR spectrum of the complex (Figure 1, spectrum "b") shows the Fenarimol band positions to be nearly identical with those in the spectrum of the pure compound (Figure 1, spectrum "a"). The only difference is the shift to 1586 cm^{-1} of the 1562- cm^{-1} band, due to a skeletal vibration of the pyrimidine ring (Lafaix and Lebas, 1970; Takahashi *et al.*, 1966).

A shift to higher frequencies is a result of the skeletal vibrations of the pyrimidine in a protic solvent (Takahashi *et al.*, 1966). It is, therefore, reasonable that Fenarimol was adsorbed by van der Waals forces and hydrogen bonding between the nitrogen (or the nitrogens) of the pyrimidine ring and the H of the solvation water of the cations.

The pyrimidinium ion was not observed in any of the Fenarimol-clay complexes. In fact, the pyrimidine-HCl spectrum showed a band in the 2500- cm^{-1} area, two bands in the region of 2000 cm^{-1} , and a band at 1605 cm^{-1} . The Fenarimol-clay complexes spectra showed no sign of any bands in the 2000- cm^{-1} and 2500- cm^{-1} regions, and nothing definite can be said about the band at 1605 cm^{-1} , which could be masked by the band of the water at 1620 cm^{-1} . The differential spectra did not clarify the situation and thin-layer chromatography revealed that only Fenarimol was present ($R_f = 0.6$).

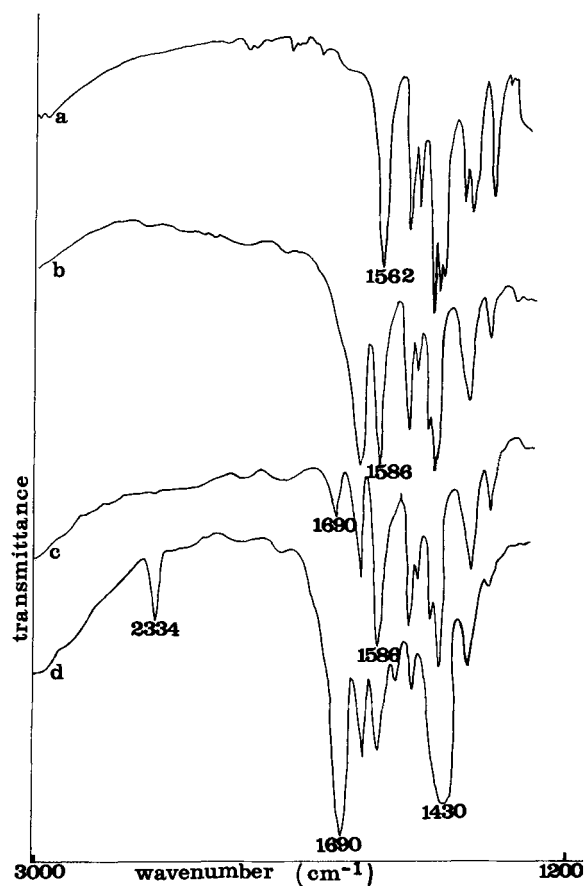
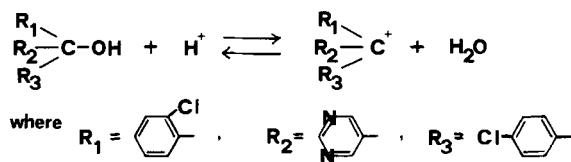


Figure 1. Infrared spectra of pure Fenarimol and of Fenarimol-Ca-montmorillonite complex: (a) pure Fenarimol (KBr disk), (b) complex at room temperature, (c) complex (b) after heating at 100°C for 8 hr and cooled in air, (d) complex (c) after heating at 100°C for 38 hr and then cooled in air.

Fenarimol-clay complexes after heating at 100°C for 8 hr

When heated at 100°C the complex assumed a pale yellow color and the UV spectrum showed a slight shoulder at 430 nm. The spectrum of Fenarimol in concentrated HCl solution shows a maximum at 430 nm which can be ascribed to the carbonium cation of the Fenarimol (Deno *et al.*, 1954). When the clay complex was equilibrated at 100% RH, the weak yellow color and the shoulder at 430 nm disappeared. The Fenarimol adsorbed on the clay surface seems to have been partially transformed into corresponding carbonium ion by interaction with the protons of the solvation water of the clay exchangeable cations. Similar results were reported with triphenylcarbinol (Fripiat *et al.*, 1964; Helsen, 1970). The reaction can be summarized as follows:

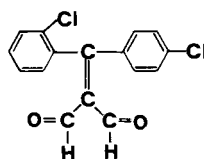


Thin-layer chromatography of the acetonic extract from the heated Fenarimol-clay complex confirmed these results; nevertheless, on the chromatographic sheet, with Fenarimol ($R_f = 0.6$), a faint spot was observed ($R_f = 0.9$) that could be ascribed to a compound that probably formed on heating. The weak band at 1690 cm^{-1} (Figure 1, spectrum "c") could be due to this compound. This band cannot be assigned to a vibration of the carbonium ion (Weston *et al.*, 1966). Moreover, the humidification does not result in its disappearance, and its intensity is markedly increased by prolonged heating at 100°C.

Fenarimol-clay complexes heated at 100°C for 38 hr

The IR spectrum of Fenarimol-clay complexes heated at 100°C for 38 hr shows a band at 2334 cm^{-1} assignable to the CO_2 -stretching vibration and another at 1430 cm^{-1} assignable to NH_4^+ . The intensity of the band at 1690 cm^{-1} (Figure 1, spectrum "d") also increased. The UV spectrum displays a shoulder or peaks at 430 nm. The film of the Fenarimol-clay complex has a definite yellow color which, unlike that previously observed, did not disappear with re-equilibration at 100% RH. The 1690- cm^{-1} band was also unaffected by humidification.

When the heated complex was treated with acetone, traces of Fenarimol and a yellow compound with $R_f = 0.9$ were extracted. An elemental analysis of this yellow compound (C = 62.64%, H = 3.36%, Cl = 23.81%, O = 10.19%) shows no nitrogen. These data, together with the information obtained from the NMR and IR spectra suggest the following formula for this compound:



calculated

C = 62.95%

H = 3.30%

Cl = 23.23%

O = 10.72%

The IR spectrum of this pure extracted compound shows bands characteristic of the aldehydic function at 2930 cm^{-1} and 2725 cm^{-1} ($-CH$ stretching) and at about 1700 cm^{-1} ($C=O$ stretching) (Rao, 1963). The spectrum of the clay complex shows this last band very clearly, while the other two at 2930 cm^{-1} and 2725 cm^{-1} are not visible, probably because of their low intensity. The proton NMR spectrum shows peaks in the 9–10 δ region of the chemical shifts which are typical of aldehydes. Thus, heating the Fenarimol adsorbed on the montmorillonite to 100°C for several hours appears to lead to the decomposition of the molecule at the level of the pyrimidine ring, with the consequent formation of a yellow-colored dialdehyde. This molecule's breakdown is confirmed by the appearance on the IR spectrum of the Fenarimol-clay complex of bands typical of CO_2 and NH_3 , the latter trapped on the clay as NH_4^+ (Figure 1, spectrum "d").

CONCLUSIONS

When triphenylcarbinol adsorbed on montmorillonite is heated in vacuum at 100°C it results in the production of the corresponding carbonium ion only. A further heating at 200°C results in a decrease of the amount of carbonium ion formed, and at 300°C the molecule decomposes with formation of uncondensable gases (Fripiat *et al.*, 1974). In contrast, the Fenarimol molecule alters at the level of the pyrimidine ring on heating at 100°C with CO_2 , NH_3 , and a dialdehydic molecule being formed.

The particular weakness of the pyrimidine ring can probably be ascribed to the delocalization of the positive charge of the carbonium ion in position 2, 4, and 6, with the consequent weakening and breakdown of the C-N-C bonds. As the resid-

ual solvation water becomes more acidic on heating, the increased proton donating properties of this water probably play an important role in the decomposition process, especially with regard to the interaction with nitrogen atoms of the pyrimidine ring.

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