

be distinguished: (i) muscovite with two small cations for each vacancy capable of accommodating a large ion (21) (Fig. 2a); (ii) xanthophyllite with two large cations for each small (Fig. 2c); and (iii) annite with all cations of the same size, or with large and small in a disordered arrangement (Fig. 2b). The xanthophyllite ordering should occur in siderophyllite, zinnwaldite,

polyolithionite, and possibly in a mica with an octahedral formula $Al_2Li_2Mg_2$. The annite arrangement applies to phlogopite, biotites, and trilithionite.

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Mode of Chemical Degradation of *s*-Triazines by Montmorillonite

Abstract. *Chemical hydrolysis of the s-triazines after interaction with less than 2-micron (equivalent spherical diameter) montmorillonite clay occurs as a result of protonation at the colloidal surface; protonation occurs even when the exchange sites are occupied by metallic cations. The adsorbed hydrolytic degradation product is not the hydroxy analog, but it is predominantly the keto form of the protonated hydroxy species. This cationic form is held tightly by the clay which may restrict vertical movement and entrance into groundwater. Protonation of the hydroxy analog occurs on the heterocyclic ring nitrogen.*

The *s*-triazines are widely used herbicides, yet their fate in soil and water has not been clearly defined. Metabolism of simazine (1, 2), atrazine (3), and ipazine (4) by soil microorganisms has been clearly shown. Recent work (2, 4) calls into question the assumption that microbial degradation is a major factor in the detoxification and loss of *s*-triazine herbicides from soil. These authors measured the evolution of CO_2 containing labeled C^{14} and concluded that very little degradation of the 2-chloro *s*-triazine derivatives occurred within a period of 4 to 16 weeks.

Chemical hydrolysis of atrazine produces hydroxyatrazine in strongly acid or basic solutions (5). The hydroxy analogs of simazine (6, 7), atrazine (8), and propazine (7) have been recovered from soils treated with the 2-chloro *s*-triazine derivatives. Thus the hydroxy analog has been proposed as the major degradation product of nonbiological degradation processes. The importance of the inorganic soil constituents in nonbiological degradation has been illustrated by Harris (7), who found that formation of the hydroxy analogs of simazine, atrazine, and propazine in five soils was not inhibited by 200 parts per million (ppm) of sodium azide. Atrazine was rapidly detoxified at 95°C in soil, but only slowly detoxified in aqueous solution at the same temperature in the absence of soil.

Direct evidence is not available on whether the degradation product of the *s*-triazine herbicides exists in the adsorbed state and whether the alkyl-amino functional group significantly affects the degradation reaction. Arm-

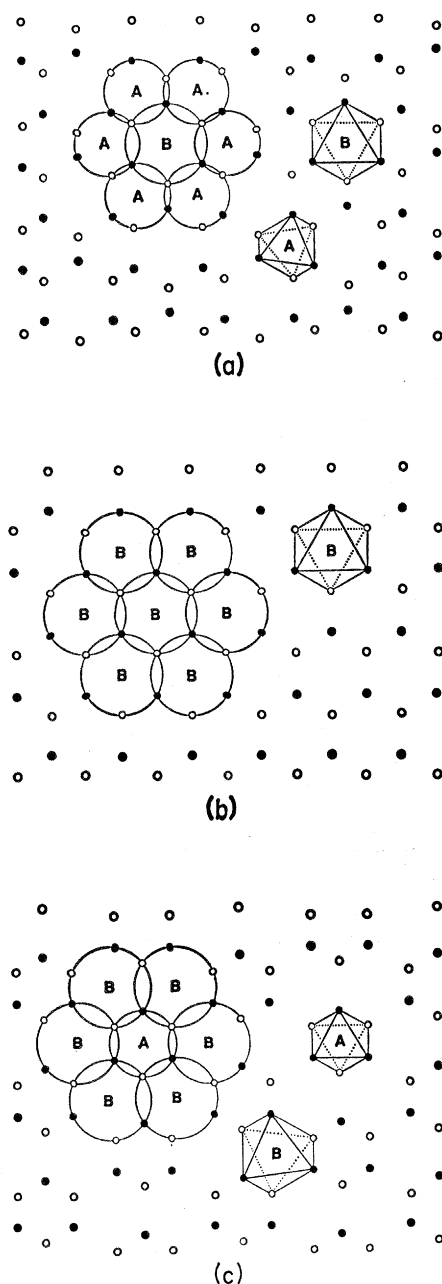


Fig. 2. Idealized octahedral anionic arrangements in the micas projected on (001) (along c^*). Octahedral cations are not shown, small (A) and large (B) sites being shown instead. The upper anion layer is shown by solid circles; open circles represent the lower layer. (a) Muscovite [modified from Veitch and Radoslovich (28)]. (b) Annite [modified from Donnay *et al.* (2)]. (c) Zinnwaldite (geometrical construction; this report).

strong, Chesters, and Harris (8) postulated that the mechanisms proposed (9) for the hydrolysis of chlorotriazines would also hold for atrazine. Acid hydrolysis might thus result from protonation of a ring or chain nitrogen atom followed by cleavage of the C-Cl bond by water. We now present spectroscopic evidence on the interaction between *s*-triazines and the silicate surface and the chemical character of the degradation product.

The montmorillonite used in this study was the <2- μ fraction of Wyoming bentonite (Upton, Wyoming). Cation saturation was effected by cation-exchange resin techniques or by repetitive washings with 1*N* chloride salt solutions. Montmorillonite was saturated with the following cations: H⁺, Na⁺, K⁺, NH₄⁺, Li⁺, Mg²⁺, Ca²⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Al³⁺, and Fe³⁺.

Montmorillonite was reacted with the chloro-, methoxy-, and methylmercapto-*s*-triazines in water, methanol, and chloroform for varying periods of time. Aqueous solutions of atrazine and its methoxy and methylmercapto derivatives (containing amounts in excess of the cation-exchange capacity of the

montmorillonite) were adjusted to pH 3.5 and reacted with a freshly prepared suspension of H-montmorillonite. In the nonaqueous systems, unsupported thin films of montmorillonite were placed in chloroform and methanol solutions of simazine and propazine and their methoxy and methylmercapto derivatives. After the excess *s*-triazine was removed, high-resolution infrared spectra of the clay-organic reaction products were recorded with the use of either unsupported films or micro-KBr techniques. The sample chamber was purged with dry nitrogen.

The *s*-triazines used were of high-purity (10). The protonated hydroxypropazine was prepared by treatment of hydroxypropazine with HCl, and then by successive recrystallizations from water and ethanol.

Infrared spectra show that both atrazine (Fig. 1, a and b) and propazine (Fig. 2, a and b) undergo significant changes as a result of interaction with the montmorillonite surface. The most obvious difference between the spectra of pure atrazine and propazine and the *s*-triazine-clay complexes is the appearance in the latter of a strong band at 1740 cm⁻¹. Carbonyl bands usually occur in this region. In addition, bands occur at approximately 1665 and 1630 cm⁻¹ in both *s*-triazine-clay complexes.

The current assumption is that degradation of chloro *s*-triazines leads to the formation of the hydroxy analogs as the principal degradation product in soils. Comparison of the infrared spectra of atrazine-clay (Fig. 1b) and propazine-clay (Fig. 2b) with those of the hydroxy analogs (Figs. 1c and 2c, respectively) shows that the adsorbed degraded species are not the hydroxy analogs.

This conclusion is further supported by the changes in the infrared spectra of the hydroxy analogs (Figs. 1c and 2c) which result from interaction with H- and NH₄-montmorillonite (Figs. 1d and 2d). The band positions of the products (Figs. 1e and 2e) resulting from treatment of the hydroxy analogs with HCl to produce the protonated form are essentially identical with those of the product of the *s*-triazine-clay reaction.

The similarity of the spectra of atrazine and propazine (when adsorbed on montmorillonite surfaces) and those of the hydroxy analogs in acidic environment indicates that the adsorbed species have been protonated and hydrolyzed as a result of interaction with the clay

surface. Degradation of the chloro *s*-triazines by interaction with the silicate surface results in the formation of the protonated hydroxy analogs of these compounds.

Infrared studies indicate that the chloro *s*-triazines are protonated even though all the exchangeable sites of the clay are occupied by metallic cations. The source of protons in these systems is probably the more highly dissociated water on the clay surface (11).

Surface acidity is an important factor in the interaction of montmorillonite systems with herbicides (12). The clay-organic interactions suggest that the surface acidity of the clay may be from 3 to 4 pH units lower than that

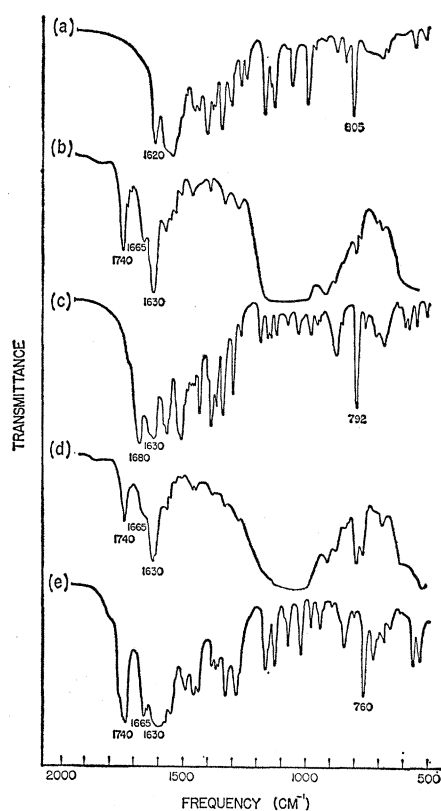


Fig. 1. Infrared spectra from 2000 to 500 cm⁻¹ of: (a) atrazine; (b) atrazine-H-montmorillonite clay complex, reaction time 5 days; (c) hydroxyatrazine; (d) hydroxyatrazine-H-montmorillonite clay complex, reaction time 30 minutes; and (e) hydroxyatrazine + 6*N* HCl.

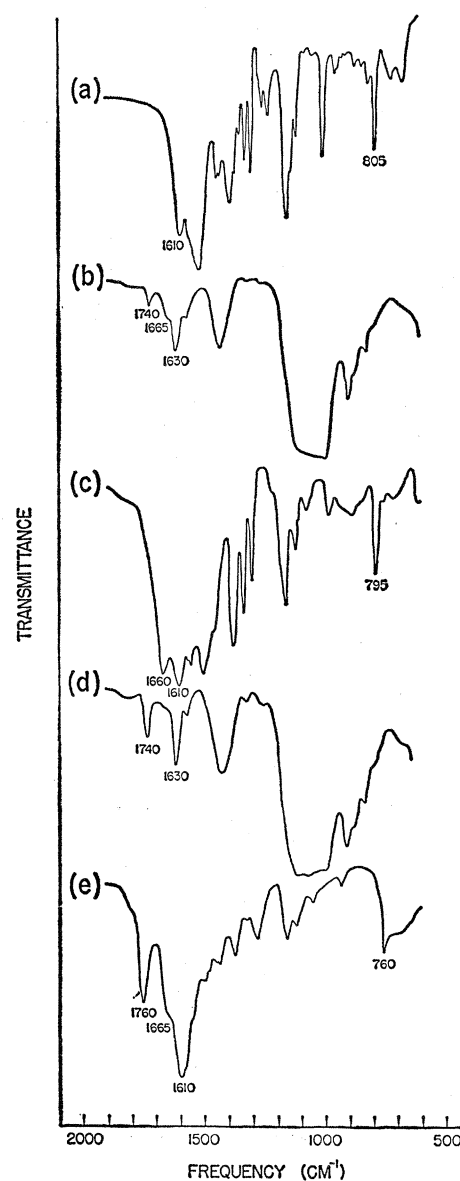


Fig. 2. Infrared spectra from 2000 to 500 cm⁻¹ of: (a) propazine; (b) propazine-NH₄-montmorillonite clay complex; (c) hydroxypropazine; (d) hydroxypropazine-NH₄-montmorillonite clay complex; and (e) propazine + HCl.

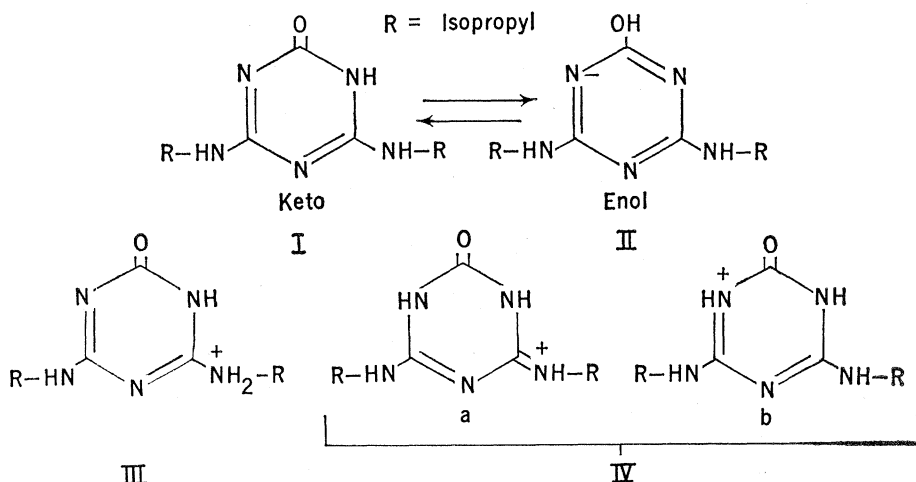


Fig. 3. Tautomeric structures (I and II) of the unprotonated and some possible tautomeric (III) and resonance (IV) structures of protonated hydroxy analogs of chloro *s*-triazines.

measured in the suspension. The fact that no degradation of atrazine was observed in a solution system at a pH of 3.5 in the absence of clay illustrates the catalytic function of the clay surface. A similar observation (8) has been reported for atrazine in soil studies. In both the low-moisture and high-moisture systems the adsorbed triazine molecules experienced high surface acidity, due in the former case to the highly dissociable water at the clay surface, and in the latter case to the presence of hydrogen as an exchangeable ion.

Two tautomeric forms of the hydroxy analogs are possible (Fig. 3). The appearance of a strong band at 1740 cm^{-1} indicates that the keto form (I) predominates in the protonated hydroxy species. This is supported by the shift of a band at 795 cm^{-1} in the hydroxy analog to 760 cm^{-1} upon protonation (13).

Protonation of the hydroxy analog has been postulated to occur either on the ring nitrogens or on the secondary amino groups of the side chains (14). Side-chain protonation would yield structure III with an NH_2^+ group, while ring protonation would result in the formation of a structure with either an exocyclic $\text{C}=\text{N}$ group and the charge on the side chain nitrogen (IVa), or one in which both proton and charge reside on a ring nitrogen (IVb). The positive charge and the proton can reside on any of the three ring nitrogens; by resonance and tautomerism structure IVb will yield five additional isomeric structures. Structure IVa has only one other tautomeric isomer, but will have two more isomers for nonidentical side chains.

Spin decoupling (double resonance) was carried out by irradiating the isopropyl CH_3 groups of protonated hydroxypropazine; this removed the coupling from between the proton of the CH group and the CH_3 groups. As shown in Fig. 4a, the CH resonance changed from a complex multiplet to a doublet upon irradiation of the CH_3

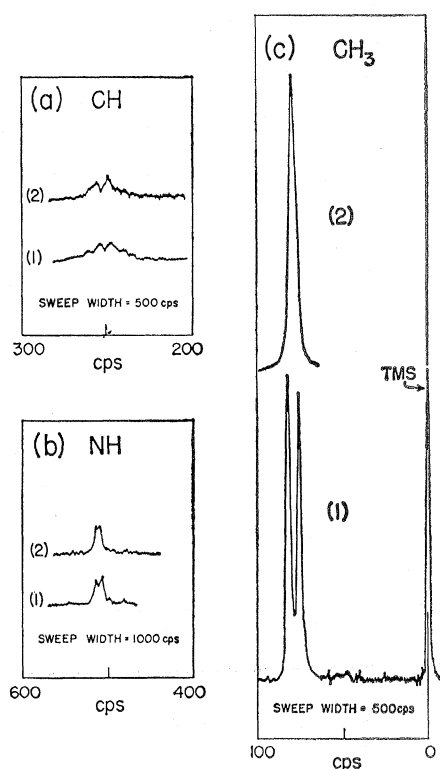


Fig. 4. Double resonance with protonated hydroxypropazine: (a) CH peaks: (1) initial spectrum; (2) CH_3 group irradiated. (b) NH peaks: (1) initial spectrum; (2) CH group irradiated. (c) CH_3 peaks: (1) initial spectrum; (2) CH group irradiated. Solvent: CHCl_3 ; sweep width, 500 cycle/sec.

groups. Irradiation of the CH proton caused the signal at 501 cycle/sec to collapse to a singlet (Fig. 4b), confirming the assignment of this absorption to the proton of the alkyl NH group. The doublet of the isopropyl CH_3 groups coalesces to a singlet upon irradiation of the CH proton (Fig. 4c). Structure III, which contains an NH_2^+ group, is ruled out by the NMR spin decoupling experiments. Thus, structure IV and its resonance and tautomeric forms are probably correct.

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