

The Adsorption of 3-Aminotriazole by Montmorillonite

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The 3-aminotriazole molecule is protonated when adsorbed on montmorillonite surfaces to produce the 3-aminotriazolium cation. In the case of montmorillonite saturated with polyvalent cations (Ca^{2+} , Cu^{2+} , Ni^{2+} , Al^{3+}), protonation is believed to be due to the highly polarized water molecules in direct coordination to these cations. The decreasing order of extent of protonation ($\text{Ca} < \text{Mg} < \text{Al}$) reflects the order of decreasing polarizing power of the cations. Infrared spectra indicate coordination

of 3-aminotriazole to Ni^{2+} and Cu^{2+} cations. The infrared absorption band at 1696 cm^{-1} is assigned to the $\text{C}=\text{N}$ stretching vibration of the exocyclic $\text{C}=\text{N}$ group. Shifts of the 1696 cm^{-1} band to 1683 and 1666 cm^{-1} upon dehydration and deuteration, respectively, suggest that the positive charge on the protonated molecule lies on the exocyclic nitrogen. The protonated molecule undergoes normal exchange reactions with other cations.

Several studies have been made of the fate of 3-amino-1,2,4-triazole in soils (Sund, 1956; Burschel and Freed, 1959; Jordan, 1960; Day *et al.*, 1961; Ashton, 1963; Ercegovich and Frear, 1964). While adsorption of aminotriazole by clay minerals was postulated by Sund (1956) and Ercegovich and Frear (1964), little is known of the interaction with pure clay minerals, particularly of the montmorillonite group. The importance of such reactions cannot be overemphasized in view of their bearing on the persistence of the herbicide in soil.

While the high solubility of aminotriazole in water (28 grams per 100 ml. at 23°C .) suggests ready leaching from whole soil, and this has been demonstrated for Californian soils by Day *et al.* (1961), this investigation indicates that if the soil contains a montmorillonite-type mineral, the aminotriazole might be resistant to leaching as a result of adsorption by the montmorillonite.

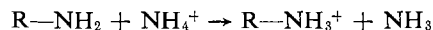
EXPERIMENTAL

The interaction between aminotriazole and montmorillonite was investigated by studying the infrared absorption spectra of sedimented montmorillonite films prepared from aqueous suspensions (1% w./v.) of homoionic montmorillonite containing dissolved aminotriazole at four levels—25, 50, 100, and 200% of the cation exchange capacity of the montmorillonite (90 mmoles per 100 grams of clay). The suspensions were slowly evaporated to dryness on thin polyethylene sheet from which the resulting clay films (2.5 to 3 mg. per sq. cm.) could be readily peeled.

DISCUSSION OF RESULTS

It is clear from the identity of the spectra in Figure 1 that the 3-aminotriazole has been converted to the triazolium cation in Mg montmorillonite. While the spectrum shown is qualitatively representative of the complexes of a range of other ionic saturations of montmorillonite (Na , NH_4 , Ca , Cu^{2+} , Ni^{2+} , Al^{3+}), the extent to which aminotriazolium cation was formed is dependent on the

exchangeable cation (Table I). The 3-aminotriazolium cation is formed, in the case of the polyvalent cations, when 3-aminotriazole becomes protonated by highly polarized water molecules which are in direct coordination to these cations. This type of reaction has been demonstrated previously for other organic bases—ethylamine (Farmer and Mortland, 1965); pyridine (Farmer and Mortland, 1966); and NH_3 (Mortland *et al.*, 1963; Russell, 1965). By contrast, in NH_4 montmorillonite, the triazolium ion is formed by the following reaction:



It is not yet clear how the aminotriazolium ion is formed in Na montmorillonite, but it is almost certainly formed by a reaction similar to the one by which NH_4^+ is formed from NH_3 (Russell, 1965), and pyridinium from pyridine (Farmer and Mortland, 1966) in this montmorillonite. Protonation of 3-aminotriazole was maximal in Al montmorillonite where the water molecules coordinated by Al^{3+} are so highly polarized that the clay is acidic. The decreasing order of extent of protonation, $\text{Ca} < \text{Mg} < \text{Al}$ (Table I), reflects the order of decreasing polarizing power of the cations.

In addition to protonation of 3-aminotriazole in both Cu and Ni montmorillonites, spectra indicated coordination of the organic base to these transition metal cations.

Table I. 3-Aminotriazolium Ion Formed in Various Cationic Saturations of Montmorillonite^a

3-Aminotriazole Added	% Exchange Capacity					
	Exchangeable Ion on Montmorillonite					
	Na	NH_4	Ca	Mg	Al	Cu Ni
25	6	17			23	3 22
50	6	28	18	29	47	12 46
100	6	48	23	45	~100	32 42
200	6	49	21	42		

^a Calculation was based on the absorbance of the 1696-cm^{-1} band of the 3-aminotriazolium cation using montmorillonite saturated with the cation as the standard. Film weights were standardized either by weight or from the absorbance of a silicate absorption band at 800 cm^{-1} .

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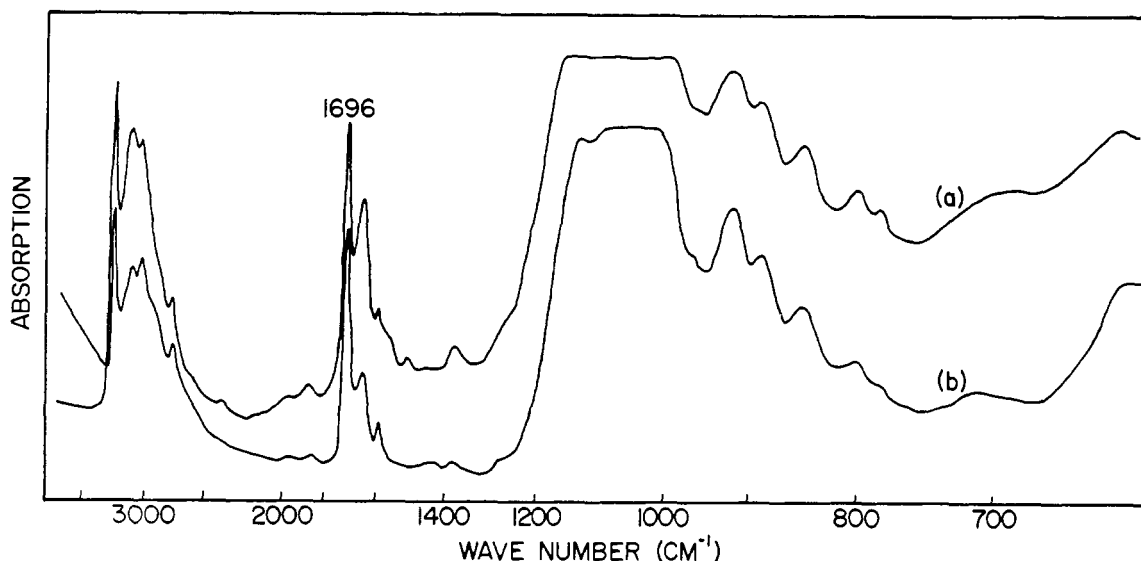


Figure 1. Infrared absorption spectra of films

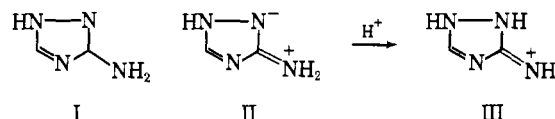
- A. Mg montmorillonite treated with 45 mmoles 3-aminotriazole per 100 grams of clay (3 mg. per sq. cm.)
 B. 3-Aminotriazolium saturated montmorillonite (1 mg. per sq. cm.)

Coordination appeared to be the more extensive reaction in the Cu system in which a blue coloration was observed. These findings are in agreement with those of Menoret and Tracez (1957) and Ashton (1963) who demonstrated the formation in solution of stable coordination complexes of 3-aminotriazole with Cu^{2+} and Ni^{2+} , and with the higher stability constants of Cu^{2+} complexes compared with Ni^{2+} .

While Mortland (1966) has observed similar protonation and coordination effects in the adsorption of urea by H and Cu montmorillonites, he found that urea was not protonated in Na, Ca, or Mg clays. This can be explained in terms of the much lower basicity of urea ($\text{p}K_B = 13.82$) compared with 3-aminotriazole ($\text{p}K_B = 9.83$; Schmidt and Gehlen, 1965). The extents of protonation of pyridine ($\text{p}K_B = 8.77$) and aminotriazole in Na, Ca, and Mg montmorillonites agree well in per cent of the exchange capacity—12, 33, and 45 for pyridine (Farmer and Mortland, 1966) and 6, 23, and 45 for aminotriazole (Table I).

Figure 2 shows spectra of the hydrogen and deuterium forms of the Cu montmorillonite complex before and after evacuation, and for comparison analogous spectra of 3-aminotriazolium montmorillonite. Deuteration was effected by flushing samples with D_2O vapor in a cell similar to that described by Angell and Schaffer (1965). The over-all similarity between the spectra of the Cu complex and the triazolium-clay suggests a similar structural form for the organic molecule.

Considering first the spectrum of aminotriazolium montmorillonite (Figure 2e) an absorption band near 1700 cm^{-1} must, in the absence of a carbonyl group in the molecule, arise from a $\text{C}=\text{N}$ group. Cipens and Grinsteins (1962) have established that while 3-aminotriazole exists in the amino (NH_2) form, its salts are in the imino ($\text{C}=\text{NH}$) form. The development of the imino cation is thought to proceed as follows:



where structure II is one of the important resonance forms contributing to the true structure of 3-aminotriazole.

Bellamy (1958) has indicated that a grouping of the

type $\begin{array}{c} \text{N} \\ \diagdown \\ \text{C}=\text{N}^+ \\ \diagup \\ \text{N} \end{array}$ would be expected to absorb near 1700 cm^{-1}

On this basis, the band at 1696 cm^{-1} is assigned

to the $\text{C}=\text{N}$ stretching vibration of the exocyclic $\text{C}=\text{N}^+$ group in structure III;

the assumption is made that the low frequency shift caused by conjugation with the double bond in the ring is compensated by the high-frequency shift brought about by the positive charge on the nitrogen, and the bonding of the carbon atom carrying the double bond to a further two nitrogens (Bellamy, 1958).

There are theoretically three further tautomeric variations of structure III in which the positive charge may lie on any of the ring nitrogen atoms. However, these variations tend to be rejected in favor of structure III on considering the behavior of the 1696-cm^{-1} band. Dehydration by evacuation at room temperature causes a shift from 1696 to 1683 cm^{-1} (Figure 2f) and deuteration a further shift to 1666 cm^{-1} (Figure 2h). Both observations indicate mechanical coupling between the exocyclic $\text{C}=\text{N}$ and $\text{N}-\text{H}$ vibrations, but the shift on dehydration has a further significance. The 3-aminotriazolium cation on exchange sites in montmorillonite lies flat in the inter-layer space—that is, with the plane of the ring parallel to the cleavage plane. In this position the ion must depend on bonding with water molecules to neutralize effectively

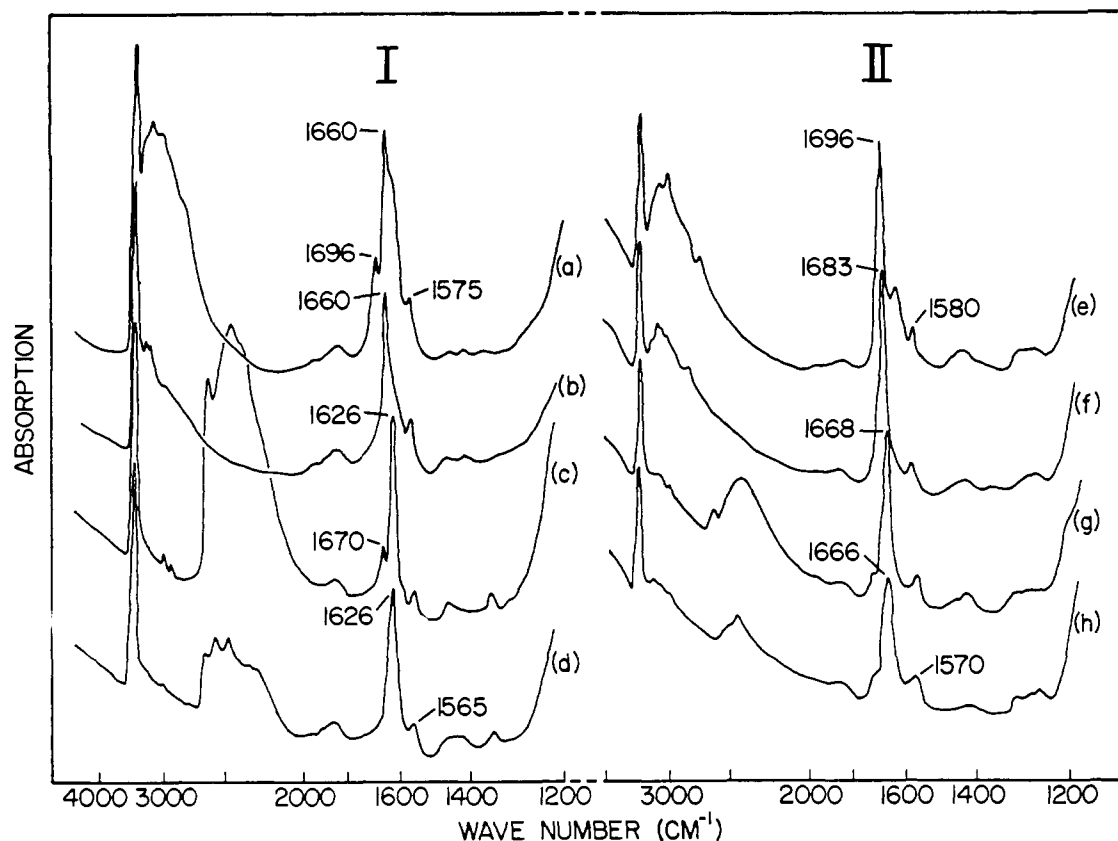


Figure 2. Infrared absorption spectra of films

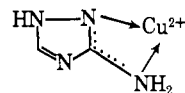
I. Cu montmorillonite treated with 22.5 mmoles 3-aminotriazole per 100 grams of clay
 II. 3-Aminotriazolium montmorillonite under various conditions: (a,e) at normal hydration; (b,f) at 0.005 mm. of Hg;
 (c,g) treated with D₂O vapor; (d,h) treated with D₂O vapor then evacuated to 0.005 mm. of Hg

negative charges on the lattice. Removal of interlayer water will result in the group carrying the positive charge being attracted towards the nearest negative lattice charge. If the positive charge resided on any of the ring nitrogen atoms, no appreciable change in the frequency of the exocyclic C=N band would be expected. If, however, the positive charge lies on the exocyclic nitrogen as shown in structure III, removal of water will cause, by the argument above, a lengthening of the exocyclic C=N bond and a shift of the stretching vibration to lower frequencies.

The weak band at 1580 cm.⁻¹ (Figure 2e) is not appreciably affected by evacuation or deuteration and is assigned to the ring C=N stretching vibration, the somewhat low frequency resulting from conjugation with the exocyclic double bond.

The arguments developed above for the structure of the aminotriazolium ion and the assignments of its absorption bands, also apply to the Cu-aminotriazole complex. The band at 1660 cm.⁻¹ is not affected by removal of interlayer water but suffers a shift to 1626 cm.⁻¹ on deuteration (Figure 2d). This leads to the conclusion that the group giving rise to the vibration is mechanically coupled to N-H, but is uncharged or only weakly so. While addition of a proton to structure II above will completely stabilize structure III, coordination of Cu²⁺ to II will not. The resulting structure of the Cu complex is thought of as

one in which the exocyclic C=N bond has partial double bond character,



and would give rise to the 1660-cm.⁻¹ band. The corresponding band in the Ni aminotriazole complex occurs at 1645 cm.⁻¹ which would be anticipated from the lower stability constants of Ni complexes.

Of considerable importance agronomically is the observation that protonation of aminotriazole is dependent on the adequate hydration of the system (except perhaps in the case of the exchange sites being saturated with NH₄) and that in the presence of H₂O, the protonated species is stable on the clay. It can be removed by extraction into ethyl alcohol or similar solvent; presumably dehydration of the clay by the alcohol causes the reaction by which the protonated species was formed to be reversed, producing the neutral aminotriazole molecule which is then dissolved by the alcohol and extracted. While the protonated molecule on the clay is stable to leaching by water, it undergoes normal exchange reactions with other cations, and could thus become available as a herbicide. Thus aminotriazole may persist as an adsorbed cation particularly in an acid soil, and could theoretically be liberated by exchange re-

actions on application of inorganic fertilizers. The magnitude of occurrence of the exchange reactions may be too small to be of practical importance.

LITERATURE CITED

- Angell, C. L., Schaffer, P. C., *J. Phys. Chem.* **69**, 3463 (1965).
Ashton, F. M., *Weeds* **11**, 167 (1963).
Bellamy, L. J., "The Infrared Spectra of Complex Molecules," p. 267, Methuen and Co., London, 1958.
Burschel, P., Freed, V. H., *Weeds* **7**, 157 (1959).
Cipens, G., Grinsteins, V., *Latv. PSR Zinat. Akad. Vest. Kim. Ser.* **3**, 401 (1962).
Day, B. E., Jordan, L. S., Hendrixson, R. T., *Weeds* **9**, 443 (1961).
Ercegovich, C. D., Frear, D. E. H., *J. AGR. FOOD CHEM.* **12**, 26 (1964).
Farmer, V. C., Mortland, M. M., *J. Phys. Chem.* **69**, 683 (1965).
Farmer, V. C., Mortland, M. M., *J. Chem. Soc.* **1966**, p. 344.
Jordan, L. S., *Proc. Ann. Calif. Weed Conf.* **78** (1960).
Menoret, Y., Tracez, J., *Compt. Rend.* **244**, 2827 (1957).
Mortland, M. M., *Clay Minerals* **6**, 143 (1966).
Mortland, M. M., Fripiat, J. J., Chaussidon, J., Uytterhoeven, J., *J. Phys. Chem.* **67**, 248 (1963).
Russell, J. D., *Trans. Faraday Soc.* **61**, 2284 (1965).
Schmidt, J., Gehlen, H., *Z. Chem.* **5**, 304 (1965).
Sund, K. A., *J. AGR. FOOD CHEM.* **4**, 57 (1956).

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