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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

THERMO-IR-SPECTROSCOPY STUDY OF THE ADSORPTION OF TERBUTHYLAZINE BY SOIL FROM THE JEZREEL VALLEY

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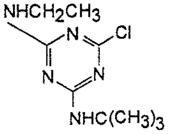
Abstract

Adsorption of the herbicide terbuthylazine by a soil from the Jezreel Valley was investigated by thermo-IR-spectroscopy. The adsorption took place mainly by the clay mineral montmorillonite. The adsorbed molecule was hydrogen bonded via the aniline groups to water molecules which were coordinated to the exchangeable metallic cations. When the sample was thermally treated at 115°C interlayer water was evolved, part of the herbicide decomposed and the other part became directly coordinated to the exchangeable metallic cations. The decomposition product contained a CO group.

Keywords: adsorption, herbicide, IR-spectroscopy, montmorillonite, soil, *s*-triazine, terbuthylazine

Introduction

The use of the herbicide terbuthylazine (2-tert-butylamino-4-chloro-6-ethylamino-1,3,5 triazine, Scheme 1) has increased in recent years in Israel, replacing other *s*-triazines, especially atrazine. This herbicide is less water soluble than



Scheme 1

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most *s*-triazines which are widely used and consequently its mobility in soil is low and it is expected that this hazardous compound will not reach ground water.

Very little is known about the interactions between soils and terbuthylazine and the fine structure of the newly formed complexes. On the other hand, there is much information available on the interactions between other *s*-triazines and soils. Most investigators believe that the binding of *s*-triazines to soils is mainly through humic substances [1]. Hydrophobic adsorption has been proposed as a mechanism for the retention of nonpolar molecules and of amphipathic molecules having predominantly nonpolar regions. The non-living soil organic material interacts with organic herbicides due to its polyelectrolytic nature and the presence of a wide variety of chemical reactive functional groups in the molecular structure. Humic and fulvic acids are rich in hydrophilic and hydrophobic functional groups and may interact with *s*-triazines by various mechanisms which include physical and chemical adsorption.

On the basis of IR studies, the following types of interactions between *s*-triazines and humic acid were identified: ionic bonding between a protonated secondary amine group of the *s*-triazine and a carboxylate anion on the humic substance [2]; a possible involvement of an acidic phenol of humic acid in proton exchange with the *s*-triazine molecule [3]; hydrogen bondings in particular with CO groups of humic substances and secondary amino groups of *s*-triazines [2–4]; *s*-triazine might be bound to humic acid in the form of electron-donor-acceptor complexes leading to a shift of the triazine CH wagging vibration absorption band towards lower frequencies [2–4]; extended aromatic structures were obtained due to covalent binding between amino groups of *s*-triazines with carbonyl or quinone groups of humic acids [3–5]. Recently, the adsorption of atrazine was investigated with the objective of quantifying the relative contributions of organic matter, silicate clays and free Fe compounds to the sorption of the herbicide by clay separated from a prominent agricultural soil [6]. Substantial differences were determined in the nature of the organic matter associated with the coarse, medium and fine clay fractions. Inorganic components (silicate clays plus free Fe compounds) represent 89% of the mass of the whole clay and contributed 32% of the affinity of the untreated whole soil for atrazine. Organic matter, comprising only 11% of the mass of the untreated whole soil and contributed 68% of the affinity of the soil for atrazine.

The objective of the present work was to study the sorption of terbuthylazine by an Israeli soil which is relatively poor in organic matter, and to determine the contribution of the mineral and organic matter to this reaction. In the first stage the soil was fractionated according to particle size and the organic fractions and the Al and Fe oxides were dissolved by selective dissolution. In the second stage the different soil fractions were dipped in an organic solution of terbuthylazine for short (2 days) and long (three months) durations. The herbicide was sorbed by all the different fractions and the fine structure of the organo-soil complexes and their thermal stability were studied by thermo-IR-spectroscopy [7]. The IR spectra of the terbuthylazine soil complexes which were obtained with the different soil fractions were compared in order to find out if there are differences between them.

Experimental

Materials

Terbuthylazine was supplied by Ciba-Geigy Inc., Basel. The technical grade material was at least 97% pure. It was further purified by recrystallization from hexane.

The soil used was a heavy clay vertisol (Chromic Haploxerets) from the top 20 cm of a commercially farmed field of Kibbutz Yifat in the Jezreel Valley. The sand, silt and clay contents were 10, 37 and 53%, respectively, and its organic carbon content was 0.59%. The soil was air-dried, crushed and sieved before use.

Methods

Selective fractionation

Forty grams of soil were dispersed over night in one liter of distilled water. The suspension was transferred to a one liter graduated cylinder and mixed. One minute after the mixing ceased the top 14 cm was decanted. The volume in the cylinder was brought back to one liter and the mixing – decanting procedure was repeated 8 times. The fraction remaining in the cylinder after the decantation contained particles of >26 μ (calculated from Stoke's Law) and designated as fraction 2a. A portion of the decanted material, <26 μ, was removed and designated fraction 2b. The remaining material was washed 3 times with 0.5N NaOH to remove humic and fulvic acids as well as amorphic Al_2O_3. This material was washed repeatedly with 0.01N $CaCl_2$ to remove all the sodium and enable sedimentation of the slurry. A portion of this material was removed and designated fraction 3. The remaining material was treated with acetic acid to remove carbonates and oxidized with H_2O_2 to remove the humin fraction. A sample, designated fraction 4, was removed and the remaining material treated with citrate-dithionate to remove iron oxides. This material was designated as fraction 5. The organic carbon content of fractions 2a, 2b, 3, 4 and 5 were 0.11, 0.86, 0.07, 0.06 and 0.03%, respectively.

Preparation of terbuthylazine-soil complex

A hexane solution of 600 mg terbuthylazine per liter (2.6 mmol L^{-1}) was prepared. The different soil fractions were dried over night at 115°C. One hundred and fifty mg of each soil fraction was slightly ground and immersed in 6 ml of the terbuthylazine solution. Two days or three months after the immersion of the soil fraction in the terbuthylazine solution, small samples of the saturated soils were separated from the hexane solutions and air dried samples were taken for IR study.

Infrared spectra

Infrared spectra of the organo-soil complexes were recorded in KBr disks by means of a Nicolet magna-FTIR spectrometer 550. Each disk was prepared by careful abrasion of the KBr (150 mg) with air-dried terbuthylazine-soil complex (3 mg). After pressing the disk, it was gently reground for a few seconds and repressed. In order to obtain reliable and reproducible IR spectra, the second preparation of the disk was essential.

Spectra were recorded immediately after the preparation of the disks and after a thermal treatment. In this treatment the disks were left for four days in a furnace at 115°C. During the thermal treatment water and organic matter was evolved. Consequently, the disks became opaque and therefore they were repressed, without regrinding, before the recording of the spectra.

A KBr disk of neat terbuthylazine was prepared, reground and repressed under the same conditions. Spectra were recorded immediately after the preparation of the KBr disk and after a thermal treatment at 115°C of four days. A spectrum of neat terbuthylazine in Nujol was also recorded.

Results

IR spectrum of terbuthylazine

The IR spectrum of terbuthylazine in a KBr disk is shown in Fig. 1. A similar spectrum was obtained after heating the disk at 115°C for four days and also in

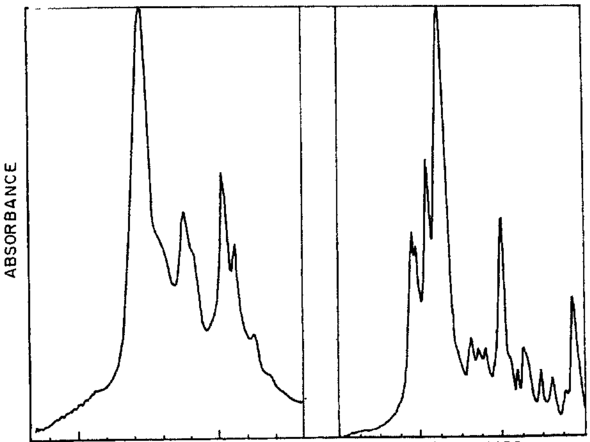


Fig. 1 IR spectrum of terbuthylazine in a KBr disk

Nujol. The locations of the different bands and their assignments are listed in Table 1. In the spectrum two N–H stretching bands, two NH...N combination bands and one N–H deformation band were identified. The splitting of the N–H stretching absorption is due to out-of-phase and in-phase combinations of the two NH groups (the terbuthyl and the ethyl amines).

Normally, a free NH group absorbs at 3470–3500 cm^{-1}. The shift to lower frequencies and the presence of NH...N combination bands [8] indicate that in KBr or in Nujol both NH groups are involved in hydrogen bonds. These groups can react as proton donors and acceptors. Due to steric hindrance it is supposed that the CH_3CH_2NH group reacts mainly as a proton acceptor, whereas the $C(CH_3)_3NH$ group reacts mainly as a proton donor. Proton donation to heterocyclic nitrogens is also possible to some extent. Normally N atoms of *s*-triazine are weak electron pair donors. However, the presence of Cl and NH groups in positions 2, 4 and 6 increases the basic strength of these hetero-nitrogens.

The effect of adsorption on the IR spectrum of TBA

Figures 2 and 3 show IR absorption spectra of soil fraction 3 (curves A) and of the same soil fraction after two days or three months, respectively, in a solution of terbuthylazine (curves B). Curves C in both figures show the subtraction of curves A from curves B. Namely, they show the IR spectra of the adsorbed terbuthylazine. In general, curves C of Figs 2 and 3 show similar features. Only small amounts of terbuthylazine were adsorbed after two days, whereas considerable amounts were adsorbed during three months. Consequently, the IR bands

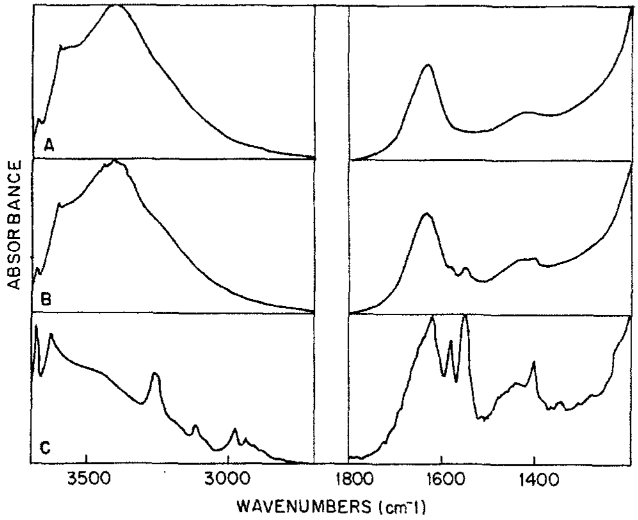


Fig. 2 IR spectra of KBr disks of (A) air-dried soil fraction 3, (B) the same soil fraction after two days in a hexane solution of terbuthylazine, and (C) subtraction of curve A from curve B

Table 1 Comparison of some characteristic IR frequencies (in cm^{-1}) of terbuthylazine recorded in a KBr disk and adsorbed on soil from Jezreel Valley, in KBr disk, unheated and heated in a KBr disk. The soil-terbuthylazine complex was recorded in a KBr disk

Assignment	Neat terbuthylazine in KBr	Terbuthylazine adsorbed on soil fraction (in KBr)	
		before thermal treatment	after thermal treatment
NH stretching	3260, 3200sh	3266	3281
NH....N	3118, 3083sh	3123	3131
CH_3	2982	2982	2977vw
CH_2	2938	2938	2939vw
CH_3	2876	2876	tr
CH_2	2825	2825	tr
decomposition product	–	1745vw *	1745s
–	–	–	1673sh
–	–	–	1624vs
triazine ring vibration	1618	1620	–
–	1608	–	–
–	1580	1583	–
N–H deformation	1548	1555	1560
triazine ring vibration	1477	1477	1477vw
–	1458	1460	1458sh

Table 1 Continued

Assignment	Neat terbuthylazine in KBr	Terbuthylazine adsorbed on soil fraction (in KBr)	
		before thermal treatment	after thermal treatment
C–H (aliphatic), CH_2	1435	1440	–
C–C (aliphatic), $C(CH_3)_3$	1399vs	1400vs	1398w
C–H (aliphatic), CH_3	1372	1372	1372vw
Ar–N	1350	1347	1338
–	1307	1303	1317
C–C (aliphatic)	1226vs	1226vs	1218vw

s=strong; m=medium; w=weak; vw=very weak; sh=shoulder; tr=trace.

* Not observed in the fresh sample. Observed after three months aging.

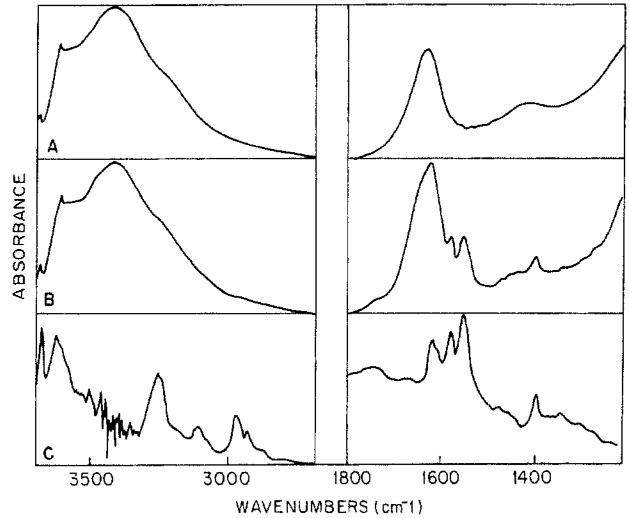


Fig. 3 IR spectra of KBr disks of (A) air-dried soil fraction 3, (B) the same soil fraction after three months in a hexane solution of terbuthylazine, and (C) subtraction of curve A from curve B

of terbuthylazine in Fig. 2 are relatively weak, whereas those in Fig. 3 are more intense. Similar spectra were obtained with all other soil fractions. The assignments and locations of the different IR bands are listed in Table 1.

The bands at 3696 and 3620 cm^{-1} which are observed in curves A and B are of OH groups of kaolinite which is one of the soil components. The baseline rise in the 3700–3620 cm^{-1} range is due to the presence of montmorillonite, which was detected by the X-ray study. This mineral has an OH band with a maximum at about 3620 cm^{-1}, which is relatively broader than this band in the spectrum of kaolinite. The broad intense absorption band at 3440–3428 cm^{-1} is attributed to the presence of water in the interlayer space of montmorillonite. The two OH bands, the baseline shift and the broad water band were observed in the spectra of all the soil fractions. Namely, they did not change by treating the soil with NaOH, H_2O_2 or dithionite to remove organic matter and the aluminum or iron oxides.

All these absorptions were detected in the spectra which were recorded after heating the KBr disks four days at 115°C (Fig. 4). However, the water bands became much weaker due to the water evolution. The thermal evolution of water was significant mainly from the samples which were saturated with terbuthylazine (compare curves B in Figs 3 and 4). This is an indication that by adsorbing the organic herbicide the hydrophobicity of the soil increases.

An NH stretching band was clearly observed in curves C (Figs 2 and 3). The location of this band was slightly shifted from its location in the spectrum of terbuthylazine in Nujol or in a KBr disk, to a higher frequency. Also the NH deformation band shifted due to adsorption from its location in the spectrum of the

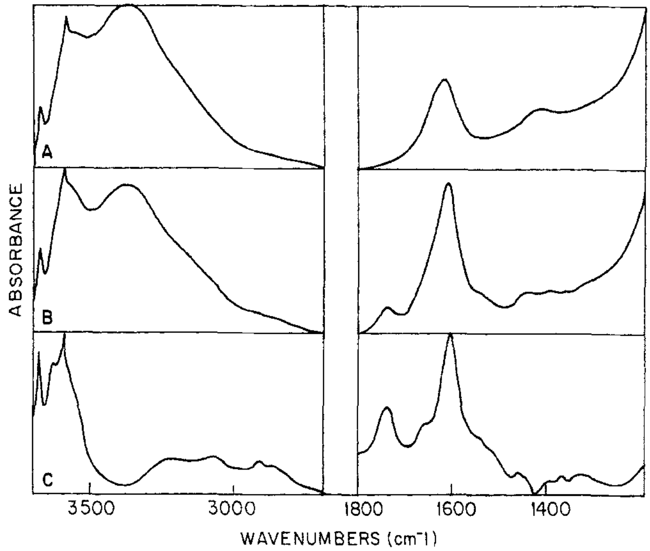


Fig. 4 IR spectra of KBr disks of (A) air-dried soil fraction 3, (B) the same soil fraction after three months in a hexane solution of terbuthylazine (both disks were thermally treated at 115°C for four days), and (C) subtraction of curve A from curve B

neat terbuthylazine to a higher frequency (Table 1). From these locations it is obvious that the adsorbed molecules were involved in hydrogen bonds. However, these shifts indicate that the hydrogen bonds in which the amine groups were involved in the adsorbed state differed from those in which they were involved in the neat herbicide.

The aliphatic CH stretching bands are located at 2700–3000 cm^{-1}. As expected, these bands were not affected by the adsorption process.

The partial protonation of the NH groups which are involved in the hydrogen bonds contribute a partial positive charge to the aromatic ring. Consequently, it is expected that these aromatic rings should take part in π interactions by accepting lone pair electrons from O atoms of the oxygen planes of the montmorillonite [9]. However, the ring vibrations in the spectra of the adsorbed terbuthylazine were similar to those in the spectrum of the neat terbuthylazine, indicating that no such π interactions were formed. This is probably due to the presence of three electron rich hetero-nitrogens which may donate lone pair electrons to the π anti-bonding orbitals of the aromatic rings and thereby preventing π interactions between the oxygen plane and the *s*-triazine. The fact that the triazine ring vibrations were not changed from the adsorption may indicate that the heterocyclic nitrogens were not protonated and were not involved in hydrogen bonds.

A weak band appeared at 1745 cm^{-1} in curve C of Fig. 3. This band was detected only after long dipping periods. It was not observed in the spectrum of neat terbuthylazine (Fig.1) or in spectra which were recorded after short dipping of the soil in the organic solution (Fig. 2). This band can be attributed to a C=O group. In the Discussion section we will show that it developed from the decomposition of terbuthylazine.

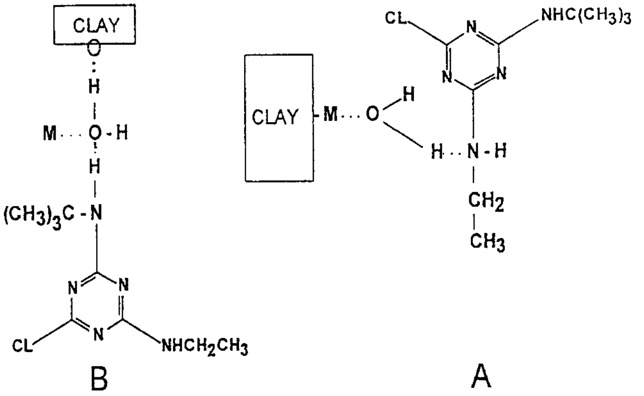
The IR spectra of adsorbed terbuthylazine which were recorded after heating the KBr disks at 115°C for four days (Fig. 4), differed from those of the non-heated disks, indicating that adsorbed azine was drastically changed during the thermal treatment. This is in contrast to the neat azine, which was not changed during a similar thermal treatment.

The thermally treated terbuthylazine gave rise to a strong band at 1623 cm^{-1} accompanied by a shoulder at 1670 cm^{-1} and a medium size band at 1745 cm^{-1}. The NH bands and the ring vibrations which characterize terbuthylazine became very weak and broad. The locations of the NH bands (Table 1) were shifted from their locations in the non-heated samples, indicating that new types of bondings were obtained after the thermal treatment, probably due to the evolution of water. The aliphatic CH vibrations also became very weak. Since this azine is not volatile and since the IR spectrum of the KBr disk of the neat terbuthylazine was not affected by a similar thermal treatment, it is concluded that a considerable amount of the adsorbed azine was decomposed during the thermal treatment with the evolution of ethylamine and iso-propylamine. The intense absorptions at 1623 and 1745 cm^{-1} should belong to a condensation product obtained from the fragments of terbuthylazine which were not evolved during the thermal treatment.

Discussion

The adsorption of terbuthylazine from an organic solvent by the different soil fractions, is a slow process. Three months were required to obtain spectra in which the intensities of the IR absorption bands were strong enough to be interpreted. The different soil fractions were obtained after selective separation and dissolutions of the soil. The end product of the fractionation process was the clay fraction which contained montmorillonite and kaolinite. The former mineral should be the principal adsorbing agent. No significant differences were observed in the spectra of the different soil fractions. It is therefore suggested that in this soil, with an organic carbon content of 0.59%, the adsorption of terbuthylazine from the organic solvent (hexane) takes place on the montmorillonite surfaces.

Cruz *et al.* [10] and Russell *et al.* [11] studied the adsorption of several *s*-triazines on montmorillonite by IR spectroscopy. From their spectra they concluded that during the adsorption, these molecules became protonated. According to these investigators, the protonation took place at N atoms in the ring rather than at N atoms in the side chains. The highly dissociable water on clay surfaces served as the source of protons for the protonation. In our study no spectroscopic evidence of protonation and formation of azinium cation was observed. The shifts of the NH vibrations which were observed are characteristic for hydrogen bonds in which the amine group was involved. It should be noted that in aqueous solutions the protonation of 2-chloro-*s*-triazines takes place at *pH* 2 or lower [12]. It is possible that the acidity of the interlayer space is not sufficiently high for a complete proton-transfer from water molecules to terbuthylazine.



Scheme 2

Based on previous studies on the adsorption of amines by montmorillonite [13], we suggest that the NH groups were bound to the clay through water molecule bridges. The bridging water molecules were coordinated to exchangeable metallic cations and, in part, also to the oxygen planes. The NH groups form hydrogen bonds with these water molecules either by proton acceptance or donation (Scheme 2). When the samples were heated at 115°C, the bridging water molecules were evolved and the NH groups were directly coordinated to the exchangeable cations. This model is supported by comparing the locations of the NH bands in the spectrum of the neat terbuthylazine (where it occurs in self-associations) to those in the spectra of the adsorbed terbuthylazine, before and after the thermal treatment (Table 1).

A weak absorption at 1745 cm^{-1} was observed in the spectra of samples which were kept for three months in the hexane solution. This absorption appears only after long contact periods. It was not observed in the spectra which were recorded after short contact of the soil fraction with the terbuthylazine solution. A similar band was previously observed by Cruz *et al.* [10, 11] during the study of the adsorption of *s*-triazines by montmorillonite. This band is characteristic of a carbonyl group which is not present in triazines. Cruz *et al.* claimed that the Cl atom in the 2nd position was hydrolyzed and replaced by an OH group, resulting in 2-hydroxytriazine. Due to a keto-enol tautomerism, a keto group was detected in the IR spectrum.

This band became very strong when the soil-terbuthylazine complex was heated. At the same time the bands which characterize the terbuthylazine became very weak. We therefore assume that this band arose from a completely different species and we attribute this band, together with a band at 1623 cm^{-1}, to a product obtained from the fragmentation of terbuthylazine. The hydrolysis may be the first step towards the decomposition of the molecule.

Nguyen [14] compared the IR spectrum of Na-montmorillonite saturated with *s*-triazine with that saturated with formamide. He concluded that within a few days the adsorbed *s*-triazine was hydrolyzed with residual bound water to form formamide which did not escape from the montmorillonite. One would expect that a similar hydrolysis of the *s*-triazine ring would take place during aging or by the thermal treatment of the terbuthylazine-soil complex. The aromatic character of *s*-triazine is less pronounced than that of benzene because the former has the contribution of a polar mesomeric form that contains an additional pair of unshared electrons on the ring N atoms and positive charge on the ring C atoms or on the Cl and aniline N atoms. The relative electron deficiency of the ring C atoms makes them susceptible to nucleophilic attack, such as by residual water in the clay. In the first stage the Cl and to some extent also the RNH groups are replaced by OH. The formation of an amide involves a subsequent ring-cleavage step.

The spectrum of the decomposition product which was obtained after the thermal treatment differed from the spectrum of terbuthylazine adsorbed by montmorillonite and also from the spectrum of formamide adsorbed by montmorillonite. The absorptions at 1670 and 1745 cm^{-1} are hydrogen bonded and non-bonded CO stretching vibrations, respectively. The intense band at 1623 cm^{-1} may be an amide NH_2 bending vibration. But NH_2 stretching vibrations were not identified in the spectra. It is possible that they overlap the H_2O stretching vibrations which are very strong. Thus we could not point to the presence of considerable amounts of formamide.

Conclusions

IR spectroscopy study showed that the adsorption of terbuthylazine from an hexane solution by a soil from the Jezreel Valley, Israel, takes place mainly by the clay mineral montmorillonite. The adsorbed molecule is hydrogen bonded via the aniline groups to water molecules which are coordinated to exchangeable metallic cations. After an aging period of three months a weak absorption band appeared at 1745 cm^{-1}. When the sample was thermally treated this band intensified. Together with this intensification, bands characteristic to terbuthylazine (ring vibrations and those which characterize tert-butylamine and ethylamine) became weak or disappeared and new bands appeared, indicating that a new decomposition product was obtained which contained a CO group but did not contain the aliphatic chains. At the same time the clay was in part dehydrated and the terbuthylazine which did not decompose, was directly coordinated to the metallic exchangeable cation.

Since the publication of Russell *et al.* [11] the appearance of an absorption band at 1730–1750 cm^{-1} was used by most investigators as proof for the presence of a protonated species in which the atom or radical at the position 2 was substituted by OH. In the present paper we show that the appearance of this band is intensified by thermal treatment and is accompanied by the disappearance of *s*-triazine bands and the appearance of new bands. It is therefore assumed that in addition to hydrolysis this band is associated with a ring cleavage followed by polymerization of the decomposition products.

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