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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

AN INSECTICIDE STABILIZED BY NATURAL ZEOLITE

A. Sopková[*] *and E. Janoková*

Department of Inorganic Chemistry, Fac. Sciences, P. J. Šafarik's University, 041 54 Košice
Slovakia

Abstract

The synthetic pyrethroide insecticide (R, S)-α-cyano-3-phenoxybenzyl-IR, S-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanocarboxylate in solid form could be enclosed in and therefore stabilized by natural clinoptilolitic zeolite. The resulting host-guest complex exhibited characteristics different from those of the starting compounds and also their physical mixtures. The product was more stabile against the tested solvents (distilled water and acetone) and also against thermal decomposition, which suggests its possible use as a slowly-releasing insecticide.

Keywords: liquid and solid form, natural clinoptilolitic zeolite, pyrethroide insecticide, slowly-releasing insecticide

Introduction

The intensification of agriculture has solved many of the worldwide problems relating to the deficiency of foodstuffs, but many ecological problems have arisen. The exhausted soils demand more and more fertilizers and the cultivation of monocultures on large areas has caused the mass appearance of insects. These adapt themselves very quickly to the insecticides used, which must be applied in ever larger amounts. Only a minor proportion of the quantities of fertilizers and insecticides applied serve the main aim. The rest of these compounds or their residues penetrate into the waters and plants, and hence into the alimentation chain. With a view to the elimination of these problems, a new kind of inclusion compounds, named slow-releasing fertilizers or agrochemicals [1, 2], have been prepared. In these, zeolites as host compounds enclose and stabilize different guest components. The sorbed compounds are partially blocked in the channels and voids of the zeolites (similarly as in montmorillonites) and they are liberated

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[*] Author to whom all correspondence should be addressed. Vihorlatská 80,04001 Košice, Slovakia

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only in a gradual process. The new products form a reserve of the effective compound for a longer time and thereby protect the waters and plant products from severe contamination. Naturally, the more effective use of the applied compounds has positive economic consequences too.

Besides other slow-releasing agrochemicals prepared in our Department [2], we set out to enclose a synthetic pyrethroid insecticide, Supercypermetrine (SCM), into a natural zeolite of clinoptilolite (CT) type. SCM was first used in our work in solid powdered form [3–5] and subsequently in liquid form [6, 7].

The problems and results relating to the inclusion of the solid form of SCM comprise the subject of this paper.

CT zeolitic material originating from different deposits in the world is used for technical purposes. The destruction of the host structure starts only at about 750°C and the crystalline compound then changes into a new hydrated amorphous phase of CT. The characteristics of an amorphous form can also be obtained without heating, but only after the sorption of a guest into the CT zeolitic host. These amorphous characteristics are found in the IR spectra [2, 8–12] for all types of fertilizers, cyclodextrins, and other pharmaceuticals enclosed at least partially in the zeolite.

The thermostability of zeolite, together with the reversible desorption and sorption of water, have proved to be advantages in many technological processes. In our Department, we have utilized zeolites from the eastern Slovakian deposit at Nižny Hrabovec to prepare for ecological purposes a series of compounds and pharmaceuticals with a slow and regulated desorption of different agrochemicals [2] and also of one or simultaneously bound two pharmaceutically effective compounds [10–13].

This CT zeolite is a nonpolar organophilic sorbent (ratio Si/Al >1). The rate of desorption of the enclosed guest may be used to study interactions between the host and guest components in the compounds formed.

As discussed previously [7], there are three possibilities for the migration of the guest molecules in the zeolites. The structure of the main mineral (57% of CT) is similar to that of mordenite. It is from the heulandite group. Its monoclinic plates, measuring about 10 μm long and 1–2 μm wide, are located differently in space and form free areas. The measured sorption capacity of zeolite as concerns H_2O (about 265 ml H_2O per g CT) suggests that about 50% of the volume in the crystals is accessible to water and H_2O-substituting guests. The pore sizes of 0.76×0.35 and 0.46×0.33 nm naturally determine which compounds may be included as guests.

As in the case of montmorillonite [14–16], the sorption of different guests in zeolites is accelerated by activation of the host structure by the presence of different cations [17]. The Cu(II) ion was found to be the most suitable [4, 7, 11] for the sorption of different guests.

The synthetic insecticides of the pyrethroid group are replacing the organophosphates, carbamates and chloro derivatives [18]. They are slightly soluble in water and may be destroyed by photolysis.

Their protection by inclusion into the zeolites is therefore advantageous. The synthetic ones imitate the action of the natural pyrethrum present in the flowers of Chrysanthemum cinerariaefolium. Their broad spectral activity against different insects, and their relatively low toxicity towards mammals, have promoted their rather rapidly widening commercialization. The SCM used in the present paper and also in [3–7] is one of the pyrethroids.

Materials, methods and equipment

The natural CT zeolite from Nižny Hrabovec, characterized chemically in [7, 19], was used in this work. Grain size: max. 0.2 mm: 2%, min. 0.09 mm: 10%. The type Nitrosorb was activated by Cu(II) ions: 500 ml of a 1 M solution of $CuC12\cdot 2H_2O$ was added to a 100 g sample of CT, and the mixture was left to stand for 10 days. The activated product (CuCT) was then decanted, washed with H_2O, centrifuged and dried in air.

The insecticide SCM forte used in this work has the formula $C_{22}H_{19}Cl_2NO_3$ (it differs from the water-soluble commercial liquid product used earlier [6, 7]: CYPER 10 EM, a product of CHEMIX, Bratislava). The product of Spolana Neratovice was used: melting temperature range: 60–80°C; mol. mass 416.29. It is well soluble in acetone, chloroform and toluene, poorly soluble in methanol and hexane, and insoluble in water.

The sorption of SCM forte (15 g in wetted form) was achieved by leaving it in contact with CuCT (15 g) for 10 days. The product was then washed with acetone, filtered off and dried. The amount of non-sorbed insecticide was determined with a GC/CHROM 4. Column length: 2 m, 3% OV 210 with Intertone AW-DMSC: T:200°C, N_2 flow rate: 60 ml min^{-1}, 1.7 kg cm^{-3}, detector FID.

The amount of sorbed insecticide was determined by CHN elementary analysis on a Hewlett-Packard instrument.

For identification, the IR spectra (Specord 80 IR) of 5 mg of sample in 500 mg of KBr, the UV/VIS spectra (Specord M 40) in the range 200–900 nm, with $BaSO_4$ for comparison, and thermal analyis (Derivatograph, MOM, Budapest) were used. TA: 100 mg sample mass, 10 °C min^{-1}, max. 900°C, TG: 100, DTA, DTG 1/5 in air.

Desorption was followed in two different media (distilled water and acetone). The former was intended to imitate the field conditions. The latter was studied for comparison because of the water-insolubility of SCM forte.

Thermoanalytical, CHN and GC control examinations (for desorption into acetone) were used for the desorption of the SCM guest.

1.5 g of product in contact with 10 ml of acetone or 100 ml of distilled water (with 2 ml of added acetone) was filtered off, dried and used for identification and analytical study.

The amount of sorbed insecticide in our product was controlled by CHN analysis before and after the desorption test, and also in the zeolite alone. The quantities of SCM present in the products were calculated from the differences.

The amount of insecticide originally sorbed in the product and the quantity desorbed into the aqueous solution were determined by GC measurements. The quantity desorbed into acetone after extraction for 10 h or 3 days was also measured.

The gradual release of the SCM insecticide from the products was studied means of thermal analysis.

Results and discussion

For the product proposed as a slowly-releasing insecticide of SCM type, we used SCM forte in solid form: this differs from the compound described and used earlier [6, 7]. The quantity of the enclosed guest (in solid form) in our product [4, 5] is in accordance with the results of CHN analysis, 14.03 g SCM/100 g zeolite, which is much higher than in the product prepared with the liquid form of SCM, described in [6, 7]. GC measurements indicated that the quantity of SCM present in the product was 16.0 g/100 g zeolite.

The presence of the enclosed guest changed the behaviour during the TA analysis, as revealed by the DTA and TG curves. The DTA changes were not very strong (Fig. 1). The mass loss of 26% on TG is about 12% higher than for the zeolitic CuCT sample alone. The thermal decompositions of the zeolitic sample CT

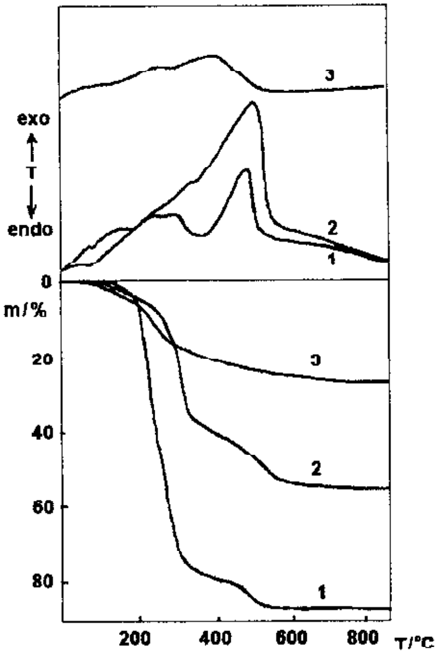

Fig. 1 Thermal analysis: 1. insecticide: SCM ; 2. physical mixture: zeolite and insecticide; 3. product: CuCT–SCM

and also CuCT have been reported in detail in [7]. The rapid decompositions of the insecticide alone and of the physical mixture of the starting materials may be observed in Fig. 1 as a very strong process on DTA. The product exhibits two exothermic changes that overlap between 200 and 490°C, but rather weaker than for CuCT alone or the physical mixture.

The endothermic change for SCM alone and for the physical mixture (70–90°C) lies close to the melting region (60–80°C) of SCM. The product does not exhibit such an endothermic process. The process of water liberation from the zeolite is associated here with insecticide decomposition. The total mass loss is 26% (14% higher than for the zeolite alone).

As a difference between the IR spectra of CT and CuCT we found two sharp bands at 3450 and 3370 cm^{-1}. These may be ascribed to interactions of Cu(II) ions with OH groups present in the zeolite. Like the other products studied in our Department [2, 7–9, 11, 12, 17], the IR spectrum of the product CuCT–SCM exhibits the ν_{as}(Si, Al–O) band as a broad band at 1240–880 cm^{-1}, while the zeolite and the physical mixture give a very sharp and relatively narrow peak. The broad band is characteristic [2] of the sorption of some guest component into the originally crystalline zeolite. Besides the overlapping bands of the insecticide, together with the intense zeolitic band, we may also find some discrete bands for the organic guest: ν (C=O) C=C (arom), δ Cl, γ Cl and ν C–Cl (described in [7]). The IR characteristics gradually decreased in intensity during the desorption control of the products [7]; mainly the narrowing of the ν as (Al, Si–O) band indicates that the SCM insecticide as guest is released in a gradual process.

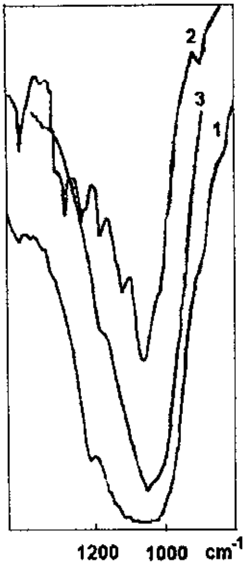

Fig. 2 IR characteristics: ν_{as} (Al, Si–O) band; 1. product: CuCT–SCM; 2. physical mixture: CuCT and SCM; 3. zeolite: CuCT

The physical mixture displays very well differentiated bands, characteristic for each of the starting materials.

The UV/VIS spectroscopic measurements on the individual starting compounds (No. 1), the products (Nos 3 and 4) and the zeolitic CT–Cu (No. 2) were compared. One minimum at 260 nm was found only in curves 4 and 3 (Fig. 3). Further, the absorption bands with maxima at 310 and 425 nm were observed only for the product. Some type of interaction between the host and guest (as yet unspecified) is revealed in this manner too.

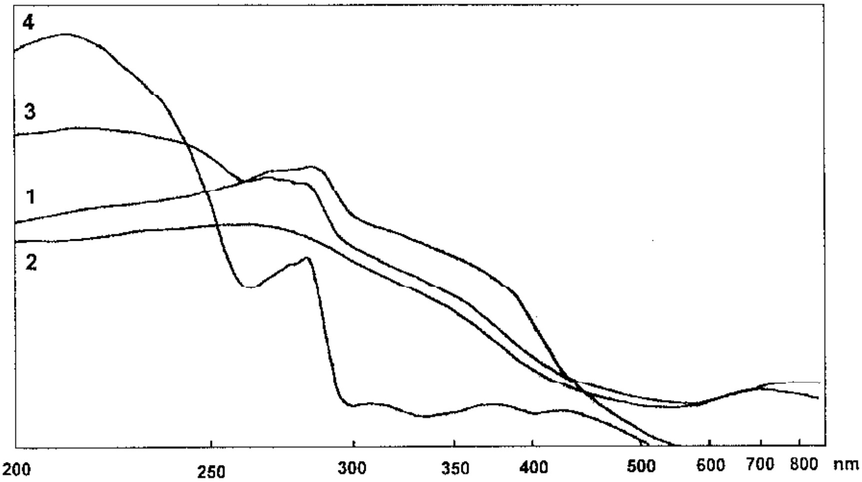

Fig. 3 UV/VIS spectra: 1. insecticide: SCM ($BaSO_4$); 2. zeolite: CuCT ($BaSO_4$); 3. product: CuCT–SCM ($BaSO_4$); 4. product: CT–SCM (zeolite)

The desorption of the SCM guest (by acetone or distilled water) was performed only in laboratory tests. In the latter medium, the insecticide is practically insoluble; this is why the medium of acetone was also chosen for the liberation control. However, the desorption in real field tests would be of interest for our new insecticide zeolitic prouduct (water as solvent, but under more drastic conditions). In this manner, the release of SCM would be effective in water too. Table 1 shows the results of the control of the original and also in a time relation for the desorbed product. The analysis demonstrated a very slight desorption of the insecticide into distilled water (only 1.43% of the SCM originally present) in 10-day desorption tests. The dissolution of the insecticide in acetone confirmed the presumed gradual release during the 3-day desorption test, total release (99.79%) being attained. This is a very considerable difference relative to the liquid insecticide form used to prepare the zeolitic product in [6, 7], where the amounts of SCM insecticide released were much lower. The total quantity of SCM bound in the CT–SCM product was lost after 28 days, as was that in the CuCT–SCM product after 30 days. However, the release in field tests is to be ex-

Table 1 Analysis of insecticide present in compounds and products of the desorption controlling test

Compounds	Insecticide after the test			Insecticide desorbed into solution					Control
	into H_2O	into CH_3COOH		H_2O	CH_3COOH				
	by CHN	by CHN	by GC	by CHN	by CHN		by GC		by TA
	g/100 g zeolite			%	%	g/100 g zeolite	%	g/100 g zeolite	Δm/%
Zeolite	0	0	0	0	0	0	0	0	14
Product before desorption	14.03	14.03	16.07	0	0	0	0	0	26
After desorption for 10 h	x	0.58	0.95	x	95.87	13.45	94.09	15.12	x
After desorption for 1 day	x	0.32	x	x	97.72	13.71	x	x	16
After desorption for 3 days	x	0.03	0	x	99.79	14.00	100	16.07	14
After desorption for 5 days	13.86	x	x	1.21	x	x	x	x	25
After desorption for 10 days	13.83	x	x	1.43	x	x	x	x	25

pected to be much slower, because the products will be used here in a much greater dilution.

Besides the dilution of the insecticide, other factors affecting the behaviour of the new product under field conditions must be assumed: temperature, pH of surroundings, climate effect and influence of microorganisms. And finally, the amounts of insecticide enclosed in our first products are much higher than those stated by the manufacturers of the insecticides to be effective against insects.

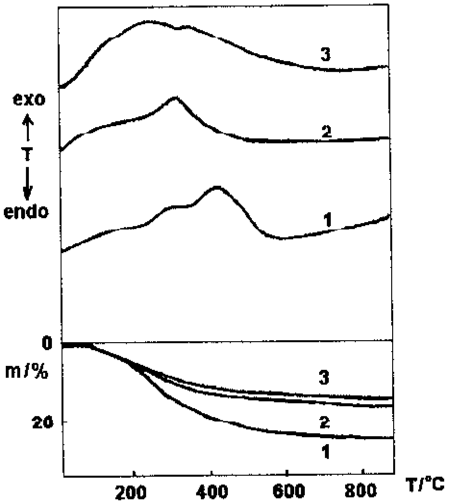

Fig. 4 Thermal analysis: 1. product (CuCT–SCM) after desorption for 5 or 10 days into distilled water; 2. product (CuCT–SCM) after desorption for 1 day into acetone; 3. product (CuCT–SCM) after desorption for 3 days into acetone

The GC measurements used for the desorption control showed the total (100%) desorption of the SCM into acetone after 3 days. We controlled thermoanalytically (mainly via the TG curves) the desorption (also partial) from the products. As only slight desorption occurs into water, the TG curves measured after desorption for 5 or 10 days differ only slightly from that for the original zeolitic product (26% and 25% Δm observed).

The desorption into acetone during a 1-day testing reached 16% and that after 3 days was 14% (the same Δm as measured for CuCT). As in the GC measurements, therefore, total insecticide release into acetone was found after a 3-day desorption control. The details of the guest desorption are to be found in [20].

Conclusions

The zeolitic product enclosing the synthetic pyrethroid insecticide either in liquid form [6, 7] or in solid powdered form may be readily prepared. It exhibits the properties of the inclusion compound, and especially of the host – guest complex in its amorphous form too. The release must be followed in field experiments and then, after evaluation of the results, the quantity of insecticide enclosed may be regulated during the preparation.

Further modelling experiments (more similar to field conditions) must be performed to examine the release of the guest insecticide under pressure.

In spite of the fact that the results gained so far originate from desorption tests performed only under very drastic conditions, the presumed gradual release of the insecticide from the proposed product was found. The observed interactions between the host and guest components indicate the enclosure and stabilization of the guest insecticide. The product to be applied in field tests will represent a reservoir of the pyrethroid insecticide for a longer time. At the same time, the waters, soils and plant alimentation products will be protected against the excess of toxic chemicals, and the insecticide SCM will be stabilized by zeolites against photolysis and release.

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