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KINETIC STUDY OF THE THERMAL DECOMPOSITION OF PESTICIDES

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ABSTRACT

The thermal decomposition kinetics of three pesticides with different chemical structures: pirimicarb (carbamate), trichlorphon (organophosphorus) and chloridazon (heterocyclic), have been studied by thermogravimetric analysis. From the thermogravimetric curves of the compounds recorded at different oven heating rates, the values of the activation energy and frequency factor are calculated for the decomposition process of each of the compounds. The determination of the rate constant and half-life for temperatures close to the maximum that can be achieved in soils reveals the influence of temperature on the stability of the compounds studied.

INTRODUCTION

The evolution of a pesticide in soil is governed by a series of processes taking place in the soil which mainly depend on the type of soil, pH, the nature of the soil colloids and the moisture content, and on a series of environmental factors such as wind, sunlight, rainfall and temperature [1–3].

Among the environmental factors, the study of the influence of temperature on the decomposition rate of pesticides has received little attention. Temperature may affect this process by modifying microbial activity and the rate of abiotic reactions. In the second case, increases in temperature can favour the development of chemical degradation reactions or may simply increase the rate of thermal decomposition of the pesticide. This process of thermal decomposition is of special interest when pesticides are applied to soils subject to a warm dry climate, particularly in certain seasons of the year when the temperature of the environment may be very high at certain times of the day [4,5]. Thermal decomposition can in some cases affect the disappearance of the compound to a greater extent than chemical or biological degradation.

In the literature there are some references to the thermal decomposition of free or clay mineral-adsorbed pesticides; in general the studies have been conducted using differential thermal analysis and thermogravimetric meth-

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ods [6–8]. However, these studies have not examined the kinetics of the thermal decomposition of the compounds.

In the present work we report on the thermal decomposition kinetics of three pesticides, all with a different chemical structure: pirimicarb (2-dimethylamino-5,6-dimethyl pyrimidin-4-yl dimethylcarbamate), trichlorphon (*O*,*O*-dimethyl (1-hydroxy-2,2,2-trichloroethyl) phosphonate) and chloridazon (4-chloro 2-phenyl 3-pyridazone) using thermogravimetric analysis (TG). Determination of the activation energy and the rate constant of this decomposition process permits an estimation of the stability of these pesticides at the temperatures they may reach during their residence in soils or plants.

EXPERIMENTAL

The pesticides were supplied by Xpectrix International Inc., Deerfield, IL (trichlorphon and chloridazon) and by Imperial Chemical Industries PLC, England (pirimicarb).

A Perkin Elmer TGS-2 thermogravimetric analyzer was employed. For each of the pesticides TG curves were obtained at oven heating rates of 5 °, 10 °, 15 ° and 20 ° C min^{-1}. In all cases, the mass of the sample was 10 mg and a dynamic atmosphere of N_2 was used (80 ml min^{-1}).

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTG curves of the three pesticides studied, obtained at an oven heating rate of 20 ° C min^{-1}. As may be seen, trichlorphon is the least stable compound of those studied, decomposing within the 112–320 ° C range. The most stable thermally is chloridazon, which decomposes in the 226–415 ° C range. Pirimicarb has an intermediate thermal stability of 151–295 ° C. In these ranges, the mass losses occurring in the three compounds are close to 100%.

In the curves obtained at lower heating rates (5 °, 10 ° and 15 ° C min^{-1}) a shift occurs in these decomposition temperature ranges towards lower temperatures. Table 1 shows the temperatures corresponding to three percentages of mass loss determined for each of the rates employed and for each of the pesticides.

Ozawa [9] and Flynn and Wall [10] have shown that the activation energy of a thermal decomposition process can be determined directly from a series of TG curves carried out at different oven heating rates. These authors reported that the logarithmic representation of the heating rate versus the reciprocal of the absolute temperature, for an identical mass loss plots as a straight line, with a slope that is directly proportional to the activation energy. This plot allows one to determine the activation energy (E) and the

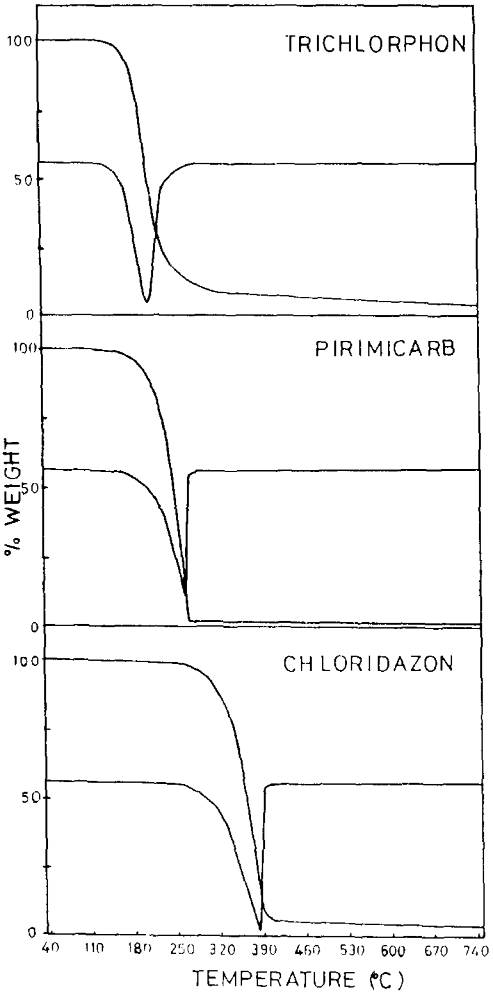

Fig. 1. TG and DTG curves of the three pesticides studied.

frequency factor (A) of the Arrhenius equation: $K = Ae^{-E/RT}$ where K is the rate constant.

Figure 2 shows the Arrhenius plots corresponding to the mass losses chosen and Table 2 shows the mean values of the activation energies and frequency factors of the Arrhenius equation obtained from the straight lines. This determination of the activation energy is independent of the order of the decomposition reaction, although later kinetic calculations require knowledge of that order. It has usually been considered that the initial portion of the TG curves can be fitted by a first-order reaction equation; taking this into account, it is possible to calculate the relationship between half-life, temperature and percent conversion. In this study, we considered low mass losses (Table 1), consistently lower than 10%, for the calculations of the activation energy from the Arrhenius equation.

TABLE 1

Temperatures corresponding to three conversions determined for different oven heating rates

Pesticide	Rate ($^\circ$C min^{-1})	Temperature ($^\circ$C)		
		4%	6%	8%
Trichlorphon	20	165	171	175
	15	162	167	172
	10	155	161	165
	5	143	149	152
Pirimicarb	20	183	192	199
	15	180	188	194
	10	169	177	183
	5	154	162	168
Chloridazon	20	285	296	304
	15	281	291	299
	10	271	281	289

Table 3 shows the values of the rate constant and half life of the three pesticides at different temperatures. The results of Table 3 show that temperature has a pronounced effect on the rate constant. In this sense, small variations, of 10 °C in temperature lead to marked variations in the

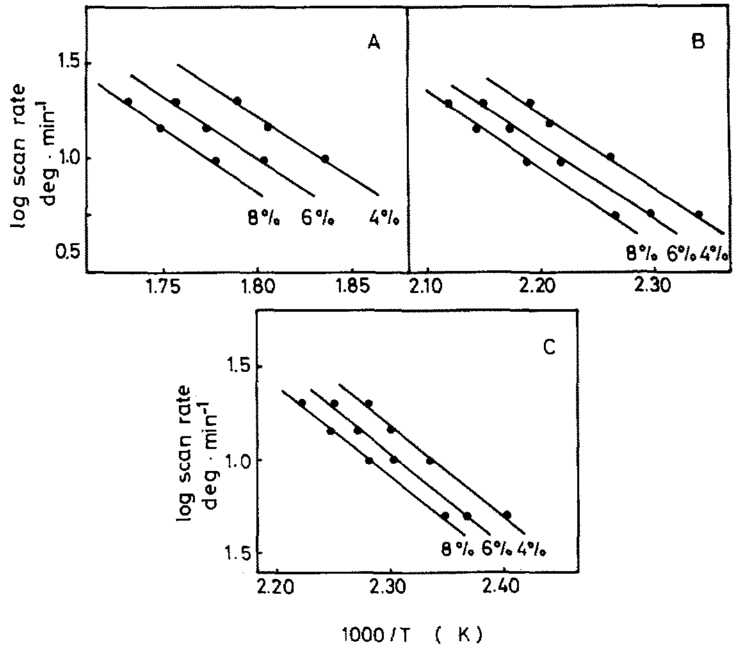

Fig. 2. Arrhenius plots corresponding to the three conversions: A, chloridazon; B, pirimicarb; C, trichlorphon.

TABLE 2

Activation energies and frequency factors (mean values) of thermal decomposition of the three pesticides

Pesticide	E (kJ mol^{-1})	A (min^{-1})
Pirimicarb	68.8	2.64×10^{6}
Trichlorphon	87.7	1.54×10^{9}
Chloridazon	111.9	1.06×10^{9}

other parameters. The extent of the influence of temperature on both parameters in turn depends on the activation energy. The variation occurring in the rate constant and the decomposition half life of the three pesticides studied with temperature is greater in the case of chloridazon, for which the activation energy of this process is much higher. The lowest variations are seen with pirimicarb, with the lowest activation energy.

In the light of such findings, it may be inferred that at the maximum temperature of 40–60 °C that is reached by the surface and subsurface layers of the soil at certain hours of the day in certain seasons and terrestrial zones [4,5] the disappearance of chloridazon from the soil by thermal decomposition, compared with the other factors that affect the evolution of the compound in soils, is practically nil. However, the influence of thermal decomposition on the persistence of trichlorphon and especially pirimicarb,

TABLE 3

Values of the rate constant (K) and half life of the three pesticides at different temperatures

Pesticide	Temperature (°C)	K (min^{-1})	Half life			
			Years	Days	Hours	Min
Pirimicarb	20	1.45×10^{-6}	–	331	3	53
	30	3.69×10^{-6}	–	130	12	22
	40	8.82×10^{-6}	–	54	14	8
	50	1.99×10^{-5}	–	24	2	21
	60	4.31×10^{-5}	–	11	4	9
Trichlorphon	20	3.64×10^{-7}	3	228	20	20
	30	1.19×10^{-6}	1	38	23	45
	40	3.62×10^{-6}	0	132	23	46
	50	1.03×10^{-5}	0	46	21	31
	60	2.73×10^{-5}	0	17	14	31
Chloridazon	20	1.22×10^{-11}	108107	42	14	24
	30	5.55×10^{-11}	23776	187	17	36
	40	2.29×10^{-10}	5760	130	7	28
	50	8.66×10^{-10}	1523	193	23	28
	60	3.02×10^{-9}	436	163	4	16

in view of their half lives at 40–50 °C, may be important even at more normal temperatures of 20 or 30 °C.

These findings in turn are of great use in discovering the half life of the compounds for a particular storage temperature or to find out the shelf-life temperature that is required to ensure a given half life. These considerations are of special interest, since apart from leading to a loss of activity in the pesticide prior to actual application, thermal decomposition in general implies the production of gases of different degrees of toxicity, according to the type of compound in question.

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