

COMMUNICATIONS

Identification of Thermal Degradation Products from Diuron and Iprodione

Diuron and iprodione were pyrolyzed at 400–1000 °C in a helium atmosphere. They showed many similarities in their thermal behavior: both emitted carbon monoxide, hydrogen chloride, and hydrogen cyanide. The N–CO bonds were the first to be split and led to an isocyanate and an amine which degraded in turn into substituted ureas and gaseous products.

With the objective of limiting the dangers resulting from chemical products, many industrial countries established regulations which have led to studies of the fate of these products. The behavior of some widely distributed pesticides when subjected to heat have already been described either for the thermal destruction of wastes and stocks (Mc Pherson et al., 1956; Kennedy et al., 1972; Holloman et al., 1976; Ahling et al., 1979) or during specific uses (Chopra et al., 1978). In our work (Gomez, 1979), we investigated the thermal behavior of iprodione (a fungicide) and diuron (a herbicide) in an inert atmosphere to detect harmful products which could evolve from incineration or fire of stocks of these pesticides.

MATERIALS AND METHODS

Materials. Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and iprodione [1-isopropylcarbamoyl-3-(3,5-dichlorophenyl)hydantoin] were of 99% + purity.

Apparatus. Pyrolysis was carried out in a helium atmosphere between 400 and 1000 °C, in a 2.7 cm i.d. ceramic tube containing baffles, placed in an horizontal tubular furnace with a heated zone of 33 cm (Bruneau et al., 1981). A helium stream swept the tube at 1.5 L/h, which gave a residence time of 7 min in the furnace. The powdered chemicals (0.5–1 g) were propelled into the furnace by means of a rubber bulb filled with helium. The effluent gas stream was directed into a gas sampling system, a cold trap cooled with ice, and two bubblers containing dilute sodium hydroxide and water, respectively.

Analysis of the Pyrolysis Products. Gaseous hydrocarbons, carbon monoxide, and hydrogen were determined by gas chromatography (GC) with a Girdel 3000 chromatograph equipped with a catharometric detector and a 300 cm × 0.5 cm stainless steel column packed with Porapak Q (100–120 mesh) at 60 °C, followed by a similar column of 13X molecular sieve (60–80 mesh) at 20 °C. Quantitation was achieved by measuring the amount of one of the pyrolysis gases by direct calibration and determining the relative amounts of each of the others by comparison of GC peaks.

The gases soluble in water (HCl; HCN; amines) were titrated, HCl and HCN with AgNO₃ (0.05 N) by potentiometry with a silver electrode in acid solution (pH 5–6) and the amines by NaOH titration of the condensate collected in 0.1 N H₂SO₄ after distillation from their initial solution with boiling 12 N NaOH. The amines were identified by GLC of the solutions from the bubblers and the cold trap on a Girdel 3000 chromatograph equipped with a 170 cm × 0.2 cm glass column packed with Chromosorb 103 (100–120 mesh) combined with a 5-cm pre-column packed with Ascarite; the column temperature was 120 °C and a flame ionization detector was used. The

Table I. Mole of Gaseous Products Obtained per Mole of Diuron (D) and Iprodione (I) Submitted to Pyrolysis at Different Temperatures^a

	mol/mol at pyrolysis temperature of							
	400 °C		600 °C		800 °C		1000 °C	
	D	I	D	I	D	I	D	I
H ₂					0.04	0.25	0.10	0.18
N ₂	0.02		0.11		0.10	0.11	0.04	0.02
CO				0.05	0.14	1.00	0.36	1.40
CH ₄			0.12	0.01	1.00	0.45	0.66	0.09
CO ₂	0.01		0.02	0.01	0.07	0.13	0.10	0.39
C ₂ H ₄					0.03	0.30	0.03	0.20
C ₂ H ₆					0.01	0.02		
HCl	0.01		0.06		0.10	0.10	0.48	0.50
HCN			0.05		0.55	0.12	0.59	0.20
amines			0.03	0.12		0.35	0.12	0.75

^a Relative retention times: H₂, 0.9; CO and N₂, 1.0 (72 s); CH₄, 1.3; CO₂, 2.0; C₂H₄, 3.0; C₂H₆, 3.8. Column: Porapak Q. Thermal conductivity detector.

condensate in the cold trap was extracted with ethyl acetate and water, and the compounds were extracted in the organic phase identified on a Varian-Mat 311 mass spectrometer coupled with a Girdel 75 chromatograph equipped with a flame ionization detector and a 140 cm × 0.2 cm stainless steel column packed with 10% Carbowax 20 M on Chromosorb WHMDS (80–100 mesh) at 140–180 °C. Identification of the compounds from the cold trap was completed by analytical liquid chromatography (HPLC) with a Varian 8500 unit, on a Lichrosorb Si 60 column (15 cm × 0.47 cm), and by preparative chromatography with a Jobin Yvon Chromatospac Prep 100 on a Merck H60 Kieselgel column (130 g; 4-cm diameter). The UV detection was at 254 nm. The composition of the mobile phase and the flow rates varied depending upon the compounds being investigated (see the text).

RESULTS AND DISCUSSIONS

Gaseous Pyrolysis Products. The pyrolysis of diuron and iprodione immediately evolved gases with relatively good reproducibility (Table I). Dimethylamine was the only amine detected in the pyrolysis of diuron; iprodione produced isopropylamine (95%), ethylamine, and a minor unidentified amine. The chlorine atoms bonded to the aromatic rings were removed only at high temperatures.

Condensed Products. Analysis of the organic fraction from diuron pyrolysis by GC–MS revealed the presence of chlorobenzene, 1,2-dichlorobenzene, benzonitrile, trichlorobenzene, aniline, 4-chloroaniline, and 3,4-dichloroaniline (in order of their retention times on Carbowax 20 M). The liquid chromatography made possible the identification of 3,4-dichlorophenyl isocyanate, bis[1,3-(3,4-

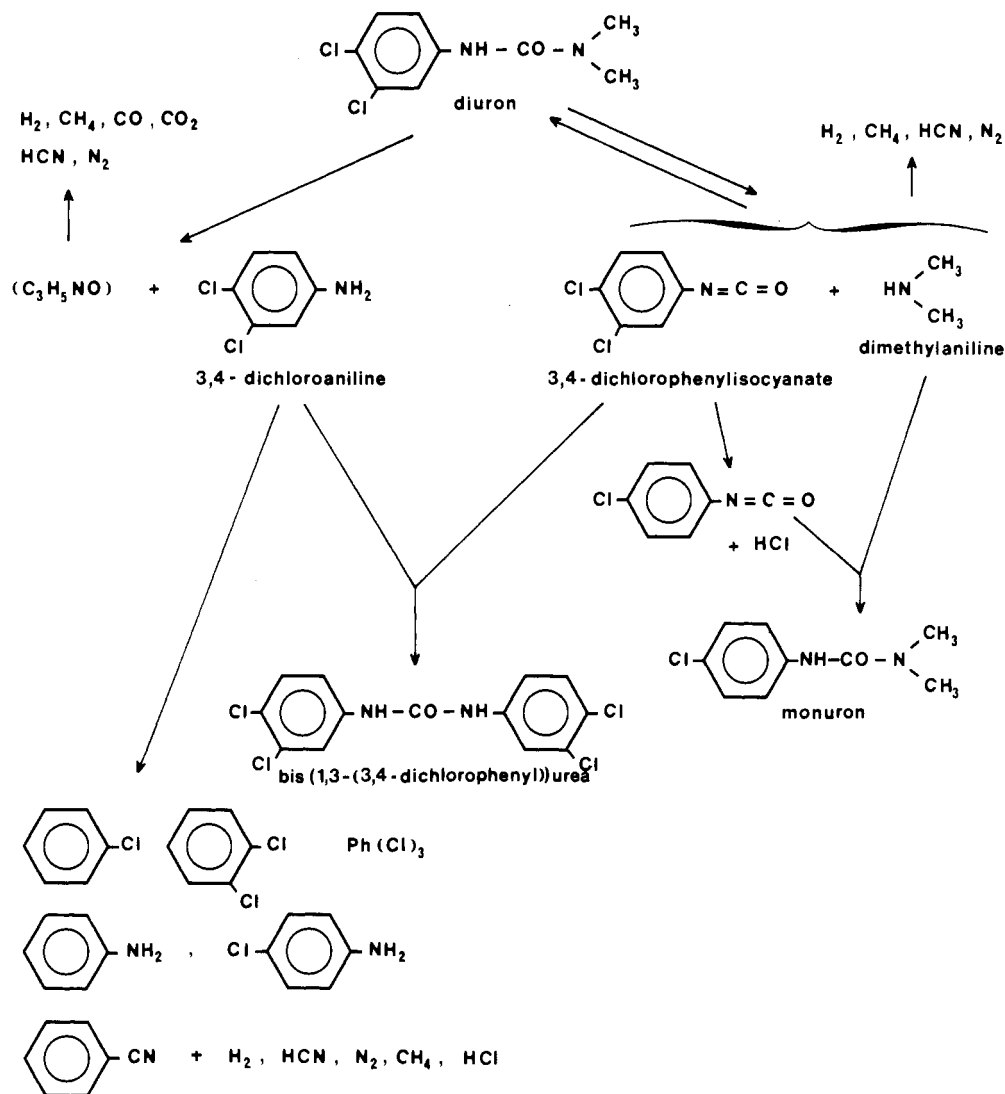


Figure 1. Thermal degradation scheme of diuron.

Table II. Mole of the Major Products Condensed in the Cold Trap per Mole of Diuron Submitted to Pyrolysis

	mol/mol at pyrolysis temperature of			
	400 °C	600 °C	800 °C	1000 °C
diuron	0.95	0.80	0.60	0.42
3,4-dichloroaniline			0.06	0.12
carbon			0.10	0.50

dichlorophenyl]urea, diuron, and monuron [3-(4-chlorophenyl)-1,1-dimethylurea] at relative retention times of 0.42, 0.35, 1.00 (214 s), and 1.55, respectively (with dichloromethane at 180 mL/h). There remained an insoluble part consisting of carbon. The presence of large amounts of diuron in the cold trap, even at high temperatures (Table II), could not be explained by nondestructive passage through the hot zone, as GLC at 240 °C (Büchert and Lokke, 1975) showed that diuron was completely decomposed into dimethylamine and 3,4-dichlorophenyl isocyanate. In our apparatus, the isocyanate and amine probably reacted to give diuron as soon as they were formed, probably in the gas phase as only traces of aryl isocyanate could be detected in the cold trap from a 1000 °C pyrolysis. Diarylureas were formed similarly from aryl isocyanates and dichloroanilines. At higher temperatures the presence of 3,4-dichloroaniline (Table II) showed that the other N-CO bond (Figure 1) was also broken. This hypothesis was supported by the fact that the thermal

weak point of the substituted ureas is the N-CO bond (Büchert and Lokke, 1975; Schwartzman and Lima, 1979) and that 3,4-dichloroaniline could not be derived from the degradation of the 3,4-dichlorophenyl isocyanate, which was thermally stable (5% decomposition at 1000 °C). These results and data from the pyrolysis of 3,4-dichloroaniline, 3,4-dichlorophenyl isocyanate, and dimethylamine suggested a general scheme for the thermal degradation of diuron in an inert atmosphere shown in Figure 1.

The decomposition of iprodione started around 300 °C, giving isopropyl isocyanate and 3-(3,5-dichlorophenyl)hydantoin. The first was identified by comparison of its IR spectra and GLC retention time with those of a pure sample of isopropyl isocyanate, and the second was identified by its mass spectrum [two most intense ions each 14 mass units above m/e 118 [124 (36), 126 (12); 113 (3), 145 (8); 147 (4), 159 (10); 160 (9), 161 (15); 174 (3), 187 (100); 188 (27), 189 (65), 244 (32), 246 (16)]] and NMR spectrum at 250 MHz in Me_2SO [4.0 (s, 2, $-\text{CH}_2-$), 7.5 (d, 2, $J = 3$ Hz, aromatic H-2 and H-6), 7.6 (t, 1, $J = 3$ Hz, aromatic H-4), 8.5 (s, 1, $-\text{NH}-$)]. Beyond 600 °C, no more isopropyl isocyanate appeared, and the hydantoin ring began to decompose to gases and products similar to those observed in the pyrolysis of diuron: anilines (3-chloroaniline; 3,5-dichloroaniline), chlorinated benzenes, and benzonitrile. From 800 to 1000 °C, the destruction of the hydantoin ring led to aryl isocyanates, anilines, and the

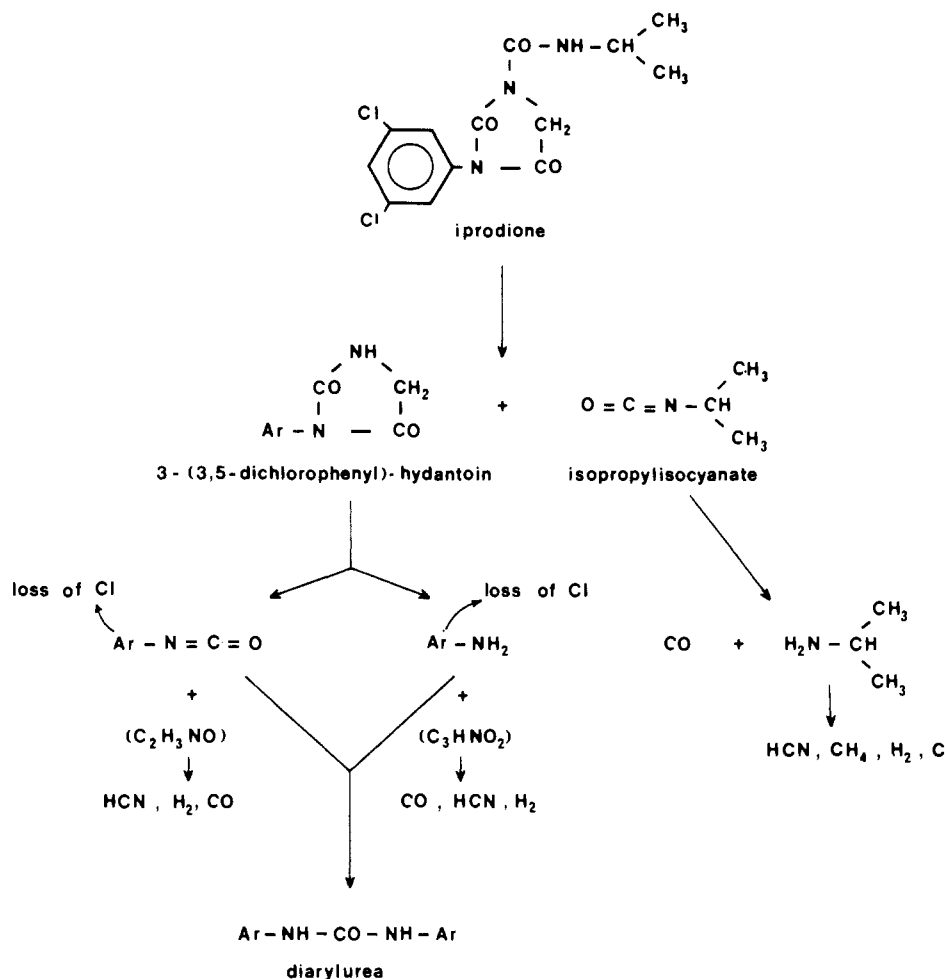


Figure 2. Thermal degradation scheme of iprodione.

Table III. Mole of the Major Products Condensed in the Cold Trap per Mole of Iprodione Submitted to Pyrolysis

	mol/mol at pyrolysis temperature of			
	400 °C	600 °C	800 °C	1000 °C
iprodione	0.5			
3-(3,5-dichloro-phenyl)hydantoin	0.5	0.92	0.78	
bis[1,3-(3,5-dichloro-phenyl)]urea			0.03	0.18
carbon			0.1	0.5

Table IV. Yields of Injurious Gases (Liters) Emitted per Kilogram of Pesticide Submitted to Pyrolysis at 1000 °C

pesticide	yield, L/kg			
	CO	HCl	HCN	amines
diuron	35	50	60	10
iprodione	90	35	15	50

corresponding diarylureas separated by HPLC with 20% ethyl acetate in heptane at 200 mL/h [retention times were 108 s for bis[1,3-(3,5-dichlorophenyl)]urea and 160 s for 1-(3-chlorophenyl)-3-(3,5-dichlorophenyl)urea] (Table III). The thermal degradation scheme proposed for the iprodione is shown in Figure 2.

The two pesticides showed many similarities in their thermal behavior, including evolution of injurious products such as carbon monoxide, hydrogen chloride, and hydrogen cyanide (Table IV). Dechlorination formed only hydrogen chloride; no chlorine or light chlorinated hydrocarbons were detected. The primary thermal reaction was for-

mation of isocyanate and amine which then generated ureas, gases, and carbon.

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