

## Thermal Degradation of Oxadiazon

The thermal degradation of oxadiazon in the presence of helium was studied in the range 300–1000 °C, in a flow reactor. The mild pyrolysis (below 450 °C) led to indazoles, carbon dioxide, and alkenes (isobutene and propene). A more vigorous degradation was obtained at higher temperatures where an important yield of nitrogen was observed. Different organic compounds were also formed in little amounts consisting especially of chlorinated or oxygenated aromatics and polyaromatic hydrocarbons. The formation of large amounts of hydrogen chloride and carbon was noticed.

In a previous paper, we exposed the reason of our studies on the thermal degradation of industrial chemicals, and we gave the results of our works on the thermal behavior of diuron and iprodione (Gomez et al., 1982). The aim of our researches is the identification and quantitative determination of products that could evolve from incineration or accidental burning of industrial chemicals. The present investigation deals with the analysis and identification of breakdown products resulting from pyrolysis of oxadiazon (an herbicide) in a helium atmosphere.

### MATERIALS AND METHODS

**Materials.** The oxadiazon (2-*tert*-butyl-4-[2,4-dichloro-5-(isopropoxy)phenyl]- $\Delta^2$ -1,3,4-oxadiazolin-5-one) was 99% + purity.

**Apparatus.** The pyrolysis was carried out between 300 and 1000 °C in an inert atmosphere consisting of helium in a flow reactor. The apparatus has already been described in our previous works (Bruneau et al., 1981) as well as the operating method for the pyrolysis of the same type of compounds (Gomez et al., 1982). The gaseous products (gases at 20 °C) were collected in a gas sampling bag or trapped in bubblers (in the case of HCl and amines). The other products collected in a cold trap cooled with ice constituted the condensate.

**Analysis of the Pyrolysis Products.** The hydrocarbons, carbon oxides, and hydrogen were determined by a Girdel 3000 chromatograph equipped with a catharometric detector. The columns used were a 300 cm  $\times$  0.5 cm stainless steel column packed with 5% Apiezon L on alumina (60–80 mesh) at 120 °C for the determination of C<sub>3</sub> and C<sub>4</sub> hydrocarbons and a 180 cm  $\times$  0.5 cm stainless steel column packed with Porapak Q (100–120 mesh) at 60 °C, followed by a similar 300 cm  $\times$  0.5 cm column packed with a 13 X molecular sieve at 20 °C.

The quantitative estimate of each gas was determined after we measured the amount of the major gas by direct calibration. The knowledge of the relative amounts of each gas was established by the internal normalization method.

The gases soluble in water (HCl, amines) were titrated by chemical and electrochemical methods after collecting them in bubblers: HCl with AgNO<sub>3</sub> (0.05 N) by potentiometry with a silver electrode in acid solution (pH 5–6); the amines by the Kjeldhal method. The identifications of the amines were made with a Girdel 3000 chromatograph equipped with a flame ionization detector. The column used was a 250 cm  $\times$  0.2 cm glass column packed with Chromosorb 103 (100–120 mesh) combined with a 5 cm long precolumn containing Ascarite at 120 °C.

The cold traps containing liquid and solid pyrolysates were washed with water and ethyl acetate. The aqueous fraction contained chloride and amines that were titrated according to the method used for the analysis of the bubblers. The compounds extracted in the organic phase were identified by GC-MS coupling, using a VG Micro-mass 7070 F mass spectrometer (electronic impact 70 eV).

Table I. Mole of Major Gaseous Product per Mole of Oxadiazon Submitted to Pyrolysis at Different Temperatures

	mol/mol at pyrolysis temperature of			
	400 °C	600 °C	800 °C	1000 °C
H <sub>2</sub>				0.49
N <sub>2</sub>			0.80	0.36
CO				0.38
CO <sub>2</sub>	0.05	0.74	0.95	0.62
CH <sub>4</sub>		0.12	0.74	0.75
C <sub>2</sub> H <sub>4</sub>		0.02	0.25	0.36
C <sub>2</sub> H <sub>6</sub>			0.16	
C <sub>3</sub> H <sub>6</sub>	0.04	0.05	0.49	0.26
C <sub>3</sub> H <sub>8</sub>		0.04	0.14	0.03
C <sub>4</sub> H <sub>8</sub>	0.02	0.55	0.60	0.03
C <sub>4</sub> H <sub>10</sub>		0.25	0.35	
HCl	0.07	0.57	0.93	1.37
amines		0.03	0.17	0.96

Their structures were assigned by comparison of their mass spectra with the data found in the literature (Heller and Milne, 1978), and some of them were confirmed by comparison of their retention times with those of standards eluted under the same chromatographic conditions. The column used was a 20-m glass capillary column coated with SE 52 programmed from 60 to 250 °C at 2 °C/min. The compounds resulting from the first splittings of the initial molecule were isolated by preparative liquid chromatography on a Merck H60 Kieselgel column using a Jobin Yvon Chromatospac Prep 100. The solvent consisted in a CH<sub>2</sub>Cl<sub>2</sub>-isooctane mixture (50:50). Their mass spectra were achieved with a Varian Mat 311 mass spectrometer and their <sup>1</sup>H NMR spectra with a JEOL MH 100 unit. Their production as a function of temperature was followed by analytical liquid chromatography with a Varian 8500 unit, on a Lichrosorb Si 60 column (15 cm  $\times$  0.47 cm). The UV detection was at 254 nm, and the mobile phase was a CH<sub>2</sub>Cl<sub>2</sub>-isooctane mixture (50:50) (flow rate 200 mL/h).

### RESULTS AND DISCUSSION

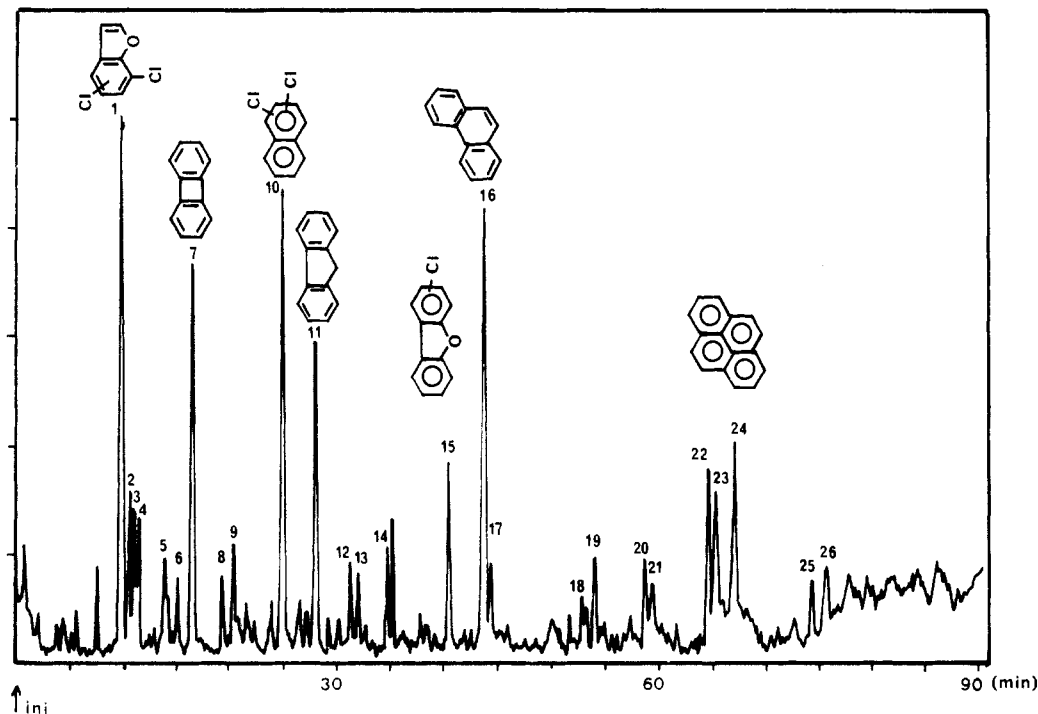
The thermal degradation began around 330 °C but the major product collected below 450 °C was the oxadiazon, which sublimated in the hot zone and was condensed in the cold trap.

**Gaseous Pyrolysis Products.** The first gases resulting from pyrolysis of oxadiazon in helium were carbon dioxide, propene, and isobutene. Then there appeared other compounds (hydrocarbons and hydrogen) coming from thermal decomposition of the former and from more vigorous pyrolysis of oxadiazon (Table I).

The formation of HCl was observed as soon as 400 °C was reached, and its yield increased with temperature. Amines were also detected, consisting essentially of ethylamine and dimethylamine.

**Condensed Products.** The yield of pyrolysate collected in the cold trap decreased with temperature, while the yields of gases and carbon increased (Tables I and II).



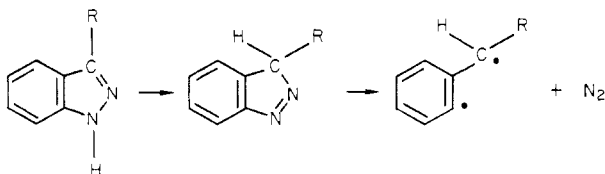


**Figure 2.** Pyrogram of oxadiazon. Products collected in the cold trap at 1000 °C. Capillary column: 20 m long, coated with SE 52; temperature programmed from 60 to 250 °C at 2 °C/min; nitrogen carrier gas inlet pressure, 0.4 atm. 1, dichlorobenzofuran; 2 and 3, chloronaphthalenes; 4, biphenyl; 5, hydroxychloronaphthalene; 6, acenaphthene; 7, biphenylene; 8, dichloromethylbenzofuran; 9, chloromethylnaphthalene; 10, dichloronaphthalene; 11, fluorene; 12, methylbiphenylene plus chlorobiphenyl or chloroacenaphthene; 13, chlorobiphenylene; 14, dichloromethylnaphthalene; 15, chlorodibenzofuran; 16, phenanthrene; 17, anthracene; 18, methylphenanthrene or methylanthracene; 19, 4*H*-cyclopenta[*def*]phenanthrene; 20, phenylnaphthalene or methyl-4*H*-cyclopenta[*def*]phenanthrene; 21, chlorophenanthrene; 22, fluoranthene; 23, benzobiphenylene; 24, pyrene; 25 and 26, benzofluorene and methylpyrene. Compounds at peaks 1–3, 5, 8–10, 12–15, 18–21, 23, 25, and 26 were identified by MS data. Compounds at peaks 4, 6, 7, 11, 16, 17, 22, and 24 were identified by MS data and retention times.

**Table II.** Yields of Condensate and Carbon from Pyrolysis of Oxadiazon at Different Temperatures

	g/g condensate and g-atom of C/mol at pyrolysis temperature of			
	400 °C	600 °C	800 °C	1000 °C
condensate	0.8	0.65	0.45	0.25
carbon		1.8	2.8	3.1

the compound A could undergo a thermal breakdown, giving also propene. It must be noticed that indazoles have already been synthesized by Reichen (1976) from 1,3,4-oxadiazol-5-ones using their ability to lose CO<sub>2</sub> by thermal treatment around 500 °C. Beyond 600 °C, a great number of aromatic compounds were formed (Figure 2) in the same time as the amount of N<sub>2</sub> increased. The main products were dichlorobenzofuran, biphenylene, dichloronaphthalenes, fluorene, chlorodibenzofuran, phenanthrene, pyrene, and fluoranthene. The formation of these compounds resulted probably from the condensation of radicals coming from the loss of N<sub>2</sub> and heteroatoms from the indazoles. Crow and Paddon-Row (1972) proposed two mechanisms to explain the elimination of N<sub>2</sub> from indazoles and showed that the predominant pathway included a hydrogen shift according to



In our case, the same type of rearrangement probably occurred, leading to compounds C (see Scheme I), but

these intermediates immediately lost a nitrogen molecule so that they could not be detected. The unspecific yield of polyaromatics was not surprising in so far as the thermal splittings in oxadiazon led to aliphatic radicals containing more than two carbon atoms. The formation of aromatic hydrocarbons from aliphatic compounds at high temperature by cyclodehydrogenation or cyclodealkylation has been known for a long time (Badger et al., 1958; Hurd et al., 1962). The arenes could also result of reactions between the benzyl radical, which is possible to be formed by nitrogen elimination, and olefins.

The yield of halogenated compounds was not very important, which agreed with the large amounts of chloride found in the gas phase.

All those remarks made possible the suggestion of a general scheme for the pyrolysis of oxadiazon at different temperatures (Scheme I).

## CONCLUSION

Oxadiazon has a relatively good thermal stability. Its degradation begins around 330 °C but becomes really effective beyond 450 °C. The oxadiazolinone ring is the weak point of the molecule and its destruction leads to carbon dioxide and an indazole. The gases emitted are not very toxic, although the yield of HCl is very important comparatively with those of other dichlorinated pesticides such as diuron or iprodione (Gomez et al., 1982). On the other hand, the formation of polyaromatic compounds is undesirable. The very important yield of carbon and the absence of HCN in this pyrolysis must be noticed.

## ACKNOWLEDGMENT

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## Use of Chromatographic Mode Sequencing for Sample Preparation in the Analysis of Caffeine and Theobromine from Beverages

Several bonded-phase sorbents in combination with the effect of several different elution solvents have been evaluated for use in the sample preparation segment of xanthine analyses in beverages. Xanthines are isolated from beverages including coffee, tea, cocoa, and colas in a rapid and highly selective procedure using solid-phase sample preparation, i.e., the use of surface-modified sorbents coupled to the technique of chromatographic mode sequencing. The resultant procedure utilizes Bond Elut columns packed with C<sub>18</sub> bonded silica (Analytichem International). Average recovery values for the three xanthines ranged from 92% to 98% with coefficients of variation of less than 5% for all three compounds. The caffeine and theobromine levels in several different brands of coffee, tea, and soft drinks were determined by using the described procedure, and the values obtained compared well with those reported by other investigators.

The determination of the levels of caffeine and related xanthines in foodstuffs is becoming increasingly important in the light of recent concern about the health effects of these compounds and their widespread consumption by the public. Several analytical methods exist for the quantitation of caffeine and/or theobromine and theophylline in coffee, tea, soft drinks, and chocolate products. These methods included titrimetry (Horowitz, 1975), spectrophotometry (Grossier, 1978), gas chromatography (Strahl, 1977), and high-pressure liquid chromatography (HPLC) using either normal-phase (Sommadossi et al., 1981) or reversed-phase modes (Kreiser and Martin, 1978). The HPLC methods have the advantages of sensitivity and improved separation, enabling individual quantitation of each of the three xanthines present in a sample. All of the above methods require some degree of sample preparation, usually consisting of a liquid-liquid extraction with a solvent such as benzene or chloroform, followed in some cases by a back-extraction into an aqueous phase to accomplish further separation of caffeine from interfering compounds.

The work described here is an example of solid-phase sample preparation, the use of specifically modified sorbents in combination with chromatographic mode changes to achieve isolation of the compounds of interest from the sample matrix. Several bonded-phase silicas were evaluated in order to determine the best solid phase for this application. Formulation of the mode sequence was based on selection of the appropriate phase together with the evaluation of several solvent systems used to elute the analytes. The objective here was to afford good recovery

of the analytes devoid of the naturally occurring chromatographic interferences such as pigments and tannins.

### EXPERIMENTAL SECTION

**Apparatus.** Extraction columns were provided by Analytichem International (Harbor City, CA). Each Bond Elut column contained 100 mg of bonded-phase silica dry packed into a 1-mL polypropylene column. The silica substrate used had a mean particle size of 40  $\mu$ m and a porosity of 60 Å. The following bonded phases were evaluated: C<sub>18</sub>, C<sub>8</sub>, phenyl, benzene sulfonic acid, carboxylic acid, and cyanopropyl. Extractions were performed by using a Vac Elut 10-place vacuum manifold, also available from Analytichem International.

Analysis was carried out by using a Varian Model 5000 liquid chromatograph equipped with a Varian Vari-chrom variable-wavelength detector (set at 280 nm) and a Linear Instruments Model 255 recorder. The column used contained Sephalyte 10  $\mu$ m, C<sub>18</sub> material in a 2.1 mm  $\times$  25 cm (narrow bore) configuration (Analytichem International). The column temperature was 55 °C; the mobile phase was acetonitrile-methanol-7 mM H<sub>3</sub>PO<sub>4</sub> (4:4:92) at a flow rate of 1.5 mL/min and a pressure of 150 atm.

**Reagents.** HPLC-grade methanol, acetonitrile, and chloroform were obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). All other solvents and inorganic reagents were reagent grade from J. T. Baker (the methanol used for standards and for column washes was HPLC grade). Distilled, deionized water was used to prepare aqueous solutions. Theobromine standard was obtained from Eastman Kodak (Rochester, NY), caffeine from