Gas Chromatographic Determination of the Rate Constant for the Hydrolysis of Heptachlor

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Introduction

Various investigators have reported the conversion of heptachlor in an aqueous solution to 1-hydroxychlordene (1-5). Ruzicka et al., (6) and, recently, Jaglan and Gunther (7), have used gas chromatographic methods to determine the rates of hydrolysis of some organophosphorous pesticides.

In the present study gas chromatography has been used to determine the rate of hydrolysis of heptachlor in distilled water.

Experimental

A stock solution of 3 ug/ml of heptachlor (Polyscience, Cat. No. 51009) in acetone (MC&B, Cat. No. AX119, 42953) was prepared. One hundred microlitres portions of this solution were added with a 100 ul syringe to a 100 ml Raysorb volumetric flask. Immediately after, 90 ml of distilled water were added and the flask placed into a constant temperature water bath. The temperature in the bath was maintained at 29.88 ± 0.03°C., and it was monitored with a quartz thermometer (Hewlett-Packard, Cat. No. 2801A).

Previously, a magnetic stirring bar was placed in each flask and then the flasks were thoroughly cleaned (chromic acid, tap water, Sparkleen, tap water, distilled water, acetone, hexane), and dried at 300°C, for at least 12 hours. Immediately before use, the flasks were taken out of the oven, let cool for 10 minutes, and then rinsed a few times with small portions of distilled water.

Distilled water of desired quality was obtained by passing tap water through a demineralizer cartridge (Corning,Cat.No.3508A) and then distilling it in all-glass distillation apparatus (Kontes Glass Co., Cat. No. WS-2).

At various time intervals flasks were removed from the bath and the contents analysed immediately for heptachlor.

The analytical procedure consisted of adding 1 ml of benzene (Anachemia, Cat. No. TG-995), stirring vigorously on a magnetic stirring plate for half an hour, and then letting the flask stand

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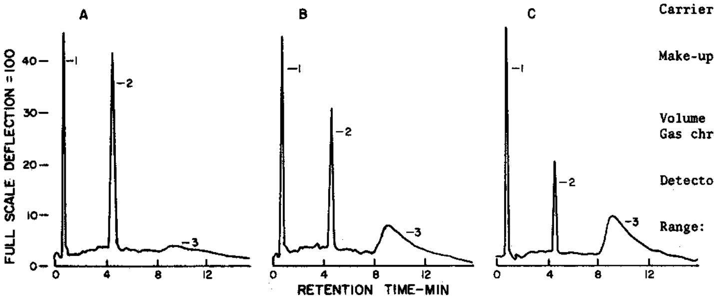
for approximately 10 minutes to allow the benzene layer to separate on top. The benzene layer was removed with a syringe, and placed in 100 ul vials for direct use in the automatic injector of the gas chromatograph. Three separate vials were filled with the benzene extract of one volumetric flask. Two separate aliquots were injected from each vial. Therefore, for each flask, six gas-chromatograms were obtained.

The gas chromatograph used in this work was a Hewlett-Packard model 7620A, equipped with a Ni (63), pulsed, electron capture detector, automatic injector (HP 7670A), and electronic integrator (HP 3370A). An eight feet, 4 mm i.d. glass column packed with 3% OV-1 on Chromosorb W, HMDS, 60-80 mesh, was used. The chromatographic conditions were kept constant during this study. They are shown together with three typical gas-chromatograms in Fig. 1.

FIG I GAS—CHROMATOGRAMS OF THE BENZENE EXTRACTS OF THE HYDROLYSIS FLASKS
PEAK I: BENZENE PEAK 2: HEPTACHLOR PEAK 3: I—HYDROXYCHLORDENE

	A		B		C	
	PEAK I	PEAK 2	I	2	I	2
RETENTION TIME (MIN)	.71	4.67	.71	4.65	.71	4.64
AREA (INTEGRATOR COUNTS)	2035	3521	1992	1911	1997	928
REACTION TIME (HRS)		6.45		35.88		59.17
UNHYDROLYSED HEPTACHLOR (CALCULATED) - ng		255		111		52
INITIAL AMOUNT OF HEPTACHLOR — ng		300		300		300



Chromatographic
conditions:
Column: glass, 8ft.
4mm i.d.
Packing: 3% OV-1 on
Chromosorb
W, H M D S,
80-100 mesh.
Temperature (°C):
Injector 235,
Column 190
Detector 340
Carrier gas: Helium,
40 psi,
45ml/min.
Make-up gas: CH_4 (5%)
+ Ar (95%),
12 psi,
45ml/min.
Volume injected: 5μl
Gas chromatograph:
Hewlett -
Packard 7600
Detector: pulsed EC,
Ni63, 150msec
pulse interval
Range: 10^4

Standard Curves: The quantity of unhydrolyzed heptachlor remaining in each flask was calculated by interpolation from a standard curve (Fig. 2). The standard curve was obtained by adding various amounts of the stock solution to 100 ml volumetric flasks. Immediately after, 90 ml of distilled water were added and then each flask was analysed for heptachlor by the method described before.

The standard points were fitted by the least squares method, to a polynomial of the form (8):

$$Y = B_0 + B_1X + B_2X^2 + B_3X^3 \qquad \ldots 1$$

or:

$$Y = B_0 + B_1X + B_2X^2 + B_3X^3 + B_4X^4 \qquad \ldots 2$$

where X was the total amount of heptachlor added to each flask, in micrograms, and Y, the area in integrator counts under the heptachlor peak, on the corresponding chromatogram. Three separate kinetics runs were performed. In each case a new standard curve was obtained. One of the curves and its corresponding polynomial are shown in Fig. 2.

The amount of unhydrolyzed heptachlor present in each hydrolysis flask was calculated by solving an equation of the form:

$$B_3X^3 + B_2X^2 + B_1X + B_0 - Y = 0 \qquad \ldots 3$$

where X was the sought quantity, and Y the area under the heptachlor peak as measured by the electronic integrator. The coefficients $B_0 \ldots B_3$ were those of the respective standard curve.

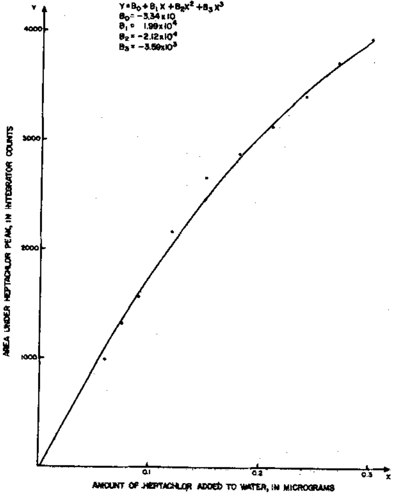
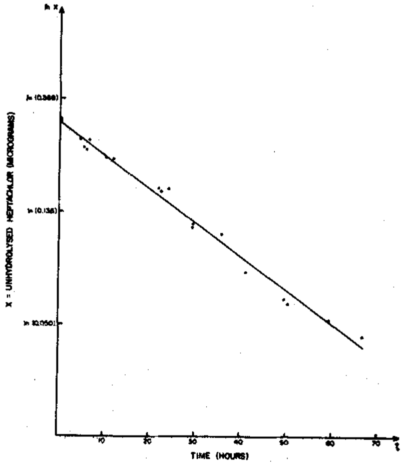


FIG. 2 STANDARD CURVE:
$Y = B_0 + B_1X + B_2X^2 + B_3X^3$
$B_0 = -3.34 \times 10$
$B_1 = 1.99 \times 10^4$
$B_2 = -2.12 \times 10^4$
$B_3 = -3.59 \times 10^3$

FIG. 3 THE HYDROLYSIS OF HEPTACHLOR IN DISTILLED WATER AT 29.96 (±0.03)°C.

$\ln X = -0.0300\ (\pm 0.0008) \times t - 1.20\ (\pm 0.02)$



Results

The results were analysed according to a first order or a pseudo-first order kinetics:

$$\ln X = kt + C$$

where X was the amount of unhydrolyzed heptachlor (in micrograms) after time t (in hours).

The hydrolysis constant k was calculated by least squares method from the points obtained in all three kinetic runs. These points and the calculated straight line fitting them are shown in Fig. 3.

The value obtained for the hydrolysis constant at 29.88°C was:

$$k = (0.0300 \pm 0.0008)h^{-1}$$

The half-life of heptachlor at the same temperature is:

$$t_{\frac{1}{2}} = 0.693/k = 23.1 \text{ h}$$

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