# ADSORPTION ISOTHERMS OF THE ALPHA, GAMMA, AND DELTA ISOMERS OF HEXACHLOROCYCLOHEXANE, AND INSTABILITY OF THE GAMMA ISOMER

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# ADSORPTION ISOTHERMS OF THE ALPHA, GAMMA, AND DELTA ISOMERS OF HEXACHLOROCYCLOHEXANE, AND INSTABILITY OF THE GAMMA ISOMER

By

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# INTRODUCTION

The compound Hexachlorocyclohexane was first prepared by Faraday, per Daasch (1) in 1825. In 1837 Meunier, per Slade (2) showed the existence of two isomers of this compound, the alpha and beta isomers. In 1912 Van der Linden, per Daasch (1) showed the existence of two additional isomers, the gamma and delta isomers. Kauer, DuVall and Alquist (3) in 1947 found another isomer, the epsilon isomer, which until now is the final isomer to be discovered. In this paper only the alpha, gamma and delta isomers were studied.

Smart, per Kauer, DuVall and Alquist (3) in 1943 isolated the gamma isomer and found it to be more toxic to weevils than was any other substance. The insecticidal action of hexachlorocyclohexane, benzene hexachloride, or 666 is due to the gamma isomer, which represents 10-12% of the crude material. According to Slade (2) less than one part of the gamma isomer will kill grain weevils as effectively as fifteen parts of D. D. T., when mixed with the grain. One theory of the insecticidal mechanism is that the structure of gamma isomer is similar to inositol, and may be absorbed from outside of the insect, distributed throughout some portion of the organism to the cells, where a vital reaction is blocked, and the organism dies.

Hexachlorocyclohexane is prepared by passing chlorine gas through benzene illuminated by ultra-violet lights (5). The structure of only the beta isomer has been determined,

but the isomers are probably similar in structure to those of hexahydroxycyclohexane (inositol) (3).

The purpose of this work is to study the adsorption isotherms of the alpha, gamma, and delta isomers of hexachlorocyclohexane, with the view of checking and extending Gilbert's (4) work, and examining the isotherms at higher concentrations. Also, some work was done on the chromotographic separation of mixtures of the isomers using Sauer's (5) method. The last part of this work is concerned with evidence of the instability of the gamma isomer, and a discussion of the possibility of conversion from this isomer to the alpha and delta forms.

## CHEMICALS

Acetone - Merck and Co., conforming to A. C. S. Standards.

Alumina - Aluminum Co. of America F-20 grade, 80-200 mesh, activated at 250° C. for four hours and was cooled in a dessicator using calcium chloride as a drying agent.

Carbon Disulfide - Mallinckrodt Chemical Works, conforming to A. C. S. Standards.

Hexachlorocyclohexane Isomers (Alpha, Gamma and Delta) - supplied by Niagara Chemical Division, Food Machinery and Chemical Corp., Middleport, N. Y.

Hexane - Eastman Kodak Co.

## APPARATUS

For the quantitative determination of the isomers, the Beckman Infrared Spectrophotometer, IR-2 was used. The temperature was 25 ± 0.4° C. A sodium chloride cell of 0.23 mm. (approximate) thickness was used.

An [illegible] was used in a constant temperature bath at 24.9° C. to allow the samples to reach equilibrium at constant temperature.

# PROCEDURE

The method used for collecting adsorption data follows: A saturated solution of each of the pure isomers in hexane was made with an excess of the isomer present, suspended in a constant temperature bath for 24 hours, then decanted off. The saturated solution thus obtained was diluted with three milliliters of hexane to 500 milliliters of solution to prevent any solid from separating out due to evaporation of the hexane.

A weighed amount of alumina was placed in a weighed Corex ampoule, then 5 to 7 milliliters of the prepared solution was placed into this ampoule and it was sealed by an oxygen torch and weighed to determine the weight of solution. At the same time a portion of this solution was placed in a weighed 10 ml. graduated flask, weighed, and analyzed on the infrared spectrophotometer. (This was a control sample, from which the correct concentration of sample placed in the ampoule was determined.) The ampoule was then placed in an under water stirrer and revolved for 72 hours in a constant temperature bath at 24.9°C. The ampoule was then broken open, and the supernatent solution filtered through No. 1 ashless filter paper into a weighed 10 ml. graduated flask, stoppered and immediately weighed to prevent any loss due to evaporation. The solvent was then evaporated, the residue was taken up in 10 ml. of carbon disulfide, and analyzed by the Beckman IR-2 Infrared Spectrophotometer. By comparing the amount of isomer after

adsorption and before adsorption, the amount adsorbed could be determined.

The method of analyzing the samples was that developed by Daasch (1), and subsequently used by Gaur (5). The mathematical operations used to derive the adsorption data were those used by Gilbert (4).

To obtain adsorption data by using a chromatographic column, the following method was used: The chromatographic column was prepared by first placing a plug of cotton in the constricted end of an 8" x ½" tube. Alumina was placed in this column, a little at a time, and tamped down with a glass rod, until an alumina column 6" x ½" was obtained. To provide a constant flow from the tube, a vacuum was applied at the lower end by means of a water aspirator. The column was wet by a solution of one part hexane and one part carbon disulfide, then the solution of isomer mixture dissolved in the solvent was poured through. To remove the last traces of isomer from the column more solvent was poured through. All liquid coming from the column (except the first wash solvent) was collected in 25 ml. graduated flasks, evaporated, and the residue taken up in carbon disulfide and analyzed by the Beckman IR-2.

Two chromatographic analyses were made with the gamma isomer alone, and the data are given on page 11.

# RESULTS

## Adsorption data tables

The following data are recorded, where:

w - grams of isomer in contact with m grams of alumina.

y - grams of isomer left in solution at the equilibrium point.

x - grams of isomer adsorbed by m grams of adsorbent.

m - grams of alumina.

m/w - grams of alumina per gram of isomer.

conc. - equilibrium concentration in grams of isomer per gram of solvent.

x/m - amount of isomer adsorbed per gram of adsorbent.

While plotting the adsorption isotherms for the samples, it was observed that some of the points on the curves were non-reproducible. The grams of alumina per gram of isomer for these samples, i.e., m/w, showed that these points represent a lower and upper limit of alumina concentration. No m/w values for gamma are given because all the gamma points fall along the ideal curve. The non-reproducible samples have an asterisk to the right of the m/w values.

# TABLE 1

## Adsorption Data of the Alpha Isomer

| w<br>grams | y<br>grams | x<br>grams | m<br>grams | m/w<br>grams/<br>gram | x/m<br>grams/<br>gram | conc.<br>grams/<br>gram |
|---|---|---|---|---|---|---|
| 0.0700 | 0.0700 | 0.0000 | 0.0065 | 0.09286* | 0.0000 | 0.0105 |
| 0.0920 | 0.0933 | -0.0013 | 0.0136 | 0.1478* | -0.0956 | 0.0145 |
| 0.0880 | 0.0977 | -0.0097 | 0.0287 | 0.3261* | -0.3376 | 0.0145 |
| 0.0612 | 0.0599 | 0.0013 | 0.0328 | 0.5360* | 0.0396 | 0.0096 |
| 0.0904 | 0.0810 | 0.0094 | 0.0533 | 0.5896* | 0.1765 | 0.0128 |
| 0.1041 | 0.1068 | -0.0027 | 0.0729 | 0.7003* | -0.0370 | 0.0134 |
| 0.0913 | 0.0898 | 0.0015 | 0.0666 | 0.7295 | 0.0225 | 0.0138 |
| 0.1014 | 0.0974 | 0.0040 | 0.0844 | 0.8323 | 0.0476 | 0.0137 |
| 0.0976 | 0.0896 | 0.0080 | 0.1153 | 1.181 | 0.0690 | 0.0131 |
| 0.0636 | 0.0547 | 0.0089 | 0.0828 | 1.302 | 0.1080 | 0.0085 |
| 0.0812 | 0.0725 | 0.0087 | 0.1585 | 1.952 | 0.0549 | 0.0118 |
| 0.0764 | 0.0634 | 0.0130 | 0.1858 | 2.432 | 0.0700 | 0.0116 |
| 0.0852 | 0.0630 | 0.0222 | 0.2905 | 3.410 | 0.0764 | 0.0097 |
| 0.0971 | 0.0546 | 0.0425 | 0.3981 | 4.100 | 0.1070 | 0.0085 |
| 0.0581 | 0.0396 | 0.0185 | 0.2571 | 4.425 | 0.0720 | 0.0067 |
| 0.0820 | 0.0538 | 0.0282 | 0.3998 | 4.876 | 0.0705 | 0.0086 |
| 0.0835 | 0.0423 | 0.0412 | 0.4605 | 5.515 | 0.0895 | 0.0074 |
| 0.0677 | 0.0372 | 0.0305 | 0.3913 | 5.780 | 0.0779 | 0.0058 |
| 0.0873 | 0.0469 | 0.0404 | 0.5326 | 6.101 | 0.0758 | 0.0076 |
| 0.0841 | 0.0304 | 0.0537 | 0.6985 | 8.316 | 0.0769 | 0.0055 |
| 0.0913 | 0.0194 | 0.0719 | 0.7887 | 8.639* | 0.0912 | 0.0040 |
| 0.0976 | 0.0896 | 0.0080 | 0.1153 | 9.262 | 0.0690 | 0.0131 |
| 0.0750 | 0.0234 | 0.0516 | 0.7641 | 10.19 | 0.0675 | 0.0043 |
| 0.0743 | 0.0240 | 0.0470 | 0.8927 | 12.01* | 0.0527 | 0.0049 |
| 0.0659 | 0.0280 | 0.0378 | 0.9074 | 13.79* | 0.0416 | 0.0048 |
| 0.0587 | 0.0127 | 0.0460 | 0.8387 | 14.29 | 0.0549 | 0.0023 |
| 0.0664 | 0.0226 | 0.0437 | 1.1188 | 16.85* | 0.0391 | 0.0028 |
| 0.0283 | 0.0048 | 0.0235 | 0.6629 | 23.42 | 0.0355 | 0.0008 |
| 0.0659 | 0.0000 | 0.0659 | 1.8989 | 28.82 | 0.0347 | 0.0000 |

# TABLE 2

## Adsorption Data of the Gamma Isomer

| w<br>grams | y<br>grams | x<br>grams | m<br>grams | x/m<br>grams/gram | conc.<br>grams/gram |
|---|---|---|---|---|---|
| 0.1417 | -0.1374 | 0.0043 | 0.0418 | 0.1029 | 0.02367 |
| 0.1567 | 0.1511 | 0.0056 | 0.0741 | 0.07557 | 0.02380 |
| 0.1533 | 0.1436 | 0.0097 | 0.0952 | 1.019 | 0.0234 |
| 0.1478 | 0.1440 | 0.0038 | 0.0540 | 0.0704 | 0.0244 |
| 0.1611 | 0.1454 | 0.0157 | 0.1092 | 0.1438 | 0.0223 |
| 0.1678 | 0.1181 | 0.0497 | 0.2379 | 0.1725 | 0.0175 |
| 0.1342 | 0.0377 | 0.0965 | 0.4505 | 0.1475 | 0.0125 |
| 0.1783 | 0.0412 | 0.1371 | 0.7779 | 0.1762 | 0.0058 |
| 0.1431 | 0.0478 | 0.0953 | 1.0149 | 0.0939 | 0.0083 |
| 0.1275 | 0.1237 | 0.0038 | 0.0520 | 0.0731 | 0.0245 |
| 0.1478 | 0.1265 | 0.0213 | 0.1188 | 0.1790 | 0.0216 |
| 0.1619 | 0.1552 | 0.0067 | 0.0722 | 0.0928 | 0.0239 |
| 0.1710 | 0.1625 | 0.0085 | 0.0854 | 0.0995 | 0.0236 |
| 0.1349 | 0.1165 | 0.0184 | 0.2020 | 0.0909 | 0.0222 |
| 0.1350 | 0.0894 | 0.0456 | 0.2750 | 0.1700 | 0.0165 |
| 0.1609 | 0.1124 | 0.0485 | 0.4216 | 0.1150 | 0.0160 |
| 0.1246 | 0.0344 | 0.0902 | 0.6656 | 0.1360 | 0.0063 |
| 0.1570 | 0.0743 | 0.0827 | 0.5248 | 0.1580 | 0.0126 |
| 0.1550 | 0.0311 | 0.1195 | 0.8425 | 0.1420 | 0.0065 |
| 0.1082 | 0.0161 | 0.0921 | 0.9375 | 0.0982 | 0.0025 |
| 0.1047 | 0.0068 | 0.0979 | 1.2072 | 0.0811 | 0.0012 |
| 0.1124 | 0.0233 | 0.0899 | 0.6577 | 0.1360 | 0.0040 |
| 0.1086 | 0.0282 | 0.0804 | 0.5774 | 0.1390 | 0.0051 |

## Table 2

## Adsorption Data of the Salt Column

| w<br>grams | y<br>grams | x<br>grams | m<br>grams | m/w<br>grams/gram | x/m<br>grams/gram | [illegible]<br>grams/gram |
|---|---|---|---|---|---|---|
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0074 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0125 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | 0.0710 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0012 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0411 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0474 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 0.0749 | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | 0.0143 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 0.1027 | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

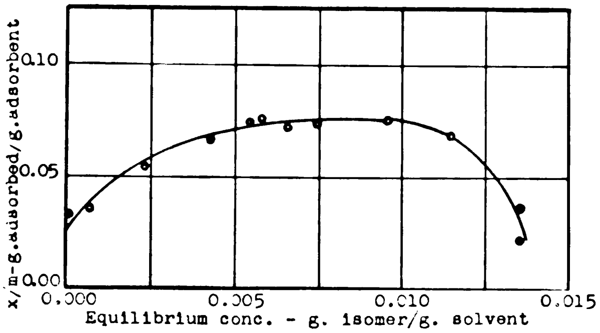

Fig. 1 Adsorption isotherm of pure alpha isomer of hexachlorocyclohexane

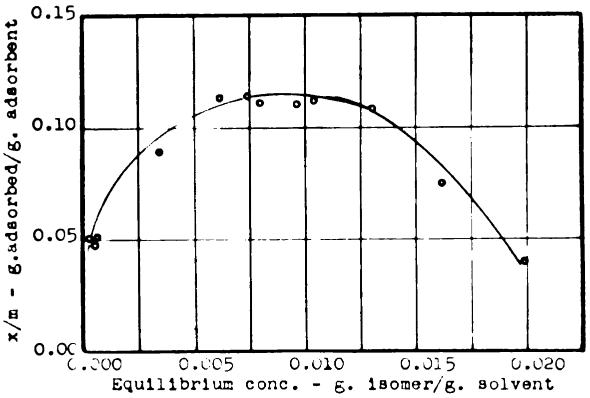

Fig. 2 Adsorption isotherm of pure delta isomer of hexachlorocyclohexane

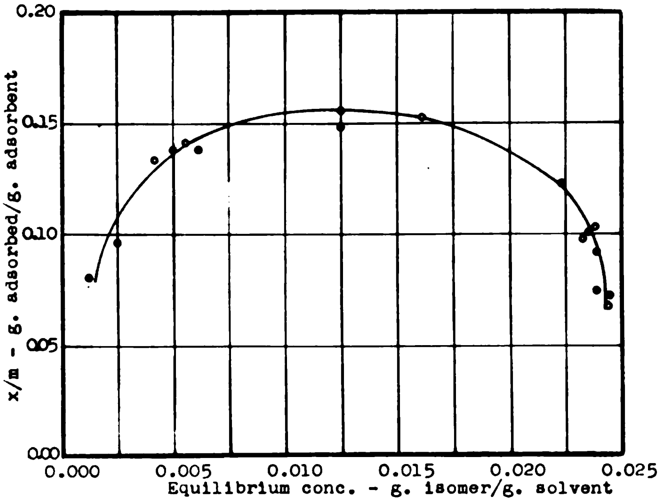

Fig. 3 Adsorption isotherm of pure gamma isomer of hexachlorocyclohexane

Separation curves of isomers

In order to verify Daur's (5) work with regard to order of elution of isomers in a mixture, a few mixtures were separated chromatographically. The results follow, and verify his order of elution, i.e., alpha first, gamma next, and delta remaining on the column. Data is also recorded for chromatographic analysis of the gamma isomer alone, Table 4.

Figure 4:

| Isomer | Sample mg. | Eluted pure mg. | Eluted mixed mg. |
|---|---|---|---|
| alpha | 227 | 17.5 | 207.5 |
| delta | 229 | 0.0 | 0.0 |
| gamma | 341 | 45.0 | 272.5 |

Figure 5:

| | | | |
|---|---|---|---|
| alpha | 297.5 | 7.5 | 255.0 |
| delta | 220.4 | 0.0 | 0.0 |
| gamma | 485.3 | 0.0 | 160.0 |

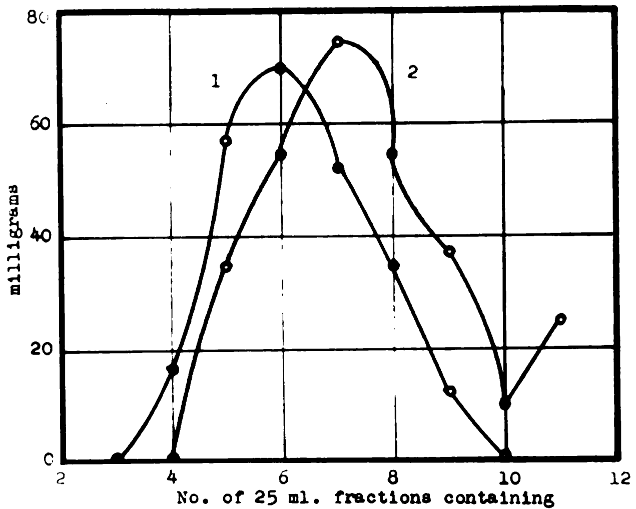

Fig. 4 (1) Alpha Isomer (2) Gamma Isomer

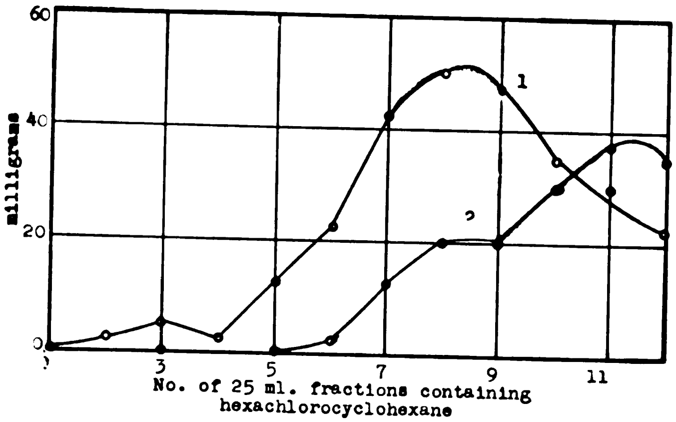

Fig. 5 (1) Alpha Isomer (2) Gamma Isomer

## TABLE 4

## Chromatographic analysis of the gamma isomer of hexachlorocyclohexane.

### I

| Fraction | grams of alpha | grams of delta | grams of gamma |
|---|---|---|---|
| Control | 0.0 | 0.0 | 0.1590 |
| 1 | 0.0 | 0.0 | 0.0850 |
| 2 | 0.0 | 0.0 | 0.3775 |
| 3 | 0.0 | 0.0 | 0.3350 |
| 4 | 0.0 | 0.0 | 0.1850 |
| 5 | 0.0 | 0.0 | 0.1400 |
| 6 | 0.0 | 0.0 | 0.1175 |
| 7 | 0.0 | 0.0 | 0.0675 |
| 8 | 0.0 | 0.0 | 0.0450 |
| 9 | 0.0 | 0.0 | 0.0300 |
| 10 | 0.0 | 0.0 | 0.0225 |
| 11 | 0.0 | 0.0 | 0.0175 |
| 12 | 0.0 | 0.0 | 0.0150 |
| 13 | 0.0 | 0.0 | 0.0100 |
| 14 | 0.0 | 0.0 | 0.0 |
| 15 | 0.0 | 0.0 | 0.0 |
| 16 | 0.0 | 0.0 | 0.0 |
|  |  |  | 1.6065 |

Original sample...... 1.6158

### II

| Fraction | grams of alpha | grams of delta | grams of gamma |
|---|---|---|---|
| 1 | 0.0 | 0.0 | 0.0025 |
| 2 | 0.0 | 0.0 | 0.0075 |
| 3 | 0.0 | 0.0 | 0.0150 |
| 4 | 0.0 | 0.0 | 0.2050 |
| 5 | 0.0 | 0.0 | 0.1475 |
| 6 | 0.0 | 0.0 | 0.0800 |
| 7 | 0.0 | 0.0 | 0.1125 |
| 8 | 0.0 | 0.0 | 0.0475 |
| 9 | 0.0 | 0.0 | 0.0400 |
| 10 | 0.0 | 0.0 | 0.0250 |
| 11 | 0.0 | 0.0 | 0.0350 |
| 12 | 0.0 | 0.0 | 0.0300 |
| 13 | 0.0 | 0.0 | 0.0150 |
| 14 | 0.0 | 0.0 | 0.0025 |
| 15 | 0.0 | 0.0 | 0.0075 |
| 16 | 0.0 | 0.0 | 0.0075 |
| 17 | 0.0 | 0.0 | 0.0225 |
|  |  |  | 0.8025 |

Original sample...... 0.8395

## Gamma conversion table

The control samples of gamma isomer showed 100% gamma, as did the chromatographic analyses of gamma isomer alone, whereas the equilibrium samples showed the following analyses:

### TABLE 5

| Sample | alpha isomer |  | delta isomer |  | gamma isomer |  |
|---|---|---|---|---|---|---|
|  | wt. | % | wt. | % | wt. | % |
| 1 | 0.014 | 9.5 | 0.023 | 15.5 | 0.111 | 75.0 |
| 2 | 0.003 | 2.4 | 0.000 | 0.0 | 0.123 | 97.6 |
| 3 | 0.004 | 3.5 | 0.000 | 0.0 | 0.115 | 96.5 |
| 4 | 0.013 | 8.7 | 0.023 | 15.4 | 0.113 | 75.9 |
| 5 | 0.007 | 5.3 | 0.013 | 9.9 | 0.111 | 84.8 |
| 6 | 0.002 | 2.6 | 0.001 | 1.3 | 0.073 | 96.1 |
| 7 | 0.003 | 4.1 | 0.014 | 18.9 | 0.057 | 77.0 |
| 8 | 0.000 | 0.0 | 0.012 | 30.8 | 0.027 | 69.2 |
| 9 | 0.000 | 0.0 | 0.011 | 22.5 | 0.038 | 77.5 |
| 10 | 0.011 | 8.7 | 0.020 | 15.8 | 0.096 | 75.5 |
| 11 | 0.006 | 5.8 | 0.010 | 9.6 | 0.088 | 84.6 |
| 12 | 0.025 | 15.1 | 0.048 | 28.9 | 0.093 | 56.0 |
| 13 | 0.008 | 7.0 | 0.017 | 14.9 | 0.089 | 78.1 |
| 14 | 0.006 | 5.7 | 0.015 | 14.2 | 0.085 | 80.1 |
| 15 | 0.009 | 9.1 | 0.023 | 23.2 | 0.067 | 67.7 |
| 16 | 0.009 | 8.3 | 0.029 | 26.9 | 0.070 | 64.8 |
| 17 | 0.000 | 0.0 | 0.007 | 22.6 | 0.024 | 77.4 |
| 18 | 0.001 | 2.0 | 0.007 | 14.3 | 0.041 | 83.7 |
| 19 | 0.002 | 7.4 | 0.011 | 40.7 | 0.014 | 51.9 |
| 20 | 0.001 | 6.3 | 0.006 | 37.5 | 0.009 | 56.2 |
| 21 | 0.001 | 14.3 | 0.004 | 57.1 | 0.002 | 28.6 |
| 22 | 0.002 | 7.7 | 0.010 | 38.5 | 0.014 | 53.8 |
| 23 | 0.000 | 0.0 | 0.007 | 29.2 | 0.017 | 70.8 |

# DISCUSSION

## Pure isomer adsorption

The adsorption curves, Figures 1, 2 and 3 verify Gilbert's (4) work up to his concentration limits. The curves represented here have higher $x/m$ values presumably because of a higher equilibrium temperature for Gilbert's work. Using smaller amounts of alumina, thereby increasing the concentration of isomer in solution, it was possible to show negative adsorption in each case. This phenomenon is described by Lewis and Squires (7) who state that if the solvent is more highly adsorbed than the solute, negative adsorption is observed although true adsorption may still be considerable. For dilute concentrations, Freundlich's equation is almost exact, but as the concentration increases, the adsorption becomes less than that indicated.

## Gamma isomer conversion

It should be noted that the adsorption isotherm for the gamma isomer is considerably higher than it should be according to chromatographic results. This may be explained by remembering that besides adsorption of the gamma isomer there seems to be considerable conversion of this isomer into the alpha and delta isomers, Table 5. Although there appears to be no rule as to the amount of alpha and delta isomers formed from the gamma isomer in connection with the amount of adsorbent or concentration of solution, it can definitely be stated that the conversion is affected by time and contact of alumina. None of the control samples

showed signs of conversion nor did any samples of gamma isomer alone on a chromatographic column (page 11). However, after allowing the samples to reach equilibrium in contact with alumina the large amounts of conversion noted occurred.

This instability may be the outcome of several of the properties of the gamma isomer. As pointed out by Baur (5) structures of greatest symmetry tend to have greater heats of vaporization, indicating greater intermolecular attraction. Therefore, the isomer with the greatest symmetry would tend to be adsorbed the most. Both the alpha and gamma isomers are adsorbed the least, and so have been tentatively assigned the 1,2,4 or 1,3 forms of structure (5). The recorded melting point of the gamma isomer, 112-112.8°C. which is the lowest of the isomers, indicates less molecular attraction than the other isomers.

Lind, Hobbs and Gross (8), found the electric moments of the isomers in benzene to be:

| | |
|---|---|
| alpha isomer | 2.12-2.30D |
| gamma isomer | 2.83-2.95D |
| delta isomer | 2.22-2.28D |

Beta had, as expected because of its symmetry, 0 moment. (It has been found by other investigators (8) that delta may have a moment of 0.) This data indicates that gamma has the highest electric moment, indicating the least symmetrical structure.

## SUMMARY

1. The order of adsorption by activated alumina of hexachlorocyclohexane isomers is delta the most strongly adsorbed, gamma the next strongest, and alpha the least strongly adsorbed.
2. At the higher concentrations of isomer per gram of solvent negative adsorption occurs.
3. The gamma isomer while in contact with alumina in a solution of hexane is unstable and forms the alpha and delta isomers.

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## ABSTRACT OF THESIS

# ADSORPTION ISOTHERMS OF THE ALPHA, GAMMA, AND DELTA ISOMERS OF HEXACHLOROCYCLOHEXANE, AND INSTABILITY OF THE GAMMA ISOMER

by Paul F. Biefeld, 1951

The compound hexachlorocyclohexane was first prepared by Faraday in 1825, and up to this date, five definite isomeric forms have been isolated, of which one, the gamma isomer, was found to be toxic to insects.

The purpose of this investigation has been to establish adsorption isotherms of three isomers of hexachlorocyclohexane on alumina, to confirm certain chromatographic adsorption studies, and to present evidence for instability of the gamma isomer when in contact with the adsorbent alumina.

To obtain the adsorption isotherms, about five milliliters of a slightly diluted hexane solution of the isomer was placed in a weighed Corex ampoule containing a known amount of alumina. The ampoule was sealed, and the exact amount of solution was obtained by weighing. Simultaneously, a portion of this solution was added to a weighed flask, and its weight determined. This was a control sample, from which the concentration before equilibrium was determined. The ampoule was placed under water at 24.9 °C., revolved for seventy-two hours, then broken open and the solution filtered and weighed. The solvent in the equilibrium mixture, as well as in the control sample, was then evaporated, the residue taken up in carbon disulfide, and analyzed in the Beckman IR-2 Spectrophotometer. By comparing the amount of isomer before and after adsorption, the amount adsorbed was determined. To obtain the isotherms, the amount of isomer adsorbed per gram of adsorbent was plotted against the

equilibrium concentration.

To confirm reported orders of the isomers on alumina, a 6" x $\frac{1}{2}$" alumina chromatographic column was used. A vacuum was applied at the lower end of the column to provide a constant flow. This column was wet by a solution of one part hexane and one part carbon disulfide, then the isomer solution was poured through, followed by successive amounts of solvent to remove traces of isomers from the column. Twenty-five milliliter fractions were collected, the solvent was evaporated, and the residue was taken up in carbon disulfide and analyzed in the Beckman IR-2. The data shows the order of adsorption to be delta the most strongly adsorbed, gamma the next strongest, and alpha the least strongly adsorbed.

While constructint the adsorption isotherms of the gamma isomer, analysis of the equilibrium solutions indicated appreciable amounts of alpha and delta isomers present, although none was found in the control samples before equilibrium, nor was any found after elution of pure gamma isomer from a chromatographic column. Although no apparent rule as to the amount of alpha and delta isomers formed from the gamma isomer was found, it can be stated that the conversion is affected by time and contact with alumina.

Definite structures of these isomers have not been determined, but data on melting points, order of elution, and electric moments indicate that the gamma isomer has less molecular attraction, and is the least symmetrical of any of the known isomers.