THE ADSORPTION OF THE ALPHA, DELTA AND GAMMA ISOMERS OF HEXACHLOROCYCLOHEXANE BY ACTIVATED ALUMINA

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Lewis Frederick Gilbert
1949

[redacted]

This is to certify that the

thesis entitled

"The Adsorption of the Alpha, Gamma and Delta Isomers of Hexachlorocycohexane by Activated Alumina".

presented by

Lewis F. Gilbert

has been accepted towards fulfillment
of the requirements for

M.S. degree in Physical Chemistry

D.T. Ewing
Major professor

Date December 2, 1949

O-169

THE ADSORPTION OF THE ALPHA, DELTA AND GAMMA ISOMERS OF HEXACHLOROCYCLOHEXANE BY ACTIVATED ALUMINA

By

Lewis Frederick Gilbert

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1949

ACKNOWLEDGMENT

The author wishes to thank Doctor D. T. Ewing for his aid and guidance, without which this work would not have been possible.

****
****
******
****
**
*

TABLE OF CONTENTS

INTRODUCTION

The complex molecule of hexachlorocyclohexane was first prepared by Faraday in 1825 (7) but few investigations were carried out on the compound until 1943, when Thomas discovered the insecticidal property of this chlorine substituted benzene. (3) Through this lack of investigation very little was known about the chemical and physical properties of the molecule. Since 1943, however, considerable effort has been directed toward investigating a number of these properties, not only for its insecticidal use but also as a study of the chemistry of a complex molecule.

Hexachlorocyclohexane is prepared by the chlorination of benzene in the presence of light. It is carried out by passing chlorine gas through benzene that is illuminated with ultra-violet light. (2) (6) There has been much speculation and many investigations concerning the structures of the six isomers of this compound. (3) As yet only the structure of the beta isomer has been determined. (1) (4) However, it has been concluded that this compound has the same isomers and structures that are possessed by inositol, which is hexahydroxycyclohexane. (3) (5)

The purpose of this work is to investigate and determine the adsorption isotherms of some of the individual isomers, singly or added in mixtures. From these we can gain not only physical data for the compound but also can reach some conclusions about the individual isomers. At the same time this data can be correlated to chromatographic data of these isomers from previous work by Saur (6) and a better understanding of chromatography can be attained.

EXPERIMENTAL

Chemicals

Acetone - J. T. Baker or Merck and Co. - was used without further purification.

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

Carbon Disulfide - Baker's Analyzed or Mallinckrodt Chemical Works - was used without further purification.

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

Hexane - Eastman Kodak Co. - commercial grade of hexane used without further purification.

Skelleysolve "B" - Skelley Oil Co.

Apparatus

Beckman Infrared Spectrophotometer, Model IR-2. The instrument was cooled to 25°±0.4° C. by water. The cell was the sodium chloride type. Cell thickness was approximately 0.28 mm.

Procedure

In general a known amount of the isomer in solution is placed in contact with a known amount of adsorbent. After a given period of time the solution is analyzed to find what amount of isomer is still in solution. The difference represents the amount which has been adsorbed. Due to the high volatility of the solvent, hexane or Skelleysolve "B", closed systems were used for the adsorption process.

The isomer or mixture of isomers, as the case may be, was dissolved in the solvent, hexane or Skelleysolve "B". A saturated solution was prepared and was then diluted by adding 50 ml. of the solvent to 200 ml. of the solution. This prevented any precipitation of the solute due to small amounts of evaporation during the preliminary work. Small amounts (5 to 7 ml.) of the solution were placed in 10 ml. glass ampules which had been weighed and contained weighed amounts of activated alumina. As each ampule was loaded with solution a sample of the same solution was placed in a weighed 10 ml. volumetric flask for analytical purposes. Immediately after the ampule was filled it was sealed by an oxygen torch. The filled ampule was then weighed to determine the weight of solution. The weight was also taken of the 10 ml. volumetric flask to determine the weight of the sample taken for analysis.

The ampule was then placed in the stirring apparatus for a period of 72 hours, the time necessary to reach equilibrium in this system. The equilibrium was attained in a constant temperature room which also maintained a constant humidity. The ampule was then broken and the solution was filtered through No. 1 ashless filter paper. The filtrate was caught in a weighed 10 ml. volumetric flask. This flask with the filtrate was again weighed to find the weight of the filtrate.

The two 10 ml. flasks, one containing a sample of the original solution and one a sample of the solution after adsorption, were then placed under vaccum and evaporated to dryness. The residue was redissolved in 10 ml. of carbon disulphide for analysis. The analysis was made by means of the infrared spectrophotometer by a method devised by Daasch (7) and modified by Saur (6).

Using the following mathematical procedure adsorption values (x/m) were obtained. The x/m was evaluated as:

$$x/m = \frac{\text{weight of isomer adsorbed}}{\text{weight of adsorbent}}$$

1. To find the weight of the isomer adsorbed (x):

   x = original weight of isomer in solution - the final weight of isomer in solution

a) Original weight of isomer in solution in contact with <u>m</u> g. of adsorbent (w_6)

$$w_6 = w_1 \times w_2/w_3$$

where:

w_1 = weight of solution in contact with the alumina

w_3 = weight of sample of original solution (in 10 ml. flask)

w_2 = weight of isomer in sample (w_3) by infrared analysis.

b) Final weight of isomer in solution at equilibrium (w_7):

$$w_7 = \frac{(w_1 - w_6) \times w_5}{w_4}$$

where:

w_4 = weight of solvent in the sample of equilibrium solution

w_5 = weight of isomer in sample of equilibrium solution (of solvent weight w_4)

w_6 = weight of isomers in the solution in contact with the alumina (this is the weight of solvent in the original solution in contact with the alumina)

c) Weight of isomer adsorbed (x):

$$x = w_6 - w_7$$

2. Concentration of equilibrium solution (in gravimetric terms):

$$\text{conc.} = \frac{w_5}{w_4}$$

3. Weight of adsorbent (m) is found by direct weighing.

TABLE I

The adsorption of the Alpha isomer of Hexachlorocyclohexane on activated alumina at 23° ± 0.5° C.

w_1 g.	w_2/w_3 g./g.	w_4 g.	w_5 g.	w_6 g.	w_1-w_6 g.	w_7 g.	m g.	x g.	x/m g./g.	conc. g./g.
4.7247	0.0012	3.1779	0.001	0.006	4.7187	0.002	0.6562	0.004	0.006	0.0003
5.9580	0.0022	4.4493	0.002	0.013	5.9450	0.003	0.5794	0.010	0.017	0.0004
5.6306	0.0056	3.7883	0.002	0.031	5.5996	0.003	0.8037	0.028	0.035	0.0006
5.6740	0.0056	3.8518	0.004	0.032	5.6420	0.005	0.6990	0.027	0.039	0.0009
5.5892	0.0056	3.8311	0.006	0.031	5.5582	0.009	0.5939	0.022	0.037	0.0015
16.1786	0.0093	7.1737	0.012	0.151	16.0276	0.027	3.0166	0.124	0.041	0.0017
5.3800	0.0056	3.5446	0.007	0.030	5.3500	0.011	0.4960	0.019	0.038	0.0020
4.9578	0.0070	3.4211	0.008	0.034	4.9238	0.011	0.6288	0.023	0.037	0.0023
5.9751	0.0056	4.3113	0.011	0.034	5.9411	0.015	0.4442	0.019	0.043	0.0026
6.0094	0.0056	4.4528	0.013	0.034	5.9754	0.017	0.4015	0.017	0.042	0.0029
4.6249	0.0095	3.1108	0.012	0.044	4.5809	0.018	0.5564	0.026	0.047	0.0038
5.5990	0.0093	3.8503	0.018	0.052	5.5470	0.026	0.6039	0.026	0.043	0.0047
22.9236	0.0081	6.8718	0.032	0.185	22.7386	0.107	1.7032	0.078	0.046	0.0047
19.8275	0.0081	7.8333	0.038	0.160	19.6675	0.096	1.3397	0.064	0.048	0.0049
5.4871	0.0093	3.9260	0.020	0.051	5.4361	0.028	0.5066	0.023	0.046	0.0051
5.7507	0.0093	4.1526	0.024	0.053	5.6977	0.033	0.4493	0.020	0.045	0.0061
5.9688	0.0105	4.4358	0.028	0.063	5.9058	0.038	0.6025	0.025	0.042	0.0063
21.4451	0.0081	7.0588	0.046	0.173	21.2721	0.140	0.7728	0.033	0.043	0.0066
5.5071	0.0105	3.7189	0.025	0.058	5.4491	0.037	0.5064	0.021	0.042	0.0067
5.6811	0.0093	4.1370	0.029	0.053	5.6281	0.040	0.3648	0.013	0.036	0.0071
5.6079	0.0105	3.7509	0.031	0.059	5.5489	0.046	0.4062	0.013	0.032	0.0083
5.4344	0.0105	3.9034	0.035	0.057	5.3774	0.049	0.2873	0.008	0.028	0.0089
6.1034	0.0105	4.3527	0.039	0.065	6.1284	0.055	0.3438	0.010	0.029	0.0089

TABLE II

The adsorption of the Delta isomer of Hexachlorocyclohexane on activated alumina at 23° ± 0.5° C.

w_1 g.	w_2/w_3 g./g.	w_4 g.	w_5 g.	w_6 g.	w_1-w_6 g.	w_7 g.	m g.	x g.	x/m g./g.	conc. g./g.
5.2350	0.0011	3.5231	0.000	0.006	5.2290	0.000	0.6849	0.006	0.009	0.0000
5.6467	0.0047	4.1050	0.001	0.026	5.6207	0.001	0.6254	0.025	0.040	0.0003
4.7099	0.0017	3.4165	0.001	0.008	4.7019	0.001	0.6679	0.007	0.010	0.0003
4.8755	0.0034	3.3270	0.001	0.016	4.8595	0.002	0.7197	0.014	0.020	0.0003
5.3708	0.0075	3.8407	0.002	0.040	5.3308	0.003	0.6708	0.037	0.055	0.0005
4.5899	0.0066	3.1486	0.002	0.030	4.5599	0.003	0.6963	0.027	0.039	0.0006
5.0383	0.0074	3.2436	0.003	0.037	5.0013	0.005	0.7341	0.032	0.044	0.0009
4.8692	0.0119	3.3538	0.005	0.058	4.8112	0.007	0.6561	0.051	0.078	0.0015
4.9996	0.0153	3.4407	0.010	0.077	4.9226	0.014	0.6445	0.063	0.098	0.0029
5.5827	0.0085	4.4041	0.028	0.047	5.5350	0.035	0.1308	0.012	0.092	0.0063
5.6381	0.0163	3.9292	0.027	0.092	5.5461	0.038	0.5368	0.054	0.100	0.0069
5.5353	0.0163	3.8731	0.031	0.090	5.4453	0.044	0.4511	0.046	0.102	0.0080
5.9774	0.0163	4.4445	0.041	0.098	5.8794	0.054	0.4101	0.044	0.107	0.0092
5.9965	0.0163	4.5505	0.047	0.098	5.8985	0.061	0.3534	0.037	0.105	0.0103
5.0174	0.0147	3.6386	0.039	0.074	4.9434	0.053	0.2089	0.021	0.100	0.0107
5.9825	0.0163	4.5303	0.050	0.098	5.8845	0.065	0.3139	0.033	0.105	0.0110
5.1828	0.0147	3.7926	0.049	0.076	5.1068	0.066	0.0996	0.010	0.100	0.0129

TABLE III

The adsorption of the Gamma isomer of Hexachlorocyclohexane on activated alumina at 23° ± 0.5° C.

w_1 g.	w_2/w_3 g./g.	w_4 g.	w_5 g.	w_6 g.	w_1-w_6 g.	w_7 g.	m g.	x g.	x/m g./g.	conc. g./g.
5.5181	0.0015	4.0108	0.000	0.008	5.5101	0.000	0.6712	0.008	0.012	0.0000
4.9760	0.0030	3.5008	0.001	0.015	4.9610	0.001	0.6702	0.014	0.021	0.0003
4.4587	0.0056	2.9658	0.002	0.025	4.4337	0.003	0.6880	0.022	0.032	0.0010
6.1905	0.0118	4.7470	0.023	0.073	6.1175	0.029	0.6257	0.044	0.070	0.0048
5.6848	0.0145	4.2031	0.026	0.082	5.6028	0.034	0.6234	0.048	0.077	0.0062
6.3525	0.0218	4.4482	0.056	0.139	6.2135	0.078	0.5993	0.061	0.102	0.0126
6.4264	0.0218	4.5997	0.062	0.140	6.2864	0.084	0.5017	0.056	0.110	0.0135
6.3828	0.0218	4.7519	0.073	0.139	6.2438	0.096	0.3989	0.043	0.108	0.0154
6.0969	0.0218	4.4609	0.078	0.132	5.9649	0.104	0.2969	0.028	0.094	0.0175
6.0272	0.0218	4.5806	0.086	0.132	5.8952	0.110	0.1978	0.022	0.110	0.0187
6.0745	0.0218	4.6914	0.097	0.135	5.9395	0.123	0.0993	0.010	0.101	0.0206

TABLE IV

The adsorption of isomers in a mixture of the Alpha and Delta isomers of Hexachlorocyclohexane on activated alumina at 23° ± 0.5° C.

ALPHA ISOMER

w_1 g.	w_2/w_3 g./g.	w_4 g.	w_5 g.	w_6 g.	w_1-w_6 g.	w_7 g.	m g.	x g.	x/m g./g.	conc. g./g.
6.3966	0.0043	4.4448	0.004	0.027	6.3396	0.006	0.7993	0.021	0.026	0.0009
6.0982	0.0047	4.4126	0.005	0.028	6.0392	0.007	0.7503	0.021	0.028	0.0011
5.5361	0.0043	4.0258	0.005	0.024	5.4861	0.007	0.7026	0.017	0.024	0.0012
6.3765	0.0047	4.7884	0.008	0.030	6.3145	0.011	0.6547	0.019	0.029	0.0017
6.2932	0.0043	4.7650	0.008	0.027	6.2372	0.011	0.6005	0.016	0.027	0.0017
6.2736	0.0043	4.8279	0.010	0.027	6.2176	0.013	0.5010	0.014	0.028	0.0021
6.2524	0.0047	4.7576	0.010	0.029	6.1914	0.013	0.5462	0.016	0.029	0.0021
6.4042	0.0047	4.8774	0.012	0.030	6.3422	0.016	0.4517	0.014	0.031	0.0025
6.1884	0.0043	4.7644	0.012	0.026	6.1334	0.015	0.3993	0.011	0.028	0.0025
5.9510	0.0047	4.5127	0.013	0.028	5.8930	0.017	0.3490	0.011	0.031	0.0029
5.8237	0.0077	4.1430	0.021	0.045	5.7227	0.029	0.5986	0.016	0.027	0.0051
6.3384	0.0078	4.5397	0.023	0.050	6.2274	0.032	0.6501	0.018	0.028	0.0051
6.5062	0.0078	4.9194	0.026	0.051	6.3922	0.034	0.5502	0.017	0.031	0.0053
6.0764	0.0078	4.5054	0.025	0.048	5.9704	0.033	0.4511	0.015	0.033	0.0056
7.0594	0.0077	5.2772	0.030	0.055	6.9364	0.039	0.4009	0.016	0.040	0.0057
6.6459	0.0077	4.9827	0.029	0.051	6.5319	0.038	0.5000	0.013	0.026	0.0058
6.2475	0.0078	4.8557	0.030	0.049	6.1385	0.037	0.3479	0.012	0.034	0.0062
6.4796	0.0077	4.9576	0.033	0.050	6.3676	0.042	0.2923	0.008	0.027	0.0067
5.9625	0.0078	4.4913	0.030	0.047	5.8585	0.039	0.2514	0.008	0.032	0.0067
5.9216	0.0078	4.7089	0.033	0.046	5.8186	0.041	0.2510	0.006	0.024	0.0070
5.8868	0.0077	4.2499	0.030	0.046	5.7848	0.041	0.2019	0.005	0.025	0.0071

(continued next page)

TABLE IV (Concluded)

DELTA ISOMER

w_1 g.	w_2/w_3 g./g.	w_4 g.	w_5 g.	w_6 g.	w_1-w_6 g.	w_7 g.	m g.	x g.	x/m g./g.	conc. g./g.
6.0982	0.0051	4.4126	0.001	0.031	6.0392	0.001	0.7503	0.030	0.040	0.0002
5.5361	0.0046	4.0258	0.001	0.026	5.4861	0.001	0.7026	0.025	0.035	0.0003
6.3765	0.0051	4.7884	0.002	0.032	6.3145	0.003	0.6547	0.029	0.044	0.0004
6.2524	0.0051	4.7576	0.002	0.032	6.1914	0.003	0.5462	0.029	0.053	0.0004
6.2932	0.0046	4.7650	0.002	0.029	6.2372	0.003	0.6005	0.026	0.043	0.0004
6.2736	0.0046	4.8279	0.003	0.029	6.2176	0.004	0.5010	0.025	0.050	0.0006
6.1884	0.0046	4.7644	0.005	0.029	6.1334	0.006	0.3993	0.023	0.058	0.0011
5.9510	0.0051	4.5127	0.006	0.030	5.8930	0.008	0.3490	0.022	0.063	0.0013
5.3617	0.0051	3.8823	0.008	0.027	5.3097	0.011	0.2533	0.016	0.063	0.0021
6.3384	0.0096	4.5397	0.010	0.061	6.2274	0.014	0.6501	0.047	0.072	0.0022
5.8237	0.0096	4.1430	0.010	0.056	5.7227	0.014	0.5986	0.042	0.070	0.0024
6.5062	0.0096	4.9194	0.015	0.063	6.3922	0.020	0.5502	0.043	0.078	0.0031
6.6459	0.0096	4.9827	0.018	0.063	6.5319	0.024	0.5000	0.039	0.078	0.0036
6.0764	0.0096	4.5054	0.017	0.058	5.9704	0.023	0.4511	0.035	0.078	0.0038
6.2475	0.0096	4.8557	0.023	0.060	6.1385	0.029	0.3479	0.031	0.089	0.0047
6.4796	0.0096	4.9576	0.026	0.062	6.3676	0.033	0.2923	0.029	0.099	0.0052
5.9625	0.0096	4.4913	0.026	0.057	5.8585	0.034	0.2514	0.023	0.092	0.0058
5.8868	0.0096	4.2499	0.026	0.056	5.7848	0.035	0.2019	0.021	0.104	0.0061
5.4887	0.0096	4.1551	0.032	0.052	5.3947	0.042	0.0989	0.010	0.101	0.0077

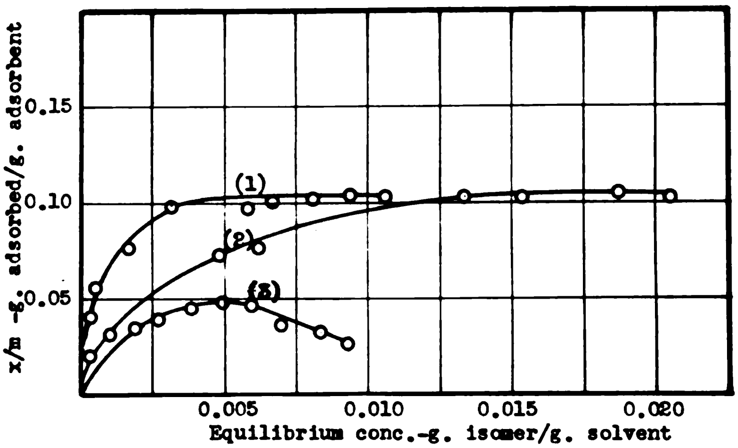

Fig. 1 Adsorption isotherms of pure isomers of Hexachlorocyclohexane. (1) Delta, (2) Gamma, (3) Alpha.

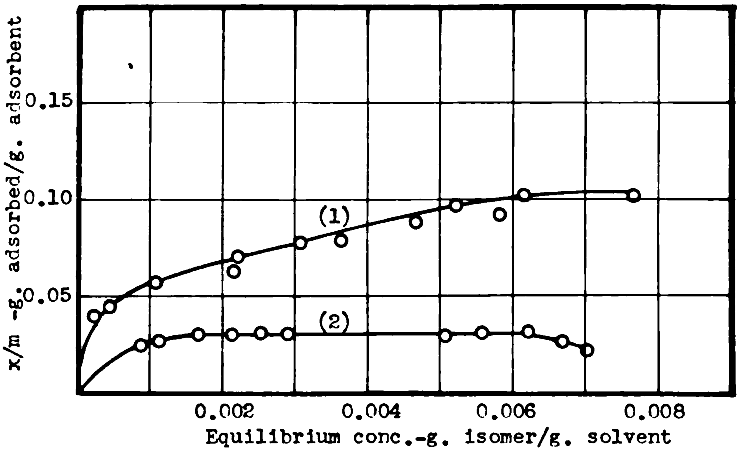

Fig. 2 Adsorption isotherms of isomers in isomer mixtures. (1) Delta, (2) Alpha.

DISCUSSION

In Figure 1, even though all of the points do not give the desired smooth curve for an adsorption isotherm, there is a definite tendency of a decided trend. Most of the difficulties can be attributed to the low solubility of the isomers in hexane, which caused a considerable portion of the work to be with low concentrations. This low solubility is a characteristic property of the isomers in most solvents as shown in the work of Slade. (3)

Solubility of Isomers at 20°C (3)

Solvent	Solubility g./100 g. solution Alpha	Gamma	Delta
Acetone	13.9	43.5	71.1
Benzene	9.9	28.9	41.1
Carbon Tetrachloride	1.8	6.7	3.6
Cyclohexane	1.4	4.6	2.7
Ethyl alcohol	1.8	6.4	24.2
Methyl alcohol	2.3	7.4	27.3
Pentane	0.9	2.2	1.6

The isotherms of alpha and delta isomers represent the true adsorption of each by activated alumina, while the isotherm for the gamma isomer represents not only the adsorption of the gamma isomer but also the conversion of this isomer to the delta isomer. Due to this conversion the isotherm is higher than the true adsorption isotherm would be for this isomer. However, the isotherm represents the removal of gamma from solution by alumina and will be useful in correlating this data to chromatographic data. The subject of the gamma isomer conversion to the delta isomer while in contact with alumina will be treated later in this paper.

It should be noted that the alpha isomer isotherm passes through a maximum and at higher concentrations the x/m value decreases. This action can possibly be accounted for by negative adsorption. This type of adsorption is not uncommon and takes place with many compounds and adsorbents. (8) The theory for negative adsorption is that the solvent is adsorbed more than the solute in high concentration of the solute, and the Langmuir and Freundlich adsorption equations hold only for low concentrations.

From the isotherms of the three isomers it can be seen that the delta isomer is adsorbed the most strongly, the gamma isomer next and the alpha isomer the least strongly. It was surprising to find that the gamma isomer increased at high equilibrium concentrations to an adsorption value equal to that of the delta isomer. But it should be noted that this concentration far surpasses the highest concentration that could be obtained for delta. The upper limit of each isotherm is necessarily fixed by the solubility of that isomer. As the solubility of delta is much lower than that of gamma it was impossible to extend the delta isotherm to the higher concentrations. Therefore only the strength of adsorption at comparable equilibrium concentrations can be correlated. When this is done the order of adsorption is then as first stated.

The discussion to this point has pertained only to the adsorption of pure isomers on alumina with the exception of the gamma isomer which contained about 5% alpha by weight. It was of interest to see how these pure isomer adsorption isotherms would be effected by having another isomer present. For this study a mixture of alpha and delta isomers was selected. The ratio of delta to alpha ranged from 1:1 to 1.5:1. As can be seen in Figure 2, the delta isomer still was adsorbed to the greatest extent although it did not reach its maximum x/m value until a higher concentration than when by its self. On the other hand, the alpha isotherm was lowered almost 50% from its pure isomer isotherm. This was entirely as expected and even though similar experiments using the gamma isomer have not been carried out as yet, it can be expected that the adsorption will be lowered just as alpha was but not to such a large extent. Further it can be expected that gamma would lower the isotherm for alpha while alpha would not have too much effect on the isotherm for gamma.

It was thought that the ratio of isomers in a mixture would have an influence on the x/m value but it was found that in the limited range of ratios used in the alpha-delta mixture that the ratio had no effect on this value. However, because the ratios were so limited no definite conclusions can be drawn. Further work is necessary over a much wider range before definite conclusions can be reached.

The correlation of this adsorption data with the chromatographic data of Saur (6) is very good. One might predict from the adsorption isotherms that the order of the isomers on the chromatographic column would be delta in the top zone, gamma in the middle and alpha in the bottom zone. Saur found this to be exactly the case when he used an alumina column to separate the isomers of commercial hexachlorocyclohexane.

His order of elution was alpha first, overlapping slightly with gamma which was eluted next. He found it almost impossible to elute the delta isomer due to its strong adsorption by alumina. If the correlation is correct and taking into consideration the overlapping of gamma and alpha on elution the isotherm of gamma is too high. As was previously noted it was believed that the isotherm was high due to conversion of gamma to delta. It was found impossible to correct this isotherm for the conversion.

The conversion was first noted in the determination of the isotherm for the gamma isomer. It was noted that the original solution of gamma contained 95% gamma and 5% alpha. At the maximum there was less than 1% of delta. However in some of the equilibrium solutions as high as 8% of delta would appear. For example in one run the original solution contained: 0.082 g. of gamma, 0.005 g. of alpha and 0.000 g. of delta. After 72 hours, in the equilibrium solution was found: 0.034 g. of gamma, 0.002 g. of alpha and 0.009 g. of delta. Here it can be seen that at least 0.009 g. of the 0.048 g. of gamma that was removed from solution was due to conversion to delta. Exactly how much gamma converted to delta is difficult to ascertain as it must be assumed that some of the delta itself was adsorbed.

The existance of a factor for the conversion of the gamma isomer to the delta isomer was carefully investigated. Having a factor would have made it possible to correct the adsorption isotherm of the gamma isomer to true adsorption values. No factor of time of contact with the alumina or mass of the isomer present was found to exist but a slight correlation was found to exist between the amount of conversion and the amount of alumina that was in contact with isomer. The amount of conversion increases as the amount of alumina increases. This correlation proved of little value in correcting the gamma isomer isotherm and work along this line was discontinued.

Interpretation of the above data leads to an interesting theory. If the conversion takes place not only during adsorption by alumina but also during any adsorption process then the use of hexachlorocyclohexane as an insecticide would be very limited even if the pure isomer of gamma was used for this purpose. The reason is that while gamma is tasteless and odorless, the delta isomer has a very displeasing odor and taste which is ever present in vegetation that it has been used on as an insecticide. It is known that the insecticide is strongly adsorbed by vegetation. Therefore if conversion takes place even the pure gamma would give traces of the displeasing delta isomer, making its use on vegetation that is used for food out of the question.

To be certain that the data being recorded was true adsorption data, some of the factors were varied. Factors such as the ratio between weight of solution and weight of adsorbent were varied over a considerable range. It was found that ratio could be varied over a considerable range, except when the amount of alumina became too small. Here it is believed that the adsorption still progresses the same as with larger amounts of alumina but the amount of isomer that is adsorbed is so small that slight errors in the analysis would appear very large in the final x/m value. The lower limit of the amount of alumina that could be used was placed at 0.1000 g. Even at this amount it is evident that any error in the amount of isomer adsorbed is magnified ten times in the x/m value.

Other factors that were varied are as follows: Some series were run by varying the concentration of the original solution and holding the amount of alumina constant. These were followed by a series with a constant solution and varying the weight of the alumina. To check the accuracy of the adsorption values found for the isomers in the small amounts that could be used in the 10 ml. ampules, a few series were run in special large glass tubes. Also the method of analysis was changed on two alpha series. In general the method of analysis was with the infrared spectrophotometer. In these two alpha series the concentrations were determined by accurate weighings. With all of these variations the values for x/m still were such that they fell on the same adsorption isotherm. From the above the method can be concluded to be correct.

The separation of the equilibrium solution from the adsorbent was made by filtering through ashless filter paper. The possibility that this procedure would introduce an error in the results due to adsorption of the isomers by the filter paper or due to loss of solvent by evaporation during the filtering process was carefully investigated. A number of solutions of the isomers were filtered under parallel conditions to those encountered in the filtering of the solutions in contact with the alumina. All filtering was carried out in a constant temperature room that also maintained a constant humidity. The temperature of the room was $23^\circ \pm 0.5^\circ$ C. and the humidity was 53-55%.

These blank runs determined that if there was adsorption of the isomers by the filter paper and loss of the solvent due to evaporation that they balanced each other in such a manner that the concentration of the solution being filtered remained unchanged during the process. As only the concentration of the filtrate is necessary in the calculation of x/m this method of separation was used throughout the work.

Another precaution was the checking of whether alumina contained any material that would effect the extinction readings of the infrared spectrophotometer. Hexane was placed in contact with alumina for a period of 72 hours and was then analysed with hexane that had not come in contact with alumina. Both of these samples were evaporated to dryness and any residue was dissolved in carbon disulphide and analysed in the spectrophotometer. Both gave the same extinction values at the wavelengths used for the isomer analysis.

More extensive work was done on the alpha and delta isomers than on the gamma isomer. There were several reasons for limiting the work done on the gamma isomer. First, the characteristic wavelength for gamma analysis by infrared analysis is 14.53 microns. This is a very low energy wavelength and requires a high amplification to observe the effects of adsorption. Slight variations in the current make it impossible to obtain steady extinction values. Readings in this range are therefore subjected to considerable error. As an alternative method of analysis direct weighing of the isomer was attempted as with the alpha isomer. Immediately the difficulty of drying the sample arose. Not only does gamma have a low melting point but as it precipitates from hexane it occludes the solvent. At no time was it possible to get constant weights as was possible with the alpha isomer. This method of analysis was discarded for the gamma isomer. As no satisfactory method of analysis was obtained for gamma and knowing that conversion of the gamma isomer to the delta isomer was taking place, only enough work was done on the gamma isomer to obtain a trend of how it was removed from solution.

CONCLUSIONS

1. The order of adsorption by activated alumina of the three principal isomers of hexachlorocyclohexane is; delta the most strongly adsorbed, gamma next and alpha the least strongly.
2. The order of adsorption by alumina is the same order as observed on a chromatographic column of alumina. That is, the delta isomer forms the top band on the column, gamma in the middle and alpha in the bottom band.
3. The gamma isomer is converted in part while in contact with the alumina, into the delta isomer.
4. In mixtures of the isomers the most strongly adsorbed isomer is not influenced too greatly by the other isomers except at low concentrations. At these low concentrations its isotherm is lowered but still remains above those of the other isomers present.

REFERENCES

1. Dickinson, R. G. and Bilicke, C., J. Am. Chem. Soc., 50, 764 (1928)
2. Smith, H. P., Noyes, W. A. Jr. and Hart, E. J., J. Am. Chem. Soc., 55, 4444-59 (1933)
3. Slade, R. E., Chem. and Ind., 1945, 314-9
4. Hendricks, S. B. and Bilicke, C., J. Am. Chem. Soc., 48, 3007 (1926)
5. Gilman, H., Organic Chemistry, An Advanced Treatise, John Wiley and Sons, New York, 1947, Vol. 1, 2nd Ed., p. 336-7
6. Saur, R. L., Michigan State College, Ph. D. Thesis (1949)
7. Daasch, L. W., Anal. Chem., 19, 779-85 (1947)
8. Lewis, W. K., Squires, L. and Broughton, G., Industrial Chemistry of Colloidal and Amorphous Materials, Macmillan Co., New York, 1948, p. 90-1

Gilbert

Gilbert

The adsorption of the alpha, delta and gamma isomers of hexachlorocyclohexane by activated alumina.

Karl Bielefeld FEB 1 '50	
SEP 2 '50	
[illegible]	