

A STUDY OF THE LIGHT CATALYZED
CHLORINATION OF BENZENE

125

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SUMMARY

In the light catalyzed chlorination of benzene to produce benzene hexachloride, conditions of the reaction were varied in an effort to find the optimum conditions for the highest yield of the gamma isomer. It was found that the most satisfactory temperature range for a liquid phase reaction lies between 20 and 40° C. When using a method of synthesis in which chlorine is passed continuously into the benzene, the highest percentage of gamma isomer is obtained when the chlorine uptake is equal to or greater than the weight of benzene used. The variation of neither temperature nor chlorine uptake produced an increase in the yield of gamma above that of the usual commercial preparation. The use of solvents, catalysts, and a few common adsorbents was also tried without success. One of the substances used as a catalyst, sodium hydroxide, was found to increase the induction period of the reaction. Alumina, when used as an adsorbent, produced the same effect and also reduced the yield of the benzene hexachloride itself. With the apparatus used, ultraviolet light also failed to affect the quantity of gamma produced. Though the evidence is inconclusive, the vapor phase reaction seems to have no advantage over that of the liquid phase.

CHAPTER I

INTRODUCTION

Definition of the Problem.--When benzene is reacted with chlorine in the presence of actinic radiation, a white crystalline solid is produced. This product is hexachlorocyclohexane, commonly called benzene hexachloride or BHC by commercial producers. The chlorine atoms are distributed one to each carbon atom of the ring. The product consists of a mixture of several geometrical isomers only one of which, the gamma isomer, is of commercial importance at the present time. This isomer has strong insecticidal properties comparable to DDT, while the other isomers are relatively inactive along these lines. Unfortunately, the gamma isomer is not the one produced in the greatest yield. In commercial BHC, the approximate percentage composition is as follows: Alpha isomer 70 per cent, beta isomer 5 per cent, gamma isomer 12 per cent, and delta isomer 13 per cent¹. The commercial product may also contain 3-4 per cent of epsilon isomer² as well as hepta- and octachlorocyclohexanes.

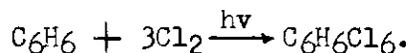
Since only the gamma isomer has strong insecticidal activity, it is apparent that it would be highly desirable to increase the yield of this isomer in relation to that of the others. It was the objective of

¹R. E. Slade, Chem. and Ind., 314 (1945).

²K. C. Kauer, R. B. Duvall, and F. N. Alquist, Ind. Eng. Chem., 39, 1335 (1947).

this research to study the light catalyzed reaction of benzene with chlorine with special attention being given to the possibility of increasing the yield of the gamma isomer. Practically nothing is known as to what factors may influence the composition of the crude product, but purely statistical considerations tend to agree with the actual results in so far as the alpha and beta isomers are concerned.¹ In this research, the various conditions under which the reaction proceeds were varied and the product analyzed for gamma isomer content. Typical of the conditions which were changed are temperature, light intensity, physical state of the reactants, and ratio of the reactants. The catalytic effect of a limited number of compounds and the effect of some common adsorbents was studied.

Historical.--In the absence of a halogen carrier, the reaction which takes place is addition of chlorine to the "double bonds" of benzene instead of substitution on the aromatic ring. This equation is written as follows:



At the present time, the reaction is believed to have some of the characteristics of the free radical mechanism and is thought to belong to this class.³ It takes place very slowly in the dark but will occur readily in the presence of sunlight or ultraviolet radiation. Also, it usually has a short induction period.

³C. E. Lane, Jr. and W. A. Noyes, Jr., J. Am. Chem. Soc., 54, 161 (1932).

It was Michael Faraday⁴ who first described the reaction of benzene and chlorine in the presence of sunlight to give a solid product which was undoubtedly benzene hexachloride.

In a later investigation of the reaction, Meunier⁵ discovered that the product was composed of a mixture of isomers. After some difficulty, he separated the alpha isomer, which melted at 157° C., and the beta isomer, which melted at a much higher undetermined temperature. T. van der Linden⁶ established the existence of four isomers having the following melting points: alpha 158° C., beta over 200° C., gamma 108-111° C., and delta 129-132° C.

Slade¹, while delivering the Hurter lecture in 1945, announced the outstanding insecticidal properties of the gamma isomer. This property had been discovered as a result of an intensive effort to find a suitable substitute for rotenone, which was in critically short supply during the war. The insecticidal activity was first noticed in a technical sample of benzene hexachloride, but different samples tended to give different results. This inconsistency led to a search for an active principle which was thought to be a possible impurity. A tedious and inefficient separation of the isomers by fractional crystallization was started. Upon isolation of the gamma isomer, it was found that almost all of the insecticidal activity of BHC was due to this one isomer alone.

⁴M. Faraday, Trans. Roy. Soc., (London), [A], 440 (1825).

⁵M. J. Meunier, Ann. Chim. et Phys., [6], 10, 223 (1887).

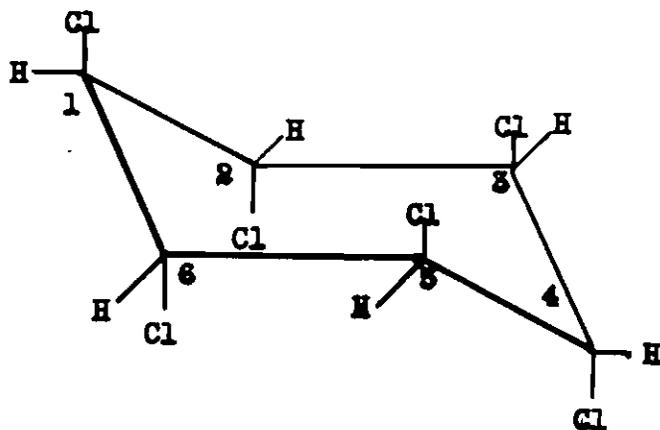
⁶T. van der Linden, Ber., 45, 231-247 (1912).

The melting points of the pure isomers were reported by Slade as follows: alpha 157.5° C., beta 309° C., gamma 112.5° C., and delta 138-139° C. An additional isomer, the epsilon isomer, present in amounts of less than two per cent, has since been discovered by Kauer² and co-workers.

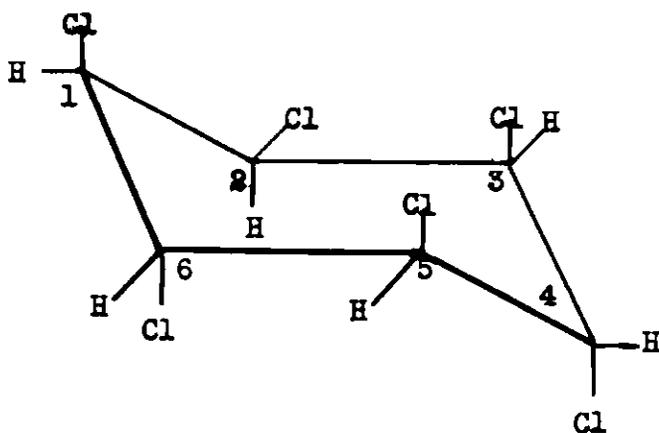
Not all authors agree as to the number of isomers which may exist. Their conclusions are apparently dependent upon what configuration is assumed for the cyclohexane ring. Slade¹, who assumes the "Z" configuration for the cyclohexane ring proposes sixteen possible isomers. However, he eliminates eleven of these because of the strain involved by too close approach of chlorine atoms to one another. Daasch⁷, who considers both the "Z" and "C" configurations arrives at the conclusion that eighteen isomers are possible in theory. Due to considerations of strain, he also eliminates many of them, stating that only seven are actually capable of formation. The 1,3,5-cis configuration is the configuration of the beta isomer and is the only one which has been proved⁸. However, most authors agree that the following configurations for the other three most common isomers are probably correct. The alpha is thought to be the 1,2,4-cis; the gamma 1,2,3,5-cis; the delta 1,2,3-cis. This method of nomenclature was devised to fit the planar concept of the cyclohexane ring and means that the chlorine atoms attached to the carbon atoms numbered are on the same side of the ring. In Fig. 1 the beta and gamma isomers are shown in the "Z" configuration of the ring. Also shown is the "C" configuration which is thought to be convertible to that of the "Z", the activation energy for the change being very low.

⁷L. W. Daasch, Anal. Chem., 19, 779 (1947).

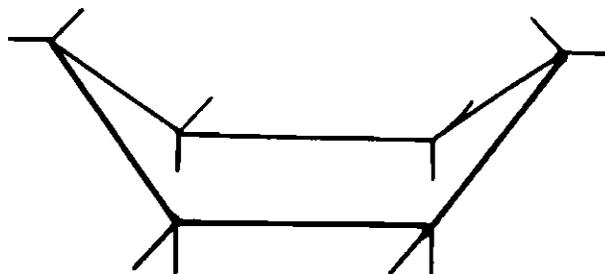
⁸R. G. Dickinson and C. Bilick, J. Am. Chem. Soc., 50, 764 (1928).



Beta Isomer, "Z" Configuration



Gamma Isomer, "Z" Configuration



"C" Configuration of Cyclohexane Ring

Fig. 1

In a large number of instances, BHC is just as satisfactory an insecticide as DDT. The following cases involving some common insects will demonstrate this effectively. The boll weevil is to a great extent unaffected by DDT, but the effect of BHC on this insect is quite deadly. It has been found that 0.09 mg./ml. of BHC or 1.6 mg./ml. of DDT is required to cause fifty per cent mortality in the case of the common housefly. After forty-eight hours both are fatal to the larvae of the anopheles mosquito when used in concentration of 0.01 parts per million⁹.

Many of the early experimenters prepared the compound simply by passing chlorine gas through benzene which contained a very dilute solution of sodium hydroxide^{10,6}. The reaction was carried out in the presence of sunlight. Usually the benzene and the base were not stirred but allowed to remain in two distinct layers. The dilute base is not necessary since the reaction will occur without it. Even though the compound has since become of great commercial importance, its preparation today is essentially the same. Several patents exist which set forth minor changes in the procedure such as the use of ultraviolet radiation of specific wave lengths or the use of polychlorinated organic solvents such as chloroform or carbon tetrachloride^{11,12,13}. A method

⁹H. L. Haller, Ind. Eng. Chem., 39, 467 (1947)

¹⁰F. E. Matthews, J. Chem. Soc., 59, 165 (1891)

¹¹J. Neil, A. E. McIlhinney, and B. G. Dunlop, Can. Chem. and Process Ind., 32, 335 (1948).

¹²Solvay and Cie, Belgian Patent 471,772 (1947).

¹³Solvay and Cie, Belgian Patent 469,299 (1947).

has been developed in which a fine spray of benzene is mixed with chlorine and then allowed to react¹⁴. Most of these patents claim a slight increase in the yield of gamma isomer.

Several techniques have been developed for analyzing the mixture of isomers which is produced. The two most popular methods are infrared spectroscopy^{7,15,16} and partition chromatography^{17,18}. In the former, it is possible to analyze for each isomer in the presence of the others. The latter method consists of a physical separation and weighing of the isomers. Other methods have also been used but are less popular, some of them having obvious limitations so far as the purpose intended here is concerned. A chemical method which consists of a rate measurement of dehydrochlorination of the various isomers is possible¹⁹. It is far too time consuming to be used when a large number of analyses are necessary. There is a cryoscopic method which requires a large quantity of pure gamma isomer as solvent²⁰. A polarographic method which permits determination of the gamma isomer in the presence of the others has been used²¹:

¹⁴A. Egart and Imperial Chemical Industries, Ltd., British Patent 504,569 (1939).

¹⁵D. H. Whiffen and H. W. Thompson, J. Chem. Soc., 1420 (1948).

¹⁶L. W. Marrison, J. Soc. Chem. Ind., 62, 192 (1949).

¹⁷O. T. Aepli, P. A. Munter, and J. F. Gall, Anal. Chem., 20, 610 (1948).

¹⁸L. L. Ramsey and W. I. Patterson, J. Assoc. Official Agr. Chem., 29, 337 (1946).

¹⁹B. La Clair, Anal. Chem., 20, 241 (1948).

²⁰C. B. Bowen and M. A. Pogorelskin, Ibid., 20, 346 (1948).

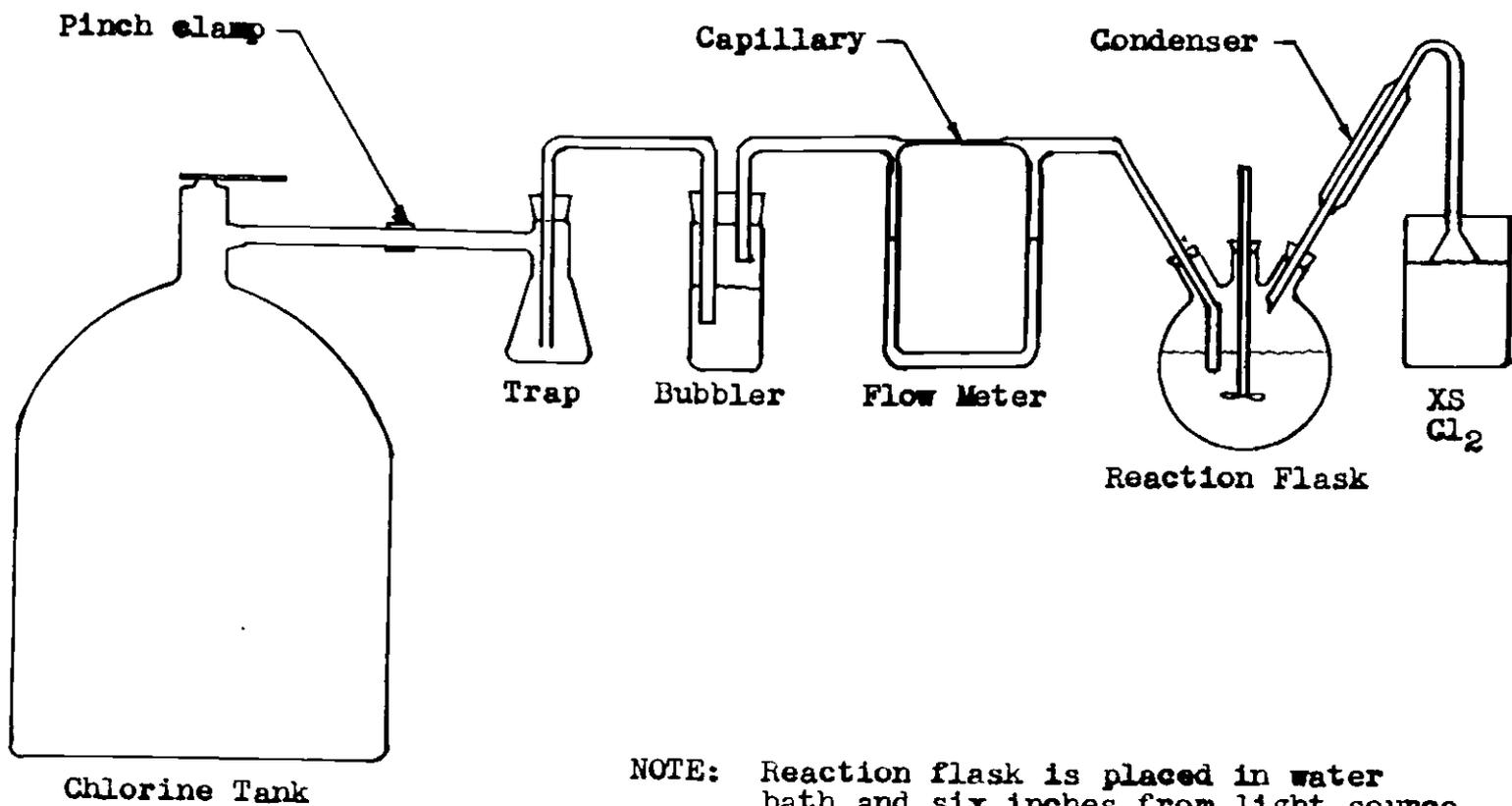
²¹G. Dragt, Ibid., 20, 737 (1948).

CHAPTER II

APPARATUS AND PROCEDURE

Apparatus.--Figure 2 shows the complete apparatus with the exception of the light source which was either an ultraviolet lamp or a three hundred watt unfrosted bulb placed about six inches from the reaction flask. Ordinary rubber stoppers were used at the reaction flask and the trap. The flow meter was used mainly as a method of maintaining, as constant as possible, the rate of introduction of chlorine. The amount of chlorine uptake was followed by actual gain in weight of the reaction mixture. A convenient method of controlling pressure was provided by the bubbler since the inlet tube could be raised or lowered, thus changing the amount of hydrostatic head to be overcome. Concentrated sulfuric acid was used in both the bubbler and flow meter. For gross control of pressure, a screw-type pinch clamp was placed just in front of the bubbler.

Pyrex glass was used throughout with the exception of connections which were made of "Tygon" plastic tubing. It is realized that pyrex glass is opaque to a large part of the ultraviolet spectrum and thus only a small part of the available light energy of this region was used. The Corning Company states that the chemical pyrex glass made by them transmits about 91 per cent in the visible range of the spectrum with transmission dropping off sharply at 3600 Angstrom units and is almost zero at 2800 Angstrom units. It was thought that sufficient transmission extended far enough into the ultraviolet range of the spectrum so that any change in the product due to light having such wave lengths would be detectable.



Apparatus Used in Synthesis of BHC

Fig. 2

The temperature of the reaction was controlled by placing the reaction flask in a water bath which could be maintained at a plus or minus one degree C. of the desired temperature. The reaction is exothermic but due to the small quantity of benzene used no difficulty was encountered in keeping the reaction mixture at the desired temperature.

The edge of the glass funnel at the end of the system was placed just beneath the surface of a beaker of concentrated sodium hydroxide. Any excess chlorine which did not react was thus absorbed by this solution.

Procedure for Making Preparation Runs.--After the reaction flask had been weighed, the apparatus was assembled and a known weight of reactants added. The inlet tube of the reaction flask was inserted and the chlorine tank, light source, and stirrer were turned on. The chlorine pressure was regulated so that it was just less than that required to bubble chlorine through the sodium hydroxide trap. The chlorination was stopped occasionally and the reaction flask weighed to determine the amount of chlorine uptake. After the desired amount of chlorine had been taken up, the reaction mixture was filtered and the excess benzene discarded. An analytical sample was prepared from the filtered and dried benzene hexachloride.

Analytical Procedure.--Analysis of the benzene hexachloride was first attempted, unsuccessfully, by a chromatographic technique, similar to that used by Aepli¹⁷ and coworkers. Due to lack of the suggested materials, it was necessary to simplify the apparatus somewhat, this perhaps accounting for the unsatisfactory results. Silica gel instead of

precipitated silicic acid was used as a support and suction by an aspirator instead of the use of positive pressure was tried. The method appeared to be effective inasmuch as the solid was separated into several distinct fractions. However, upon taking melting points of these fractions, little separation of the isomers was found to have occurred.

The next method of analysis tried was that of infrared spectroscopy. Several articles have been published on this method and the critical wave lengths and most satisfactory solvents are well known. The spectra of geometrical isomers usually have several absorption bands which coincide, but, in general, there will be one or more wave lengths at which there will be sufficient difference in absorption for analytical purposes. The gamma isomer has distinctive absorption peaks at 11.81 microns and at 14.53 microns⁷.

The equipment available for this work was the Beckman Model IR-2 Infrared Spectrophotometer equipped with a Brown automatic recording potentiometer. The solvent used to dissolve the analytical sample should be capable of dissolving enough BHC to give sufficiently strong absorption bands at a cell length small enough to keep the absorption of the solvent from overlapping that of the solute too much. The solvent should also be fairly non-volatile and readily obtainable in a pure condition. Carbon disulfide was first tried as a solvent but was found to dissolve so little of the gamma isomer that it could not be used with the spectrophotometer available. Nitromethane, though not quite so satisfactory from the viewpoint of transparency, was a better solvent. From preliminary transmission curves, it was found that a cell of longer light path than the standard 0.1 mm. was needed. A liquid absorption

cell of cell length 0.6350 mm. was constructed. In all cases, this machine was operated by sweeping through the desired wave length, a permanent record being made by the recording potentiometer. A spot analysis at one wave length by needle deflection was not attempted because of a tendency for the wave length to drift slightly.

In the absence of molecular interaction, the absorption of a solution should obey the law of Beer and Lambert. This relationship is as follows:

$$E = \log_{10} \frac{I_0}{I_s} = kcl.$$

where E equals extinction, I_0 equals light transmitted by the solvent, I_s equals light transmitted by the solution, k equals the extinction coefficient of the absorbing material, c equals concentration, and l equals length of solution path. If k and l are held constant, E plotted against c should be a straight line with a slope of kl. Several standard samples of pure gamma isomer in nitromethane were prepared and their transmission curves run*. At least ten such curves were run for each standard with an average E being computed for each. This average E was plotted against the concentration in grams per liter. The working curve obtained was almost a straight line, but a slight deviation from the Beer and Lambert law was observed at about twelve grams per liter. The standard samples were chosen so that they would have the same quantity of gamma isomer as an unknown sample ranging from zero to thirty per

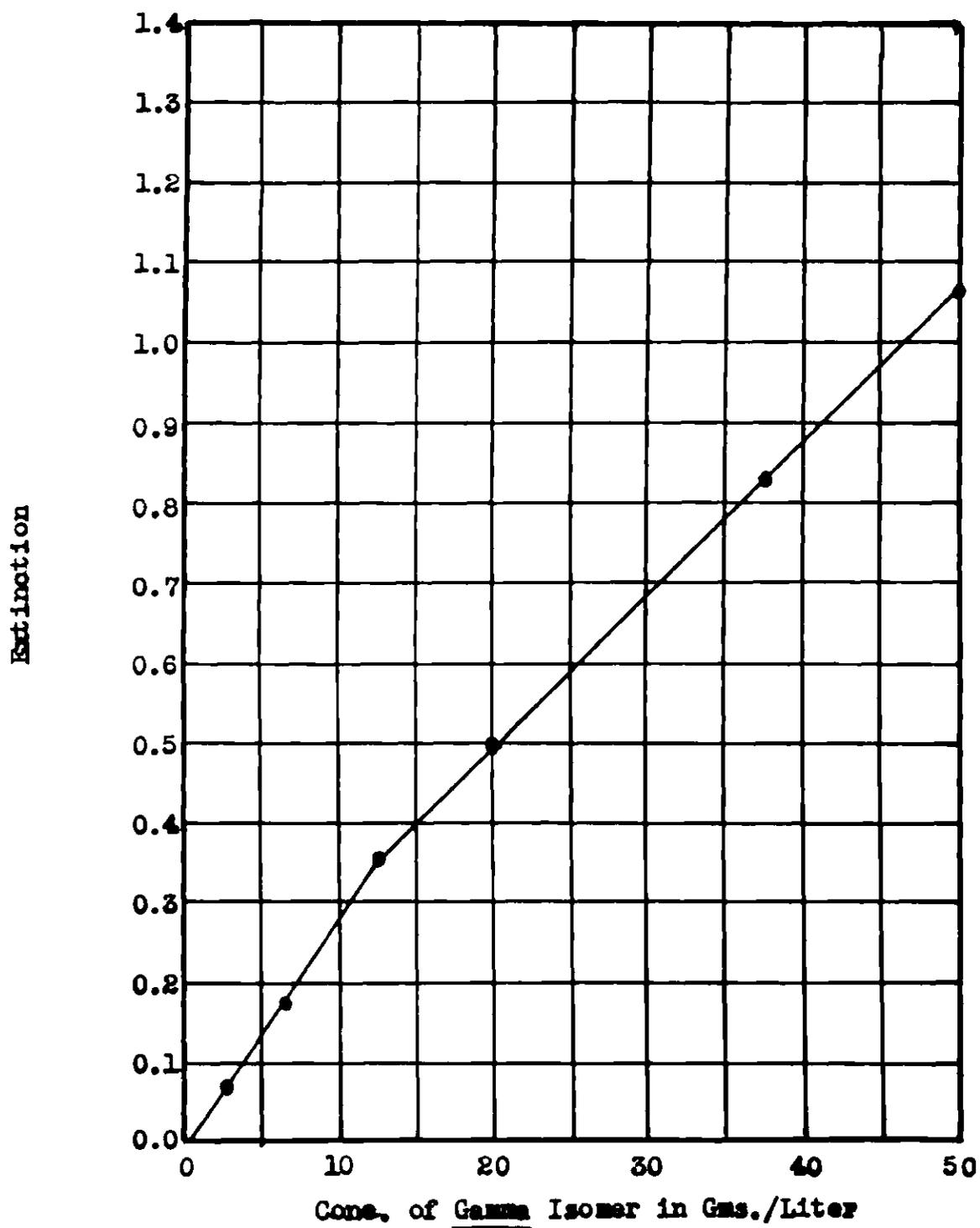
*The gamma isomer used was that obtained by fractional crystallization from a commercial sample furnished by the Tennessee Products and Chemical Corporation. It melted at 111.4-112.1 (uncorrected).

cent. Ten ml. of nitromethane was the quantity of solvent used in preparing both the standards and unknown samples. In the case of the standards just the required weight of pure gamma isomer was used. The unknowns were composed of 1.000 grams of the filtered product from a preparation run. In the case of the unknowns not all of the sample dissolved in the solvent. A check was made to see if any gamma isomer was left undissolved and it was found that the quantity remaining undissolved was negligible. By use of this working curve, i.e., the plot of E vs. concentration, it is possible to determine the concentration of gamma isomer in an unknown sample by finding the E at the critical wave length. This procedure was tested on four known samples and found to give results within a plus or minus three per cent of the actual gamma content.

In the infrared analysis of complex mixtures, the accuracy obtainable for a single component is a function of the composition of the whole sample and the spectroscopic nature of the solvent used. In the technique used here, some accuracy has been sacrificed for speed but the analysis is expected to be as accurate as that indicated above. The greatest single factor introducing error is that the transmission curves cannot be read more accurately than a plus or minus one per cent. This could be corrected to a great extent if a large number of transmission curves were taken for each sample and their average extinction used. This is obviously time consuming. Table 1 contains the data from which the working curve was constructed. Figures 3 and 4 are the working curve and a sample transmission curve of an unknown respectively. Figure 5 is a sample calculation of the gamma isomer content of the unknown of Figure 4.

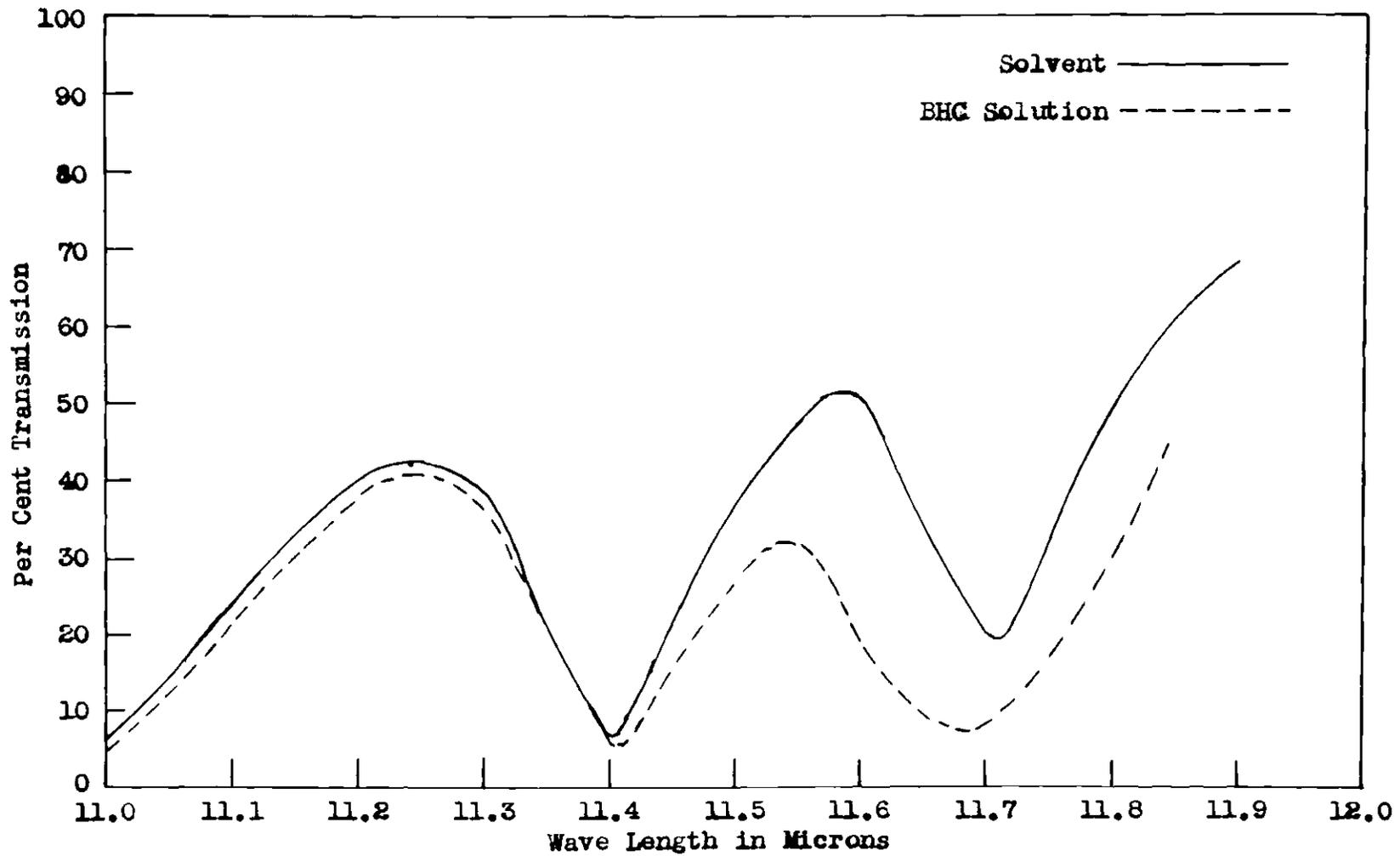
Table 1. Analytical Standards.

Standard	Gms. <u>gamma</u> isomer per 10 ml. of nitromethane	Average E	Concentration in gms. per liter
1	0.1250	0.3572	12.50
2	0.2500	0.5970	25.00
3	0.3750	0.8301	37.50
4	0.5000	1.0602	50.00
5	0.0250	0.0815	2.50
6	0.0625	0.1702	6.25



Analytical Working Curve

Fig. 3



Sample Transmission Curve

Fig. 4

1. Run number 52, the vapor phase run, will be used for this example. 1.000 gms. of the unknown was treated with 10.00 ml. of nitromethane. Upon conversion, this becomes 100.0 gms. per liter.

2. Obtain E of the unknown from the transmission curve, i.e., Figure 4, by reading I_0 and I_{unk} at 11.81 microns.

$$I_0 = 53.5$$

$$I_{unk} = 33.3$$

$$E = \log_{10} \frac{I_0}{I_{unk}} = 0.20575$$

3. Use Figure 3 to obtain the concentration of the gamma isomer. This is found to be 7.0 gms. per liter.

4. Compute the per cent gamma isomer in the sample as follows:

$$\frac{7.0}{100} \text{ times } 100 = 7.0\% \text{ gamma isomer.}$$

Sample Calculation of Per Cent Gamma Isomer

CHAPTER III

RESULTS AND CONCLUSIONS

Preliminary Runs and Separation of the Isomers.--The first part of the laboratory work was aimed at familiarization with the ordinary method of preparation and the properties of BHC, especially the separation of the various isomers. The second stage of the work was to be the establishing of a rapid method of analysis and the third stage that of increasing the yield of gamma isomer.

For familiarization, three preparation runs were made using benzene and chlorine and an unfrosted three hundred watt bulb as a light source. After each run, an attempt was made to separate the isomers using the method of Slade. Except for the alpha isomer which could be separated in a pure condition, none of the other isomers could be obtained pure. Other workers had encountered this same difficulty in separating the isomers and had turned to other methods, one of which was partition chromatography. As stated previously, this method was tried without success.

In order to obtain a sizable sample of the pure gamma isomer, five pounds of commercial BHC, specified to contain 14.2 per cent gamma isomer, was obtained from the Tennessee Products and Chemical Corporation. Using the same method of fractional crystallization, thirteen grams of gamma isomer was separated from the commercial BHC. This quantity of gamma was considered sufficient for making standard samples for the analytical procedure.

In none of these first three runs was the entire quantity of benzene reacted. While increasing the reaction time would increase the quantity of chlorine taken up, the time required for complete reaction would be prohibitive. The excess benzene was removed from the reaction mixture by distilling under reduced pressure. This procedure resulted in a dark colored product, probably due to some decomposition. On subsequent runs, the excess benzene was removed by filtration. Since the gamma isomer is more soluble in benzene than the alpha and beta isomers¹, filtration would cause the analytical result to be somewhat lower than the true gamma content.

Chlorination in the Presence of Sodium Hydroxide.--The use of sodium hydroxide as a possible method of increasing the gamma isomer yield was suggested by Gunther who, in a laboratory preparation, claimed a yield of 42.0 per cent gamma. His method consisted of simply chlorinating an emulsion of benzene and dilute sodium hydroxide under ultraviolet radiation. The preparation of the compound was incidental to the actual research and was thus not investigated further²².

The data for the runs using sodium hydroxide is contained in Table 2. All of these runs were made at 30° C., using a three hundred watt unfrosted bulb as a light source. The reaction mixture was filtered to obtain the product. A small piece of solid aerosol, usually about 0.3 grams, was used to obtain a satisfactory emulsion.

It is obvious that none of these runs produced results comparable to those of Gunther, and due to the limited accuracy of the analytical

²²F. A. Gunther, Chem. and Ind., 399 (1946).

Table 2. Effect of Sodium Hydroxide

Run	Ml. of benzene	Ml. of NaOH sol.	Conc. of NaOH sol.	Gms. NaOH per ml. of benzene	Time in hours	Wt. of product in gms.	% <u>gamma isomer</u>
8	20	40	3.0%	0.0590	4.0	5.86	5.4
9	20	40	1.0%	0.0191	4.0	6.82	11.0
27	20	40	0.5%	0.0096	2.3	5.08	7.8
46	20	10	0.1%	0.0005	2.3	11.90	7.1

method, little can be deduced of a general nature regarding the gamma isomer yield. It was found, however, that sodium hydroxide solutions of concentrations above three per cent tend to give inorganic salts in the product and leave the product strongly acid. Since this acid is extremely difficult to wash out or neutralize, analysis is difficult because of the danger of etching the rock salt crystals of the absorption cell. It was also noticed that the induction period of these runs was longer than that of runs using pure benzene. As can be seen from the data presented here, the best yield of gamma was obtained from a ratio of 0.019 grams of sodium hydroxide per ml. of benzene with the yield decreasing on either side of this value.

Chlorination in the Presence of Pyridine.---When the sodium hydroxide runs produced no improvements in the yield or the reaction, it was decided that possibly a weaker base might give the desired results. For this reason, pyridine, an organic base, was tried. The data for these runs is contained in Table 3.

In all cases, there was an immediate reaction of the chlorine to produce a white precipitate which was probably pyridine hydrochloride. Upon further chlorination, the product yielded chloropyridine of an undetermined structure. The evidence for this is that the final color of the precipitate was yellow to orange and could not be washed out with a base which would have been true of pyridine hydrochloride. Actually these products of chlorine and pyridine proved very troublesome. Various methods of removing them were tried without success; hot water, acids, and bases had very little effect on them. All of these runs were made at 29° C. with the unfrosted bulb as a light source, and the product was

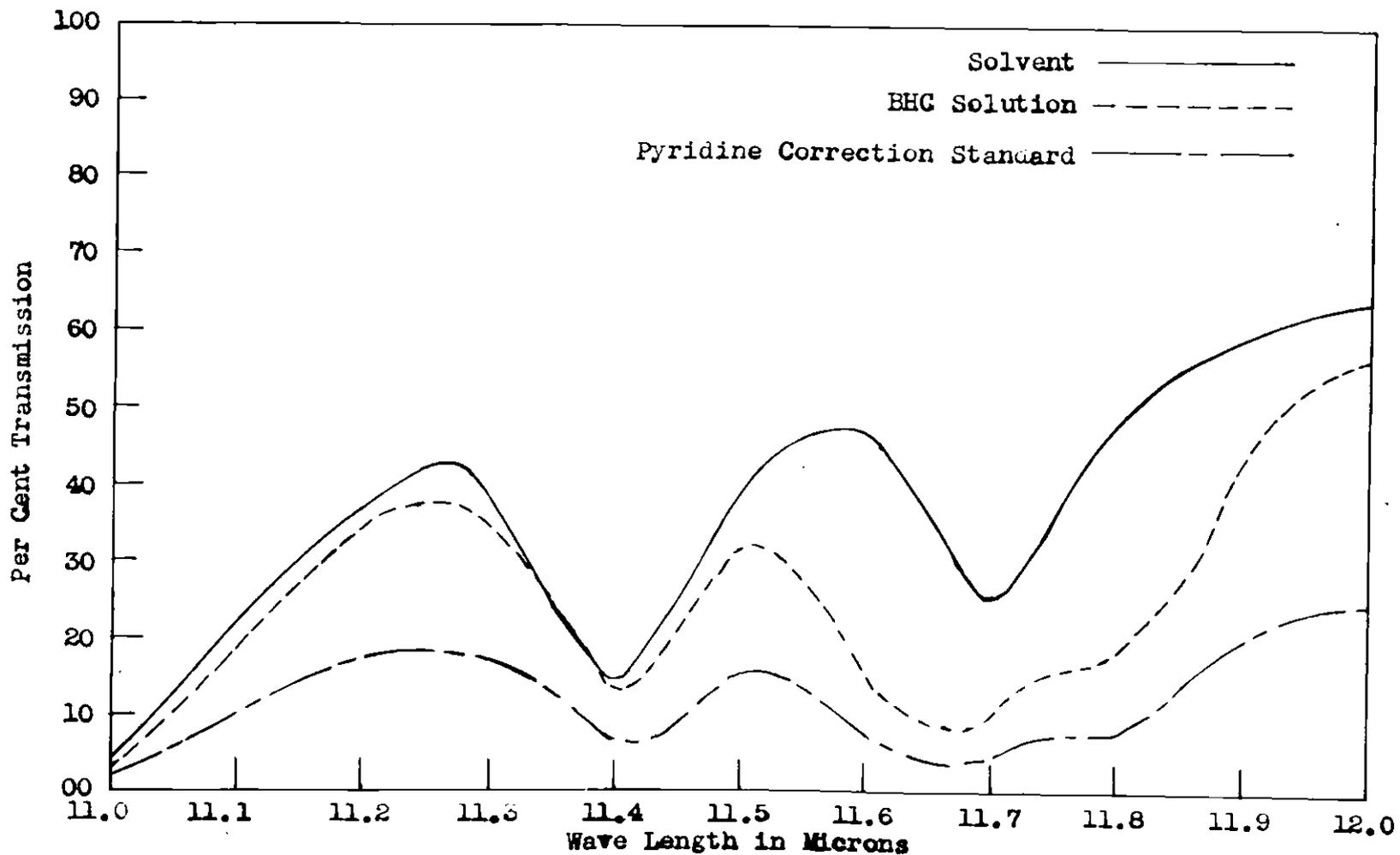
Table 3. Effect of Pyridine.

Run*	Ml. of pyridine	Time in hours	Wt. of product in gms.	% <u>gamma</u>	% <u>gamma</u> corrected
11	1.2	4.0	14.13	13.9	11.5
12	2.4	4.0	34.22	18.0	15.1
13	7.2	4.0	13.44	16.7	12.5
20	2.4	4.0	46.50	16.3	11.4
31	1.2	1.5	27.59	17.8	
32	2.4	2.0	12.64	16.0	

*Twenty ml. of benzene was used in all runs.

obtained by filtering the reaction mixture.

When analyzing these runs with the chloropyridines present, there was no assurance that the gamma isomer content observed was correct. It would be extremely unlikely that the impurities present would not absorb at the critical wave length. The observed absorption would thus be greater than that actually due to the gamma isomer of BHC. It was thought that if a wave length could be found at which the absorption of none of the isomers of BHC exceeded that of the solvent, but at which the absorption of the chloropyridines did, a correction could be made for the absorption of the chloropyridines at 11.81 microns. The complete spectrum of BHC in nitromethane was examined in relation to that of pure nitromethane. At 11.36 microns, the transmission curves were found to satisfy the above conditions and several standards were prepared from which it was believed the desired relationship could be obtained. These standards contained weighed amounts of BHC and chloropyridines, the BHC being of known gamma content. The chloropyridines were prepared by chlorinating small quantities of pyridine in the same manner as in the preparation runs with the exception that it was dissolved in carbon tetrachloride. It was necessary to assume that the product so produced was of the same composition as the chloropyridines obtained in the preparation runs. Figure 6 is a sample transmission curve of one of these standards. It shows the absorption of the pure solvent, a solution of BHC in nitromethane, and the standard. It will be noted that the curves of the pure solvent and the solution of BHC are coincident at 11.36 microns. If the gamma isomer content of the BHC solution and that of the standard are computed by the method previously described, a difference of 7.9 per cent

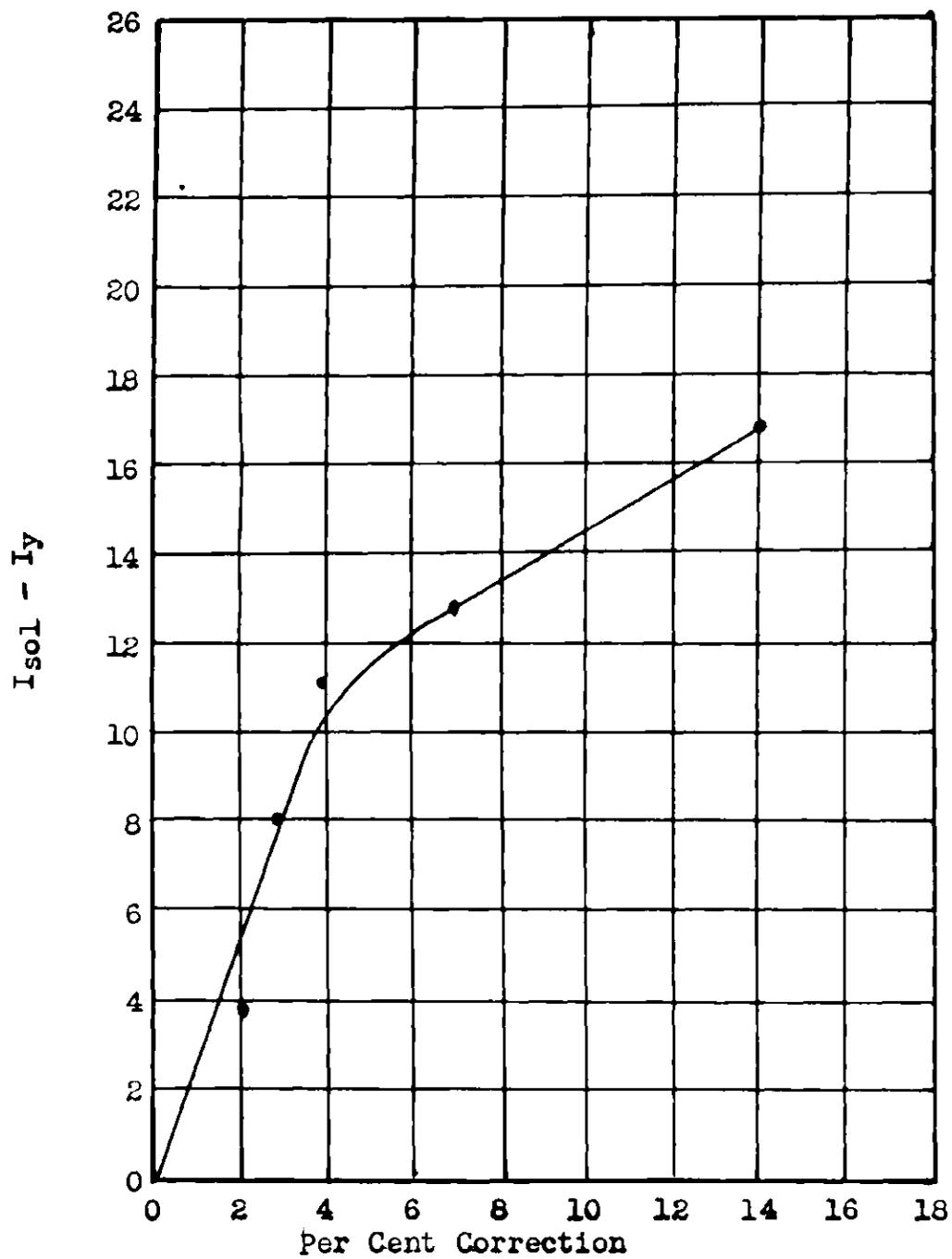


Sample Transmission Curve of Pyridine Standard

Fig. 6

will be found. At 11.36 microns, the transmission of the BHC solution is 23.0 and that of the standard is 10.2; there is a difference of 12.8. The transmission of the solution is designated I_{S01} and that of the standard I_y . If a plot of the per cent correction vs. I_{S01} minus I_y is made for all standards, the curve of Fig. 7 is obtained. Table 4 contains the data from which this curve was constructed. In analyzing an unknown containing chloropyridines, it is now possible to get I_{S01} minus I_y at 11.36 microns from the transmission curve and thus obtain the correction to be applied to the apparent gamma content from Fig. 7. Since this is an empirical correction, it would not be necessary that the absorption of the chloropyridines follow the Beer and Lambert law, but only that the transmission curves of an unknown be obtained under the same conditions and in the same range of concentrations as those of the standards. The corrected values of the gamma isomer content of the pyridine runs are given with the data in Table 3, and it can be seen that no substantial increase was effected. The first four runs and their corrections are averages of several transmission curves. In the last two runs, the correction method apparently failed. It was later found that the controls of the spectrophotometer had been changed thus changing the conditions from those under which the standards were run. This may account for the failure of the method in these two runs.

Chlorination in the Presence of Triethylamine.--In this series of runs another organic base was tried. In all cases, the reaction mixture was filtered and the residue washed with several small volumes of water. A large quantity of water soluble material, probably triethylamine hydrochloride, was removed. There was no increase in the yield of gamma isomer.



Pyridine Correction Curve

Fig. 7

Table 4. Standards for Correction of Gamma Content of Pyridine Runs.

Standards*	BHC in gms	Chloropyridines in gms.	$I_{sol} - I_y$ at 11.36 microns	Apparent % <u>gamma</u>	% Correction
BHC sol.	1.75	0.0	0.0	8.3	0.0
1	1.00	0.10	3.8	10.3	2.0
2	0.583	0.50	16.9	22.3	14.0
BHC sol.	1.000	0.0	0.0	13.6	0.0
3	1.000	0.52	12.8	21.5	7.9
BHC sol.	1.75	0.0	0.0	9.1	0.0
4	1.75	0.28	8.0	12.0	2.9
5	1.75	0.41	11.1	13.0	3.9

*Standards are grouped with the BHC solutions with which they were run.

The data for these runs is included in Table 5.

Chlorination in the Presence of Benzoyl Peroxide.--Since the addition of chlorine to benzene to form BHC is light catalyzed, it is thought to be a free radical reaction. Though little is known of the actual steps involved, it is safe to assume that because light is necessary the initial step is the formation of free chlorine atoms. This of course need not be the rate determining step of the reaction. If it were the slow step, however, the usual catalysts capable of promoting the formation of free radicals should catalyze the reaction. Benzoyl peroxide is such a compound. It is well known that it decomposes eventually to a phenyl radical²³ which in turn could react with a chlorine molecule to produce chlorobenzene and a chlorine atom. The results of these runs did not indicate that catalytic amounts of this peroxide increased the yield of gamma isomer. In the third run of this series, the rate of introducing chlorine was approximately doubled. Although this wasted considerable chlorine by absorption in sodium hydroxide at the end of the system, it also greatly increased the amount of BHC produced. All of these runs were made at 29° C., and the product was obtained by filtering the reaction mixture. The data for these runs is contained in Table 6.

Variation of Temperature.--Several runs were made in which the temperature was varied, at ten degree intervals, from 0 to 40° C. The reaction mixtures were allowed to come to room temperature before filtering. An attempt was made to chlorinate each run to approximately the same amount

²³R. C. Fuson, Advanced Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 12.

Table 5. Effect of Triethylamine.

Run*	Ml. of triethylamine	Wt. of product after washing in gms.	% <u>gamma</u>
14	2.10	8.11	9.2
15	4.15	4.91	9.2
50	12.50	9.05	11.8

*All of these runs were made with twenty ml. of benzene and were chlorinated for four hours.

Table 6. Effect of Benzoyl Peroxide.

Run*	Benzoyl peroxide in gms.	Wt. of product in gms.	% <u>gamma</u>
18	2.7	4.73	8.6
19	5.4	6.49	14.7
21#	5.4	43.9	12.3

*All of these runs were made with twenty ml. of benzene and chlorinated for four hours.

#Rate of introducing chlorine was doubled in this run.

of chlorine uptake. The results indicate that from about 20° to 40° C. the percentage of gamma isomer reaches a maximum of about 9 per cent. Because of the possibility of getting too much vapor phase reaction, runs were not made at temperatures higher than 40° C. The lower gamma content of the lower temperature runs indicated that the lowest feasible temperature for this reaction would be about 20° C. The data for these runs is contained in Table 7.

Variation in Chlorine Uptake.--This series of runs was designed to show whether there was a relationship between the quantity of chlorine taken up by the benzene and the yield of gamma isomer. All of these runs were made at 30° C. and the product was obtained by filtering the reaction mixture. By plotting the chlorine taken up in grams vs. the per cent gamma obtained, it was found that the yield of the desired isomer approached a maximum of about 12.5 per cent when the amount of chlorine taken up equalled or exceeded the weight of benzene reacted. Below this value, the gamma content of the product dropped off sharply. This can readily be seen by reference to Fig. 8. The data for these runs is contained in Table 8. It appears that for the most desirable results, an amount of chlorine equal to the amount of benzene must be used.

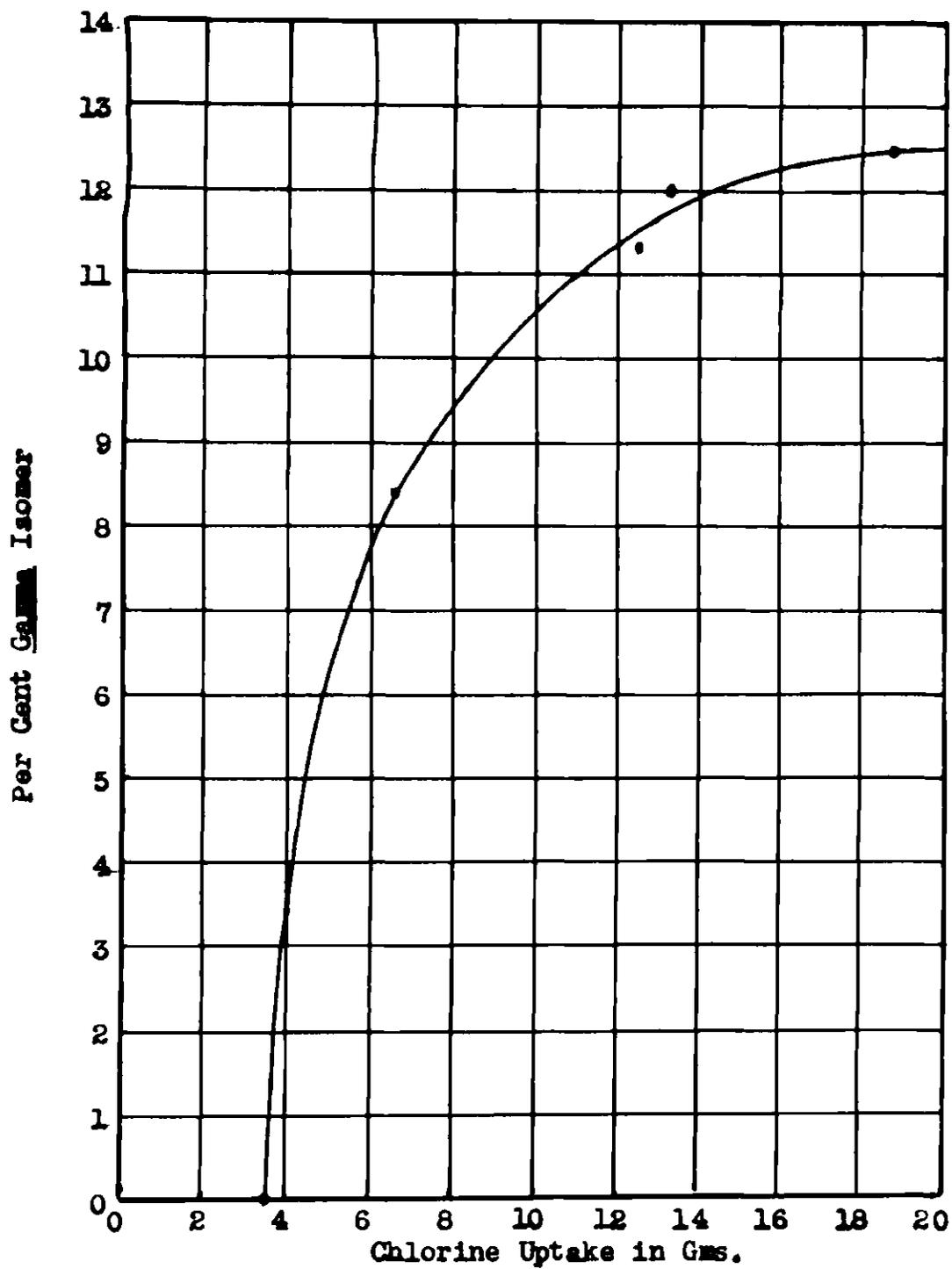
Chlorination in the Presence of Ultraviolet Radiation.--In some cases of commercial production, ultraviolet light has been used to irradiate the reaction mixture¹¹. In one case, however, this type of radiation was thought to decrease the gamma isomer content of the product²⁴. It was decided to try ultraviolet light and compare the results with runs in

²⁴A. P. H. Dupire, Brit. Patent 613,519 (1948).

Table 7. Effect of Temperature.

Runs*	Temperature in degrees Centigrade	Cl ₂ uptake in gms.	Time in hours	Wt. of product in gms.	% <u>gamma</u>
22	0	12.9	1.6	3.025	4.5
23	10	12.4	1.3	6.93	7.6
26	20	14.9	1.0	15.56	10.8
26A	20	13.4	0.8	12.10	9.3
29	30		1.0	8.87	8.8
25	40	11.4	1.0	12.14	9.1

*Twenty ml. of benzene was used in all runs.



Effect of Variation in Chlorine Uptake

Fig. 8

Table 8. Effect of Variation in Chlorine Uptake

Run*	Cl ₂ uptake in gms.	Time in hours	Wt. of product in gms.	<u>% gamma</u>
37	3.4	0.5	0.193	0.0
34	6.4	0.75	4.00	8.4
33	12.4	1.75	14.82	11.3
36	13.4	2.00	19.59	12.0
35	18.9	2.00	27.21	12.5

*Twenty ml. of benzene was used in all runs.

which the three hundred watt unfrosted bulb had been used. The lamp used was of the fused quartz mercury vapor type*. The data on these runs is contained in Table 9. Under the conditions used here, ultra-violet light produced no increase in the gamma isomer content.

Use of Methylene Chloride as a Solvent.--Two runs were made in which fifty ml. of methylene chloride was used as a solvent, one of them also containing 2.5 grams of benzoyl peroxide. Both runs were made at 30° C. for a duration of 2.5 hours. Because of a net loss of weight of the reaction mixtures, it was impossible to obtain the amount of chlorine uptake. This was due to evaporation of the solvent or its mechanical carry-over by chlorine. An unfrosted three hundred watt bulb was used as a light source. In order to remove most of the methylene chloride, the reaction mixtures were worked up by evaporation at 60° C. The remaining benzene was filtered. No significant change in the yield of gamma isomer was noted in these runs. The first run, number 41, produced 14.8 grams of product which was 9.0 per cent gamma. The second, number 42, produced 12.83 grams of product which was 8.3 per cent gamma.

Chlorination in the Presence of Adsorbents.--It was decided to test the reaction for the possibility that adsorption of one of the reactants or some intermediate on the surface of a foreign substance might be desirable. Alumina, powdered glass, and activated charcoal were chosen as substances commonly used for this purpose. No increase in the gamma isomer content was obtained. In the case of alumina, the induction period was lengthened and the yield of BHC was low. The BHC was recovered

*See above, p. 8

Table 9. Effect of Radiation.

Run*	Cl ₂ uptake in gms.	Wt. of product in gms.	Time in hours	Type of radia- tion	% <u>gamma</u>
39	11.9	17.71	2.0	uv	11.0
40#	9.4	11.57	2.0	uv	11.8
29		8.37	1.0	visible	8.8
33	12.4	14.62	1.8	visible	11.3
36	13.4	19.59	2.0	visible	12.0
49	11.9	10.62	2.0	visible	7.8

*All of these runs were made at 30° C. and twenty ml. of benzene was used.

#This run contained 1.2 ml. of pyridine and the value for the gamma content is uncorrected.

by filtering the reaction mixtures and washing the residues repeatedly with small quantities of acetone. The acetone solutions were evaporated under reduced pressure at room temperature. All of these runs were made at 30° C., and with the three hundred unfrosted bulb used as a light source. The data for these runs is contained in Table 10.

Comparison of Filtration and Evaporation as Methods of Treating Reaction Mixtures.—One disadvantage of the technique of filtering the reaction

mixture is that the gamma isomer is relatively more soluble in benzene than are the alpha and beta isomers. The residue from a filtration process should actually consist of the excess of each isomer above that required to saturate the unreacted benzene. If the reaction mixture could be evaporated without coloration of the product occurring to too great an extent, the per cent gamma in the residue should be higher than that obtained by filtration. The runs listed in Table 11 were intended to determine this difference. Some of these runs have been listed in previous tables, but the conditions used were such that they should be included here for comparison. Run number 47 was evaporated at 60° C. under reduced pressure, but a small amount of discoloration occurred indicating a slight decomposition. Run number 48 was evaporated at room temperature under reduced pressure without decomposition. If averages are taken of both the filtered runs and evaporated runs respectively, there is a difference of 5.6 per cent in the gamma content. This indicates that the best commercial method of production would be one in which all of the BHC is recovered from the unreacted benzene. Both methods have been used; a third method also exists in which the unreacted benzene is removed by steam distillation¹¹.

Table 10. Effect of Adsorbents

Run*	Adsorbent	Wt. of adsorbent in gms.	Time in hours	Cl ₂ uptake in gms.	Wt. of product in gms.	% <u>gamma</u>
43	Alumina	5.00	3.0	11.9	3.45	9.8
44	Powdered glass	7.96	2.0	11.9	11.95	5.3
45	Activated charcoal	3.80	2.4	13.6	9.05	9.9

*Twenty ml. of benzene was used in all runs.

Table 11. Comparison of Filtered and Evaporated Runs.

Run*	Treatment	Gms. of product	% <u>gamma</u>
47	Evaporated	19.92	16.3
48	Evaporated	13.26	14.8
49	Filtered	10.62	7.8
29	Filtered	8.87	8.8
33	Filtered	14.82	11.3
36	Filtered	19.59	12.0

*Twenty ml. of benzene was used in all of these runs and the chlorine uptake and time were approximately the same. The light source was an unfrosted three hundred watt bulb.

A Comparison of Thermal Treatment of the Product.--The following procedure was used to determine whether a thermal equilibrium existed between the isomers. Twenty ml. of benzene was chlorinated at 30° C. for one hour. The reaction mixture was decanted and the residue weighed while damp. It was found to weigh 15.08 grams and was divided into three equal parts which were designated as parts one, two, and three. The same was done to the decanted benzene. One of the three parts of solid was allowed to dry in air and the other two parts were each returned to one-third of the liquid. Part one was analyzed immediately and was found to have 13.1 per cent gamma. Part two was placed in a constant temperature water bath and maintained at 50° C. for two weeks. It was then filtered and analyzed and found to contain 9.1 per cent gamma. After having been placed in the refrigerator at 5° C. for two weeks, part three was filtered and analyzed and found to contain 8.3 per cent gamma. The gamma contents of parts two and three are within experimental error of being the same. The higher gamma content of part one could be explained by the fact that this portion of the BHC was allowed to dry in air instead of being filtered. It would appear that subsequent changes in temperature of the reaction mixture do not materially affect the per cent gamma in the product.

Vapor Phase Reaction.--For this vapor phase run, the apparatus was modified only to the extent of using another inlet tube which did not go below the surface of the reaction mixture and was curved upward to avoid entrapping benzene vapors. Also a heating mantle was used instead of a water bath. Twenty ml. of benzene was chlorinated for 3.5 hours at the boiling point of benzene, ultraviolet light being used for irradiation.

The reaction was expected to take place above the surface of the benzene and in the condenser. A considerable quantity of product was formed in the condenser and had to be scraped out at the conclusion of the reaction. Throughout the reaction, dense white fumes were visible in the condenser and were thought to be hydrogen chloride from a substitution reaction. Condensing benzene carried large quantities of product down into the reaction flask where it remained until the mixture was cooled to room temperature. At the end of the reaction, it was found that 20.9 grams of chlorine had been taken up and 18.25 grams of EHC produced. The product was found to contain 7.0 per cent gamma isomer.

CHAPTER IV

RECOMMENDATIONS

It would appear that the conditions of reactions which have been varied here are not factors which determine the composition of benzene hexachloride. There are, however, at least two more series of runs which might give information on the yield of BHC itself.

In the work done here, a constant rate of introduction of chlorine was maintained by the use of a crude flow meter. Not all of the chlorine which was introduced remained in contact with the benzene. It might well be worth while to make a series of runs in which a given quantity of chlorine was introduced and the reaction vessel sealed. It could then be shaken in the presence of a strong light until reaction ceased. This would eliminate the wastage of chlorine and would give more definite information on the most desirable ratio of reactants than can be obtained by measuring different chlorine uptakes as done here. Another series of runs could be designed to measure the effect of pressure on the reaction. It is possible that maintaining a high concentration of chlorine by the use of pressure might increase the reaction rate and thus increase the yield of crude BHC obtained in a given time.

The vapor phase reaction should be investigated more thoroughly. The fact that large quantities of product formed in the condenser during the vapor phase reaction here might indicate that surfaces are more important in this type of reaction than in the liquid phase.

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