THE QUANTUM YIELD OF PHOTODECOMPOSITION OF

BENZENE SOLUTIONS AT ROOM TEMPERATURE

By

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INTRODUCTION

The study of chemical and physical changes in a system brought about by absorption of light is called photochemistry. Light as used here includes the infrared and ultraviolet regions of the spectrum, as well as the visible region, i. e., the wave length range from about 1,000 Å to about 10,000 Å.

Light incident upon a system can be reflected, transmitted, scattered, or absorbed. The law of Grotthuss and Draper, sometimes called the first law of photochemistry, states that only the light that is absorbed can produce a chemical change. However, light which is absorbed will not always cause a reaction. Shortly after the advent of the quantum theory, Einstein proposed another law of paramount importance in the interpretation of photochemical reactions, the law of photochemical equivalence. He stated the rule that one quantum of absorbed radiation activates one molecule of the absorbent, but this activated molecule does not necessarily undergo chemical reaction. This law applies only to the absorption process. If a molecule absorbs a quantum of radiation and then decomposes, and the products do not further react, the number of quanta absorbed will equal the number of molecules which react. However, an activated molecule can be deactivated by collision with other molecules, or it may re-emit the energy as fluorescence, in which cases the number of quanta absorbed will be larger than the number of molecules which react. Again, an activated molecule may initiate a chain of thermal reactions, which will lead to a larger number for reacting molecules

than for the number of quanta absorbed.

To express the relation between the number of molecules reacting and the number of quanta absorbed, the quantum yield or quantum efficiency, ϕ, of a process is introduced. This quantity is defined as

$$\frac{\text{number of molecules reacting in a given time}}{\text{number of quanta of light absorbed in the same time}}.$$

The quantum yield of a reaction may be anywhere from near zero to 10^6 (13, 15).

The primary aim of this research was to establish whether or not benzene solutions may be photochemically decomposed at room temperature, and if so, to measure the quantum yield for the process.

HISTORICAL

No quantitative measurements of the photodecomposition of benzene have been reported in the literature. Baxendael and Smithies (4), Burton and Patrick (5), and Gordon and Burton (11) have investigated the effects of 190 KV x-rays, 100 electron volt gamma radiation, and 1.5 MV electrons, respectively, on several organic compounds, including benzene. However, the energies of such radiations are considerably higher than the energy of ultraviolet light, and the mechanisms of reactions caused by gamma rays and electrons are ionic. As would be expected, a variety of products resulted: hydrogen, acetylene, phenol and hydrogen peroxide (in the presence of water), and other species.

In 1939, Krassina (12) and Prilezhaeva (14) studied the vapor phase photodecomposition of benzene. Using various sparks as sources, they found that no reaction was predominant; biphenyl was detected in small amounts from the absorption spectrum.

Allsopp and Szigeti (1, 2), while studying the effect of ultraviolet light on carcinogenic hydrocarbons, noted that the solvent used had a pronounced effect on the photoreactions of various polycyclic aromatic hydrocarbons. When benzene was used as the solvent anomalous results were obtained; accordingly, these workers studied the effect of ultraviolet light on benzene alone. They irradiated pure benzene and solutions of benzene in cyclohexane contained in an open Petri dish, using a mercury resonance lamp as a source of light. After a large number of aliquots had been irradiated, the resulting solution was

evaporated to 5% of its original volume, diluted with carbon tetra-
chloride, and chromatographed, using dry alumina. Five fractions were
obtained, none of which could be characterized with any certainty.
They believed that biphenyl was formed, and that one of the fractions
had a carbonyl group in its structure because a precipitate was formed
with 2,4-dinitrophenylhydrazine and also with p-bromophenylhydrazine.
However, not enough precipitate was obtained to get a melting point.

In 1953, Gibson, Blake, and Kalm (7) reported results obtained by
irradiating rigid glass solutions of benzene at the boiling point of
liquid nitrogen. They first noticed a decrease in fluorescence with
continued irradiation, and, on melting and refreezing the sample, the
fluorescence increased some but did not quite reach its original level.
They attributed this to decomposition of the benzene, by supposing
that the decomposition products formed an opaque layer on the outer
edge of the cell, thereby decreasing the fluorescence. After a solu-
tion was melted, the products would then become evenly distributed
throughout the cell, thus allowing the fluorescence to build up nearly
to its original level. No decomposition was observed at room tempera-
ture. Water and oxygen were shown to have no part in the reaction,
by virtue of the fact that a water- and oxygen-free solution behaved
in exactly the same manner as solutions from which water and oxygen
were not removed. The ultraviolet absorption spectrum of the product
was obtained in either of two ways: by using the original solution
as the "blank" in the spectrophotometer, or by purification of the
product by distillation. It was shown also that the product was un-
saturated, and that it evidently polymerized after standing in contact
with air for three weeks. It was concluded that the product was 1,3,5-

hexatriene. The solvent in this case was postulated to act as a hydro-
gen contributor, two atoms of hydrogen being needed to form the 1,3,5-
hexatriene from benzene. When perfluoro-2-methylpentane was used as
a solvent, an entirely different product was formed, the spectrum of
which resembled that of biphenyl.

Gilmore (9) found indications that photodecomposition took place
at room temperature: a dilute solution of benzene in 2,2,4-trimethyl-
pentane effused a characteristic acetylenic odor after being used as
a short wave length cut-off filter in fluorescence experiments.

EXPERIMENTAL

Chemicals Used. The benzene used was Merck Reagent grade thiophene-free; this was distilled, and a small center fraction of constant boiling point was collected. The cyclohexane and 2,2,4-trimethylpentane were Phillips Petroleum Company Spectro grade, used with no further purification. The hydrogen was Matheson electrolytic, 99.8%. The chloroacetic acid used was Eastman Kodak Company white label.

Apparatus. The source of ultraviolet light used was a fused silica helical mercury resonance lamp, manufactured by Hanovia Chemical and Manufacturing Company. According to Hanovia, 95% of the ultraviolet light put out by this lamp is mercury resonance radiation of wave length 2537 Å. The lamp was powered by a 5,000 volt luminous tube transformer, which was operated directly from line current.

The first irradiations were carried out in a #7900 Vycor test tube which was supported in the center of the helical lamp; the solutions were stirred by hand. It was found that extensive heating occurred, so a finger condenser was constructed to fit inside the test tube, and a helical stirring rod was made to fit around the condenser inside the test tube. The stirring rod was powered by means of the level-wind device on a fishing reel. Since evaporation could occur in this cell, it was desirable to have a totally enclosed cell which could be cooled, and at the same time the contents of which could be stirred. This was achieved by placing a water cooling jacket around the cell, and by magnetic stirring. The final apparatus is shown in Figure 1. The cooling
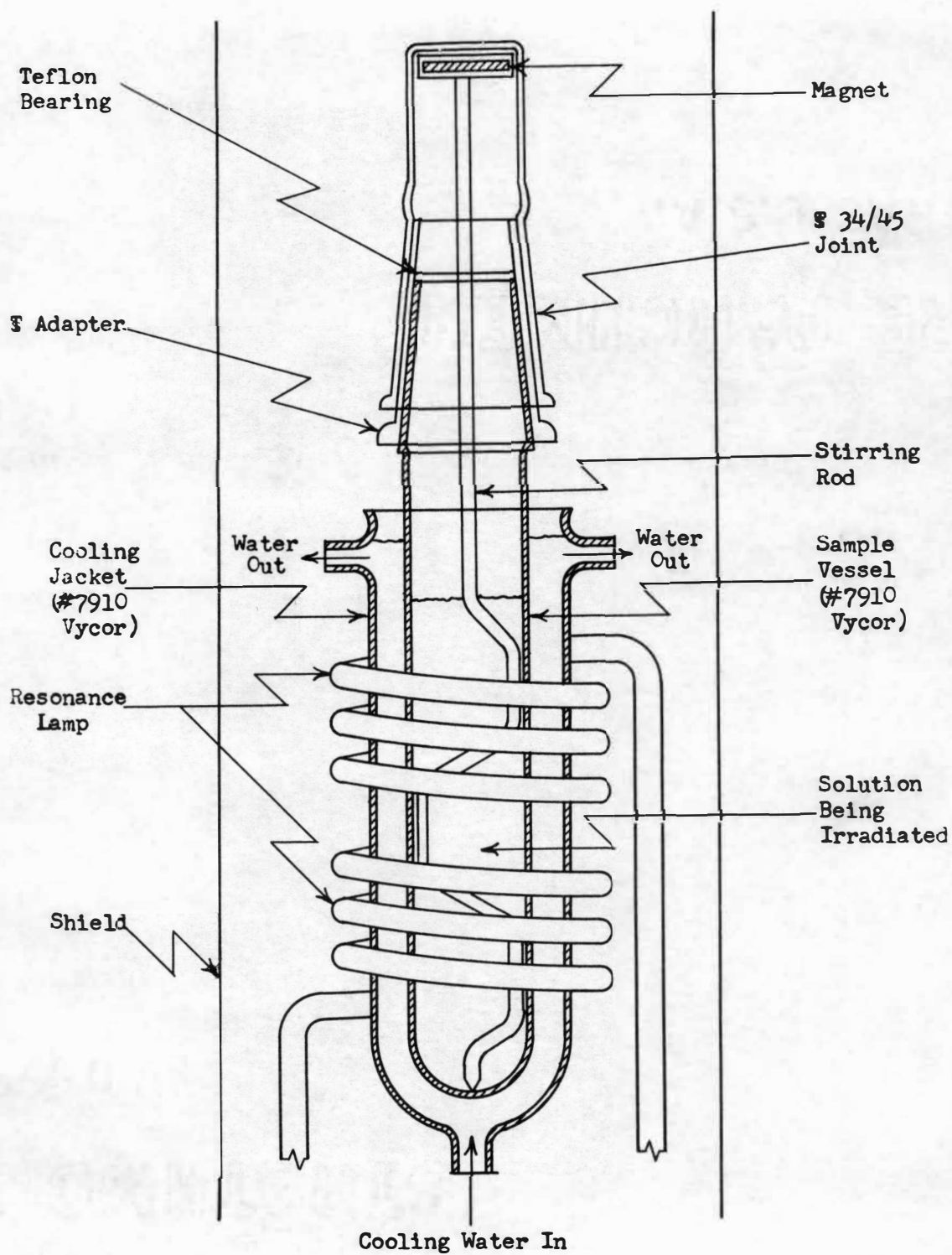
Irradiating Apparatus

Figure 1

jacket and the main body of the irradiation cell were ordered from Corning Glass Works, and were constructed of #7910 Vycor, which is much more transparent to ultraviolet light than the #7900 Vycor.

All absorption spectra were obtained on the Beckman Model DU Quartz Spectrophotometer with the Beckman Hydrogen Lamp as a source and with a photomultiplier as a detector. Silica cells of one centimeter path length with silica blocks 0.9 centimeter thick were used to hold the samples, so that the final path length was one millimeter.

Procedure. It was shown first that photodecomposition actually occurs at room temperature, and that it is due to the 2537 Å radiation rather than to the 1849 Å line of the lamp. Approximately 0.01 molar solutions of benzene in 2,2,4-trimethylpentane and in cyclohexane were irradiated, and the optical density of both solutions increased the same for equal periods of irradiation. A reaction was definitely indicated. Figure 2 shows this increase with cyclohexane as the solvent. Irradiation of either solvent alone produced no change in the spectrum of the solvent. Cyclohexane was used as the solvent for the solutions on which final measurements were made, but there is little doubt that 2,2,4-trimethylpentane would serve equally well.

That the reaction observed is not due to the 1849 Å line was shown by replacing the water in the cooling jacket with a filter solution, which consisted of a 0.2 g/l solution of dihydropyran in 2,2,4-trimethylpentane; this filter solution does not transmit below about 2300 Å (3). A similar increase in optical density with irradiation was observed with this filter solution in place.

It was then shown that the reaction was not due to oxygen or to water, which are present in small amounts in the hydrocarbons described
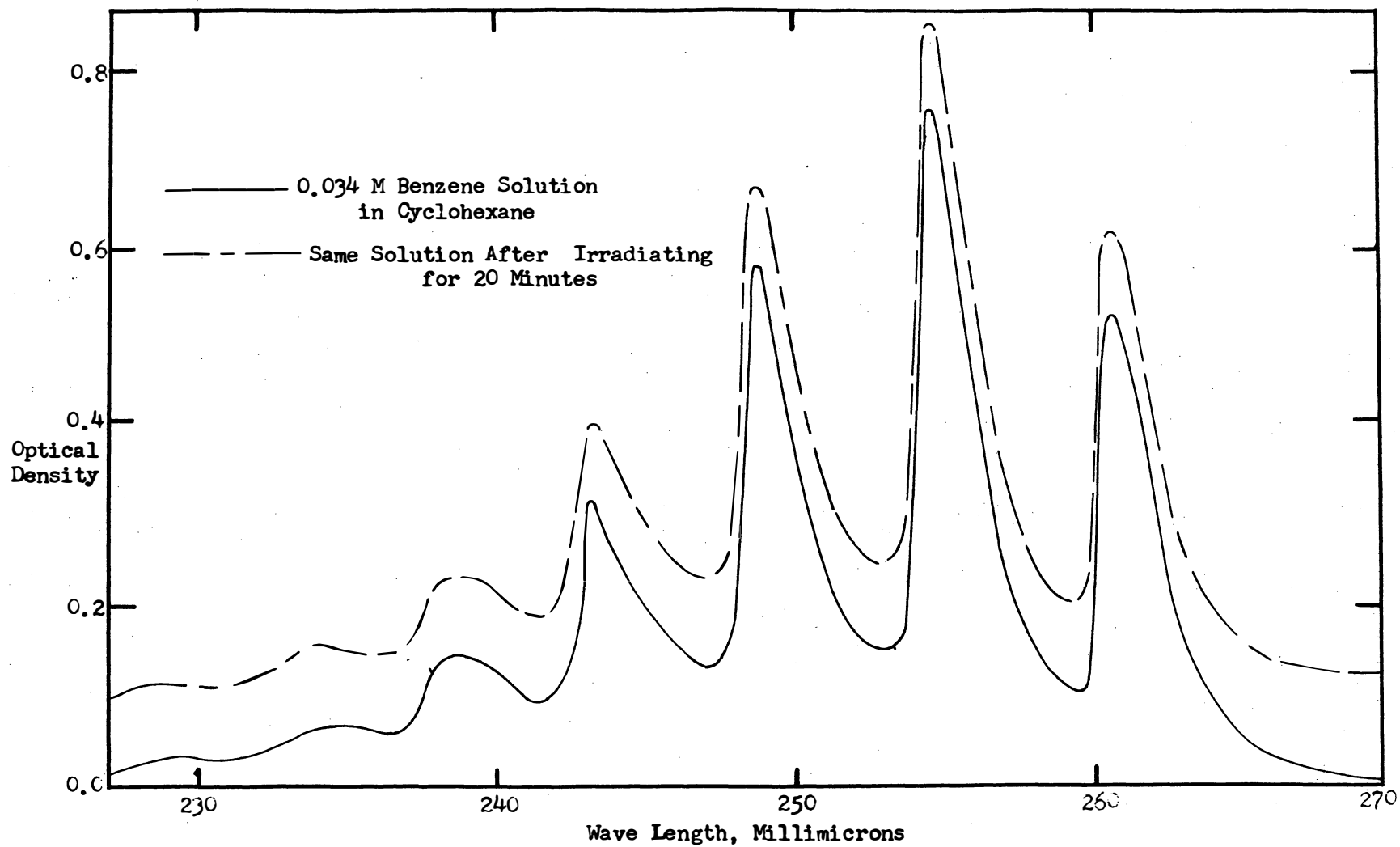
Effect of Irradiation on Spectrum of Benzene

Figure 2

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above. A solution of benzene in cyclohexane was refluxed over sodium metal four hours, and was then distilled off into the dry irradiation cell. The solution was then frozen with dry ice-acetone, and the cell was evacuated. The solution was then allowed to melt; this freezing-evacuating-melting cycle was repeated four more times, and then the vacuum was relieved with dry nitrogen. A small sample was removed for analysis, and then the solution in the cell was irradiated. A similar increase in optical density was observed; thus it was indicated that water and oxygen play no part in the reaction.

As seen in Figure 2, the absorption of the irradiated solution increased a uniform amount over the entire absorption spectrum of benzene in the ultraviolet range. No characteristic new spectrum appeared. Irradiation for an eight hour period did not destroy the benzene spectrum.

The irradiated solution was shown to decolorize dilute potassium permanganate solution. Since Gibson, Blake, and Kalm (7) gave good evidence for the formation of 1,3,5-hexatriene at low temperatures, it was decided to proceed on the assumption that the same or a similar olefinic product was obtained at room temperature, and in order to determine the remaining benzene, several means of removing the product without removing any benzene were tried.

Woods and Schwartzman (18) found that 1,3,5-hexatriene hydrogenates easily with Adams catalyst (platinum black). This process was tried, in a glass container with 15 psig hydrogen pressure, with the catalyst prepared according to Gilman and Blatt (8). The stopcock grease dissolved enough to allow the hydrogen and some solution to escape, and the procedure did not work.

A portion of the irradiated solution was shaken in a separatory funnel with concentrated sulfuric acid, using the acid as a stopcock lubricant. The acid layer took on a reddish-brown color, but it did not remove quite all of the light-absorbing substances other than benzene: the optical density did not consistently go below that of the original solution. Upon washing the original solution with sulfuric acid there resulted a very slight but regular decrease in absorption, for which a correction might have been made.

A 4 $\underline{N}$ solution of sodium hydroxide which was saturated with potassium permanganate also was used to remove the product. This attempt to remove the product proved unsuccessful; inconsistent results were obtained.

Bromination was tried on solutions made from both the solvents. The bromine reacted with the 2,2,4-trimethylpentane, and when sodium hydroxide solution was used to remove excess bromine from the cyclohexane solution, a turbid solution resulted that could not be analyzed with the spectrophotometer.

Fuming sulfuric acid (2%) was tried, and the same results were obtained as with concentrated sulfuric acid. Potassium dichromate removed very little of the product, and chromic acid reacted with the cyclohexane.

The best and only consistent results were obtained by hydrogenation of the irradiated solution at a higher pressure than was first tried. The process this time was carried out in the Aminco high-pressure hydrogenation apparatus, using the glass-lined bomb. The pressure was maintained at 72-75 psig by the pressure regulator for four hours. The same catalyst was used as before. The absorption spectrum of the

irradiated-hydrogenated solution is compared with the spectrum of the original benzene solution in Figure 3. All calculations were made from data obtained from hydrogenation experiments.

To measure the light output of the lamp, a chemical actinometer was used. Chloroacetic acid was chosen for this work. Ultraviolet light causes hydrolysis of aqueous solutions of this acid to glycolic acid and hydrochloric acid. The quantum yield for this reaction is known (16, 17). By titrating the hydrochloric acid formed, one may calculate the number of quanta absorbed by the solution. A solution of chloroacetic acid was made up so as to have the same absorbency as the benzene solutions at 2537 Å, and samples were irradiated for various periods of time. The chloride ion was titrated potentiometrically with standard silver nitrate solution, by using a Leeds and Northrup Student Potentiometer and a General Electric galvanometer. A silver wire dipping into the actinometer solution formed one half cell, and a saturated calomel half cell connected to the actinometer solution via an ammonium nitrate-agar salt bridge was used to complete the cell.
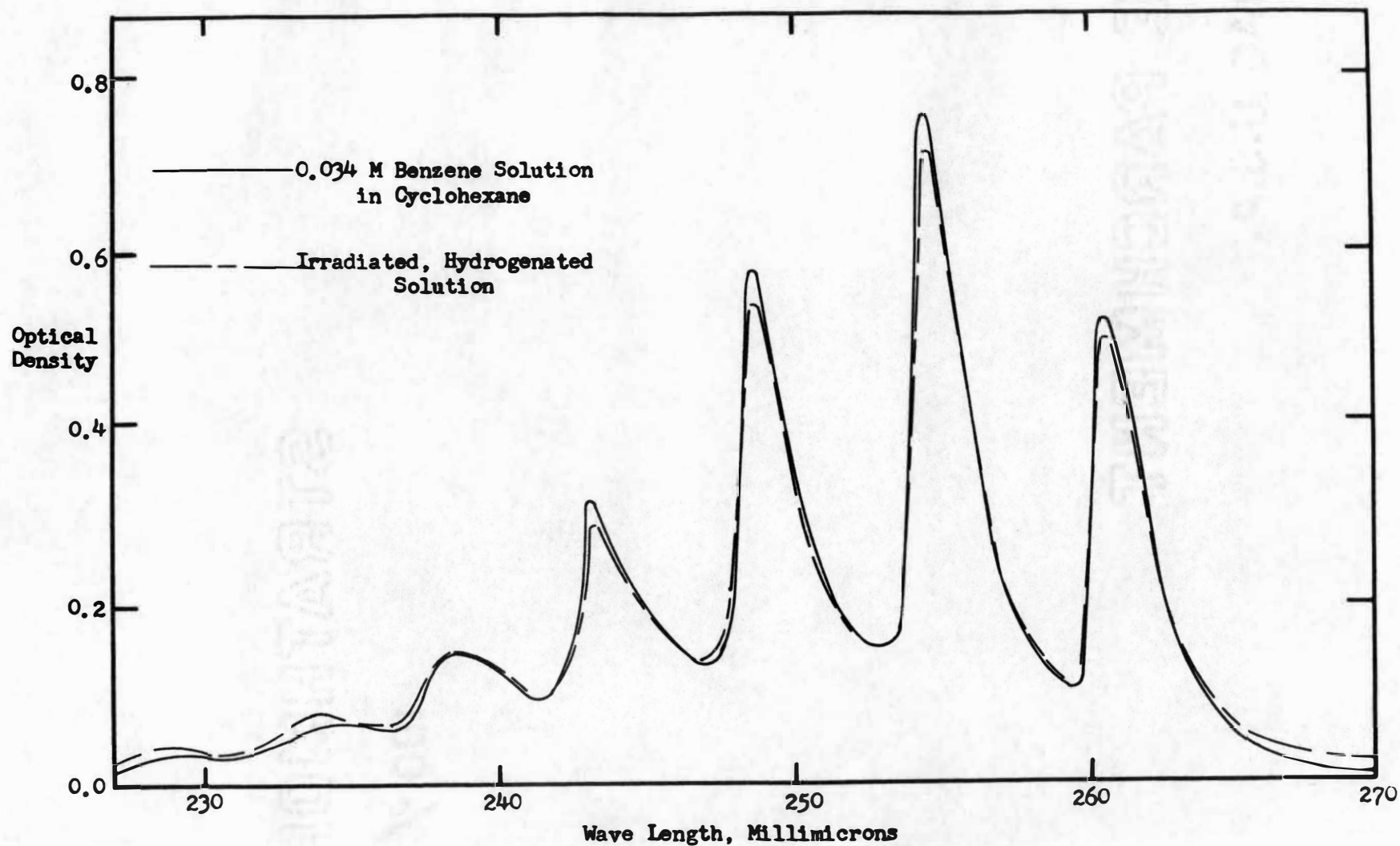
Removal of Product by Hydrogenation

Figure 3

CALCULATIONS

It can be seen from Figure 3 that the hydrogenation process either did not remove all the uv-absorbing product, or that it introduced some other substance which decreased the light transmission. If nothing new had been introduced, and if the hydrogenation had removed all the uv-absorbing product, the spectrum of the irradiated hydrogenated solution would have fallen below that of the original solution. At both extremities of the spectrum, in regions of low absorption, the irradiated hydrogenated solution absorbed a nearly uniform amount more than the original solution. This incremental increase in absorption may be due to colloidal platinum, which would scatter the light, or it may be due to some product which is not changed by hydrogenation. If it is assumed that this same absorption occurs in the region of high absorption, then a correction factor may be applied over the entire spectrum, effectively lowering the spectrum so that in regions of low absorption the irradiated hydrogenated solution spectrum falls on that of the original solution. The result of such a correction factor is shown in Figure 4. The three highest peaks on the corrected curves then show agreement within 3% for the decrease in benzene concentration. From the data for this Figure,

at $\lambda = 2487$ Å, $\qquad$ at $\lambda = 2545$ Å, $\qquad$ at $\lambda = 2606$ Å,

$$\epsilon = \frac{O.D.}{cl} = \frac{0.582}{0.00337}; \qquad \epsilon = 225; \qquad \epsilon = 154;$$

$$= 173;$$

$$\Delta C_{20 \text{ min}} = \frac{\Delta O.D.}{\epsilon l};$$

$$= \frac{0.037}{17.3};$$

$$= 0.00214 \text{ M/l};$$

$$\Delta C_{43 \text{ min}} = 0.00324 \text{ M/l}.$$

$$\Delta C_{20 \text{ min}} = 0.00209 \text{ M/l}; \quad \Delta C_{20 \text{ min}} = 0.00208 \text{ M/l};$$

$$\Delta C_{43 \text{ min}} = 0.00320 \text{ M/l}. \quad \Delta C_{43 \text{ min}} = 0.00324 \text{ M/l}.$$

The above values for the extinction coefficients at the three wave lengths compare with 182, 219, and 156, respectively, as given by Friedel and Orchin (6).

When the number of quanta absorbed by the benzene during these same periods of irradiation is known, one can calculate the quantum yield for the process. From the actinometric measurements, the output of the lamp incident on the solution in the cell may be calculated as follows: 11.2 ml of 0.0075 $\underline{N}$ AgNO$_3$ solution was needed to titrate the HCl formed during a four minute irradiation period; this is equivalent to $\frac{11.2 \times 0.0075 \times 6.02 \times 10^{23}}{1000} = 5.06 \times 10^{19}$ molecules; since the quantum yield for the hydrolysis of chloroacetic acid is 0.33, the output of the lamp in the four minutes was $\frac{5.06 \times 10^{19}}{0.33} = 1.53 \times 10^{20}$ quanta; this is equivalent to 6.39×10^{17} quanta per second. Six such determinations gave 6.20×10^{17} quanta per second as an average.

The above number times the total time of irradiation in seconds gives the number of quanta absorbed in the benzene solution in the cell during the irradiation. The fraction absorbed by the benzene at any given instant is given by the ratio of the optical density of a solution containing only benzene at the same concentration, to the optical density of the irradiated solution at the given instant. The fraction absorbed over a period of time is obtained from a graph-
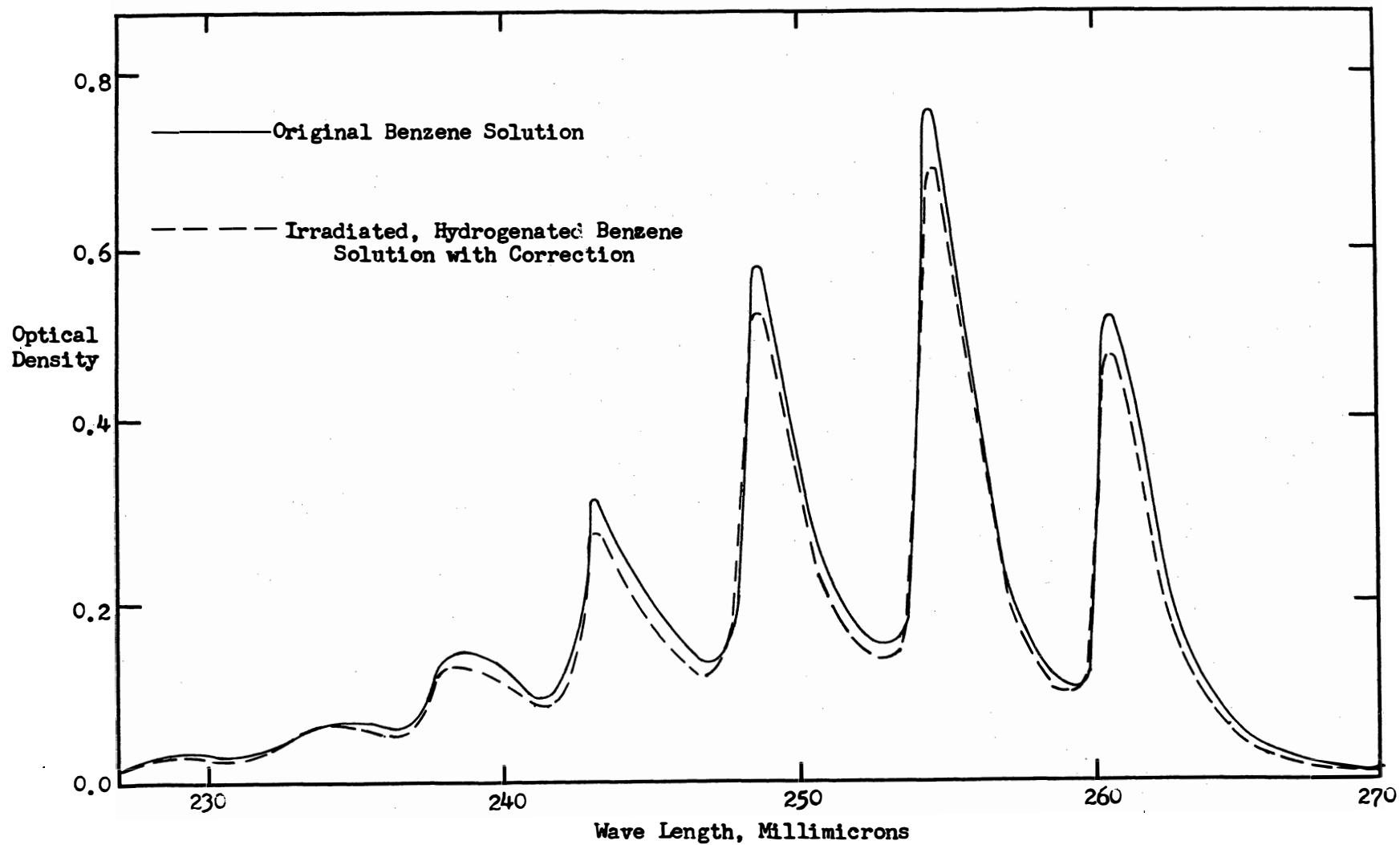
Result of Correction for Incomplete Removal of Product

Figure 4

ical integration of these ratios. Such an integration was carried out for this process, as shown in Figure 5. The area under the ~~upper~~ *lower* curve represents the numerator of the desired ratio, and the area under the upper curve the denominator. Data for the upper curve were obtained by finding the optical density of a solution of benzene in cyclohexane as a function of irradiation time. Data for the lower curve were obtained by finding the optical densities of samples of the irradiated solution which had been hydrogenated. The DU was set as close to 2537 $\mathring{A}$ as possible, by means of a mercury vapor lamp, for obtaining the above data. A planimeter gave the following results for the graphical integration (f_t = fraction absorbed by the benzene over time t):

$$f_{20} = 0.740; \qquad\qquad f_{43} = 0.597.$$

The quantum yield follows as

$$\phi_{20} = \frac{0.00210 \text{ mole/liter x } 6.02 \text{ x } 10^{23} \text{ molecules/mole x } 0.060 \text{ liter}}{6.20 \text{ x } 10^{17} \text{ quanta/sec x 20 minutes x 60 sec/minute x } 0.740},$$

$$= 0.138;$$

$$\phi_{43} = \frac{0.00323 \text{ x } 6.02 \text{ x } 10^{23} \text{ x } 0.060}{6.20 \text{ x } 10^{17} \text{ x 43 x 60 x } 0.597};$$
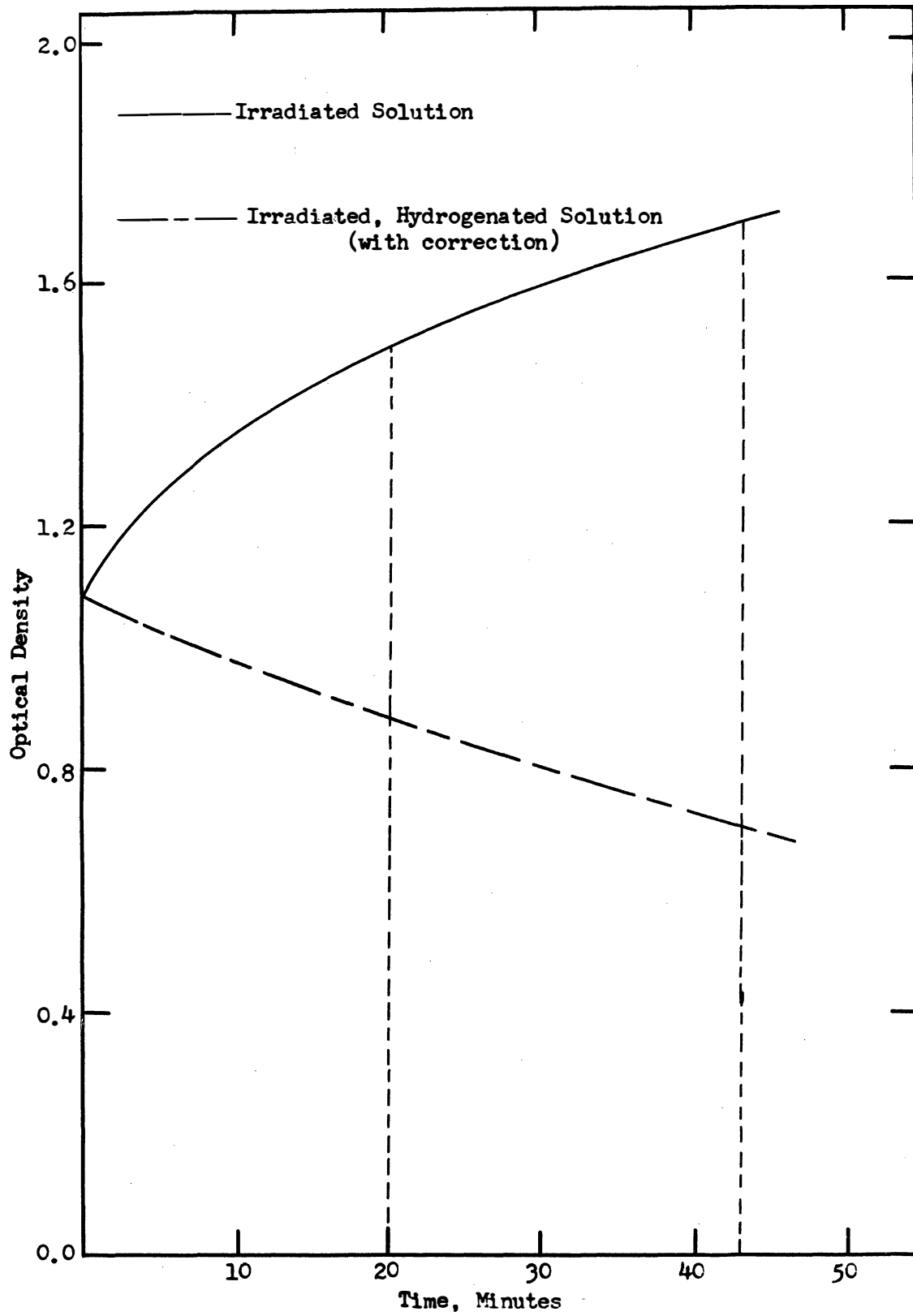
$$= 0.122.$$

Figure 5--Graphical Integration

DISCUSSION OF RESULTS

The two results for two periods of irradiation are not as close as one may desire, but they do lie within the range of experimental error, as best as it may be calculated. Variations in the results for the output of the lamp as high as $\pm 10\%$ were observed, and the quantum yield results lie within $\pm 10\%$ of 0.13. Since no quantitative measurements of this reaction have been reported, it is rather difficult to state a range of accuracy. One change which might lead to more precise results would be to power the lamp from a regulated source, either AC or DC. Another improvement might be to use the uranyl oxalate actinometer instead of the chloroacetic acid. This actinometer has been refined to a higher degree, and is not subject to reaction in the dark; the dark reaction for the hydrolysis of chloroacetic acid is about 1% as fast as the reaction caused by light at 25° C. Perhaps the largest error is in the approximation made in order to determine the final benzene concentration. It would be desirable to characterize the product and to investigate any secondary reactions which may occur; the little effort which was expended in this direction gave no conclusive results.

The quantum yield measurements are not inconsistent with the luminescence quantum efficiency of benzene as reported by Gilmore, Gibson, and McClure (10), in that the sum of the decomposition quantum yield and the luminescence quantum yield does not exceed unity. The latter datum was measured at 77° K, and may be somewhat higher than

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reported, because no allowance was made for decomposition of the

benzene.

SUMMARY

It has been shown that benzene dissolved in either cyclohexane or 2,2,4-trimethylpentane decomposes when exposed to strong ultraviolet irradiation of wave length 2537 Å. However, the ultraviolet absorption spectra of irradiated solutions maintain the general shape of the benzene spectrum; the absorbance increases a nearly uniform amount over the entire range of the benzene spectrum. No new characteristic absorption bands appear.

Several methods were tried to remove the product without removing any benzene, in order to be able to measure the remaining benzene concentration so as to calculate the quantum yield for the decomposition. The best method found was hydrogenation at 75 psig pressure using platinum black as a catalyst. However, even this method was not entirely satisfactory.

By making certain assumptions, the quantum yield was calculated to be 0.13 ±0.01.

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