

PHOTOLYSES OF ISOMERIC DINITROBENZENES
IN SOLUTION AT ROOM TEMPERATURE

By

CHARLES WILLIAM JONES

Bachelor of Arts

Western State College

Gunnison, Colorado

1954

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1957

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
AUG 12 1957

PHOTOLYSES OF ISOMERIC DINITROBENZENES
IN SOLUTION AT ROOM TEMPERATURE

Thesis Approved:

Earl H. Gilmore

Thesis Adviser

O. D. Dorman

Robert F. Maurice

Dean of the Graduate School

383090

ACKNOWLEDGMENT

The author wishes to express grateful acknowledgment to Dr. Earl H. Gilmore, thesis adviser, for his assistance and guidance throughout this work.

Acknowledgment is also made of financial aid by the Department of Chemistry and the Research Foundation of Oklahoma Agricultural and Mechanical College in the form of a research assistantship supported by the Office of Ordnance Research under Contracts No. Da-23-072-ORD-877 and No. DA-23-072-ORD-581.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. HISTORICAL	5
III. EXPERIMENTAL	7
Chemicals Used	7
Solvents	7
Isomeric Dinitrobenzenes	8
Actinometer	8
Instruments Used	9
Spectrophotometers	9
Monochromator	9
Monitor	9
Titration Instruments	9
Manner of Irradiation	9
Experiments Performed	11
<u>m</u> -Dinitrobenzene	11
<u>o</u> -Dinitrobenzene	17
<u>p</u> -Dinitrobenzene	19
IV. CALCULATIONS	28
Full Lamp Intensity	29
Calculation of Q	29
Calculation of dP_r/dt	29
Calculation of ϕ	29
Lamp With Screen	29
Calculation of Q	29
Calculation of dP_r/dt	31
Calculation of ϕ	31
V. DISCUSSION OF RESULTS	32
VI. SUMMARY	34
BIBLIOGRAPHY	36
APPENDIX	38

LIST OF TABLES

Table	Page
I. Summary of Changes in the Absorption Spectra of Isomeric Dinitrobenzenes Due to Exposure to a Wave Length of 253.7 m μ	35

LIST OF FIGURES

Figure	Page
1. Irradiating Apparatus	12
2. Absorption Spectrum of <u>m</u> -Dinitrobenzene in 2,2,4-Trimethylpentane	13
3. Absorption Spectrum of <u>m</u> -Dinitrobenzene in Ethanol	16
4. Absorption Spectra of <u>o</u> -Dinitrobenzene in 2,2,4-Trimethylpentane Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 m μ	18
5. Absorption Spectra of <u>o</u> -Dinitrobenzene in Ethanol Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 m μ	20
6. Absorption Spectra of <u>p</u> -Dinitrobenzene in 2,2,4-Trimethylpentane Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 m μ	21
7. Absorption Spectra of <u>p</u> -Dinitrobenzene in Ethanol Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 m μ	23
8. Absorption Spectra of <u>p</u> -Dinitrobenzene in Cyclohexane Before and After Irradiation With a Wave Length of 253.7 m μ	26
9. Absorption Spectra of <u>p</u> -Dinitrobenzene in Cyclohexane Before and After Irradiation With a Wave Length of 253.7 m μ When a Screen Was Inserted in the Irradiating Apparatus	27
10. Optical Density at 253.7 m μ of <u>p</u> -Dinitrobenzene in Cyclohexane as a Function of the Time of Irradiation With a Wave Length of 253.7 m μ	30

CHAPTER I

INTRODUCTION

Radiation chemistry is the study of chemical reactions resulting directly or indirectly from exposure of a system to radiation with electromagnetic waves, high velocity electrons, or other corpuscular beams obtained either from nuclear reactions or from electric accelerators. Photochemistry, a subdivision of radiation chemistry, is the science of the chemical effects of the electromagnetic waves ranging from the ultraviolet through the infrared, i.e., from about 100 $m\mu$ to 1000 $m\mu$. Usually, radiation chemistry refers to the science of the chemical effects of the higher-energy ionizing rays, so that the whole subject is divided into photochemistry and radiation chemistry on energetic grounds.

According to the quantum theory, a beam of light consists of many units of radiation called photons. A quantum of energy is the energy of one photon and depends upon the wave length of the light, the shorter wave lengths being more energetic. All of the photons in monochromatic light of a given wave length have the same energy according to Einstein's fundamental relationship,

$$E = h\nu,$$

in which E is the energy in one quantum, h is Planck's constant, and ν is the frequency of the light.

Light, when striking a substance, can be transmitted, scattered,

reflected, or absorbed. The logarithm of the fraction of incident light absorbed by a medium is proportional to the thickness of the medium traversed. This law was originally stated in a memoir by Bouguer, in 1729. It was later rediscovered by Lambert. In 1852, Beer showed that the logarithm of the fraction of incident light absorbed by a solution is proportional to the concentration of the solute for many solutions of absorbing compounds in practically transparent solvents. The two laws may be combined to form the Beer-Lambert law, which is

$$\rho = \log \frac{I_0}{I} = \epsilon cl,$$

where ρ is the optical density, I_0 is the intensity of the incident light, I is the intensity of the transmitted light, ϵ is the molar extinction coefficient, c is the molarity of the solution, and l is the number of centimeters of absorbing medium through which the beam of light passes.

In 1818, Grotthuss and Draper stated the principle that only light which is absorbed can produce a chemical change. It does not follow, however, that absorbed radiation must produce a chemical reaction. The absorbed radiation may simply be converted into heat or it may be re-emitted as light of either the same or a different wave length. The latter phenomenon is known as fluorescence or phosphorescence. In general, the wave length of the incident radiation is shorter than that of the re-emitted radiation, indicating that the molecule has absorbed some energy, since the light re-emitted has less energy. This relationship was first stated by Stokes; however, numerous exceptions have been found. Formerly, the differentiation between fluorescence and phosphorescence was based on the duration of the

afterglow. A slow decay of luminescence was called phosphorescence. Currently, the distinction of these terms is based on a difference in the mechanism for re-emission of light. In fluorescence, the quantum is absorbed and re-emitted from the excited state reached, either back to the initial state (resonance radiation) or to a different state. In exceptional cases, the re-emission may occur slowly, leading to a long afterglow. In phosphorescence, after the initial excitation to a certain energy level, the molecule makes a transition to a nearby level, which may be a metastable level, in that the transition from it to lower levels is unlikely because of low quantum mechanical transition probabilities. Considerable time may elapse before the molecule can acquire from suitable collisions enough energy to jump back up to the original excited state, from which the molecule can re-emit a quantum of light. Hence, the afterglow usually has an appreciable duration in phosphorescence, because the excited molecule has become "trapped in a metastable state." (11).

Einstein's law of the photochemical equivalent states that in the primary photochemical process each molecule is activated by the absorption of one photon, but the activated molecule does not necessarily undergo chemical reaction. For a gram mole of a substance, in this simple primary process, there should be 6.023×10^{23} quanta absorbed. The energy of a "gram mole" of quanta is called an einstein. Frequently, the Einstein law is marked by secondary reactions and complicating circumstances which prevent a simple one-to-one relationship between the number of quanta absorbed and the final number of molecules of products in the reaction. The quantum yield or quantum efficiency, ϕ , is defined by the relationship,

$$\phi = \frac{\text{number of molecules reacting chemically.}}{\text{number of quanta absorbed}}$$

It provides a means for describing the experimental facts and offers valuable information from which conclusions can be made as to the mechanism of a reaction. (1).

The main purpose of this research was to discover whether or not the isomeric dinitrobenzenes undergo photolysis in solution when irradiated with ultraviolet light from a mercury resonance lamp (253.7 m μ) at room temperature, and, in the event that photolyses were found, to measure the quantum yield of the processes.

CHAPTER II

HISTORICAL

In 1939, Shelegova (13) determined the absorption spectra of nitrobenzene in the vapor phase from -80° C to $+50^{\circ}$ C. A yellow tarnish formed on the walls of the reaction chamber when the vapor was irradiated with a wave length of around $217\text{ m}\mu$, which indicated that the absorption was accompanied by photodecomposition of the nitrobenzene. Shelegova postulated that excited and unexcited NO_2 formed and that the active NO_2 reacted with nitrobenzene to give di- and trinitrobenzene.

A mechanism of nitration was proposed by Gorislavets and Prilezhaeva (7), in 1941, on the basis of the absorption spectra of nitro compounds and the photochemical decomposition of nitrobenzene. They postulated that the electron atmosphere of NO_2 is distorted considerably by the interaction of NO_2 with aromatic molecules. The chemically active form of NO_2 is $^+\text{N}(:\text{O})\text{O}^-$, into which state the NO_2 molecule can be transformed by action of light. The NO_2 group is detached from the nitro compounds in the same electronic state as that produced by electronic excitation of a molecule of NO_2 . Hence, direct nitration by nitrogen oxides should proceed with catalysts that lead to the proper rearrangement of the electron atmosphere of the NO_2 molecule.

In 1943, Gorislavets (6) studied the photochemical reaction of NO_2 (and N_2O_4) with benzene in the gas and liquid phases and with nitrobenzene in the gas and liquid phases. He found that photochemical

decomposition of nitrobenzene showed that it is accompanied by formation of NO_2 . He proposed the following reaction equations:



Five years later, Hastings and Matsen (8) irradiated nitrobenzene with nitrogen as a carrier and obtained a mixture of products, which consisted chiefly of nitrosobenzene and *p*-nitrophenol. The products were identified spectrophotometrically. There was no evidence obtained to show the presence of NO_2 or polynitrobenzenes. The main reactions were:



Since the nitro group is ortho-para directing for free radicals, the presence of para, rather than meta, should be expected. (17).

Sollazzo (16), in 1933, found that vessels containing a mixture of *m*-dinitrobenzene, ethanol and ammonia underwent a photochemical reaction when exposed to sunlight at an altitude of 2812 meters above sea level. This was the only case in the literature survey in which dinitrobenzene was used in an experiment on photolysis.

CHAPTER III

EXPERIMENTAL

Chemicals Used

Solvents. Only a small amount of data on absorption curves for the isomeric dinitrobenzenes is to be found in the literature (2, 3, 4, 9, 10 and 12.) and these are for strongly polar solvents. 2,2,4-Trimethylpentane was selected as a solvent because it is non-polar and, therefore, a minimum of interaction should be expected between the solvent and solute molecules. Cyclohexane was used as a non-polar solvent in the later experiments, because it was thought that cyclohexane would be less apt to enter into secondary reactions than the 2,2,4-trimethylpentane on account of the tertiary hydrogen atoms on the latter. The 2,2,4-trimethylpentane and cyclohexane used were Phillips Petroleum Company Spectro Grade.

In order to have a polar solvent for comparison, ethanol was used. Commercial absolute ethanol was not used as a solvent, because it contains traces of benzene and the benzene absorbs in the same region of the ultraviolet as the isomeric dinitrobenzenes. Absolute ethanol was prepared by placing a liter of 95 percent ethanol in a two liter round bottom flask with about 3/4 of a pound of lumpy calcium oxide. The mixture was refluxed for several hours and then the flask was attached to a distilling apparatus, using standard taper joints throughout. The flask was heated with a glas-col until the reaction

started and then the heat was turned down. The distillate was collected in a round bottom flask. The distillation was stopped when the mixture in the pot became a white crust. About 600 ml of alcohol was obtained. At this point, the alcohol was supposed to be around 99.5 percent ethanol and 0.5 percent water. The receiver was removed and 80 ml of the distillate was put into a two liter round bottom flask with $\frac{1}{2}$ of a gram of iodine and about five grams of magnesium. The mixture was refluxed until much of the magnesium had reacted. The rest of the distillate was then added and the mixture was refluxed for an hour. After the refluxing, the pot was connected with ground glass joints to a distillation apparatus. The outlet on the receiver was fitted with a calcium chloride tube in order to prevent the admission of moisture to the system. A little more than 400 ml of the "anhydrous" ethanol distilled at 77° C. A silica cell was filled with this ethanol and distilled water was put into a matched cell for a reference. The absorption spectrum of the ethanol was determined. The ethanol did not absorb appreciably from 350 $m\mu$ to 255 $m\mu$, but the optical density increased from 250 $m\mu$ to 220 $m\mu$.

Isomeric Dinitrobenzenes. Coleman and Bell pure m-dinitrobenzene was purified by recrystallization from ethanol. Sapon Laboratories o-dinitrobenzene was recrystallized twice from ethanol, yielding white crystals with a melting point of 114-115° C. p-Dinitrobenzene, from the Matheson Co., Inc., was used. It was brownish-orange and had a melting point of 170-171° C. p-Dinitrobenzene, prepared by N. Karamian, was purified by sublimation and used in the later work. White needles, with a melting point of 172° C, were obtained.

Actinometer. The monochloroacetic acid used was Eastman Kodak Company (best grade) and the silver nitrate was Mallinckrodt analytical

reagent.

Instruments Used

Spectrophotometers. In the first part of the research, the absorption spectra were determined with a Beckman Model DU quartz spectrophotometer, equipped with a hydrogen discharge tube. A photomultiplier was used as a detector with the Model DU for the intermediate work. The absorption spectra in the later work were obtained with a Beckman Model DK2 ratio recording spectrophotometer. Silica cells were used throughout to hold the samples. Cells with a path length of one cm were used most, but in some cases a nine mm quartz block was inserted in the cell, so that the path length was one mm.

Monochromator. A Bausch and Lomb grating monochromator was used to isolate the 296.7 m μ mercury line. The mercury tube sold by Bausch and Lomb with the instrument was used as a source of light.

Monitor. A Heathkit vacuum tube voltmeter was used with a photo tube to monitor the light. The leads in the circuit were shielded so that the oscillations of the needle on the voltmeter due to pickup of stray 60 cycle field were held to a minimum.

Titration Instruments. A Rubicon Type B potentiometer and a General Electric galvanometer were used for the potentiometric titrations.

Manner of Irradiation

The means of irradiating the solutions was changed from time to time throughout the experimental work as better methods of irradiation were developed. A description of the various irradiation apparatuses follows in the order that they were used.

The solution to be irradiated was put in a silica cell and

placed in the cell holder from the spectrophotometer in front of the exit slit of a Bausch and Lomb Grating Monochromator. The 296.7 $m\mu$ line of mercury was isolated with the slit widths and heights set at two and ten mm, respectively.

In order to obtain a more intense source of light, a helical spiral mercury resonance lamp, made by the Hanovia Chemical and Manufacturing Company, was used. According to the manufacturer, 95 percent of the ultraviolet irradiation from the fused silica lamp is in the 253.7 $m\mu$ line. The lamp was powered by a 5,000 volt luminous tube transformer connected directly to the line. The solution to be irradiated was placed in a test tube made from 20 mm #7900 Vycor tubing. The Vycor vessel was used because it is transparent to the 253.7 $m\mu$ line and opaque to the 184.9 $m\mu$ line of mercury. It was assumed, therefore, that any photochemical change occurring was initiated by absorption of the 253.7 $m\mu$ mercury line, since the compounds do not absorb appreciably at longer wave lengths. The test tube was supported in the center of the spiral. The solution was stirred during irradiation by means of a bent rod propelled in an up and down direction by a fish reel. The stirrer wound around a finger condenser. The inlet of the condenser was connected to a water tap and the outlet ran into a beaker in which a thermometer was placed. The lamp was placed in a stove pipe which was coated on the inside with magnesium oxide.

Since it was desired to have an enclosed cell that could be stirred, a 25 mm (O. D.) #7910 Vycor tube that had a ground glass joint at the top was used for the reaction vessel. A glass stirrer with a magnet in the top end of it was placed in the vessel and a standard taper cap was put on the tube. The tube was situated in the center of a 45 mm (O. D.) #7910 Vycor tube which had water running through it

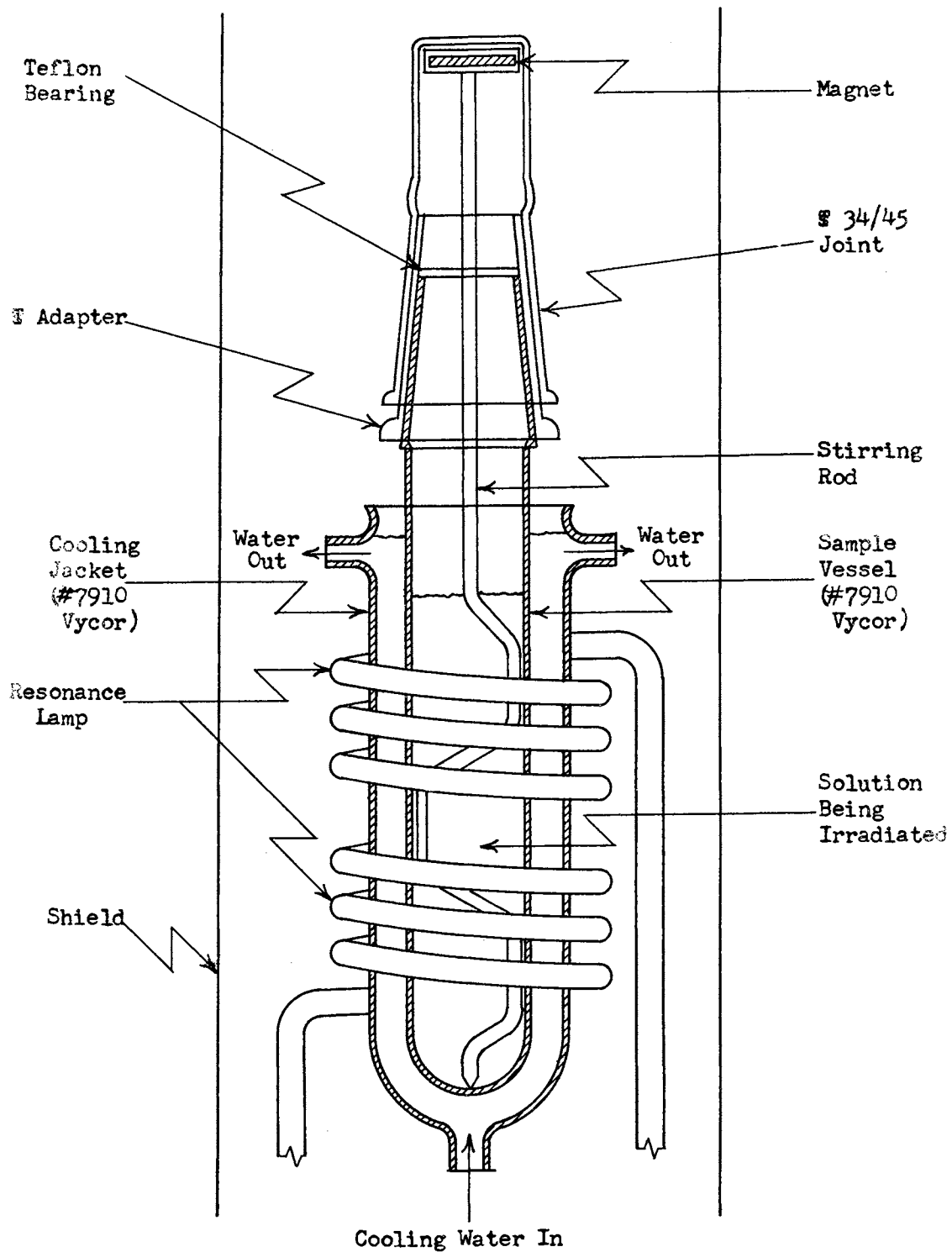
from the tap, so that the solution was kept at constant temperature. The tubes were supported between the coils of the helical spiral mercury resonance lamp, which was powered as before. The lamp was encircled by a sheet of galvanized metal and had a galvanized sheet for a cover. The diameter of the shield was ten inches. The stirrer was propelled by means of a magnet attached to a motor. The outlet from the outer tube ran into a beaker and a thermometer was inserted in the beaker. The apparatus is shown in Fig 1. The #7910 Vycor tubes were ordered from Corning Glass Works. The #7910 Vycor is more transparent to ultraviolet light than the #7900 Vycor.

The apparatus just described was used in all of the later work. Additions, such as a filter for the water jacket and a monitor for the light were made in some of the experiments. Some changes in the apparatus, such as the method of removing the irradiated solution from the reaction vessel and removal of the shield, were also made. These changes and additions are described in the next section.

Experiments Performed

m-Dinitrobenzene. A solution of 1.7×10^{-3} M m-dinitrobenzene in 2,2,4-trimethylpentane was prepared and the absorption spectrum determined from 220 $m\mu$ to 350 $m\mu$ with the solvent used as a reference. The absorption spectrum showed a very high maximum around 228 $m\mu$ and maxima at about 285 $m\mu$ and 296 $m\mu$. The curve is shown in Fig. 2.

It was decided to see if any evidence of photochemical decomposition could be found when 2,2,4-trimethylpentane solutions of the m-dinitrobenzene were irradiated in the 280-300 $m\mu$ region of the spectrum. The solution was irradiated for 30 minutes with the 296.7 $m\mu$ line of mercury, using the Bausch and Lomb grating monochromator.



Irradiating Apparatus

Figure 1

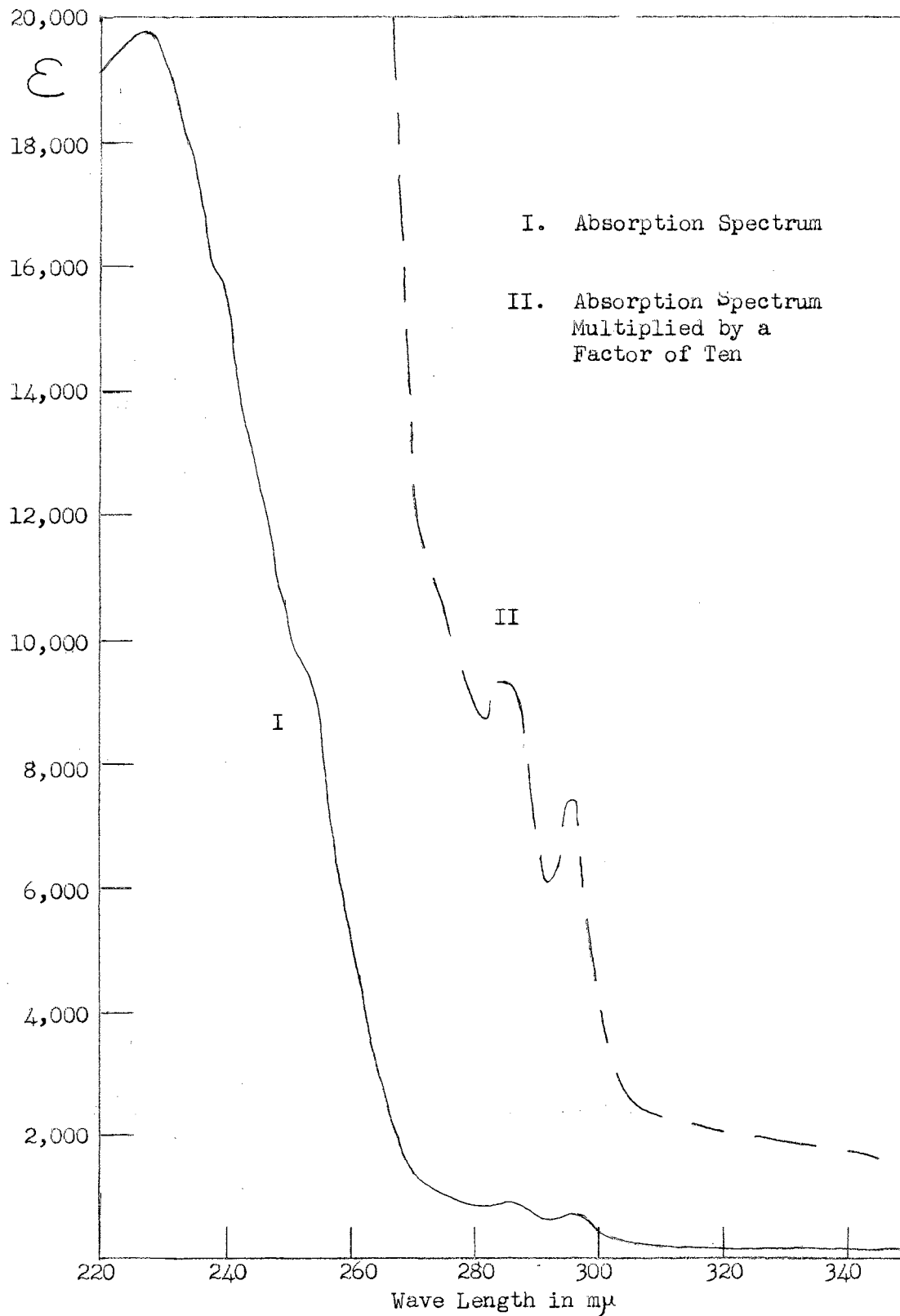


Fig. 2. Absorption Spectrum of *m*-Dinitrobenzene in 2,2,4-Tri-methylpentane.

The absorption spectrum of the solution showed the same characteristic curve as before irradiation, but it was higher throughout. It was thought that photochemical decomposition may have taken place. It was suspected, however, that the increase in absorption was due to evaporation of the solvent, thus increasing the concentration of the solution, so experiments were carried out to correct for any evaporation.

The unirradiated solution was put in a silica cell and weighed. A 30 minute irradiation was done in the same manner as before, and after the absorption spectrum of the irradiated solution was procured the cell was weighed again. It was found that 14.6 percent by weight of the solvent had evaporated. The number of moles of m-dinitrobenzene in the cell was calculated from the molarity of the solution and the number of milliliters of solvent lost was determined from the density of the 2,2,4-trimethylpentane. The concentration of the solution after evaporation was determined and the absorption spectrum was resolved using the calculated value for the concentration to compute the molar extinction coefficients. When this correction was applied, the absorption spectrum was almost identical to the curve before irradiation, so that there was no evidence of a photochemical change.

As another check, two matched stoppered silica cells were filled with the solution and placed in the spectrophotometer cell holder. The solution in one of the cells was irradiated with the 296.7 μ mercury line with the monochromator as before. The absorption spectrum was determined using the unirradiated solution as a reference and the absorption was found to be negligible. The main disadvantages of this method of irradiation were that the temperature could not be controlled and the solution could not be stirred.

It was thought that the exciting source may have been insufficiently intense, because other experiments, done by N. Smith (14), showed that benzene in 2,2,4-trimethylpentane solutions is photodecomposed at room temperature when excited in its long wave length absorption band.

In order to have a more intense source of light, the solution of m-dinitrobenzene in 2,2,4-trimethylpentane was irradiated for 30 minutes with the mercury resonance lamp (253.7 $m\mu$), using the apparatus involving the open Vycor reaction vessel described on the top of page ten. There was no visible change in the solution or change in odor due to the irradiation. The absorption spectrum was secured and it was found that the absorption of the whole curve increased and that the peaks of the original curve had not shifted. There were no new peaks.

Again, it was suspected that this change was due to evaporation of the solvent. The experiment was repeated, the only difference being that the solution was placed in a Pyrex test tube when it was irradiated. Pyrex is opaque to the 253.7 $m\mu$ line, so the ultraviolet light could not penetrate into the solution and cause a photochemical change. Hence, if any change in the spectrum were observed, it would probably have been due to the heat of the lamp. There was not a significant difference between the spectrum of the solution irradiated in Vycor and the solution irradiated in Pyrex.

A clear solution of 1.1×10^{-3} M m-dinitrobenzene in ethanol was prepared and the absorption spectrum determined with ethanol used as the reference. The spectrum had a high absorption peak at about 233 $m\mu$ and there were smeared out shoulders in the 280-300 $m\mu$ region instead of the peaks obtained in 2,2,4-trimethylpentane. See Fig. 3.

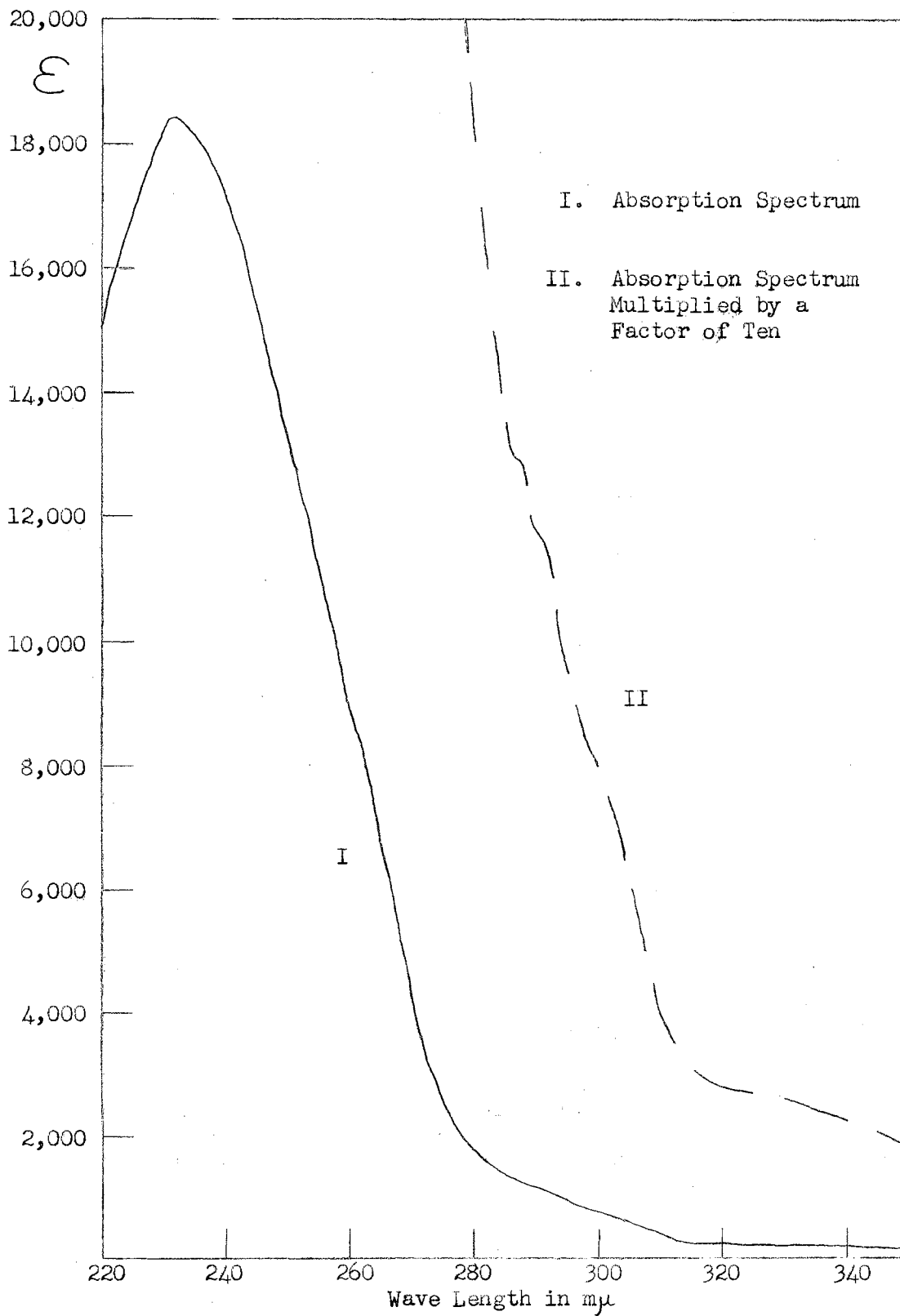


Fig. 3. Absorption Spectrum of *m*-Dinitrobenzene in Ethanol.

The solution of m-dinitrobenzene in ethanol was irradiated with the mercury resonance lamp (253.7 $m\mu$), using the apparatus shown in Fig. 1, for 30 minutes. The irradiated solution appeared to have a slightly yellow color. The absorption spectrum was determined using ethanol as the reference. The curve obtained had the same general shape as before irradiation. In the longer wave lengths the solution absorbed a little more after irradiation. The absorption spectrum was determined from 350 $m\mu$ to 1000 $m\mu$ by using a tungsten lamp for a source of light. The optical density decreased from 350 $m\mu$ to about 470 $m\mu$ and was zero from there to 1000 $m\mu$. The curve did not change sufficiently for one to conclude that a photochemical change had occurred.

o-Dinitrobenzene. Several solutions of around 10^{-4} M o-dinitrobenzene in 2,2,4-trimethylpentane were prepared and the absorption spectra were determined, using the solvent as a reference. It was very difficult to get the o-dinitrobenzene to go into solution. The absorption curves increased rapidly from 270 $m\mu$ to 220 $m\mu$. See Fig. 4 for the curve.

A solution of the o-dinitrobenzene in 2,2,4-trimethylpentane was irradiated for 30 minutes with the mercury resonance lamp (253.7 $m\mu$) using the apparatus pictured in Fig. 1. The irradiated solution appeared to be a little darker and when the absorption spectrum was examined, using the solvent as a reference, it was found that the solution absorbed less below about 257 $m\mu$ and more above 257 $m\mu$. The spectrum of the irradiated solution exhibited an isosbestic point¹

¹The term isosbestic point is applied to any wave length where the absorbancy indexes are the same for two materials which are interconvertible.

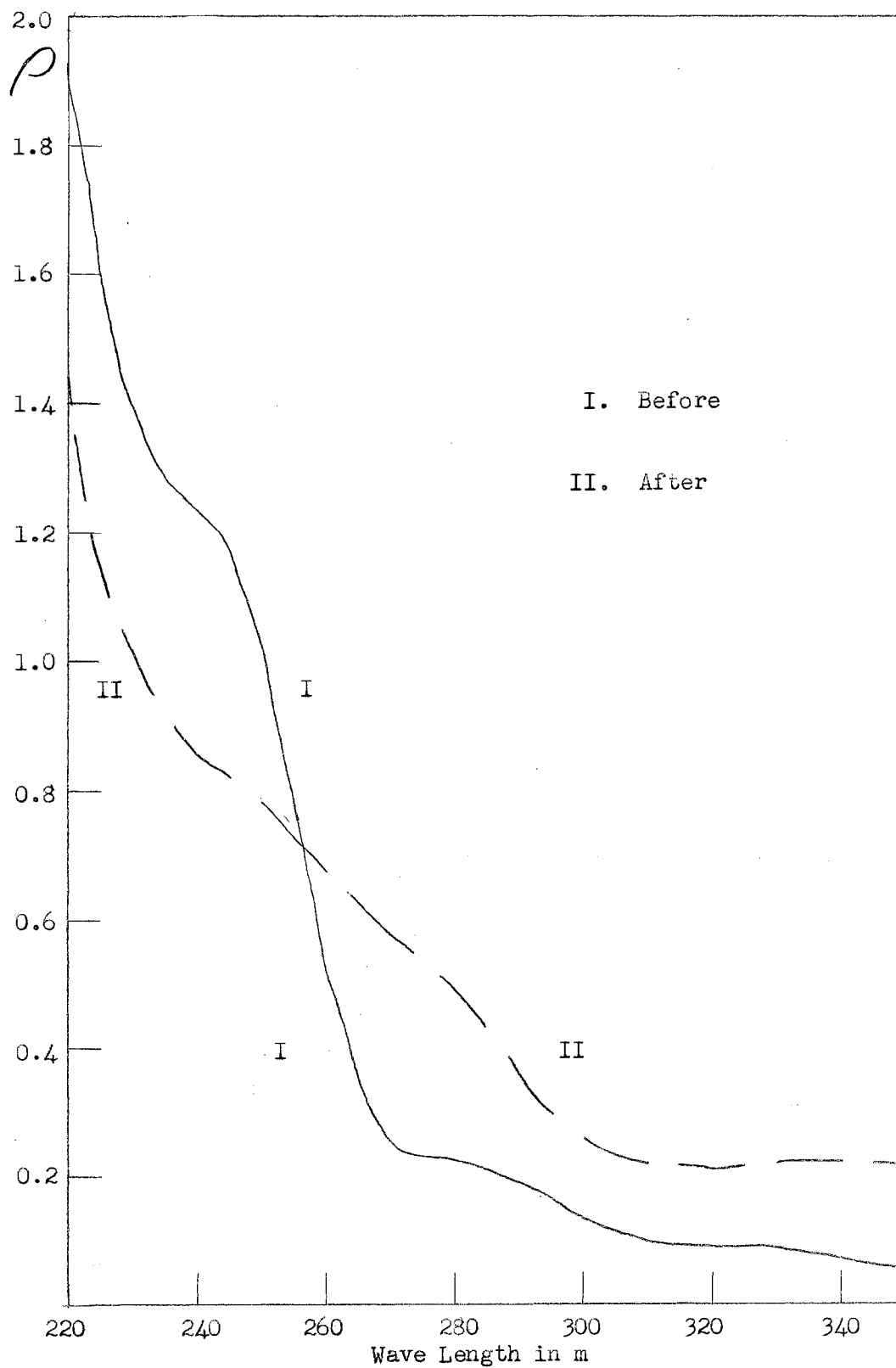


Fig. 4. Absorption Spectra of *o*-Dinitrobenzene in 2,2,4-Tri-methylpentane Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 μ .

with the initial solution. The change in the absorption spectrum, as shown in Fig. 4, was significant enough to indicate that a photochemical change had taken place.

A 2.0×10^{-4} molar solution of o-dinitrobenzene in ethanol was prepared. The solution was clear and the solute dissolved more readily in ethanol than in 2,2,4-trimethylpentane. The absorption spectrum was obtained using ethanol as a reference. The compound showed no peaks from 220 $m\mu$ to 350 $m\mu$ and its absorption increased from 310 $m\mu$ to 220 $m\mu$. The absorption spectrum is shown in Fig. 5.

The solution was irradiated for 30 minutes with the mercury resonance lamp (253.7 $m\mu$), using a setup as shown in Fig. 1. After irradiation the solution had a pale yellow color. There was no noticeable change in odor. The solvent was used as a reference and the absorption spectrum was obtained. After irradiation the solution absorbed less from 220 $m\mu$ to about 268 $m\mu$ and more from 268 $m\mu$ to 350 $m\mu$, as is shown in Fig. 5. The spectrum of the irradiated solution was measured to 500 $m\mu$, using a tungsten lamp for a source of light, and it was found that the optical density decreased to zero as the wave length increased. An isosbestic point was present around 268 $m\mu$. There was little doubt that photolysis had occurred.

p-Dinitrobenzene. A clear solution of 1.0×10^{-4} M p-dinitrobenzene in 2,2,4-trimethylpentane was prepared. p-Dinitrobenzene dissolves with difficulty in 2,2,4-trimethylpentane. The absorption spectrum was obtained, using the solvent as a reference, and a high peak was found at 256 $m\mu$. The absorption curve is shown in Fig. 6.

The solution was irradiated for 30 minutes with the mercury resonance lamp (253.7 $m\mu$) in the apparatus shown in Fig. 1. The solution underwent no visible change, nor was there a change in odor

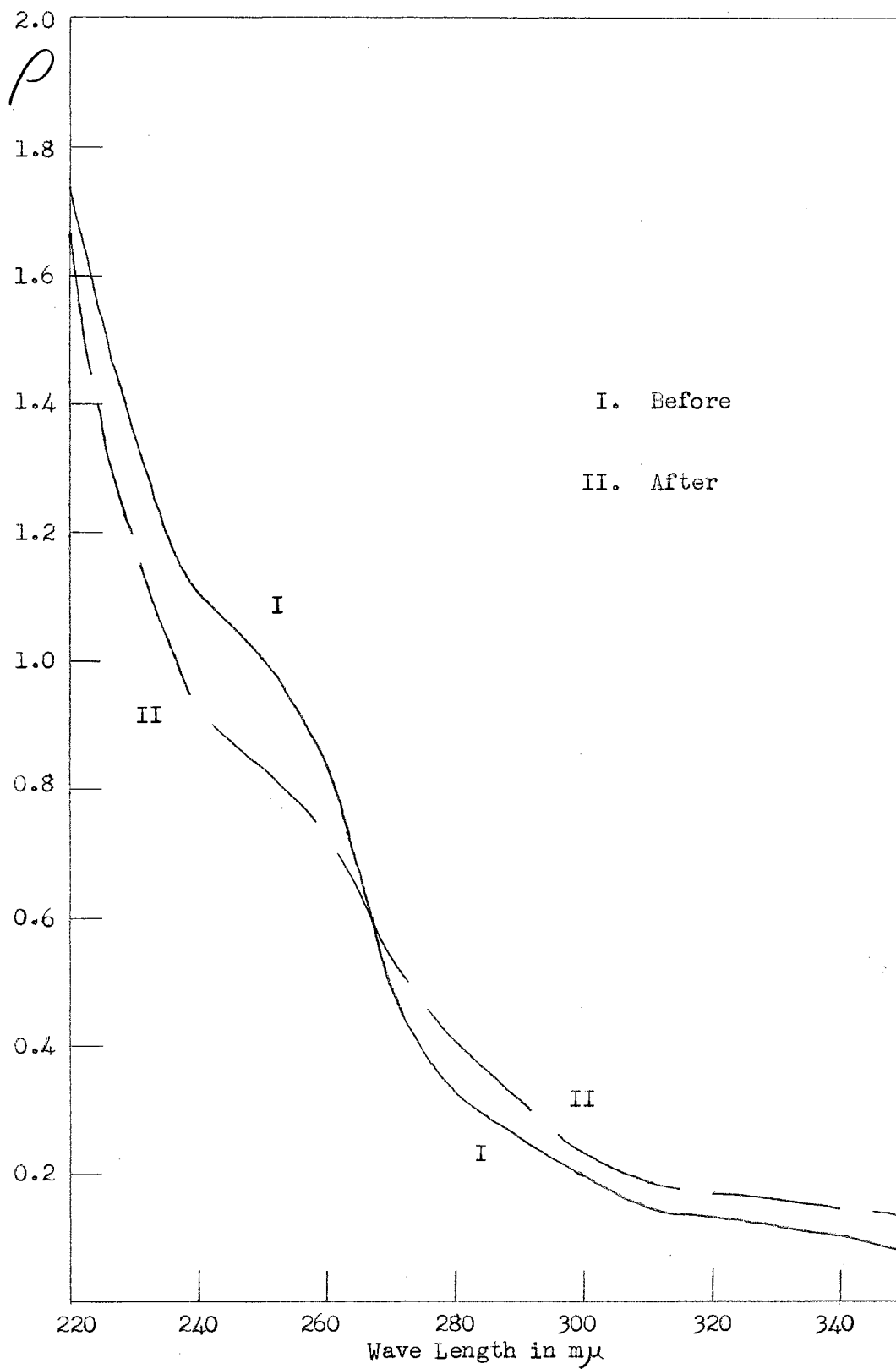


Fig. 5. Absorption Spectra of *o*-Dinitrobenzene in Ethanol Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 $m\mu$.

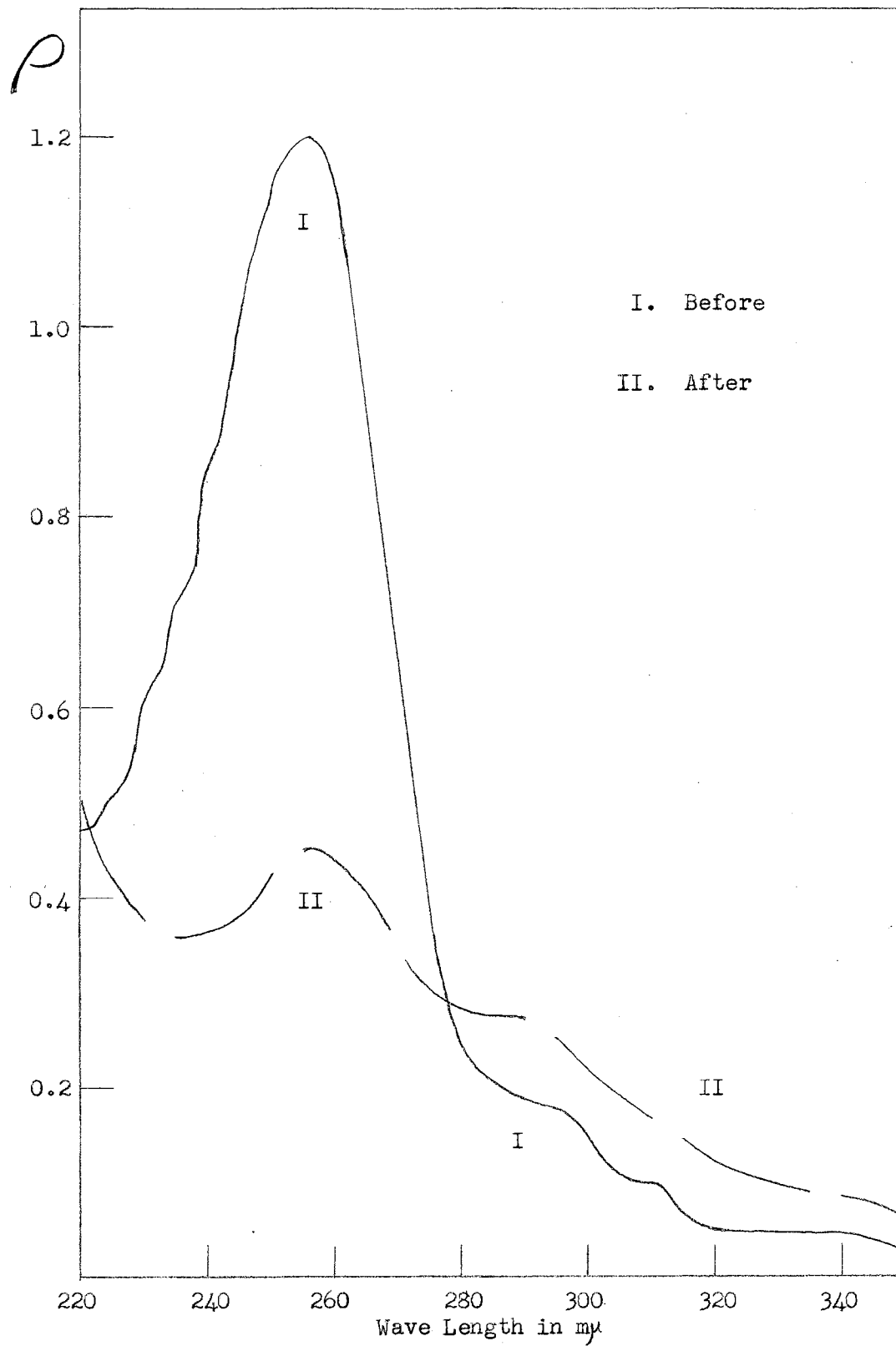


Fig. 6. Absorption Spectra of *p*-Dinitrobenzene in 2,2,4-Tri-methylpentane Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 $m\mu$.

due to irradiation. The absorption spectrum, however, with the solvent as a reference, showed a marked change. See Fig. 6. The compound absorbed considerably less below 278 $m\mu$ and more above 278 $m\mu$ after irradiation. There was a relative minimum around 236 $m\mu$. There was an isosbestic point at 278 $m\mu$ and perhaps another one around 222 $m\mu$. The marked change in the spectrum showed that a photochemical change had taken place.

A 2.0×10^{-4} molar solution of *p*-dinitrobenzene in ethanol was prepared and irradiated for 30 minutes with the mercury resonance lamp (253.7 $m\mu$) using the apparatus shown in Fig. 1. The irradiated solution appeared to be a little darker, but again there was no noticeable change in the odor. The absorption spectra before and after irradiation were determined using ethanol as a reference and are shown in Fig. 7. The solution had a high peak at 260 $m\mu$ before irradiation. After irradiation there was a large change in the nature of the curve. The irradiated solution absorbed less than the initial solution from 220 $m\mu$ to about 285 $m\mu$ and more above 285 $m\mu$. There was a relative minimum at 260 $m\mu$. An isosbestic point exists near 285 $m\mu$. There was definitely a photochemical change.

A clear solution of 1.3×10^{-4} M *p*-dinitrobenzene in cyclohexane was prepared. Solution of the *p*-dinitrobenzene was quite difficult. The absorption spectrum was determined, using cyclohexane as the reference. The curve showed a high peak at 255 $m\mu$.

Three portions of the solution were irradiated for periods of 10, 20, and 30 minutes, respectively, and the absorption spectra were resolved for the three samples, using cyclohexane as a reference. The irradiation was done with the mercury resonance lamp (253.7 $m\mu$) in the apparatus shown in Fig. 1. It was found that as the length of time of

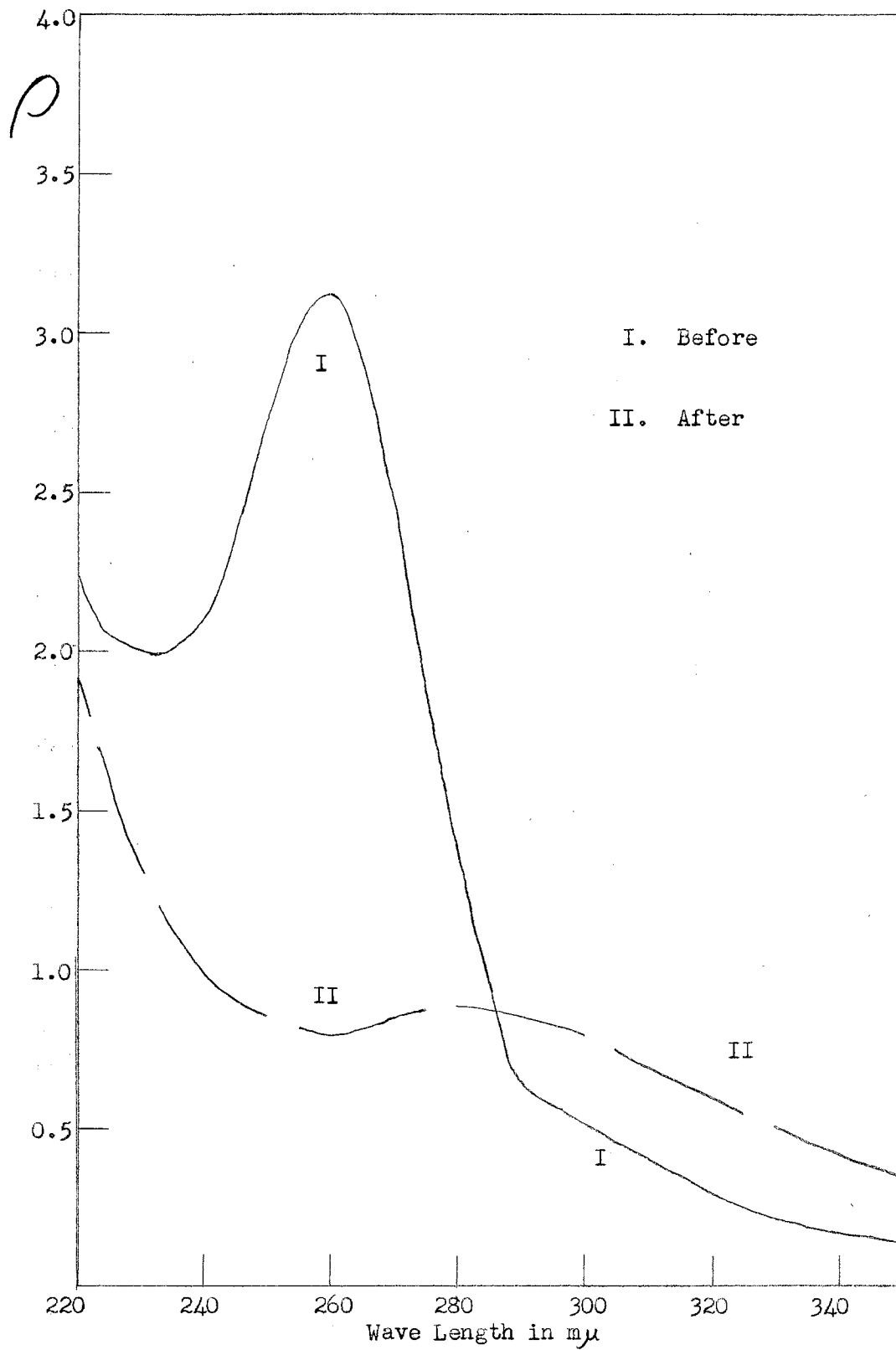


Fig. 7. Absorption Spectra of *p*-Dinitrobenzene in Ethanol Before and After Irradiation for 30 Minutes With a Wave Length of 253.7 $m\mu$.

irradiation was increased the solution absorbed less and less from about 230 $m\mu$ to about 275 $m\mu$ and more and more from 275 $m\mu$ to 350 $m\mu$. There are isosbestic points at about 275 $m\mu$ and around 230 $m\mu$. Photolysis takes place.

Another solution of *p*-dinitrobenzene in cyclohexane (1.2×10^{-4} M) was prepared from cyclohexane that had been refluxed with sodium in an attempt to remove traces of water. The absorption spectrum was determined again and the experiment in the above paragraph was repeated, except that the lengths of time for irradiation were 15, 30, and 60 minutes. The absorption spectra changed in a manner similar to the changes observed in the preceding experiment.

The order of the reaction with respect to the exciting quanta is of considerable interest. In order to determine this quantity it is necessary to know how the absorption curves change when the number of quanta entering the solution per second is changed.

A 5.7×10^{-5} molar solution of *p*-dinitrobenzene in cyclohexane was prepared. Six 50 ml portions of the solution were irradiated for periods of 5, 10, 15, 20, 30, and 60 minutes, respectively, with the mercury resonance lamp (253.7 $m\mu$) using the apparatus shown in Fig. 1. The following additions were made. An ammeter was placed in series with the lamp and the transformer in order to monitor the current. A water filter was placed between the tap and the cooling vessel to keep it from becoming contaminated. The reaction vessel was held rigidly and the solutions were removed with an aspirator so that it was not necessary to move the vessel between runs. The system was monitored with a photo cell to see if the radiant output of the lamp was constant. The absorption spectra of the solutions before and after irradiation

were determined and are shown in Fig. 8.

The output of the lamp under the same conditions was determined actinometrically. Monochloroacetic acid was used as an actinometer, because it is sensitive only to radiation of wave length 253.7 $m\mu$ and less and can, therefore, be used in ordinary room light (15). Its aqueous solutions are hydrolyzed by ultraviolet light to give glycolic acid and hydrochloric acid. The number of quanta absorbed by the solution can be calculated by titrating the hydrochloric acid formed, because the quantum yield for the reaction is known.

An aqueous solution of monochloroacetic acid with the same optical density as the *p*-dinitrobenzene solution at 253.7 $m\mu$ was prepared. Several 50 ml portions were irradiated for periods of ten minutes. The chloride ion was titrated potentiometrically with standard silver nitrate solution. A silver wire was used as an indicator electrode. The reference electrode, a saturated calomel half cell, was connected to the solution by an ammonium nitrate-agar salt bridge.

A 5.8×10^{-5} molar solution of *p*-dinitrobenzene in cyclohexane was prepared and six 50 ml portions were irradiated for periods of 5, 10, 15, 20, 45, and 60 minutes, respectively, with the mercury resonance lamp (253.7 $m\mu$), using the apparatus described on the bottom of page twenty-four with the following changes. A galvanized screen was placed in the water jacket around the reaction vessel to cut out some of the light. The shield was removed and the apparatus was covered with a black cloth. The absorption spectra of the solution before and after irradiation were determined and are shown in Fig. 9.

The output of the lamp under the same conditions was determined in the same manner as before. The actinometer solutions were irradiated for periods of 15 minutes.

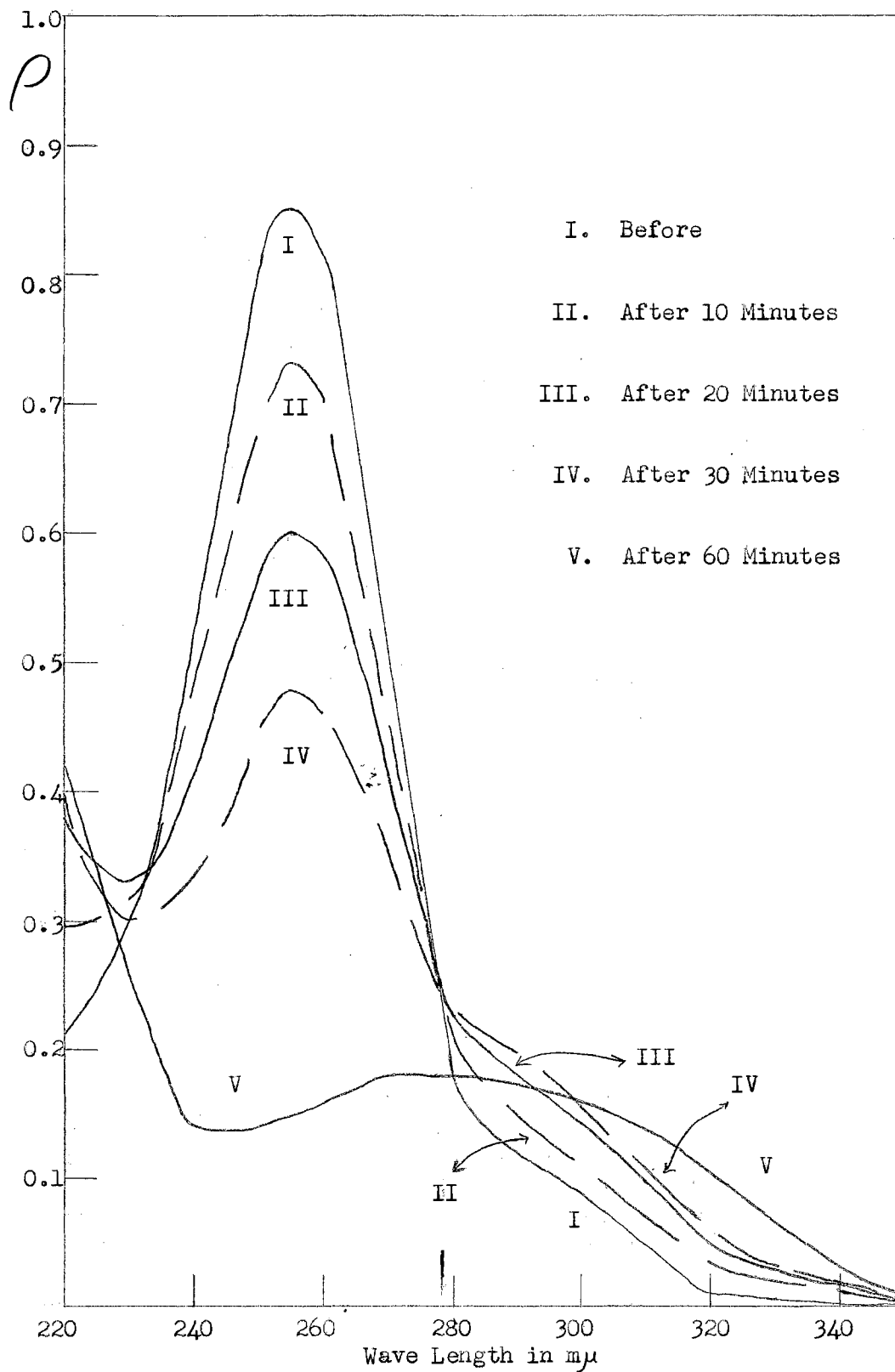


Fig. 8. Absorption Spectra of p-Dinitrobenzene in Cyclohexane Before and After Irradiation With a Wave Length of 253.7 $m\mu$.

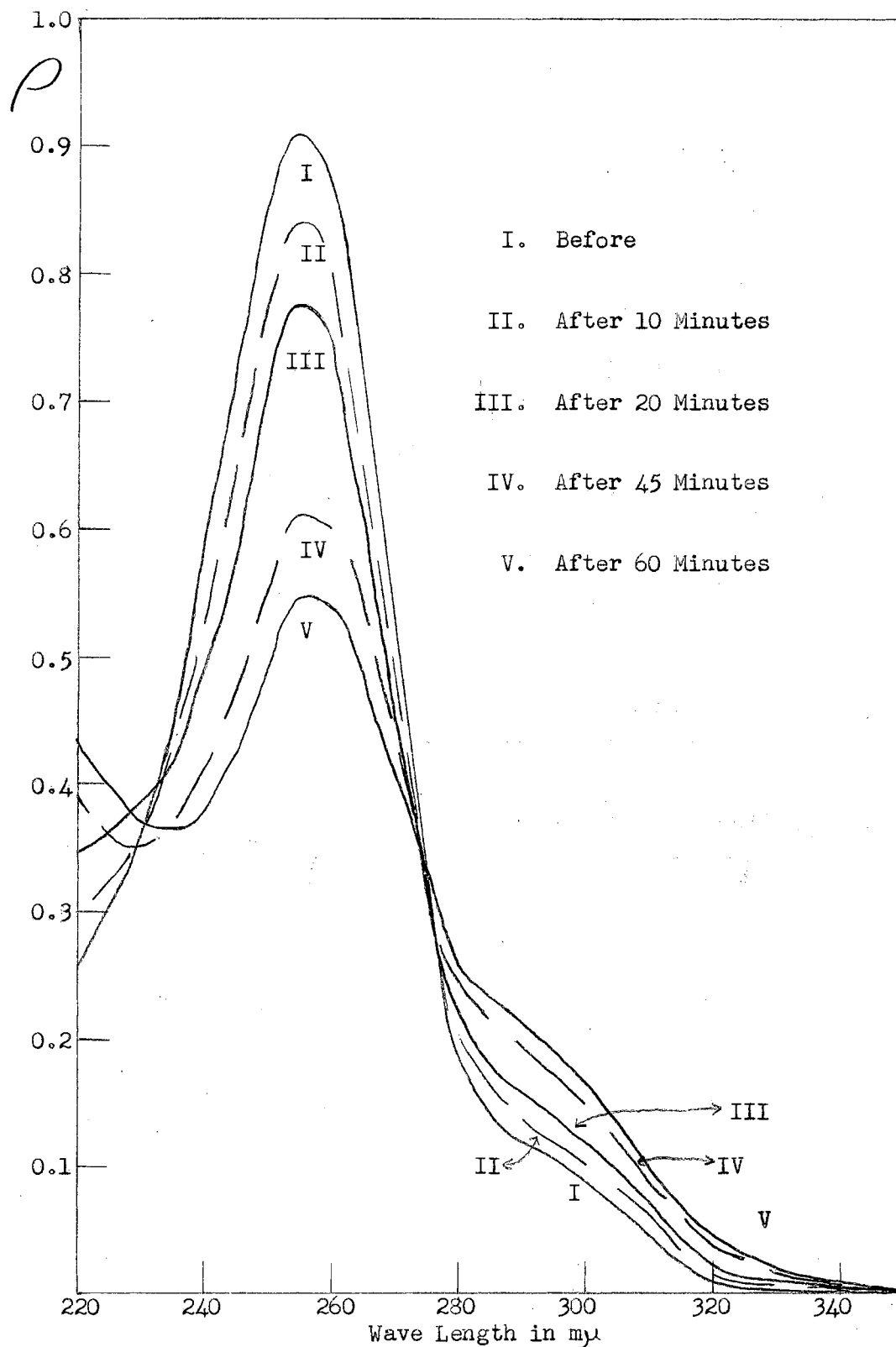


Fig. 9. Absorption Spectra of p-Dinitrobenzene in Cyclohexane Before and After Irradiation With a Wave Length of 253.7 $m\mu$ When a Screen Was Inserted in the Irradiating Apparatus.

CHAPTER IV

CALCULATIONS

The optical density at the wave length of the excitation of the photolyzed solution is a linear function of the time of irradiation. It is shown in the appendix that under such circumstances, the time rate of change of the optical density is related to the quantum yield by the expression

$$\frac{d\rho_r}{dt} = - \frac{Q \phi \epsilon_r}{N V} = - \frac{Q \phi \rho_r}{N V C_r} \quad (1)$$

In this expression ($d\rho_r/dt$) is the change in optical density at the excitation wave length of the photolyzed solution with respect to time, Q is the number of quanta absorbed per second by the solution, ϕ is the quantum yield, N is Avogadro's number, V is the volume of the solution in liters, ϵ_r is the molar extinction coefficient of the reactant, and ρ_r is the optical density at the excitation wave length of the reactant at concentration C_r .

Since ρ_r , N , V , and C_r are known, the quantum yield of the reaction can be calculated, if Q and ($d\rho_r/dt$) can be obtained, from the equation,

$$\phi = - \frac{N V C_r}{Q \rho_r} \cdot \frac{d\rho_r}{dt} \quad (2)$$

Full Lamp Intensity

Calculation of Q. Three solutions of monochloroacetic acid, which had the same optical density at 253.7 μ as that of the p-dinitrobenzene solution, were irradiated with the same apparatus for periods of ten minutes. The irradiated solutions were titrated with 0.01227 M silver nitrate and an average of 18.2 ml was required. The number of molecules reacting was $0.0182 \times 0.01227 \times 6.023 \times 10^{23}$. The quantum yield for the reaction at the temperature that the experiment was run (30° C) is known (16) to be 0.35 and the number of seconds that the solution was irradiated was 600. Therefore, the number of quanta absorbed per second by the solution, Q, was $(0.0182 \times 0.01227 \times 6.023 \times 10^{23}) / (0.35 \times 600) = 6.4 \times 10^{17}$.

Calculation of $(d\rho_r/dt)$. From Fig. 10, it is seen that the optical density of the photolyzed solution at 253.7 μ is a linear function of time. The slope of the line, $(d\rho_r/dt)$, was found to be $(-0.525/2700)$ or -1.94×10^{-4} .

Calculation of ϕ . Substituting all of the known values into equation (2), the quantum yield is obtained. Hence,

$$\phi = \frac{N \quad V \quad C_r \quad d\rho_r/dt}{(6.4 \times 10^{17})(0.85)} = \frac{(6.023 \times 10^{23})(0.050)(5.7 \times 10^{-5})(-1.94 \times 10^{-4})}{(6.4 \times 10^{17})(0.85)}$$

or

$$\phi = 6.1 \times 10^{-4}$$

Lamp With Screen

Calculation of Q. Six solutions of monochloroacetic acid of the proper optical density were irradiated with the apparatus involving

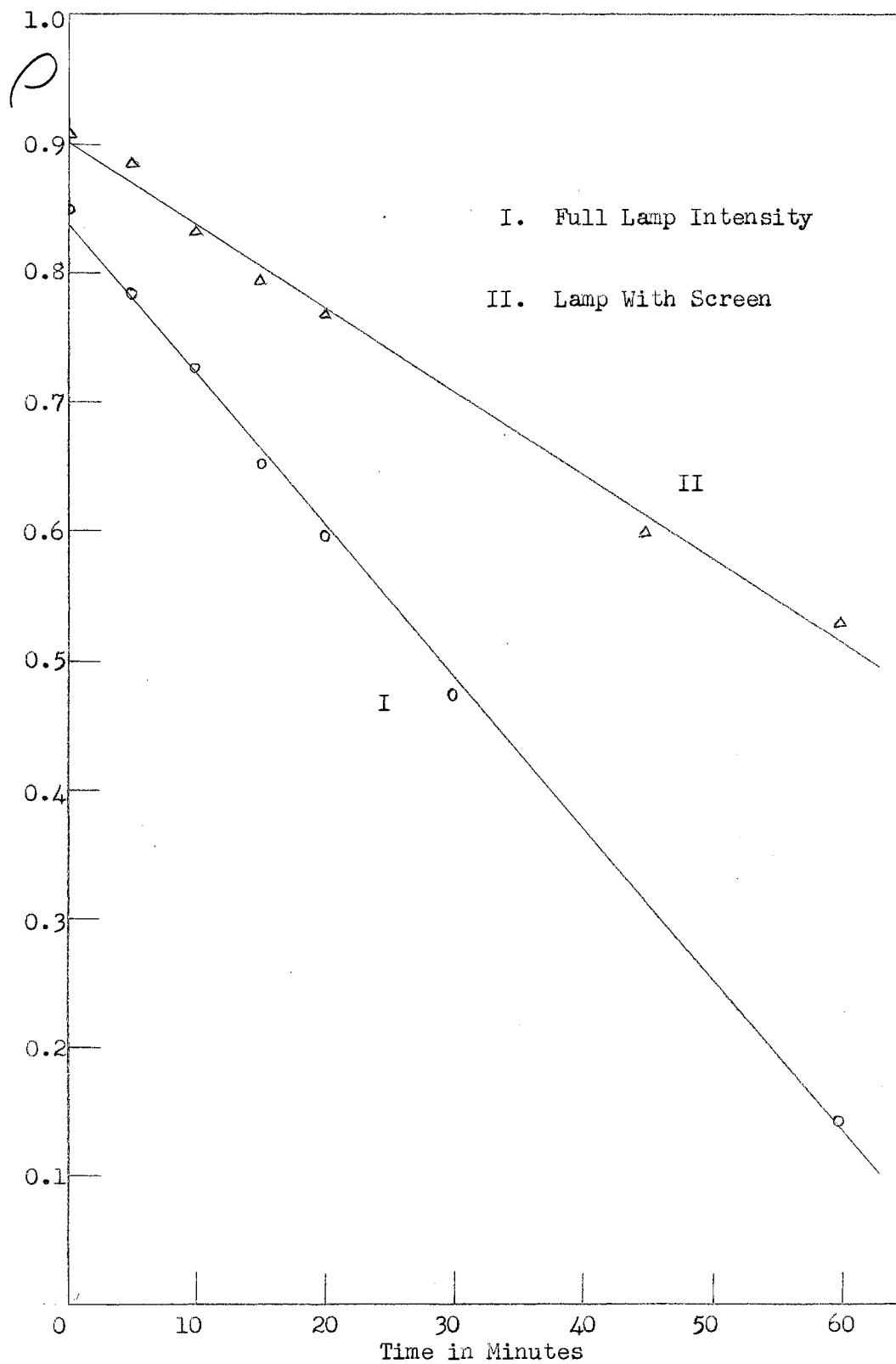


Fig. 10. Optical Density at $253.7 \text{ m}\mu$ of *p*-Dinitrobenzene in Cyclohexane as a Function of the Time of Irradiation With a Wave Length of $253.7 \text{ m}\mu$.

the screen for periods of 15 minutes. The irradiated solutions were titrated with 0.01227 M silver nitrate and an average of 13.6 ml was required. The number of molecules reacting was $0.0136 \times 0.01227 \times 6.023 \times 10^{23}$. Since the quantum yield for the reaction (16) at 29° C (the temperature of the actinometric solution during irradiation) is 0.34 and the time of irradiation was 900 seconds, the number of quanta absorbed per second by the solution, Q , was $0.0136 \times 0.01227 \times 6.023 \times 10^{23} / (0.33 \times 900)$ or 3.4×10^{17} .

Calculation of $(d\rho_r/dt)$. The optical density at 253.7 $m\mu$ of the photolyzed solution is seen to be a linear function of time. See Fig. 10. The change in optical density with respect to time, $(d\rho_r/dt)$, was found to be $(-0.325/3000)$ or -1.08×10^{-4} .

Calculation of ϕ . The quantum yield is given by

$$\phi = \frac{N \quad V \quad C_r \quad d\rho_r/dt}{(3.4 \times 10^{17})(0.91)}$$

$$\phi = \frac{(6.023 \times 10^{23})(0.050)(5.8 \times 10^{-5})(-1.08 \times 10^{-4})}{(3.4 \times 10^{17})(0.91)}$$

or

$$\phi = 6.1 \times 10^{-4}$$

CHAPTER V

DISCUSSION OF RESULTS

Since the m-dinitrobenzene does not undergo photolysis and the other two compounds do, this indicates that the results of the photochemical behavior of the three compounds can be related to the differences in electron densities, on an aromatic ring with a meta orienting group, at the 2- and 4-positions as compared with the 3-position.

The experimental results for the irradiation of p-dinitrobenzene in cyclohexane with the mercury resonance lamp show that a linear relationship exists between the optical density of the solution and the time of exposure. It seems reasonable, therefore, to interpret the photolyses of the p-dinitrobenzene solutions as simple photodecomposition in which molecules of a single species are produced from the molecules of p-dinitrobenzene. It is regarded as improbable that more than one species is produced because nearly all molecules of any degree of complexity have significant absorption at 253.7 μ . The probability that two or more molecules with little or no absorption at 253.7 μ be formed in the reaction is much less than the probability of having one such molecule formed. It is also possible that several very simple molecules are formed, but the degree of breakdown required makes this possibility unlikely. In addition, the product molecules absorb appreciably more at a longer wave length than do the reactant molecules. Such is quite unlikely to be the case if the product molecules are simple molecules.

The precision of the values of the quantum yield obtained lie within the range of experimental error. More precise results might be obtained if the lamp were powered from a regulated source. It would probably be better to use uranyl oxalate, instead of monochloroacetic acid, for an actinometer. Uranyl oxalate does not react in the dark, whereas, monochloroacetic acid undergoes hydrolysis in the dark about one percent as fast as when it is exposed to a wave length of 253.7 $m\mu$ at 25° C.

CHAPTER VI

SUMMARY

It has been shown that m-dinitrobenzene dissolved in either 2,2,4-trimethylpentane or ethanol does not show an appreciable change in its absorption spectrum when it is irradiated with ultraviolet light of wave length 253.7 μ . When o-dinitrobenzene and p-dinitrobenzene are exposed to a wave length of 253.7 μ in either 2,2,4-trimethylpentane or ethanol there are enough changes in the absorption spectra to show that photolyses have occurred. The results obtained are summarized in Table I.

It was decided to calculate the quantum yield for the photolysis of p-dinitrobenzene in cyclohexane. By making certain assumptions, a value of 0.0006 was obtained with the error estimated to be five percent. The output of the lamp was reduced and the reaction was found to be first order with respect to the quanta.

Plans are being made to identify the products of the photodecomposition chromatographically.

TABLE I

Summary of Changes in the Absorption Spectra of Isomeric Dinitrobenzenes

Due to Exposure to a Wave Length of 253.7 $m\mu$

Compound	Solvent	Change in Spectrum
<u>m</u> -Dinitrobenzene	2,2,4-Trimethylpentane	Practically none
<u>m</u> -Dinitrobenzene	Absolute Ethanol	Slight
<u>o</u> -Dinitrobenzene	2,2,4-Trimethylpentane	Absorption is less from 220 $m\mu$ to 257 $m\mu$, and is greater from 257 $m\mu$ to 350 $m\mu$ than before irradiation.
<u>o</u> -Dinitrobenzene	Absolute Ethanol	Absorption is less from 220 $m\mu$ to 268 $m\mu$, and is greater from 268 $m\mu$ to 500 $m\mu$ than before irradiation
<u>p</u> -Dinitrobenzene	2,2,4-Trimethylpentane	Absorption is much less from about 222 $m\mu$ to 278 $m\mu$, and is greater from 278 $m\mu$ to 350 $m\mu$ than before irradiation
<u>p</u> -Dinitrobenzene	Absolute Ethanol	Absorption is much less from about 220 $m\mu$ to 285 $m\mu$, and is greater from 285 $m\mu$ to 350 $m\mu$ than before irradiation
<u>p</u> -Dinitrobenzene	Cyclohexane	Absorption is much less from about 230 $m\mu$ to 275 $m\mu$, and is greater from 275 $m\mu$ to 350 $m\mu$ than before irradiation

BIBLIOGRAPHY

1. Daniels, Farrington: Outlines of Physical Chemistry, John Wiley and Sons, Inc., New York, 1948, Chapter 20.
2. Doub, Leonard, and J. M. Vandenbelt, J. Am. Chem. Soc. 69, 2714-23 (1947).
3. Doub, Leonard, and J. M. Vandenbelt, J. Am. Chem. Soc. 71, 2414-20 (1949).
4. Fielding, P., and R. J. W. Le Fevre, J. Chem. Soc. 1950, 2812-3.
5. Gilmore, Earl H., Quarterly Status Report No. 6, Contract DA-23-072-ORD-581, March 15, 1956.
6. Gorislavets, I. O., J. Phys. Chem. (U. S. S. R.) 17, 102-7 (1943).
7. Gorislavets, I. O., and N. A. Prilezhaeva, Bull. acad. sci. U. R. S. S., Ser. phys. 1941, 115-9 (English Summary).
8. Hastings, S. H., and F. A. Matsen, J. Am. Chem. Soc. 70, 3514-5 (1948).
9. Kiss, Árpád, and J. Hyross, Acta Univ. Szeged., Chem. et Phys. 2, 76-82 (1948).
10. Kortüm, G., Z. physik. Chem. B42, 39-66 (1939).
11. Moore, Walter J.: Physical Chemistry, Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1955, Chapter 18.
12. Shatenshtein, A. I., and Ya M. Varshavskii, (Karpov Inst. Phys.-Chem., Moscow). J. Phys. Chem. (U. S. S. R.) 22, 529-39 (1948).
13. Shelegova, O. N., J. Exptl. Theoret. Phys. (U. S. S. R.) 9, 1527-9 (1939).
14. Smith, Norris K.: The Quantum Yield of Photodecomposition of Benzene Solutions at Room Temperature, Unpublished thesis, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, 1956.
15. Smith, R. Nelson, Phillip A. Leighton, and Wesley G. Leighton, J. Am. Chem. Soc. 61, 2299-301 (1939).
16. Sollazzo, G., Boll. chim.-farm. 72, 913-5 (1933).

17. Wheland, G. W.: The Theory of Resonance, John Wiley and Sons, Inc., New York, 1944, page 262.

APPENDIX

The Use of Absorption Spectra Data in the Study of Photochemical Processes in Solutions. (5).

In general, the absorption spectrum of an irradiated solution in which photodecomposition is occurring changes in a complicated manner, both as a function of time and as a function of the wave length. The absorption of the initial species decreases with time, and the absorption of the product or products increases; and since their spectra are usually quite different, the complicated spectral changes result. The situation may be further complicated if one or more of the product molecules is decomposed by the radiation causing the photolysis of the initial species, or by radiation of another wave length that may be present in the source. To predict the behavior of the total absorption spectrum of some of the more complicated situations is clearly difficult. One can, however, develop analyses of the behaviors of some of the simpler situations which are of great value in the study of photochemical processes for which the analyses are valid.

Case I.

The first case to be considered is that of a solution, which, upon being irradiated, undergoes photochemical changes in accordance with the following conditions:

1. The solution is irradiated by monochromatic radiation.
2. The relative numbers of product molecules produced by the photolysis of the initial species are independent of the time.

3. The product species are not further photodecomposed.
4. The solution is perfectly stirred.
5. The absorption of each species present is unaffected by the presence of the other species.
6. The incident radiation is essentially completely absorbed in all the solutions considered.

A. Behavior of the Optical Density During Irradiation.

The optical density, at any arbitrarily chosen wave length when measured in a cell of unit length, is given by

$$\rho = \epsilon_r C_r + \sum_{i=1}^n \epsilon_i C_i, \quad \text{Eq. (1)}$$

in which ρ is the optical density, ϵ_r and ϵ_i are the absorption coefficients of the reactant and the i^{th} product species respectively for the arbitrarily chosen wave lengths, and C_r and C_i are the concentrations of the reactant and i^{th} product species respectively. The time rate at which the optical density changes is given, therefore, by

$$(d\rho/dt) = \epsilon_r (dC_r/dt) + \sum_{i=1}^n \epsilon_i (dC_i/dt). \quad \text{Eq. (2)}$$

The derivative dC_r/dt of Eq. (2) can be written

$$dC_r/dt = - (Q\phi/NV)f_r \quad \text{Eq. (3)}$$

in which Q is the rate at which quanta are delivered to the solution, ϕ is the photodecomposition yield of the reactant species, N is Avogadro's number, V is the volume of the solution, and f_r is the instantaneous fraction of the quanta absorbed by the reactant species. The quantity f_r can be written as

$$f_r = \epsilon_r C_r / \rho, \quad \text{Eq. (4)}$$

by virtue of conditions 4, 5, and 6, when ϵ_r and ρ are measured at the wave length of the excitation (condition 1 requires that there be only one such wave length). Equation (3) may now be written

$$dC_r/dt = -(\mathcal{Q}/NV) \epsilon_r C_r / \rho. \quad \text{Eq. (5)}$$

The rate at which the concentration of the i^{th} product changes with time is obtained in terms of C_r by differentiating the equation

$$C_i = (C_0 - C_r) P_i. \quad \text{Eq. (6)}$$

The result is

$$\begin{aligned} dC_i/dt &= P_i d(C_0 - C_r)/dt \\ &= -P_i dC_r/dt, \end{aligned} \quad \text{Eq. (7)}$$

in which C_0 is the starting concentration of the reactant species and P_i is the probability that a molecule of the i^{th} product species will be formed when a molecule of the reactant decomposes. Equation (6) is valid if conditions 2 and 3 are met.

Then

$$dC_i/dt = (P_i \mathcal{Q}/NV) \epsilon_r C_r / \rho, \quad \text{Eq. (8)}$$

hence

$$\sum_{i=1}^n \epsilon_i (dC_i/dt) = (\mathcal{Q}/NV) (\epsilon_r C_r / \rho) \sum_{i=1}^n C_i P_i. \quad \text{Eq. (9)}$$

Substituting from Eqs. (9) and (5) into Eq. (2), there is obtained the result

$$d\rho/dt = (Q\phi/NV) \sum_{i=1}^n (\epsilon_i P_i - \epsilon_r) \epsilon_r C_r / \rho. \quad \text{Eq. (10)}$$

The expression for $d\rho/dt$ given in Eq. (10) can be integrated provided $\epsilon_r C_r$ can be found as a function of ρ . Such a function can be found by solving Eqs. (6) and (1) simultaneously.

The result is

$$\epsilon_r C_r = \epsilon_r (\rho - K_1) / K, \quad \text{Eq. (11)}$$

When one sets $K_1 = C_0 \sum_{i=1}^n \epsilon_i P_i$ and $K = \epsilon_r - \sum_{i=1}^n \epsilon_i P_i$. These quantities are constants as long as conditions 2 and 3 are satisfied. Substituting the expression for $\epsilon_r C_r$ given by Eq. (11), into Eq. (10), the differential equation

$$d\rho/dt = -K_2 \epsilon_r (1 - K_1/\rho) \quad \text{Eq. (12)}$$

is obtained when one sets $(Q\phi/NV) = K_2$.

Many interesting facts can be deduced concerning the processes occurring by studying Eq. (12). The slope of the curve of ρ vs. t behaves in characteristic ways depending upon the relative values of K_1 and ρ_0 .

Four different situations of interest are considered in the following:

1. If $K_1 = 0$, then $d\rho/dt = -K_2 \epsilon_r$ and the optical density of the photolyzed solution will be a linear function of the time.
2. If $0 < K_1 < \rho_0$, then $d\rho/dt < 0$ for all $t < \infty$ but

$$\lim_{t \rightarrow \infty} \frac{d\rho}{dt} = 0 \quad \text{since} \quad \lim_{t \rightarrow \infty} \rho = K_1. \quad \text{The curve of } \rho \text{ vs } t \text{ will}$$

start with a finite negative slope and approach a limiting value.

3. If $K_1 = \rho$, then $d\rho/dt = 0$ and the optical density is independent of the duration of the irradiation. Such is the condition which will give an isosbestic point.
4. If $K_1 > \rho$, then $d\rho/dt > 0$ and the curve of ρ vs. t will start with a finite positive slope but will tend to reach a limiting value of ρ equal to K_1 as $t \rightarrow \infty$.

Once the behaviors of the concentrations of reactants and products can be predicted from what is happening at the wave length of excitation, the behavior of the optical densities at other wave lengths can be predicted if the corresponding molar extinction coefficients are known. Conversely, if the behaviors of optical densities at other wave lengths are known, together with a knowledge of the behaviors of the concentrations of product and reactant species, then information can be derived on the absorption coefficients of the products.

VITA

Charles William Jones
candidate for the degree of
Master of Science

Thesis: PHOTOLYSES OF ISOMERIC DINITROBENZENES IN SOLUTIONS AT
ROOM TEMPERATURE

Major Field: Chemistry

Biographical and Other Items:

Born: July 25, 1932, at Upland, California, the son of Henry A.
and Dorothy L. Jones.

Undergraduate Study: Western State College, Gunnison, Colorado,
1950-1954.

Graduate Study: Oklahoma Agricultural and Mechanical College,
Stillwater, Oklahoma, 1954-1957.

Experience: Teaching Assistant, Department of Chemistry, Okla-
homa Agricultural and Mechanical College, 1954-1955;
Research Assistant, Department of Chemistry, Oklahoma
Agricultural and Mechanical College, 1955-1956.

Organizations: Phi Lambda Upsilon, Sigma Pi Sigma, Lambda
Delta Lambda, and American Chemical Society.

Date of Final Examination: March, 1957.

THESIS TITLE: PHOTOLYSES OF ISOMERIC DINITROBENZENES IN SOLUTION
AT ROOM TEMPERATURE

AUTHOR: Charles William Jones

THESIS ADVISER: Dr. Earl H. Gilmore

The content and form have been checked and approved by the author and thesis adviser. The Graduate School assumes no responsibility for errors either in form or in content. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: Jean Kroll