PHOTOCHEMICAL STUDIES OF THE ISOMERIC MONONITRONAPHTHALENES

By

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369912

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TABLE OF CONTENTS

Chapter		Page
I.	INTRODUCTION	1
II.	HISTORICAL BACKGROUND	6
III.	EXPERIMENTATION	8
IV.	INTERPRETATIONS OF RESULTS	27
V.	CALCULATIONS	39
VI.	SUMMARY	45
BIBLIOGRAPHY		46

LIST OF FIGURES

Figure		Page
1.	Sublimation Apparatus	9
2.	Absorption Spectra of 1-nitronaphthalene	11
3.	Absorption Spectra of 2-nitronaphthalene	12
4.	Irradiation Apparatus	14
5.	Effect of Irradiation on Spectra of Mononitronaphthalenes in 95% Ethanol	16
6.	Effect of Irradiation on Spectra of Mononitronaphthalenes in Cyclohexane	17
7.	Monochromatic Irradiator	18
8.	Filter Train Irradiator	20
9.	Transmission Spectra of Diphenylbutadiene	22
10.	Resonance Lamp Irradiator	24
11.	Effect of Mercury Resonance Line on Spectrum of 2-nitronaphthalene in Cyclohexane	25
12.	Effect of Mercury Resonance Line on Spectrum of 1-nitronaphthalene in 95% Ethanol	26
13.	Optical Density vs Time of Exposure for 2-nitronaphthalene in Cyclohexane	28
14.	Optical Density vs Time of Exposure for 1-nitronaphthalene in 95% Ethanol	31
15.	Graphical Determination of $\lim_{t \to 0} (d\ /dt)$	38

CHAPTER I

INTRODUCTION

Photochemistry is a specialized subdivision of the moore general field, radiation chemistry. It is concerned with the interaction of matter with light of the infrared, visible, and ultraviolet regions of the spectrum, i. e., light with wavelengths ranging from about 1,000 to about 10,000 Å. Quanta in this range have energies in the order of 23 to 230 kcal per mole. Since such energies are comparable in magnitude to the bonding energies between atoms in molecules, the absorption of a quantum of light might, under favorable conditions, be expected to sever a chemical bond. When a bond is broken in this manner, the molecule is said to have decomposed photochemically.

Light incident upon a system can be transmitted, reflected, scattered, refracted, or absorbed, or be subject to any combination of these processes. In 1818 Grotthuss and Draper pointed out that only light which is absorbed can be effective in producing a photochemical change; this fact is often designated as the first law of photochemistry. Not all light which is absorbed, however, must produce a chemical change. Often the atom or molecule is merely excited to a higher energy state in which the sys-

tem possesses additional energy equal in magnitude to the energy of the absorbed quantum. Such an excited system can conceivably return to the ground state by emitting the excess energy as luminescence, or it can transfer its excess energy to surrounding molecules as heat, thereby passing by a radiationless process to the ground level. The molecule can also rid itself of the energy of excitation by a photolytic process, as discussed earlier, but in that case the molecule does not return to its own ground state.

In order to excite electrons in a molecule to a higher energy level, radiation in the visible or ultraviolet regions is ordinarily required. It is now generally accepted that molecules with an even number of electrons have singlet and triplet electronic levels analogous to atoms with even numbers of electrons.[1] Research recently has indicated that singlet levels are those from which fluorescence (short-lived) emission originates, and that triplet levels are those from which phosphorescence (long-lived) emission originates.[2] Phosphorescence from molecules can usually be observed only when conditions are such that the rate of energy transfer between molecules is greatly reduced, i. e., at low temperatures, in rigid solutions, or both. Molecules can change from the singlet

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[1]Lewis, G. N. and Kasha, M., J. Am. Chem. Soc., 66, (1944).

[2]Moore, W. J., Physical Chemistry, Prentice-Hall, Inc., New York, N. Y., 1955, Ed. 2, p. 595.

to the triplet level spontaneously because the energy of of the triplet level is lower than that of the singlet. The rate of this process is low, however, because of a quantum mechanical prohibition of transitions involving changes of multiplicities. Nevertheless, electronically excited molecules in the singlet state can proceed to the ground state by at least two different paths. (1) directly, or (2) via the triplet state.

There is also evidence that some molecules while in the triplet state may absorb a second quantum of light thereby gaining sufficient energy to eject an electron or otherwise undergo photodecomposition.[3] This mechanism can explain the natures of some photochemical reactions which have been shown to be second order with respect to the photons.

Another law of fundamental importance in understanding photochemical phenomena is the law of photochemical equivalence or the second law of photochemistry. This law was originally proposed by Einstein and states that the excitation of an atom or a molecule by light is a quantum process; that is that one quantum of absorbed radiation activates one atom or molecule of absorbent. The second law says nothing about what happens to the system after activation; therefore we can make no a priori statement

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[3]Lewis and Kasha, p. 2102.

concerning the extent of a photochemical reaction. Instead we define the quantum yeild, ϕ, by the expression

$$\phi = \frac{\text{number of molecules reacting per unit time}}{\text{number of quanta absorbed per unit time}}$$

This quantity has been measured for many photochemical reactions; it was found to have values ranging from near zero to about 10^6.[4]

Two other laws of photochemical importance are the light absorption laws of Bouguer and Beer. The former, moore commonly, although erroneously, attributed to J. Lambert is expressed by the equation

$$I = I_0 e^{-\epsilon' l}$$

in which I_0 is the intensity of the incident light, and I is its intensity after traversing an absorbing material of thickness l and extinction coefficient equal to ϵ'.

In 1852 Beer showed that often for the case of absorbing solutes in nonabsorbing solvents, the extinction coefficient is directly proportional to the concentration of the solute. Solutions which exhibit this property are said to obey Beer's law

$$I = I_0 e^{-\epsilon C l}$$

in which ϵ is the molar extinction coefficient, and C is the molar concentration of the solute.

These absorption laws make possible the spectrophotometric study and analysis of photochemical systems; they

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[4]Prutton, C. F. and Maron, S. H., Fundamental Principles of Physical Chemistry, The Macmillan Co., New York, N. Y., 1951, p. 765.

are strictly true only for monochromatic light.

It was decided to investigate the photochemical behavior of the mononitronaphthalenes in both polar and nonpolar media. Suitable solutions were irradiated with various sources of ultraviolet light; marked changes in their absorption spectra were taken as adequate proof of photochemical activity.

CHAPTER II

HISTORICAL BACKGROUND

An intensive investigation of the available chemical literature uncovered no reports concerning the photochemical behavior of 2-nitronaphthalene and only one such report for 1-nitronaphthalene. Lewis and Kasha have shown that at the temperature of liquid air 1-nitronaphthalene in rigid EPA solution (5 parts ether, 5 parts isopentane, 2 parts ethanol, by volume) undergoes photodecomposition when exposed to intense ultraviolet radiation.[5] The extent of the photochemical activity was found by these workers to be proportional to the time of exposure and to the square of the intensity of the incident radiation. As previously mentioned, they explained such reactions, which are second order with respect to the photons, by assuming a second excitation of the molecule while it is in the triplet state.

The light absorption properties of the mononitronaphthalenes have received considerably more attention in the chemical literature. Their infrared absorption spectra have been reported by such workers as Kamada, Nishino, and

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[5]Lewis and Kasha, p. 2102.

Lecomte.[6, 7] Hertel studied the complete absorption spectra of both compounds from 2,500 to 10,000 Å.[8] Hodgson and Hathway studied the ultraviolet absorption spectra of the mononitronaphthalenes in absolute ethanol.[9]

The only available report of an absorption spectrum of interest to this research, however, was made by Schroeder and coworkers.[10] They found for 1-nitronaphthalene in absolute ethanol an absorption band with a peak at 333 mμ with a corresponding molar extinction coefficient equal to 4090. They also found an absorption minimum at 278 mμ and a rather flat band near 240 mμ. Subsequent measurements in the present research yeilded results in precise agreement with these data.

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[6] Kamada, H. and Nishino, Y., Japan. Analyst, 2, 338-42 (1953).

[7] Lecomte, J., Compt. rend. 208, 1636-8 (1939).

[8] Hertel, E., Z. Electrochem., 47, 813-19 (1941).

[9] Hodgson, H. H. and Hathway, D. E., Trans. Faraday Soc., 41, 115-21 (1945).

[10] Schroeder, Wilcox, Trueblood, and Depper, Anal. Chem., 23, 1740-7 (1951).

CHAPTER III

EXPERIMENTATION

Source of Chemicals

The 1-nitronaphthalene was Matheson's technical grade. The 2-nitronaphthalene was synthesized by the method of Hodgson and Ward.[11] The ethanol was commercial 95%, and the cyclohexane was Phillip's spectro grade.

Purification of Chemicals

The chemical literature suggests in general the purification of the mononitronaphthalenes by crystallization.[12] Since this research called for only very small samples of the pure chemicals (in the order of a few milligrams) and since the chance for occluded impurities seemed to be greater for crystallization than for sublimation, it was decided to try the latter method, the simple apparatus shown schematically in figure 1 prooved most effective in refining the crude substances. It consists of a sintered glass Buchner funnel inverted inside a slightly larger

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[11] Hodgson, H. and Ward, E., J. Chem. Soc., 1947, 127.

[12] Telushkin, M. P. and Minaev, P. E., Russ. 57, 915, Sept. 30, 1940.

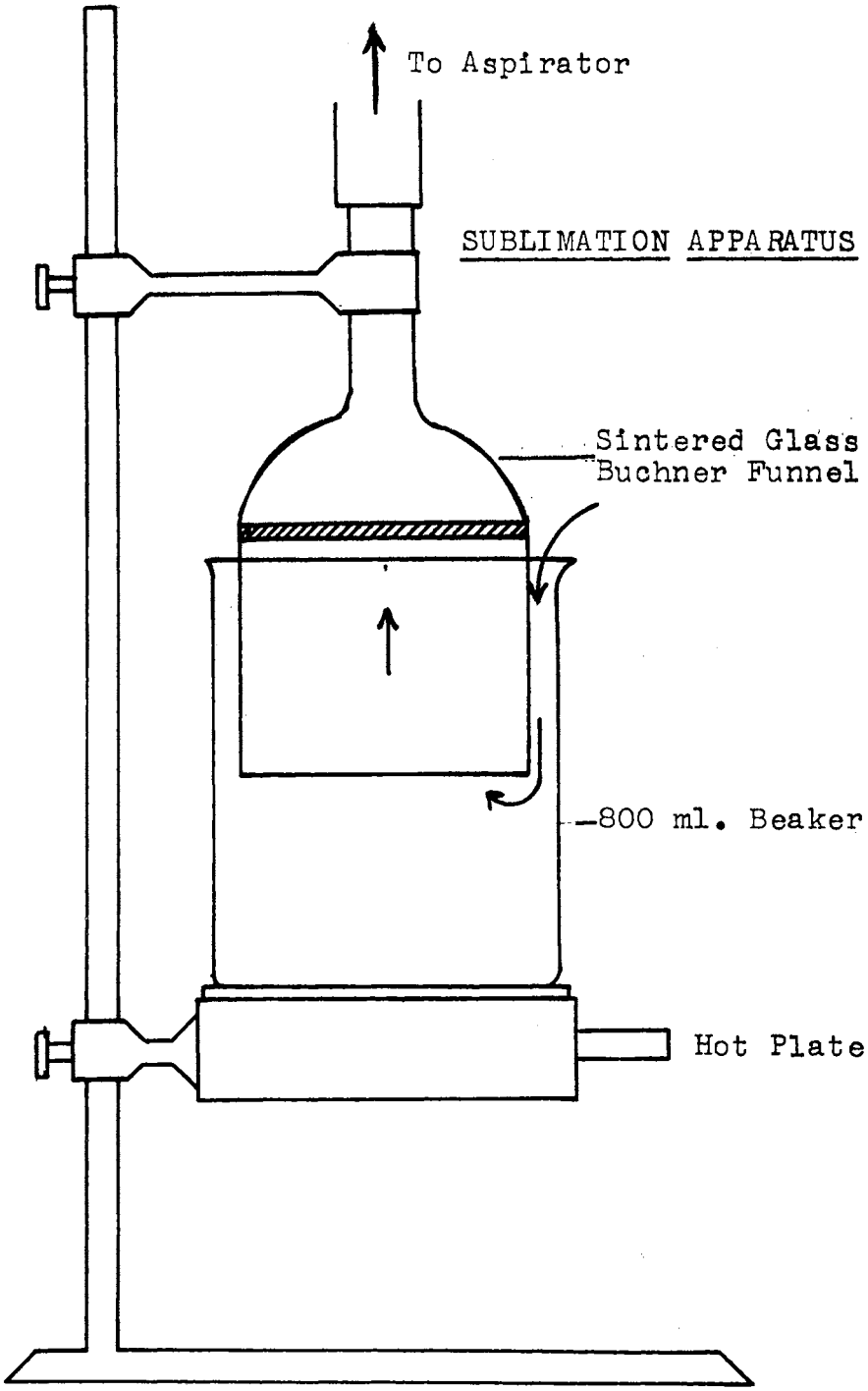
To Aspirator
SUBLIMATION APPARATUS
Sintered Glass
Buchner Funnel
800 ml. Beaker
Hot Plate

Figure 1

Pyrex beaker. The sample to be purified was placed in the beaker and heated with the small electric hot plate; its vapors were pulled upward by the gentle current of air which was drawn through the aspirator. The vapors were condensed on the lower surface of the sintered glass disc. Long well defined needle-like crystals of both 1- and 2-nitronaphthalenes were collected this way. Observed melting point ranges of the crystals were 0.5 and 1.0° for the 1- and 2-nitronaphthalenes respectively.

The cyclohexane and the 95% ethanol were used without further treatment.

Apparatus

Several irradiating devices were employed in the course of this work. Each of them is discussed later. All absorption spectra were obtained with a Beckman Quartz spectrophotometer model DU equipped with 1 cm. fused silica absorption cells.

Procedures

Solutions of 1- and 2-nitronaphthalenes in cyclohexane and in 95% ethanol were prepared and their absorption spectra carefully determined. These spectra are shown in figures 2 and 3. The polar solution of 1-nitronaphthalene exhibits absorption maxima at 333 and 243 mμ. When the polarity of the solution is decreased, these maxima are shifted to slightly shorter wavelengths, i. e., 327 and

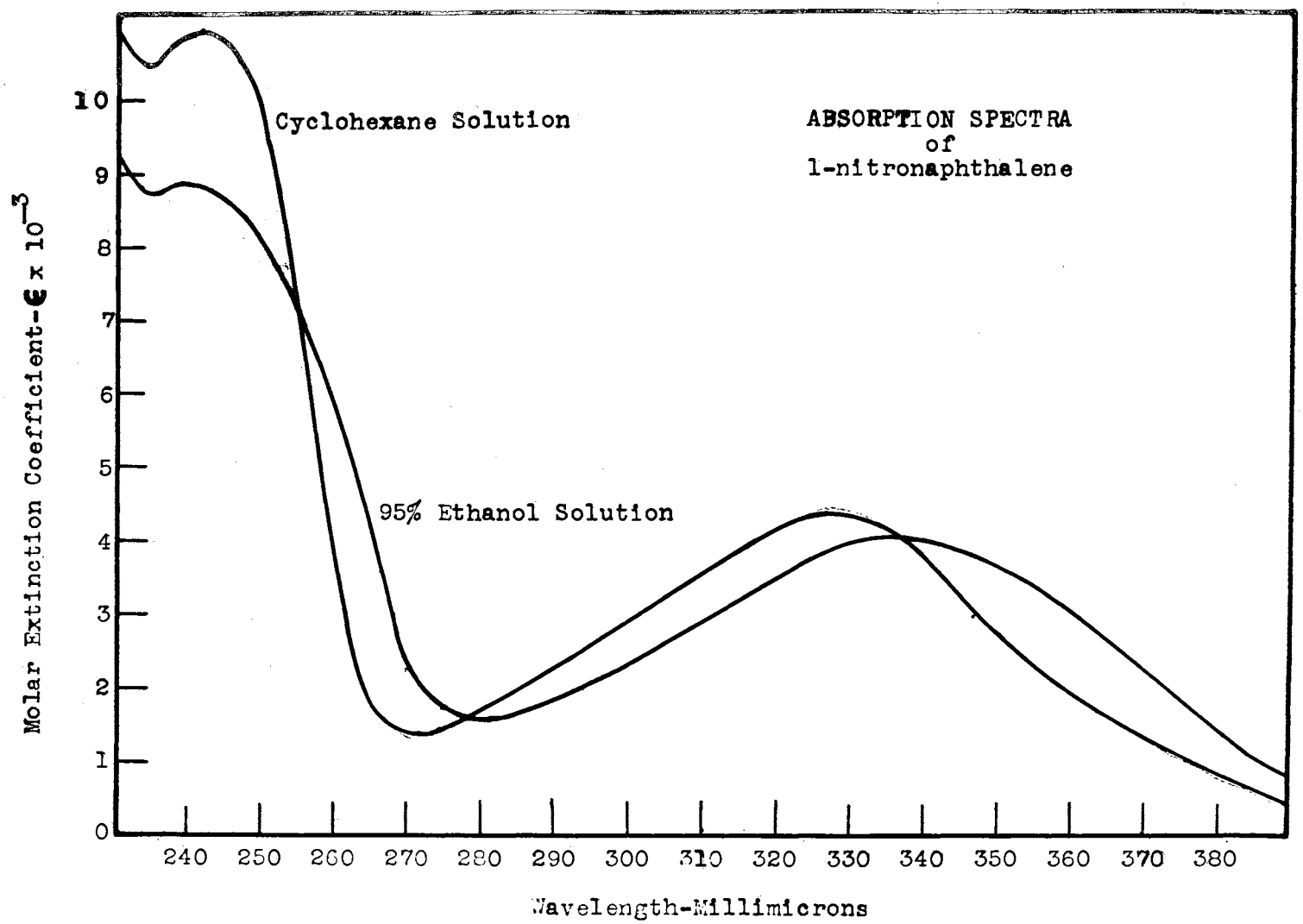
ABSORPTION SPECTRA
of
1-nitronaphthalene
Cyclohexane Solution
95% Ethanol Solution
Molar Extinction Coefficient-ε x 10^-3
0
1
2
3
4
5
6
7
8
9
10
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
Wavelength-Millimicrons

Figure 2

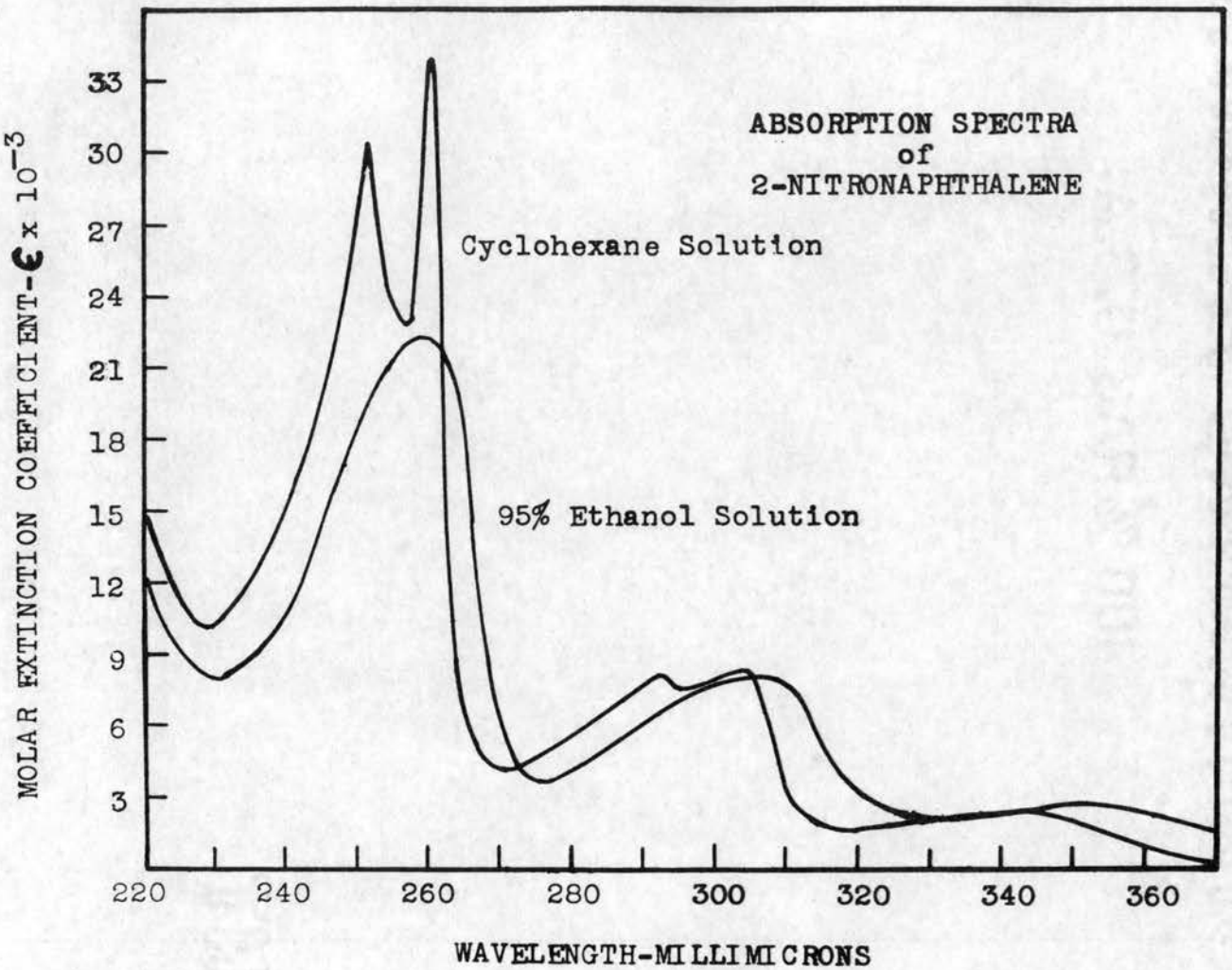
ABSORPTION SPECTRA
of
2-NITRONAPHTHALENE
Cyclohexane Solution
95% Ethanol Solution
MOLAR EXTINCTION COEFFICIENT-ε x 10⁻³
33
30
27
24
21
18
15
12
9
6
3
220
240
260
280
300
320
340
360
WAVELENGTH-MILLIMICRONS

Figure 3

242 mμ respecitvely in cyclohexane. The corresponding molar extinction coefficients are somewhat increased.

The absorption spectra of 2-nitronaphthalene in the two solvents exhibit some much more striking dissimilarities, the features of which can be seen in figure 3. The two absorption peaks at 260 and 305 mμ in 95% ethanol are each resolved into a pair of peaks in cyclohexane. They occur at 251.5 and 260 mμ and at 292 and 304 mμ respectively, and although the effect is too small to be apparent in the drawing, the absorption maximum at 350 mμ in 95% ethanol is also resolved into a pair of peaks at 331 and 343 mμ in cyclohexane. The molar extinction coefficient of 2-nitronaphthalene at 260 mμ is much greater in cyclohexane than in 95% ethanol. These results suggest that a strong interaction occurs between the 2-nitronaphthalene and the solvent in the ethanol solutions that is not present in the cyclohexane solutions.

To ascertain whether or not the above solutions are photochemically unstable, the irradiation apparatus shown in figure 4 was designed and constructed from Pyrex brand glass. This method allowed for the simultaneous stirring and cooling of the sample during its exposure to the mercury lamp. Measurments of the transmissivity of Pyrex, however, showed it to be opaque to light of wavelengths below about 2800 Å. Much of the mercury arc spectrum, which is rich in lines below this limit was, therefore, not available for producing photochemical processes in the

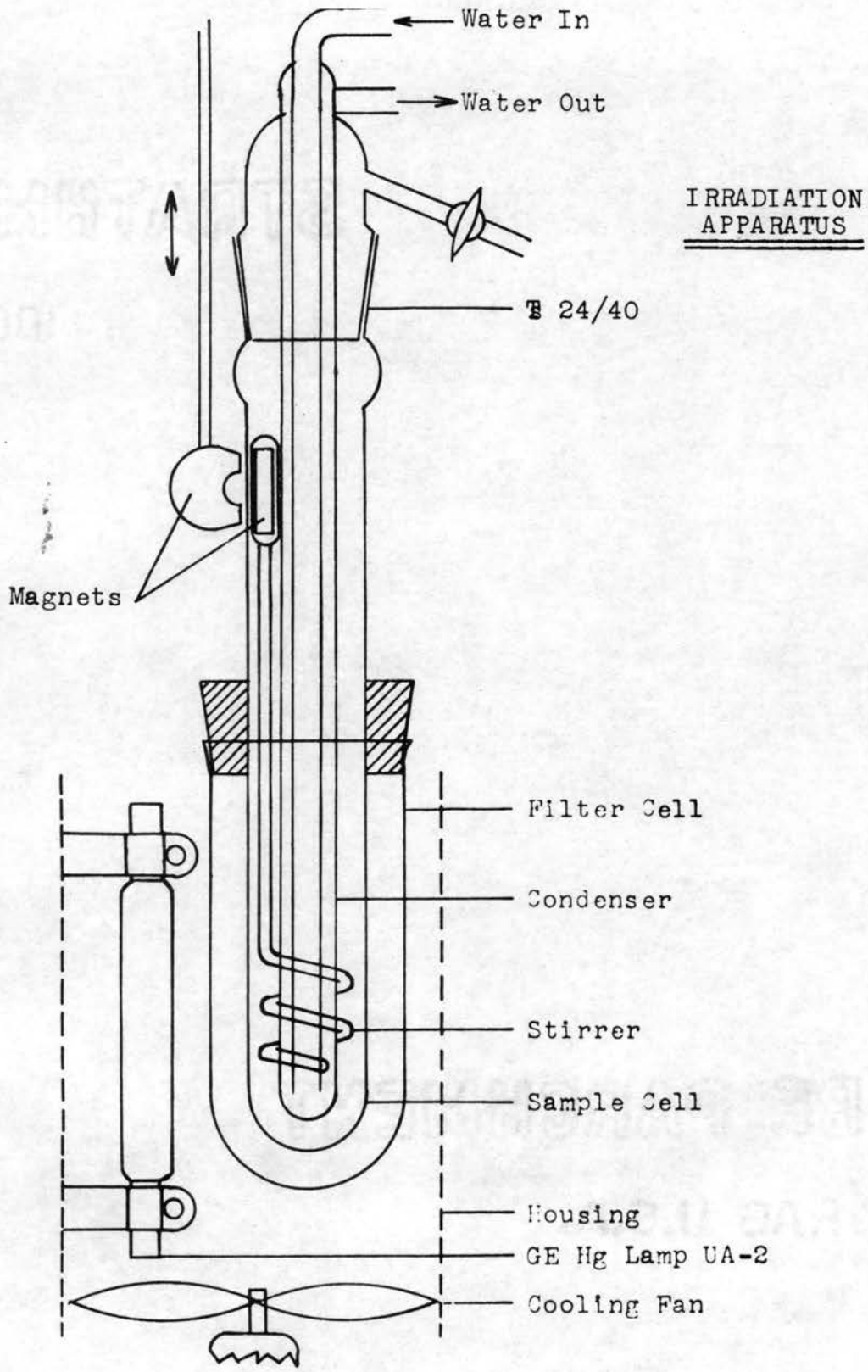
Water In
Water Out
IRRADIATION APPARATUS
T 24/40
Magnets
Filter Cell
Condenser
Stirrer
Sample Cell
Housing
GE Hg Lamp UA-2
Cooling Fan

Figure 4

Pyrex apparatus.

When exposed to the light from a General Electric mercury lamp type UA-2, the solutions of both mononitronaphthalenes in 95% ethanol decomposed rapidly in the Pyrex irradiator. Figure 5 shows their absorption spectra after fifteen minute exposures; the solutions, before irradiation were those from which the data for figure 2 were obtained.

In cyclohexane, however, both compounds are quite stable in the Pyrex container. To determine the stability of the latter solutions when exposed to wavelengths below the transmission limit of Pyrex, they were irrariated in fused silica vessels. In this manner they too were shown to be highly unstable. Figure 6 gives their absorption spectra after fifteen minute exposures to the G.E. UA-2 mercury lamp in the fused silica vessels.

Next it was decided to determine which line(s) of the mercury arc spectrum were responsible for the photochemical changes. The first efforts to do so involved the adaptation of the Bausch and Lomb grating monochromator to be used as a source of monochromatic ultraviolet light for photochemical irradiations. The apparatus is depicted schematically in figure 7. The cell holder was constructed so that an image of the grating was brought to a focus inside the fused silica reaction cell. The spectral lines were located and identified with the aid of a fluorescent glass plate. In this manner each of the above solutions

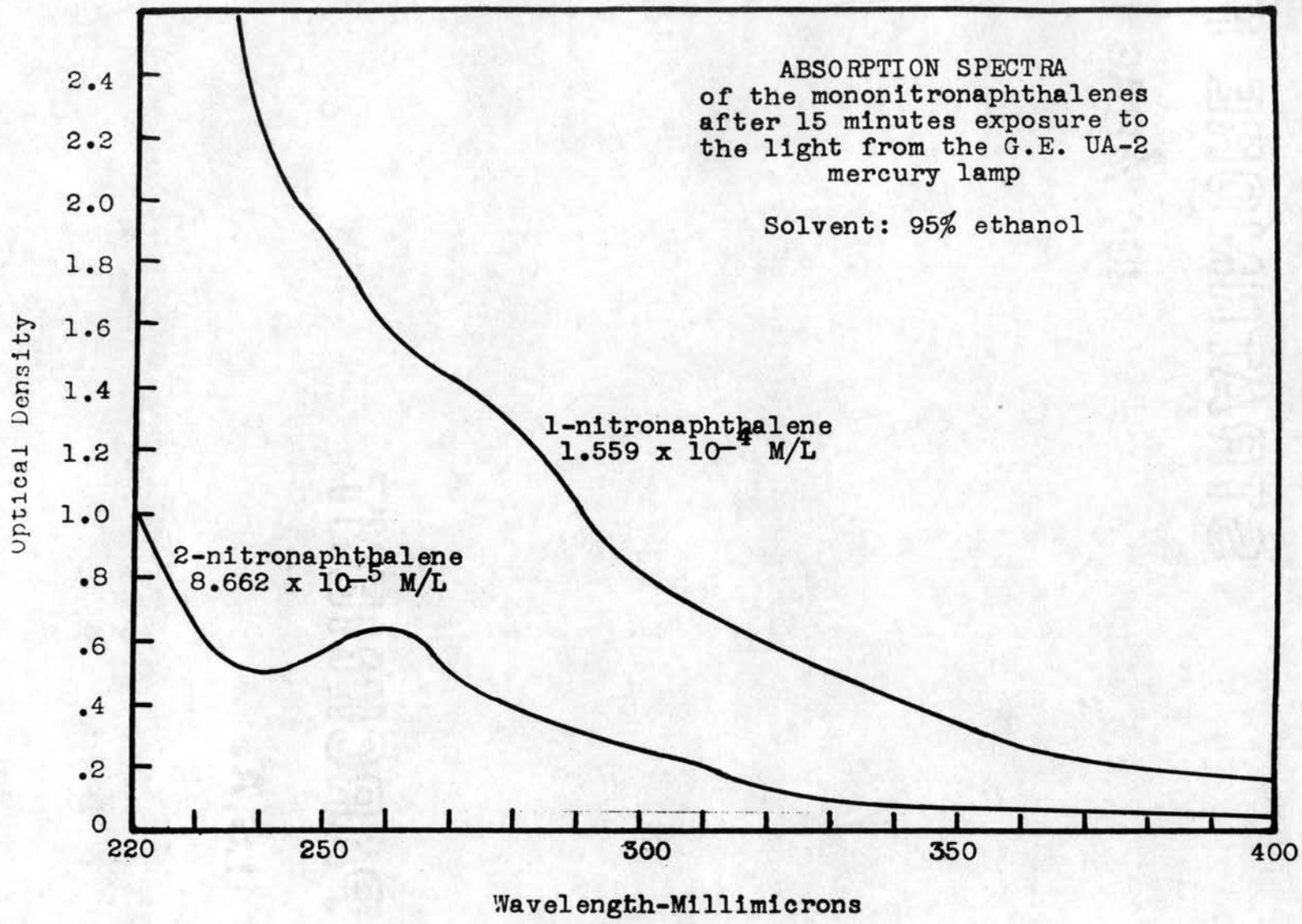
ABSORPTION SPECTRA
of the mononitronaphthalenes
after 15 minutes exposure to
the light from the G.E. UA-2
mercury lamp
Solvent: 95% ethanol
1-nitronaphthalene
1.559 x 10⁻⁴ M/L
2-nitronaphthalene
8.662 x 10⁻⁵ M/L
Optical Density
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
220
250
300
350
400
Wavelength-Millimicrons

Figure 5

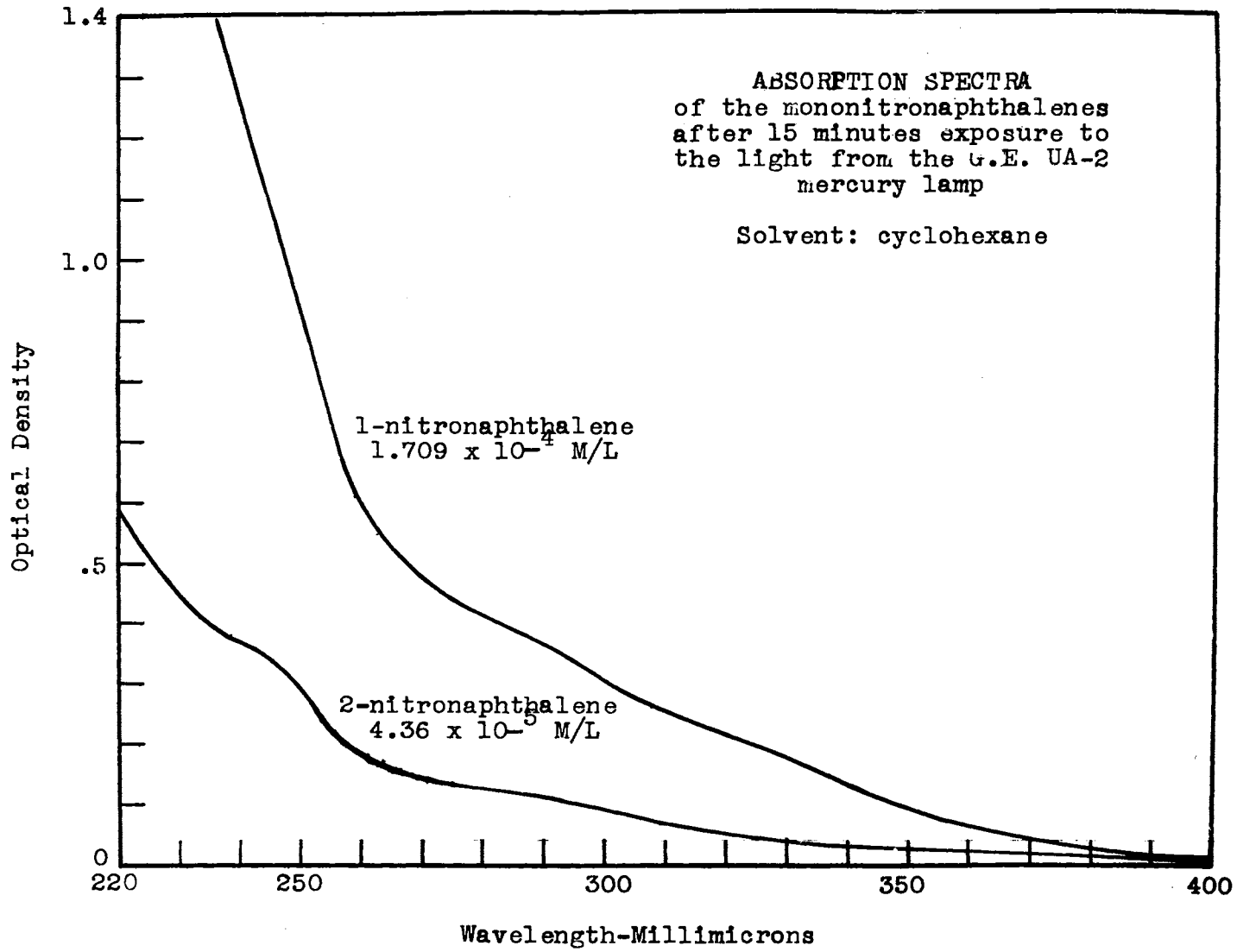
ABSORPTION SPECTRA
of the mononitronaphthalenes
after 15 minutes exposure to
the light from the G.E. UA-2
mercury lamp
Solvent: cyclohexane
1-nitronaphthalene
1.709 x 10-4 M/L
2-nitronaphthalene
4.36 x 10-5 M/L
Optical Density
1.4
1.0
.5
0
220
250
300
350
400
Wavelength-Millimicrons

Figure 6

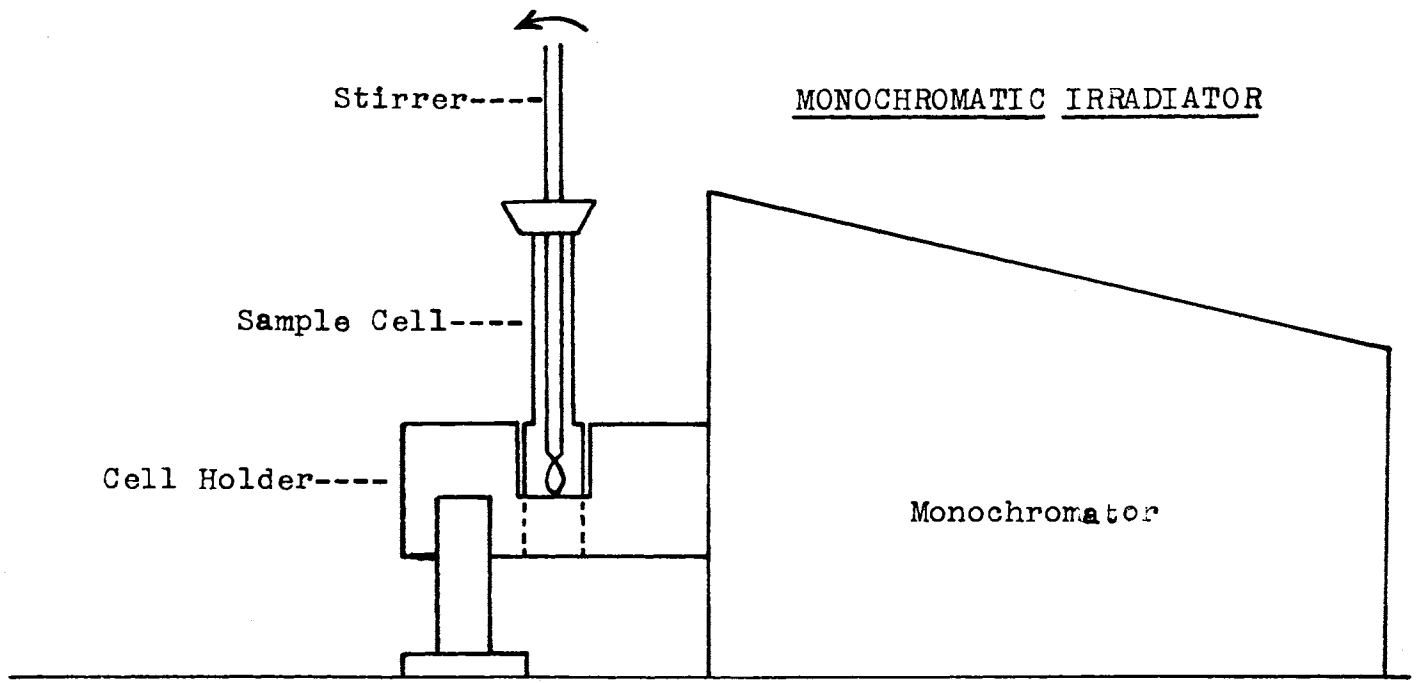
MONOCHROMATIC IRRADIATOR
Stirrer----
Sample Cell----
Cell Holder----
Monochromator

Figure 7

was irradiated with each strong line of the mercury arc spectrum from 2537 to 3341 Å. Although the exposures were continued for several hours, no significant changes were observed in any of the absorption spectra.

The failure of this apparatus to be useful for photochemical irradiations was attributed to the severe loss in intensity of the light passing through the multicomponent optical system. In an effort to counteract this loss, the Bausch and Lomb monochromator mercury lamp was replaced with a General Electric Mercury arc lamp type C85-H3. Even though the latter is a much stronger source of the ultraviolet, it too was inadequate for rendering the monochromator a practical light source for photochemical studies.

Kasha has devised a series of multicomponent transmission filters for the ultraviolet.[13] To isolate narrow wavelength bands with these filters, the irradiation apparatus shown in figure 8 was constructed. The 5 cm. absorption cell was designed and fabricated from two inch copper tubing and equipped with replacable quartz windows. The filter components that were placed in this cell (aqueous solutions of nickel and cobalt salts) all reacted with the cell itself to produce radical changes in their transmission characteristics. All of the organic liquid filter components, which were placed in the 1 cm. fused silica

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[13]Kasha, M., J. Opt. Soc. Am., 38, No. 11, 929-34 (1948).

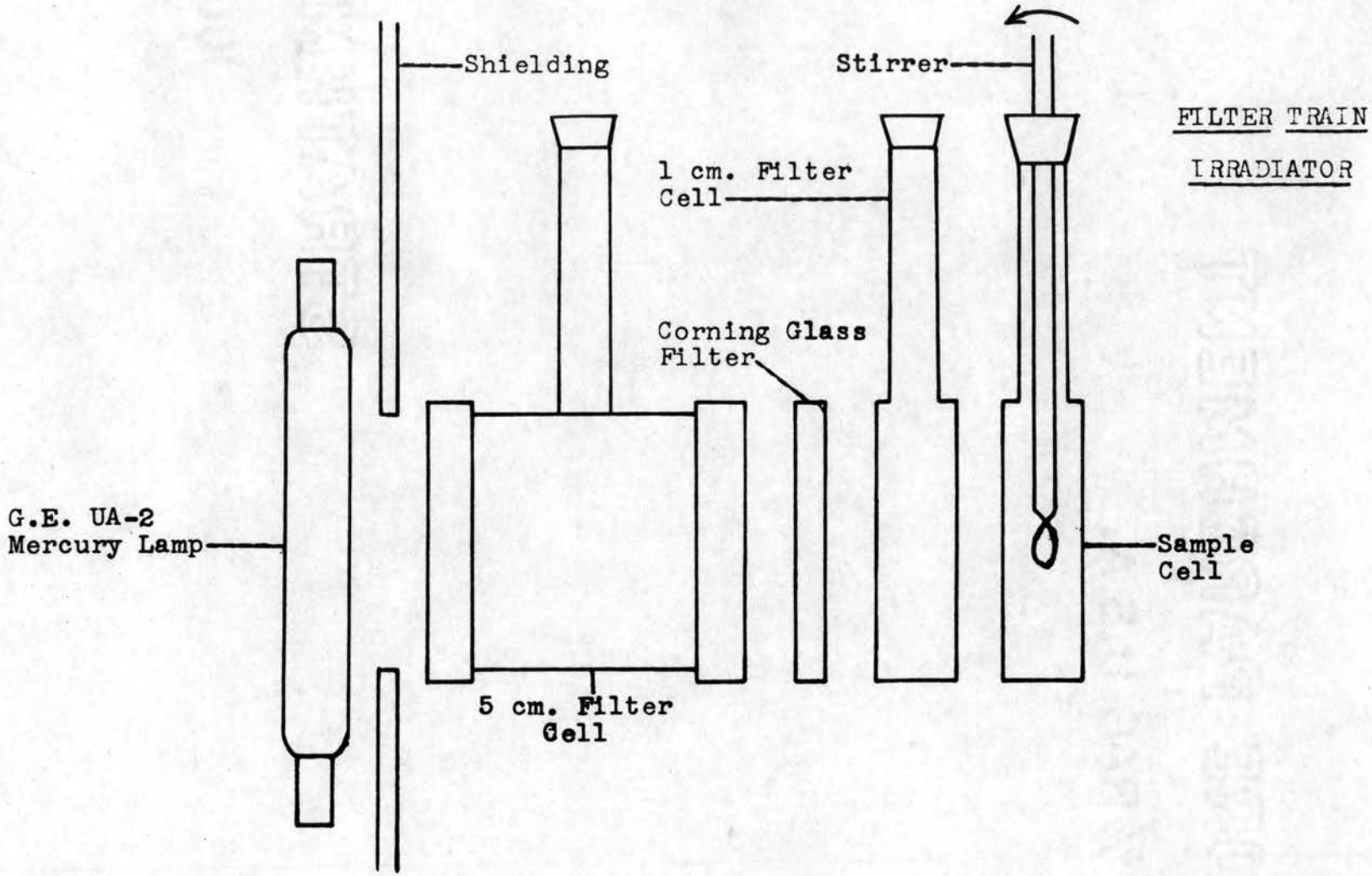
Shielding
Stirrer
FILTER TRAIN
IRRADIATOR
1 cm. Filter
Cell
Corning Glass
Filter
G.E. UA-2
Mercury Lamp
Sample
Cell
5 cm. Filter
Cell

Figure 8

cell underwent very rapid photochemical changes resulting in modified transmission properties. For these reasons no positive information regarding the photochemistry of the mononitronaphthalenes was obtained with these filters

In his same paper, however, Kasha mentioned the transmission properties of diphenylbutadiene in diethylether solutions.[14] Such solutions have the desirable property of isolating the 2537 Å line from the mercury arc spectrum. Figure 9 shows the transmission spectrum of a solution containing 4.24 mg. diphenylbutadiene in 100 ml. of diethylether. The lower curve is for the same solution after a ten minute exposure to the GE UA-2 mercury lamp. Although the solution is photochemically unstable, the only change in its transmission spectrum is a decrease in the amount of transmitted energy; therefore by using this solution as the only filter component in the apparatus of figure 8, and replacing the decomposed solution after each ten minute exposure, it was shown that the 2537 Å resonance line does produce photochemical change in both the polar and nonpolar solutions of both the mononitronaphthalenes.

The photochemical instability of the diphenylbutadiene filter solution rendered it unsuitable for quantitative investigations of the reactions induced by the 2537 Å mercury resonance line. Instead use was made of a spiral

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[14] Ibid. p. 932.

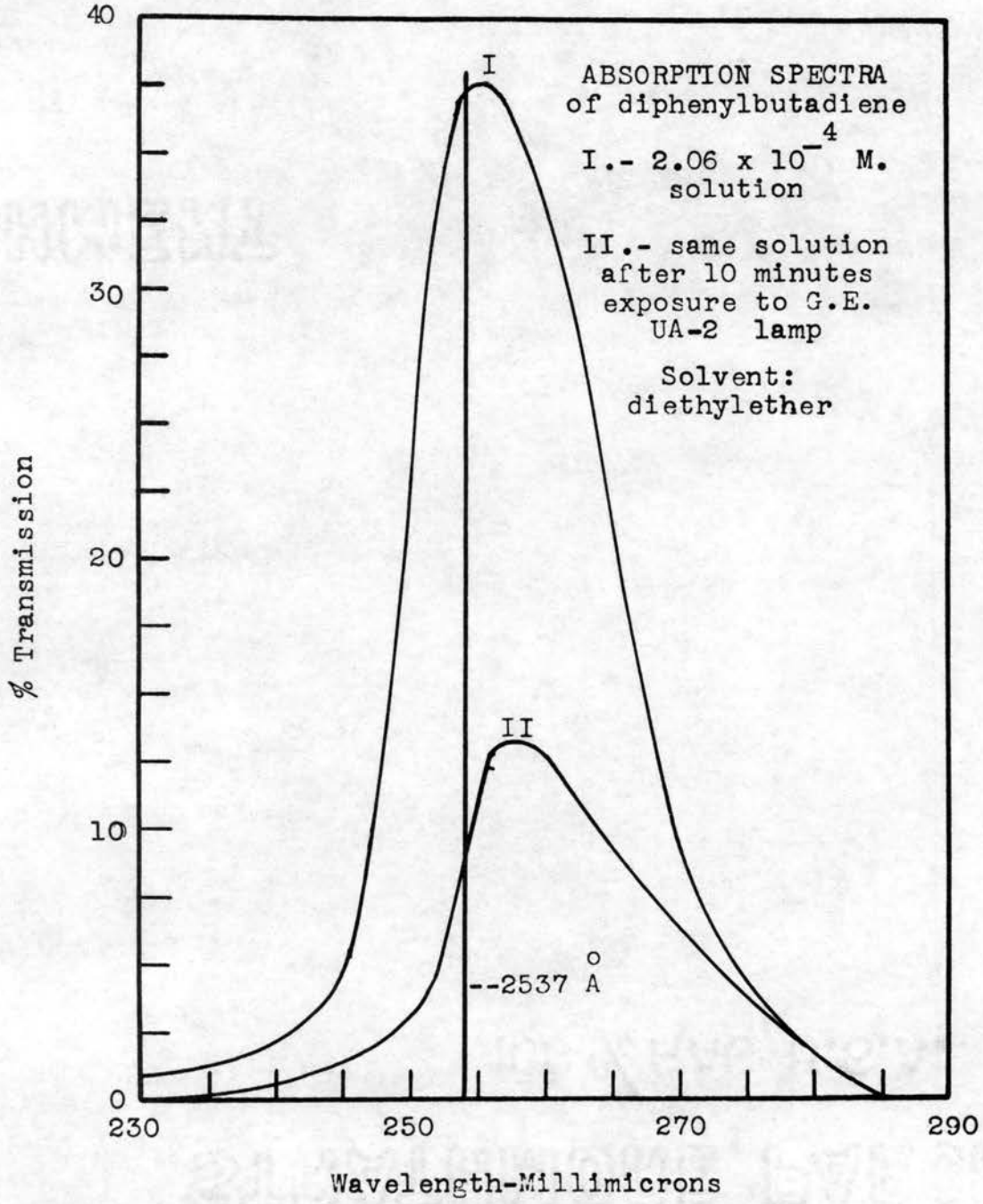
ABSORPTION SPECTRA
of diphenylbutadiene
I.- 2.06 x 10⁻⁴ M.
solution
II.- same solution
after 10 minutes
exposure to G.E.
UA-2 lamp
Solvent:
diethylether
I
II
--2537 Å
% Transmission
40
30
20
10
0
230
250
270
290
Wavelength-Millimicrons

Figure 9

mercury resonance lamp which according to its makers, the Hanovia Chemical and Manufacturing Company, produces 95% of its ultraviolet radiation at 2537 Å. This lamp was mounted in the apparatus described by Smith.[15] His drawing of it is reproduced here in figure 10. The lamp was standardized actinometrically with monochloroacetic acid. The latter absorbs 2537 Å photons and hydrolyzes according to the equation

$$CH_2ClCOOH + H_2O = CH_2OHCOOH + HCl$$

The quantum yield for this reaction is known.[16, 17] By titrating the liberated hydrochloric acid with standard silver nitrate solution, the number of quanta delivered to the solution per unit time were determined.

Each of the mononitronaphthalene solutions was irradiated with the resonance lamp for increasing time intervals, and its absorption spectrum was determined after each exposure. Figures 11 and 12 illustrate typical results.

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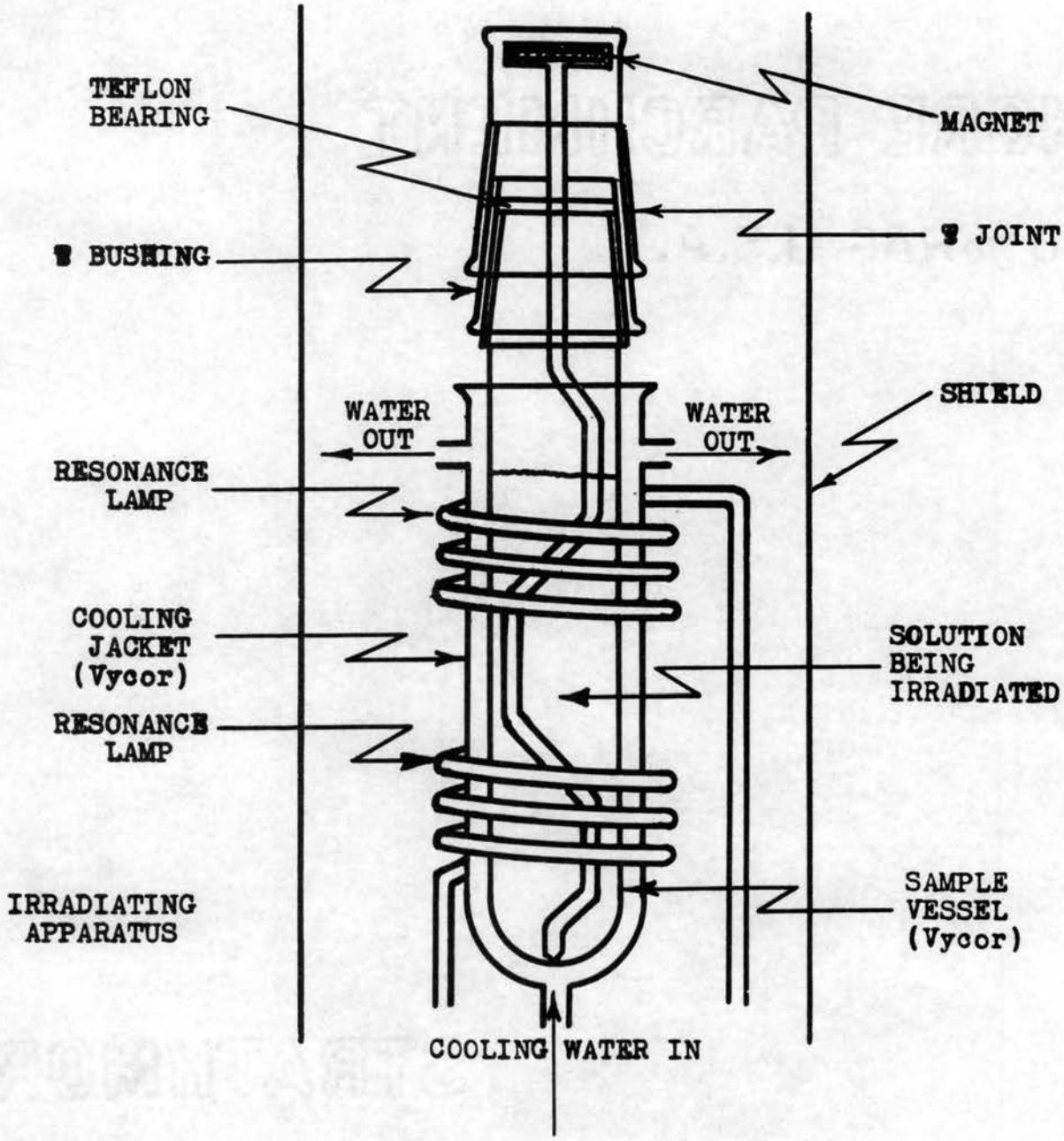
[15] Smith, N. K., "The Quantum Yield of Photodecomposition of Benzene Solutions at Room Temperature" (unpub. M. S. thesis Oklahoma Agricultural and Mechanical College, 1956) p. 7.

[16] Smith, R. N., Leighton, P. A. and Leighton, W. G., J. Am. Chem. Soc., 61, 2299 (1939).

[17] Thomas, L. B., J. Am. Chem. Soc., 62, 1879-80 (1940).



RESONANCE LAMP IRRADIATOR

Figure 10

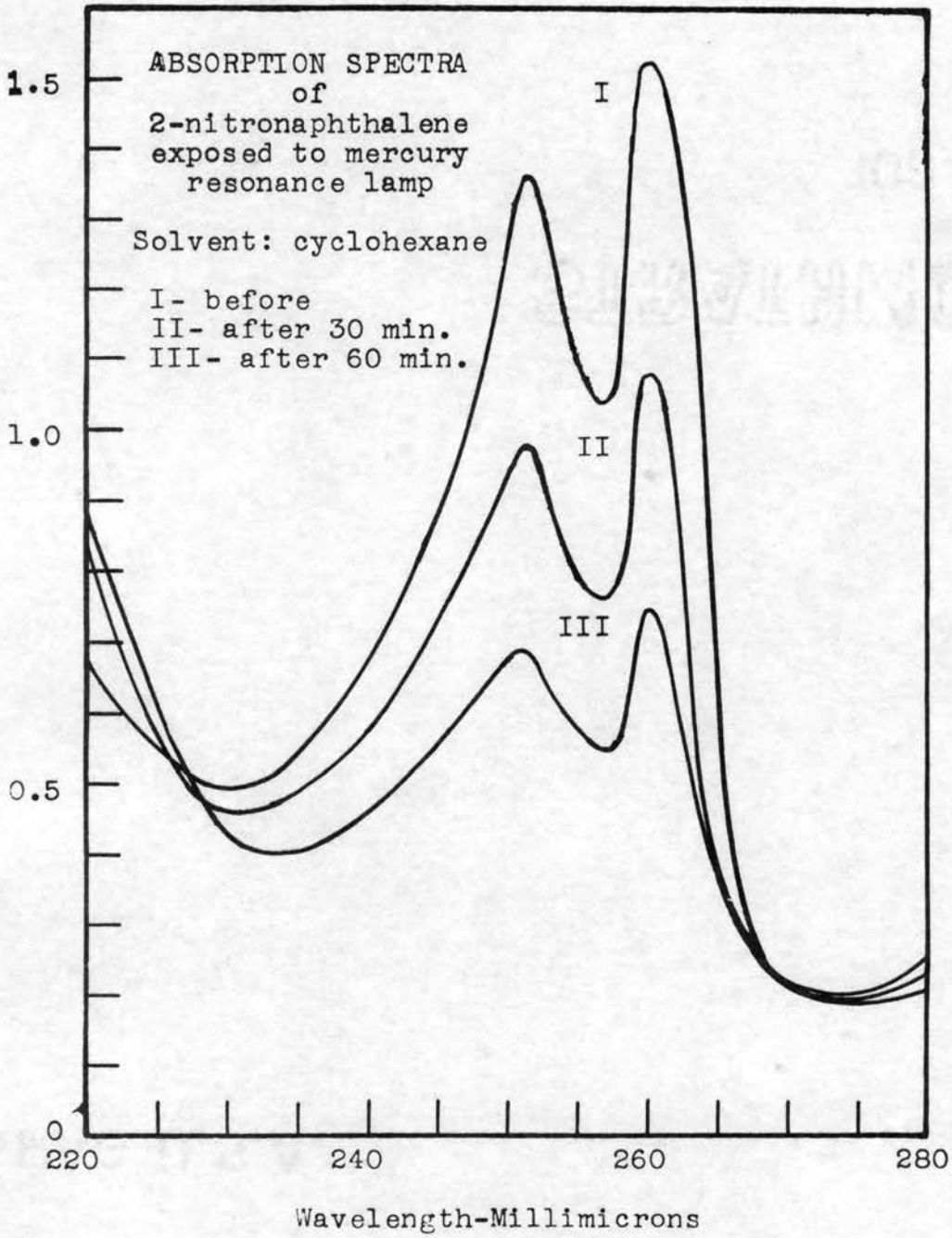

ABSORPTION SPECTRA
of
2-nitronaphthalene
exposed to mercury
resonance lamp
Solvent: cyclohexane
I- before
II- after 30 min.
III- after 60 min.
I
II
III
1.5
1.0
0.5
0
220
240
260
280
Wavelength-Millimicrons

Figure 11

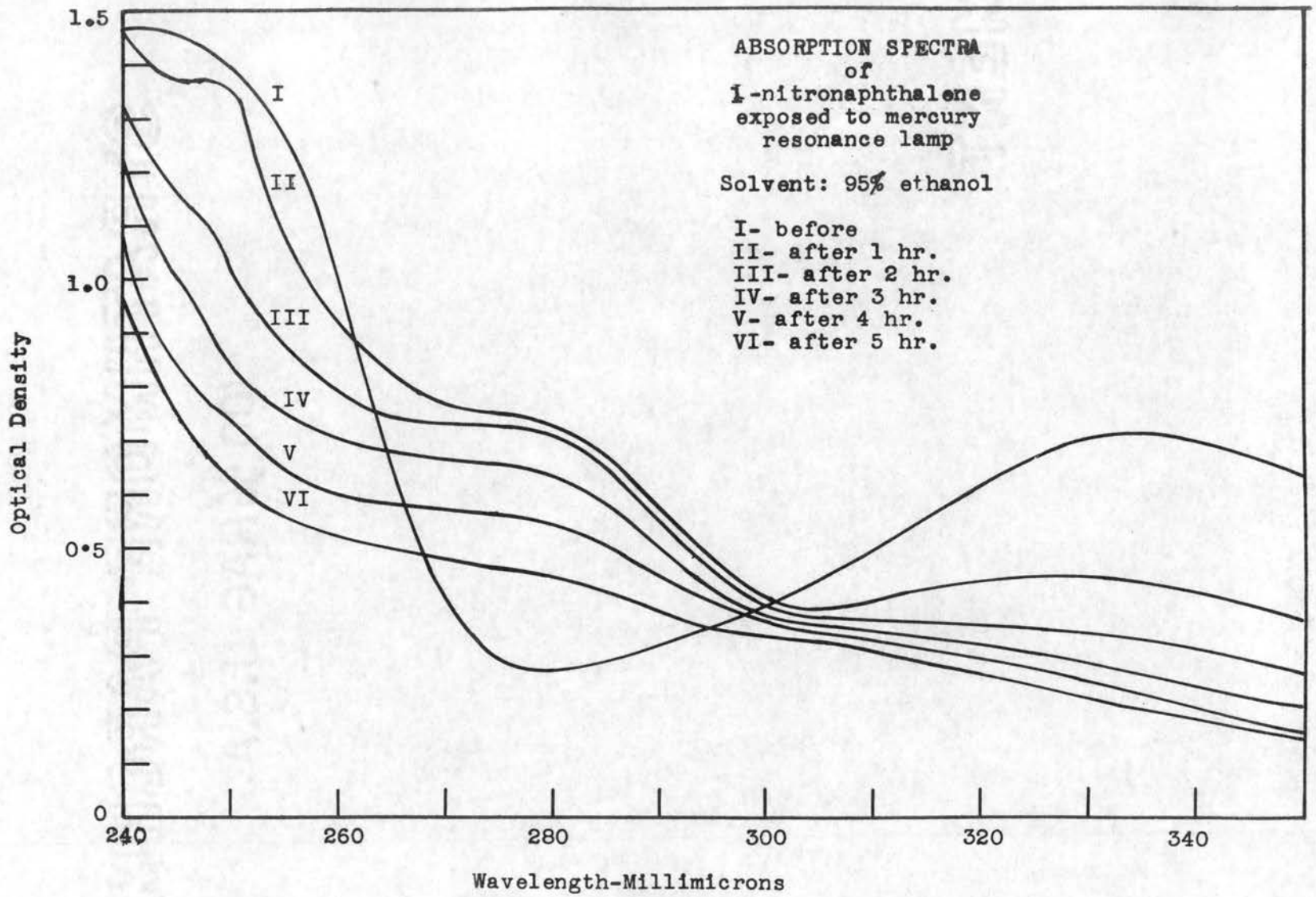

ABSORPTION SPECTRA
of
1-nitronaphthalene
exposed to mercury
resonance lamp
Solvent: 95% ethanol
I- before
II- after 1 hr.
III- after 2 hr.
IV- after 3 hr.
V- after 4 hr.
VI- after 5 hr.
I
II
III
IV
V
VI
Optical Density
1.5
1.0
0.5
0
240
260
280
300
320
340
Wavelength-Millimicrons

Figure 12

CHAPTER IV

INTERPRETATIONS OF RESULTS

Determination of Quantum Yields of Photochemical Processes Occuring in 2-nitronaphthalene Solutions

Often the light absorption of a solution undergoing photochemical reaction changes in a complicated manner, but occasionally the changes are simpler. In the latter cases much valuable information can be obtained from a knowledge of the behaviors of the absorption spectra with changes in time. From figure 11 one can see that the reaction induced by the 2537 Å mercury line incident on 2-nitronaphthalene in cyclohexane solution is indeed one of the simpler cases. The change in optical density at the wavelength of excitation is, in fact, a linear function of the time of exposure, figure 13. The same is true for 2-nitronaphthalene in 95% ethanol. Such reactions can be explained if they proceed in accordance with the following conditions:

1. The solution is irradiated with monochromatic light.
2. The relative numbers of product molecules pro-

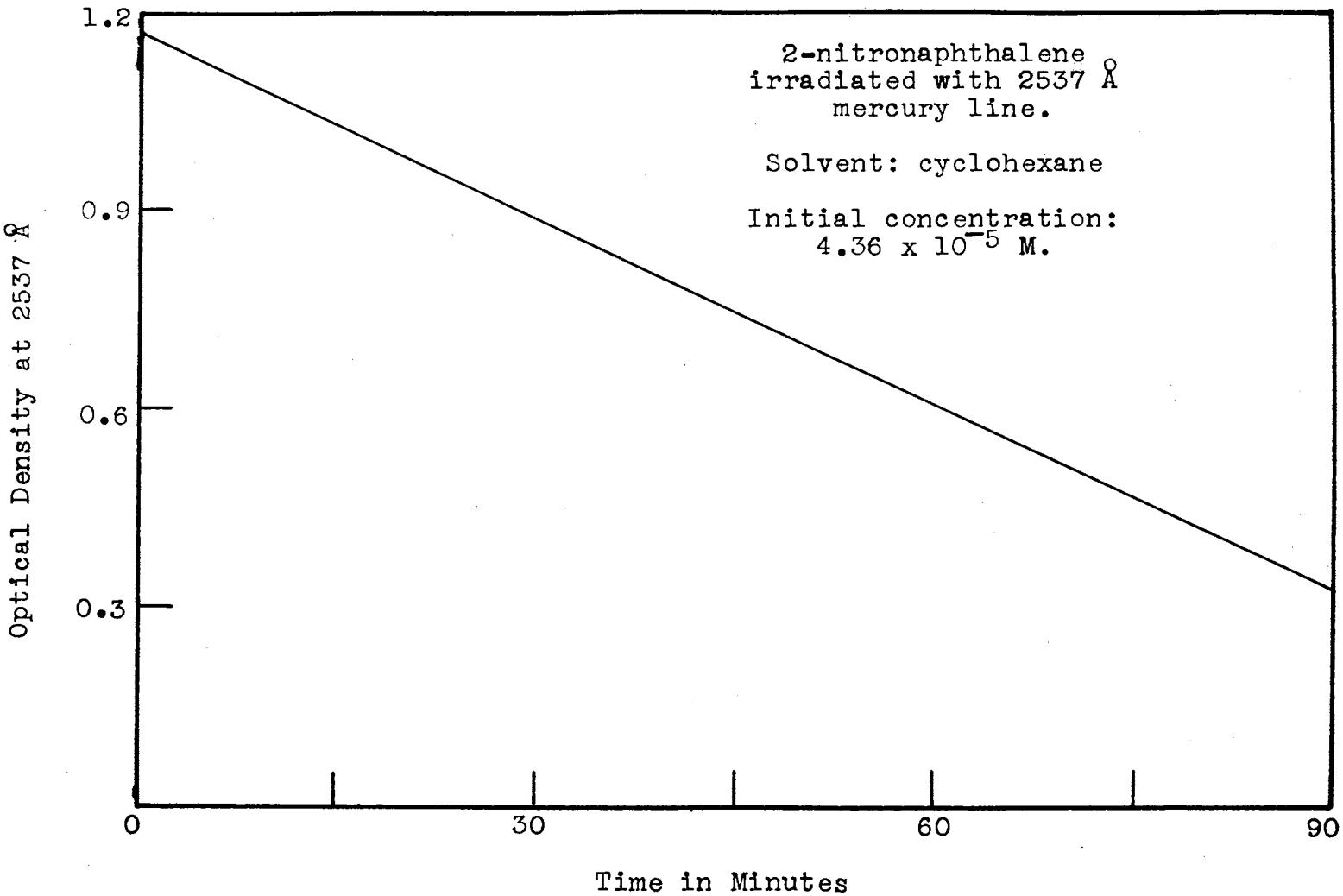

2-nitronaphthalene
irradiated with 2537 Å
mercury line.
Solvent: cyclohexane
Initial concentration:
4.36 x 10⁻⁵ M.
1.2
0.9
0.6
0.3
Optical Density at 2537 Å
0
30
60
90
Time in Minutes

Figure 13

duced by the photolysis of the initial species are independent of the time.

3. The products are photochemically stable.
4. The solution is perfectly stirred.
5. The absorption of each species present is unaffected by the presence of the others.
6. The incident radiation is essentially completely absorbed by the solution.
7. The product molecules do not absorb appreciably at the wavelength of excitation.

The optical density, P, of a solution undergoing photochemical change is given by the general expression

$$P = \epsilon_A C_A + \sum_{i=1}^{n} \epsilon_i C_i . \qquad \text{Eq. (1)}$$

where the ϵ's are molar extinction coefficients, the C's are molar concentrations, and the subscript A refers to the initial reactant while the i's refer to the ith product species. For the case described above, however, condition (7) requires that for each product $\epsilon_i = 0$; therefore the expression for the total optical density becomes merely

$$P = \epsilon_A C_A . \qquad \text{Eq (2)}$$

and the time rate of change of P is

$$(dP/dt) = \epsilon_A (dC_A/dt) . \qquad \text{Eq. (3)}$$

(dC_A/dt) can be shown to be expressible as

$$(dC_A/dt) = -(Q\phi/NV). \qquad \text{Eq. (4)}$$

where Q is the rate at which quanta are delivered to the solution, ϕ is the quantum yield of the reaction, N is Avagadro's number, and V is the volume of the irradiated solution.

Substituting equation (4) into equation (3) and solving for ϕ gives

$$\phi = (NV/2\epsilon_A)(dP/dt). \qquad \text{Eq. (5)}$$

Since all of the terms on the right side of equation (5) are known or measurable, the quantum yield for the reaction can be determined from a knowledge of the behavior of the absorption of the solution at the wavelength of the excitation.

Determination of Quantum Yields of Photochemical Processes Occuring in 1-nitronaphthalene Solutions

Figure 12 shows the photochemical reaction of 1-nitronaphthalene to be considerably more complicated than that for 2-nitronaphhthalene. The data illustrated are for the reaction in 95% ethanol, but the behavior of 1-nitronaphthalene in cyclohexane is entirely analogous. The optical density at the wavelength of excitation is not a linear function of the time of exposure as can be seen in figure 14. The same figure also shows the behavior at

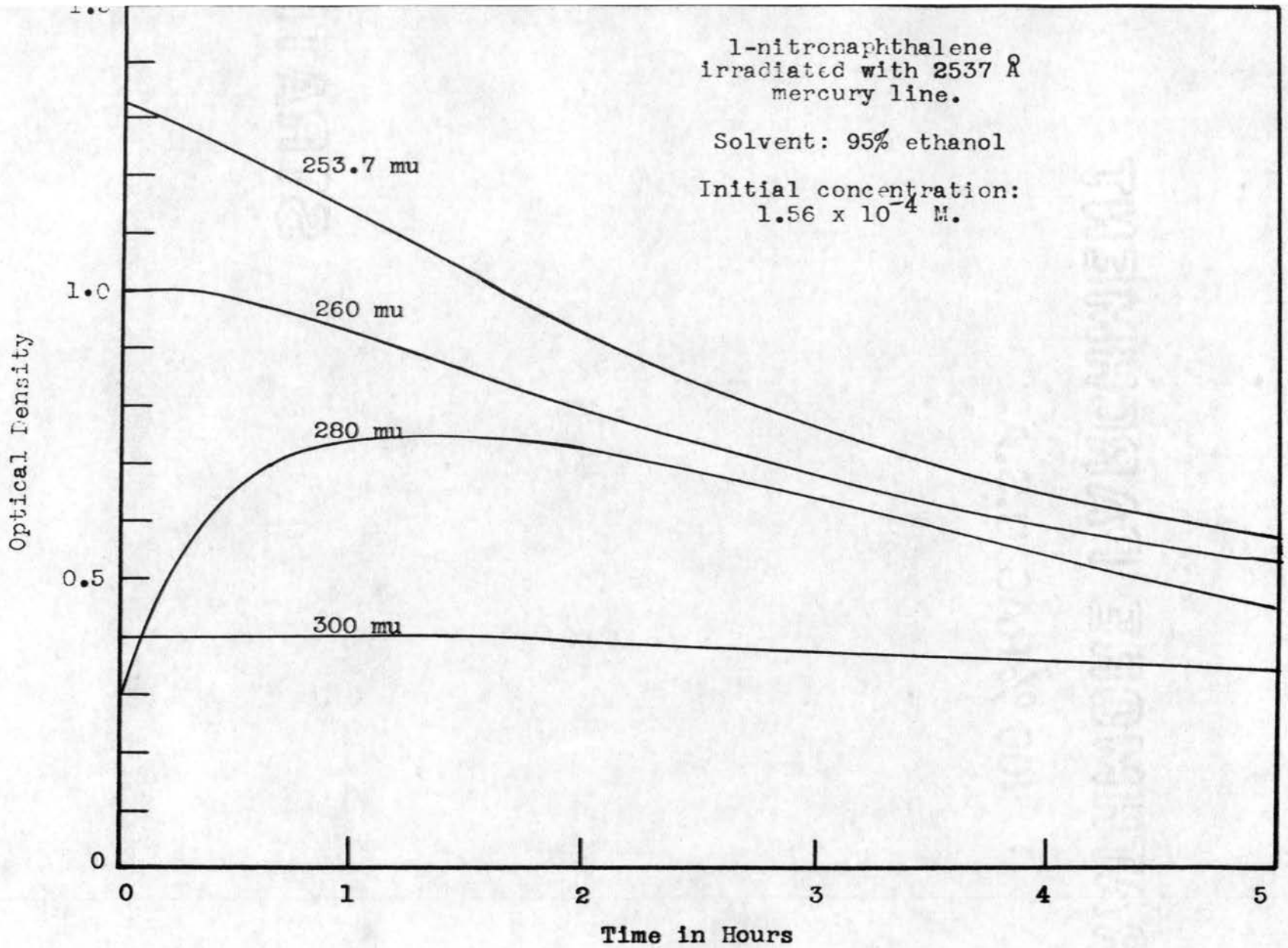

1-nitronaphthalene
irradiated with 2537 Å
mercury line.
Solvent: 95% ethanol
Initial concentration:
1.56 x 10^-4 M.
253.7 mu
260 mu
280 mu
300 mu
Optical Density
1.0
0.5
0
0
1
2
3
4
5
Time in Hours

Figure 14

other wavelengths. At 280 mμ the optical density rises until it reaches a maximum value then drops off to a lower limiting value with continued exposure. At 260 and 300 mμ the optical density remains constant for a period and then drops off slowly with increased exposure time.

The above phenomona can be readily explained if it is assumed that the process involved consists of two consecutive photochemical reactions; that is that the initial species absorbs a quantum of light and decomposes to yield a product which absorbs a second quantum of light and decomposes to yield a second and final product.

$$A + \text{photon} = B. \qquad \text{Eq. (6)}$$

$$B + \text{photon} = C. \qquad \text{Eq. (7)}$$

where A is the initial reactant and B and C are the intermediate and final products respectively.

The conditions for a maximum in the optical density versus time plot are merely, $\epsilon_A < \epsilon_B$ and $\epsilon_C < \epsilon_B$; these conditions hold at 280 mμ for the system: 1-nitronaphthalene in 95% ethanol. For a minimum in the curve, it is necessary only that $\epsilon_B < \epsilon_A$ and $\epsilon_B < \epsilon_C$; these conditions are not met by the system under consideration. The behavior at 260 and 300 mμ requires that $\epsilon_A = \epsilon_B > \epsilon_C$, while at 253.7 m$\mu$ (the exciting wavelength) $\epsilon_A > \epsilon_B > \epsilon_C$.

Even more information regarding such rather complicated reactions may be determined from these plots if they proceed in accordance with the following set of conditions:

1. The solution is irradiated with monochromatic light.
2. The relative number of intermediate product molecules produced by the photolysis of the initial species is independent of the time.
3. The relative number of final product molecules produced by the photolysis of the intermediate product is independent of the time.
4. The final product is photochemically stable.
5. The solution is perfectly stirred.
6. The light absorption of each species present is unaffected by the presence of the others.
7. The incident radiation is essentially completely absorbed by the solution.

For such a system the total optical density is given by

$$P = \epsilon_A C_A + \epsilon_B C_B + \epsilon_C C_C. \qquad \text{Eq. (8)}$$

The time rate of change of P is then

$$(dP/dt) = \epsilon_A (dC_A/dt) + \epsilon_B (dC_B/dt) + \epsilon_C (dC_C/dt). \qquad \text{Eq. (9)}$$

The rate of change of the initial species is given by

$$(dC_A/dt) = -(Q\phi_1/NV) f_A. \qquad \text{Eq. (10)}$$

where Q, N, and V have the same meanings as before (page 30), ϕ_1 is the quantum yield of the first of the consecutive reactions, equation (6), and f_A is the fraction of the in-

cident light absorbed by species A. When P and the extinction coefficients are measured at the wavelength of excitation, this fraction may be written

$$f_A = (\epsilon_A C_A/P). \qquad \text{Eq. (11)}$$

Letting

$$(Q\phi_1\epsilon_A/NV) = K_1. \qquad \text{Eq. (12)}$$

then substituting equations (11) and (12) into equation (10), the latter becomes

$$(dC_A/dt) = -(K_1 C_A/P). \qquad \text{Eq. (13)}$$

By analogous reasoning the time rate of change of the final product is

$$(dC_C/dt) = (Q\phi_2/NV)(\epsilon_B C_B/P). \qquad \text{Eq. (14)}$$

where ϕ_2 is the quantum yield of the second of the consecutive reactions, equation (7). Letting

$$(Q\phi_2\epsilon_B/NV) = K_2. \qquad \text{Eq. (15)}$$

equation (14) becomes

$$(dC_C/dt) = (K_2 C_B/P). \qquad \text{Eq. (16)}$$

The time rate of change of the intermediate product can be shown to be

$$(dC_B/dt) = \frac{(K_1 C_A - K_2 C_B)}{P}. \qquad \text{Eq. (17)}$$

Combining equations (13), (16), and (17) with equation (9) gives

$$(dP/dt) = \frac{K_1 C_A(\epsilon_B - \epsilon_A) - K_2 C_B(\epsilon_C - \epsilon_B)}{P}. \qquad \text{Eq. (18)}$$

In the limit as $t \to 0$, $C_B \to 0$, $C_A \to C_o$, and $P \to \epsilon_A C_o$, where C_o is the concentration of the initial species before the

irradiation. By virtue of these conditions, equation (18) becomes in the limit

$$\lim_{t \to 0} (dP/dt) = \frac{K_1(\epsilon_B - \epsilon_A)}{\epsilon_A}. \qquad \text{Eq. (19)}$$

Substituting for K_1 in equation (19), the latter becomes

$$\lim_{t \to 0} (dP/dt) = (Q\phi_1/NV)(\epsilon_B - \epsilon_A). \qquad \text{Eq. (20)}$$

Thus if the value of ϵ_B at the wavelength of excitation is known, ϕ_1 can be determined from absorption spectral data.

To obtain ϕ_2 from spectrophotometric data, it is necessary to eliminate the concentration variables from the expression relating optical density and time. To do this equation (18) was differentiated with respect to time, and the resulting time derivatives of the concentrations of A and B were replaced by their equlivents, equations (13) and (17). The result of these operations is the second order differential equation

$$P^2\ddot{P} + P\dot{P}^2 = (K_1K_2K_4 - K_1^2K_3)C_A + K_2^2K_4C_B. \qquad \text{Eq. (21)}$$

in which

$$K_3 = \epsilon_B - \epsilon_A. \qquad \text{Eq. (22)}$$

and

$$K_4 = \epsilon_C - \epsilon_B. \qquad \text{Eq. (23)}$$

The dots over the P's indicate differentiation with respect to time.

The same operations were applied to equation (21) resulting in the third order differential equation

$$P^3 \dddot{P} + 4P^2\dot{P}\ddot{P} + P\dot{P}^3 =$$

$$(K_1^3K_3-K_1^2K_2K_4-K_1K_2^2K_4)C_A + K_2^3K_4C_B. \qquad \text{Eq. (24)}$$

Equations (18), (21), and (24) are three simultaneous differential equations; the elimination of the concentration variables, C_A and C_B, from them yields the third order differential equation

$$P^3 \dddot{P} + 4P^2\dot{P}\ddot{P} + P\dot{P}^3 +$$

$$(K_1+K_2)(P^2\ddot{P}+P\dot{P}^2) + K_1K_2P\dot{P} = 0. \qquad \text{Eq. (25)}$$

Dividing equation (25) by P and intergrating once gives the second order differential equation

$$P^2\ddot{P} + P\dot{P}^2 + (K_1+K_2)P\dot{P} + K_1K_2P = C_1. \qquad \text{Eq. (26)}$$

All attempts to intergrate this equation were unsuccessful, But it was put into the form of a first order differential equation by making the substitution

$$(dP/dt) = \alpha. \qquad \text{Eq. (27)}$$

Equation (26) then becomes

$$\alpha P^2(d\alpha/dP) + P(\alpha+K_1)(\alpha+K_2) = C_1. \qquad \text{Eq. (28)}$$

To evaluate the constant of intergration, C_1, the behavior of the system at very large values of t was used, for as $t \to \infty$, $\alpha \to 0$, and $P \to \epsilon_C C_o$; therefore C_1 is given by

$$C_1 = K_1K_2\epsilon_C C_o. \qquad \text{Eq. (29)}$$

Using this value for C_1 and replacing $\alpha P^2(d\alpha/dP)$ with its equivalent, $P^2(d\alpha/dt)$, equation (28) becomes

$$P^2(d\alpha/dt) + P(\alpha-K_1)(\alpha-K_2) = K_1K_2\epsilon_C C_o. \qquad \text{Eq. (30)}$$

Now ϵ_C may be determined from the limiting value of P as

$t \to \infty$. The limiting values of P and α are known as $t \to 0$, and the value of $(d\alpha/dt)$ as $t \to 0$ may be determined graphically, figure 15; therefore since K_1 is known from a knowledge of ϕ_1, equation (12), only K_2 remains unknown in equation (30). Solving for K_2 and substituting back into equation (15) gives the value of ϕ_2.

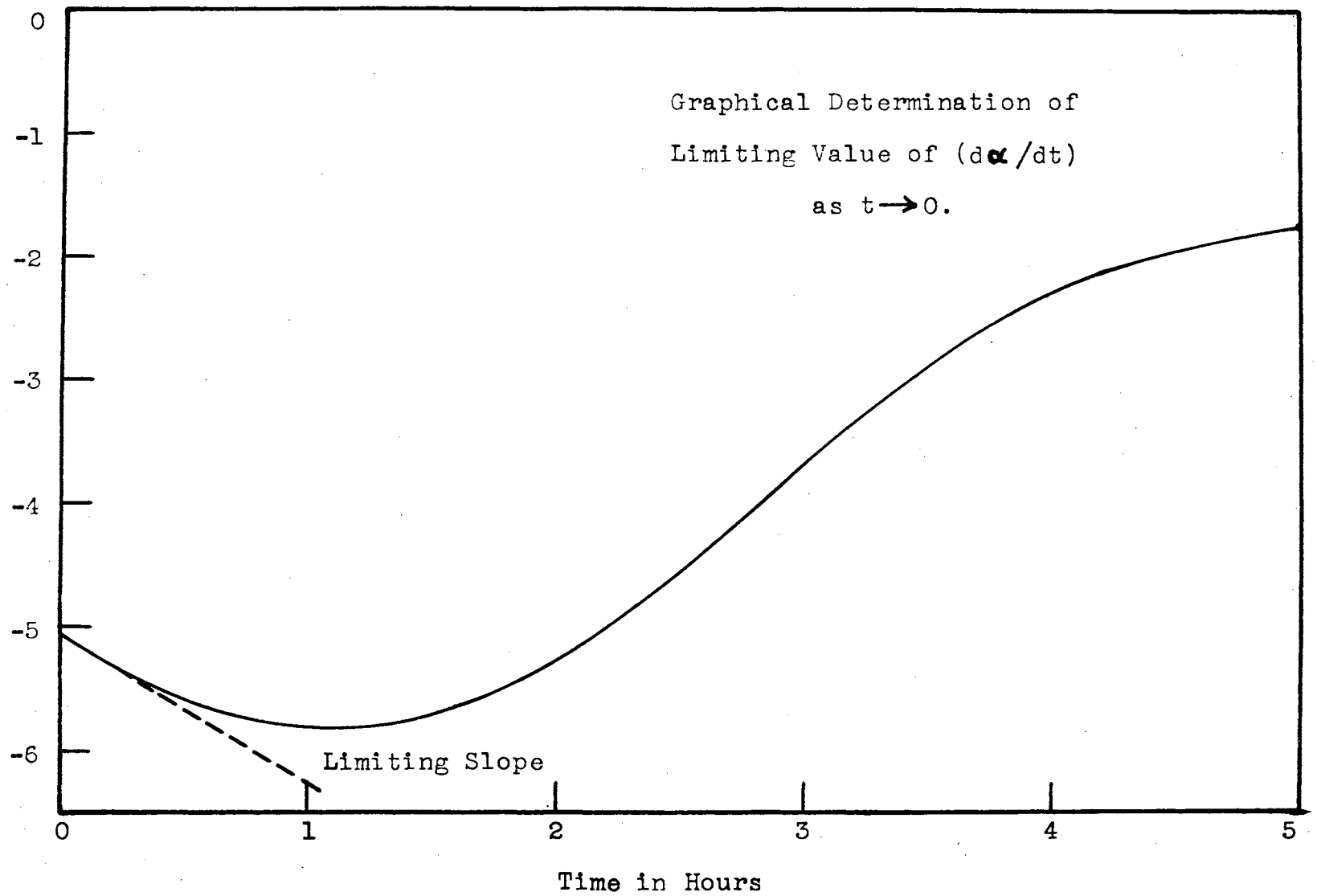

Graphical Determination of
Limiting Value of (dα/dt)
as t→0.
Limiting Slope
0
-1
-2
-3
-4
-5
-6
0
1
2
3
4
5
Time in Hours

Figure 15

CHAPTER V

CALCULATIONS

If the photochemical reactions induced by the 2537 Å mercury resonance line in solutions of the mononitronaphthalenes proceed in accordance with the conditions outlined in chapter IV, the quantum yields of the processes must all lie between zero and unity. To arrive at suitable values for these quantum yields, it was necessary to measure the output of the mercury resonance lamp. Using the monochloroacetic acid actinometer, several determinations were made. The following illustrates the calculation of Q from typical data: forty milliliters of an aqueous solution of monochloroacetic acid (optical density at 2537 Å = 1.22) were irradiated for fifteen minutes in the resonance lamp apparatus. Ten milliliters of this solution required 5.75 milliliters of 0.01227 N. silver nitrate solution to precipitate the liberated chloride ion. The quantum yield for the hydrolysis of monochloroacetic acid is 0.33.[16,17] Q then is given by

$$\frac{(5.75\ \text{ml})(1.227\times10^{-2}\ \text{moles/lit})(6.023\times10^{23}\ \text{molecules/mole})}{(0.33\ \text{molecules/quantum})(1000\ \text{ml/lit})(900\ \text{sec})}$$

from which

$$Q = 1.228\times10^{17}\ \text{quanta/sec.}$$

Five such determinations yielded 1.275×10^{17} quanta/sec for an average value of Q.

To determine the value of ϕ for the photodecomposition of 2-nitronaphthalene in cyclohexane the following data were obtained: volume of irradiated solution, V, = 40 ml, $(dP/dt) = -1.88 \times 10^{-4}$/sec, ϵ_A at 2537 Å = 26,900. Substitution of these values into equation (5) gives

$$\phi = \frac{(6.023 \times 10^{23} \text{ molecules/mole})(4 \times 10^{-2} \text{ lit})(1.88 \times 10^{-4}/\text{sec})}{(1.275 \times 10^{17} \text{quanta/sec})(2.69 \times 10^{4} \text{lit/mole})}$$

from which

$$\phi = 0.0013 \text{ molecules/quantum.}$$

For the photodecomposition of 2-nitronaphthalene in 95% ethanol, the following data were obtained: V = 40 ml, $(dP/dt) = -2.36 \times 10^{-3}$/sec, and ϵ_A at 2537 Å = 22,000. Using these values in equation (5), the quantum yield for this reaction was found to be

$$\phi = 0.0202 \text{ molecules/quantum.}$$

Since no attempts were made to identify the products of photodecomposition, the extinction coefficients of the intermediate products of the processes occuring in solutions of 1-nitronaphthalene are unknown. The quantum yields of these processes have, therefore, not been determined, but from the behaviors of the optical densities of these solutions at the exciting wavelength, definite limits can be placed on the values of the products' extinction coefficients.

Since the optical density at 2537 Å for solutions of

1-nitronaphthalene decreases with time of exposure, the value of ϵ_B in each system must be less than that of ϵ_A, i. e., $0 < \epsilon_B < \epsilon_A$. Although the ranges of possible values of the ϵ_B's are rather large, they do place certain restrictions on the quantum yield values for the consecutive reactions. These restrictions are calculated below.

For the photodecomposition of 1-nitronaphthalene in cyclohexane, the following data were obtained: at 2537 Å $\epsilon_A = 8850$, $\epsilon_C = 2300$, $V = 40$ ml, $\lim_{t \to 0} (dP/dt) = \alpha_o = -1.483 \times 10^{-4}$/sec, $\lim_{t \to 0} (d\alpha/dt) = -1.73 \times 10^{-7}/\text{sec}^2$, $C_o = 1.71 \times 10^{-4}$ moles/lit, and $\lim_{t \to 0} P = P_o = 1.512$.

Substitution of the proper values into equation (20) gave for ϕ_1 for this system

$$\frac{(6.023 \times 10^{23} \text{ molecules/mole})(4 \times 10^{-2} \text{ lit})(-1.483 \times 10^{-4}/\text{sec})}{[(\epsilon_B - 8850)\text{lit/mole}](1.275 \times 10^{17} \text{quanta/sec})}$$

from which

$$\phi_1 = -\frac{28.0}{\epsilon_B - 8850}$$

The upper limit of ϕ_1 is unity, which incidentally further restricts the range of permissible values of ϵ_B, i. e., $\epsilon_{B_{max}} = 8850 - 28 = 8822$. The lower limit of ϕ_1 is found by letting ϵ_B equal zero.

$$\phi_{1_{min}} = 0.00317 \text{ molecules/quantum.}$$

The calculation of ϕ_2 for the reactions of 1-nitronaphthalene is considerably more complicated, because ϕ_2, unlike ϕ_1, is not a simple function of ϵ_B. To show this, equations (15) and (30) were solved simultaneously for

ϕ_2. The result is the equation

$$\phi_2 = \frac{NV\left[P_o^2 \lim_{t\to 0} (d\alpha/dt) + \alpha_o P_o(\alpha_o + K_1)\right]}{Q\epsilon_B\left[K_1\epsilon_C C_o - P_o(\alpha_o + K_1)\right]}$$

Next equation (18) was solved for K_1 in the limit as t approaches zero. This gave

$$K_1 = \frac{\alpha_o \epsilon_A}{\epsilon_B - \epsilon_A}$$

Making this substitution for K_1 in the above expression for ϕ_2 and noting that $P_o = \epsilon_A C_o$, yielded

$$\phi_2 = \frac{NV\left[\lim_{t\to 0} (d\alpha/dt)(\epsilon_B - \epsilon_A)\epsilon_A C_o + \alpha_o^2 \epsilon_B\right]}{Q\alpha_o \epsilon_B(\epsilon_C - \epsilon_B)}$$

Solution of this equation using the appropriate values for 1-nitronaphthalene in cyclohexane gave values for ϕ_2 corresponding to chosen values of ϵ_B. If $\epsilon_B = \epsilon_{B_{max}}$, $\phi_2 = 0.0059$ molecules/quantum. If $\epsilon_B = 0$, $\phi_2 = 0$, i. e., product B can undergo no photodecomposition if it absorbs none of the incident radiation.

For the reaction of 1-nitronaphthalene in 95% ethanol the following data were obtained: $\epsilon_A = 7540$, $\epsilon_C = 1000$, $\epsilon_{B_{max}} = 7535$, V = 40 ml, $\alpha_o = -2.67\times10^{-5}$/sec, $\lim_{t\to 0} (d\alpha/dt) = -3.0\times10^{-9}/\text{sec}^2$, and $C_o = 1.71\times10^{-4}$ moles/lit.

Using the above values, equation (20) yielded for ϕ_1

$$\phi_1 = -\frac{5.05}{\epsilon_B - 7540}$$

Substituting $\epsilon_B = 0$ into the above equation, the lower limit of ϕ_1 was found to be 6.71×10^{-4} molecules/quanta. The value of ϕ_2 for this system when $\epsilon_B = \epsilon_{B_{max}}$ was found

to be 7.63×10^{-4} molecules/mole.

It was shown in the previous chapter that to calculate the quantum yields of two consecutive photochemical reactions, the value of ϵ_B at the wavelength of excitation must be known. To this end future plans for the extension of this research include the isolation of the intermediate products by chromatographic techniques. If sufficient amounts of these products can be collected to permit molecular weight determinations (micro methods) and absorption spectral analysis, the desired extinction coefficients can be readily calculated.

Also included in plans for future work are experiments to determine the order of the photochemical reactions occuring in solutions of the mononitronaphthalenes. By far most of the photochemical reactions that have been studied are first order with respect to the photons, and, indeed, this research has assumed that the reactions it concerns are of the first order. Strong evidence exists in support of this assumption even without recourse to experimentation when one considers the fraction of the total number of molecules that is in an excited state at any particular instant. This fraction is roughly determined in the following manner: in the solutions of this research the number of reactant molecules that were initially present in the irradiation cell was on the order of 10^{18}; the number of these that were activated per second was on the order of 10^{17}. The average time that a molecule exists in

such an excited state before losing its excess energy is about 10^{-7} second; therefore at any instant there are $(10^{17})(10^{-7})$ or 10^{10} molecules in an excited state, this represents $10^{10}/10^{18}$ or 10^{-6}% of the total number of molecules. For the order of a photochemical reaction to be higher than one, molecules in an excited state must absorb photons and undergo subsequent reaction. The probability of an excited mononitronaphthalene molecule colliding with a photon is quite low because of the small percent of the former which is present at any time; therefore the photochemical reactions of these molecules in solution are most likely of the first order with respect to the photons.

CHAPTER VI

SUMMARY

Solutions of both 1- and 2-nitronaphthalenes in cyclohexane and in 95% ethanol were shown to be unstable when exposed to the 2537 Å line of the mercury arc spectrum. Changes in the absorption spectra of the irradiated solutions indicate that the photochemical processes occuring in the 1-nitronaphthalene solutions are two consecutive photochemical reactions. The photodecompositions of the 2-nitronaphthalene solutions yield products which do not absorb at the wavelength of excitation. For the reactions of 2-nitronaphthalene the quantum yields were calculated from spectrophotometric data. They are 0.0013 for the cyclohexane solution and 0.0202 for the 95% ethanol solution.

A mathematical treatment of the spectrophotometric data for consecutive photochemical reactions was developed. This treatment allows for the calculation of both ϕ_1 and ϕ_2 for such reactions if the extinction coefficient at the wavelength of excitation of the intermediate product is known.

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