INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again – beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

74-16,979

GINSBURG, Paul Howard, 1945-
REACTIONS OF ELECTRONICALLY EXCITED
NAPHTHOQUINONE.

The City University of New York, Ph.D., 1974
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

REACTIONS OF ELECTRONICALLY
EXCITED NAPHTHOQUINONE

by

Paul Howard Ginsburg

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment of the requirements for the degree
of Doctor of Philosophy, The City
University of New York.

1974

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

This manuscript has been read and approved for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

2/13/74
date

Joseph Rennert
Chairman of Examining Committee

2/19/74
date

Leonard H. Schwartz
Executive Officer

Professor Takanobu Ishida
Professor Joseph Rennert
Professor Irving Waltcher

Supervisory Committee

The City University of New York

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Abstract

REACTIONS OF ELECTRONICALLY EXCITED NAPHTHOQUINONE

Paul H. Ginsburg

Adviser: Professor Joseph Rennert

Photoreduction of 1,4-naphthoquinone in benzene, a major competing reaction to photodimerization, was shown to occur by identification of the complex formed by 1,4-naphthoquinone and 1,4-naphthalenediol upon rapid freezing, by identification of the quinhydrone complex of 1,4-naphthoquinone and 1,4-naphthalenediol formed when the solvent is evaporated, and by isolation of 1,4-naphthalenediol from the photoproduct mixture. Di-naphthoquinone was shown to have no effect on 1,4-naphthalenediol formation by excited 1,4-naphthoquinone in benzene, and photoreduction did not occur in carbon tetrachloride, indicating that the benzene solvent was the hydrogen donor. Several products other than di-naphthoquinone and 1,4-naphthalenediol were found in both solvents.

The quantum yield of photoreduction was found to be the same at 334 nm and 436 nm, corresponding to the π,π^* and n,π^* transitions, indicating that 100 percent efficient conversion of the π,π^* state to the lower lying n,π^* state occurs. Photoreduction was sensitized by acridine yellow, and quenched by

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

anthracene indicating that photoreduction occurs via the first excited triplet state. Complex formation by acridine yellow a and 1,4-naphthoquinone in a glass at liquid nitrogen temperature, and by anthracene and 1,4-naphthoquinone in solution was observed. It was suggested that complex formation and energy transfer may be due to similar interactions.

The quantum yield determinations were made possible primarily by the apparatus developed for quantitative chemistry, which enabled accurate measurement of the fraction of light absorbed. Other features of the apparatus are provision for cross illumination, and a corrected response photomultiplier tube.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

To Marlene

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ACKNOWLEDGEMENTS

I wish to express my deep appreciation to my mentor Professor Joseph Rennert for his advice, assistance and concern during the course of this research. I wish to thank Professors Takanobu Ishida and Irving Waltcher, of my thesis guidance committee, for their counsel and cooperation.

Messrs. B. Slutsky and M. Alpay, supported by the N.S.F.U.R.P., assisted in the separation of photo-products.

Messrs. R. Bardell (Schoeffel Instrument Co.), J. LaRubbio, J. Russo, O. Safferling, H. Schimatz and R. Walker assisted in the construction of apparatus.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

TABLE OF CONTENTS

APPROVAL PAGE ii

ABSTRACT iii

DEDICATION PAGE v

ACKNOWLEDGEMENTS vi

TABLE OF CONTENTS vii

LIST OF TABLES xi

LIST OF FIGURES xii

1. INTRODUCTION 1

  1.1 Photoreduction of Quinones 1

    1.1.1. Early Investigations of Quinone Photoreduction 1

    1.1.2. Determinations of Quantum Yields and The Effect of Different Variables 2

    1.1.3. Mechanism of Reaction 4

    1.1.4. Hydrogen Transfer to Quinones 13

    1.1.5. n,π^* and π,π^* Excited States 14

    1.1.6. Determination of the Multiplicity of The Excited State 17

    1.1.7. Photoreduction of Quinones in Benzene 21

  1.2. Photodimerization of Quinones 22

    1.2.1. Synthesis of Photodimers 22

    1.2.2. Mechanism and Electronic States of Dimerization 26

    1.2.3. Photodimerization of Nucleic Acids 27

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1.3. Scope of This Research 29

2. MATERIALS 31

2.1. 1,4-Naphthoquinone 31

2.2. 1,4-Naphthalenediol 31

2.3. Di-naphthoquinone 31

2.4. Solvents 32

2.5. Purification of Benzene By Fractional Crystallization 32

2.6. Chromatographic Materials 33

2.7. Actinometry 33

2.8. Sensitizers and Quenchers 33

2.9. Other Materials 34

3. EQUIPMENT 35

3.1. Apparatus For Photochemical Irradiation 35

3.2. Photochemical Reactor Irradiation Apparatus 35

3.3. Instrumental Analysis 37

3.4. Degassing 37

3.5. Degassing Manifold 39

3.6. Photochemical Reaction Vessels 41

3.7. Photochemical Reaction Vessel With Sealed in Fritted Glass Filter 41

4. APPARATUS FOR QUANTITATIVE PHOTOCHEMISTRY 44

4.1. Quantum Yield 44

4.2. Actinometry 44

4.3. Determination of the Number of Photons Incident on a Solution 45

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4. Determination of the Number of Photons Incident When all of the Incident LIght is not Absorbed 46

4.5. System Design 47

4.6. Sample Compartment 50

4.7. Light Source and Optics 50

4.8. Detection of Incident Radiation 51

4.9. Luminescence and Cross Illumination Measurements 52

4.10. Deciding Which Detector to Use for Measurement of Incident Intensity and Fraction of Light Absorbed 52

4.11. Choice of Detector in This Work 54

4.12. Use of the System for Quantum Yield Determinations 55

4.13. Construction of the Apparatus 56

4.14. Procedure for Calibration of the Thermistor-Bolometer 59

4.15. Calculation of a Calibration Constant From the Actinometry Data 61

4.16. Calculation of the Quantum Yield of 1,4-Naphthoquinone Photoreduction at 436 nm 62

4.17. Calculation of the Quantum Yield of 1,4-Naphthoquinone Photoreduction at 334 nm 63

5. EXPERIMENTAL 67

5.1. Irradiation of 1,4-Naphthoquinone in Benzene 67

5.2. Irradiation of 1,4-Naphthoquinone in Benzene for Long Periods of Time Following Precipitation of Di-naphthoquinone 71

5.3. Thermochromism of Irradiated Benzene Solutions of 1,4-Naphthoquinone 73

5.4. Verification of the Photoreduction of 1,4-Naphthoquinone 74

5.5. Exclusion of Di-naphthoquinone as a Hydrogen Donor 80

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.6. Identification of the Hydrogen Donor in the Photoreduction of 1,4-Naphthoquinone 82

5.7. Other Products of 1,4-Naphthoquinone Irradiated in Benzene or in Carbon Tetrachloride 82

5.8. Photochemistry of 1,4-Naphthoquinone in Other Solvents 85

5.9. Determination of Quantum Yields for the Photoreduction of 1,4-Naphthoquinone in 2-Propanol 87

5.10. Sensitization of the Photoreduction of 1,4-Naphthoquinone 87

5.11. Quenching of 1,4-Naphthoquinone Photoreduction 102

5.12. Complex Formation of 1,4-Naphthoquinone with Anthracene and With Acridine Yellow 103

6. DISCUSSION AND CONCLUSIONS 116

6.1. Photoreduction of 1,4-Naphthoquinone in Benzene 116

6.2. Indentification of the Hydrogen Donor 117

6.3. Photoreduction of Other Quinones in Benzene 117

6.4. Mechanism for Photoreduction of 1,4-Naphthoquinone in Benzene 118

6.5. Reactions of 1,4-Naphthoquinone in Carbon Tetrachloride 120

6.6. Complex Formation Between 1,4-Naphthoquinone and 1,4-Naphthalenediol 120

6.7. The Excited State in Photoreduction 121

6.8. Importance of the Apparatus for Quantitative Photochemistry 122

6.9. Multiplicity of the Excited State in Photoreduction 123

6.10. Complex Formation With Acridine Yellow and Anthracene 124

7. BIBLIOGRAPHY 125

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

List of Tables

1 Absorbances of Degassed Benzene Solutions of 1,4-Naphthoquinone After Prolonged Irradiation 72

2 Effect of Di-naphthoquinone on the Photoreduction of 1,4-Naphthoquinone in Benzene 81

3 Mass Spectral Data for Photoproducts of 1,4-Naphthoquinone in Benzene and in Carbon Tetrachloride 84

4 Photoproducts of 1,4-Naphthoquinone in Various Solvents 86

5 Quantum Yields for the Photoreduction of 1,4-Naphthoquinone in 2-Propanol 89

6 Absorbance Changes of Irradiated 2-Propanol Solutions of Acridine Yellow and 1,4-Naphthoquinone and Acridine Yellow Only 94

7 Absorbance Changes of Irradiated Degassed Acetone Solutions of Acridine Yellow and 1,4-Naphthoquinone and Acridine Yellow Only 101

8 Determination of K_a and ε_{QA} for the Complex Formed by 1,4-Naphthoquinone and Anthracene in 4:1 Benzene:2-Propanol 110

9 Absorbance Changes of 2-Propanol Solutions of 1,4-Naphthoquinone and Acridine Yellow Upon Mixing 113

10 Absorbance of Ethanol Solutions of 1,4-Naphthoquinone, Acridine Yellow and a Mixture of 1,4-Naphthoquinone and Acridine Yellow 115

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF FIGURES

1. Corning Filter Irradiation Apparatus 36
2. Chemical Reactor Irradiation Apparatus 38
3. Degassing Manifold 40
4. Spectrophotometer Cell Degassing Assembly 42
5. Fritted Disc Filter Degassing Assembly 43
6. Apparatus For Quantitative Photochemistry, Side View 48
7. Apparatus For Quantitative Photochemistry, Top View 49
8. Ultraviolet Spectrum of 1,4-Naphthoquinone in 2-Propanol 64
9. Ultraviolet Spectrum of 1,4-Naphthalenediol in 2-Propanol 65
10. Visible Irradiation of 1,4-Naphthoquinone in Benzene 68
11. Ultraviolet Irradiation of 1,4-Naphthoquinone in Benzene 69
12. Ultraviolet Spectrum of Di-naphthoquinone in Benzene 70
13. Flow Chart for the Isolation of Quinhydrone From an Irradiated Solution of 1,4-Naphthoquinone in Benzene 75
14. Infrared Spectrum of the Quinhydrone of 1,4-Naphthoquinone and 1,4-Naphthalenediol 77
15. Split Compartment Mixing Cell for Difference Spectroscopy 78
16. Fluorescence Spectrum of 1,4-Naphthalenediol 79
17. Visible Spectrum of 1,4-Naphthoquinone in 2-Propanol 88
18. Triplet and Singlet Energies of a Sensitizer for 1,4-Naphthoquinone 90
19. Triplet and Singlet Energies of a Quencher for 1,4-Naphthoquinone 92

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

20. Ultraviolet Spectrum of Acridine Yellow in 2-Propanol 93

21a. Visible Spectra of a Degassed Irradiated Solution of 1,4-Naphthoquinone and Acridine Yellow in 2-Propanol 96

21b. Visible Spectra of a Degassed Irradiated Solution of 1,4-Naphthoquinone and Acridine Yellow in 2-Propanol 97

22a. Visible Spectra of a Degassed Irradiated Solution of 1,4-Naphthoquinone and Acridine Yellow in Acetone 99

22b. Visible Spectra of a Degassed Irradiated Solution of 1,4-Naphthoquinone and Acridine Yellow in Acetone 100

23. Visible Spectrum of Anthracene in 1:4 Benzene: 2-Propanol 104

24. Visible Absorption Spectra of Solutions of 1,4-Naphthoquinone and Anthracene and 1,4-Naphthoquinone Only in 4:1 Benzene:2-Propanol 105

25. Determination of the Composition of the Complex Formed by 1,4-Naphthoquinone and Anthracene in 4:1 Benzene:2-Propanol 107

26. Determination of the K_a and ε_{QA} for the Complex Formed by 1,4-Naphthoquinone and Anthracene in 4:1 Benzene:2-Propanol 109

27. Spectrum of 6.84×10^{-2}M 1,4-Naphthoquinone and 2.28×10^{-3}M Anthracene In 4:1 Benzene:2-Propanol v. a Reference Solution of 6.84×10^{-2}M 1,4-Naphthoquinone in 4:1 Benzene:2-Propanol 111

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1. INTRODUCTION

1.1. Photoreduction of Quinones

1.1.1. Early Investigations of Quinone Photoreduction

Ciamician[1] observed that when an ethanol solution of p-benzoquinone is exposed to sunlight, hydroquinone and quinhydrone are produced, and the alcohol is oxidized to acetaldehyde. Klinger[2] found that phenanthraquinone in alcohol was photoreduced to its hydroquinone, and that acetaldehyde was produced. Ciamician and Silber[3] then found that 2-propanol could be used as a reducing agent for the photoreduction of p-benzoquinone, and that acetone was then formed. Schönberg and his associates, interested in photochemistry from the synthetic point of view, worked on a number of reactions of quinones. Schönberg and Mustafa[4] found that p-benzoquinone abstracts hydrogen from diphenylmethane, fluorene, xanthen, anthrone and dinaphthapyran, forming quinhydrone, and ethane derivatives. They subsequently reported[5] that p-benzoquinone converts thioxanthen to dithioxanthyl as quinhydrone is produced, and that phenanthraquinone causes thioxanthen to be converted to dithioxanthyl, and diphenylmethane to be converted to s.-tetraphenylethane. Mustafa[6] found that p-benzoquinone, toluquinone, chloranil, and phenanthraquinone were

---

[1] G. Ciamician, Gazz. Chim. Stal., 16, 111 (1 86).
[2] H. Klinger, Ber., 19, 1862 (1886).
[3] G. Ciamician and P. Silber, Per., 34, 1530 (1901).
[4] A. Schönberg and A. Mustafa, J. Chem. Soc., 1944, 67.
[5] A. Schönberg and A. Mustafa, J. Chem. Soc., 1945, 657.
[6] A. Mustafa, Nature, 162, 856 (1948).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

photochemically reduced by ethylorthoformate to the corresponding hydroquinones. Schönberg and Mustafa[7] discussed photochemical dehydrogenation by quinones in a review of the photochemistry of ketones.

1.1.2. Determinations of Quantum Yields and the Effect of Different Variables

Leighton and Forbes[8] were the first to investigate the photoreduction of quinones from the perspective of physical chemistry and to determine quantum yields. They studied the photochemical decomposition of p-benzoquinone in water and in ethanol under a nitrogen atmosphere, because they noticed that oxygen retards photoreduction. It was found that in water, initially little reduction occurred, but the absorbance changed. This was attributed to dimerization. After an initial period, more photoreduction occurred. The quantum yield of photoreduction was 0.16 at 435.0 nm and 0.9 for 366 nm and 253.7 nm. In alcohol the quantum yield was 0.2 at 546.0 nm and increased to 0.5 at 435.0 nm, but was constant between 435.0 nm and 253.7 nm, measured at several wavelengths. In alcohol, the quantum yield was independent of concentration. The temperature coefficient $\Delta K_{10°}$ was near unity for the reaction in water.

---

[7] A. Schonberg and A. Mustafa, Chem. Revs., 40, 181 (1947).

[8] P.A. Leighton and G.S. Forbes, J. Amer. Chem. Soc., 51, 3549 (1929).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Quantitative study of the photoreduction of quinones was continued by Berthoud and Porret[9]. They found that the efficiency of the reaction between p-benzoquinone and isopropyl alcohol in aqueous solution decreased by 50% when the alcohol concentration was reduced from 5M to 0.02M. With ethyl alcohol the efficiency also varied with alcohol concentration. Using p-benzoquinone with high concentrations of ethyl alcohol and blue light, they found that the quantum yield was independent of quinone concentration, intensity of illumination and temperature, and in disagreement with Leighton and Forbes[8] that the quantum yield was unity.

Atkinson and Di[10], in work suggested by these findings, studied the effect of light intensity and ethanol concentration on p-benzoquinone photoreduction in carbon tetrachloride under a nitrogen atmosphere at 25°C. and with irradiation of 435.8 nm. They found that when the alcohol concentration was at least 0.185M the light intensity, a range from 0.07×10^{-8} einst. sec^{-1} to lo^{-8} einst. sec^{-1}, did not affect the quantum yield. At an alcohol concentration of 0.185M the quantum yield was constant for p-benzoquinone concentrations of 10^{-3} to 10^{-2}M. With a benzoquinone concentration of 5×10^{-3}M the quantum yield was constant for alcohol concentrations of 0.18M to 5M. With alcohol concentrations below

---

9. A. Berthoud and D. Porret, Helv. Chim. Acta., 17, 694 (1934).
8. P.A. Leighton and G.S. Forbes, J. Amer. Chem. Soc., 51, 3549 (1929).
10. B. Atkinson and M. Di, Trans. Faraday Soc., 54, 1331 (1958).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

10^{-1}M the quantum yield decreased with decreasing alcohol concentrations, and in the range 10^{-1} to 10^{-3}M alcohol a marked dependence of the quantum yield on the light intensity was observed. Quantum efficiencies for the photochemical oxidation of ethyl, n-propyl, and isopropyl alcohols by p-benzoquinone at high alcohol concentrations were 0.78, 0.77 and 0.78.

Tickle and Wilkinson[11] found that at low anthraquinone concentrations and with high rates of absorption of light, the quantum yield of photoreduction of anthraquinone in 2-propanol approaches a lower limit of 0.5, while at high concentrations and low intensities, the upper limit is 1.0. There was no wavelength dependence comparing 366.0 nm and 313.0 nm.

1.1.3. Mechanism of Reaction

As certain anthraquinoid vat dyes were known in the textile industry as accelerators of the photodegradation of cellulose, Bolland and Cooper[12] studied the oxidation of ethanol by oxygen to yield acetaldehyde, acetic acid, and hydrogen peroxide, photosensitized by anthraqqinone 2,6 disodium sulfonate. They found that the quantum yield of oxygen absorption was unity, that the quantum yields of aldehyde, acid,and hydrogen peroxide production were fractional, and that the rate of oxygen uptake was insensitive to

---

[11] K. Tickle and F. Wilkinson, Trans. Faraday Soc., 61, 1981 (1965).

[12] J.L. Bolland and H.R. Cooper, Proc. Roy. Soc., A225, 405 (1954).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

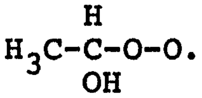
variations in the reactant concentrations and in temperature. They concluded that the reaction occurred by a non-chain process. They also found that the photosensitizer operated by a cyclic mechanism which enabled large numbers of oxygen molecules to take part in photo-oxidation without concomitant destruction of the sensitizer. However, when the alcohol concentration was below 0.8M (water was the diluent), side reactions involving the sensitizer became significant. Colored derivatives, having no efficiency as photosensitizers, were formed.

Bolland and Cooper suggested that the quinone abstracted hydrogen from the alcohol to form a semiquinone radical which reacted further to give the products. The following mechanism was proposed:

$$A + h\nu \rightarrow A^*$$
$$A^* + RH \rightarrow AH\cdot + R\cdot$$
$$R\cdot + O_2 \rightarrow RO_2\cdot$$
$$AH\cdot + O_2 \rightarrow A + HO_2\cdot$$
$$R\cdot + A \rightarrow AH\cdot + \text{aldehyde}$$
$$RO_2\cdot + RO_2\cdot \rightarrow 2\ \text{acid} + H_2O_2$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$
$$RO_2\cdot + HO_2\cdot \rightarrow \text{aldehyde} + H_2O_2 + O_2$$
$$R\cdot + R\cdot \rightarrow$$
$$R\cdot + RO_2\cdot \rightarrow$$
$$R\cdot + HO_2\cdot \rightarrow$$

A represents the anthraquinoid sensitizer, A* represents the excited sensitizer molecule, AH· represents the semiquinone radical, R· represents the radical $H_3C\text{-}\overset{H}{\underset{H}{C}}\cdot$, and $RO_2\cdot$ represents

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

the radical  $H_3C-\overset{H}{\underset{OH}{C}}-O-O.$

A kinetic analysis of this proposed reaction scheme led to expressions relating the product yields to experimental conditions which were in accordance with the observed results.

That semiquinone radicals actually resulted from photoreduction was shown by Linschitz, Rennert and Korn[13] who found that irradiation of either p-benzoquinone or hydroquinone in a glass yields a semiquinone. Both ultraviolet-visible and e.s.r. spectra were obtained.

The development of flash photolysis enabled the direct observation of triplets and radicals in solution. Porter and Windsor[14] made the first observation of a possible quinone triplet in solution when they found that p-benzoquinone flashed in liquid paraffin formed a transient. Bridge and Porter[15] observed transient spectra of intermediates upon flashing benzoquinone, duroquinone, toluquinone, xyloquinone, naphthoquinone and anthraquinones in various solvents. They made a detailed study of duroquinone. Transients were identified arising from the following main intermediates:

1) The semiquinone radical which appeared in all solvents containing abstractable hydrogen at pH 7 and below.

---

13. H. Linschitz, J. Rennert and T.M. Korn, J. Amer. Chem. Soc., 76, 5839 (1954).
14. G. Porter and M.W. Windsor, Nature, 180, 187 (1957).
15. N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 259 (1958).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2) The semiquinone radical ion which appears only at pH 7 and above.
3) The triplet state which is observed strongly in the viscous solvent liquid paraffin and has a relatively short life.

Bridge and Porter[16] measured rate or equilibrium constants for the following reactions of duroquinone:

$$
\begin{array}{l}
Q^{*} \rightarrow Q_T \\
Q_T \rightarrow Q \\
Q^{*} + RH \rightarrow QH\cdot + R \\
Q_T + RH \rightarrow QH\cdot + R \\
2QH\cdot \rightarrow Q + QH_2 \\
QH\cdot \rightarrow Q\cdot^{-} + H^{+} \\
2Q\cdot^{-} \rightarrow Q + Q^{2-} \\
Q^{-} + H^{+} \rightarrow QH\cdot \\
QH\cdot \rightleftarrows Q\cdot^{-} + H^{+}
\end{array}
$$

Wilkinson[17], who found evidence that the triplet state of anthraquinone was the photochemically reactive state, suggested the following mechanism for photoreduction in 2 propanol in the absence of oxygen:

$$
\begin{array}{l}
AQ + h\nu \rightarrow AQ^{*}\ (\text{Singlet, S}) \\
AQ^{*}(S) \rightarrow AQ^{*}\ (\text{Triplet, T}) \\
AQ^{*}(T) + (CH_3)_2CHOH \rightarrow AQH\cdot + (CH_3)_2\cdot COH \\
(CH_3)_2\cdot COH + AQ \rightarrow AQH\cdot + (CH_3)_2C{=}O \\
2AQH\cdot \rightarrow AQ + AQH_2
\end{array}
$$

---

[16] N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 276 (1958).
[17] F. Wilkinson, J. Phys. Chem., 66, 2569 (1962).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Tickle and Wilkinson[11] added the following to this proposed mechanism:

$$2R_2\dot{C}OH \rightarrow R_2CO + R_2CHOH$$

Walker[18] determined quantum yields for the photochemical oxidation of ethanol by phenanthraquinone at 435 nm in solutions of ethanol in benzene, degassed by bubbling through nitrogen. At high concentrations of ethanol a quantum efficiency of 4 was attained indicating a chain reaction. The products of the photo-oxidation were acetaldehyde and phenanthrenediol. The following mechanism was proposed:

$$PQ + h\nu \rightarrow PQ^*$$
$$PQ^* + PQ \rightarrow 2PQ$$
$$PQ^* + CH_3CH_2OH \rightarrow PQH\cdot + CH_3\dot{C}HOH$$
$$PQH\cdot + CH_3CH_2OH \rightarrow PQH_2 + CH_3\dot{C}HOH$$
$$CH_3\dot{C}HOH + PQ \rightarrow PQH\cdot + CH_3CHO$$
$$2CH_3\dot{C}HOH \rightarrow CH_3CH_2OH + CH_3CHO$$
$$2PQH\cdot \rightarrow PQH_2 + PQ$$

Schulte-Frohlinde and Sonntag[19] found that addition of sodium hydroxide to aqueous solutions of anthraquinone and 2-propanol resulted in formation of the semiquinone radical in quantum yields as high as 2. This may be rationalized by

---

[11] K. Tickle and F. Wilkinson, Trans. Faraday Soc., 61 1981 (1965).

[18] P. Walker, J. Chem. Soc., 1963, 5545.

[19] D. Schulte-Frohlinde and C. von Sonntag, Z. Physik. Chem. N.F., 44, 313 (1965).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

assuming that the acid base reaction

$$AQH\cdot + OH^- \rightarrow AQ\cdot^- + H_2O$$

competes effectively with the disproportionation of the semiquinone radical, $2AQH\cdot \rightarrow AQ + AQH_2$. In deoxygenated solutions $AQ\cdot^-$ is stable.

Hales and Bolton[20] followed the decay of the chloranil semiquinone radical anion produced in methanol and ethanol by flash photolysis and determined the rate constants.

Nafisi-Movaghar and Wilkinson[21] subjected large volumes of concentrated solutions of duroquinone in deaerated 2-propanol to prolonged irradiation. Five products were detected. These included durohydroquinone, diduroquinone and three other compounds produced in very small yields. Flash photolysis experiments by Nafisi-Movaghar and Wilkinson[22] showed that when a certain concentration of durohydroquinone was present, photoreduction was prevented but transient durosemiquinone was produced in a yield twice that produced when duroquinone alone is flashed, indicating that quenching by durohydroquinone is chemical, producing 2 semiquinone radicals:

$$AQ^* + AQH_2 \rightarrow 2AQH\cdot$$

---

20. B.J. Hales and J.R. Bolton, Photochem. Photobiol., 12, 239 (1970).
21. J. Nafisi-Movaghar and F. Wilkinson, Trans. Faraday Soc., 66, 2257 (1970).
22. J. Nafisi-Movaghar and F. Wilkinson, Trans. Faraday Soc., 66, 2268 (1970).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The transient spectrum obtained when duroquinone is flashed in the presence of added diduroquinone was not identical to that observed from duroquinone alone or from duroquinone in the presence of added durohydroquinone, indicating that chemical quenching accurred. Flashing duroquinone in a solution of water and 2-propanol gave initially little transient, indicating that the quenching was physical. Hydrogen bonding with water may facilitate intersystem crossing.

Wong et. al.[23] irradiated 1,4-benzoquinone, 1,4-naphthoquinone and duroquinone in 2-propanol and dioxane, obtained e.s.r. spectra and measured the rate constants for decay of the semiquinone radicals. Photolysis of anthraquinone in 2-propanol gave e.s.r. spectra of the anthrasemiquinone radical ion. The mechanism for its suggested decay was the one suggested by Bridge and Porter[16] for durosemiquinone radical ion in neutral solution:

$$Q\cdot^{-} + H^{+} \xrightarrow{Ka} QH\cdot$$

$$2QH\cdot \rightarrow Q + QH_2$$

The differential rate equation for the disappearance of $Q\cdot^{-}$ would be second order

$$\frac{d[Q\cdot^{-}]}{dt} = \frac{k[H^{+}]}{Ka}[DSQ^{-}]^2$$

---

23. S.K. Wong, W. Sytnyk and J.K.S. Wan, Can. J. Chem., 50, 3052 (1972).
16. N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 276 (1958).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

E.s.r. was also used by Kamiya et. al.[24] who studied the photosensitized decomposition of methyl alcohol in the presence of p-benzoquinone by continuous irradiation of the frozen solution. Four kinds of e.s.r. spectra were distinguished; these were attributed to CH_2OH, CHO, CH_3 and p-benzosemiquinone radicals. The decay of methyl radical was found to be second order.

Rennert et. al.[25] showed that irradiation of degassed solutions of phenanthraquinone in ethanol in the presence of divalent metal ions results in a blue-green intermediate which is a cation-semiquinone complex. The intermediate could be further photoreduced to the colorless 9,10-phenanthrenediol.

Further study of the effects of concentration and light intensity prompted greater understanding of quinone photoreduction reaction mechanisms. Carapelluci et. al.[26] showed that the photolysis of phenanthraquinone in 2-propanol gives rise to 9,10-phenanthenediol and acetone. The quantum yield of the disappearance of phenanthraquinone in 2-propanol-benzene mixtures was found to be independent of the incident light intensity, and to increase with the alcohol concentration to reach a maximum value of 1.6 in pure 2-propanol.

---

[24] M. Kamiya, K. Hatano and T. Kwan, Chem. Pharm. Bull, 15, 932 (1967).

[25] J. Rennert, M. Mayer, J. Levy and J. Kaplan, Photochem. Photobiol., 10, 267 (1969).

[26] P.A. Carapellucci, H.P. Wolf and K. Weiss, J. Amer. Chem. Soc., 91, 4635 (1969).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

A mechanism consistent with the intensity dependence and the quantum yield greater than unity was proposed:

$Q \rightarrow Q^*(S)$
$Q^*(S) \rightarrow Q^*(T)$
$Q^*(T) \rightarrow Q$
$Q^*(S) \rightarrow Q$
$Q^*(S) + RH_2 \rightarrow QH' + RH\cdot$
$QH' + RH_2 \rightarrow QH_2 + RH\cdot$
$QH' \rightarrow QH\cdot$
$RH\cdot + Q \rightarrow QH\cdot + R$
$2QH\cdot \rightarrow QH_2 + Q$

where Q' is a vibrationally excited semiquinone radical. The 2-hydroxyl-2-propyl radical is represented by RH· and acetone by R.

In a study of duroquinone photoreduction in deaerated 2-propanol by Nafisi-Movaghar and Wilkinson[21] no concentration or intensity dependence was observed.

Carlson and Hercules[27] extended the use of flash photolysis further to the red than previous investigators of quinone photochemistry. Bridge and Porter[15] had attempted to study the anthrasemiquinone radical by flash photolysis, but found its absorption overlapped greatly with that of 9,10-dihydroxyanthracene, and it was therefore not possible for them to obtain a spectrum or any kinetic data. Carlson and Hercules[27] obtained the absorption spectrum of anthrasemiquinone

---

21. J. Nafisi-Movaghar and F. Wilkinson, Trans. Faraday Soc., 66, 2257 (1970).
27. S.A. Carlson and D.M. Hercules, Photochem. Photobiol., 17, 123 (1973).
15. N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 259 (1958).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

radical in the region of 550-700 nm where complications from absorption by 9,10-dihydroxyanthracene were not encountered. They also observed an absorption band of anthrasemiquinone radical ion in the 600-900 nm region. The rate constant for disproportionation of the radical in ethanol was estimated. Carlson and Hercules also studied the photoreduction of anthraquinone and hexane, and pointed out that the low quantum yield of 0.11 could be due to dimerization and disproportionation of solvent radicals and also to the reaction:

$$AQH\cdot + R\cdot \rightarrow AQ + RH$$

1.1.4. Hydrogen Transfer to Quinones

In a study of irradiated, oxygenated aqueous solutions of sodium anthraquinone-2-sulfonate, with added methanol, ethanol, isopropanol and tert-butanol, Wells[28] concluded from the low reactivity of tert-butanol that only hydrogen atoms on the carbon atom α to the hydroxyl group are removed by the photoexcited quinone, i.e., hydrogen atoms on the hydroxyl oxygen atom or on β carbon atoms are not attacked. From the fact that the reactivity is a hundredfold lower for t-butanol, rather than two or three fold lower, he concluded that direct hydrogen transfer rather than electron transfer is the primary oxidative act.

---

[28] C.F. Wells, Trans. Faraday Soc., 57, 1703 (1961).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

At high sensitizer concentration, low isopropyl alcohol concentration and high oxygen pressure, Wells found that a competing reaction of the photosensitizer with oxygen occurred, resulting in colored products. He also found that in ethanol, 2-propanol, and cis-1,2-cyclohexanediol, the rate constants for either hydrogen abstraction or reversion to the ground state by the excited quinone were independent of temperature.

Wells[29] also determined the reactivities of a number of alcohols, ethers and ketones for hydrogen transfer to sodium anthraquinone-2-sulfonate. He found that increasing alkylation increases the reactivity of the hydrogen atoms on the α carbon atoms of alcohols. Increasing alkylation in ethers causes a retardation of hydrogen transfer from alpha carbon atoms.

1.1.5. n,π* and π,π* Excited States

It was known that the tendering ability of anthraquinoid dyes with different substituents differed widely. Interest in this area led to research identifying particular excited states as photochemically reactive. Abrahamson and Panik[30] suggested that the lack of tendering ability of some anthraquinoid dyes could be explained by the fact that their n,π* states lie at higher energies than their π,π* states and that

---

[29] C.F. Wells, Trans. Faraday Soc., 57, 1719 (1961).

[30] E.W. Abrahamson and I. Panik, "The Spectroscopy and Photochemistry of Anthraquinone Dyes," Advances In Molecular Spectroscopy, Vol.,I, Pergamon Press, Oxford, 1962, p354-62.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

the π,π^* states were unreactive. The relative positions of the n,π^* and π,π^* states are affected by substitution and the non-tendering substituted quinones considered by Abrahamson and Panik had substituent groups that would have been expected to affect the energies so that the π,π^* state was lower in energy. Experiments on the effect of acid on the photochemistry of 2,7-anthraquinone in 20 per cent ethanol were consistent with this hypothesis. When a degassed slightly acid ($\approx 10^{-3}$M H_2SO_4) solution was flash illuminated, an absorption band at approximately 390 nm, characteristic of the semiquinone, appears. In concentrated sulfuric acid, with 5 per cent ethanol, the absorption changes on flash illumination are almost negligible. In 10^{-3}M H_2SO_4 solution the peak assumed to be the $n \rightarrow \pi^*$ peak underwent a blue shift. In concentrated acid the $n \rightarrow \pi^*$ transition was assumed to be shifted to a much higher energy than the $\pi \rightarrow \pi^*$ transition.

Schulte-Frohlinde and von Sonntag[19] determined quantum yields for a number of substituted anthraquinones in 2-propanol and water and in 2-propanol only. Several were unreactive and a few were lower in reactivity than unsubstituted anthraquinone. They also found that addition of hydrochloric acid to aqueous solutions of anthraquinone and 2-propanol reduced the quantum yield of anthraquinone photoreduction measured at 313 nm. These results were in accord

---

[19] D. Schulte-Frohlinde and C. von Sonntag, Z. Physik. Chem. N.F., 44, 313 (1965).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

with the hypothesis of Abrahamson and Panik[30]. Schulte-Frohlinde and von Sonntag[19] also determined quantum yields for the photoreduction of 1,4-benzoquinone and 1,4-naphthoquinone, in both 2-propanol and water.

Nagakura and Kuboyama[31] showed that the absorption of 1,4-naphthoquinone in the visible had a low molar extinction coefficient and was shifted to shorter wavelengths with increasing dielectric constant of the solvent. He concluded that the absorption was due to the singlet-singlet $n \rightarrow \pi^*$ transition.

Rennert et. al.[32] determined the quantum yields of photoreduction of 1,4-naphthoquinone in 2-propanol at 313 nm and 405 nm for a 6 x 10^{-3}M solution. At 313 nm for a deoxygenated solution the quantum yield was unity. For non-degassed solutions the quantum yields were 0.80 for 313 nm and 0.87 for 405 nm. Schulte-Frohlinde and von Sonntag[19] had determined the quantum yield at 313 nm, for a solution that had been degassed by bubbling nitrogen, to be 0.85. Rennert et. al.[32] concluded that since the quantum yields at 313 nm and 405 nm were practically the same and that since these wavelengths corresponded to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively, that photoreduction took place in the n,π^* state reached via either direct

---

30. E.W. Abrahamson and I. Panik, "The Spectroscopy and Photochemistry of Anthraquinone Dyes," Advances In Molecular Spectroscopy, Vol. I, Pergamon Press, Oxford, 1962, p. 354-62.
19. D. Schulte-Frohlinde and C.von Sonntag, Z. Physik. Chem. N.F., 44, 313 (1965).
31. S. Nagakura and A. Kuboyama, J. Amer. Chem. Soc., 76, 1003(1954).
32. J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

transition, or by a 100 per cent efficient interval conversion from the higher lying π,π^* state.

1.1.6. Determination of the Multiplicity of the Excited State

In a kinetic study of duroquinone by flash photolysis, Bridge and Porter[16] found that the transient identified as the triplet did not decay to give rise to the semiquinone radical, and concluded that the latter was due to the first excited singlet state. They also found that the semiquinone radical was formed very rapidly after the flash and concluded that hydrogen transfer rather than electron transfer was the primary process.

Wilkinson[17] studied the photoreduction of anthraquinone to anthraquinol, in the absence of oxygen, in 2-propanol solutions. He found that photoreduction was quenched by anthracene, and demonstrated, by flash photolysis, that energy transfer resulting in the formation of triplet anthracene was possible. He concluded that anthraquinone is photoreduced via the triplet state. In the presence of a triplet energy accepter, A, of lower triplet energy than anthraquinone, the following reaction occurs:

$$AQ^*(T) + A(S) \rightarrow AQ(S) + A^*(T)$$

---

[16] N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 276 (1958).
[17] F. Wilkinson, J. Phys. Chem., 66, 2569 (1962).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Dearman and Chan[33] found that observation of phosphorescence for substituted anthraquinones was a requisite for photoproduction of semiquinones in alkaline methanol, detected by e.s.r. This was taken as evidence that the triplet state is the photochemically reactive state.

Flash photolysis of duroquinone, solutions in the presence and absence of triplet energy acceptors, by Wilkinson, et. al.[34] established the triplet state of duroquinone as the precursor of the durosemiquinone radical. Experiments in which duroquinone solutions in 2-propanol were subjected to continuous irradiation, in the presence and absence of antracene, indicated that the triplet state was responsible for all detectable duroquinone photoconversions including those to give duroquinol and diduroquinone.

Energy transfer experiments by Carapelluci et. al.[26] identified a transient, that had been observed during flash photolysis of phenanthraquinone, as a triplet. In the presence of anthracene the phenanthraquinone transient was not observed upon excitation of phenanthraquinone only, but the anthracene triplet was observed. It was also shown that the quantum yield of phenanthraquinone photoreduction was lowered by addition of anthracene.

---

[33] H.H. Dearman and A. Chan, J. Chem. Phys., 44, 416 (1966).

[34] F. Wilkinson, G.M. Seddon and K. Tickle, Ber. Bunsenges. Phys. Chem., 72, 315 (1968).

[26] P.A. Carapelluci, H.P. Wolf and K. Weiss, J. Amer. Chem. Soc., 91, 4635 (1969).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Rubin and Neuwirth-Weiss[35] found that photoreduction of phenanthraquinone in degassed benzene to yield biphenyl, the monophenyl ether of 9,10-dihydroxyphenanthrene, and 9,10-dihydroxyphenanthrene and some uncharacterized material. It was later shown[36] that the reaction was completely quenched by 10^{-2} M anthracene, indicating that all products were formed from the n,π^* triplet.

Carlson and Hercules[37] observed delayed thermal fluorescence of anthraquinone. This implied that triplet quenching experiments had not firmly established the triplet as the reactive state, because the triplet could repopulate the singlet state. However, a consideration of the effect of various hydrogen donors on the quantum yield of luminescence showed that the rate constants for hydrogen abstraction in ethanol and 2-propanol were so high that it could be concluded that photoreduction from the triplet is the bulk of the reaction, but that previous work with triplet quenchers does not preclude a small fraction of the reaction being from the singlet, and does not mean that the singlet is unreactive. In order for a singlet state to account for a significant part of the reaction, it should have $\Delta E_{ST} < 1500$ cm^{-1} and the reaction should have a low quantum yield.

---

35. M.B. Rubin and Z. Neuwirth-Weiss, Chem. Commun., 1968,1607.
36. M.B. Rubin and Z. Neuwirth-Weiss, J. Amer. Chem. Soc., 94, 6048 (1972).
37. S.A. Carlson and D.M. Hercules, J. Amer. Chem. Soc., 93, 5611 (1971).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

From the relative changes of absorption with time at 405 nm, and at 490 nm, following flash illumination of duroquinone in liquid paraffin, Bridge and Porter[16] had concluded that the triplet state of duroquinone did not decay to give the semiquinone radical, while Wilkinson et. al.[34] had shown from energy transfer experiments that the semiquinone radical is formed from the triplet state. In an attempt to resolve this descrepancy, Kemp and Porter[38] investigated duroquinone using the nanosecond flash photolysis technique. The transient absorption at 490 nm, originally identified as the triplet by Bridge and Porter[15], was shown to decay faster in ethanol, isopropanol, liquid paraffin and benzene upon addition of anthracene. The presence of naphthalene in benzene and in liquid paraffin had no effect, in accord with the observations of Wilkinson et. al.[34]. The kinetic observations of Bridge and Porter[16] were explained by finding that there is an overlap of the absorption of durosemiquinone radical by the triplet at 405 nm. Whether the triplet decays to give durosemiquinone radical in liquid paraffin, was not proven but was no longer excluded. The kinetics of the semiquinone radical in ethanol were also investigated.

---

[16] N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 276 (1958).

[34] F. Wilkinson, G.M. Seddon and K. Tickle, Ber. Bunsenges. Phys. Chem., 72, 315 (1968).

[38] D.R. Kemp and G. Porter, Proc. Roy. Soc., A326, 117 (1971).

[15] N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 259 (1958).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Wong and Wan[39] observed e.s.r. emission from naphthasemiquinone radicals produced by irradiation of a degassed solution of 1,4-naphthaquinone in 2-propanol with intermittent radiation from a mercury lamp and a rotating disc. Wong et. al.[40] attributed this to the 1,4-naphthaquinone triplet being in the emissive mode, and hydrogen atom abstraction occurring before depolarization via spin-lattice relaxation, so that emission occurred from the semiquinone radical as well. Thus, e.s.r. emission was taken as evidence that the triplet state was the photochemically reactive state.

1.1.7. Photoreduction of Quinones in Benzene

Paoloni and Marini-Bettolo[41] reported the photoreduction of 1,4-benzoquinone in benzene. Rubin and Neuwirth-Weiss[35] found that irradiation of phenanthraquinone in benzene yields biphenyl, the monophenyl ether of 9,10-dihydroxyphenthrene, 9,10-dihydroxyphenanthrene and some uncharacterized material. Isotope studies[36] were consistent with addition of a phenyl radical to benzene to give biphenyl rather than with addition of a phenyl radical to another phenyl radical. Addition of iodine to the reaction mixture resulted in formation

---

[39] S.K. Wong and J.K.S. Wan, J. Amer. Chem. Soc., <u>94</u>, 7197 (1972).

[40] S.K. Wong, D.A. Hutchinson and J.K.S. Wan, J. Chem. Phys., <u>58</u>, 985 (1973).

[41] L. Paoloni and G.B. Marini-Bettolo, Gazz. Chim. Ital., <u>87</u>, 395 (1957).

[35] M.B. Rubin and Z. Neuwirth-Weiss, Chem. Commun., 1968, 1607.

[36] M.B. Rubin and Z. Neuwirth-Weiss, J. Amer. Chem. Soc., <u>94</u>, 6048 (1972).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

of iodobenzene rather than of biphenyl, but the monophenylether was formed. This suggested that the monophenylether can be formed via direct addition of phenanthraquinone to benzene, resulting in formation of a diradical, which converts to the ether.

1.2. Photodimerization of Quinones

1.2.1. Synthesis of Photodimers

Photodimerization of quinones, as photoreduction of quinones, was studied very early in the history of photochemistry. Lieberman and Ilinski[42] reported that thymoquinone in ether, exposed to sunlight, forms a polymerization product, which on heating, dissociates with the formation of thymoquinone. Hartley and Leonard[43] found that 1,4-benzoquinone in water, exposed to sunlight, yields a dimer. Madinaveitia[44] reported that exposure of crystalline 2-methyl-1,4-naphthoquinone to sunlight yields a dimer believed to be a cyclobutane derivative.

Schönberg et. al.[45] prepared di-naphthoquinone by exposing 1,4-naphthoquinone in benzene, in a sealed tube with carbon dioxide, to sunlight. Solid 1,4-naphthoquinone exposed to sunlight did not yield dimer. However, 2-methyl-1,4-naphthoquinone did dimerize when the solid was exposed to sunlight.

---

[42] C. Lieberman and M. Ilinski, Ber., 18, 3193 (1885).

[43] W.N. Hartley and A.G.G. Leonard, J. Chem. Soc., 1909, 34.

[44] J. Madinaveitia, Rev. Acad. Cienc. Madrid, 31, 617 (1934).

[45] A. Schönberg, A. Mustafa, M.Z. Barakat, N. Latif, R. Moubasher, and A. Mustafa, J. Chem. Soc., 1948, 2126.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2,3-dimethyl-1,4-naphthoquinone proved to be stable in both solid and benzene solution.

The interest of photochemists came to be focused upon determining the relative orientation of the monomers in quinone photodimers, and also in attempting to synthesize cage structures photochemically. Zavarin[46] prepared a trans photodimer of thymoquinone. Cookson and Hudec[47] found that irradiation of 2,5-dimethylbenzoquinone in ethyl acetate yielded a trans dimer and that irradiation of crystalline 2,5-dimethylbenzoquinone resulted in formation of a cage dimer. Bruce[48] converted di-naphthoquinone to 1,4,5,8-tetrahydroxy 2,3:6,7-dibenzobiphenylene and derivatives. Cookson et. al.[49] exposed crystalline 2,6-dimethylbenzoquinone and 2,5-dimethylbenzoquinone to sunlight. Both yielded cis and trans dimers. Crystalline 2,3-dimethylbenzoquinone, exposed to sunlight yielded a cis dimer. The trans dimers were stable to further irradiation, but the cis dimers cyclized once again to form saturated box shaped molecules. Thymoquinone dimer did not yield a saturated isomer upon further irradiation. They, therefore, concluded that it had a trans structure. Bryce-Smith reported in a letter to Gold and Ginsburg[50] that

---

[46] E. Zavarin, J. Org. Chem., 23, 47 (1958).

[47] R.C. Cookson and J. Hudec, Proc. Chem. Soc., 1959, 11.

[48] J.M. Bruce, J. Chem. Soc., 1962, 2782.

[49] R.C. Cookson, D.A. Cox and J. Hudec, J. Chem. Soc., 1967, 4499.

[50] E.H. Gold and D. Ginsburg, J. Chem. Soc. (C), 1967, 15.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

he had prepared a cage dimer of 1,4-benzoquinone by irradiation of the quinone in the presence of durene and other aromatic hydrocarbons. Irradiation of 1,4-benzoquinone in molten maleic anhydride or benzophenone by Gold and Ginsburg[50] resulted in formation of a trans dimer.

Rabinovich and Schmidt[51] reviewed the solid state chemistry of quinones. They attempted to explain why Cookson et. al.[49] had found that irradiation of crystalline p-benzoquinone, or its mono-,tri-, or tetra-methyl derivatives produced no dimer but resulted in formation of an insoluble, unsublimable polymer, containing hydroxyl groups. Inability of quinones to form dimers in the solid state may be the result of absence of short parallel contacts. The formation of polymeric material results from the presence of short contacts between carbon atoms of nearest neighbor, non-parallel, carbon-carbon double bonds. Dimer diradicals are formed that cannot terminate by ring closure, but may instead initiate polymerization.

In work prompted by interest in bacterial quinones and the effect of radiation on bacteria, Werbin and Strom[52] prepared head to head and head to tail, syn and anti cyclobutane

---

[50] E.H. Gold and D. Ginsburg, J. Chem. Soc. (C), 1967, 15.
[51] D. Rabinovich and G.M.S. Schmidt, J. Chem. Soc. (B), 1967, 144.
[49] R.C. Cookson, D.A. Cox and J. Hudec, J. Chem. Soc., 1967, 4499.
[52] H. Werbin and E.T. Strom, J. Amer. Chem. Soc., <u>90</u>, 7296 (1968).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

dimers of 2-methyl-1,4-naphthoquinone, as well as an oxetane dimer. The syn dimers were prepared by irradiation of the solid quinone with sunlight. The anti dimers were prepared by irradiation of a quinone solution in acetone or by irradiation of the quinone adsorbed on silica gel. The oxetane dimer was also prepared by irradiation of the quinone adsorbed on silica gel.

Dekker et. al.[53] prepared the anti dimer of 1,4-naphthoquinone, which was the isomer prepared by previous workers, in acetic anhydride, and the syn dimer by irradiation of the solid. As Schönberg et. al.[45] had not been able to prepare di-naphthoquinone by irradiation of solid quinone, it may be that Dekker et. al.[53] had actually melted the quinone. Derivatives of both the syn and anti dimers were prepared.[53] The enolization of the dimers was studied by Venter and Dekker[54].

Creed et. al.[55] continuing the research effort of Werbin and Strom[52] on biologically important quinones, studied the photochemistry of plastoquinone-1, i.e. 2,3-dimethyl-5-(3-methylbut-2-enyl)-1,4-benzoquinone. During irradiation in solution, under nitrogen, two isomeric dimers were formed, among other products. These dimers were not, however, cyclobutane dimers. One bond of the dimers, involved a quinone oxygen.

---

53. J. Dekker, P.J. van Vuuren and D.P. Venter, J. Org. Chem., 33, 464 (1968).
45. A. Schönberg, A. Mustafa, M.Z. Barakat, N. Latif, R. Moubasher and A. Mustafa, J. Chem. Soc., 1948, 2126.
54. D.P. Venter and J. Dekker, J. Org. Chem., 34, 2224 (1969).
55. D. Creed, H. Werbin and E.T. Strom, J. Amer. Chem. Soc., 93, 502 (1971).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1.2.2. Mechanism and Electronic States of Dimerization

By irradiating a frozen solution of 1,4-naphthoquinone in benzene, Rennert et. al.[32] observed no dimer formation, suggesting that the dimerization reaction did not take place in an associated species of quinoid molecules existing in the dark. Additional evidence for the lack of a ground state complex being a precursor to photodimer was the fact that the relative efficiency of the dimerization reaction was shown to be proportional to the 0.4 power of the quinone concentration. Since the yield was not a strong function of the 1,4-naphthoquinone concentration, it was concluded that the dimer forming reaction involves one excited molecule with another molecule in the ground state. The quantum yield for dimerization was 3×10^{-2} for both 313 nm and 405 nm, indicating that the n,π^* state was the reactive state.

Wilkinson et. al.[34] irradiated solutions of duroquinone in 2-propanol in the presence and absence of anthracene. They concluded that the triplet state was responsible for all detectable duroquinone photoconversions, including that to give diduroquinone.

---

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967).

[34] F. Wilkinson, G.M. Seddon and K. Tickle, Ber. Bunsenges. Phys. Chem., 72, 315 (1968).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1.2.3. Photodimerization of Nucleic Acids

Photodimerization of nucleic acids to form cyclobutane derivatives similar to those formed by quinones is a major area of investigation in photochemistry and photobiology. The photochemistry of nucleic acids has been reviewed by Setlow[56] and by Burr[57]. Photosensitization in biological systems and triplet-triplet energy transfer to DNA has been reviewed by Lamola[58]. Although conclusions drawn from researches in nucleic acid chemistry cannot necessarily be used to decide which electronic states are reactive in the photodimerization of quinones, some recent papers in the field suggest experimental approaches which might be applied to quinone photodimerization.

Eisinger and Lamola[59] prepared isolated pairs of thymine molecules, having the necessary relative orientations for dimerization, by photochemically splitting the dimers in a rigid matrix, and studied the kinetics of the redimerization of such pairs as well as their absorption and emission

---

[56] J.K. Setlow, "The Molecular Basis of Biological Effects of Ultraviolet Radiation and Photoreactivation", Current Topics in Radiation Research, Vol. 2, ed. by M. Ebert and A. Howard, North-Holland Publishing Company, Amsterdam, 1966, pp. 195-248.

[57] J.G. Burr, "Advances in the Photochemistry of Nucleic Acid Derivatives", Advances in Photochemistry, Vol. 6, ed. by W.A. Noyes, Jr., G.S. Hammond and J.N. Pitts, Jr., Interscience Publishers, a division of John Wiley and Sons, New York, 1968, pp. 193-299.

[58] A.A. Lamola, Mol. Photochem., 4, 107 (1972).

[59] J. Eisinger and A.A. Lamola, Mol. Photochem., 1, 209 (1969).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

properties. The quantum yields for remaking of three dimethythymine dimers ranged from 0.7 to 1.1. In considering a dimerization mechanism by way of the triplet state, the observed quantum yields of dimerization require that totally efficient intersystem crossings occur. The intersystem crossing rate in the monomer is known, and the rate of intersystem crossing in the broken dimer would have to be at least ten thousand times faster than it is in the monomer. This ten thousand fold increase in the intersystem crossing rate demanded by a triplet mechanism for redimerization of the broken dimers was judged unlikely, but could not be excluded by experiment.

Lamola[60], using 313 nm irradiation, performed sensitization experiments involving triplet-triplet energy transfer from acetophenone to Escherichia coli DNA. Cyclobutane type thymine dimers were formed, apparantly via the triplet state.

Golankiewicz and Strekowski[61] determined quantum yields for photodimerization of 1,1'-polymethylene bis-5-alkyluracils in solution. For EtU-C_3-EtU, EtU-C_3-T, and T-C_3-T the oxygen effect was negligible, and photodimerization took place even in the presence of 3M KBr which would have been expected to inhibit triplet states. It was concluded that these photodimerizations proceeded via the singlet.

---

60. A.A. Lamola, Pure Appl. Chem., 24, 599 (1970).
61. K. Golankiewicz and L. Strekowski, Mol. Photochem., 4, 189 (1972).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

In similar pentamethylene compounds there was an evident oxygen effect, and the photodimerizations were judged to proceed via the triplet.

1.3. Scope of This Research

The work of Rennert et. al.[32], in determining the quantum yields of photoreduction and photodimerization of 1,4-naphthoquinone at 313 nm and at 405 nm, appeared to establish that in both reactions the n,π* state was the photochemically reactive state. 313 nm was below the absorption peak in the 330 nm region, and 405 nm was closer to the π→π* peak than was experimentally possible. It was decided that irradiation at 334 nm, which closely corresponds to the first ultraviolet absorption maximum, and 436 nm, which is farther to the red and less likely to represent π→π* transitions, was desirable from the point of view of confirming that the n,π* state was the photochemically reactive state.

Further study of the dimerization reaction showed that it was far more complicated than heretofore expected. The reaction in various solvents was accompanied by the formation of several products. In view of this complexity, major emphasis was then placed on studies of the photoreduction reaction, in order to clearly establish that the n,π* state was the photochemically reactive state, by determining the quantum yield for photoreduction at 334 nm and at 436 nm,

---

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., <u>6</u>, 485 (1967).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and in order to determine the multiplicity of the excited state. The sensitization and quenching experiments involving triplet-triplet energy transfer described above suggested that similar experiments might be a fruitful approach in determining the multiplicity of the excited state in 1,4-naphthoquinone photoreduction.

In order to perform these experiments an apparatus for quantitative photochemistry was designed which permitted accurate measurements of the fraction of light absorbed and which has a number of useful features which are of interest to photochemists. The apparatus was particularly useful in determinations of quantum yields at 436 nm. At this wavelength, the solubility of 1,4-naphthoquinone in 2-propanol is limited, and it was impossible to prepare a solution that would absorb nearly all of the incident radiation. An accurate measurement of the fraction of light absorbed was therefore required.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2. MATERIALS

2.1. 1,4-Naphthoquinone

The 1,4-naphthoquinone (J.T. Baker, practical grade) was purified by extraction with petroleum ether in a Soxhlet extractor. After precipitation, it was collected by filtration and was then recrystallized three times from methanol. It was dried at 50°C in a vacuum oven (m.p. 125°-126°C.). For use in quantum yield measurements, it was further purified by sublimation under high vacuum.

2.2. 1,4-Naphthalenediol

The 1,4-naphthalenediol was prepared in a nitrogen atmosphere, within a glove bag, by addition of 1,4-naphthoquinone, in glacial acetic acid, to boiling hydrochloric acid and tin.[62] The hot solution was rapidly filtered, and the filtrate was then chilled. The colorless precipitate was recrystallized from boiling hydrochloric acid and tin. It was dried by pumping overnight with a Welch Model 1405 vacuum pump (m.p. 176°-177°C.).

2.3. Di-naphthoquinone

Di-naphthoquinone was prepared by the method of Rennert et. al.[32] It was dried in a vacuum dessicator by several hours of pumping. (m.p. 241°-242°C.)

---

[62] R.T. Plimpton, J. Chem. Soc., <u>37</u>, 635 (1880).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2.4. Solvents

The following solvents were used as supplied: benzene (for chromatography), dimethylformamide, dimethylsulfoxide, methanol and petroleum ether (Malinckrodt, Analytical Reagent); benzene, carbon tetrachloride and 2-propanol (J.T. Baker, G.C.- Spectroscopic); toluene (Fisher, 99 mole percent pure); methylcyclohexane (Eastman Organic, Spectro); acetone (J.T. Baker, "Baker Analyzed" Reagent); cyclohexane (Fisher, Spectrophotometric); glacial acetic acid, and hydrochloric acid (Fisher, A.C.S. Reagent); and absolute ethanol (Pharmco).

2.5. Purification of Benzene by Fractional Crystallization

The benzene used for preparation of the solution described in section 5.4 was purified by the modified method of Stull.[63] Benzene (Malinckrodt, Analytical Reagent) was frozen in an ice bath, with stirring, and liquid (at least one-quarter) was discarded. After six successive separations, the purified benzene was dried on an alumina column (Woelm basic aluminum oxide). Ten percent of the starting material remained after purification.

---

63. D. Stull, J. Amer. Chem. Soc., 59, 2726 (1937).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2.6. Chromatographic Materials

Woelm silica gel for dry column chromatography, and Eastman "Chromagram" sheets of silica gel with a fluorescent indicator were used for separations. The solvent generally used was ten percent methanol in benzene. The solvent used in testing for the presence of polyphenyls was cyclohexane.

2.7. Actinometry

Ferric potassium oxalate (Amend, Pure) was recrystallized three times from water.

The following were also used: sodium acetate and 1-10-phenanthroline (J.T. Baker, "Baker Analyzed" Reagent); and sulfuric acid (Fisher, A.C.S. Reagent).

2.8. Sensitizers and Quenchers

Trans piperylene (Aldrich, 99%) was further purified, in order to remove polymeric material, by five bulb-to bulb distillations on a high vacuum line, discarding the least volatile portion in each case. About half of the original material was discarded in all.[64]

Anthracene (Aldrich, Zone Refined), and acridine yellow, i,e., 2,7-dimethyl-3,6-diaminoacridine (Pfaltz and Bauer, 99+%) were used as a quencher and sensitizer respectively.

---

[64] D. Grossman, Ph.D. thesis, City University of New York, 1973.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2.9. Other Materials

The following materials were used without further purification: biphenyl, o-terphenyl, m-terphenyl and p-terphenyl (Eastman); nitrogen (J.T. Baker, Prepurified, 99.99%); tin (J.T. Baker, "Baker Analyzed" Reagent); and cupric chloride (Baker and Adamson, Reagent).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

3. EQUIPMENT

3.1. Apparatus for Photochemical Irradiation

The apparatus used for irradiation in the experiments described in sections 5.1. - 5.4. and 5.7. is shown in Figure 1. The emission of an HBO 500 watt Osram mercury lamp, in a Schoeffel Instrument Co. Model LH151N housing, filtered by a pyrex water filter (path length of one and one-quarter inches) containing distilled water, was further filtered by the following Corning filters: two 3-75 filters (cut off below 365 nm) for "visible" radiation, or one 7-37 filter (cut off below 313 nm) for "ultraviolet" radiation (section 5.1); two 0-51 filters (cut off below 365 nm, section 5.2.); two 3-75 filters (sections 5.3., 5.5. and 5.7.).

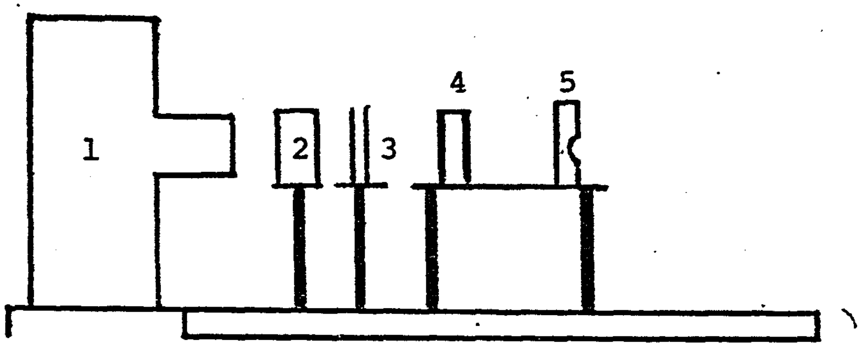
A Yellow Springs Instrument Co. Y.S.I.-Kettering radiometer probe, encased in a housing, and a Cary square cell holder were mounted on a stand that was placed on the optical bench. The cell holder was masked at the top and bottom so that the area of the solution irradiated was reproducible. When switching from irradiation to an intensity measurement the stand was removed from the optical bench, rotated 180 degrees, and then replaced. If test tubes rather than cells were used, they were held in the path of the beam by a clamp.

3.2. Photochemical Reactor Irradiation Apparatus

An Hanovia 450 watt high pressure mercury lamp was placed in a water cooled quartz immersion well. Wavelengths

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 1: Corning Filter Irradiation Apparatus



Key: 1, light source; 2, water filter; 3, filters; 4, cell; 5, thermistor-bolometer detector.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

shorter than 300 nm were filtered out by a tube of Corning Pyrex glass. The well was placed in a water-jacketed photochemical reaction vessel filled with a copper chloride filter solution, which was stirred for more effective heat transfer. The solution, of pathlength 0.7 cm, had an absorbance of 3.0 at 370 nm and an absorbance of 0.6 at 405 nm. Sample tubes, to be irradiated, were placed around the outside of the reaction vessel (Fig. 2).

3.3. Instrumental Analysis

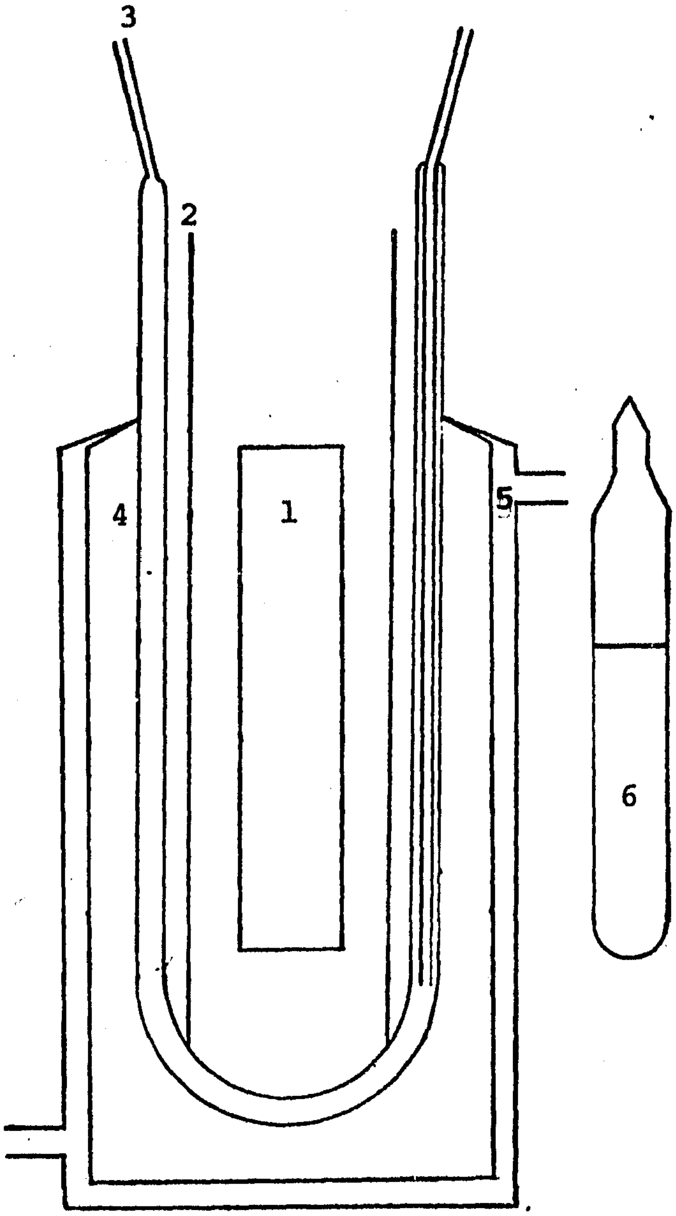
Absorption spectra were obtained on a Cary Model 14R Recording Spectrophotometer. Perkin-Elmer Model 203 and Model MPF-2A Fluorescence Spectrophotometers were employed for fluorescence measurements. The Cary Model 14R and the Perkin Elmer Model MPF-2A were fitted with extended sample compartment covers so that cells attached by graded seals to degassing assemblies could be accomodated. Infrared spectra were obtained on a Perkin-Elmer Model 137 Infrared Spectrophotometer. Mass spectra were obtained on a Varian CH-5 single focusing 90 degree sector spectrometer. A Hewlett Packard Model 302B Vapor Pressure Osmometer was used for molecular weight determinations.

3.4. Degassing

Solutions described in sections 5.4. and 5.8. were degassed by several freeze thaw cycles with a Welch Model 1405 high vacuum pump and sealed with a teflon stopcock in

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 2: Chemical Reactor Irradiation Apparatus



Key: 1, mercury lamp; 2, pyrex tube;
3, quart immersion well; 4, filter solution;
5, water jacketed reaction vessel;
6, solution to be irradiated

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

a large pyrex test tube. Other solutions were degassed by several freeze thaw cycles on a high vacuum line and sealed off with a torch under vacuum.

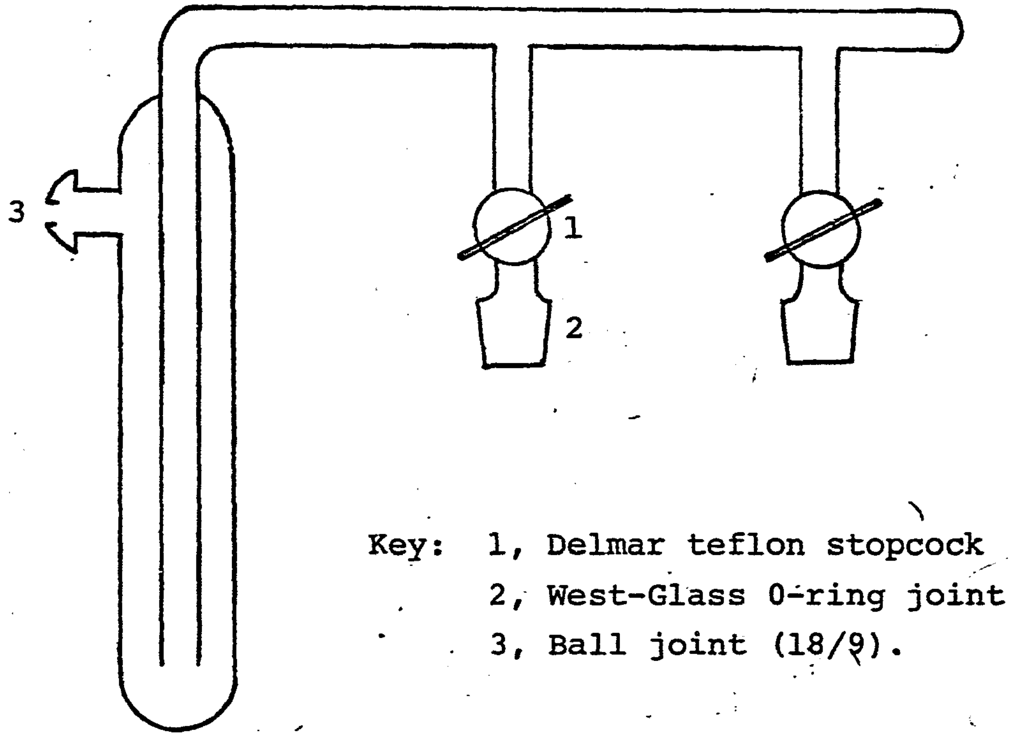
For the experiments prior to the quantum efficiency measurements a two stage mercury diffusion pump was used for the high vacuum line, and pressures were monitored by a Consolidated Vacuum discharge gauge. Pressures attained were 5 x 10^{-5} torr. Subsequently, a three stage oil diffusion pump was used, and pressures were monitored by a Distillation Products Industries ionization gauge with a VG1A ionization gauge tube. Pressures attained were 2 x 10^{-5} torr.

3.5. Degassing Manifold

In order to minimize contamination from the high vacuum line to degassed solutions, a detachable manifold, connected to the high vacuum line by a ball joint, was designed (Fig. 3). There was a trap adjacent to the ball joint, and no grease was used on any part of the manifold on the other side of the trap. The stopcocks were Delmar 0-4 mm high vacuum teflon stopcocks with viton O-rings. The joints used were West-Glas 14/35 inner joints with viton O-rings. Degassing assemblies were, therefore, fitted with West-Glas 14/35 outer joints. The use of these joints limited the pressures attained to those mentioned in section 3.4.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 3: Degassing Manifold



Key: 1, Delmar teflon stopcock (0-4mm.);
2, West-Glass O-ring joint (14/35);
3, Ball joint (18/9).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

3.6. Photochemical Reaction Vessels

Solutions that were to be irradiated but of which spectra were not to be taken, were placed in pyrex test tubes. The test tubes were either sealed with teflon stopcocks or with a torch.

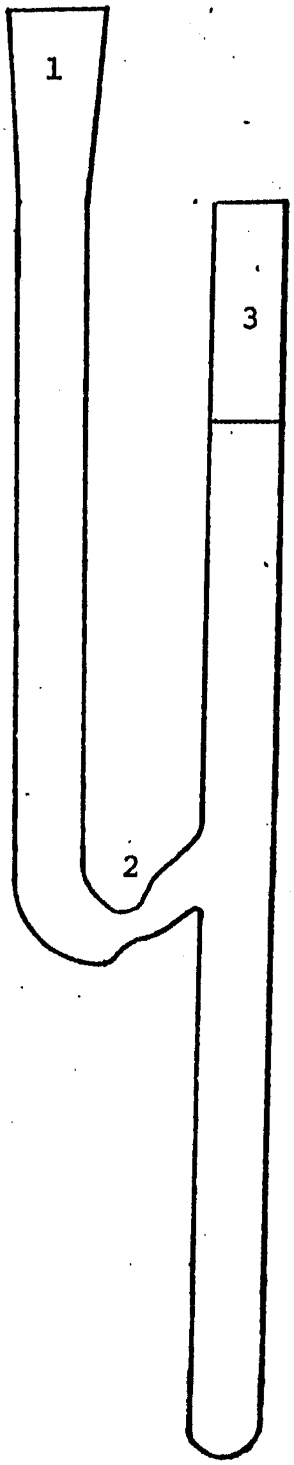
Reaction vessels with quartz spectrophotometer cells attached to quartz to pyrex graded seals (Fig. 4) were used if spectrophotometric analysis was required. Quartz fluorescence cells were used, in addition, for fluorimetric analysis.

3.7. Photochemical Reaction Vessel with Sealed in Fritted Glass Filter

In order to eliminate light scattering when taking spectra of degassed irradiated solutions after the occurrence of precipitation, a photochemical reaction vessel was designed that permitted separation of precipitate prior to taking spectra (Fig. 5). The degassed solution was irradiated in the pyrex test tube and then poured on top of the sealed in "fine" fritted glass filter. Chilling the test tube end on the cell side of the filter resulted in a drop in pressure due to condensation of the vapor that was in equilibrium with the solvent. This created a sufficient pressure differential between the two sides of the filter to cause the solution to flow through the filter. The filter was sufficiently porous so that it did not appreciably inhibit distillation of solvent from one side to another when preparing dilutions of irradiated solutions.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 4: Spectrophotometer Cell Degassing Assembly

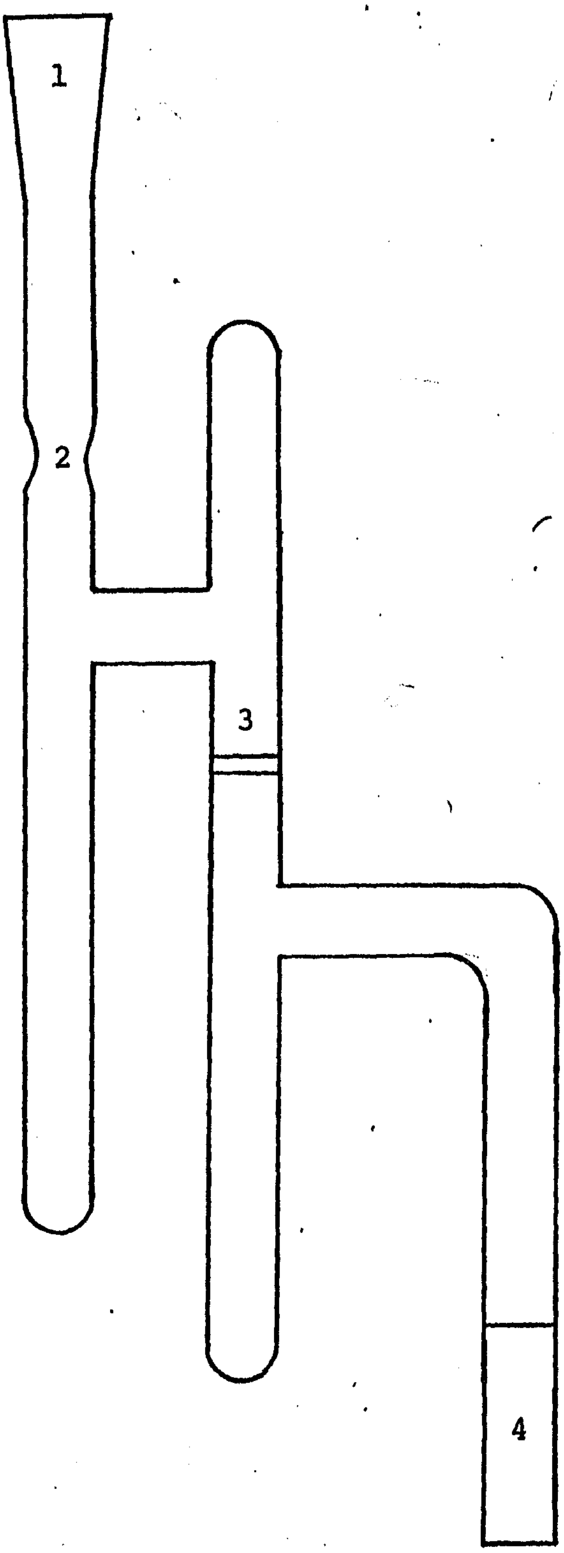


Key: 1, West-Glass outer joint (14/35); 2, constriction for sealing OFF; 3, spectrophotometer cell (1 cm.)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 5: Fritted Disc Filter Degassing Assembly

Key: 1, West-Glass outer joint (14/35); 2, constriction for sealing off; 3, sealed in glass fritted disc (fine); 4, spectrophotometer cell (1 cm).



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4. APPARATUS FOR QUANTITATIVE PHOTOCHEMISTRY

4.1. Quantum Yield

The quantum yield, Φ, is a measure of the extent of photochemical reaction following the absorption of electromagnetic radiation. Generally

$$\Phi = \frac{\text{moles reacted}}{\text{einsteins absorbed}} = \frac{\text{moles reacted}}{\text{photons absorbed}}$$

The quantum yield may refer to the photochemical yield of a particular species of molecule which must then be specified. Determination of the quantum yield, therefore, requires both a quantitative analysis of chemical reaction, and a measurement of the corresponding total radiant energy absorbed.

4.2. Actinometry

Measurement of the number of quanta absorbed involves a determination of the light intensity incident on, and the fraction of light absorbed by, the photosensitive material. There are both physical and chemical methods available for this purpose. Among the detectors that have been used are thermopiles, thermistor-balometers, photo-tubes and photomultiplier tubes. The method of chemical actinometry used most frequently in recent years has been the ferrioxalate method of Hatchard and Parker.[65]

---

[65] C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A235, 518 (1956).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The use of a detector connected to either a meter or recorder is preferable to chemical actinometry because greater speed of measurement is possible. It is necessary to calibrate the detector initially either with a standard lamp or by chemical actinometry. Chemical actinometry is preferable because it does not require disturbing the geometry of the system, and because it makes corrections for differences in source intensity and corrections for various reflections unnecessary.

4.3. Determination of the Number of Photons Incident on a Solution

If a detector is positioned behind the reaction vessel so that when the vessel is removed, light is incident on the detector, a measurement of the incident intensity with the detector would be followed by irradiation of a ferrioxalate solution that absorbed all incident radiation. Analysis of the extent of reaction of the ferrioxalate solution would serve to calibrate the detector. Two other possible arrangements of detector and solution involve the use of a turntable so that they may be placed in the beam of exciting radiation alternately, or the use of a beam splitter so that the intensity may be continuously monitored. After the detector has been calibrated, a photosensitive solution may be placed in the reaction vessel. It its absorbance is sufficiently high so that the light can be considered as being completely absorbed, it will absorb the same number of photons for a given detector response, as did the chemical actinometer.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4. Determination of the Number of Photons Incident When All of the Incident Light is not Absorbed

The number of photons absorbed by a solution is given by

$$I = I_oQt$$

where I_o is the incident intensity in photons per second, Q is the fraction of radiation absorbed and t is the time in seconds.

The fraction of radiation absorbed is related to the absorbance, A, as follows:

$$Q = 1-e^{-A}$$

If the photosensitive material in solution is not the only absorbing species present, the fraction of radiation absorbed by the photosensitive material, Q corrected, is obtained by

$$Q_{corrected} = \frac{A\ \text{photosensitive material}}{A\ \text{total}}\ Q$$

where A is the absorbance.

If one wishes to irradiate a solution which does not absorb all of the incident radiation, provision must be made for measuring the fraction of light absorbed. Spectrophotometric analysis of a solution in a commercial spectrophotometer will not give an accurate value for the fraction of radiation absorbed by the solution during a photochemical irradiation. The major difficulty rests in a high radiation intensity requirement for photochemical irradiation, versus the advantages of low radiant power in measuring light beams

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

of spectrophotometers. This results in the use of differing dispersion elements, light sources and other optics, and consequently in differences in the spectral energy distribution of exciting and measuring beams.

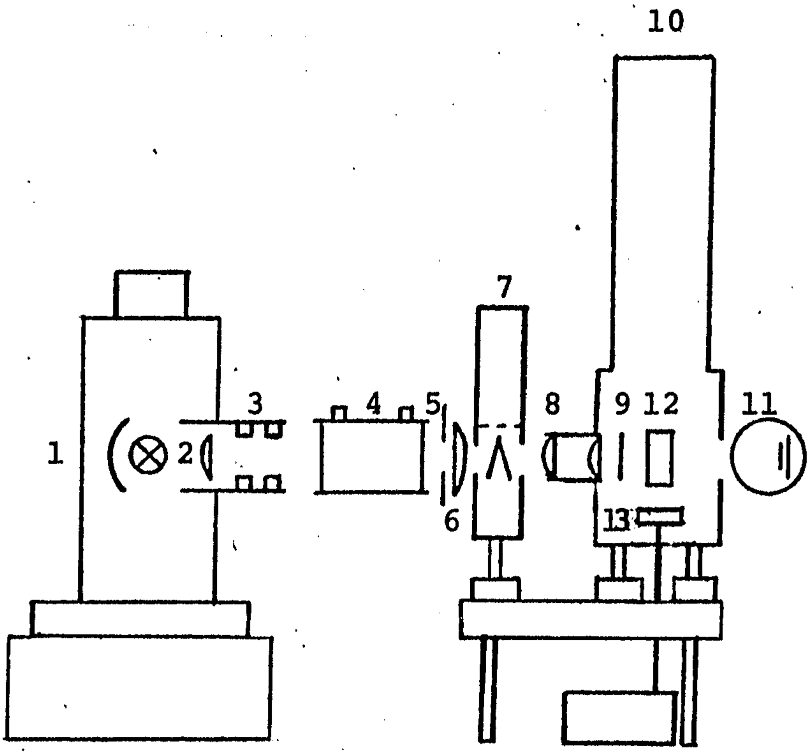
Measurement of the fraction of light absorbed with the system described in section 4.3 requires first measuring the intensity of radiation transmitted by a cell filled with solvent only, and then measuring the intensity of radiation transmitted by a cell filled with the solution in question. Measurement of the fraction of light absorbed when more than one species is present is discussed further in section 4.16.

4.5. System Design

A photochemical irradiation set-up (Figs. 6 and 7) was therefore designed in which the same source and optics are used both for irradiation and for measurement of the fraction of light absorbed. Large monochromator slit widths may be used because the sensitivities of the detector systems utilized do not vary greatly with wavelength. The system is also designed for fluorescence measurements, and for monitoring reactions where either the starting material, or a product fluoresce. Cross illumination provides for continuous monitoring of the reaction at a wavelength different from that used for irradiation, or for simultaneously taking spectra without interrupting the irradiation by removing the solution. Cross illumination may also be used for taking spectra of transient species, if they have sufficiently high absorbance,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

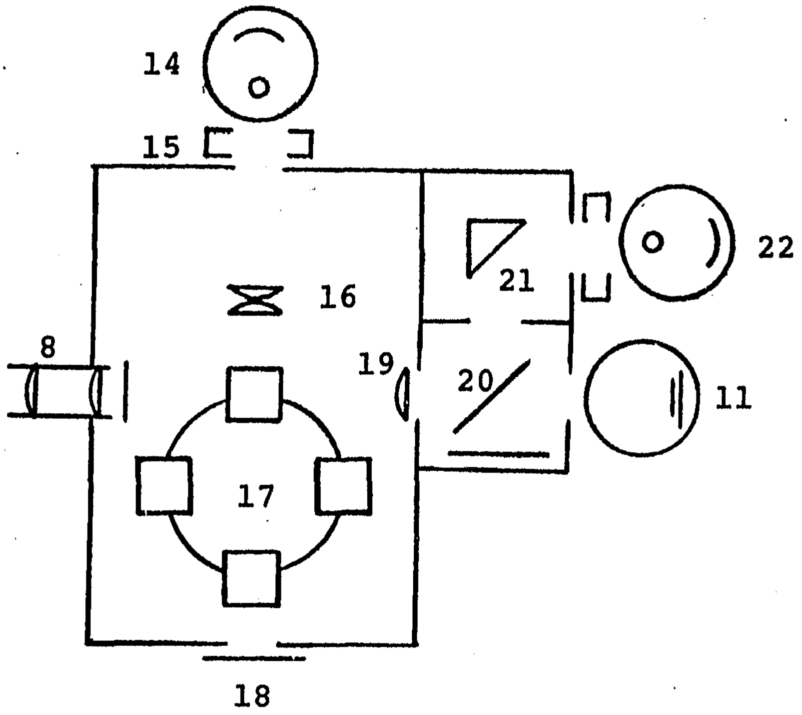
Figure 6: Apparatus for Quantitative Photochemistry (side view)



Key: 1, lamp housing; 2, 50 mm. F.L. lens; 3, shutter; 4, 100 mm. water filter; 5, mask; 6, 75 mm. F.L. lens; 7, monochromator; 8, two 50 mm. F.L. lenses; 9, U.V. cut-off filter; 10, sample compartment; 11, thermistor-bolometer detector; 12, cell; 13, magnetic stirrer.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 7: Apparatus for Quantitative Photochemistry (top view)



Key: 14, photomultiplier tube; 15, filter holder; 16, two 50 mm. F.L. lenses; 17, rotating turret cell holder; 18, light plug; 19, 50 mm. F.L. lens; 20, mirror box; 21, triangular cell; 22, photomultiplier tube.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and if their steady state concentration is sufficiently high.

The principal components of the system, described in the following sections, are the sample compartment, light sources and optics, and detectors.

4.6. Sample Compartment

The central component of the system is a sample compartment (10) with a rotating turret cell holder (17), in which one or more solutions to be irradiated, a reference solution, a fluorescence standard, and an actinometer solution may be placed. Solutions are stirred with a built in magnetic stirrer (13) so that accumulation of absorbing photoproduct within the path of the beam is avoided, in order to prevent uncertainty as to the fraction of light absorbed by the photosensitive material.

4.7. Light Source and Optics

The light source (1) and associated optics were used for both irradiation and absorbance measurements. An ultraviolet cut-off filter (9) is placed after the lens (8) at the sample compartment entrance port for wavelengths greater than 400 nm.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.8. Detection of Incident Radiation

A mirror box (20) with 0°, 90° and 180° ports, with a swing mirror for 90° and straight-through light paths, is mounted at the exit port of the sample compartment. A thermistor-balometer (11), and a photomultiplier tube (22) with a corrected spectral response accessory are mounted on the mirror box. Measurements are made by direct irradiation of the thermistor-balometer, or by swinging the mirror into the path of the beam of radiation for measurement by the 1P28 photomultiplier tube. The triangular cell (21) in the photomultiplier tube corrected spectral response accessory is filled with a solution of a substance whose fluorescence quantum efficiency does not vary with wavelength. A suitable cut-off filter is placed in front of the photomultiplier tube and the fluorescence is measured. The fluorescence measured will be proportional to the number of photons absorbed by the solution. This corrects for the fact that the spectral sensitivity of the photomultiplier tube varies with wavelength. If this variation is not of concern, the triangular cell can be replaced with a mirror, or the photomultiplier tube can be attached directly to the mirror box. Another method for correcting the spectral response of the photomultiplier tube involves replacing the triangular cell with two quartz plates, between which a layer of liumogen or other suitable solid has been deposited. The luminescence of this material is then measured. If a high intensity beam is used, it may be necessary

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

to place a neutral density filter between the mirror and the corrected spectra accessory.

The availability of the two detectors in the system permits measurements of radiant power incident on the reaction vessel, or transmitted by it in a range of intensities from the least sensitive range for the Yellow Springs Instrument Co. YSI-Kettering Model 65 Radiometer thermistor balometer (10^6 ergs/cm^2-sec full scale) to the most sensitive range for the photomultiplier tube (10^{-6} ergs/cm^2-sec full scale if used with Aminco Photomultiplier Microphotometer). The upper intensity limit may be extended with the use of neutral density filters.

4.9. Luminescence and Cross Illumination Measurements

A photomultiplier tube housing (14), with a filter holder (15) and a shutter, mounted on the side of the sample compartment, is used for fluorescence measurements. An entrance port across from the fluorescence photomultiplier tube provides for an additional light source and monochromator for cross illumination. A single cell holder is substituted for the rotating cell holder.

4.10. Deciding Which Detector to Use for Measurement of Incident Intensity and Fraction of Light Absorbed

The corrected photomultiplier tube "counts" photons correctly and is very sensitive but lacks long term stability. The thermistor-bolometer has long term stability but lacks

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

sensitivity. An additional problem is that the thermistor-bolometer has a response that measures energy rather than photons. Two photons of different energy will result in different responses on such a detector. Over a bandwidth of a few nanometers, however, the energy of a photon may not vary sufficiently to result in a significant error. Another factor to be considered is that the response time of the thermistor-bolometer is about twenty-seconds, while that of the photomultiplier tube is very fast. The thermistor-bolometer response time is not a problem if the fraction of light absorbed changes slowly.

If the incident intensity is sufficiently high to give a response on the thermistor-bolometer, that instrument should be used to measure the intensity of the incident light with no cells in the path. The corrected photomultiplier tube should then be used for measuring the fraction of light absorbed. If the incident intensity is too low for use of the thermistor bolometer a fluorescent standard, which may however have to be replaced after each measurement, may be placed in the triangular cell. It should not usually be necessary, however, to use very narrow slit widths which result in low intensity. The solution used to correct the photomultiplier tube response may change with irradiation. If this occurs, and if the photoproduct formed does not absorb at the wavelength used for irradiation, the solution

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

may be used until its absorbance is too low. However, if this solution exhibits a significant change with one exposure, the second measurement should be corrected. Liumogen films were found to turn cloudy, as a result of partial recrystallization, after a few days or weeks of storage at room temperature. The transparancy of such films were found to be slightly lower, but there was no change in the luminescence stability.[65a.] This suggests that such films are suitable for correcting photomultiplier tube response, and would be suitable for measurement of the fraction of light absorbed, but would not be suitable for measurement of incident intensity.

4.11. Choice of Detector in this Work

The deficiencies of the thermistor-bolometer mentioned above were not judged to result in a significant error in this work. A slit width of 0.5 mm was used in the quantum yield determinations and a calculation showed that photons at 432 nm and 438 nm (the extremes of the band of radiation used at a wavelength of 436 nm) differed in energy by 2 percent. At 334 nm, the peak irradiated was very broad and the variation of response with wavelength was judged even less significant a problem. The fraction of light absorbed changed relatively slowly with wavelength and the 30 seconds that were taken for an intensity measurement did not cause a significant error.

65a. R. Stair, W.E. Schneider and J.K. Jackson, Applied Optics, 2, 1151 (1963).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.12. Use of the System for Quantum Yield Determinations

The YSI-Kettering Model 65 Radiometer calibrated by ferrioxalate actinometry[65] was used as the detector system. Measurements were made after 30 seconds of irradiation. The intensity of radiation passing through a cell filled with distilled deionized water was measured. This is referred to as the incident intensity. As the solvents used did not absorb radiation of the wavelengths used, a measurement of solvent absorbance was omitted. At the beginning of the irradiation period, the intensity of radiation transmitted by the solution being irradiated was measured. The cells containing the solution to be irradiated were furnished with spectrophotometer cell stirring magnets encased in teflon (manufactured by Bel-Art). Some teflon was sanded off the perimeter of the cell stirrers so that they would fit into the cells with graded seals. The magnets did not block the light beam in the system, but could not be left in position when spectra were taken in a Cary 14R spectrophotometer. In order to take spectra the magnets were raised by means of a small magnet on the outside of the cell and were held in place above the cell when the outer magnet was fastened with adhesive tape.

The apparatus was used for measurement of the fraction of light absorbed. Analysis to determine the number of moles reacted was performed on the Cary Model 14R spectrophotometer. Greater accuracy in measuring small absorbance changes was

---

65. C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A235, 518(1956).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

therefore possible, particularly when an expanded scale slidewire (0-0.1 or 0.1-0.2 absorbance, full scale) was used.

4.13 Construction of the Apparatus

The LH151N lamp housing and the GM100 monochromator(7), with a reciprocal linear dispersion of 8.5 nm/mm slitwidth were obtained from the Schoeffel Instrument Co. The water filter (4) was supplied with deionized water by an Illinois Water Treatment Co. "Research" cartridge. The Osram HBO 500 watt mercury lamp was powered by a George W. Gates and Co. P-510-D power supply connected to a LRK 500 low ripple kit. Both the power supply and the thermistor-bolometer were connected to the output of a variable transformer, so that the line voltage could be periodically adjusted to 117 volts.

A shutter (3) was constructed by placing two aluminum rings, held in place by set screws, in the lamp housing focusing sleeve, on either side of an open slot that was on top of the focusing sleeve. An aluminum plate was slipped between the rings to cut off the light.

The sample compartment was constructed by modification of a Schoeffel fluorescence spectrophotometer sample compartment. Two additional threaded holes were added to the sample compartment, so that there were threaded holes on all four sides. Threaded fittings, which accommodate tubes with a one inch outer diameter were placed in the entrance port,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and in the two ports at right angles to it. A threaded tube with a one inch outer diameter was placed in the port directly opposite the entrance port. This tube extends into the mirror box. The threaded holes that were not in use were covered with threaded plugs (18).

The lens (6) between the water filter and the monochromator is mounted within an adapter that connects the two. The lens adjacent to the exit port of the monochromator is mounted in a threaded tube that is attached to the monochromator. The threaded fitting on the entrance port of the sample compartment also has a lens mounted within. The lenses (16) used for fluorescence measurements are mounted in a threaded tube that is connected to the inside of the fluorescence port. The lens (19) at the rear of the sample compartment is mounted in a monochromator window mount. The ultraviolet cut-off filter, when it is in use, is mounted in a monochromator window mount which is attached to the threaded fitting extending into the entrance port of the sample compartment by a female-female fitting.

The YSI-Kettering radiometer probe is mounted in a polyethylene tube with a hole in front of the probe. The tube was encased in a brass tube with a hole on one side, corresponding to the hole in the polyethylene tube, so that the probe could be exposed to incident radiation. The tube was inserted in a solid aluminum block which had a large hole drilled completely through it from top to bottom so that

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

the tube could be rotated and moved up and down within the block. A hole was drilled through one side of the block facing the probe. A one inch outer diameter tube was inserted into this hole and held in place by set screws. The other end of the tube was inserted into a fitting on the mirror box. Set screws on the aluminum block held the metal tube containing the radiometer probe in place after the probe was centered within the beam of exciting radiation.

The magnetic stirrer was constructed by removing the outer case and top of a Thermolyne heater-stirrer, and replacing the shaft, to which the magnet was attached by a longer shaft of stainless steel that extended through a hole in the optical bench and then through a hole in the bottom of the sample compartment. The back of a plastic meter case was placed over the magnet that had been repositioned on top of the stainless steel shaft. The meter case back was fastened to the bottom of the sample compartment in order to exclude light.

An 18 inch extension tube was added to the top of the sample compartment, and the rotating turret control rod was extended, so that degassing assemblies or dewar vessels could be accommodated.

An Aminco photomultiplier tube housing, with variable slits, and a filter holder for two inch square filters, was modified by fastening it to a plate, on which was machined a one inch outer diameter tube, so that it could be connected to the sample compartment.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The photomultiplier tube response correction accessory, when set up for use with a fluorescent solution, consists of a photomultiplier tube housing, a triangular cell holder and housing (available from Schoeffel), and a triangular cell (available from Perkin-Elmer). For use of the system with a solid phosphor, one substitutes a box with two one inch outer diameter tubes mounted at a right angle, with mounted quartz plates, for the triangular cell holder and housing, and the triangular cell.

4.14. Procedure For Calibration of the Thermistor-Balometer

The YSI-Kettering Model 65 Radiometer thermistor-bolometer was calibrated by ferrioxalate actinometry. The method of Hatchard and Parker[65] was modified in order to minimize the number of pipetting operations, so that both the error and the exposure to light of the actinometry samples and blanks might be reduced.

1) Actinometer Solution

A 0.006 M Actinometer solution was prepared by dissolving 2.947g of potassium ferrioxalate in 800 ml. of water, adding 100 ml. of 1.0 N-sulfuric acid, diluting to 1 l. and mixing.

2) Buffer Solution

The buffer solution was prepared by mixing 600 ml. of 1.0 N-sodium acetate and 360 ml. of 1.0 N-sulfuric acid, and diluting to 1 l.

---

[65] C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A235, 518 (1956).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

3) Phenanthroline Solution

The phenanthroline solution was 0.1% 1,10-phenanthroline monohydrate in water.

3 ml. of actinometer solution were pipetted into three square cells with a pathlength of 1 cm. The cells each contained a spectrophotometer cell stirrer with a sealed in magnet. The total height of a cell, the attached quartz-pyrex graded seal, and pyrex tubing was about six inches. The cells were sealed with Parafilm. Two cells were placed in the irradiation apparatus, and one was used as a blank.

A 2:1 buffer-phenanthroline solution was prepared by mixing the buffer and phenanthroline solutions described above. 3 ml. portions of this solution were added to each 1 cm. cell. After thorough mixing, the cells were left in the dark for 45 minutes. The absorbance of each cell versus distilled water, at 510.0 nm was then measured.

During the procedure, the solutions used were exposed only to the light of a 25 watt General Electric orange colored light bulb. This light was shown to have had a minimal photochemical effect, because of the negligible absorbance changes observed for blank solutions that were not irradiated in the apparatus. Other photosensitive solutions were likewise exposed only to this light.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.15. Calculation of a Calibration Constant From the Actinometry Data

The data obtained during an irradiation, and the spectrophotometric data obtained afterwards permit the calculation of a calibration constant for the thermistor-balometer. The constant is multiplied by the meter reading in order to determine the number of einsteins per second incident on a solution contained in a sample cell in the apparatus.

The calibration constant C is give by:

$$C = \frac{[\Sigma t I_Z Q] \quad (11040)}{0.006\ \Delta A}$$

Σ indicates that the product in brackets for the number of irradiation periods are added, and then multiplied by the rest of the numerator, t is the time, I_Z is the average incident intensity, Q is the fraction of light absorbed, is the quantum yield determined by Hatchard and Parker[65], 11040 is the absorbance of the ferrous phenanthroline complex at 510 nm, 0.006 is the volume of the solution in the cell after buffer and 1,10-phenanthroline have been added, and Δt is the measured difference in absorbance between the irradiated sample and the blank.

---

[65] C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A235, 518 (1956).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The fraction of light absorbed, Q, is given by:

$$Q = 1 - I_x/I_{y1}$$

I_x is the intensity of the light transmitted by the cell filled with the actinometer solution, and I_{y1} is the intensity of the light transmitted by a cell filled with distilled water, measured at the beginning of the irradiation period.

The average incident intensity, I_Z, is given by:

$$I_Z = (I_{y1} + I_{y2})/2$$

I_{y2} is the intensity of the light measured after the irradiation period.

4.16. Calculation of the Quantum Yield of 1,4-Naphthoquinone Photoreduction at 436 nm

The quantum yield, , is given by:

$$= \frac{0.003\ \Delta A}{[\Sigma t I_Z\ Q_{avg}]C(43.0)}$$

0.003 is the volume of solution, ΔA is the change in absorbance at 421.0 nm, t is the time, I_Z is the average incident intensity, Q_{avg} is the average fraction of light absorbed, C is the calibration constant determined by actinometry, and 43.0 is the absorptivity of 1,4-naphthoquinone.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

I_z, the average incident intensity is obtained as shown in section 4.14. Q is obtained by measurements made at the beginning of an irradiation period as shown in Section 4.14. Q_{avg} is obtained by averaging the values of Q obtained for two successive periods of irradiation, each measurement having been taken at the beginning of a period.

4.17. Calculation of the Quantum Yield of 1,4-Naphthoquinone Photoreduction at 334 nm

At 334 nm both 1,4-naphthoquinone (Fig. 8) and 1,4-naphthalenediol (Fig. 9) absorb radiation. If 1,4-naphthoquinone is photoreduced to 1,4-naphthalenediol, the fraction of radiation absorbed by 1,4-naphthoquinone, after some photoreduction has taken place, is a fraction of the radiation absorbed by the solution.

The average fraction of light absorbed by 1,4-naphthoquinone, $(Q_{NQ})_{avg}$, is given by:

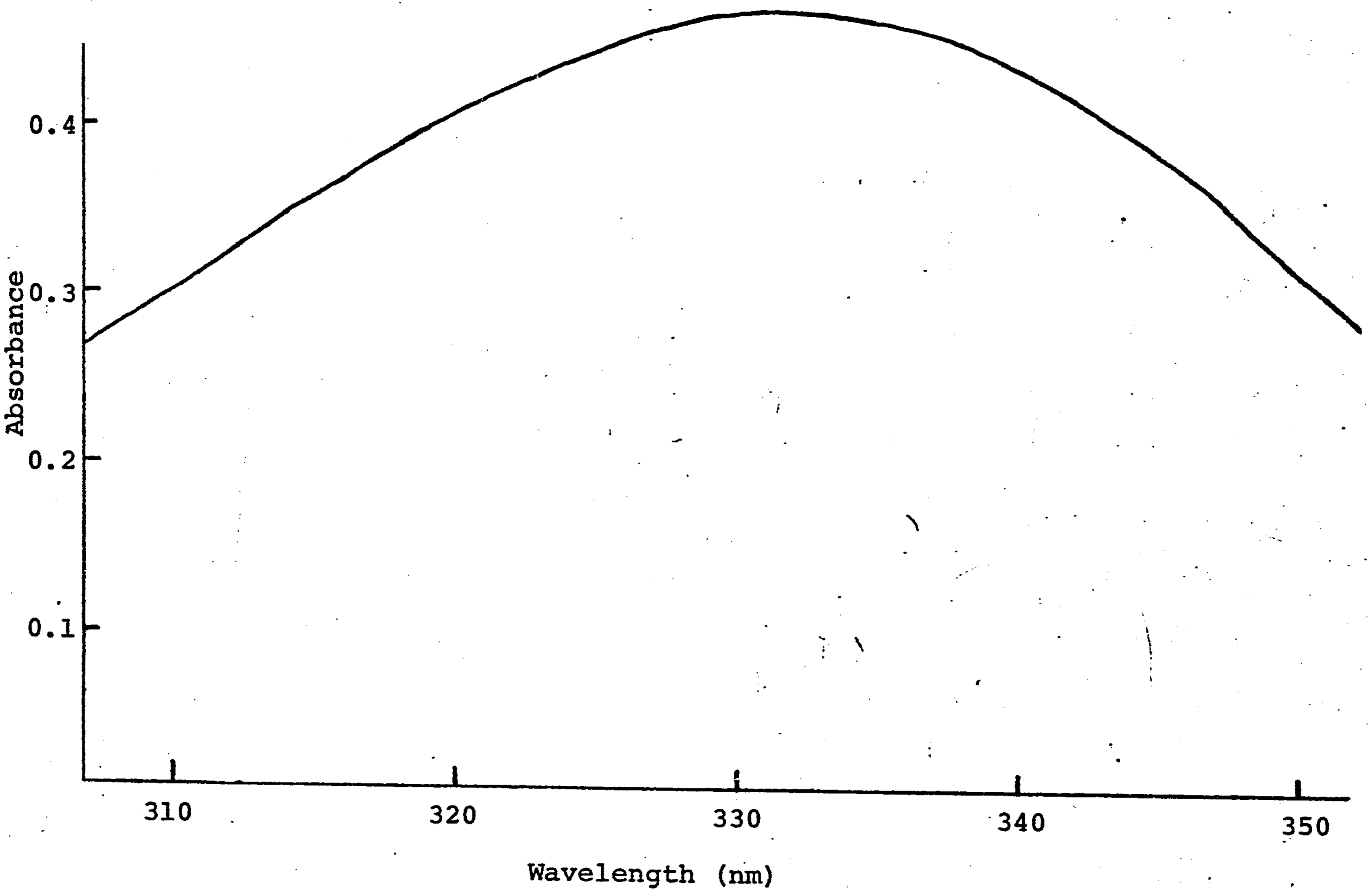
$$(Q_{NQ})_{avg} = \frac{Q_{avg}\ (A_{NQ})_{avg}}{A_{avg}}$$

Q_{avg} is the average fraction of light absorbed by the solution, $(A_{NQ})_{avg}$ is the average absorbance, in the photochemical apparatus, of the 1,4-naphthoquinone present during the period of irradiation, and A_{avg} is the average absorbance of a solution in the photochemical apparatus, which is calculated from the fraction of light transmitted. The average of values determined at the beginning of two successive

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

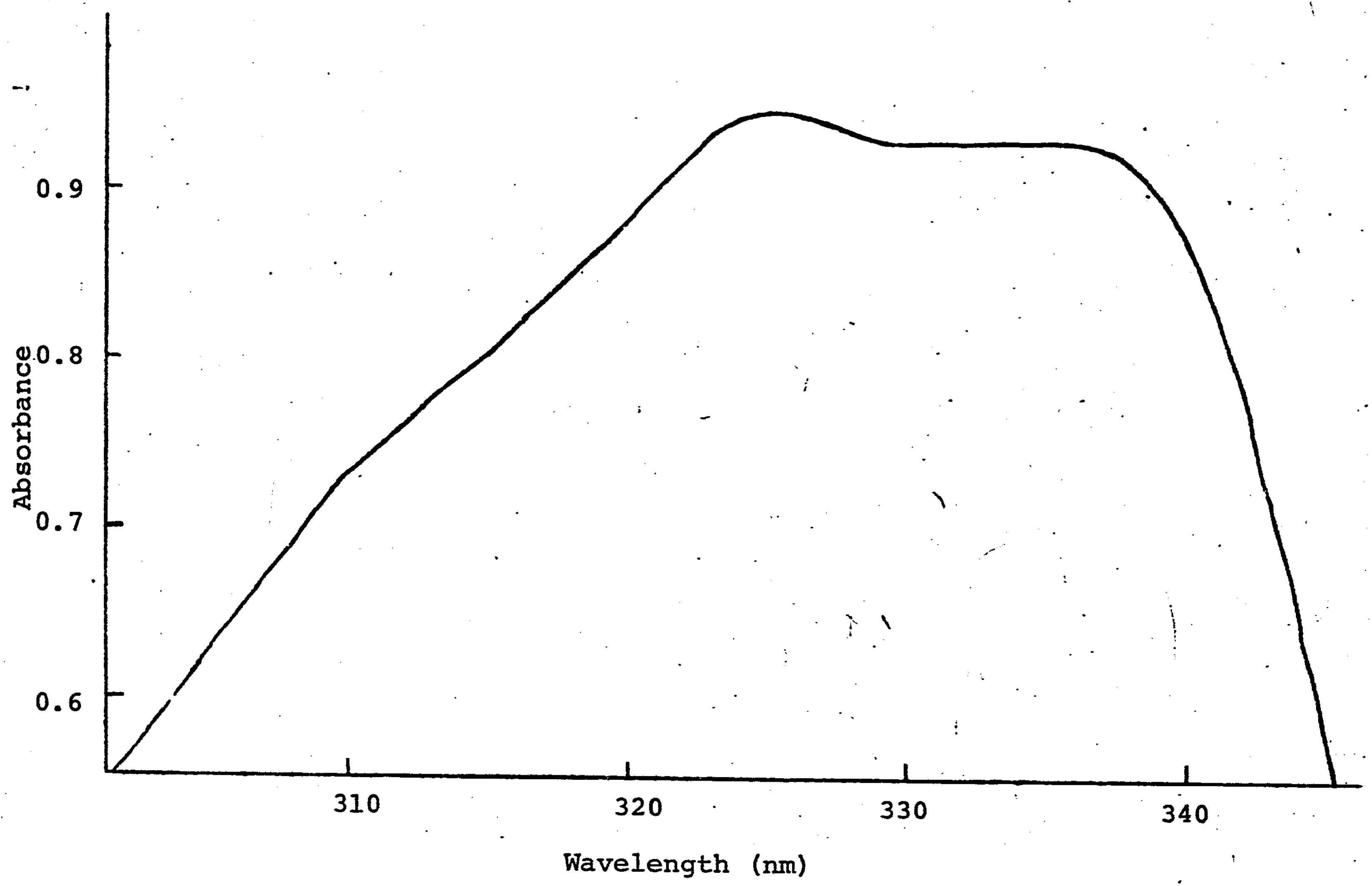
Figure 8: Ultraviolet Spectrum of 1,4-Naphthoquinone in 2-Propanol

(concentration: 1.49 x 10^{-4}M)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 9: Ultraviolet Spectrum of 1,4-Naphthalenediol in 2-Propanol (concentration: 1.62×10^{-4}M)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

periods is taken. Q_{avg} is obtained as described in section 4.14. The absorptivity of 1,4-naphthoquinone at 331.0 nm was 3024, and the absorptivity of 1,4-naphthalenediol at 331.0 nm was 5724. Thus, when 1,4-naphthoquinone is photoreduced to 1,4-naphthalenediol, there is an absorbance increase of 2699 per mole. An irradiated solution of 1,4-naphthoquinone in 2-propanol can therefore be analyzed spectrophotometrically, and both the amount of 1,4-naphthalenediol produced can be calculated. The average amount of 1,4-naphthoquinone present during each irradiation period, NQ_{avg}, was calculated. The absorbance of 1,4-naphthoquinone in the photochemical intrument at the beginning of the first irradiation period, (A_{NQ})initial, was calculated from the fraction of light transmitted. The following relation gave the average absorbance of 1,4-naphthoquinone:

$$(A_{NQ})_{avg} = (A_{NQ})_{initial} \frac{NQ_{avg}}{NQ_{initial}}$$

Once $(Q_{NQ})_{avg}$ is determined, the calculation proceeds similarly to that of section 4.15. The following changes are made in the equation given:

$(Q_{NQ})_{avg}$ is substituted for Q_{avg}, C for 343 is substituted for C for 436 and 2699 is substituted for 43.0.

Only one intensity measurement was made per period for this experiment, as the irradiation time was short. I_Z here, thus, is a single measurement, rather than an average.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5. EXPERIMENTAL

5.1. Irradiation of 1,4-Naphthoquinone in Benzene

When a degassed solution of 1,4-naphthoquinone in benzene, 3 x 10^{-2}M, is exposed to the exciting visible radiation of a high pressure mercury lamp, the absorbance of the solution, at 420 nm, decreases initially, and thereafter increases (Fig. 10). Irradiation of a degassed solution of 1,4-naphthoquinone in benzene, 2 x 10^{-4}M, with short wavelength ultraviolet radiation, in order to measure the spectrum at short wavelengths, results in a continued decrease in absorbance at 330 nm, and an increase in absorbance, followed by a decrease in absorbance, at 300 nm (Fig. 11).

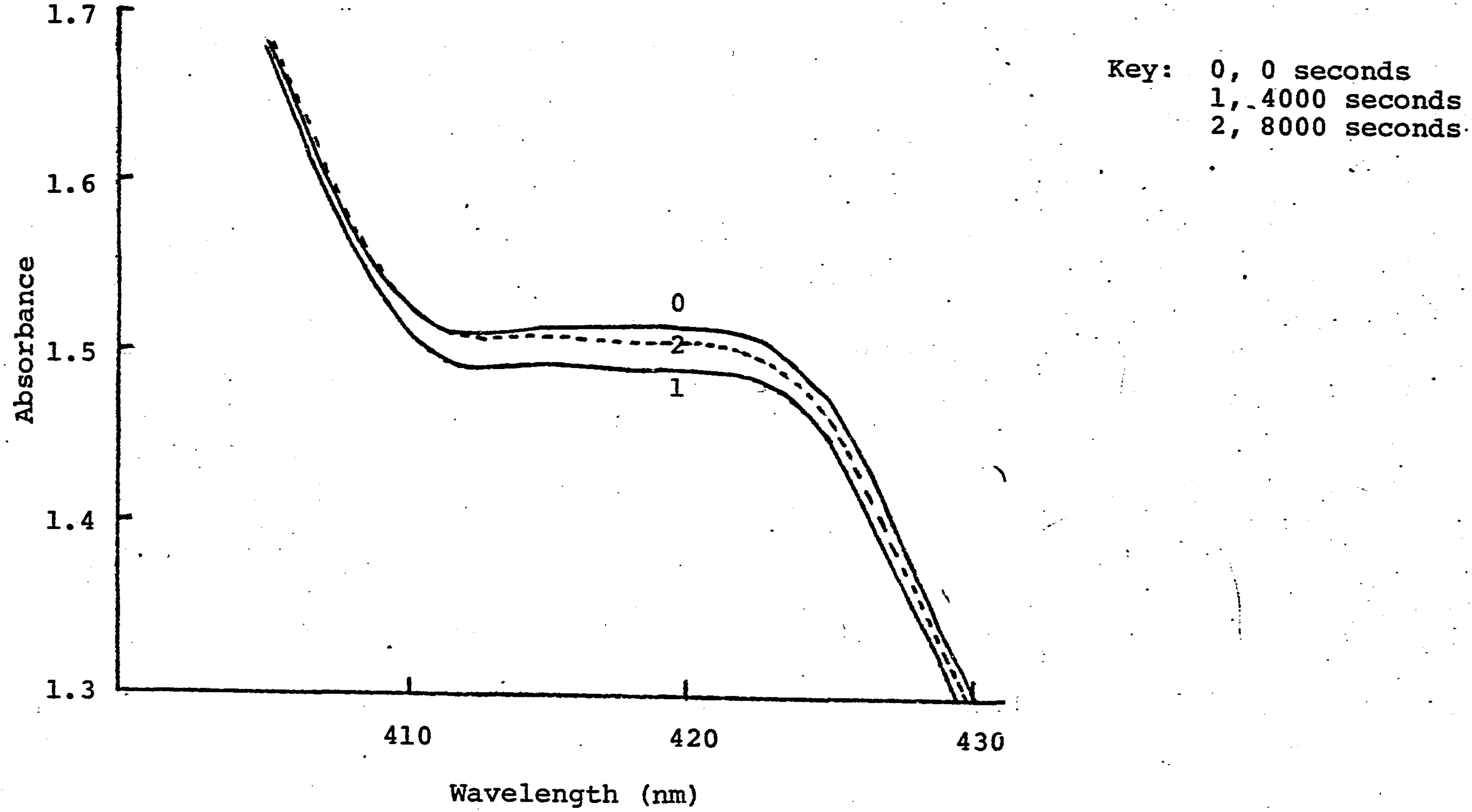
The absorbance decreases at 330 nm and at 420 nm, and the absorbance increase at 300 nm are not inconsistent with dimerization, as the absorbance of di-naphthoquinone (Fig. 12) is greater than that of 1,4-naphthoquinone at 300 nm, and less than that of 1,4-naphthoquinone at 330 nm and at 420 nm. The absorbance decrease at 300 nm and the absorbance increase at 420 upon further irradiation are inconsistent with the assumption that di-naphthoquinone formation is the only reaction that occurs.

The absorbance changes at 300 nm suggest that di-naphthoquinone is initially formed, and then reacts further. The changes at long wavelengths suggest that an intermediate to di-naphthoquinone is formed, or that one or more additional

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 10: Visible Irradiation of 1,4-Naphthoquinone in Benzene (initial concentration: 3.42×10^{-2}M)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 11: Ultraviolet Irradiation of 1,4-Naphthoquinone in Benzene (initial concentration: 1.51×10^{-4})

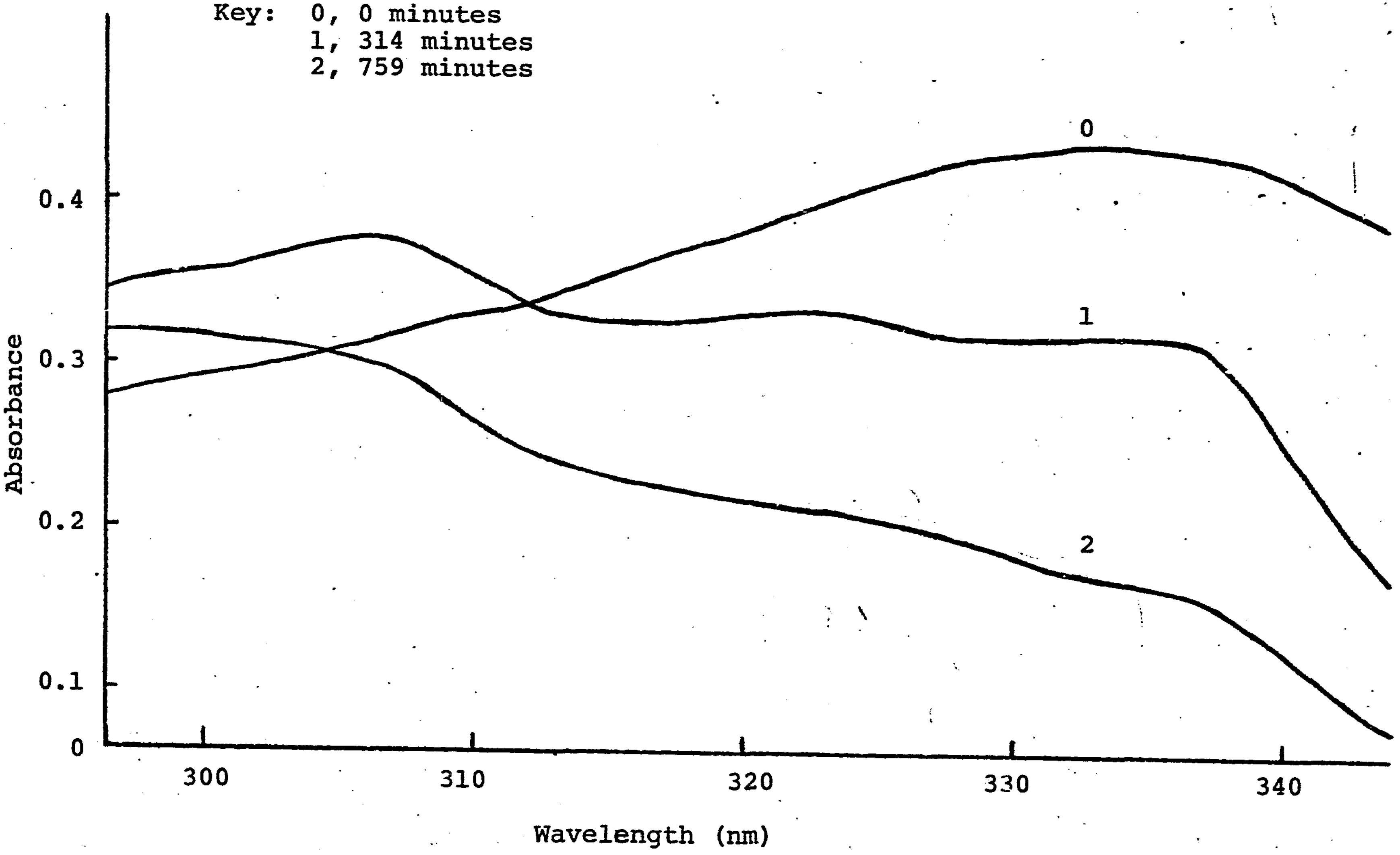
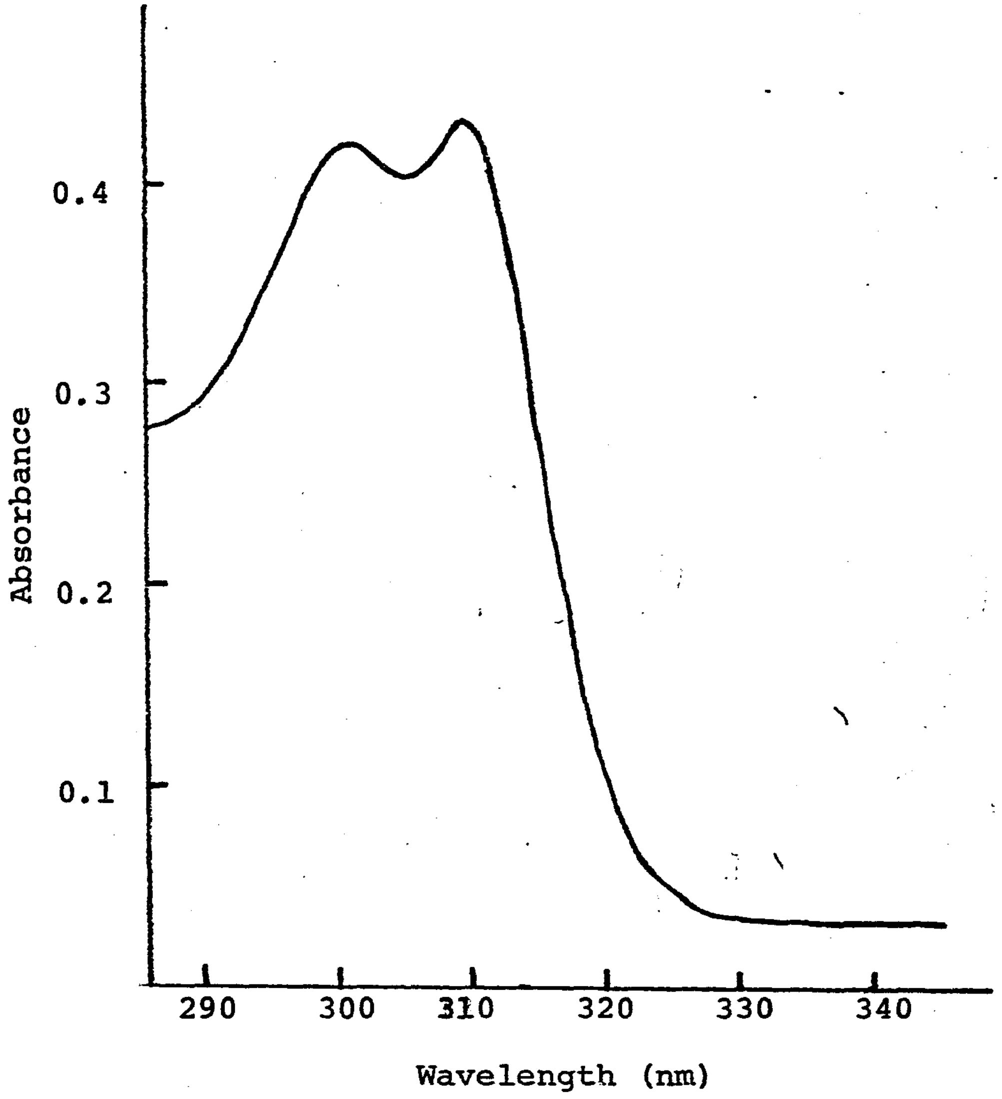


Figure 12: Ultraviolet Spectrum of Di-naphthoquinone in Benzene

(concentration: 1.41×10^{-4}M)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

reactions occur. Further study of the photochemistry of 1,4-naphthoquinone in benzene was undertaken.

5.2. Irradiation of 1,4-Naphthoquinone in Benzene for Long Periods of Time Following Precipitation of Di-naphthoquinone

In order to check if the darkening of irradiated degassed solutions of 1,4-naphthoquinone in benzene was due to the formation of intermediates, a degassed solution of 1,4-naphthoquinone in benzene was irradiated for long periods after the occurrence of precipitation. Spectra were taken of the solution after filtration through the sealed in fritted glass disc.

In order to follow absorbance increases when the absorbance became greater than 2, dilutions were made by first pouring a small amount of irradiated solution through the filter, and then distilling additional solvent from the tube where the remainder of the solution was, to the tube containing the filtrate, by chilling the tube with liquid nitrogen.

Prolonged irradiation resulted in continued absorbance (Table 1) and the irradiated solutions became darker and darker. As no subsequent decrease in absorbance was observed, these changes were apparently not due to the formation of a photochemical intermediate, but rather due to the formation of products of other reactions.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 1: Absorbances of Degassed Benzene Solutions of 1,4-Naphthoquinone After Prolonged Irradiation

Time (hours)	Absorbance	
	600.0 nm	420.0 nm
0	0.005	1.597
3	0.025	1.618
8	0.097	1.884
15	0.232	2.64
25	0.381	3.24
40	0.607	4.60
61	0.754	5.54
90	1.042	6.84
118	1.334	8.7

Precipitation occurred during the second period of irradiation. Absorbances at 420.0 nm greater than 2 were obtained by multiplying the absorbance of a diluted solution at 420.0 nm by the ratio of the absorbances of the undiluted solution and the diluted solution at 560.0 nm.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.3. Thermochromism of Irradiated Benzene Solutions of 1,4-Naphthoquinone

Freezing of an irradiated benzene solution of 1,4-naphthoquinone, when necessary to distill solvent from one tube to another in the previous experiment, resulted in observation of thermochromism. Degassed benzene solutions of 1,4-naphthoquinone, after several hours of irradiation freeze to a red solid upon being immersed in liquid nitrogen or dry ice-acetone. When the vessels are removed from the cooling bath, and allowed to warm slightly, the frozen solid turns blue. The blue color persists as long as the solution remains frozen, even if the temperature is then lowered to that of liquid nitrogen once again, or raised to that of ice water. After melting, the original yellow color of the solution is restored. Freezing the solution in ice water, on the other hand, does not give a red or blue solid.

The quinhydrone of 1,4-naphthoquinone precipitates as a blue solid when concentrated benzene solutions of 1,4-naphthoquinone and 1,4-naphthalenediol, each nearly saturated, are mixed. The supernatant liquid, on freezing, exhibits the same thermochromism as the irradiated 1,4-naphthoquinone solutions. It was, therefore, suspected that the blue color of the frozen irradiated solutions was due to quinhydrone or semiquinone formation.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

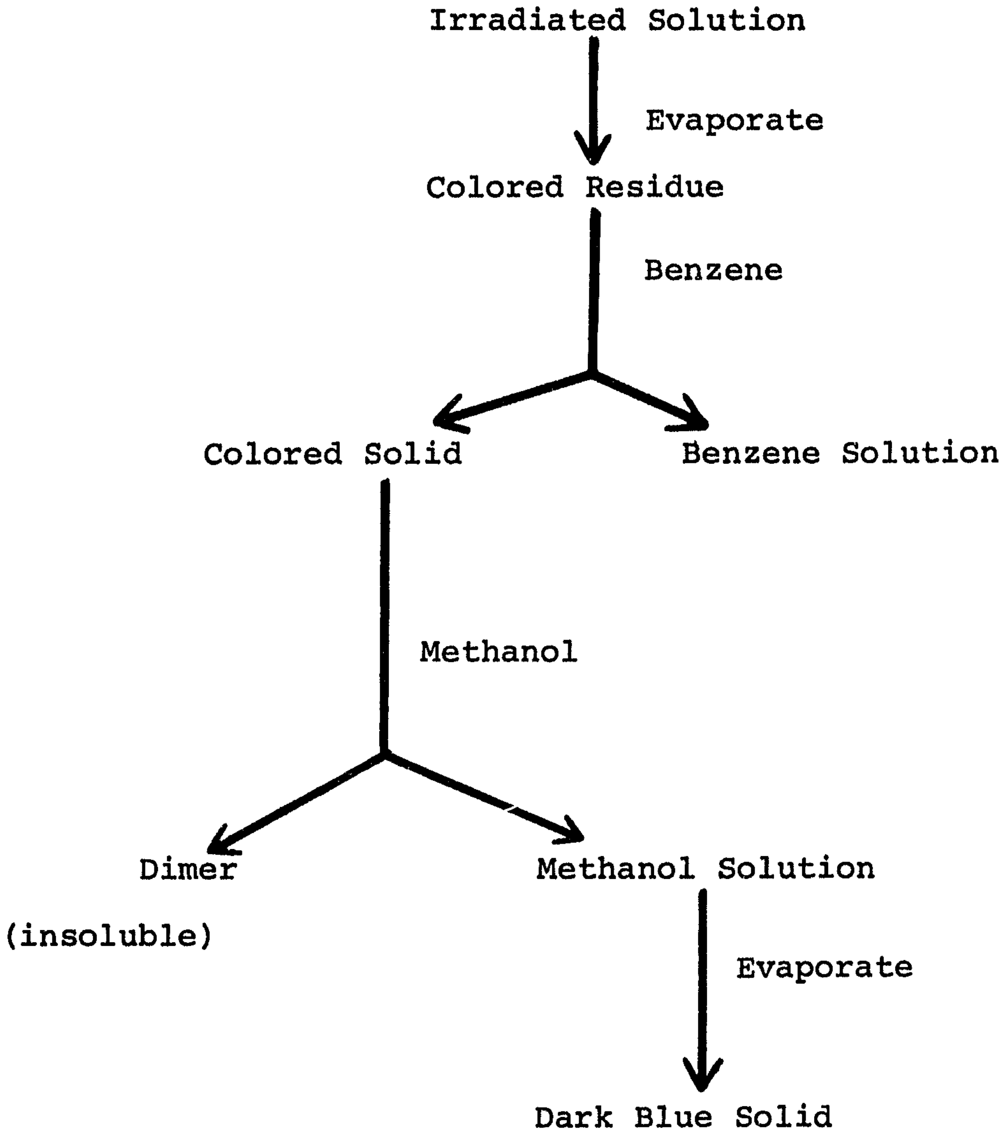
5.4. Verification of the Photoreduction of 1,4-Naphthoquinone

After prolonged irradiation of a degassed solution of 1,4-naphthoquinone in benzene in a degassing assembly with a sealed in fritted glass filter, it was noticed that evaporation of the solvent from one tube to another left a blue precipitate on the sides of the tube. The color of this precipitate called to mind some interesting observations on the behavior of 1,4-naphthalenediol exposed to air. 1,4-Naphthalediol on standing for a few weeks turns pink, and after a few months, turns blue. The thermochromism observed in irradiated solutions, that was identical with that observed for solutions which contained both 1,4-naphthoquinone and 1,4-naphthalenediol, together with observation of a blue precipitate when irradiated solutions were evaporated, suggested that photoreduction of 1,4-naphthoquinone was occurring in benzene solutions. An attempt was then made to isolate the blue precipitate.

A degassed benzene solution, $3 \times 10^{-2}M$ in 1,4-naphthoquinone, was exposed to the filtered radiation of the Hanovia mercury lamp for one week. The white di-naphthoquinone precipitate was filtered. The colored residue remaining on evaporation of the solvent was washed with a small volume of benzene. The residue was then treated with methanol, leaving undissolved di-naphthoquinone. The methanol solution was evaporated, leaving a dark blue solid (Fig. 13). The infra-red spectrum of this material was identical with that of the

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 13: Flow Chart for the Isolation of Quinhydrone From an Irradiated Solution of 1,4-Naphthoquinone in Benzene



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

quinhydrone precipitated by mixing 1,4-naphthoquinone and 1,4-naphthalenediol solutions (fig. 14). Bands were observed at 3300 cm^{-1}, 1670 cm^{-1}, 1620 cm^{-1}, 1300 cm^{-1}, 1075 cm^{-1} and 760 cm^{-1}. The yields of di-naphthoquinone and quinhydrone were both about ten percent.

The complex of 1,4-naphthoquinone and 1,4-naphthalenediol is not stable in solution at ambient temperature. This was demonstrated spectrophotometrically by comparing the absorption spectrum of benzene solutions of 1,4-naphthoquinone and 1,4-naphthalenediol contained in separate compartments of a "split compartment mixing cell for difference spectroscopy"[66] with the spectrum obtained when the contents of the separate compartments were mixed (Fig. 15). The spectra were identical.

It was possible to effect a separation of some 1,4-naphthalenediol, from the blue solid obtained from the photoproduct mixture, by leaching out the quinone with benzene. A small amount of undissolved white solid was obtained. Its fluorescence spectrum (λ_{max}= 385 nm) in benzene solution was identical with that of 1,4-naphthalenediol (Fig. 16).

The quantum yield of the photoreduction of 1,4-naphthoquinone in benzene, obtained by gravimetric analysis of the major products, di-naphthoquinone and the quinhydrone of 1,4-naphthoquinone was 10^{-2}. This is much lower than that in

---

66. J.A. Yankeelov, Jr., Anal. Biochem., 6, 287 (1963).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 14: Infrared Spectrum of the Quinhydrone of 1,4-Naphthoquinone and 1,4-Naphthalenediol

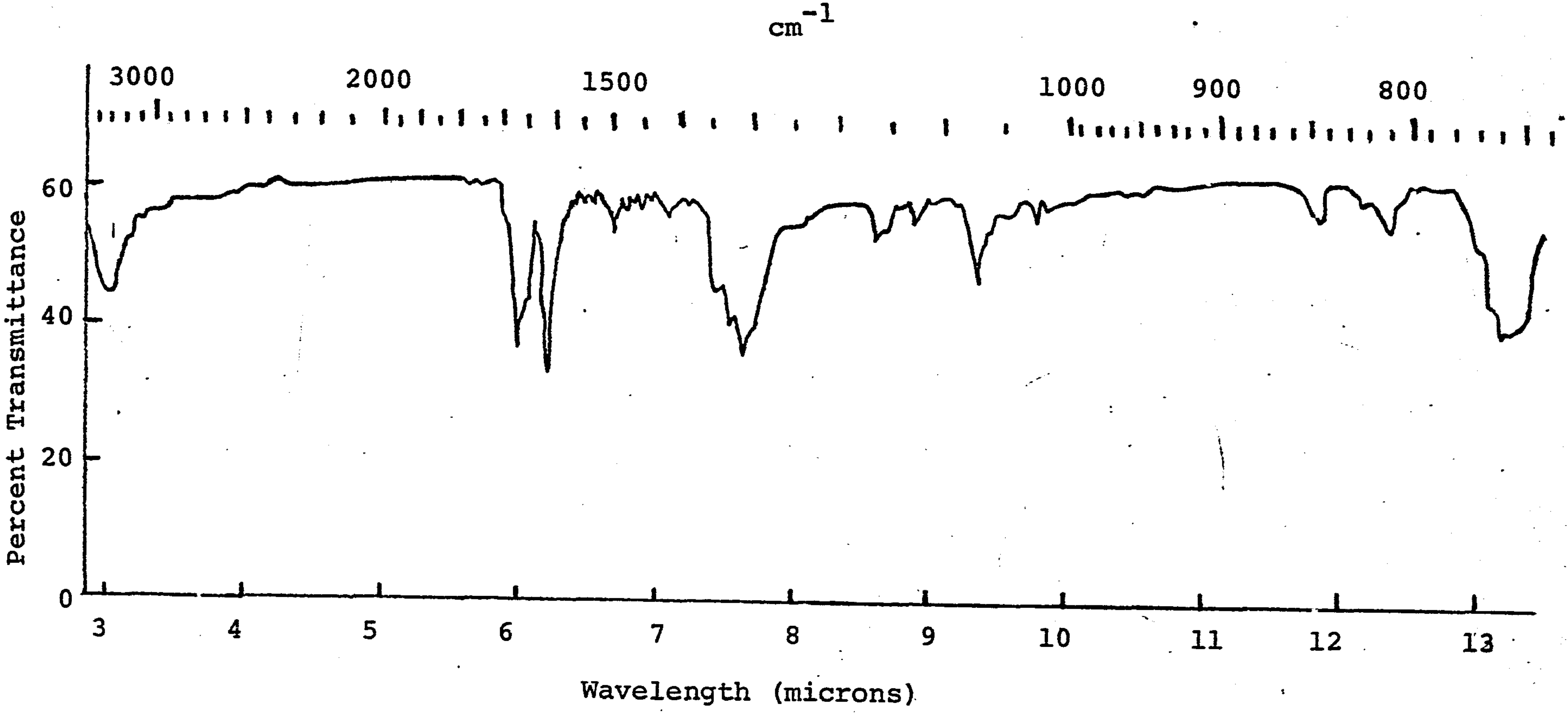
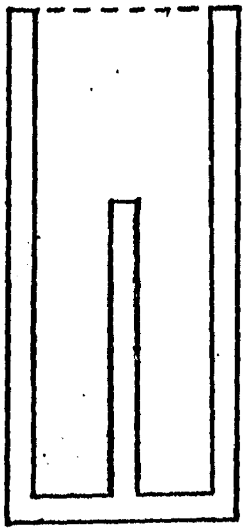
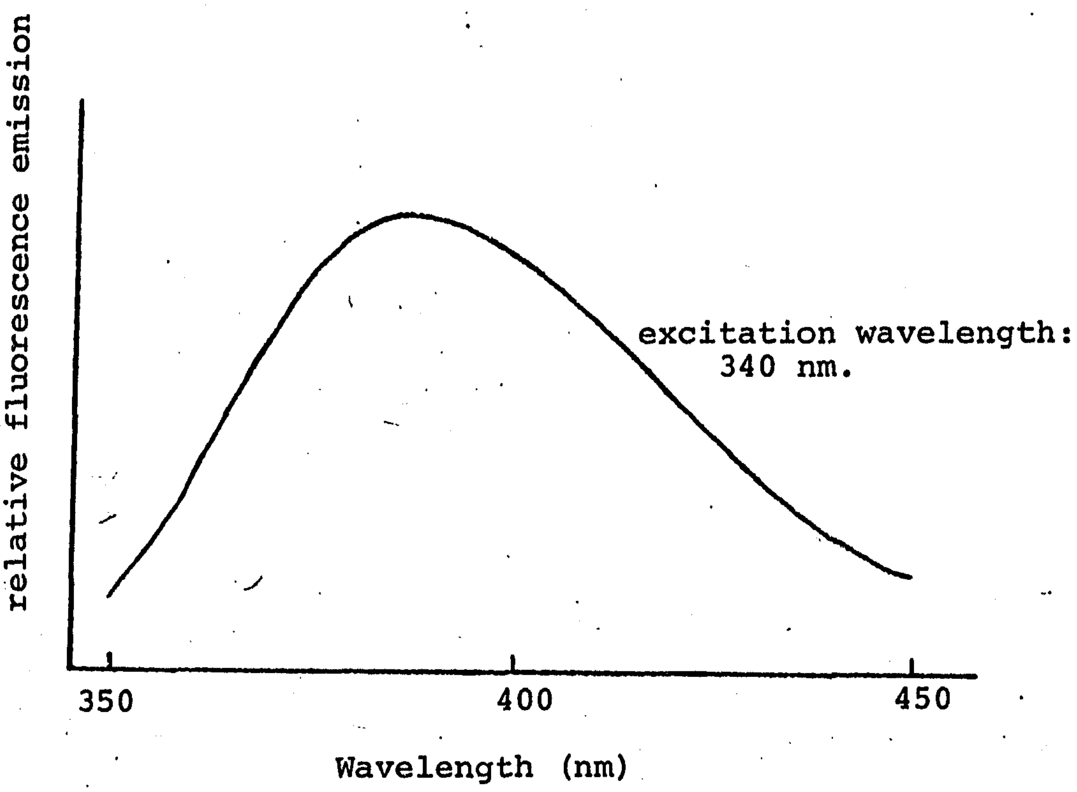


Figure 15: Split Compartment Mixing Cell for Difference Spectroscopy



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 16: Fluorescence Spectrum of 1,4-Naphthalenediol (Perkin-Elmer Model 203 Fluorescence Spectrophotometer)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2-propanol ($\Phi = 0.9$), but of the same order of magnitude as that of the photo-dimerization.[32] This is taken to mean that the same excited state is involved in both reactions.

5.5. Exclusion of Di-naphthoquinone as a Hydrogen Donor

It was established that photoreduction of 1,4-naphthoquinone in benzene had occurred, but the hydrogen donor had not yet been identified. The possible hydrogen donors were the di-naphthoquinone produced photochemically, 1,4-naphthoquinone itself, and the benzene solvent. In order to determine if the di-naphthoquinone was a hydrogen donor, the effect of added dimer, in a benzene solution of 1,4-naphthoquinone, on the rate of photochemical 1,4-naphthalenediol formation was investigated. A solution of 3×10^{-2}M 1,4-naphthoquinone in benzene was prepared. A portion of this solution was used to prepare a solution that was also 3×10^{-5}M in di-naphthoquinone. The blank (1,4-naphthoquinone alone) and dimer (1,4-naphthoquinone with di-naphthoquinone added) solutions were degassed, and were then exposed alternately to long wavelength radiation absorbed by the 1,4-naphthoquinone only. After equal total photon absorptions by the blank and dimer solutions, the solutions were analyzed for 1,4-naphthalenediol peak, using the Perkin-Elmer MPF-2A fluorescence spectrophotometer. No difference in the rate of 1,4-naphthalenediol formation was found (Table 2). Di-naphthoquinone was thus excluded as the hydrogen donor.

---

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol. 6, 485 (1967).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 2: Effect of Di-naphthoquinone on the Photoreduction of 1,4-Naphthoquinone in Benzene (fluorescence emission measured with a Perkin-Elmer Model MPF-2A Fluorescence Spectrophotometer)

	Relative Fluorescence Emission of 1,4-Naphthalenediol at 400 nm (excitation at 336 nm)	
Solution	Time of Irradiation	
	4000 seconds	8000 seconds
3.42×10^{-2}M 1,4-Naphthoquinone	2.8	9.9
3.42×10^{-2}M 1,4-Naphthoquinone and 2.91×10^{-4}M Di-Naphthoquinone	2.7	9.8

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.6. Identification of the Hydrogen Donor in the Photoreduction of 1,4-Naphthoquinone

As dimer had been excluded as a possible hydrogen donor, the remaining possibilities were the 1,4-naphthoquinone itself and the benzene solvent. The method chosen for identification of the hydrogen donor was irradiation of 1,4-naphthoquinone in a solvent that was hydrogen-free, and therefore, could not be a hydrogen donor.

A degassed carbon tetrachloride solution, 3 x 10^{-2} M in 1,4-naphthoquinone, was irradiated for one week. The solution darkened, and there was a large quantity of di-naphthoquinone precipitating. The precipitate's identity was confirmed by infrared and mass spectra. Thermochromism was not observed. The solution was concentrated and tested for the presence of 1,4-naphthalenediol by thin layer chromatography. No 1,4-naphthalenediol was found, confirming that the 1,4-naphthoquinone itself was not a hydrogen donor, but rather that the benzene solvent was responsible for photoreduction of 1,4-naphthoquinone.

5.7. Other Products of 1,4-Naphthoquinone Irradiated in Benzene or in Carbon Tetrachloride

Thin layer chromatography of irradiated degassed solutions, initially 3 x 10^{-2}M, of 1,4-naphthoquinone in benzene or in carbon tetrachloride indicated the presence of many products in each case. An irradiated, degassed solution of

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1,4-naphthoquinone in benzene was checked for the presence of biphenyl and terphenyls by spotting samples of these materials and a sample of photoproduct on a thin layer chromatography plate. Biphenyl and terphenyls were not found in the photoproduct mixture.

An attempt was made to isolate some of the products from the above benzene solution, and from the carbon tetrachloride solution described in section 5.6. A few products were separated by dry column chromatography. These were shown to be homogeneous by thin layer chromatography as no further separation occurred. Mass spectra of these products were taken (Table 3). Peaks corresponding to compounds of three naphthoquinones were observed for carbon tetrachloride and benzene samples. A peak corresponding to a compound of four naphthoquinones was observed for one benzene sample. A few other samples had peaks above 400. A problem that was encountered in taking mass spectra of these products was that the products had low vapor pressures at lower temperatures. It is conceivable that decomposition of the samples occurred at the higher temperatures that had to be used in order to get sufficiently high pressures. Possible structures of these products are discussed in section 6.4.

It was not possible to assign more exact molecular weights to these products by using vapor pressure osmometry. The vapor pressure osmometer used gave results for these samples that were highly uncertain because the solubilities

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 3: Mass Spectral Data for Photoproducts of 1,4-Naphthoquinone in Benzene and in Carbon Tetrachloride

Solvent	Color	Approximate Percentage Yield	Sample Temperature (°C.)	Highest Mass Peak
benzene	purple	2	150	472
benzene	purple	3	275	632
benzene	yellow	0.5	150	462
benzene	yellow	3	275	504
benzene	brown	3	225	430
carbon tetrachloride	brown	1	200	472

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

were very low (about 5g/kg. solvent). The limited solubility does, however, suggest that these products are polymeric materials.

5.8. Photochemistry of 1,4-Naphthoquinone in Other Solvents

In order to check if other solvents might be suitable for further study of either the photoreduction reaction or the photodimerization reaction of 1,4-naphthoquinone, solutions of 1,4-naphthoquinone in several solvents were degassed, and were then irradiated until appreciable darkening occurred. The irradiated solutions were tested for the presence of 1,4-naphthalenediol and di-naphthoquinone by thin layer chromatography (Table 4). Dimerization occurred in acetic anhydride, acetone and carbon disulfide. 1,4-Naphthalenediol was found in acetic anhydride, acetone and cyclohexane. The absence of 1,4-naphthalenediol in the photoproduct mixture in carbon disulfide was expected, because carbon disulfide contains no abstractable hydrogens. Cyclohexane appeared to be a very good hydrogen donor, as 1,4-naphthalenediol was formed to the exclusion of di-naphthoquinone. Those solutions that yielded 1,4-naphthalenediol and/or di-naphthoquinone had other products as well. Irradiation of 1,4-naphthoquinone in dimethylformamide yielded a product that was identified by thin layer chromatography as the product that is also formed when di-naphthoquinone solutions of dimethylformamide are heated.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 4: Photoproducts of 1,4-Naphthoquinone in Various Solvents (X indicates photoproduct formed)

Solvent	Di-naphthoquinone	1,4-Naphthalenediol
acetic anhydride	X	X
acetone	X	X
benzene	X	X
carbon disulfide	X	
carbon tetrachloride	X	
cyclohexane		X
dimethylformamide		

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.9. Determination of Quantum Yields for the Photoreduction of 1,4-Naphthoquinone in 2-Propanol

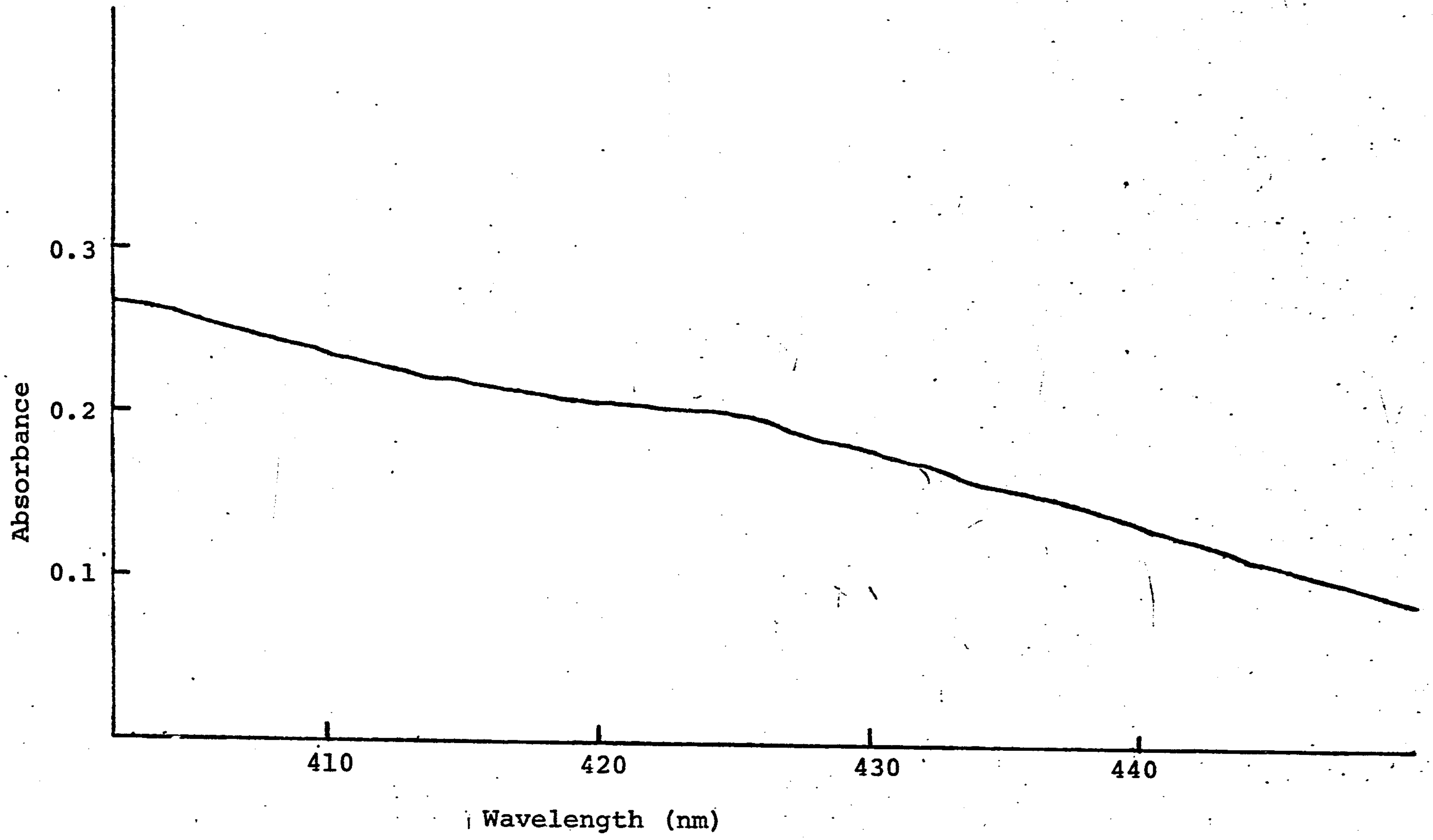
Degassed solutions of 1,4-naphthoquinone in 2-propanonol (Fig. 17) were irradiated in both the $\pi \rightarrow \pi^*$ (334 nm) and the $n \rightarrow \pi^*$ (436 nm) bands. At 334 nm for a 3.23×10^{-4}M solution the quantum yield was 0.93, and for a 3.04×10^{-5}M solution it was 0.89. At 436 nm for a 3.58×10^{-3}M solution it was 0.90 (Table 5). Within the experimental error the quantum yields were independent of wavelength and of concentration. It was concluded (section 6.7.) that the n,π^* state is the photochemically reactive state.

5.10. Sensitization of the Photoreduction of 1,4-Naphthoquinone

The n,π^* state had been established as the photochemically reactive state, but the multiplicity of the photochemically reactive state had not yet been determined. It was decided to attempt to determine if the photochemically reactive state was an excited singlet or an excited triplet. This was done by checking if sensitization of the photoreduction reaction with a triplet sensitizer, or quenching the photoreduction reaction with a triplet quencher was possible. In these types of experiments, in order to obtain unambiguous results, energy transfer should be possible only between the triplet states of the donor and acceptor in question. A suitable sensitizer would have a higher triplet energy and a lower singlet energy than 1,4-naphthoquinone (Fig. 18), so that energy transfer from the sensitizer singlet to the 1,4-naphthoquinone singlet could not occur. A suitable quencher would have a higher lying excited

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 17: Visible Spectrum of 1,4-Naphthoquinone in 2-Propanol
(concentration: 4.79×10^{-3})



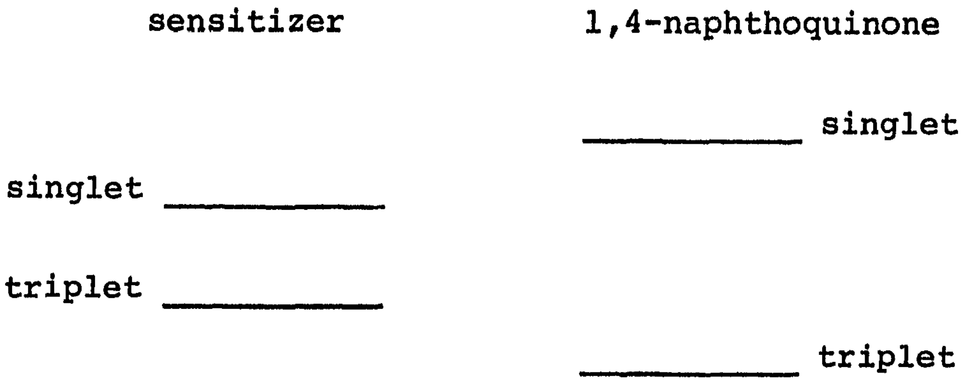
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 5: Quantum Yields for the Photoreduction of 1,4-Naphthoquinone in 2-Propanol

Wavelength (nm)	Concentration	Quantum Yield
436	3.58×10^{-3} M	0.90
334	3.26×10^{-4} M	0.93
334	3.04×10^{-5} M	0.89

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 18: Triplet and Singlet Energies of a Sensitizer For 1,4-Naphthoquinone



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

singlet energy, and a lower triplet energy than 1,4-naphthoquinone (Fig. 19). A substance with a lower lying singlet state would not be suitable because it could quench either the singlet or the triplet.

Lewis and Kasha[67] determined from its phosphorescence spectrum that the triplet energy of acridine yellow was 58 kcal. They pointed out that if the value for acridine yellow was calculated using a correction factor for the broadness of the phosphorescence band a value of 61 kcal. is obtained. Calculation of the triplet energy of 1,4-naphthoquinone from the phosphorescence spectrum obtained by Kuboyama and Matsuzaki[68] yields uncorrected and corrected values of 57 kcal. and 58 kcal. respectively.

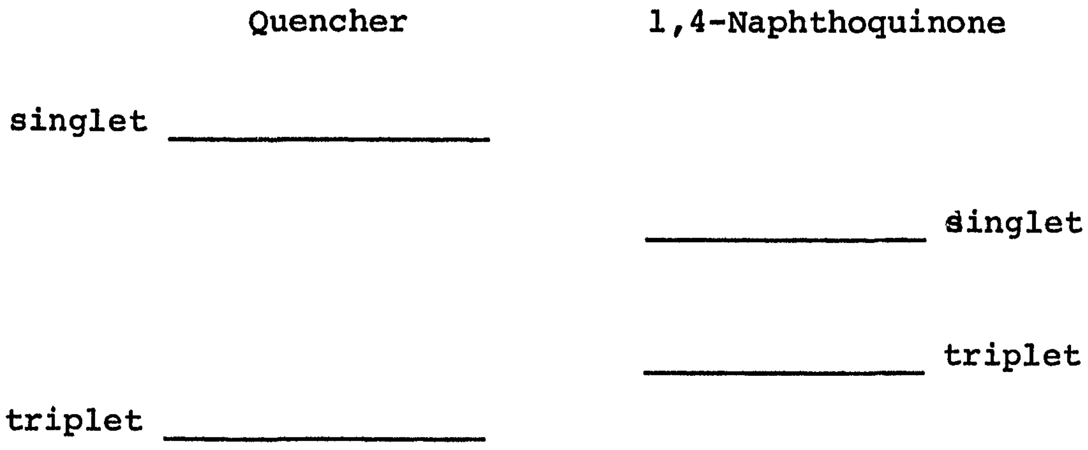
Irradiation of a degassed solution of 1,4-naphthoquinone and acridine yellow in 2-propanol at 436 nm resulted in an increase in absorbance at the 1,4-naphthalenediol peak, corresponding to the production of 0.40×10^{-7} moles of 1,4-naphthalenediol (Fig. 20 and Table 6). A fluorescence spectrum confirmed the production of 1,4-naphthalenediol. The quantities of 1,4-naphthoquinone present at the beginning and at the end of an irradiation period were calculated from the absorbance changes at 331.0 nm. The absorptivity of 1,4-naphthoquinone in the apparatus, calculated from the fraction of light transmitted

---

67. G.N. Lewis and M. Kasha, J. Amer. Chem. Soc., 66, 2100 (1944).
68. A. Kuboyama and S. Matsuzaki, Reports of the Government Chemical Industrial Research Institute, Tokyo, Vol. 64, No. 3, pp. 105-10 (1969).

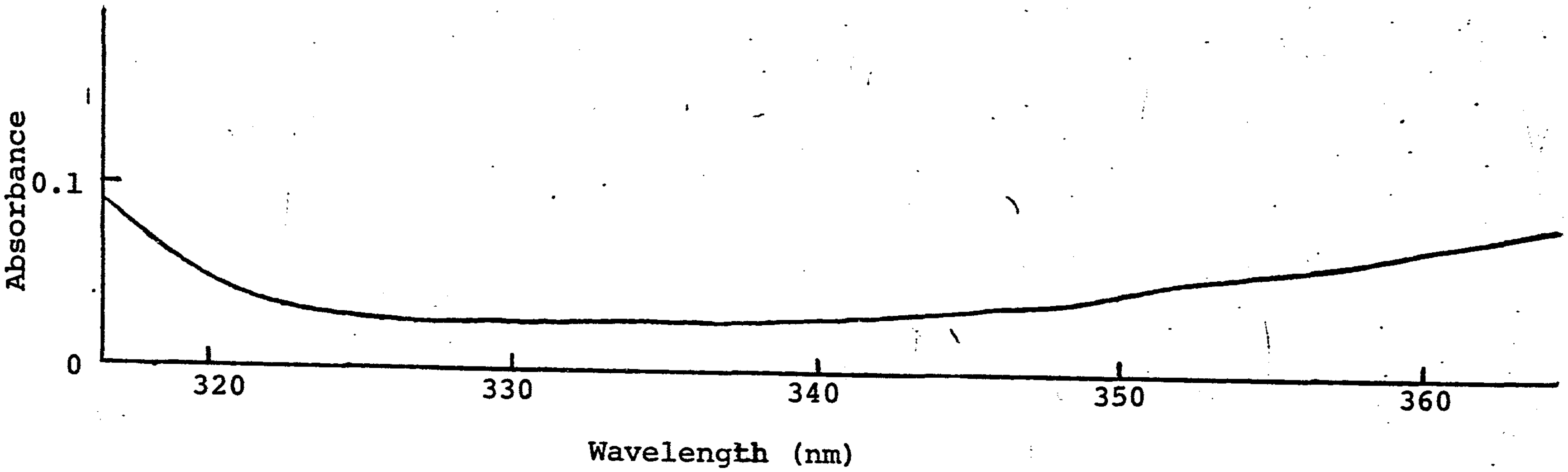
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 19: Triplet and Singlet Energies of a Quencher For 1,4-Naphthoquinone



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 20: Ultraviolet Spectrum of Acridine Yellow in 2-Propanol (concentration: 1.71 x 10^{-4})



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 6: Absorbance Changes For Irradiated 2-Propanol Solutions of Acridine Yellow and 1,4-Naphthoquinone and Acridine Yellow Only

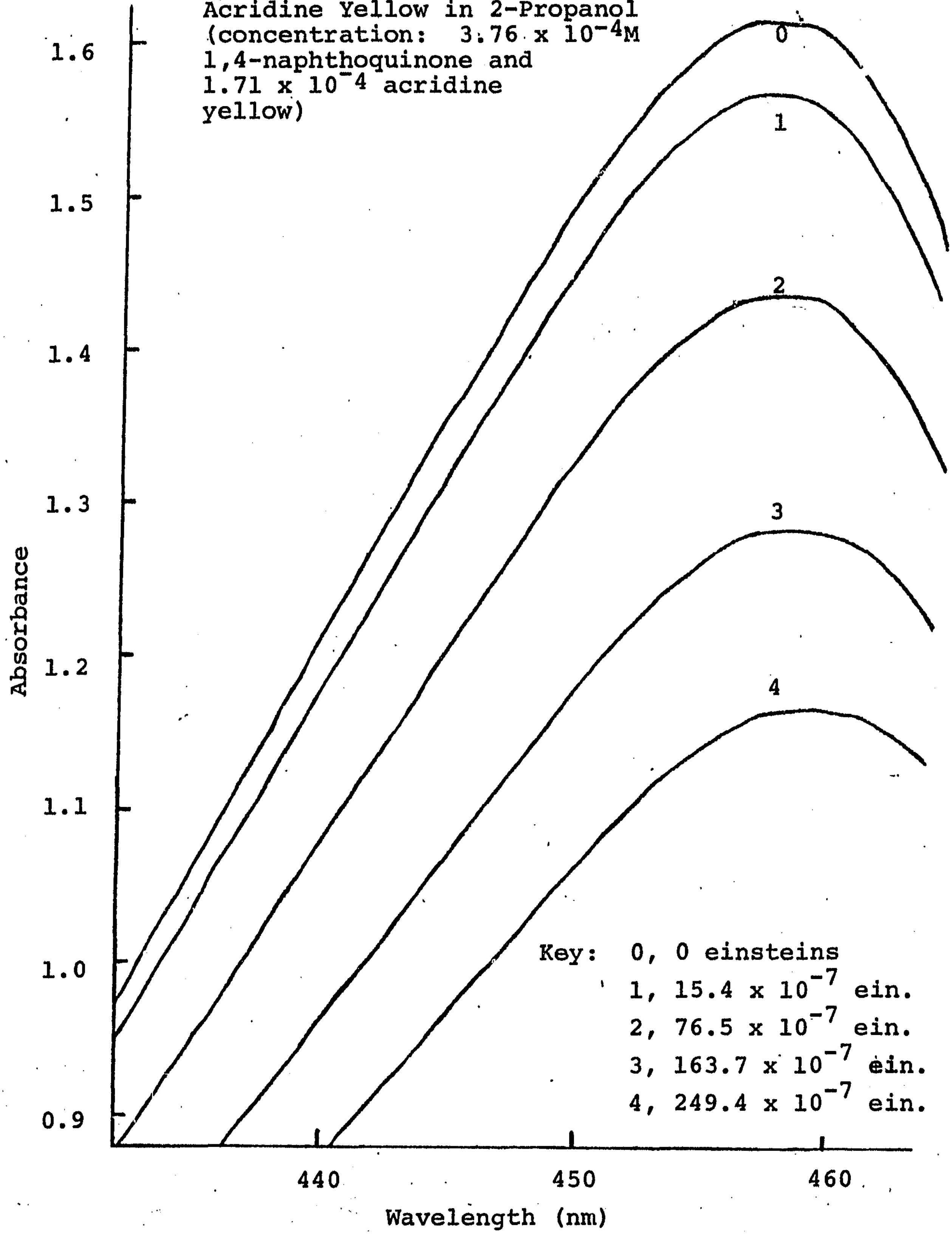
Solution	Einsteins Absorbed During the Interval (436 nm)	Absorbance Change		Moles of 1,4-Naphthalenediol Produced	Fraction of Radiation Absorbed by 1,4-Naphthoquinone	Moles of 1,4-Naphthalenediol Produced by Direct Excitation
		458.0nm	331.0nm			
3.76×10^{-4}M 1,4-naphthoquinone and 1.71×10^{-4}M acridine yellow degassed	15.4×10^{-7}	-0.047	+0.036	0.40×10^{-7}	0.0110	0.19×10^{-7}
	61.1×10^{-7}	-0.130	+0.120	1.33×10^{-7}	0.0129	0.71×10^{-7}
	87.2×10^{-7}	-0.152	+0.158	1.76×10^{-7}	0.0113	0.89×10^{-7}
	85.7×10^{-7}	-0.120	+0.141	1.57×10^{-7}	0.00939	0.72×10^{-7}
1.71×10^{-4}M acridine yellow degassed	15.2×10^{-7}	+0.001	+0.001			
	62.1×10^{-7}	-0.005	+0.002			
	91.8×10^{-7}	-0.010	+0.007			
	91.1×10^{-7}	-0.008	+0.004			
4.95×10^{-4}M 1,4-naphthoquinone and 1.70×10^{-4}M acridine yellow not degassed	14.1×10^{-7}	-0.060	+0.004			
	51.1×10^{-7}	-0.075	-0.022			
	53.1×10^{-7}	-0.056	-0.005			
	275.7×10^{-7}	-0.210	-0.085			
	321.1×10^{-7}	-0.149	-0.160			
1.71×10^{-4}M acridine yellow not degassed	77.6×10^{-7}	-0.013	+0.005			

by solutions of 1,4-naphthoquinone in 2-propanol, was 34.5 at 436 nm. The calculated average absorbance of 1,4-naphthoquinone during the first irradiation period was 0.0128. The average total absorbance of the irradiated solution in the apparatus was 1.16. Dividing the absorbances yields 0.0110, the fraction of radiation absorbed by 1,4-naphthoquinone. Since 1,4-naphthoquinone was known to have absorbed radiation at 436 nm, the amount of 1,4-naphthalenediol that would have been produced by direct excitation of 1,4-naphthoquinone was calculated. The calibration factor for irradiation at 436 nm, was obtained by using solutions of 1,4-naphthoquinone in 2-propanol as actinometers. The quantum efficiency had been determined to be 0.90 (Table 5). The calculation showed that 0.19×10^{-7} moles of 1,4-naphthalenediol could have resulted from direct excitation, less than half the amount produced in actuality (Table 6). Calculations were similarly performed for succeeding periods of irradiation.

It is evident (Figs. 21a and 21b) that the sensitized reaction was also accompanied by another reaction which resulted in a decrease in absorbance at the acridine peak and an increase in absorbance at longer wavelengths. As irradiation of a degassed acridine yellow solution containing no 1,4-naphthoquinone resulted in no significant absorbance changes (Table 6), it appeared that 1,4-naphthoquinone played a role in this reaction, either as a reactant or as a catalyst. Irradiation of an undegassed solution, of approximately the

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

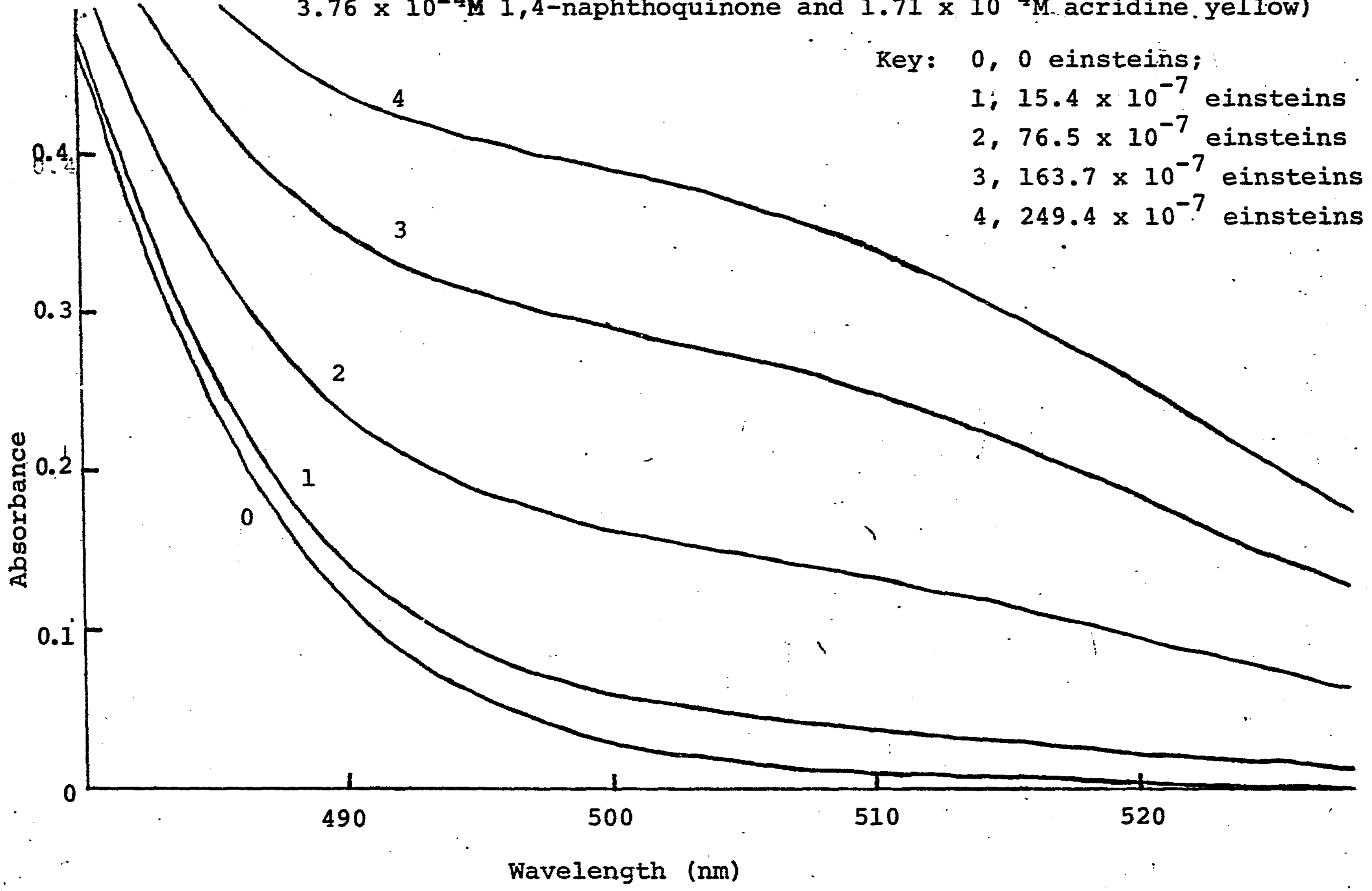
Figure 21a: Visible Spectra of a Degassed Irradiated (at 436 nm) Solution of 1,4-Naphthoquinone and Acridine Yellow in 2-Propanol (concentration: 3.76 x 10^{-4}M 1,4-naphthoquinone and 1.71 x 10^{-4} acridine yellow)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 21b: Visible Spectra of a Degassed Irradiated (at 436 nm) Solution of 1,4-Naphthoquinone and Acridine Yellow in 2-Propanol (concentrations: 3.76×10^{-4}M 1,4-naphthoquinone and 1.71×10^{-4}M acridine yellow)

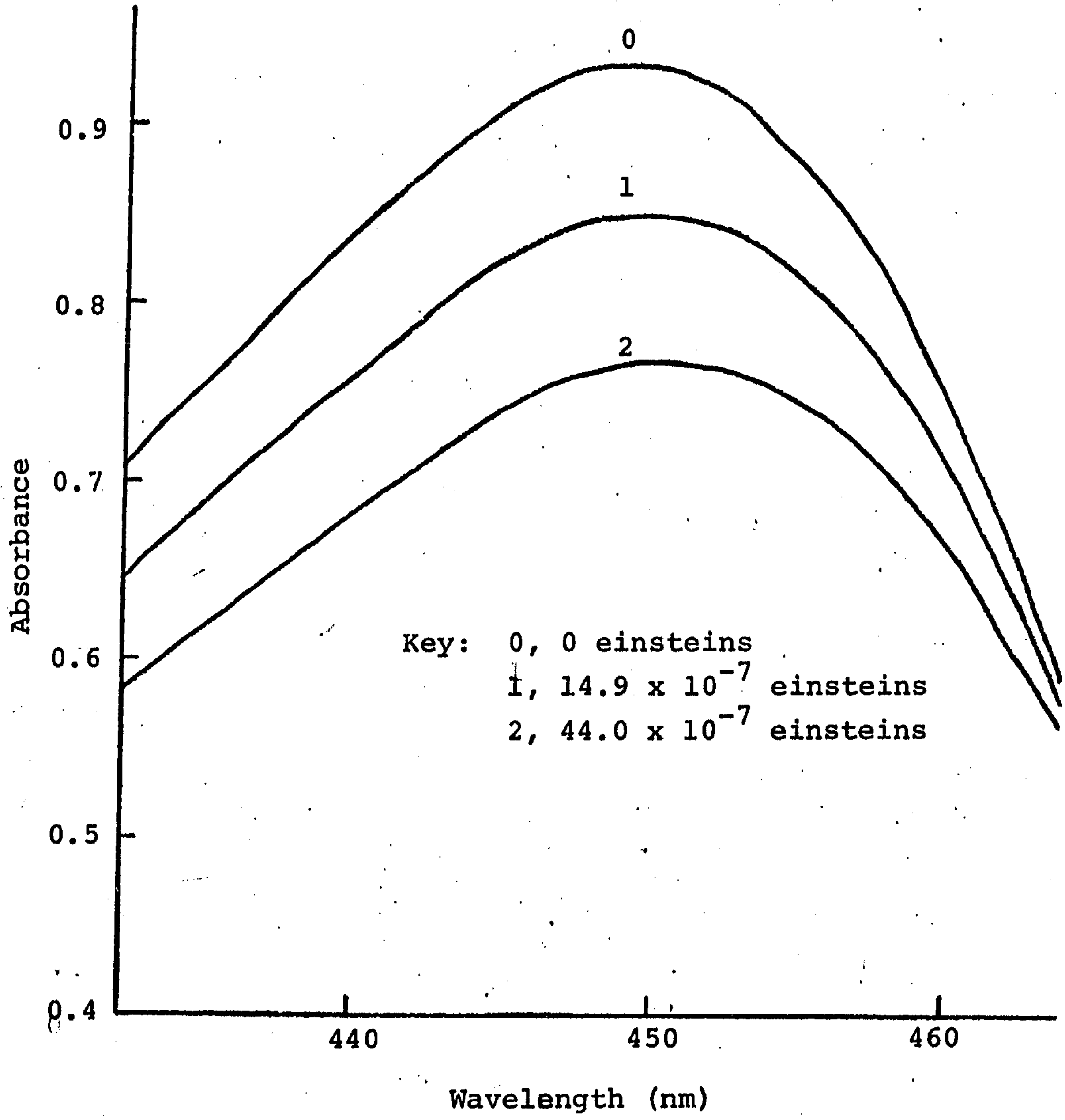


same concentrations of 1,4-naphthoquinone and acridine yellow, where 1,4-naphthalenediol would either not form, or would be reoxidized to 1,4-naphthoquinone on standing, showed a decrease in absorbance at the 1,4-naphthoquinone peak of 0.004 corresponding to a decrease in absorbance at the acridine yellow peak of 0.060, and an increase in absorbance at longer wavelengths (Table 6). Irradiation of an undegassed solution of acridine yellow containing no 1,4-naphthoquinone resulted in no significant absorbance changes (Table 6). The absorbance changes observed in the presence of 1,4-naphthoquinone (Table 6) are apparantly due to a reaction between acridine yellow and 1,4-naphthoquinone.

Whether the observed reaction between 1,4-naphthoquinone and acridine yellow occurred between excited acridine yellow and 1,4-naphthoquinone, or between excited 1,4-naphthoquinone and acridine yellow had not been determined. A degassed solution of acridine yellow and 1,4-naphthoquinone in acetone, irradiated at 436 nm showed the same changes at the acridine yellow peak and at longer wavelengths as the 2-propanol solution (Figs. 22a and 22b), while a degassed solution of acridine yellow in acetone containing no 1,4-naphthoquinone showed no significant changes (Table 7). When the solution of 1,4-naphthoquinone and acridine yellow in acetone was irradiated with radiation of 334 nm, absorbed by the quinone, there were no significant absorbance changes at either the acridine yellow peak or at longer wavelengths (Table 7). Apparently,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 22a: Visible Spectra of a Degassed Irradiated Solution (at 436 nm) of 1,4-Naphthoquinone And Acridine Yellow in Acetone (concentrations: 4.28 x 10^{-4}M 1,4-naphthoquinone and 1.08 x 10^{-4}M acridine yellow)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 22b: Visible Spectra of A Degassed Irradiated (at 436 nm) Solution of 1,4-Naphthoquinone and Acridine Yellow in Acetone (Concentrations: 4.28 x 10^{-4}M 1,4-naphthoquinone and 1.08 x 10^{-4}M acridine yellow)

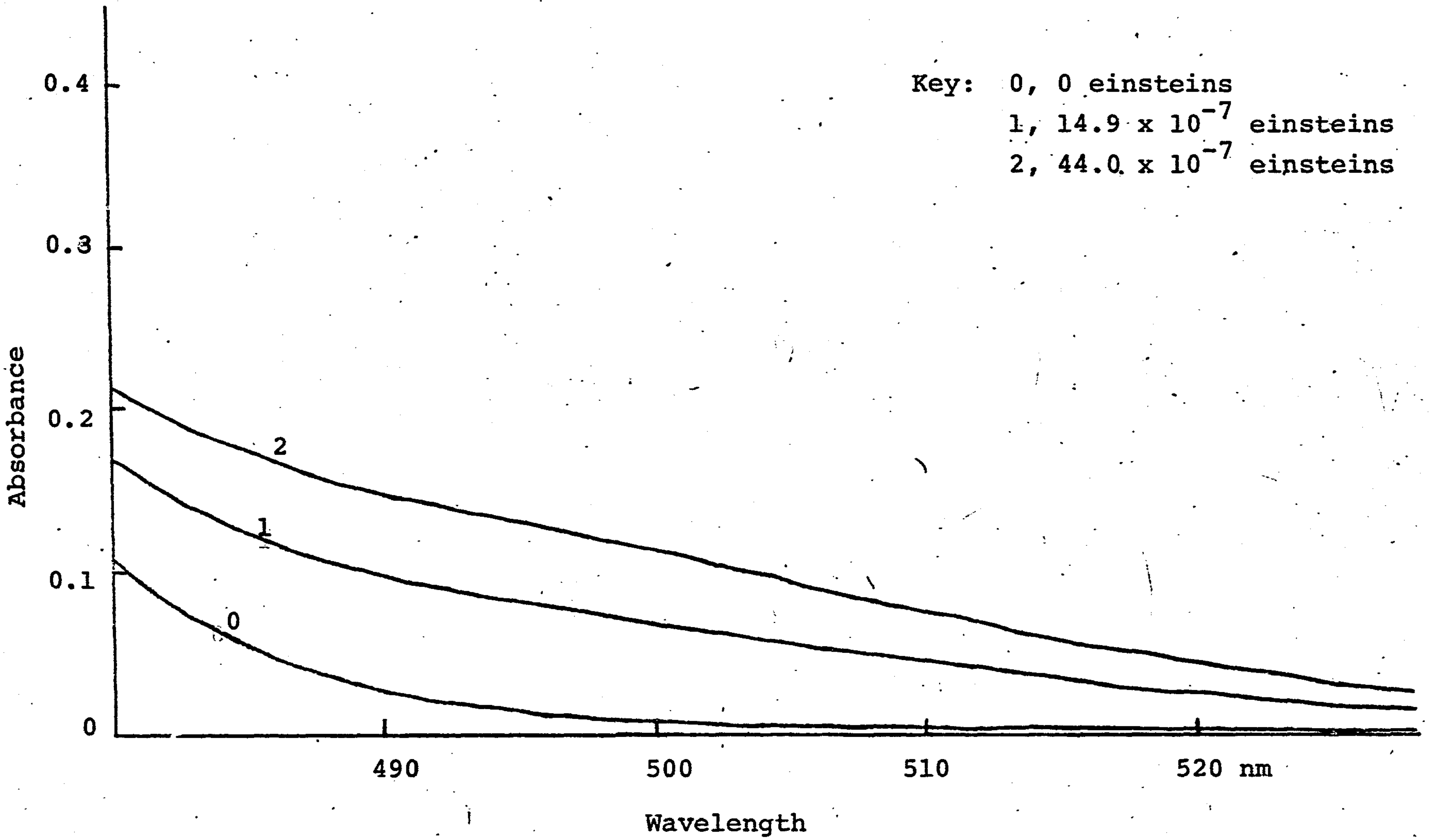


Table 7: Absorbance Changes of Irradiated Degassed Acetone Solutions of Acridine Yellow and 1,4-Naphthoquinone and Acridine Yellow Only

Solution	Wavelength of Irradiation (nm)	Einsteins Absorbed During the Interval	Absorbance change	
			448.0 nm	490.0 nm
4.28×10^{-4}M 1,4-naphthoquinone and 1.08×10^{-4}M acridine yellow	436	14.9×10^{-7}	-0.086	+0.069
	436	29.1×10^{-7}	-0.074	+0.53
	334	7.02×10^{-7}	+0.007	0
1.08×10^{-4}M acridine yellow	436	15.1×10^{-7}	-0.003	+0.003
	436	28.9×10^{-7}	-0.012	+0.008
	334	3.69×10^{-7}	-0.010	0

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

excited acridine yellow reacts with unexcited 1,4-naphthoquinone, but excited 1,4-naphthoquinone does not react with unexcited acridine yellow.

5.11. Quenching of 1,4-Naphthoquinone Photoreduction by Anthracene

Dienes, trienes and polycyclic aromatics are frequently used as triplet quenchers in photochemical reactions because they have high singlet energies ($>10^2$ kcal/mole) and low triplet energies (in the order of 5×10^1 kcal/mole). It was found that trans-piperylene reacts with 1,4-naphthoquinone in the dark, presumably via a Diels-Alder reaction. Therefore, dienes and trienes were not found suitable for further tests as possible triplet quenchers. Polycyclic aromatics were thought to be more stable in the presence of 1,4-naphthoquinone. Lewis and Kasha[67] determined from its phosphorescence spectrum that the triplet energy of anthracene was 42 kcal. Anthracene was the lowest molecular weight polycyclic aromatic with a lower triplet energy and a higher singlet energy than 1,4-naphthoquinone.

For a degassed solution containing 2:1 anthracene: 1,4-naphthoquinone in 2-propanol no quenching was observed. A higher ratio of anthracene to 1,4-naphthoquinone could not be used because of the limited solubility of anthracene in

---

[67] G.N. Lewis and M. Kasha, J. Amer. Chem. Soc., 66, 2100 (1944).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

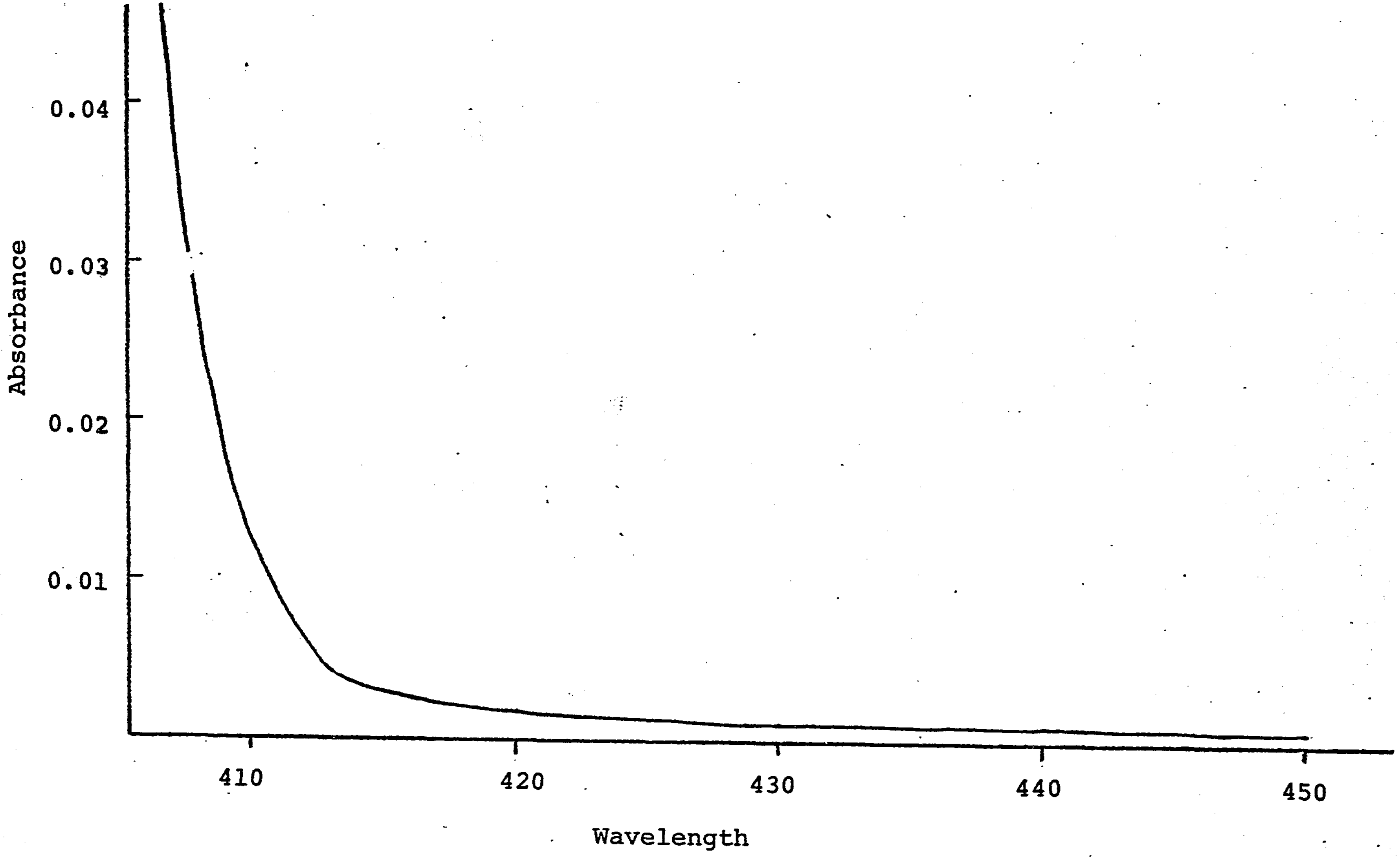
2-propanol. As anthracene was much more soluble in benzene than in 2-propanol, a mixed solvent system consisting of 4:1 benzene:2-propanol was chosen. A degassed solution 2.46×10^{-3}M in 1,4-naphthoquinone and 2.28×10^{-2}M in anthracene and a degassed solution containing the same concentration of 1,4-naphthoquinone only were irradiated at 436 nm. Where the absorbance of anthracene is negligible (Fig. 23) 1,4-naphthalenediol, identified by its fluorescence spectrum, precipitated from each and settled to the bottom of the cell. Quantum yields were determined by measuring the absorbance decrease at 422.0 nm corresponding to disappearance of 1,4-naphthoquinone. In determining the number of einsteins absorbed correction was made for complex formation (Sec 5.12). The number of moles of 1,4-naphthoquinone reacted for the solution containing anthracene was 2.06×10^{-6} for 6.49×10^{-6} einsteins absorbed. In the absence of anthracene 2.55×10^{-6} moles reacted for 6.94×10^{-6} einsteins absorbed. The quantum efficiencies were 0.32 in the presence of anthracene and 0.37 in the absence of anthracene.

5.12. Complex Formation of 1,4-Naphthoquinone With Anthracene and With Acridine Yellow

It was observed that a solution containing 1,4-naphthoquinone and anthracene in 4:1 benzene:2-propanol showed spectral differences from a solution containing 1,4-naphthoquinone only (Fig. 24), and that when nearly saturated solutions of 1,4-naphthoquinone and anthracene in a mixed solvent of

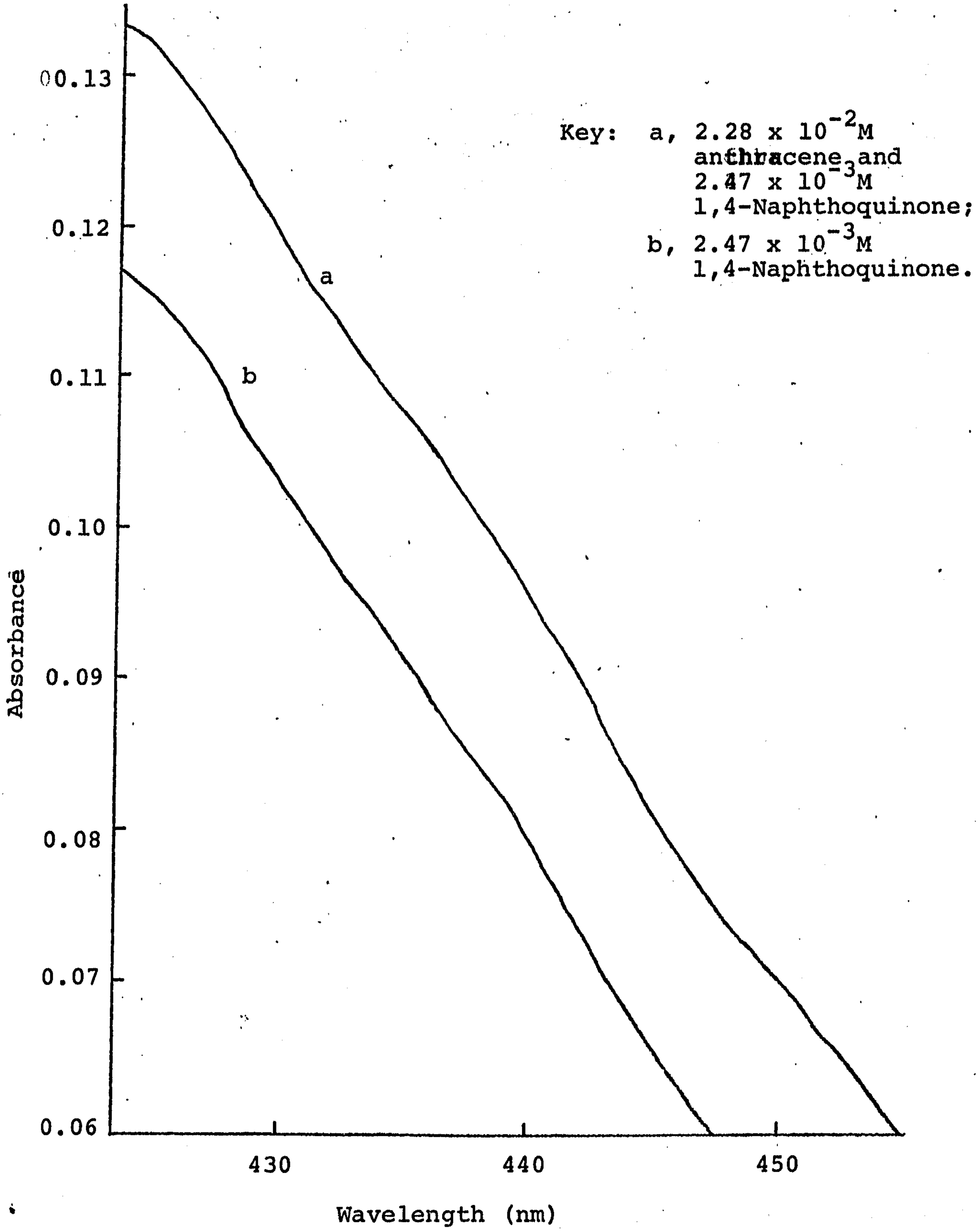
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 23: Visible Spectrum of Anthracene in 4:1 Benzene:2-Propanol
(concentration: 2.28×10^{-2}M)



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 24: Visible Absorption Spectra of Solutions of 1,4-Naphthoquin one and Anthracene and 1,4-Naphthoquinone Only in 4:1 Benzene:2-Propanol



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2:1 methylcyclohexane:toluene is frozen in liquid nitrogen, the resultant glass appears reddish rather than yellow. These observations suggested complex formation.

The composition of the complex formed by 1,4-naphthoquinone and anthracene in 4:1 benzene:2-propanol was determined by Job's[69,70] method. Solutions of 2.28 x 10^{-2}M 1,4-naphthoquinone and 2.28 x 10^{-2}M anthracene were mixed. X ml. of the 1,4-naphthoquinone solution were added to (1 - X_ ml. of the anthracene solution. Y shows the values of the difference between the measured absorbance, at 450.0 nm, and that calculated from the absorbance at the same wavelength of the pure 1,4-naphthoquinone solution assuming no reaction on mixing the two solutions. The peak at X = 0.5 indicated that a 1:1 complex was formed.

An equation derived by Brittain et. al.[71], when applied to the case of 1,4-naphthoquinone and anthracene in 4:1 benzene:2-propanol becomes:

$$\frac{Q_i 1}{A_{obs}-A^{f}_{obs}} = \frac{1}{K_a(\ _{QA}-\ _{Q})}\ \frac{1}{A_i} + \frac{1}{(\ _{QA}-\ _{Q})}$$

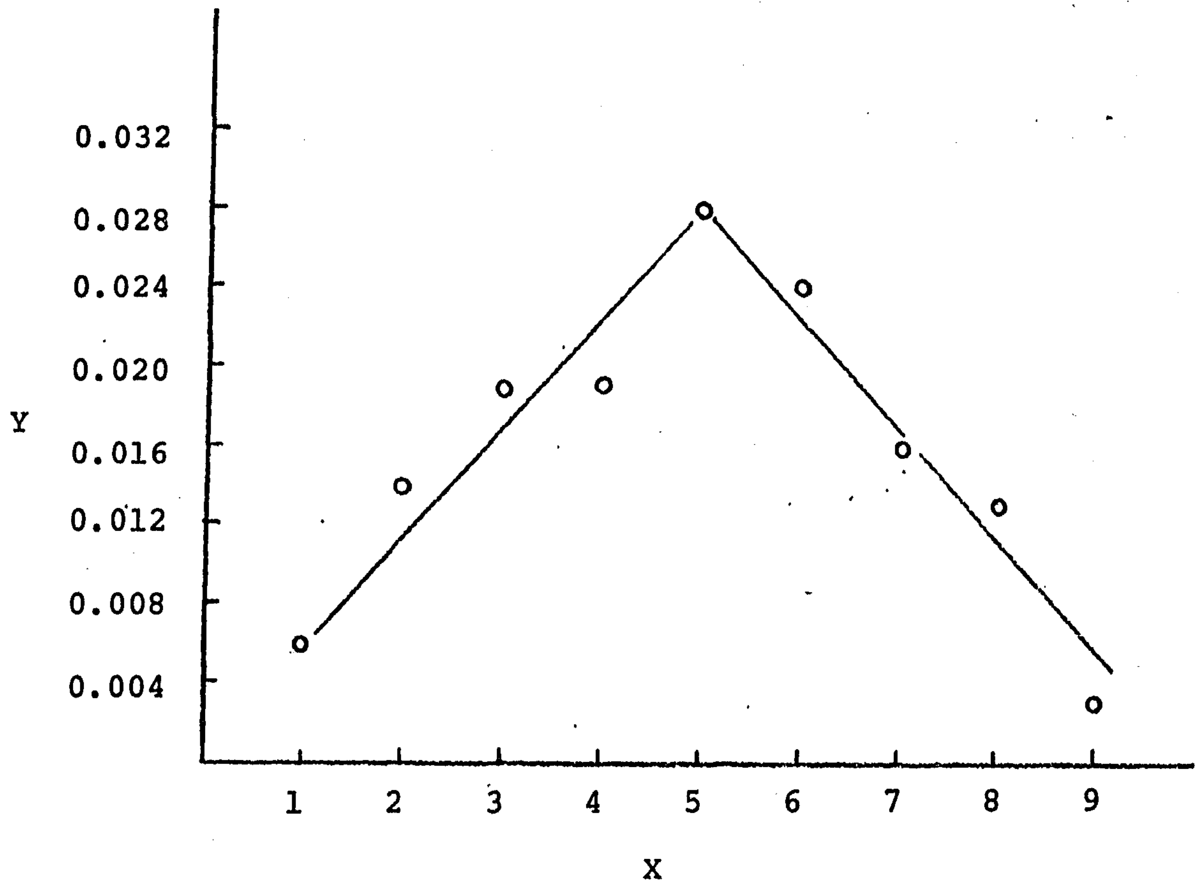
where 1 is the path length, Q_i is the initial concentration of the quinone, A_{obs} is the absorbance observed, A^{f}_{obs} is the absorbance of the

---

69. P. Job, Ann. Chim., [10] 9, 113 (1928).
70. W.C. Vosburgh and G.C. Cooper, J. Amer. Chem. Soc., 63, 437 (1941).
71. E.F.H. Brittain, W.O. George and C.H.J. Wells, Introduction to Molecular Spectroscopy, Academic Press, London, 1970,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 25: Determination of the Composition of the Complex Formed by 1,4-Naphthoquinone and Anthracene In 4:1 Benzene:2-Propanol



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

free quinone, and K_a is the equilibrium constant for complex formation.

If the left hand side of the equation is plotted (Fig. 25) against $1/A_i$, the value of K_a may be calculated from the slope of the line and the intercept of the line on the y axis. From the data in Table 8 K_a was found by the method of least squares, to be 12.8 as ε_Q was determined to be 0.91 at 490.0 nm, ε_{QA} was calculated to be 11.6. A spectrum of the complex is shown in Figure .

Since

$$\text{Abs} = {}_{QA}\,QA + {}_{Q}\,Q_f$$

where Abs is the absorbance at 490.0 nm, QA is the concentration of complex, and Qf is the concentration of uncomplexed quinone and

$$QA = Q_i - Q_f$$

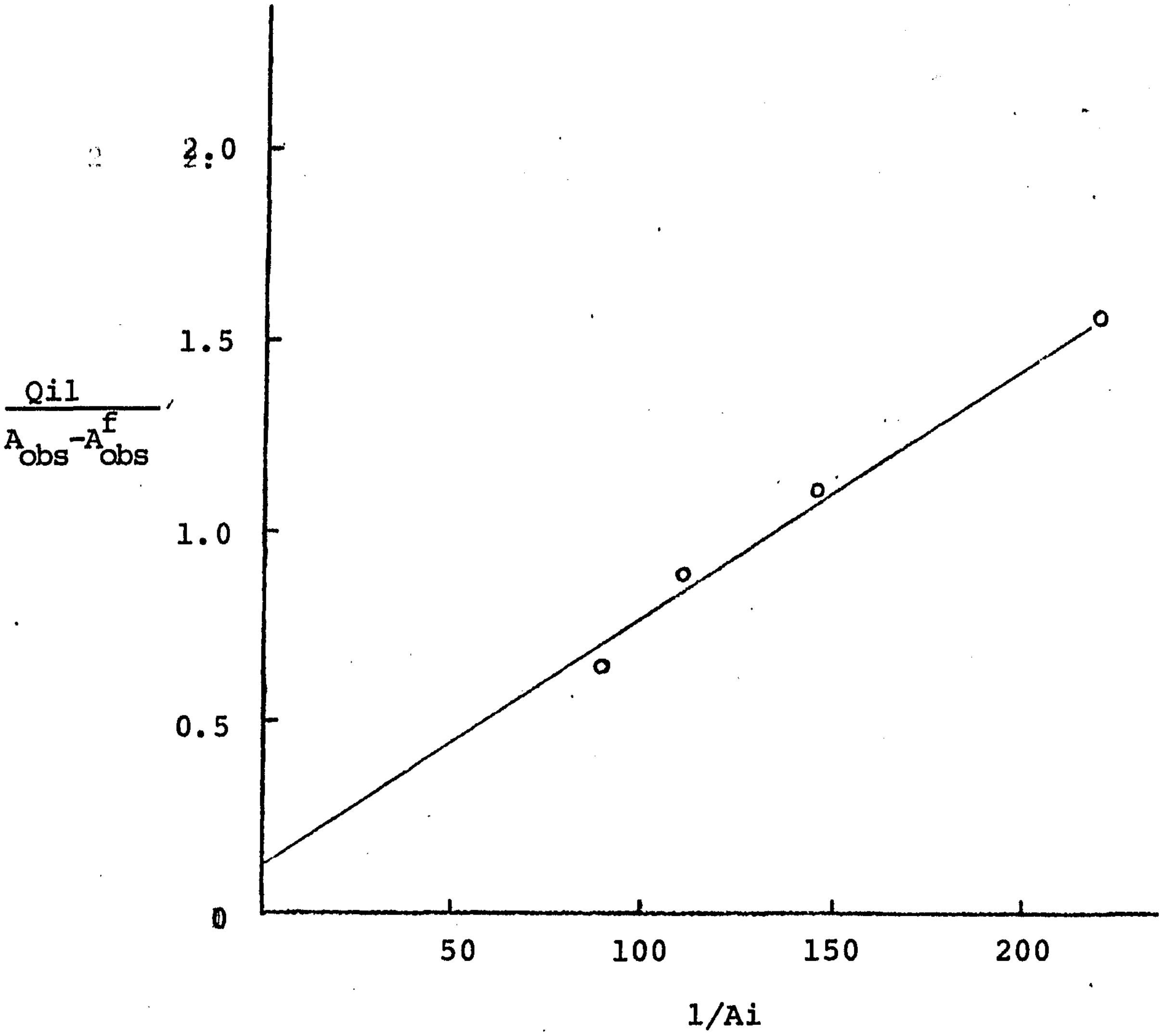
where Q_i is the initial concentration of quinone. therefore

$$Q_f = \frac{\text{Abs} - \varepsilon_{QA}\,Q_i}{\varepsilon_Q - \varepsilon_{QA}}$$

This relation was used to determine the fraction of radiation absorbed by the uncomplexed quinone in the quenching experiment (Sec. 5.11.). As the initial concentration of

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 26: Determination of the K_a and $_{QA}$ for the Complex Formed by 1,4-Naphthoquinone and Anthracene In 4:1 Benzene:2-Propanol



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 8 : Determination of K_a and ε_{QA} For The Complex Formed By 1,4-Naphthoquinone and Anthracene in 4:1 Benzene:2-Propanol

Initial Concentrations (M)				
A_i	Q_i	$A_{abs}-A^f_{obs}$	$Q_i 1/A_{abs}-A^f_{obs}$	$1/A_i$
0.00456	0.0684	0.0440	1.55	219
0.00684	0.0684	0.0650	1.05	146
0.00912	0.0684	0.0775	0.882	110
0.0114	0.0684	0.1070	0.639	87.7

By the method of least squares:

$$\text{slope} = \frac{1}{K_a(\varepsilon_{QA}-\varepsilon_Q)} \neq 0.00671$$

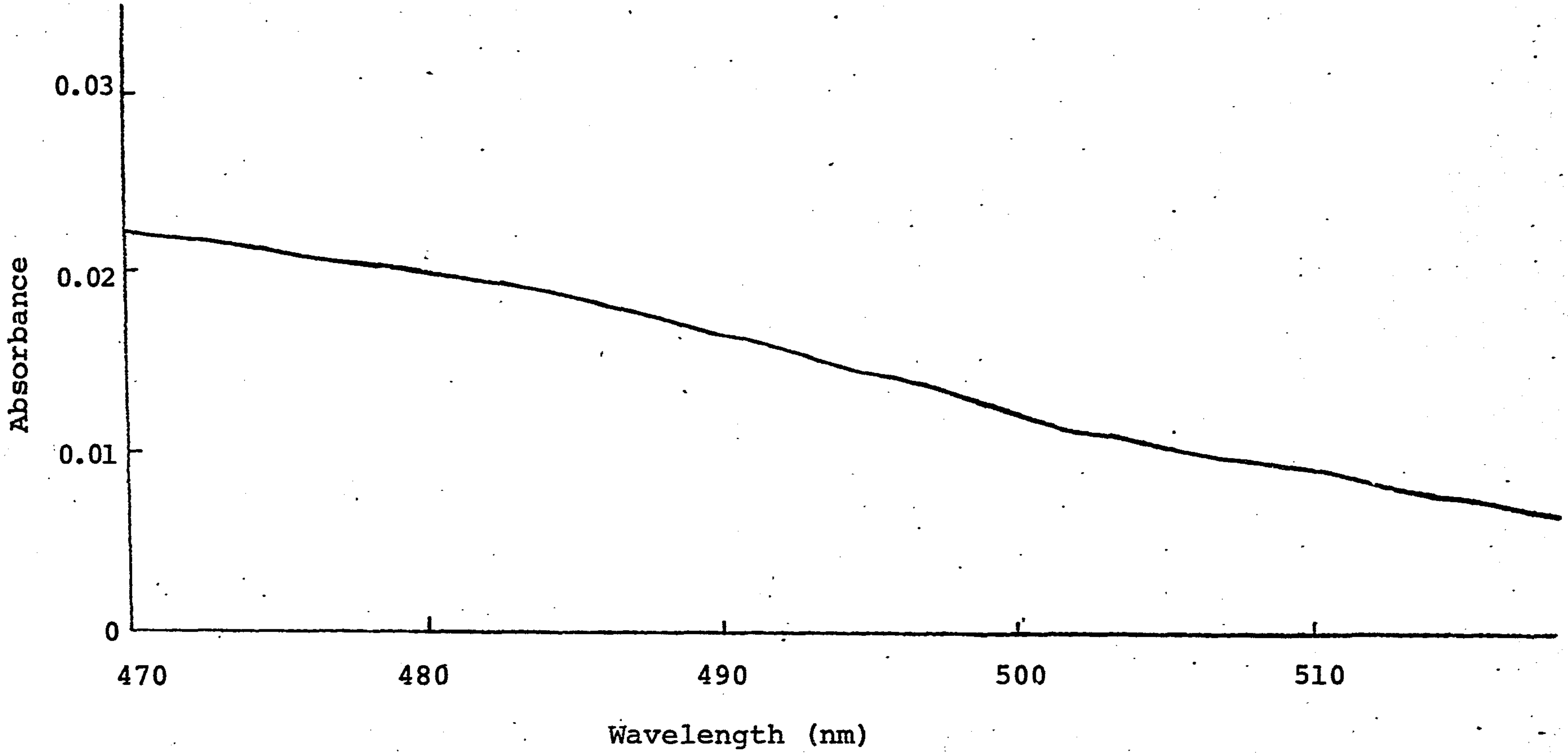
$$\text{intercept} = \frac{1}{(\varepsilon_{QA}-\varepsilon_Q)} = 0.0860$$

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Figure 27: Spectrum of 6.84 x 10^{-2}M* 1,4-Naphthoquinone and 2.28 x 10^{-3}M* Anthracene In 4:1 Benzene:2-Propanol v. a Reference Solution of 6.84 x 10^{-2}M 1,4-Naphthoquinone in 4:1 Benzene:2-Propanol.

*initial concentrations before complex formation



1,4-naphthoquinone present was known, and conversion of 1,4-naphthoquinone to 1,4-naphthalenediol was followed by absorbance decreases at 422.0 nm, it was possible to calculate the total quantity of 1,4-naphthoquinone present, after an irradiation. Measurement of the absorbance at 490.0 nm enabled a calculation, using the equation derived above, of the concentration of uncomplexed quinone. The absorptivity of 1,4-naphthoquinone in the irradiation apparatus was calculated from the initial fraction of radiation absorbed by the solution containing 1,4-naphthoquinone only. It was then possible to calculate the absorbance of the uncomplexed 1,4-naphthoquinone in the irradiated solution, and thus the quantity of radiation absorbed by the uncomplexed quinone could also be calculated.

Spectra were taken of 2-propanol solutions of 6.3×10^{-4}M acridine yellow and 9.6×10^{-4}M 1,4-naphthoquinone in a split cell, before and after mixing. The small differences (Table 9) suggest that in the acridine yellow and 1,4-naphthoquinone solutions discussed in section 5.10 very little complex was formed, and that its absorbance at 436 nm was negligible. However, when an ethanol solution (both acridine yellow and

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 9: Absorbance Changes of 2-Propanol Solutions of 1,4-Naphthoquinone and Acridine Yellow Upon Mixing

Wavelength (nm)	Absorbance before mixing	Absorbance change upon mixing
490.0	0.097	+0.006
458.0	1.296	-0.004
436.0	0.882	0.000
331.0	1.215	+0.003

concentrations: 9.6×10^{-4}M 1,4-naphthoquinone
6.3×10^{-4}M acridine yellow

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1,4-naphthoquinone are more soluble in ethanol than in 2-propanol) 10^{-2}M in both acridine yellow and 1,4-naphthoquinone is frozen in liquid nitrogen, the resultant glass appears reddish. In order to check if complex formation occurred in solution, in the case of more concentrated solutions than those described in section 5.10., stock solutions of 3.53×10^{-2}M 1,4-naphthoquinone in ethanol and 3.32×10^{-2}M acridine yellow in ethanol (both nearly saturated) were prepared. Each solution was added to an equal volume of ethanol to give a solution of one-half the concentration. Equal volumes of the stock solutions were combined to give a third solution. Spectra of these three solutions were obtained, using 0.05 mm. path length cells, and it was found that the spectrum of the solution containing both quinone and dye differed only slightly from the spectrum obtained by adding the spectra of the quinone and dye solutions (Table 10). It was concluded that very little complex formation occurred in this case as well.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table 10 : Absorbances of Ethanol Solutions of 1,4-Naphthoquinone, Acridine Yellow and A Mixture of 1,4-Naphthoquinone and Acridine Yellow

	Wavelength (nm)			
	490.0	458.0	436.0	331.0
1) 1.77 x 10^{-2}M 1,4-naphthoquinone	0.002	0.004	0.005	0.342
2) 1.66 x 10^{-2}M acridine yellow	0.094	1.488	1.035	0.015
3) 1.77 x 10^{-2}M 1,4-naphthoquinone and 1.66 x 10^{-2}M acridine yellow	0.099	1.474	1.022	0.359
calculated absorbance of solution 3 (sum of absorbances for solutions 1 and 2)	0.096	1.492	1.040	0.357
difference between observed and calculated absorbances for solution 3	+0.003	-0.018	-0.018	+0.002

absorbance

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

6. DISCUSSION AND CONCLUSIONS

6.1. Photoreduction of 1,4-Naphthoquinone in Benzene

Previous workers may have overlooked the photoreduction of 1,4-naphthoquinone in benzene for a number of reasons. Upon irradiation of 1,4-naphthoquinone in benzene neither the quinhydrone of 1,4-naphthoquinone and 1,4-naphthalenediol nor 1,4-naphthalenediol itself precipitate. Di-naphthoquinone does precipitate and it may have been assumed that any other products present were polymeric in nature. Rennert et. al.[32] studied the dimerization reaction for very small initial increments of reaction and apparantly assumed that dimerization was the only reaction taking place initially. This was a valid assumption as long as any additional products were assumed to be polymeric. If a solution of 1,4-naphthalenediol is exposed to air, the 1,4-naphthalenediol will become oxidized. This may also have prevented its detection. Indeed, it was the fortuitous observation of the thermochromism of irradiated benzene solutions of 1,4-naphthoquinone that first suggested that photoreduction was a possibility.

Photoreduction of 1,4-naphthoquinone in benzene to 1,4-naphthalenediol was shown to occur by identification of the complex formed by 1,4-naphthoquinone and 1,4-naphthalenediol upon rapid freezing, by identification of the quinhydrone complex of 1,4-naphthoquinone and 1,4-naphthalenediol formed when the solvent is evaporated, and by isolation of 1,4-

---

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

naphthalenediol from the photoproduct mixture. Comparison of the yields of di-naphthoquinone and quinhydrone showed that photoreduction of 1,4-naphthoquinone in benzene is a major competing reaction to photodimerization.

6.2. Identification of the Hydrogen Donor

The benzene solvent was identified as the hydrogen donor by a process of elimination. Di-naphthoquinone was shown to have no effect on formation of 1,4-naphthalenediol by irradiated 1,4-naphthoquinone in benzene, measured fluorimetrically, when the initial concentration of added di-naphthoquinone was near saturation. Dimerization of 1,4-naphthoquinone in carbon tetrachloride, but lack of 1,4-naphthalenediol formation in this hydrogen free solvent, indicated that the benzene solvent, rather than the 1,4-naphthoquinone itself, or the di-naphthoquinone photoproduct, was the hydrogen donor.

6.3. Photoreduction of Other Quinones in Benzene

Benzene has also been shown to reduce benzoquinone and phenanthraquinone. Paoloni and Marini-Bettolo[41] found that irradiation of benzoquinone in benzene yields quinhydrone. Rubin and Neuwirth-Weiss[35] found that irradiation of phenanthraquinone in benzene yielded phenanthraquinhydrone, biphenyl, an adduct of phenanthraquinone and benzene, and

---

[41] L. Paoloni and G.B. Marini-Bettolo, Gazz. Chim. Ital., 87, 395 (1957).

[35] M.B. Rubin and Z. Neuwirth-Weiss, Chem. Commun., 1968, 1607.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

uncharacterized material as the products. They suggested that the presence of biphenyl and a quinhydrone suggest the intermediacy of phenyl and phenanthraquinone semiquinone radicals, resulting from abstraction of a hydrogen atom from benzene by excited phenanthraquinone.

6.4. Mechanism for Photoreduction of 1,4-Naphthoquinone in Benzene

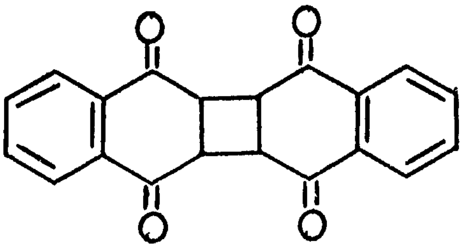
The mechanism proposed by Rubin and Neuwirth-Weiss[35] for the photoreduction of phenanthraquinone in benzene seems applicable to the photoreduction of 1,4-naphthoquinone as well. The absence of biphenyl or terphenyls in the case of 1,4-naphthoquinone in benzene can be accounted for by the hundred-fold larger concentration of quinone present (3×10^{-2}M) in this study, resulting in effective competition of 1,4-naphthoquinone with phenyl radical for other phenyl radicals. In this case as well, the complexity of the photoproduct mixture suggests that there are quite a few entities present that might also react with phenyl radical. Among the possibilities are semiquinone radicals, which reacted with benzene in the study of Rubin and Neuwirth-Weiss[35], di-naphthoquinone, and compounds containing two, three or four 1,4-naphthoquinones. The presence of compounds containing multiples of 1,4-naphthoquinone was suggested by the mass spectral data, but no attempt was made to analyze the isolated products.

---

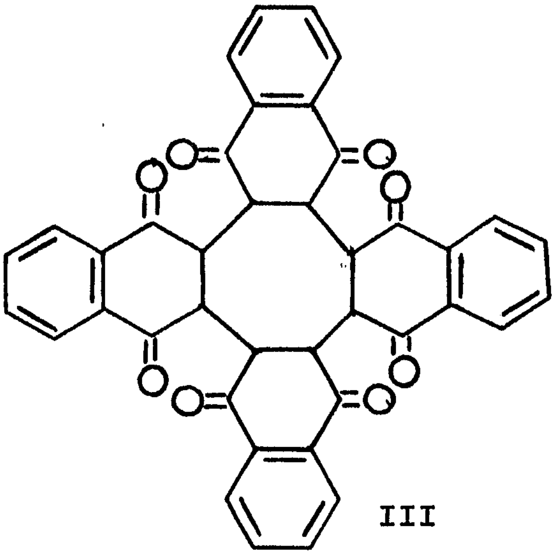
35. M.B. Rubin and Z. Neuwirth-Weiss, Chem. Commun., 1968, 1607.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

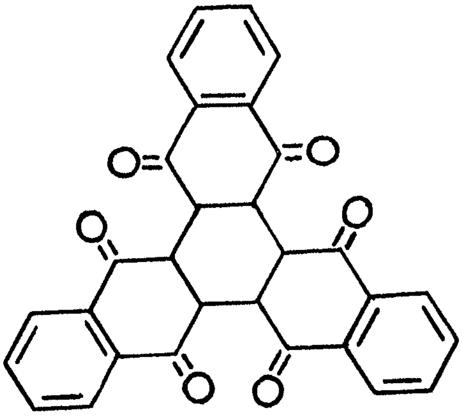
The structures shown below in addition to di-naphthoquinone(I) which is known to be present are possible exocyclic addition products (II and III), a possible oxetane dimer IV and linear polymers V:



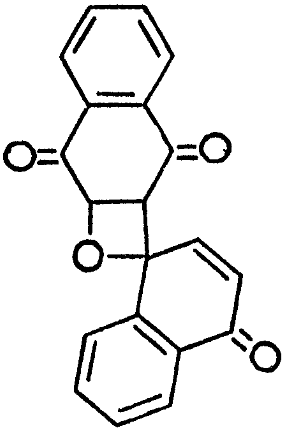
I



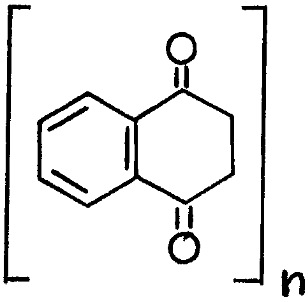
III



II



IV



V

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

6.5. Reactions of 1,4-Naphthoquinone in Carbon Tetrachloride

The fact that several products in addition to 1,4-naphthoquinone were found in carbon tetrachloride, and that these products did not contain chlorine, suggests that it would not be possible to find a solvent in which dimerization only occurred. In view of the fact that carbon tetrachloride would be expected to react with free radicals,[72] and chlorine was not found in the products, the dimerization and other reactions of 1,4-naphthoquinone with other 1,4-naphthoquinones or with di-naphthoquinone do not proceed via free radical intermediates.

6.6. Complex Formation Between 1,4-Naphthoquinone and 1,4-Naphthalenediol

Thermochromic changes observed in irradiated solutions of 1,4-naphthoquinone are ascribed to molecular complex formation similar to that suggested for p-benzoquinone and hydroquinone by Szent-Gyorgyi.[73] He observed that sudden freezing at dry ice temperatures of a mixture of p-hydroquinone and p-quinone in solution results in formation of a dark ultramarine blue solid. If to one part 10^{-2}M quinone one adds one part 10^{-2}M quinhydrone, and one part 10% glucose, sudden freezing results in the formation of a carrot red color. If the tube is allowed to warm, the carrot-red color shoots

---

[72] J. Saltiel, H.C. Curtis and B. Jones, Mol. Photochem., 2, 331 (1970).

[73] A. Szent-Gyorgyi, Introduction to a Submolecular Biology, Academic Press, New York, 1960, pp. 76-80.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

over into ultramarine blue. As in the benzoquinone system, the red complex in the 1,4-naphthoquinone and 1,4-naphthalenediol system may be the metastable form of the blue molecular complex. Ultraviolet-visible spectrophotometric evidence, with the use of a split compartment mixing cell for difference spectroscopy, was presented for the dissociation of the complex of 1,4-naphthalenediol and 1,4-naphthoquinone in benzene at ambient temperature. In a study of this complex, Kotera[74] showed this to be the case in cyclohexane by infrared spectroscopy. By making mixtures of 1,4-naphthoquinone and 1,4-naphthalenediol in ether in various molar ratios, and then stripping off the solvent and taking infrared spectra of the solid residue, Katera showed that the complex of 1,4-naphthoquinone and 1,4-naphthalenediol was a 1:1 complex.

6.7. Identity of the Excited State in Photoreduction

The quantum yield of photoreduction of 1,4-naphthoquinone was shown to vary neither with wavelength, nor with concentration differences spanning two orders of magnitude. This is consistent with the work reported by Rennert et. al.[32] Their contention that the n,π* state is the photochemically reactive state is confirmed. The experiments reported in this work are a stronger proof than previously offered because the quantum yield for the π,π* transition was determined at the

---

[74] K. Kotera, Yakugaku Zasshi, 80, 659 (1960).

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

absorption peak of 1,4-naphthoquinone, and because the quantum yield for the n,π* transition was determined farther to the red and was at a point less likely to represent overlap with the π,π* transition, any uncertainty in ascribing this transition to the n,π* excited state was removed. Within the experimental error one may conclude that 100 percent efficient conversion of the π,π* state to the lower lying n,π* state occurs. The somewhat higher values for the quantum yields determined are ascribed to more complete degassing, and to better quantitative measurements. These measurements firmly establish the hypothesis of Rennert et al.[32] and Schulte-Frohlinde and von Sonntag[19], whose measurements were not as definitive, however, as those reported here.

6.8. Importance of the Apparatus for Quantitative Photochemistry

The quantum yield determinations were made possible primarily by the apparatus developed for quantitative photochemistry. Accurate measurement of the fraction of light absorbed was particularly important for the dilute solution at 334 nanometers because of the low concentration used, and for the solution at 436 nm, where the concentration was high but the absorbance was low. Two important features of the instrument that were not utilized in this work but are expected to be very useful to photochemists in the future are the

---

[32] J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967).

[19] D. Schulte-Frohlinde and C. von Sonntag, Z. Physik. Chem. N.F., 44, 313 (1965).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

provisions for cross illumination, and the incorporation of a corrected response photomultiplier tube. This detector enables the use of very wide bandwidths to attain high incident intensities without sacrificing accuracy in the measurement of the number of photons absorbed.

6.9. Multiplicity of the Excited State in Photoreduction

The sensitizing and quenching experiments performed provide evidence that the first excited triplet state rather than the first excited singlet state is the photochemically reactive state. Irradiation of a mixture of 1,4-naphthoquinone and acridine yellow, which has a higher triplet energy than 1,4-naphthoquinone, but a lower singlet energy, resulted in sensitization of 1,4-naphthoquinone photoreduction, and also in formation of a product of 1,4-naphthoquinone and acridine yellow. This product was shown to be formed by excited acridine yellow and ground state 1,4-naphthoquinone rather than between excited 1,4-naphthoquinone and ground state acridine yellow. Millich and Oster[75] reported that acridine yellow, in an aqueous solution of pH 4, is photoreduced in the presence of allylthiourea. The quantum yield was not reported. However, the quantum yield for photoreduction of an aqueous solution of 2×10^{-5}M 3,6-diaminoacridine and 1×10^{-2}M allylthiourea concentration at pH 4 was reported

---

[75] F. Millich and G. Oster, J. Amer. Chem. Soc., <u>81</u>, 1357 (1959).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

to be 1.0 x 10^{-2} mole/einstein. The reaction was said to be "less proficient" at higher pH, but quantitative information was not supplied. The relatively short periods of irradiation and the neutral pH in this research apparently resulted in relatively little photoreduction of acridine yellow.

Addition of anthracene, which has a lower triplet energy than 1,4-naphthoquinone but a higher singlet energy, to 1,4-naphthoquinone in a mixed solvent system of 4:1 benzene: 2-propanol resulted in quenching of the photoreduction reaction.

6.10. Complex Formation With Acridine Yellow and Anthracene

The fact that 1,4-naphthoquinone forms complexes with both anthracene and acridine yellow, although such complex formation was not significant in the sensitizing experiment performed, suggests a possible mode of interaction for energy transfer to take place. Just as 1,4-naphthoquinone and 1,4-naphthalenediol form a complex via interaction of their π orbitals it may be that the complexes formed between anthracene and 1,4-naphthoquinone and between acridine yellow and 1,4-naphthoquinone, as well as the energy transfer observed, are due to similar interactions.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

7. Bibliography

E.W. Abrahamson and I. Panik, "The Spectroscopy and Photochemistry of Anthraquinone Dyes", Advances in Molecular Spectroscopy, Vol.I, Pergamon Press, Oxford, 1962, pp. 354-62. [30]*

B. Atkinson and M. Di, Trans. Faraday Soc., 54, 1331 (1958). [10]

A. Berthoud and D. Porret, Helv. Chim. Acta., 17, 694 (1934). [9]

J. Beutel, R.J. Ruszkay and J.F. Brennan, J. Phys. Chem., 73, 3240 (1969).

J.L. Bolland and H.R. Cooper, Proc. Roy. Soc., A225, 405 (1954). [12]

G.J. Brearly and M. Kasha, J. Amer. Chem. Soc., 77, 4462 (1955).

N.K. Bridge, Trans. Faraday Soc., 56, 1001 (1960).

N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 259 (1958). [15]

N.K. Bridge and G. Porter, Proc. Roy. Soc., A244, 276 (1958). [16]

E.F.H. Brittain, W.O. George and C.H.J. Wells, Introduction to Molecular Spectroscopy, Academic Press, London, 1970, pp. 102-106. [71]

J.M. Bruce, J. Chem. Soc., 1962, 2782. [48]

J.M. Bruce, Quart. Rev. Chem. Soc., 21, 405 (1967).

D. Bryce-Smith and A. Gilbert, J. Chem. Soc., 1964, 2428.

J.G. Burr, "Advances in the Photochemistry of Nucleic Acid Derivatives", Advances in Photochemistry, Vol. 6, ed. by W.A. Noyes Jr., G.S. Hammond, and J.N. Pitts, Jr., Interscience Publishers, a division of John Wiley and Sons, New York, 1968, 193-299. [57]

---

*Numbers in brackets after references refer to footnotes in the text.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

J.G. Calvert and J.N. Pitts, Jr., Photochemistry, John Wiley and Sons, Inc., New York, 1966.

P.A. Carapellucci, H.P. Wolf and K. Weiss, J. Amer. Chem. Soc., 91, 4635 (1969). [26]

S.A. Carlson and D.M. Hercules, J. Amer. Chem. Soc., 93, 5611 (1971). [37]

S.A. Carlson and D.M. Hercules, Photochem. Photociol., 17, 123 (1973). [27]

G. Ciamician, Gazz. Chim. Ital., 16, 111 (1886). [1]

G. Ciamician and P. Silber, Ber. dtsch. Chem. Ges., 19, 2899 (1886).

G. Ciamician and P. Silber, Ber. dtsch. Chem. Ges., 34, 1530 (1901). [3]

R.C. Cookson, D.A. Cox and J. Hudec, J. Chem. Soc., 1967, 4499. [49]

R.C. Cookson and J. Hudec, Proc. Chem. Soc., 1959, 11. [47]

D. Creed, H. Werbin and E.T. Strom, J. Amer. Chem. Soc., 93, 502 (1971). [55]

H.H. Dearman and A. Chan, J. Chem. Phys., 44, 416 (1966). [33]

J. Dekker, P.J. von Vuuren and D.P. Venter, J. Org. Chem., 33, 464 (1968) [53]

J. Eisinger and A.A. Lamola, Mol. Photochem., 1, 209 (1969). [59]

P.S. Engel and B.M. Monroe, "Complications in Photosensitized Reactions", Advances in Photochemistry, Vol. 8, ed. by J.N. Pitts, Jr., G.S. Hammond, and W.A. Noyes, Jr., Interscience Publishers, a division of John Wiley and Sons, New York, 1971, pp. 245-313.

K. Golankiewicz and L. Strekowski. Mol. Photochem., 4, 189 (1972). [61]

E.H. Gold and D. Ginsburg, J. Chem. Soc. (C), 1967, 15. [50]

U. von Gizycki, Liebigs Ann. Chem., 753, 1 (1971).

D. Grossman, Ph.D. thesis, City University of New York, 1973. [64]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

B.J. Hales and J.R. Bolton, Photochem. Photobiol., **12**, 239 (1970). [20]

W.N. Hartley and A.G.G. Leonard, J. Chem. Soc., 1909, 34. [43]

C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., **A235**, 518 (1956). [65]

H. Hermann and G.O. Schenck, Photochem. Photobiol., **8**, 255 (1968).

P. Job, Ann. Chim., [10] **9**, 113 (1928). [69]

M. Kamiya, T. Hamaoka and T. Kwan, Chem. Pharm. Bull., **14**, 358 (1966).

M. Kamiya, K. Hatano and T. Kwan, Chem. Pharm. Bull., **15**, 932 (1967). [24]

R.O. Kan, *Organic Photochemistry*, McGraw Hill Book Company, New York, 1966, pp. 169-72.

D.R. Kemp and G. Porter, Chem. Commun., 1969, 1029.

D.R. Kemp and G. Porter, Proc. Roy. Soc., A326, 117 (1971). [38]

H. Klinger, Ber. dtsch. chem. Ges., **19**, 1862 (1886). [2]

K. Kotera, Yakugaku Zasshi, **80**, 659 (1960). [74]

A. Kuboyama and S. Matsuzaki, Reports of the Government Chemical Industrial Research Institute, Tokyo, Vol. 64, No. 3, pp. 105-110 (1969). [68]

A.A. Lamola, "Electronic Energy Transfer in Solution: Theory and Applications", *Energy Transfer and Organic Photochemistry*, ed. by A.A. Lamola and N.J. Turro, Vol. 14 of *Technique of Organic Chemistry*, ed. by P.A. Leermakers and A. Weissberger, Interscience Publishers, a division of John Wiley and Sons, New York, 1969, pp. 17-132.

A.A. Lamola, Mol. Photochem., **4**, 107 (1972). [58]

A.A. Lamola, Pure Appl. Chem., **24**, 599 (1970). [60]

P.A. Leighton and G.S. Forbes, J. Amer. Chem. Soc., **51**, 3549 (1929). [8]

G.N. Lewis and M. Kasha, J. Amer. Chem. Soc., **66**, 2100 (1944). [67]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

C. Lieberman and M. Ilinski, Ber. dtsch. chem. Ges., 18, 3193 (1885). [42]

H. Linschitz, J. Rennert and T.M. Korn, J. Amer. Chem. Soc., 76, 5839 (1954). [13]

J. Madinaveitia, Rev. acad. cienc. Madrid, 31, 617 (1934). [44]

L. Michaelis and M.P. Schubert, Chem. Rev., 22, 437 (1938).

F. Millich and G. Oster, J. Amer. Chem. Soc., 81, 1357 (1959). [75]

A. Mustafa, Nature, 162, 856 (1948). [6]

J. Nafisi-Movaghar and F. Wilkinson, Trans. Faraday Soc., 66, 2257 (1970). [21]

J. Nafisi-Movaghar and F. Wilkinson, Trans. Faraday Soc., 66, 2268 (1970). [22]

S. Nagakura and A. Kuboyama, J. Amer. Chem. Soc., 76, 1003 (1954). [31]

W.A. Noyes, Jr. and P.A. Leighton, The Photochemistry of Gases, Reinhold Publishing Corporation, New York, 1941.

L. Paoloni and G.B. Marini-Bettolo, Gazz. Chim. Ital., 87, 395 (1957). [41]

R.T. Plimpton, J. Chem. Soc., 37, 635 (1880). [62]

G. Porter and M.W. Windsor, Nature, 180, 187 (1957). [14]

D. Rabinovich and G.M.J. Schmidt, J. Chem. Soc. (B), 1967, 144. [51]

J. Rennert, S. Japar and M. Guttman, Photochem. Photobiol., 6, 485 (1967). [32]

J. Rennert, M. Mayer, J. Levy and J. Kaplan, Photochem. Photobiol., 10, 267 (1969). [25]

R.D. Rieke and W.E. Rich, J. Amer. Chem. Soc., 92, 7349 (1970).

M.B. Rubin, Fortschr. Chem. Forschung, 13, 251 (1969).

M.B. Rubin and Z. Neuwirth-Weiss, Chem. Commun., 1968, 1607. [35]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

M.B. Rubin and Z. Neuwirth-Weiss, J. Amer. Chem. Soc., 94, 6048 (1972). [36]

J. Saltiel, H.C. Curtis and B. Jones, Mol. Photochem., 2(4), 331 (1970). [72]

A. Schönberg and A. Mustafa, Chem. Revs., 40, 181 (1947). [7]

A. Schönberg and A. Mustafa, J. Chem. Soc., 1944, 67. [4]

A. Schönberg and A. Mustafa, J. Chem. Soc., 1945, 657. [5]

A. Schönberg, A. Mustafa, M.Z. Barakat, N. Latif, R. Moubasher and A. Mustafa, J. Chem. Soc., 1948, 2126. [45]

D. Schulte-Frohlinde and C. von Sonntag, Z. Physik. Chem. N.F. 44, 313 (1965). [19]

J.K. Setlow, "The Molecular Basis of Biological Effects of Ultraviolet Radiation and Photoreactivation", Current Topics in Radiation Research, Vol. 2, ed. by M. Ebert and A. Howard, North-Holland Publishing Compnay, Amsterdam, 1966, pp. 195-248. [56]

R. Stair, W.E. Schneider and J.K. Jackson, Applied Optics, 2, 1151 (1963). [65a]

D. Stull, J. Amer. Chem. Soc., 59, 2726 (1937). [63]

A. Szent-Györgyi, Introduction to a Submolecular Biology, Academic Press, New York, 1960, pp. 76-80. [80]

K. Tickle and F. Wilkinson, Trans Faraday Soc., 61, 1981 (1965). [11]

N.J. Turro, Molecular Photochemistry, W.A. Benjamin, Inc., New York, 1965.

D.P. Venter and J. Dekker, J. Org. Chem., 34, 2224 (1969). [54]

W.C. Vosburgh and G.C. Cooper, J. Amer. Chem. Soc., 63, 437 (1941). [70]

P. Walker, J. Chem. Soc., 1963, 5545. [18]

P.J. Wagner and G.S. Hammond, "Properties and Reactions of Organic Molecules in Their Triplet States", Advances in Photochemistry, Vol. 5, ed. by W.A. Nöyes, Jr., G.S. Hammond, and J.N. Pitts, Jr., Interscience Publishers, a division of John Wiley and Sons, New York, 1968, pp. 21-156.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

C.F. Wells, Trans. Faraday Soc., 57, 1703 (1961). [28]

C.F. Wells, Trans. Faraday Soc., 57, 1719 (1961). [29]

H. Werbin and E.T. Strom, J. Amer. Chem. Soc., 90, 7296 (1968). [52]

F. Wilkinson, J. Phys. Chem., 66, 2569 (1962). [17]

F. Wilkinson, G.M. Seddon and K. Tickle, Ber. Bunsenges. Phys. Chem. 72, 315 (1968). [34]

H.P. Wolf, J.J. Bohning, P.A. Schnieper and K. Weiss, Photochem. Photobiol., 6, 321 (1967).

S.K. Wong, D.A. Hutchinson and J.K.S. Wan, J. Chem. Phys., 58, 985 (1973). [40]

S.K. Wong, W. Sytnyk and J.K.S. Wan, Can. J. Chem., 50, 3052 (1972). [23]

S.K. Wong and J.K.S. Wan, J. Amer. Chem. Soc., 94, 7197 (1972). [39]

J.A. Yankeelov, Jr., Anal. Biochem., 6, 287 (1963). [66]

E. Zavarin, J. Org. Chem., 23, 47 (1958). [46]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.