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RADIATION INDUCED REACTIONS IN NONAQUEOUS SOLUTIONS

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Berkeley, California

October 25, 1956

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Re: Errata - UCRL-3422

Please make the following corrections in your copies of UCRL-3422:

Page 49	Figure 18 represents data for reaction in bromobenzene, not reaction in chlorobenzene.
Page 62	Reference to Fig. 30, not Fig. 26.
Page 63	In Eq. III-5, replace 5/2 with 11/2.
Page 63	In Table XI, divide all values by 2.2.
Page 81	References 8, 9, and 10 are to J. chim. phys., not J. Chem. Phys.

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Laddie Ray Griffith

July, 1956

(Ph.D. Thesis)

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RADIATION INDUCED REACTIONS IN NONAQUEOUS SOLUTIONS

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Department of Chemistry and Chemical Engineering
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July, 1956

ABSTRACT

The photoinduced disappearance of 1,1-diphenyl-2-picryl-hydrazyl, DPPH, in solution in several organic liquids was studied.

Solutions of DPPH in cyclohexane, benzene, toluene, chlorobenzene and bromobenzene were irradiated with ultraviolet light of wave length 3126 to 3130 A. The initial rates of the disappearance of DPPH were studied spectrophotometrically and were found to be nearly independent of the amount of light absorbed by DPPH except for DPPH in cyclohexane. The rates were, however, proportional to the amount of light absorbed by the solvent.

The results indicate that the reaction is one of short-lived excited species of the solvent molecules in benzene, toluene, chlorobenzene, and bromobenzene. Furthermore, the excited species responsible for the reaction is the lowest triplet state of the solvent molecule. A reaction of free radicals produced by the photodissociation of bromobenzene probably contributes to the rate of disappearance of DPPH in bromobenzene.

Reactions of excited singlet states would not be observed in the DPPH concentration range studied because the lifetimes of the excited singlet states of these molecules are short compared with the time between collisions of these excited states with DPPH.

Investigators using the rate of disappearance of DPPH as a free-radical counting technique in radiation chemistry must consider that DPPH also reacts with at least some of the excited species present in the irradiated solutions.

I. INTRODUCTION

The mechanism by which energy is transferred from high-energy radiation -- i.e., x-rays, γ-rays, protons, etc. -- to matter is very complex and not clearly understood. It is known, for instance, that one of the primary processes is ionization,[17,20] yielding still another high-energy particle, the electron, which must lose its energy by more processes of ionization, excitation, and ultimately the combination of this electron with a positively charged species to yield an excited state of a stable molecule. Other primary processes that may occur are excitation to unstable states which dissociate into reactive fragments or stable molecules, excitation to excited states of stable molecules, and direct production of reactive free radicals.

It would be of great interest to the field of radiation chemistry if the relative importances of the many primary acts involved in the absorption of high energy radiation could be determined quantitatively.

An attempt has been made by Prevost-Bernas et al.,[32] to establish quantitatively the number of free radicals produced when organic liquids are irradiated with high-energy radiations such as γ-rays, x-rays, protons, fast neutrons, etc. The method used by Prevost-Bernas et al. depends upon the reaction of the stable organic free radical α,α-diphenyl-β-picryl-hydrazyl, hereafter abbreviated DPPH, with the free radicals produced when the high-energy radiation is absorbed by the organic liquids.

During the last six or seven years, the use of DPPH as a free radical scavenger in the liquid phase has attracted considerable attention. The stability of DPPH and its presence in the monomeric form, both in the solid state and in solution in many organic liquids, adds immeasurably to

the convenience of its use for this purpose. The intense absorption band in the visible spectrum of DPPH makes simple colorimetric analysis practical when the reaction products do not display appreciable absorption in the same region.

Bawn and Mellish[a] state that they have demonstrated the efficiency of DPPH as a free-radical scavenger of thermally produced free radicals in the thermal disproportionation of benzoyl peroxide and azobisisobutyronitrile. The efficiency of DPPH as a free-radical scavenger has been questioned by Bevington[a] in the thermal disproportionation of azobisisobutyronitrile. The efficiency of free-radical scavengers at low scavenger concentrations has been questioned theoretically by Richard Noyes.[a]

The inefficiency of DPPH in the cases mentioned is commonly accepted as the inability of DPPH to compete with the recombination of the radicals before diffusive displacements of the free radicals carries them sufficiently far from the neighborhood of the primary reaction that their recombination is unlikely. This effect was first explained by Frank and Rabinowitch[12] and was termed the "cage effect."

Goldschmidt and Renn[14] first prepared and characterized DPPH in 1922. They reported a characteristic visible and ultraviolet absorption spectrum of DPPH with maxima at 3300 A ($\log \epsilon = 4.2$) and at 5300 A ($\log \epsilon = 3.81$) in chloroform. Benington[3] in 1952 further characterized the structure of DPPH by studying the infrared, ultraviolet, and visible spectra of DPPH and several related compounds. The accepted structure of DPPH is usually represented by

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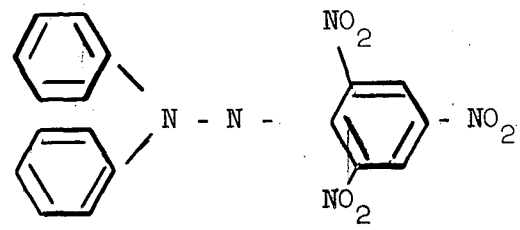
[a]Discussed in detail later in the section



It has been established that DPPH does not dimerize in solution and does not react with oxygen.[14]

Bartlett and Kwart[1] studied the behavior of DPPH as an inhibitor of the benzoyl peroxide-induced polymerization of vinyl acetate at 45°C kinetically by a dilatometric method. At concentrations of DPPH of about 10^{-5} mole/liter of solution, the polymerization was inhibited completely until the DPPH color nearly disappeared; at this time the polymerization commenced and gradually reached its normal rate.

It was concluded by Bartlett and Kwart that DPPH stops one chain or "growing radical" per molecule of DPPH present, since the polymerization was completely inhibited until the DPPH was all or mostly used up.

In the same manner Matheson, Auer, Bevilacqua, and Hart[23] concluded that DPPH stops one chain per molecule of DPPH in the polymerization of styrene.

Interpreting the works by Bartlett and Kwart and by Matheson, Auer, Bevilacqua, and Hart as meaning that DPPH reacts with all radicals produced in the thermal disproportionation of benzoyl peroxide, Bawn and Mellish[2] used DPPH to measure the rate of the thermal disproportionation reactions of benzoyl peroxide and azobisisobutyronitrile.

$$(CH_3)_2C(CN) \cdot N{:}N \cdot C(CN)(CH_3)_2 \longrightarrow 2(CH_3)_2\,C(CN)\cdot + N_{2(g)} \qquad \text{(I-1)}$$

$$C_6H_5\ COOOOC\ C_6H_5 \longrightarrow 2\ C_6H_5CO_2\ . \qquad \text{(I-2)}$$

Activation energies measured by this method agree well with those determined by previous workers who measured the rate of the reactions by different methods, e.g., nitrogen evolution in the thermal disproportionation of azobisisobutyronitrile; however, the absolute rates observed by Bawn and Mellish in these thermal disproportionation reactions were somewhat slower than those observed previously.[36]

This discrepancy can be explained by saying that some of the radicals produced combine in the Frank-Rabinowitch "caging effect" and do not react with DPPH. That each DPPH molecule stops one "growing chain" in a radical-induced polymerization is not sufficient evidence for saying that DPPH reacts with all of the radicals produced. Radicals that combine in the "caging effect" would not be effective in polymerization initiation.

Experimental verification of this theory can be seen in the experimental results of J. C. Bevington.[4] Bevington, using larger DPPH concentrations in benzene solution, showed that DPPH reacts with only about 70% of the radicals produced in the thermal disproportionation of azobisisobutyronitrile.

Henglein[16] has attempted to measure the rate of ultrasonic irradiation-induced depolymerization by the rate of disappearance of DPPH in solutions of polymers. Radicals produced in this manner are very large and reactions with DPPH are complicated.

Finally, it may be stated that very little is known about the products of the reactions causing the fading of the DPPH solutions. One product,

diphenylpicrylhydrazine, has been tentatively identified by Wild.[37] Many other products are observed but no others have been identified. Furthermore, attempts to prepare compounds with the formula DPPHR have not been successful.

The research of Prevost-Bernas et al. and Chapiro[8-10] has shown that in several organic liquids, the rate of disappearance of DPPH is dependent only upon the quantity of high-energy radiation (γ-rays, x-rays, protons, and fast neutrons) absorbed by the solution. This rate of disappearance of DPPH has been interpreted by these authors as a measure of the number of free radicals produced by the high-energy radiation in the solvent.

To explain their results, Prevost-Bernas et al. and Chapiro have proposed a simplified mechanism for the disappearance of DPPH involving the reaction of DPPH with all the free radicals produced, and only the free radicals.

$$S \rightsquigarrow R\cdot + R\cdot \qquad \text{(I-3)}$$

$$R\cdot + R\cdot \longrightarrow S \qquad \text{(I-4)}$$

$$R\cdot + \text{DPPH} \longrightarrow \text{DPPHR} \qquad \text{(I-5)}$$

That most of the high-energy radiation absorbed by the solvents in most cases does not lead to compound formation or radical production is evident from known yields of products[11,15] and estimates of radical yields as determined by Prevost-Bernas et al. It then seems reasonable that a large number of molecules in these solutions do not have enough energy to disproportionate to radicals, but may have enough energy to insure reaction with DPPH.

In addition to radicals and excited molecules, these solutions under high-energy irradiation (γ-rays, x-rays, and protons) contain ions that

may or may not react with DPPH and, in some cases, unsaturated compounds, which are known to react with DPPH.[11,15,32]

It then seems that the nature of the reactions induced by the high-energy radiation used by Prevost-Bernas et al. and Chapiro is too complex to interpret very simply, because of the formation of so many excited species.

In order to determine whether DPPH reacts with excited molecules, Magat[22] irradiated a solution of DPPH in methanol with infrared radiation in an attempt to excite the OH vibration of methanol and thereby induce a reaction of methanol with DPPH. This attempt was unsuccessful.

One might have expected that Magat's approach -- to investigate the possibility of the reaction of methanol excited by infrared irradiation with DPPH -- would not be successful. Since the excited vibrational levels are always thermally populated to some extent, the success of this experiment depends upon substantially increasing the population of the excited vibrational levels. The major problem involved in a study of this type would be one of lifetimes of the excited vibrational states. The lifetimes of excited vibrational states in solution are much shorter than the lifetimes of nonforbidden electronic transitions in solution. This conclusion is based on the fact that fluorescence is observed only from the ground states of the excited electronic states in solution.

The lifetimes of the excited vibrational states are probably on the order of 10^{-11} to 10^{-12} second, since the collisions are reasonably efficient in the deactivation process.[20] Since diffusive displacements occur with a frequency of about 10^{11} per second, it is seen that the excited vibrational state probably makes no diffusive displacements, on

the average, before deactivation by collision occurs. It would then require a very large mole fraction of DPPH in methanol in order for any collisions between DPPH and the activated methanol to occur. Detection of very small changes in DPPH concentration at $N_{DPPH} = 0.1$ to 0.5 would be extremely difficult. It is very doubtful that any effect could be seen in the above experiment.

It is interesting to note that the number of quanta emitted in the frequency range 3550 to 3650 cm^{-1} from one square centimeter of an infrared source operating at $1000^{o}K$ is approximately 5×10^{17} per second or about 7.5×10^{-3} calorie per second, as calculated from the Planck Radiation Law. This number of quanta is comparable with the number of quanta used in medium-intensity photochemical studies using ultraviolet light; however, one quantum of ultraviolet light excites the molecule to a reactive level, whereas with infrared, many quanta are necessary to elevate the molecule to a reactive level. With intensities such as can be obtained from infrared sources, the probability of exciting one molecule to progressively higher states of excitation is prohibitively small. The extremely short lifetimes of these excited vibrational levels makes the previously-mentioned probability even less.

In order to test the assumption that excited species produced when various organic liquids are irradiated with high-energy radiation do not react with DPPH, one must produce molecules in excited electronic states in the liquid phase in the presence of DPPH. One must also be certain that the exciting radiation has insufficient energy to cause disproportionation of the absorbing molecule.

It is generally accepted that the primarily excited states produced by high-energy radiation are essentially like those which are excited by absorption of ultraviolet light.[17] The absorption of electromagnetic radiation of the wave length 2000 to 8000 A is usually a much less complicated process than the absorption of high-energy radiation such as x-rays and γ-rays. The absorption of the quantum of energy occurs as a single process involving the quantum of energy and the absorbing molecule. The products of the primary process are similarly reactive and can often be identified, and the rate of their formation can sometimes be stated. Almost always the nature of the activated species can be understood.

In general, the difficulties in interpreting the absorption spectra of polyatomic molecules are very great; however, in some highly symmetric molecules the absorption spectra are well understood. One such molecule is benzene. The absorption spectrum of liquid benzene is given in Fig. 1.[21]

The portion of this spectrum that is of interest in this work is the region from 3000 A to 3400 A. The series of four bands appearing in this region arises from an absorption from the ground state of the benzene molecule to the lowest triplet and first excited singlet states. The energy of the absorbed radiation at 3000 A is about 90 kcal per mole, which is insufficient to cause dissociation of the molecule. Light of wave length below 2200 A is necessary to show a quantum yield of 10^{-3} for the decomposition of benzene.[38]

Several organic liquids with fairly well-defined ultraviolet absorption spectra are known not to disproportionate when irradiated with light of wave lengths near but below their ultraviolet absorption thresholds. For these reasons a study of the photochemical processes that occur when

solutions of DPPH in several organic liquids are irradiated with ultraviolet light was initiated to give information on the reactivity of DPPH with excited electronic states of molecules in solution. Of course it is necessary that the quantum yield of the reaction of the excited DPPH molecule with the solvent be small.

When solutions of DPPH in organic liquids are exposed to ultraviolet light of a frequency that is absorbed by both DPPH and the solvent, there are two types of reactions that can occur; (a) reactions initiated by excited DPPH molecules and (b) reactions initiated by excited solvent molecules.

(a) $DPPH + h\nu \longrightarrow DPPH^*$ (I-6)

$DPPH^* \longrightarrow Products$ (I-7)

$DPPH^* + Solvent \longrightarrow Products$ (I-8)

$DPPH^* \longrightarrow DPPH + h\nu$ (I-9)

$DPPH^* + S \longrightarrow DPPH + S$ (I-10)

(b) $S + h\nu \longrightarrow S^*$ (I-11)

$S^* + DPPH \longrightarrow Products$ (I-12)

$S^* \longrightarrow S + h\nu$ (I-13)

$S^* + M \longrightarrow S + M$ (I-14)

In Series (a), the rate of the process is a function of the number of quanta of light absorbed by the DPPH. A reaction of this type can be identified by studying the rate of the reaction as a function of the DPPH concentration (or as a function of the number of quanta absorbed by the DPPH).

In Process (b), however, the rate of the process is not a function of the DPPH concentration, but rather of the amount of light absorbed

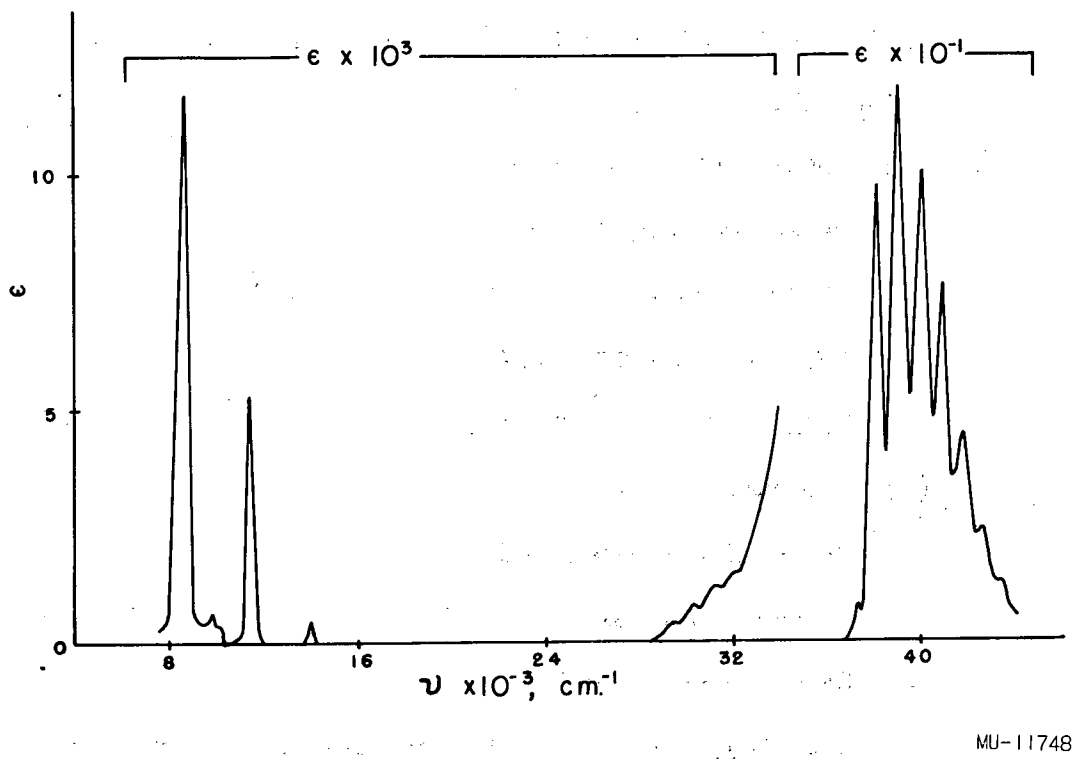


Fig. 1. The complete molal extinction curve of liquid benzene (a, determined with 10 cm of pure liquid; b, determined with dilute solution of benzene in ethanol) at room temperature, from 12,500 to 2,200 Å [18].

by the solvent -- with one provision, namely, that the DPPH concentration is great enough so that the activated solvent molecules S* react with DPPH in a time shorter than their fluorescent lifetimes or before they can lose their energy by collision or internal conversion (i.e., that Reactions I-13 and I-14 do not compete with Reaction I-12).

In this case, then, a study of the rate of the reaction as a function of DPPH concentration should show no dependence of the rate on DPPH concentration at concentrations of DPPH where Process I-12 is the predominant one, provided that the optical path through the solution be short or that a correction be made for the inner filter effect of DPPH absorption, i.e., the progressive reduction of light intensity within the solution because of light absorption by DPPH. It is possible, of course, for both effects to be present. This complication necessitates resolving the experimental data into two unique sets describing the two separate processes. This may or may not always be feasible.

The rates of Reactions I-7, I-8, and I-12 can be measured conveniently by measuring the rate of disappearance of DPPH in the solution. This is accomplished by spectrophotometrically measuring the decrease in the optical density of the DPPH absorption band at 5300 A. For this method to be successful it must be established that the products of the reactions studied show little or no absorption at this wave length.

Both Processes (a) and (b) would be expected to be proportional to the intensity of the incident radiation. Neither Process (a) nor (b) would be expected to be a sensitive function of temperature.

II. EXPERIMENTAL

1. Materials

(a) DPPH

Diphenyl-picryl-hydrazyl was prepared in the following way. Twenty-two grams of diphenylhydrazine hydrachloride (unsymmetrical) in 250 ml of absolute ethyl alcohol at 25°C was treated with 21 g of sodium bicarbonate and with 24.8 g of picryl chloride. After most of the CO_2 had come off, the solution was boiled gently for 15 minutes. Two hundred fifty ml of chloroform was added and the solid residue was filtered off while the solution was warm. The filtrate was washed with two 250-ml portions of water, concentrated on a steam bath to 150 ml and diluted with 150 ml of warm absolute ethyl alcohol. This solution was let stand overnight and filtered, and the crystals of diphenyl-picryl-hydrazine were recrystallized from 90 ml of chloroform and 60 ml of ethyl alcohol.

Twenty-five grams of the diphenyl-picryl-hydrazine, 25 g of sodium sulfate, and 150 g of lead dioxide were stired for 2 hours in 500 ml of benzene. The lead dioxide sediment was filtered off. An equal volume of normal pentane was added to the filtrate, and this solution was let stand for several hours and the DPPH was obtained by filtration.

The DPPH was recrystallized twice from a benzene-pentane solution. The crystals thus obtained were dried in a vacuum oven at 40°C for 72 hours. The crystals melted at 139-141°C.

Analyzing for C, H, and N yielded C, 61.1%; H, 3.9%; and N, 15.0%; calculated for DPPH · C_6H_6, C, 61.0%; H, 3.8%; and N, 14.8%.

(b) Potassium Ferrioxalate

One hundred sixty-seven ml of 1.5 M ferric chloride was treated with 500 ml of 1.5 M potassium oxalate in a darkroom illuminated with two safe-lights. The solution was placed in a dark storage space for 1 hour.

The potassium ferrioxalate was filtered from the solution, and re-dissolved in hot water, cooled, and filtered. After three recrystallizations from hot water the crystals of potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) were dried in a current of air at about 40°C.

(c) Benzene

Baker's "Analyzed" reagent-grade thiophene-free benzene was recrystallized in an ice water bath until the ultraviolet absorption spectrum between 3000 A and 3500 A was reproducible. Since the molar extinction coefficients of benzene in this region are approximately 10^{-3}, this offers a very good criterion of purity for the photolysis with light of wave length 3126 A.

(d) Toluene

Baker's "Analyzed" reagent-grade toluene was distilled through a ratio-controlled magnetic-head fractionating column with about 37 theoretical plates; the middle fraction, boiling at 111.0 ± .2°C (uncorrected), was used in the experiments.

(e) Chlorobenzene

Eastman Kodak Co. reagent-grade chlorobenzene was distilled through the 37-plate fractionating column; the middle fraction, boiling at 132.0 ± .1°C (uncorrected), was used in the experiments.

(f) Bromobenzene

Baker's "Analyzed" reagent-grade bromobenzene was distilled in the

37-plate fractionating column; the middle fraction, boiling at 156.2 $\pm$ .2°C (uncorrected), was taken for the experiments. Bromobenzene purified in this manner showed a considerable thermal reaction with DPPH, which was accelerated by the removal of dissolved air. The impurity responsible for this thermal reaction was removed by treating the bromobenzene with an excess of DPPH at 45° to 50°C for several hours, followed by two vacuum distillations of the bromobenzene from DPPH solutions. Bromobenzene prepared in this manner gave stable solutions of DPPH.

(g) Cyclohexane

Eastman Kodak Co. "spectro" grade cyclohexane also showed a considerable thermal reaction with DPPH; pure cyclohexane was obtained in the same manner as was the bromobenzene. Solutions prepared with cyclohexane purified in this manner were stable; however, some impurities were present which absorbed at 3126 A, making these solutions useless for photolysis purposes. Some products of the reaction of DPPH with the impurities evidently are volatile.

2. Equipment

(a) Spectrophotometers

All optical density measurements taken following the photolyses of solutions were made with a Beckman Model DU Quartz spectrophotometer using one-centimeter matched quartz solution cells.

Measurements of extinction coefficients were made with Cary Recording Spectrophotometers (Models 14M and 11) or with the Beckman Model DU.

(b) Light Sources

The light source used for the photolyses of the solutions was a Hanovia Type S-100 medium-pressure mercury arc operating on the 110-volt ac line, with a Sorensen Voltage Regulator to control the input voltage. The total light intensity of this source did not vary more than ± 5% during the entire investigation. The intensity was monitored with a Photronic barrier layer cell, as described in paragraph (d), and was checked every time an experiment was run.

(c) Irradiation Cells

Two types of irradiation cells were used. Type 1 cell (Fig. 2) was used in the horizontal irradiation apparatus illustrated in Fig. 3. The cell contained two compartments -- A, which contained the solution to be photolyzed or the actinometer solution, and B, which contained an absorbing solution to reduce reflection at the rear wall of the radiation cell to a minimum. This cell was placed in a reproducible position in a fitted brass cylinder as shown in Fig. 3. Compartment A inside dimensions were 34 mm in diameter and 11.3 mm in length.

Type 2 cell was used in the horizontal irradiation apparatus

exactly as Cell 1. This cell was made entirely of Pyrex glass, with polished optically flat windows. It was used in the determination of the rates of the reactions in air-free solutions. Its inside diameter was 34 mm and its inside length 11 mm.

(d) Monitors

Photronix barrier layer cells were used in series with a microammeter to determine fluctuations in light intensities of the light sources. These cells were not calibrated, but were used only to determine the constancy of the intensities over certain periods of time.

(e) Filter Combinations

Light of wave length 2900 A to 3200 A was obtained by using this filter system: 2 cm of saturated $NiSO_4 \cdot 6H_2O$; and Corning glass filters, nos. 9863 and 9700, each 2 mm thick. In this spectral region the two important lines of the source are at wave length 3126 and 3130 A.

(f) Equipment for Degassing Solutions

A conventional high-vacuum system with a two-stage mercury diffusion pump backed by a Duo Seal high-vacuum pump was used in the degassing procedure. A trap cooled by liquid nitrogen was always kept between the mercury diffusion pump and the cell being degassed. All stopcocks were greased with either Apiezon "N" or "T" stopcock grease, and joints were greased with a Silicone stopcock grease.

(g) Irradiation Arrangement

The apparatus used for the irradiation of the solutions is shown in Fig. 3. A is the light source focused by lens B so that the high-intensity light beam covers the entire area of the opening in the shutter F, the light traveling through filters C, D, and E. The irradiation cell

is placed in the fitted brass cylinder G. Monitor cell H was in a reflected part of the light beam. All parts of the system were placed on the optical bench I. J is a light shield.

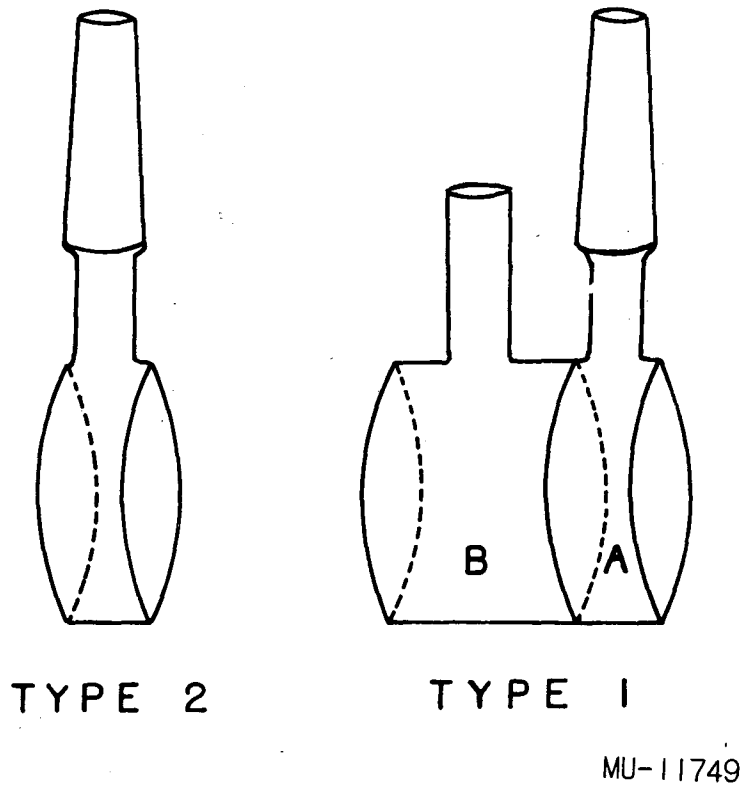


Fig. 2. The irradiation cells.

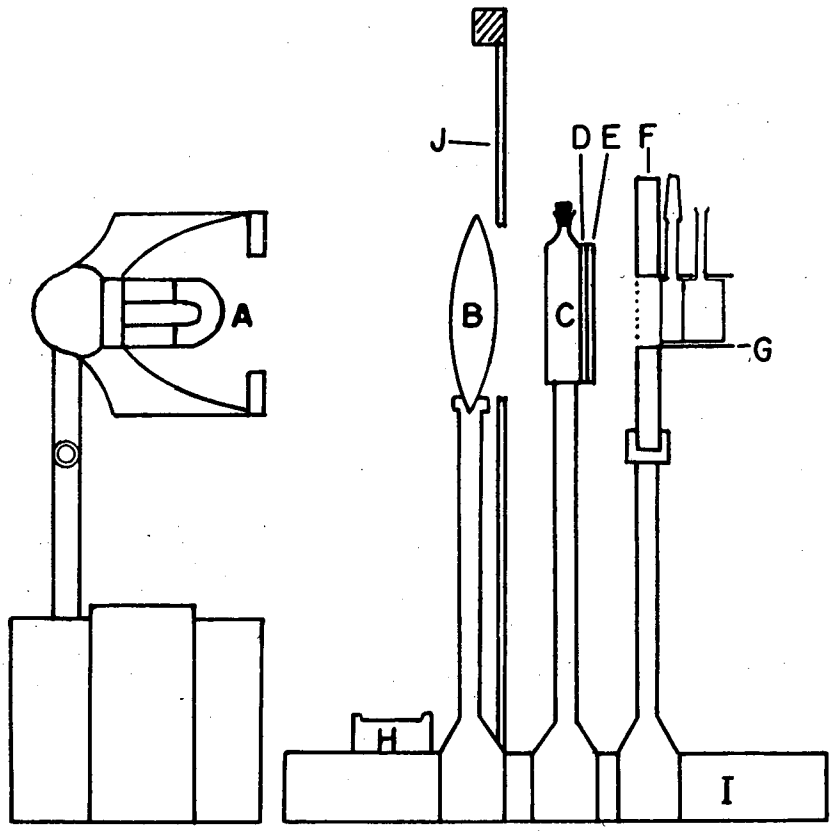


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Fig. 3. Irradiation apparatus: A, the Hanovia ultraviolet source; B, a quartz lens; C, D, and E, light filters; G, a brass cylinder; H, the monitor cell; I, the optical bench; and J, a light shield.

3. Experimental Procedures

Extinction coefficients of DPPH in the various solvents used were determined in the usual manner. A weighed sample of DPPH (solvated with benzene in a 1:1 molar ratio) was dissolved in a known amount of solution and the optical density was measured on the Beckman Model DU spectrophotometer or on the Cary Model 14M recording spectrophotometer. In all determinations with the Beckman DU, matched quartz cells were used, with pure solvent in the reference cell. In all determinations on the Cary a baseline was run with pure solvent in both cells. All determinations were done at room temperature ($25 \pm 2^{\circ}C$).

In obtaining the kinetic data, the method of initial rates was used. Air-saturated samples of known concentration of DPPH were introduced into the radiation cell, which was then placed in the brass cylinder in the horizontal radiation apparatus already described. The shutter was opened and the vessel irradiated for the desired time. All times were measured with a stopwatch. After the shutter was closed, the irradiated solutions were stirred by shaking and transferred to the Beckman cell, and the optical density was taken. This procedure took about 2 minutes. The optical density was then read several times in the next few minutes to see if any postirradiation reaction had taken place.

The change of optical density of DPPH (for the first 5% to 25% of the reaction) per second divided by the extinction coefficient of DPPH was taken to be the initial rate of the reaction. In no case was the reaction found to be nonlinear with time of exposure for this amount of reaction.

In order to determine the rates of the reactions in degassed samples a method of relative rates was used. An air-saturated solution of known concentration of DPPH was introduced into the cell, and the cell was attached to the evacuating system via a stopcock fitted with ground glass tapered joints. The solution was frozen with liquid nitrogen, evacuated, and allowed to just melt. This procedure was repeated until no gas bubbles were seen to form when the solution melted. The procedure was then repeated once more. The solution was allowed to come to room temperature and irradiated as previously described. The stopcock was removed and the optical density taken as described before. Again this procedure took only about two minutes. The cell was immediately refilled with the air-saturated solution of the same concentration and irradiated exactly as the degassed sample. It had previously been established that degassing did not change the optical density of the solution.

In order to obtain the quantum efficiency of the observed reaction one must determine the intensity of the incident radiation and the extinction coefficient of the absorbing material. Several methods are available for determining the former. The latter is determined directly from optical density measurements.

For determining the intensity of the incident radiation, a calibrated thermopole-galvanometer system may be used to measure the absolute energy of radiation of all wave lengths; however, this procedure measures beam intensities, and when absorption cells are placed in the beam, corrections must be made for reflection at the interfaces, for absorption of radiation by the windows, and for area of absorption.

Barrier-layer cells, or photovoltaic cells, are sometimes used in the same manner as the thermopile, and the same inconveniences are evident.

A more convenient method for measuring the absolute intensity of light that actually enters the absorption cell is the use of a calibrated chemical actinometer, such as the potassium ferrioxalate actinometer described by Parker.[29]

When a standardized chemical actinometer of this type is used, a very accurate measurement of the number of quanta entering the cell may be obtained. Therefore the absolute intensity of the incident radiation was determined by the following procedure.

A solution of 0.006 M potassium ferrioxalate in 0.1 N sulfuric acid solution was irradiated for 2 minutes in the irradiation cell placed in the horizontal irradiation apparatus. Ten ml of the photolyzed solution was transfereed to a 20-ml calibrated flask. Two ml of 1:10 orthophenanthroline solution (0.1% orthophenathroline monohydrate in water) was added, followed by 5 ml of a buffer solution (600 ml of 1.0 N sodium acetate plus 360 ml 1.0 N sulfuric acid made up to a liter of solution). Distilled water was then added to make 20 ml of solution. After the solution was made up and mixed, the liquid was allowed to stand for 30 minutes to allow complete reaction. Its absorption was then measured at 5100 A on the Beckman spectrophotometer, with the reference solution developed in the same manner but using unexposed potassium ferrioxalate solution instead of the photolyte.

Taking the extinction coefficient for the ferrous-orthophenanthroline complex as 11050 and the quantum yield of the photolysis of potassium ferrioxalate at 3126 A as 1.09, an optical density of 2.8 was then found for the developed solution which showed an absolute intensity of 2.3×10^{18} quanta/second/liter actually entering the radiation vessel used in this study.

4. Experimental Results

(a) Extinction Coefficients of Solvents and of DPPH in the Various Solvents

The absorption spectra of the various solvents used in this investigation are shown in Figs. 4, 5, 6, and 7. The extinction coefficients for the various solvents at 3126 A are given in Table I.

Table I

The extinction coefficients of solvents at 3126 A

Solvent	$\epsilon_{3126\ A}$
Cyclohexane	--
Benzene	$(1.53 \pm 0.10) \times 10^{-3}$
Toluene	$(4.6 \pm 0.5) \times 10^{-3}$
Chlorobenzene	$(7.2 \pm 0.7) \times 10^{-3}$
Bromobenzene	$(84.0 \pm 1.0) \times 10^{-3}$

Wave lengths and extinction coefficients of observed bands in benzene and bromobenzene are given in Table II.

Table II

The extinction coefficients of the observed bands in benzene and bromobenzene in the spectral region 3000 to 3400 A

Solvent	ν, cm^{-1}	ϵ
Benzene	29,400[a]	4×10^{-4}
	30,300[a]	1.0×10^{-3}
	31,200[a]	1.3×10^{-3}
	32,100[a]	1.5×10^{-3}
	29,500	5×10^{-4}
	30,400	0.8×10^{-3}
	31,200	1.25×10^{-3}
	32,100	1.53×10^{-3}
Bromobenzene	30,500	0.085
	31,300	0.090
	32,000	0.083
	33,000	0.074

[a]See Reference (18)

DPPH shows the same characteristic absorption spectrum in all solvents used. The absorption spectrum of DPPH in benzene is given in Fig. 8. Extinction coeffients of DPPH at various wave lengths are given in Table III for DPPH in various solvents.

Table III

The extinction coefficients of DPPH in several solvents

Solvent	λ_{max},A	ϵ_{max}	$\epsilon_{3126\ A}$	$\epsilon_{5300\ A}$
Benzene	5200	11,900	11,700	11,700
	3280	15,100		
Toluene	5200	13,900	14,500	13,300
	3280	18,000		
Bromobenzene	5290	13,300	11,300	13,300
	3330	15,800		
Chlorobenzene	5260	13,300	13,500	13,300
	3300	16,900		
Cyclohexane	5100	-	-	-
	3240	-	-	-
Chloroform	5250	13,200	14,300	13,000*
	3240	15,300		13,100**
				14,500[a]
				11,500[b]
				6,500[c]

*Determined from DPPH recrystallized from chloroform.

**Determined from DPPH recrystallized from benzene.

[a]See Reference (3)
[b]See Reference (32)
[c]See Reference (14)

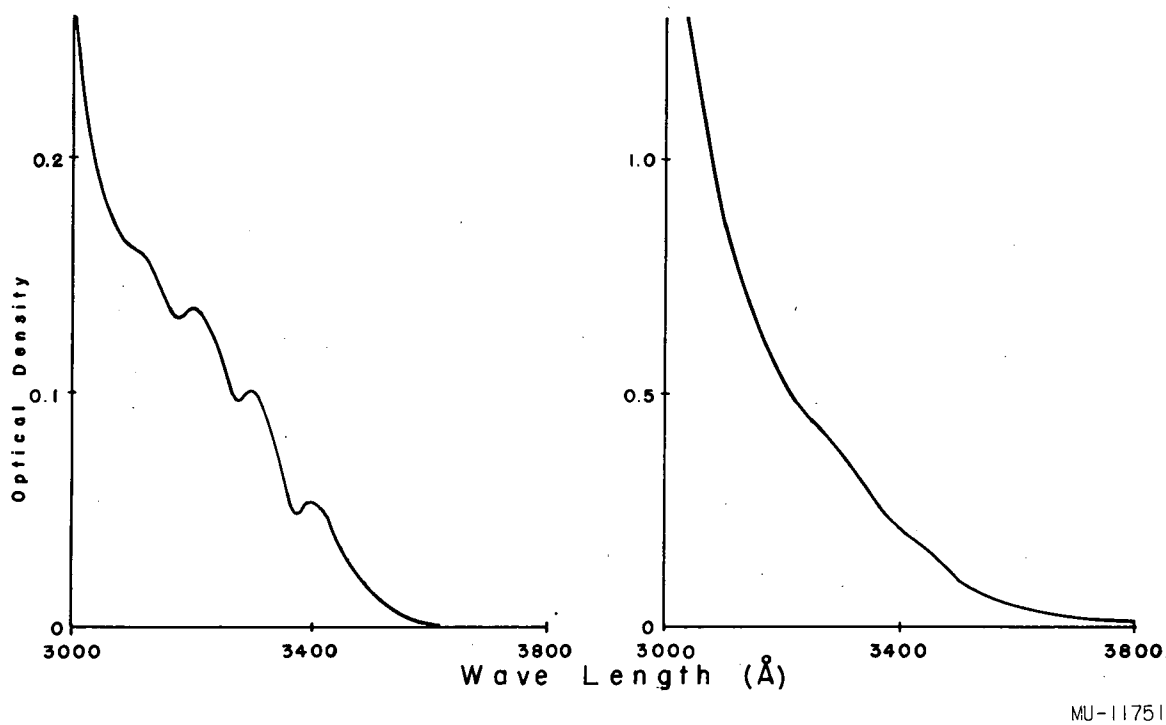

Fig. 4. The absorption curve of 10 cm of pure liquid benzene at room temperature from 3000 to 3800 Å.

Fig. 5. The absorption curve of 10 cm of pure liquid toluene at room temperature from 3000 to 3800 Å.

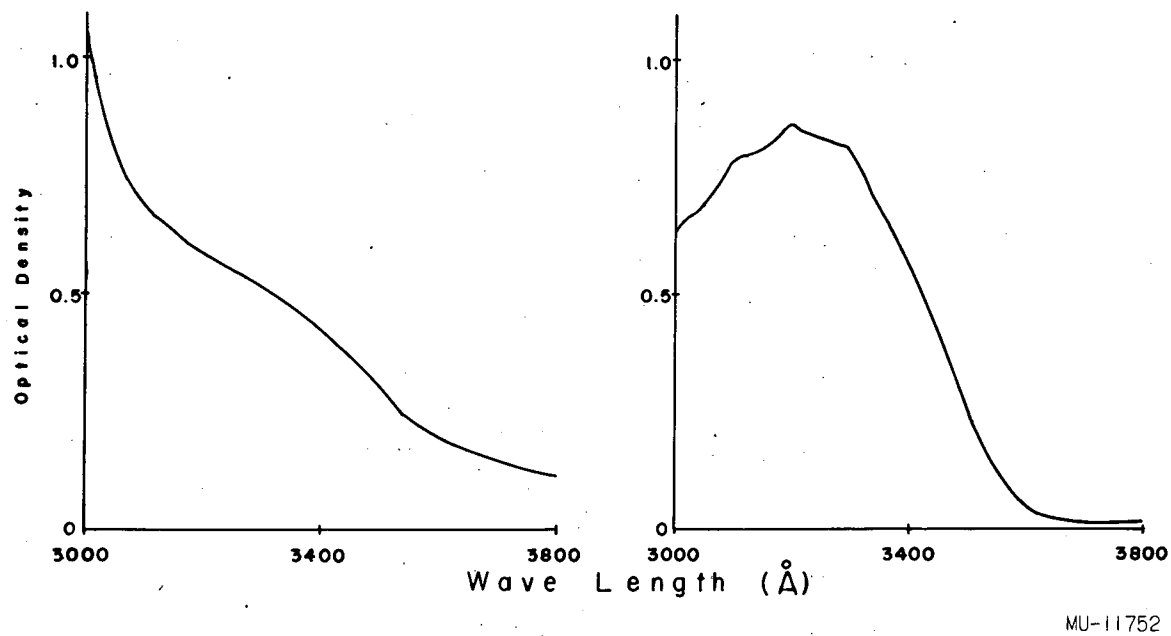

Fig. 6. The absorption curve of 10 cm of pure liquid chlorobenzene at room temperature from 3000 to 3800 Å.

Fig. 7. The absorption curve of 1 cm of pure liquid bromobenzene at room temperature from 3000 to 3800 Å.

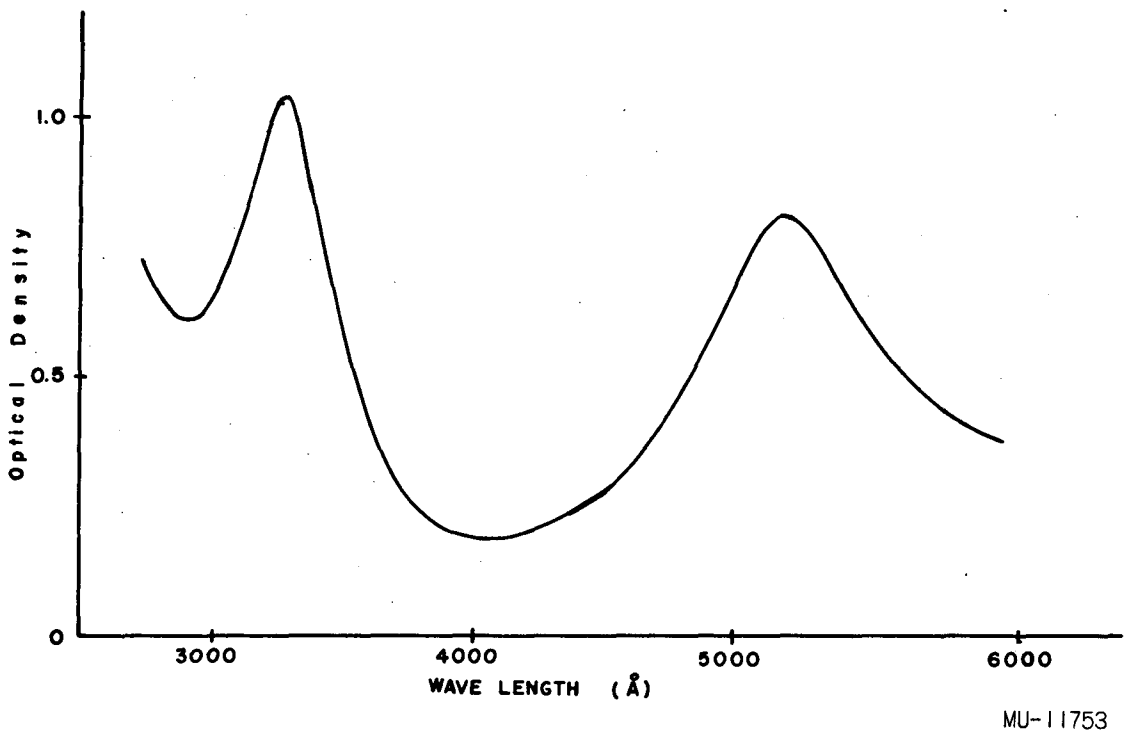

Fig. 8. The absorption spectrum of DPPH in benzene (8.1 mg of DPPH · C_6H_6 disolved in 250 ml of benzene solution at 25° C).

(b) Kinetics of the Rate of Disappearance of DPPH

The observed rates of disppearance of DPPH in cyclohexane, benzene, toluene, chlorobenzene, and bromobenzene are given in Tables IV, V, VI, VII, and VIII for both air-saturated and degassed solutions.

Plots of these initial rates versus the amount of light absorbed by the DPPH in the solution have been made, and are shown in Figs. 9, 10, 11, 12, and 13. Plots have also been made of the initial rates versus the concentration of DPPH in Figs. 14, 15, 16, 17, and 18. In all cases the results from both the air-saturated and degassed solutions are shown in one figure.

In plotting the curves of initial rate versus DPPH concentration and of initial rates versus amount of light absorbed by the DPPH, a smooth curve was drawn through the data obtained in the air-saturated solutions; this smooth curve was then used as a basis for determining the curve for the degassed solutions from the relative-rate data.

Table IX compares the observed maximum rates of the photoinduced disappearance of DPPH in the solvents studied.

Table IV

The observed rate of disappearance of DPPH in cyclohexane

Key	$O.D._{0(DPPH)}^{5200A}$	$t_{(min)}$	$O.D._t$	Δ O.D.	$\frac{\Delta \text{ O.D.}}{30 \text{ min}}$	$O.D._{0(DPPH)}^{3125A}$ (1.13 cm)	$\%I_o$ abs.*
ab	0.011	30	0.004	0.007	0.007	0.0153	3.5
ab	0.039	30	0.028	0.011	0.011	0.054	18
ab	0.022	30	0.012	0.010	0.010	0.031	6.8
ab	0.022	15	0.018	0.004	0.008	0.031	6.8
ab	0.378	60	0.333	0.045	0.022	0.527	70.2
ab	0.354	70	0.300	0.054	0.023	0.494	68
ab	0.335	60	0.293	0.042	0.021	0.467	66
ab	0.405	30	0.385	0.020	0.020	0.564	72.7
ab	0.148	30	0.134	0.014	0.014	0.205	37.7
ab	0.085	30	0.074	0.011	0.011	0.118	23.8
ab	0.056	30	0.046	0.010	0.010	0.078	16.6
ab	0.038	30	0.028	0.010	0.010	0.052	11.2
ab	0.023	38	0.010	0.013	0.010	0.032	7.0
ab	0.165	30	0.152	0.013	0.013	0.23	41.2
ab	0.176	30	0.163	0.013	0.013	0.245	43.2
ab	0.220	30	0.205	0.015	0.015	0.306	50.6
ab	0.812	30	0.793	0.019	0.019	1.13	92.6

Key: a, air saturated solution,
b, irradiated in cell 1,
c, irradiated in cell 2,
d, irradiated with light of wavelength 2900-3500 A from a G. E. AH-6 arc, using a vertical light path and a partially filled cylindrical quartz irradiation vessel,
*, (Solvent absorption neglected).

Table V

The observed rate of disappearance of DPPH in benzene

Key	$O.D._{0}^{5300A}$ (DPPH)	t (min)	$O.D._{t}$	Δ O.D.	$\frac{\Delta\ O.D.}{10\ min}$	$O.D._{0}^{3126\ A}$ (1.13 cm)	$\%I_{o}$ abs.*
ab	0.409	20	0.387	0.022	0.011	0.462	65.4
ab	0.348	20	0.327	0.021	0.0105	0.393	59.5
ab	0.231	20	0.209	0.022	0.011	0.261	45.1
ab	0.133	20	0.112	0.021	0.0105	0.150	29.3
ab	0.104	20	0.082	0.022	0.011	0.118	23.8
ab	0.043	10	0.034	0.009	0.009	0.049	10.6
ab	1.23	80	1.16	0.070	0.0088	1.39	96
ab	0.895	20	0.878	0.017	0.0085	1.01	90.2
ab	0.737	10	0.728	0.009	0.009	0.832	85.3
ab	0.572	10	0.562	0.010	0.010	0.646	77.4
ab	0.496	10	0.486	0.010	0.010	0.560	72.4
ab	0.320	10	0.309	0.011	0.011	0.362	56.7
ab	0.186	10	0.175	0.011	0.011	0.210	38.4
ab	0.092	10	0.080	0.012	0.012	0.104	21.3
ab	0.043	10	0.030	0.010	0.010	0.049	10.6
ab	0.033	10	0.023	0.010	0.010	0.037	8.3
ab	1.165	40	1.130	0.0088	0.0088	1.318	95.0
ab	0.930	30	0.900	0.010	0.010	1.05	91.0
ab	0.656	40	0.620	0.009	0.009	0.741	81.9
c	0.153	30	0.140	0.013			
ac	0.153	30	0.136	0.017			
d	0.317	10	0.292	0.025			
ad	0.317	10	0.288	0.029			
d	0.404	10	0.385	0.019			
ad	0.404	10	0.380	0.024			
d	0.162	10	0.139	0.023			
ad	0.162	10	0.132	0.030			

(See Table IV for Key)

Table VI

The observed rate of disappearance of DPPH in toluene

Key	$O.D._{0(DPPH)}^{5300\ A}$	t (sec)	$O.D._t$	Δ O.D.	$\frac{\Delta\ O.D.}{1\ min}$	$O.D._{0(DPPH)}^{3126\ A}$ (1.13 cm)	$\%I_o$ abs.*
ab	1.342	150	1.298	0.044	0.018	1.66	97.8
ab	0.568	120	0.527	0.041	0.022	0.700	80
ab	0.567	60	0.545	0.022	0.022	0.700	80
ab	0.268	60	0.243	0.025	0.025	0.331	53.4
ab	0.269	60	0.244	0.025	0.025	0.332	53.5
ab	0.097	30	0.085	0.012	0.024	0.120	24.2
ab	0.097	60	0.073	0.024	0.024	0.120	24.2
ab	0.043	20	0.035	0.008	0.024	0.053	11.5
ab	0.023	15	0.018	0.005	0.020	0.0284	6.3
ab	0.275	60	0.250	0.025	0.025	0.340	54.2
ab	0.265	60	0.231	0.024	0.024	0.327	53
c	0.732	180	0.714	0.018			
ac	0.732	180	0.698	0.034			
c	0.238	180	0.220	0.018			
ac	0.238	180	0.196	0.042			
c	0.238	180	0.218	0.020			
ac	0.238	180	0.196	0.042			
c	0.118	120	0.105	0.013			
ac	0.118	60	0.103	0.015			
c	0.118	120	0.105	0.013			
d	0.233	60	0.200	0.033			
ad	0.233	60	0.168	0.065			
d	0.229	60	0.190	0.039			
ad	0.229	60	0.166	0.063			

(See Table IV for key)

Table VII

The observed rate of disappearance of DPPH in chlorobenzene

Key	$O.D._{o(DPPH)}^{5300\ A}$	$t_{(sec)}$	$O.D._t$	Δ O.D.	$\frac{\Delta\ O.D.}{1\ min}$	$O.D._{o(DPPH)}^{3126\ A}$ (1.13 cm)	$\%I_o$ abs.*
ab	1.07	120	1.01	0.06	0.03	1.23	94.2
ab	0.506	60	0.470	0.036	0.036	0.584	74.0
ab	0.506	120	0.433	0.073	0.0365	0.584	74.0
ab	0.720	120	0.651	0.069	0.0335	0.830	85.2
ab	0.409	60	0.373	0.036	0.036	0.472	66.3
ab	0.293	60	0.255	0.036	0.036	0.338	54.2
ab	0.239	60	0.202	0.037	0.037	0.276	47.0
ab	0.146	30	0.128	0.018	0.036	0.168	32.2
ab	0.109	20	0.097	0.012	0.036	0.126	25.2
ab	0.065	20	0.055	0.010	0.030	0.075	15.9
ab	0.046	20	0.037	0.009	0.027	0.053	11.6
ab	0.025	20	0.018	0.007	0.021	0.0288	6.4
ab	0.088	20	0.077	0.011	0.033	0.101	20.8
c	0.130	60	0.112	0.018			
ac	0.130	60	0.108	0.022			
c	0.130	75	0.106	0.024			
ac	0.130	75	0.103	0.027			
c	0.436	60	0.419	0.017			
ac	0.436	60	0.416	0.020			
c	0.064	30	0.054	0.010			
ac	0.064	30	0.053	0.011			
c	1.21	180	1.16	0.05			
ac	1.21	180	1.155	0.055			

(See Table IV for key)

Table VIII

The observed rate of disappearance of DPPH in bromobenzene

Key	$O.D._{0(DPPH)}^{5300\ A}$	t (sec)	$O.D._t$	Δ O.D.	$\frac{\Delta\ O.D.}{1\ min}$	$O.D._{0(DPPH)}^{3126\ A}$ (1.13 cm)	$\%I_{eff}$ abs.
ab	1.187	60	1.070	0.117	0.117	1.15	92.9
ab	0.887	60	0.774	0.113	0.113	0.862	86.3
ab	0.364	30	0.298	0.066	0.132	0.354	55.7
ab	0.255	15	0.219	0.036	0.144	0.248	43.6
ab	0.081	5	0.068	0.013	0.156	0.079	16.6
ab	0.715	60	0.603	0.112	0.112	0.695	79.8
ab	0.246	15	0.207	0.039	0.156	0.239	32.4
ab	0.246	15	0.206	0.040	0.160	0.239	32.4
ab	0.094	10	0.068	0.026	0.156	0.0915	18.9
ab	0.055	5	0.041	0.014	0.168	0.0535	11.7
ab	0.026	5	0.017	0.009	0.108	0.0253	5.7
ab	0.026	5	0.016	0.010	0.120	0.0253	5.7
ab	0.045	5	0.033	0.012	0.144	0.0438	9.5
c	0.487	60	0.390	0.097			
ac	0.487	60	0.396	0.093			
c	0.120	30	0.055	0.065			
ac	0.120	30	0.065	0.055			
ac	0.120	30	0.065	0.055			
c	0.700	60	0.616	0.084			
ac	0.700	60	0.616	0.084			
c	0.912	60	0.812	0.100			
ac	0.912	60	0.822	0.090			
c	0.504	40	0.434	0.070			
ac	0.504	40	0.445	0.059			
c	0.280	30	0.211	0.069			
ac	0.280	30	0.223	0.057			
c	0.115	20	0.062	0.053			
ac	0.115	20	0.073	0.042			

Table IX

The comparison of the observed maximum rates of the photoinduced disappearance of DPPH in the solvents studied

Solvent	Δ O.D./min (degassed)	Δ O.D./min (Air saturated)	$\Delta c \frac{\text{moles}}{\text{liter-min}}$ (degassed)	$\Delta c \frac{\text{moles}}{\text{liter-min}}$ (Air saturated)
	---	0.0007	---	$\sim 5 \times 10^{-8}$
Benzene	.0009	0.0011	8×10^{-8}	9.4×10^{-8}
Toluene	0.011	0.025	83×10^{-8}	190×10^{-8}
Chloro-benzene	0.032	0.037	240×10^{-8}	280×10^{-8}
Bromo-benzene	0.203	0.165	1530×10^{-8}	1240×10^{-8}

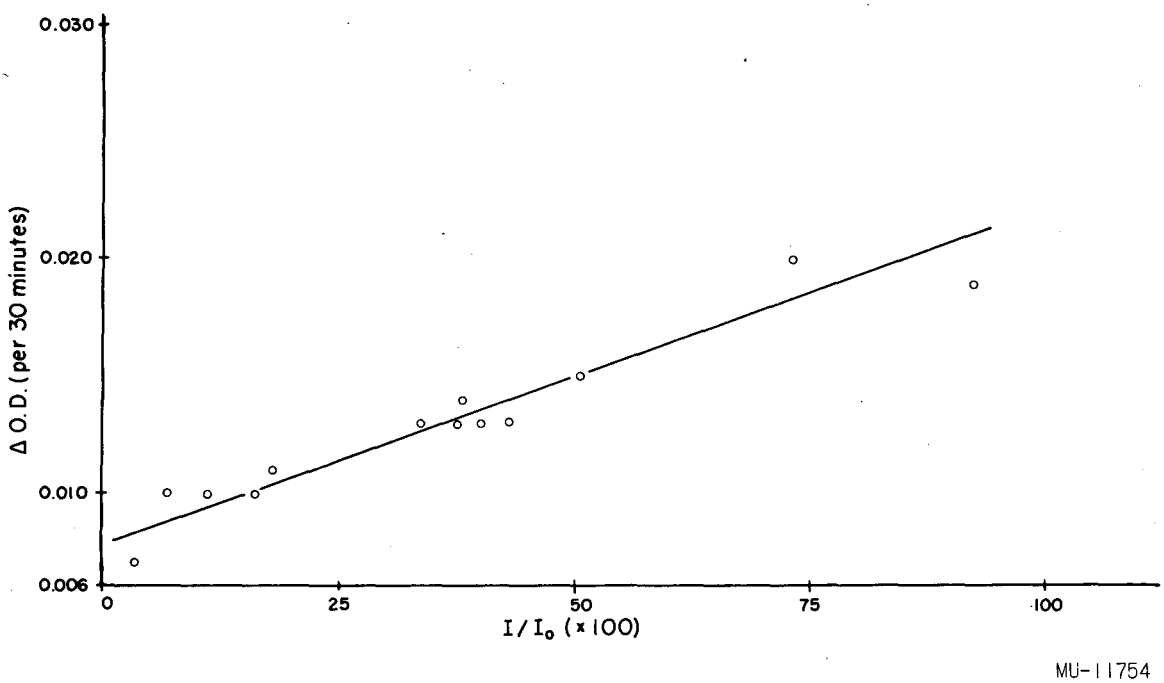

Fig. 9. The initial rate of the disappearance of DPPH on cyclohexane as a function of I/I_0, the fraction of the incident light intensity absorbed by the DPPH.

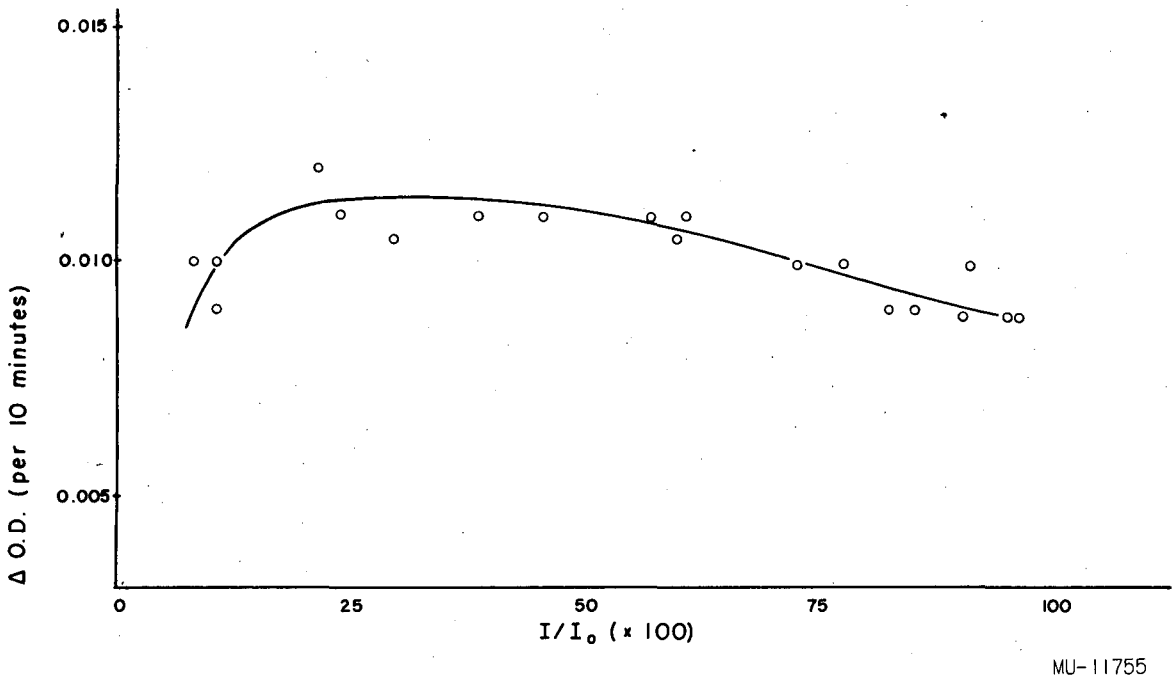

Fig. 10. The initial rate of the disappearance of DPPH in benzene as a function of I/I_0, the fraction of the incident light intensity absorbed by the DPPH.

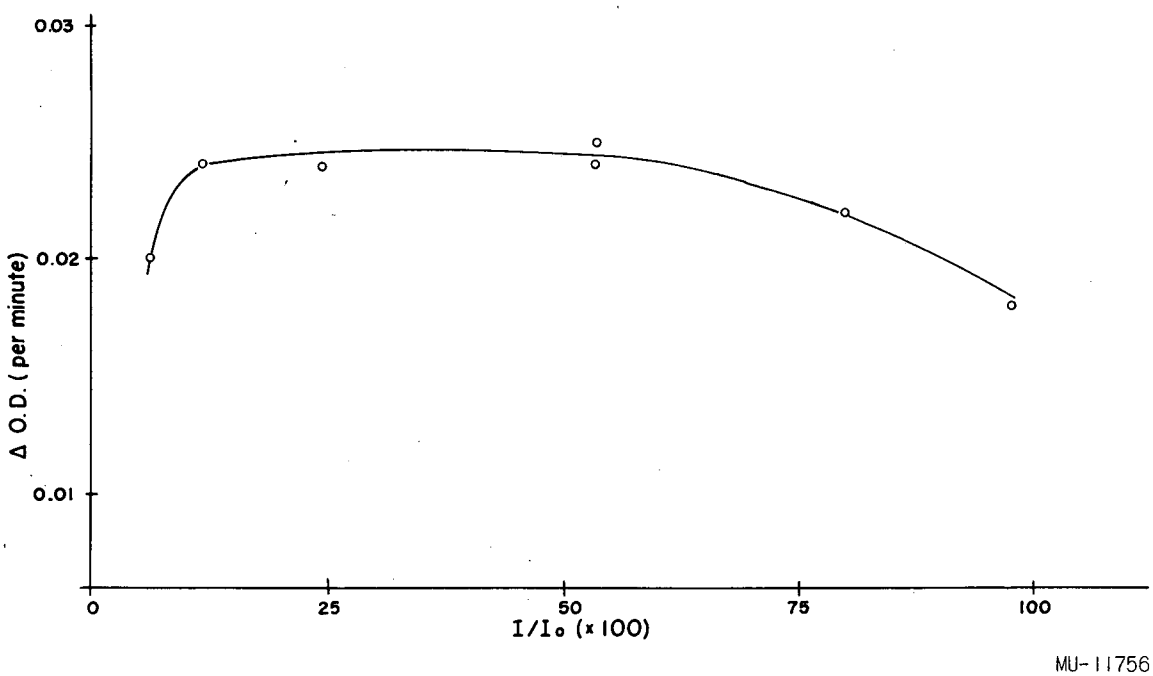

Fig. 11. The initial rate of the disappearance of DPPH in toluene as a function of I/I_0, the fraction of the incident-light intensity absorbed by the DPPH.

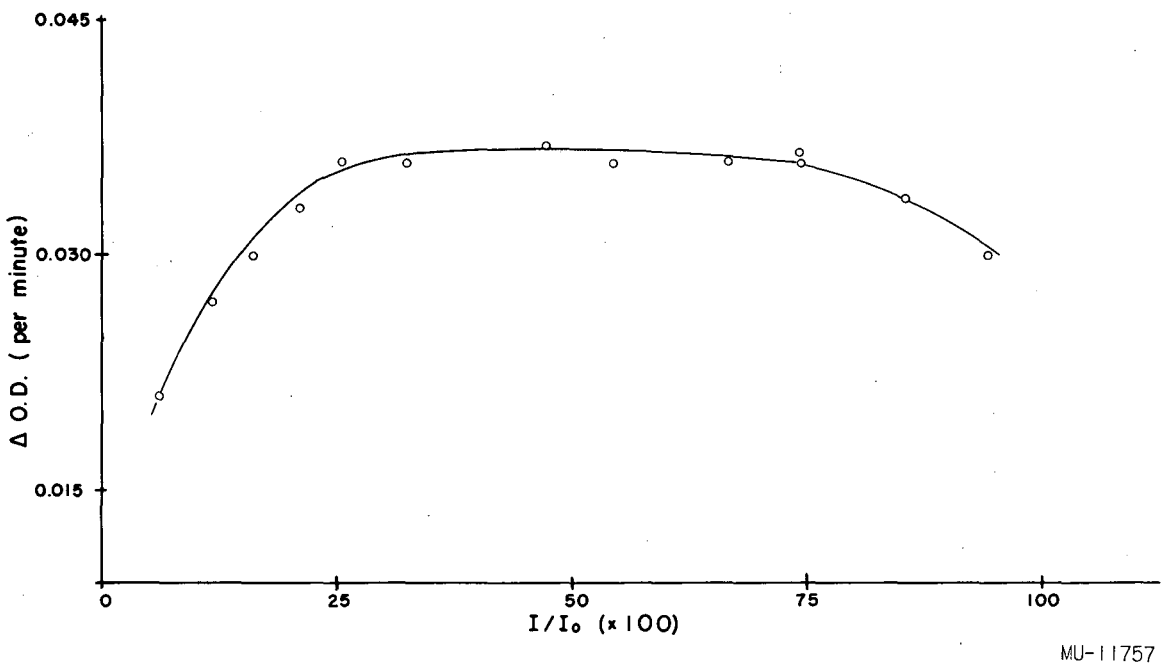

Fig. 12. The initial rate of the disappearance of DPPH in chlorobenzene as a function of I/I_0, the fraction of the incident-light intensity absorbed by the DPPH.

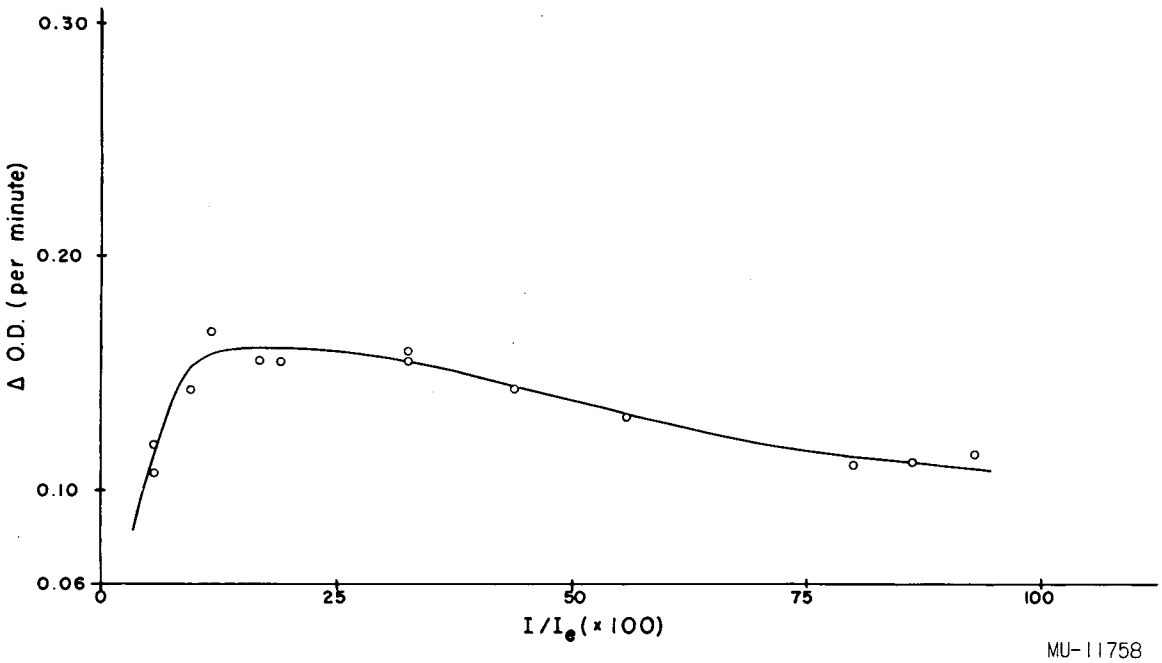

Fig. 13. The initial rate of the disappearance of DPPH in bromobenzene as a function of I/I_e, the fraction of the effective light intensity absorbed by the DPPH.

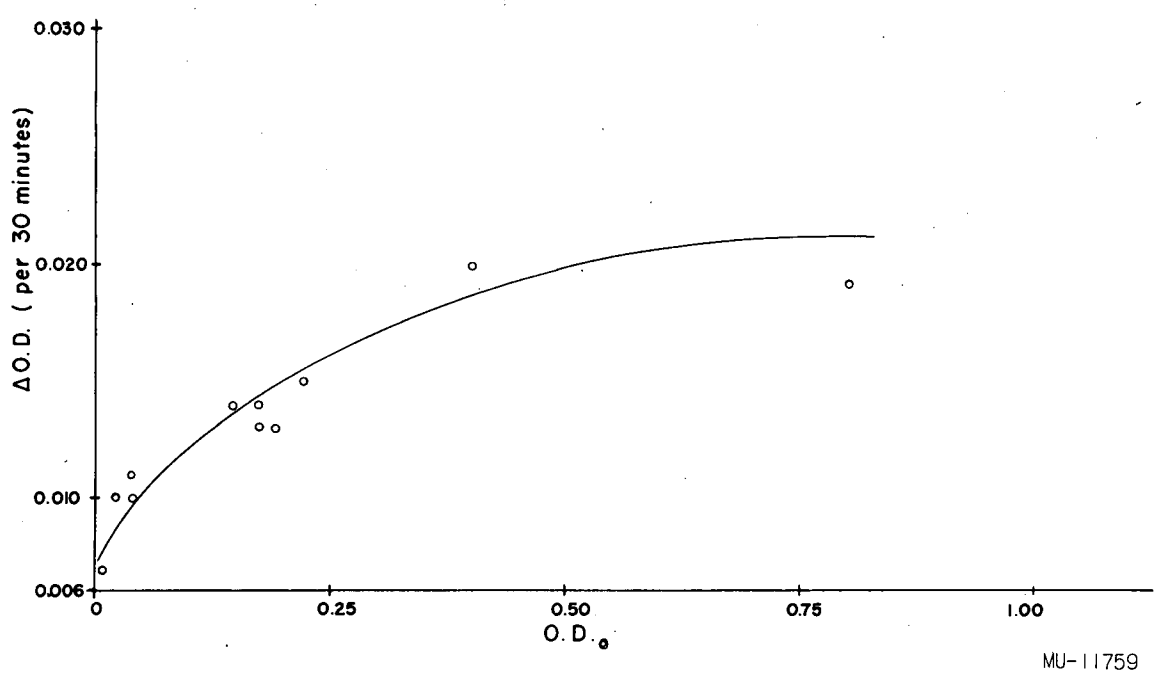

Fig. 14. The initial rate of the disappearance of DPPH in cyclohexane as a function of the initial concentration, expressed in optical density, of DPPH. The solutions were air-saturated.

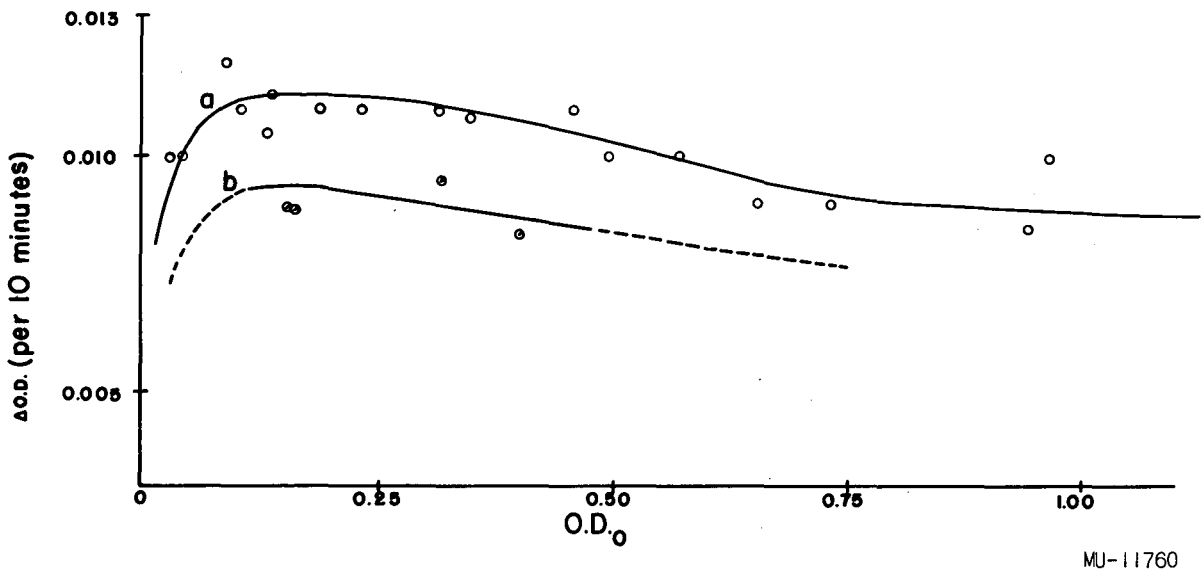

Fig. 15. The initial rate of the disappearance of DPPH in benzene as a function of the initial concentration, expressed in optical density, of DPPH. Curve a represents the initial rates in air-saturated solutions; Curve b represents the initial rates in degassed solutions.

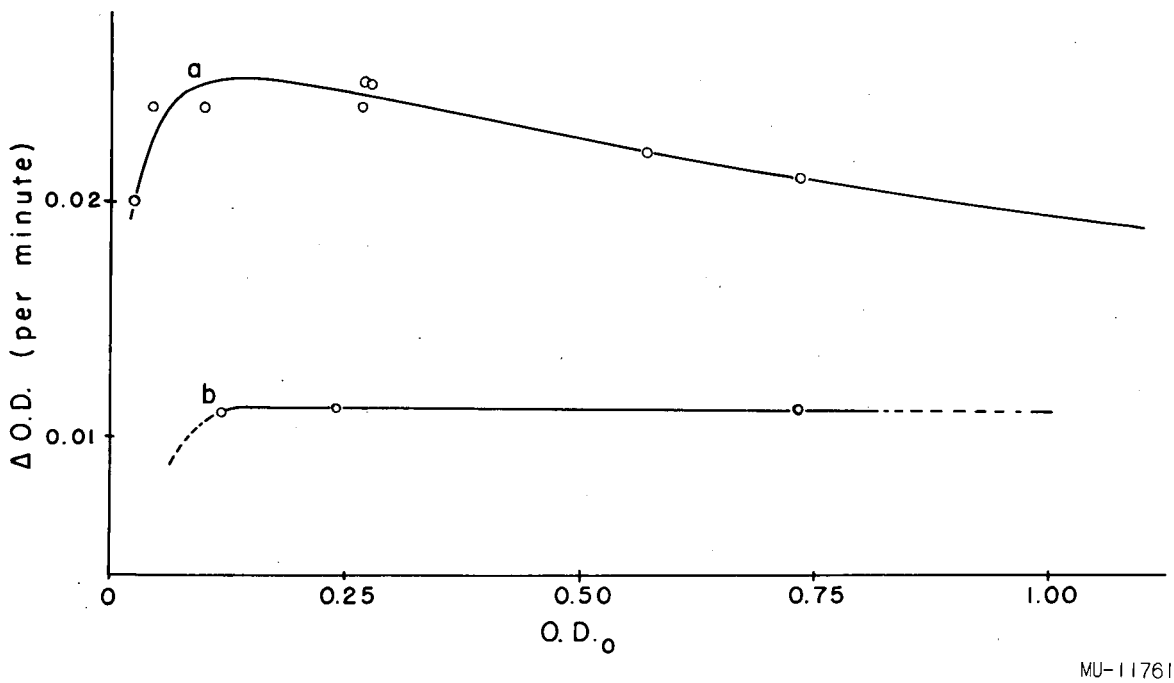

Fig. 16. The initial rate of the disappearance of DPPH in toluene as a function of the initial concentration, expressed in optical density, of DPPH. Curve a represents the initial rates in air-saturated solutions; Curve b represents the initial rates in degassed solutions.

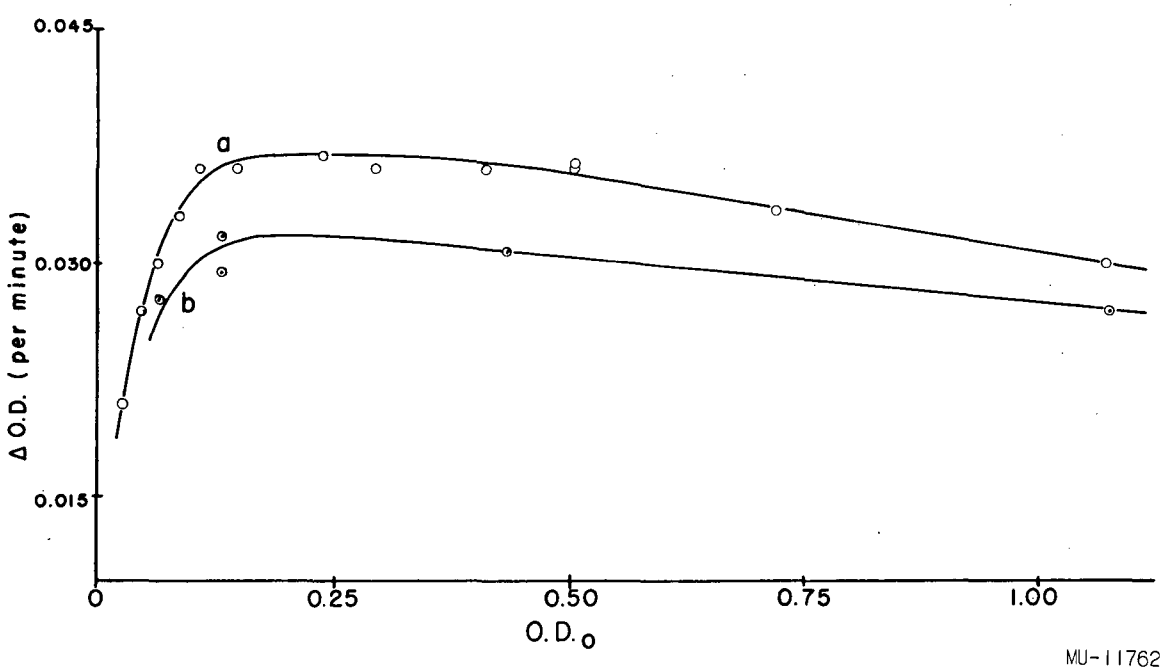

Fig. 17. The initial rate of the disappearance of DPPH in chlorobenzene as a function of the initial concentration, expressed in optical density of DPPH. Curve a represents the initial rates in air-saturated solutions; Curve b represents the initial rates in degassed solutions.

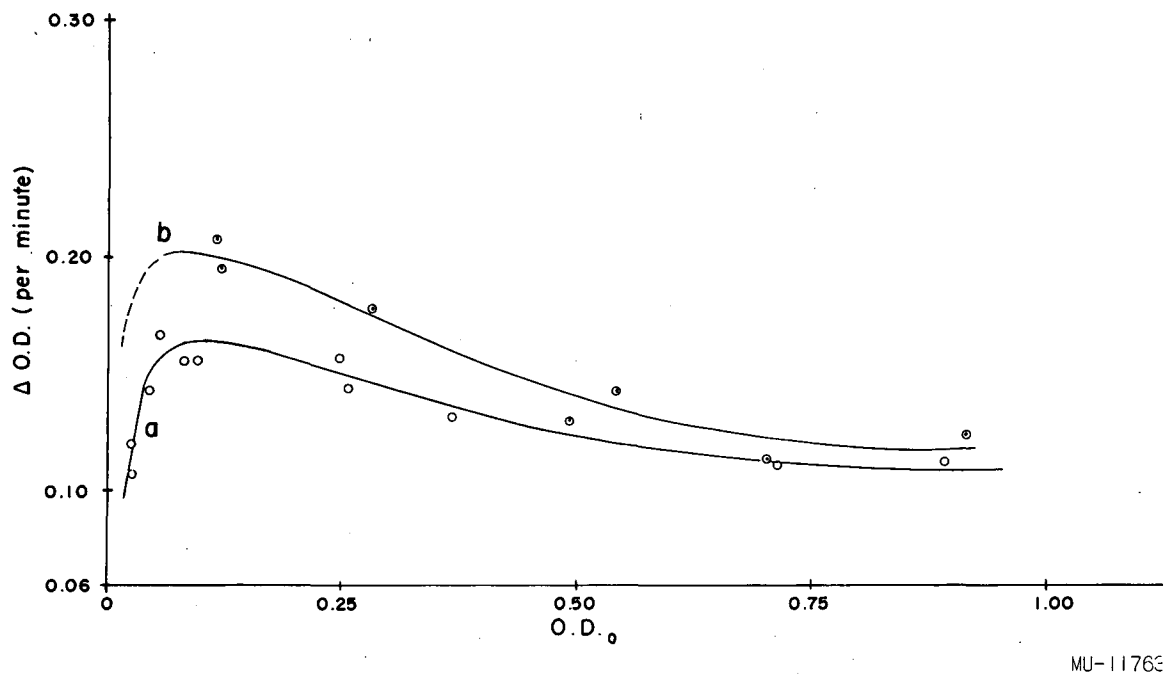

Fig. 18. The initial rate of the disappearance of DPPH in chlorobenzene as a function of the initial concentration, expressed in optical density, of DPPH. Curve a represents the initial rates in air-saturated solutions; Curve b represents the rates in degassed solutions.

III. DISCUSSION OF RESULTS

Preliminary qualitative experiments established that ultraviolet light induced reactions resulting in the disappearance of DPPH for solutions of DPPH in each of the following solvents: chloroform, carbon tetrachloride, ammonia, methanol, acetone, benzene, toluene, chlorobenzene, n-hexane, cyclohexane, heptane, and bromobenzene.

An attempt was made to study the photolysis of solutions of DPPH in chloroform and in carbon tetrachloride. The rates of disappearance of DPPH in these solutions were not linear with time of exposure, but showed an increase of rate with time of irradiation. This acceleration of the rate with time of exposure was assumed to indicate either that the products of the reaction were unstable -- the fragments of the decompositions reacting with DPPH -- or that metastable products of the photolysis had lifetimes of the order of minutes, thus showing the observed increase in the rate. Important postirradiation reactions resulting in the disappearance of DPPH were also observed, which can be attributed to the same reasons just mentioned.

Several colored products were also separable from the photolyzed solution, indicating that a very complicated reaction occurs.

A more extensive study was undertaken of the photolysis of DPPH in cyclohexane, benzene, toluene, chlorobenzene, and bromobenzene. In all these cases the rates of the reactions were linear with time of exposure or very nearly so, and some information about the products indicated that straightforward interpretations could be put forth.[a]

Upon inspection of the plots of the initial rates of the disappearance of DPPH versus the amount of light absorbed by the DPPH in the

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[a]Discussed later in the section

solutions, it is seen that for benzene, toluene, chlorobenzene, and bromobenzene the rate of disappearance of the DPPH in these solutions appears to be independent of the amount of light absorbed by the DPPH except at low concentrations of DPPH. It then appears that the reaction

$$\text{DPPH} + h\nu \longrightarrow \text{DPPH}^*$$

followed by the reaction of DPPH* with the solvent or by DPPH* decomposition is not the major process occurring. One sees, however, that in the irradiation of cyclohexane-DPPH solutions, the rate of the photoinduced reaction is directly proportional to the amount of light absorbed by the DPPH in the solution, indicating that the major reaction is indeed

$$\text{DPPH} + h\nu \longrightarrow \text{DPPH}^* ,$$

followed by some reaction of DPPH* that results in the disappearance of DPPH*.

It must be concluded, then, that the disappearance of DPPH in benzene, toluene, chlorobenzene, and bromobenzene involves a process due to the absorption of energy by the solvent, i.e.,

$$S + h\nu \longrightarrow S^*,$$

followed by

$$S^* + \text{DPPH} \longrightarrow \text{Products}.$$

Let us examine the possible excited species of the solvent at wave length 3126 A.

The lowest-lying triplet states for many molecules have been found in recent years by studying the phosphorescence spectra of these molecules in rigid glasses.[21] Electronic transitions between triplet states have been observed by McClure[25] in rigid glasses.

In solution, at room temperatures, these materials which phosphoresce in the solid glass show only normal fluorescence, generally with a decay

time of about 10^{-8} second. This indicates either that the interconversion from excited singlet state to lowest triplet state does not occur in the liquid media, or that the molecule formed in the lowest triplet state is deactivated with great efficiency before it radiates.

Evidence from both spectroscopy and photochemistry indicates that it is a case of deactivation. Bowen[6] postulates that the photooxidation of anthracene in solution has the lowest triplet state of anthracene as an intermediate in the oxidation. If triplet states are actually involved in photochemical reactions, it seems reasonable that the lifetimes of the triplet states in solution are greater than those of the singlet states.

By a flash photolysis technique, Porter and Windsor[30] have observed transient spectra with half lives as short as about 50 μsec in solutions of naphthalene, phenanthrene, naphthacene, triphenylene, chrysene, pyrene, and others. The spectra were interpreted by Porter and Windsor to be due to triplet states of these molecules in solutions. These transient spectra were not observed in very simple aromatic compounds, probably because the lifetimes are too short for them to be observed by the technique used.

Porter and Windsor conclude that the formation of triplet states as well as singlet states by photolysis is a general phenomenon, even though the triplet states are not formed by a direct absorption process. It is also a phenomenon of major importance, as is shown by the fact that there is in some cases about 50% conversion of the excited singlet states to the triplet state by a single flash, in Porter and Windsor's experiments.

With some substances, such as benzene and dichlorobenzene, direct absorption to the triplet level has been previously observed.[18] Direct absorption to the lowest triplet state probably occurs in chlorobenzene and toluene, and is very prominent in bromobenzene.

Therefore, in benzene, toluene, chlorobenzene, and bromobenzene, there are produced by direct absorption at wave length 3126 A both the first excited singlet states and the lowest triplet states of the molecules. In addition to the production of the triplet state by direct absorption, it has been postulated that in aromatic systems the production of the triplet state from the first excited singlet state by a process of internal conversion occurs to some extent.[31]

Finally there is the possibility of direct photodissociation or predissociation of the absorbing aromatic molecules. For benzene, toluene, and chlorobenzene, no evidence has been found for photodissociation at wave length 3126 A.[13,17,34,38] Bromobenzene, however, has been pyrolyzed with an activation energy of about 71 kcal/mole for the production of bromine atoms and phenyl radicals.[19] One might then expect that bromobenzene would photolyze at wave length 3126 A (corresponding to 91 kcal/mole) to give phenyl radicals and bromine atoms. The spectrum of bromobenzene in the near ultraviolet is apparently not a continuum, which suggests that if phenyl radicals and bromine atoms are produced, it is by a predissociation process involving either the singlet or triplet state.

Two types of reactions resulting from light absorption by the solvent would show no dependence on the DPPH concentration, providing that corrections are made for the inner filtering effect of the DPPH absorption. These types are

A. The photoproduction of radicals followed by the reaction of DPPH with all the radicals that escape a primary recombination (providing that the DPPH concentration is great enough to compete with the combination reaction of radicals that escape primary recombination).

B. The photoproduction of excited molecules followed by the reaction of DPPH with a major fraction of the excited molecules before the excited molecules lose their energy by fluorescence, internal conversion, or some other form of deactivation.

If the excited molecules have a finite lifetime, then at low concentrations of DPPH -- where the time between collisions of the excited state with DPPH is greater than the average lifetime of the excited state -- the process of deactivation would compete with the reaction of the excited state with DPPH. As the concentration of the DPPH is increased, so that the time between collisions is less than the average lifetime of the excited state, the rate of the reaction would become independent of the DPPH concentration.

A plot of the rate versus the DPPH concentration for processes A and B would be of the form shown in Fig. 19, neglecting the inner filtering effect of the solvent but correcting for the inner filtering effect of DPPH absorption.[b] The solid line would be observed if all radicals produced reacted with DPPH (no recombination of the radicals), or if the activated states had infinite lifetimes, insuring collision and reaction with DPPH. The dotted line indicates what would be observed if there were recombination of the radicals at low DPPH concentrations or if the activated species had a short lifetime.

Since the observed rate versus DPPH concentration plots are of the form just described by the dotted line on Fig. 19, the photoinduced disappearance of DPPH in benzene, toluene, chlorobenzene, and bromobenzene is attributed to the reaction of DPPH with excited states of the

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[b]The method of applying the corrections for the inner filter effect is given in Appendix I.

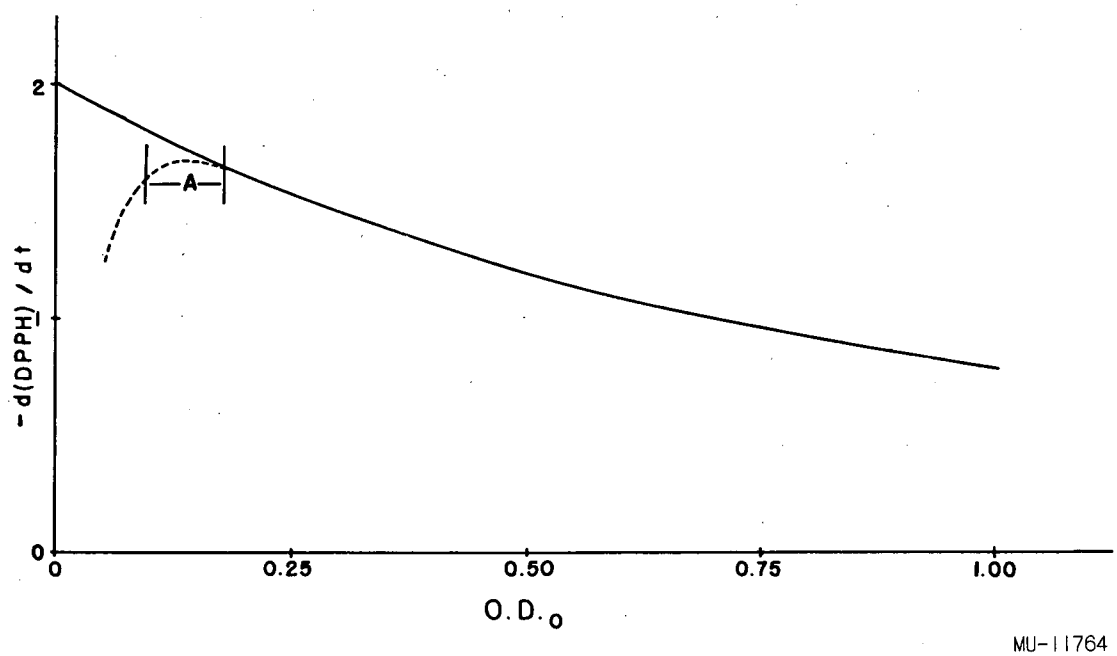

Fig. 19. The effect of light absorption by DPPH on processes A and B (page 49). The broken line represents the expected form of the curve if the disappearance of DPPH is due to short-lived species.

solvent molecules or to the reaction of DPPH with photoproduced free radicals. As was stated before, no evidence has been found for photodissociation of benzene, toluene, or chlorobenzene at wave length 3126 A, but some photodissociation of bromobenzene probably occurs at this wave length. Quantum yields for the photodissociation of benzene at 1900 A are less than 10^{-2},[38] and for toluene at 2537 A, less than 10^{-4}.[17]

The experimental results do not fit the above picture precisely, but suggest that a second reaction, which is proportional to the DPPH concentration, is occurring. Since a reaction of this type was observed in cyclohexane it seems reasonable that it would occur in the other solvents. It was found that the experimentally determined curves of rate versus the DPPH concentration could be resolved into two unique curves; curve ad (Figs. 20-22), which describes the DPPH and S* reaction (assuming that DPPH reacts with all S* formed), and curve oe which describes the DPPH* and S reaction. The method used to determine the two curves was one of successive approximations and is illustrated for chlorobenzene in Appendix II. The curves determined for benzene, toluene, and chlorobenzene by this method are given in Figs. 20, 21, and 22.

The sum of the two curves, ad and oe, is given by curve ac in Figs. 20, 21, and 22. The original data are plotted to give curve bc. Then the actual rate of disappearance of DPPH vs DPPH concentration is given by ad - (ac-bc), the dotted curve on Figs. 20, 21, and 22.

The quantum yields for both reactions determined in this manner are given in Table X.

Table X

Limiting quantum yields for the disappearance of DPPH by reaction with S* and by the reaction of DPPH* at wave length 3126 A calculated by method shown in Appendix II

Solvent	Reaction with S*	Reaction of DPPH[c]
Cyclohexane	- -	~ 0.0001
Benzene	0.01 ± .002	0.00013
Toluene	0.037 ± .005	0.003
Chlorobenzene	0.073 ± .004	0.005
Bromobenzene	0.18 ± .02	- - [c]

[c]This reaction was so small compared to the other that it could not be evaluated.

If one assumes that the rate of the reaction of the excited state with DPPH is diffusion-controlled for low concentrations of DPPH, then one would expect that some information could be obtained by estimating what lifetime the excited state would have to have in order to show the concentration dependence observed in the DPPH concentration range of 10^{-5} mole/liter.

This can be done very roughly by estimating the distance through which the excited states diffuse from the point of their formation in the lifetime of the excited state. The radial distance R by which the excited state diffuses from the source, as calculated for a three-

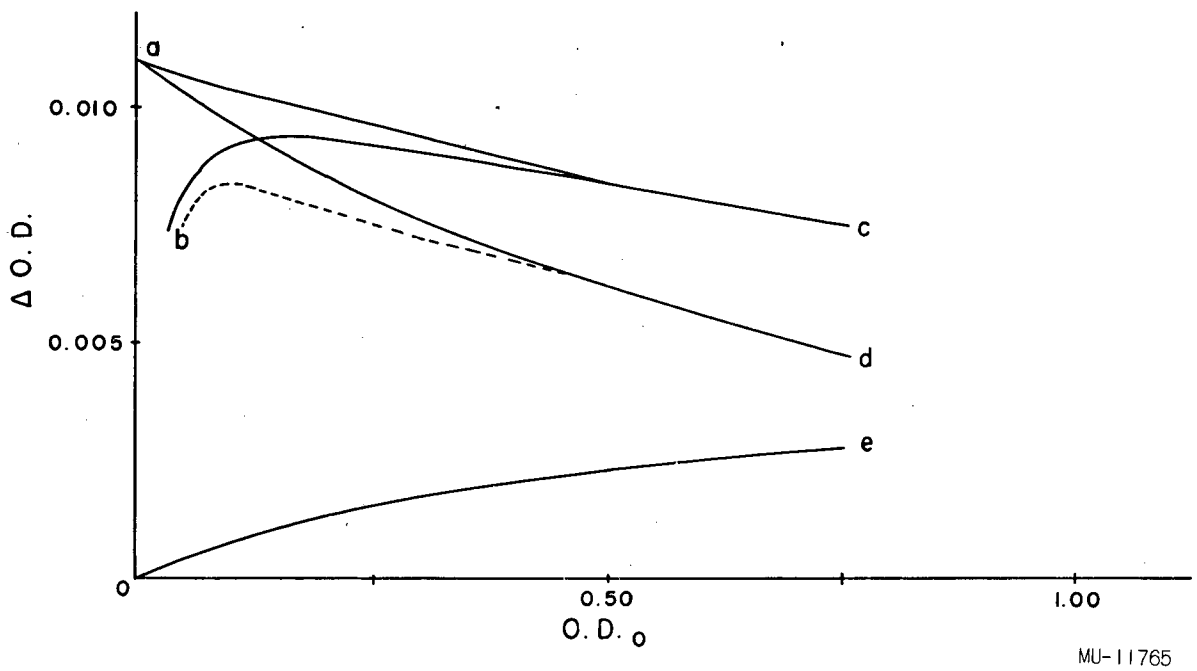

Fig. 20. The determination of Curves ad and oe, which describe reactions of Type I-12 and I-8 respectively, from the experimental Curve bc. The broken curve describes the rate of disappearance of DPPH due to a short-lived species. The broken curve is determined by ad-(ac-bc).

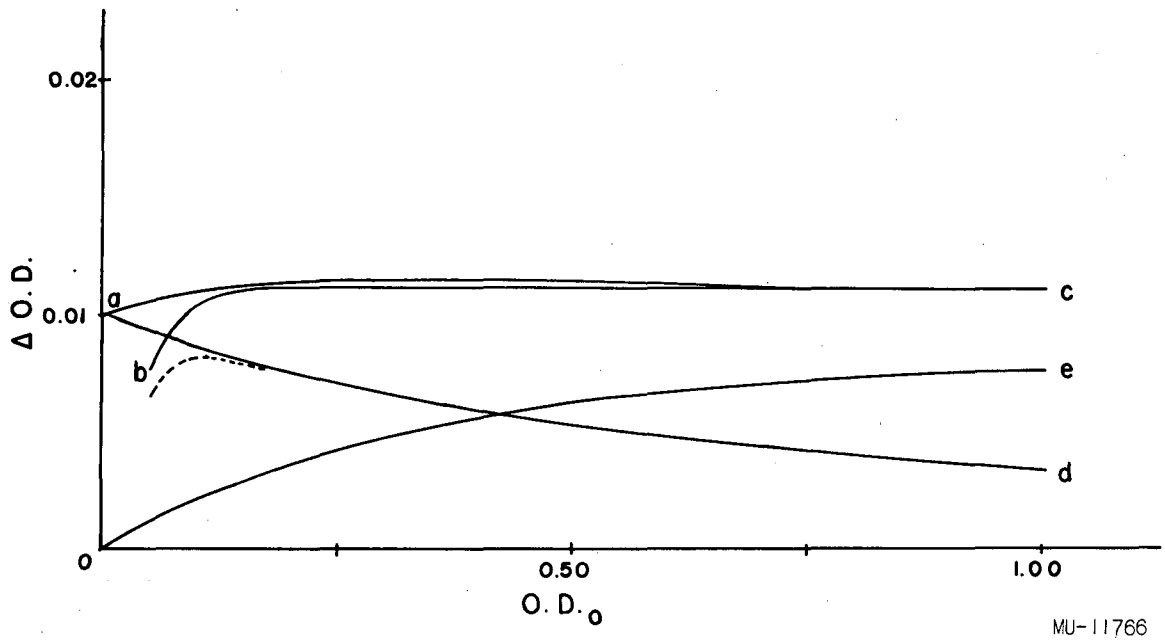

Fig. 21. The determination of Curves ad and oe, which describe reactions of Types I-12 and I-8 respectively, from the experimental Curve bc. The broken curve describes the rate of disappearance of DPPH due to a short-lived species. The broken curve is determined by ad-(ac-bc).

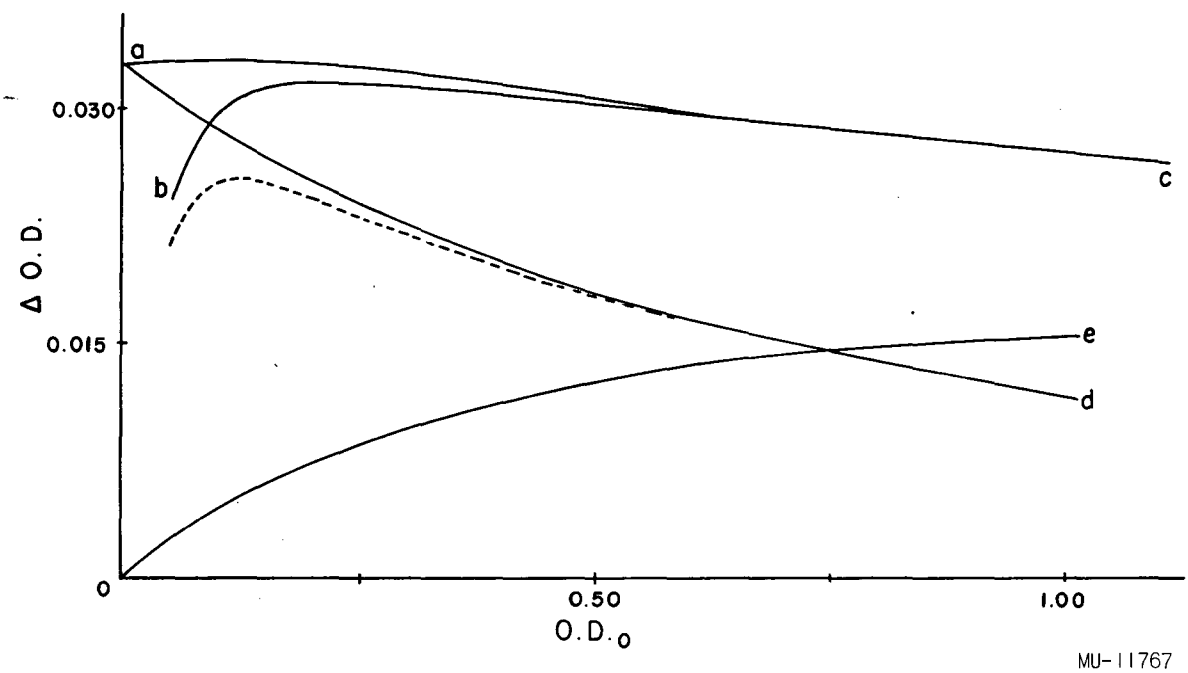

Fig. 22. The determination of Curves ad and oe, which describe reactions of Types I-12 and I-8 respectively, from the experimental Curve bc. The broken curve describes the rate of disappearance of DPPH due to a short-lived species. The broken curve is determined by ad-(ac-bc).

dimensional random walk process, is given by

$$R = 2\, r_0 \left(\frac{n}{6}\right)^{1/2}, \qquad \text{III-1}$$

where r_0 is the spacing of nearest neighbors and n is the number of diffusive displacements during the lifetime of the state.[7] Assuming then that the frequency factor of diffusive displacements is about 10^{11} per second, we can calculate the radial displacement R for an activated species of lifetime 10^{-9} second and one of lifetime 10^{-5} second (corresponding to the expected lifetimes of the first excited singlet and lowest triplet states in benzene).

The collison diameter of benzene is about 5.7 A; with this as the value for the spacing of nearest neighbors, we have

$$R = 5.7 \times 2 \left(\frac{10^{11} \times 10^{-8}}{6}\right)^{1/2} \text{ for } \tau = 10^{-9} \text{ sec,}$$

or

$$R \cong 50 \text{ A;}$$

and

$$R = 5.7 \times 2 \left(\frac{10^{11} \times 10^{-5}}{6}\right)^{1/2} \text{ for } \tau = 10^{-5} \text{ sec,}$$

or

$$R \cong 6000 \text{ A.}$$

As the average distance between DPPH molecules in benzene solution at a DPPH concentration of 10^{-5} M is about 550 A, it seems reasonable to say that the species with the 10^{-9}-sec lifetime would not react appreciably with the DPPH at this concentration.

This estimation indicates that the reactive species is one of longer lifetime than the first excited state of benzene, and is evidence that the reactive species is the triplet state of benzene.

In an attempt to predict the shape of the curve for the rate vs DPPH concentration for a reaction of an excited species with an average

lifetime τ, one may consider the rate of disappearance of activated solvent molecules, $\frac{dS^*}{dt}$, as a function of the diffusive displacement frequency ν, the average lifetime τ of the excited state S*, and the mole fraction N_D of DPPH. Then we have

$$dS^*/dt = -(11/12\,\nu\, N_D\, 6)n - n/\tau, \qquad \text{(III-2)}$$

where n is the number of activated states produced per unit time, 11/12 is a correction factor for the probability that on the average one displacement in twelve would take the activated state into the same solvent shell from which it had just come, and 6 is the average number of different molecules that S* sees with each diffusive displacement.

Then the fraction reacted with DPPH at any time t and at any rate of formation of S* is given by

$$F = \frac{11/2\, N_D\, \nu}{11/2\, N_D \nu + 1/\tau} \quad . \qquad \text{(III-3)}$$

The curves predicted by Eq. (III-3) for $\tau = 5 \times 10^{-6}$ sec, 10^{-5} sec, 5×10^{-5} sec, and 10^{-8} sec are given in Fig. 23.

For benzene and chlorobenzene, curves of the type predicted by Eq. (III-3) are readily obtained from the experimental plots of initial rate of disappearance of DPPH vs DPPH concentration and from the two curves describing the DPPH —— S* reaction and the DPPH* - S reaction illustrated in Appendix II. Referring to Fig. 26, we see that the type of curve predicted by Eq. (III-3) is obtained by subtracting the differences of curves Z"A and BCA from curve Z"D". Thus

*The average lifetime of benzene fluorescence in pure liquid benzene, air-saturated and at room temperature, has recently been found to be $4.5 \pm .8 \times 10^{-10}$ second by Paul R. Kromann in this laboratory.

$$[Z''D'' - (Z'A - BCA)] = R$$

is of the form predicted by Eq. (III-3).

Then R/OZ" is equal to the fraction of the excited species formed that reacts with DPPH, and from Eq. (III-3) we have

$$R = \frac{11/2 \; N_D \nu}{11/2 \; N_D \nu + \frac{1}{\tau}} \qquad \text{(III-4)}$$

and

$$\frac{1}{R} = 1 + \frac{1}{5/2 \nu \tau \; N_D} \; . \qquad \text{(III-5)}$$

It is seen that a plot of $1/R$ vs $1/N_D$ should give a straight line with slope $(5/2\nu\tau)^{-1}$. Such a plot for the DPPH-chlorobenzene reaction is given in Fig. 24.

Values of $\nu\tau$ for the triplet states of benzene, toluene, and chlorobenzene calculated in this manner are given in Table XI.

Table XI

Values for $\nu\tau$ for triplet states in solutions

Solvent	$\nu\tau$	τ(assuming $\nu = 10^{11}$/sec)
Benzene	$\sim 3 \times 10^6$	3×10^{-5} sec
Toluene	$\sim 2.5 \times 10^6$	2.5×10^{-5} sec
Chlorobenzene	$2.2 \pm 0.2 \times 10^6$	2.2×10^{-5} sec

It should be pointed out that the values of $\nu\tau$ in Table XI are subject to high experimental error, since the values are determined from

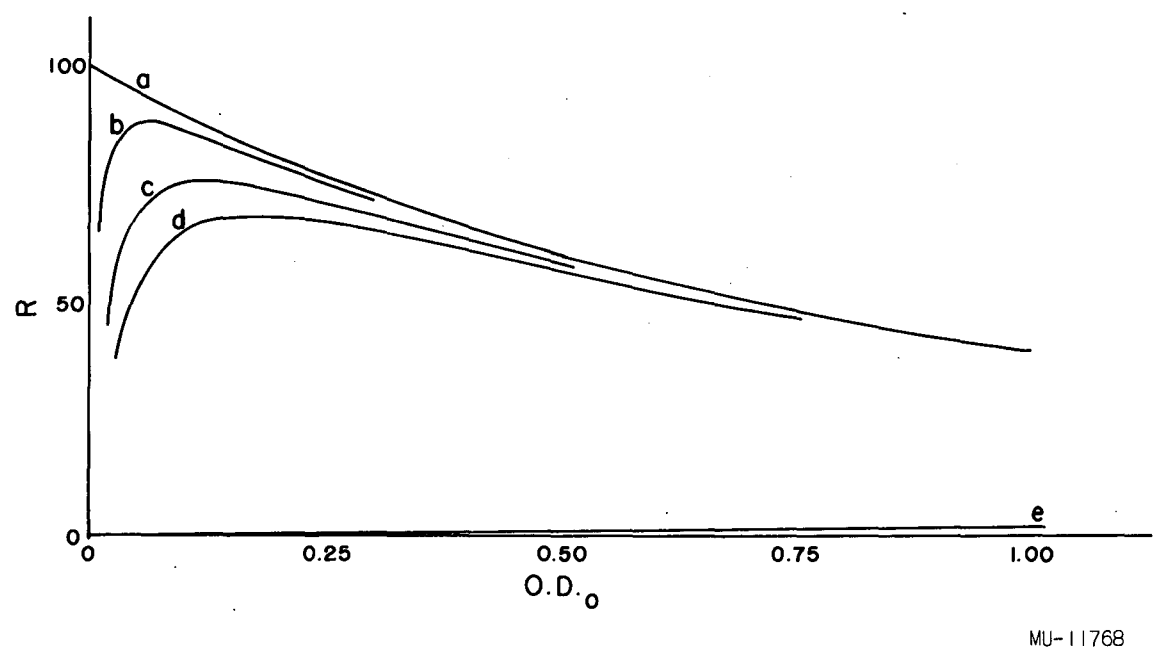

Fig. 23. The initial rates R of the disappearance of DPPH as a function of DPPH concentration for activated species of several average lifetimes (a, infinite; b, 5×10^{-5} sec; c, 1×10^{-5} sec; d, 5×10^{-6} sec; and e, 1×10^{-8} sec). These curves are predicted by Eq. III-3 and the inner filtering effect.

the portion of the experimental curve that is at very low DPPH concentrations, and can be considered only as approximations.

The region A of Fig. 19 is of interest in the compounds irradiated. It is noted that as the mass (or atomic number) of the substituted group or atom increases Region A moves to a higher DPPH concentration (with the exception of bromobenzene), and that the limiting quantum yield of Reaction (I-12) increases. This suggests that the lifetime of the excited state responsible for the reaction is decreasing with increasing mass (or atomic number) of the substituent group. In substituted benzene molecules, as the atomic number of the substituent group increases, the singlet-triplet transition probability increases owing to the gradual change of the electron coupling from L·S to j·j, and the lifetime of the triplet states decreases.[24]

The differences in the rates in air-saturated and degassed solutions are also of interest. In benzene, toluene, and chlorobenzene it is noted that the presence of air causes an increase in the rates of the reactions. It has been shown by Bowen[5] that oxygen quenches the fluorescence of benzene and toluene in solution by a reaction of the oxygen with the excited singlet state to give a stable peroxide. This effect in toluene is roughly twice as great as in benzene. It has been shown by Magat[22] that DPPH is extremely sensitive to peroxides in solution. One would then expect that if oxygen is present in the solution of DPPH in benzene and toluene, an increase in the rate of the photoinduced reaction would be observed owing to the peroxides formed when oxygen quenches the singlet-state fluorescence. An effect of this type is present. Fluorescence of chlorobenzene is not observed in solution, but the peroxide formation during the deactivation process probably occurs.

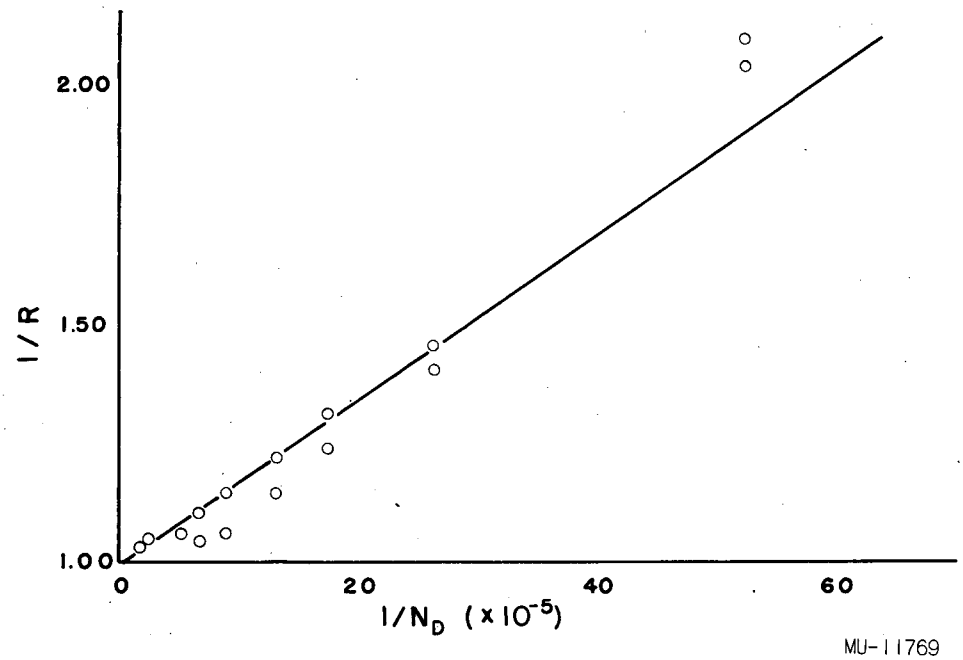

Fig. 24. A plot of 1/R vs $1/N_D$ (from Eq. III-5) for the DPPH-chlorobenzene reaction.

In bromobenzene, removal of air causes the rate of the photoinduced disappearance of DPPH to increase. This is possibly evidence that at least part of the reaction in bromobenzene is of a different nature from the reactions in the other solvents. Further evidence that at least part of the reaction in bromobenzene is of a different nature from that in the other solvents is that Region A (Fig. 19) is at lower DPPH concentrations than in chlorobenzene. If the reaction in bromobenzene were only a reaction of the triplet state of bromobenzene with DPPH, Region A should fall at higher DPPH concentrations than for chlorobenzene, since the triplet state of bromobenzene is expected to be shorter-lived than the triplet state of chlorobenzene. Region A for bromobenzene is a lower DPPH concentration than it is for chlorobenzene.

Since the activation energy of the reaction

$$C_6H_5Br \longrightarrow C_6H_5\cdot + Br\cdot \qquad \text{(III-6)}$$

has been determined to be about 71 kcal per mole, and since the energy at 3126 A is about 90 kcal per mole, it is quite possible that the photodissociation of bromobenzene followed by the reaction of the DPPH with the free radicals produced contributes to the over-all rate of disappearance of DPPH in bromobenzene. That the triplet state of bromobenzene contributes significantly to the rate of disappearance of DPPH is evident from the quantum yield of 0.18. This is significantly higher than would be expected if the reaction were only that of DPPH and free radical produced by photodecomposition, since the quantum yield for the production of radicals in iodobenzene is only 0.033 at these wave lengths.[28]

An attempt was made to separate the products of the photolysis by the use of chromatographic columns of silicic acid, using the solvent as the

elutant. Previous work by Wild[37] had shown that DPPH is reduced on alumina columns. DPPH was found to be stable on silicic acid columns.

Only one product was observed from the photolysis of benzene in air-free solutions. In air-saturated solutions a small amount of a second product was observed, indicating that oxygen actually participated in the reaction. The spectra of the products are given in Figs. 25, 26, 27, 28, and 29.

Two products could be separated from the photolyzed air-free solution of DPPH in toluene. It could not be determined that the two products were not produced on the chromatographic column. Again, in the presence of air, an alteration of the spectra of the products indicated that oxygen participated in the reaction.

In no case was the product diphenylpicrylhydrazine, which has a characteristic absorption spectrum that can be easily identified. This clearly eliminates reactions such as

$$\text{DPPH} + \text{H}\cdot \longrightarrow \text{DPPH-H}$$

and

$$\text{DPPH} + \text{S} \longrightarrow \text{DPPH-H} + \text{R}\cdot \quad .$$

Photolyzed solutions of DPPH in toluene and benzene could be reoxidized with lead dioxide to the characteristic color of DPPH, but the spectrum was different than that of DPPH. Again this is evidence that the product formed was not the simple hydrazine of DPPH.

Because of the difficulties involved with trace amounts of large molecules, which hold solvents very tenaciously, decompose on chromatographic columns, and do not lend themselves to gravimetric analysis, no further work on product determination was undertaken.

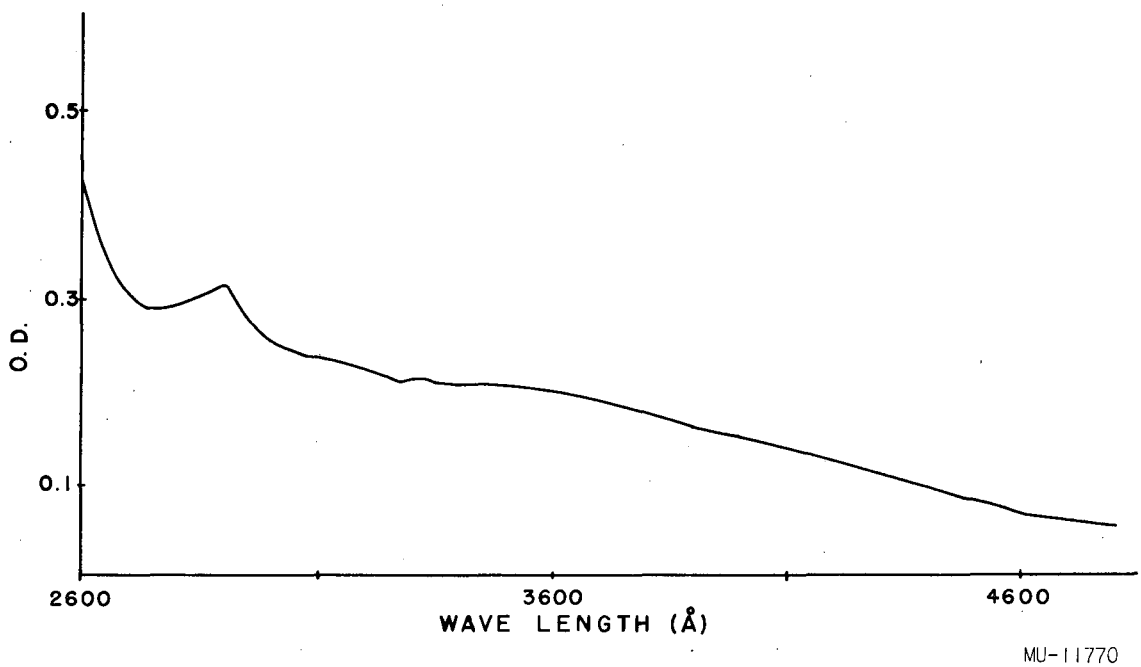

Fig. 25. The absorption spectrum of the final products of the photolysis of an air-saturated DPPH-cyclohexane solution. The initial optical density of DPPH was approximately 0.3.

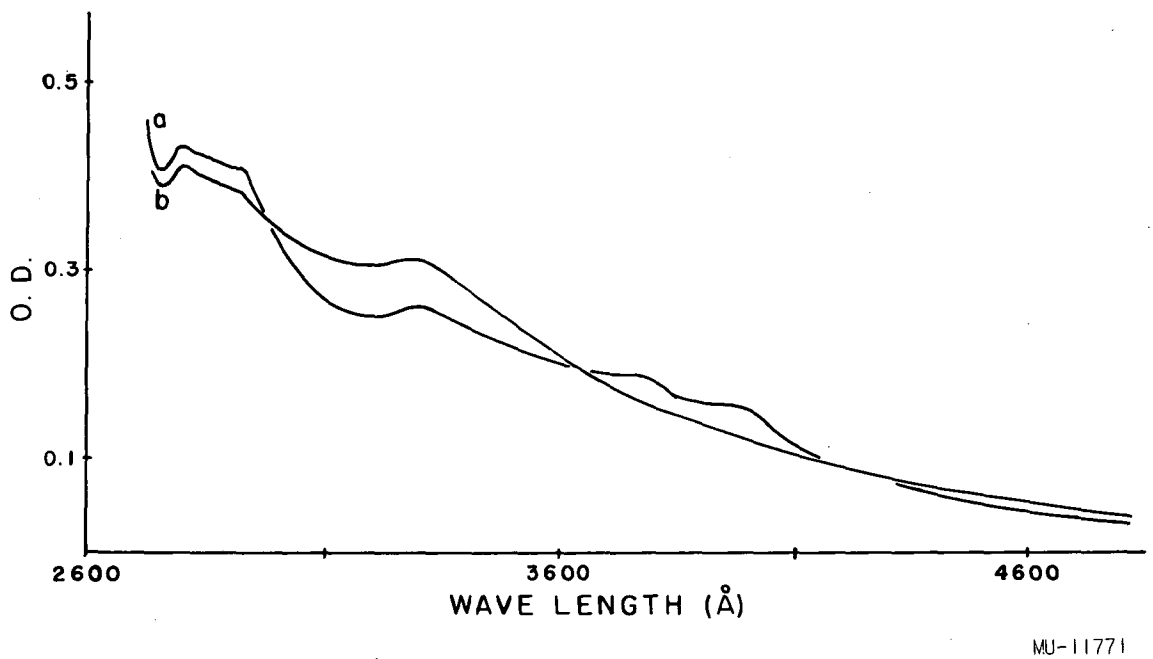

Fig. 26. The absorption spectra of the final products of the photolysis of DPPH-benzene solutions. Curve a represents the products in an air-saturated solution; Curve b represents the products in a degassed solution. $O.D._0 = 0.325$.

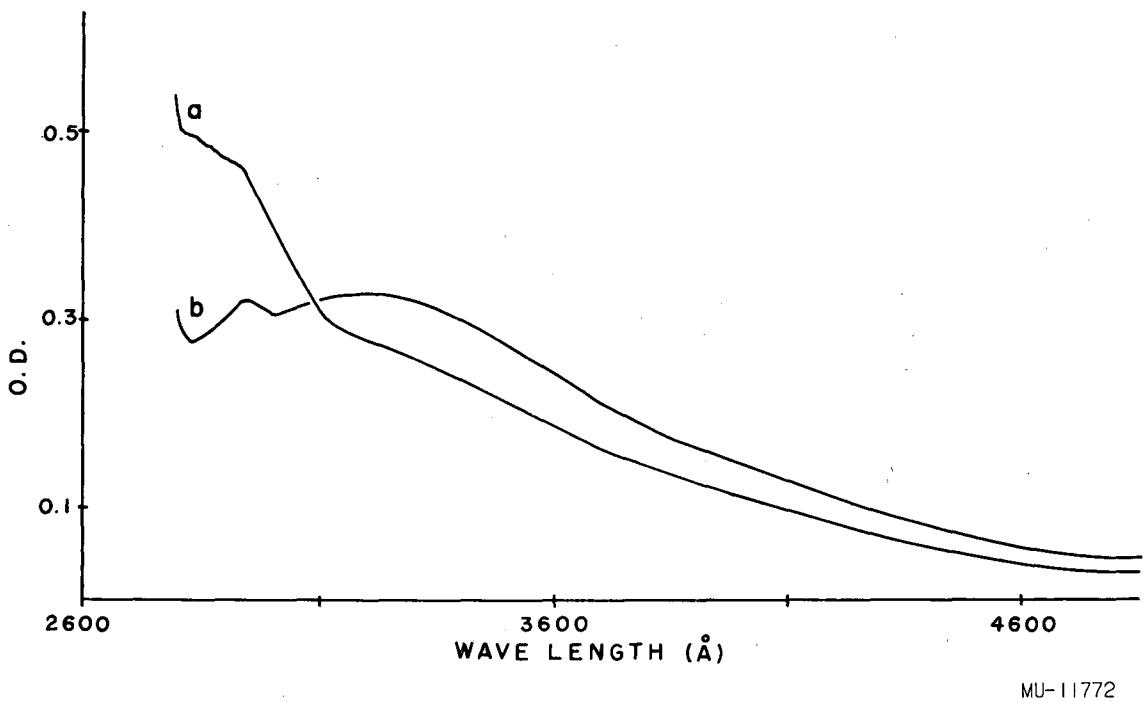

Fig. 27. The absorption spectra of the final products of the photolysis of DPPH-toluene solutions. Curve a represents the products in an air-saturated solution; Curve b represents the products in a degassed solution. $O.D._0^{5300A} = 0.330$.

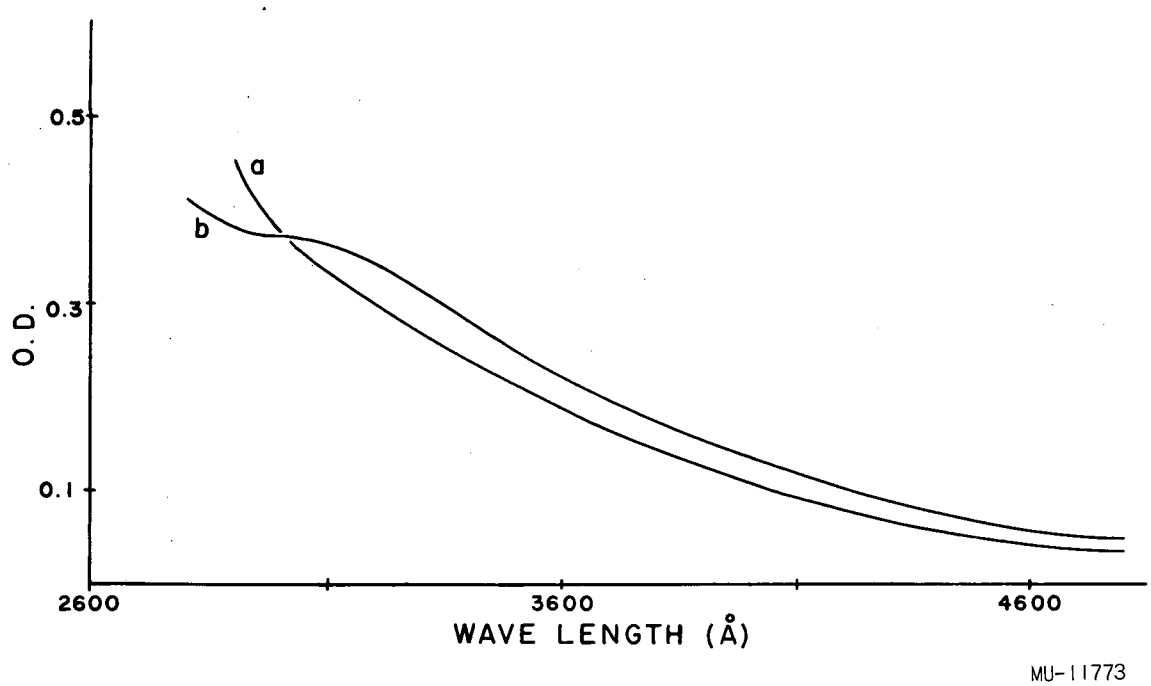

Fig. 28. The absorption spectra of the final products of the photolysis of DPPH-chlorobenzene solutions. Curve a represents the products in an air-saturated solution; Curve b represents the products in a degassed solution. O. D. $_{5300A}$ = 0.335.

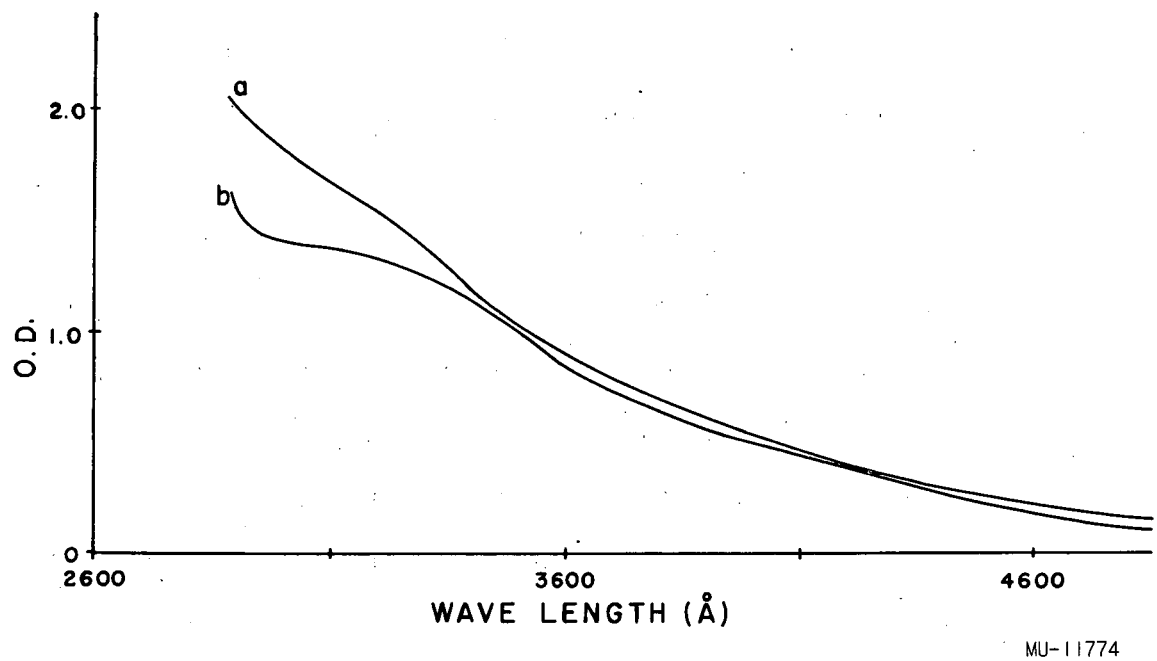

Fig. 29. The absorption spectra of the final products of the photolysis of DPPH-bromobenzene solutions. Curve a represents the products in an air-saturated solution; Curve b represents the products in a degassed solution. $O.D._0^{5300} = 1.3$.

IV. CONCLUSION

The rates of the photoinduced disappearance of DPPH from solutions of DPPH in cyclohexane, benzene, toluene, chlorobenzene and bromobenzene have been studied by use of ultraviolet light of wave length 3126-3130 A. At least two types of reactions occur in the solutions studied. These two types of reactions were identified as (a) the reaction of an excited triplet state of the solvent molecule with DPPH, and (b) a reaction involving the excited DPPH molecule. This reaction involving DPPH does not result in the abstraction of a solvent hydrogen atom by DPPH.

These results indicate that the assumption by Prevost-Bernas[32] et al. and Chapiro[8-10] that activated molecules do not react with DPPH, is invalid. Therefore, the use of DPPH as a radical scavenger in the presence of electronically activated species must be considered qualitative unless the reaction of DPPH with free radicals can be identified uniquely.

The presence of air in the photolyzed systems complicated the reactions somewhat. This complication is not well understood, but oxygen is known to form peroxides with excited solvent molecules which react with DPPH. In the absence of oxygen these species would not react with DPPH directly because their lifetimes are so short that reaction with DPPH is improbable.

Since, in general, it is believed that aromatic molecules in excited singlet states yield triplet states of lower energy (when they exist) by a radiationless process, it is suggested that a study of the rate of disappearance of DPPH due to the reaction of DPPH with molecules in triplet states as a function of the wave length of the incident radiation, might give information concerning the rate of the interconversion process. Several complications to a study of this type are evident. As the wave

length of the incident light is decreased the photodissociation process may contribute significantly to the rate of disappearance of DPPH. Direct absorption to excited triplet levels, not measurable, may contribute to the rate of disappearance of DPPH. As the wave length of the incident light is decreased, the photolysis of DPPH itself becomes more important.

The identification of the products formed by the reaction of excited species and free radicals with DPPH is essential for a complete understanding of the scavenger properties of DPPH.

Acknowledgment

I am indebted to the late Professor Gerhard K. Rollefson, whose advice, encouragement, and friendship during the initial stages of my graduate career were indispensable.

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Appendix I - Corrections for Inner Filter Effects

In order to determine the quantum yields of the reactions where light absorption in the reaction vessel is not negligible, it is always necessary to apply a correction for this inner filtering effect.

The absorption laws of Beer and Lambert give

$$\frac{I}{I_0} = e^{-\epsilon CX} \quad , \qquad \text{(V-1)}$$

where C is the concentration of the absorbing substance in moles/liter; X is the thickness of the absorbing layer in centimeters; ϵ is the absorption coefficient of the absorber; I_0 is the incident light intensity; and I is the intensity at thickness X.

The effective intensity or average intensity of the light over a thickness X is given by

$$I_{eff} = \frac{\int_0^X I dX}{\int_0^X dX} \quad . \qquad \text{(V-2)}$$

Substituting 5a in 5b, one obtains

$$I_{eff} = \frac{\int_0^X I_0 \, e^{-\epsilon CX} \, dX}{X} = \frac{I_0 \, (1 - e^{-\epsilon CX})}{\epsilon \, C \, X} \qquad \text{(V-3)}$$

or, in terms of optical density of the solution,

$$I_{eff} = \frac{I_0 (1 - e^{-(O.D.)})}{(O.D.)} \qquad \text{(V-4)}$$

where O.D. is the optical density and is defined as

$$O.D. = \epsilon CX \qquad \text{(V-5)}$$

If two substances with different extinction coefficients are present as absorbers, Eq. (5d) becomes

$$I_{eff} = \frac{I_0 \left(1 - e^{-(O.D._1 + O.D._2)}\right)}{(O.D.)_1 + (O.D.)_2} \qquad \text{(V-6)}$$

Appendix II

The method of successive approximations for determining the curves that describe the two Reactions (I-12) and (I-8) from the original data is represented by Fig. 30.

Curve ACB is a plot of the observed rate of disappearance of DPPH versus the optical density of DPPH (optical density is proportional to the concentration). At point C, the maximum of curve ACB, where O.D. = X, a correction is made for the inner filter effect of the DPPH absorption, assuming that most of the reaction at this point is caused by the activated solvent molecules. Line zy, then, represents approximately the rate of disappearance of DPPH if no inner filter effect were present. Curve zD is then drawn so that it describes the reaction

$$S^* + DPPH \longrightarrow \text{products}$$

as it would be observed with the inner filter effect of DPPH absorption present. The amount of reaction AD was assumed then to be due to another reaction, (I-8).

Curve OF is then drawn so that it describes Reaction (I-8) which is proportional to the amount of light absorbed by DPPH (the inner filter effect of the solvent is neglected): EF = A.D.

It is seen, then, that at O.D. = X, the inner filter correction should not be applied to the amount of reaction represented by WX. This lowers curve zD at z by the amount WX multiplied by the correction for the inner filter effect at X. This correction, made successively, gives curves z"D' and OF' which describe the two reactions, (I-12) and (I-8); and which when added together give curve z"A. Curve z"A is then the curve that would be expected if S* had a lifetime that was very long compared to the time between collisions of S* and DPPH.

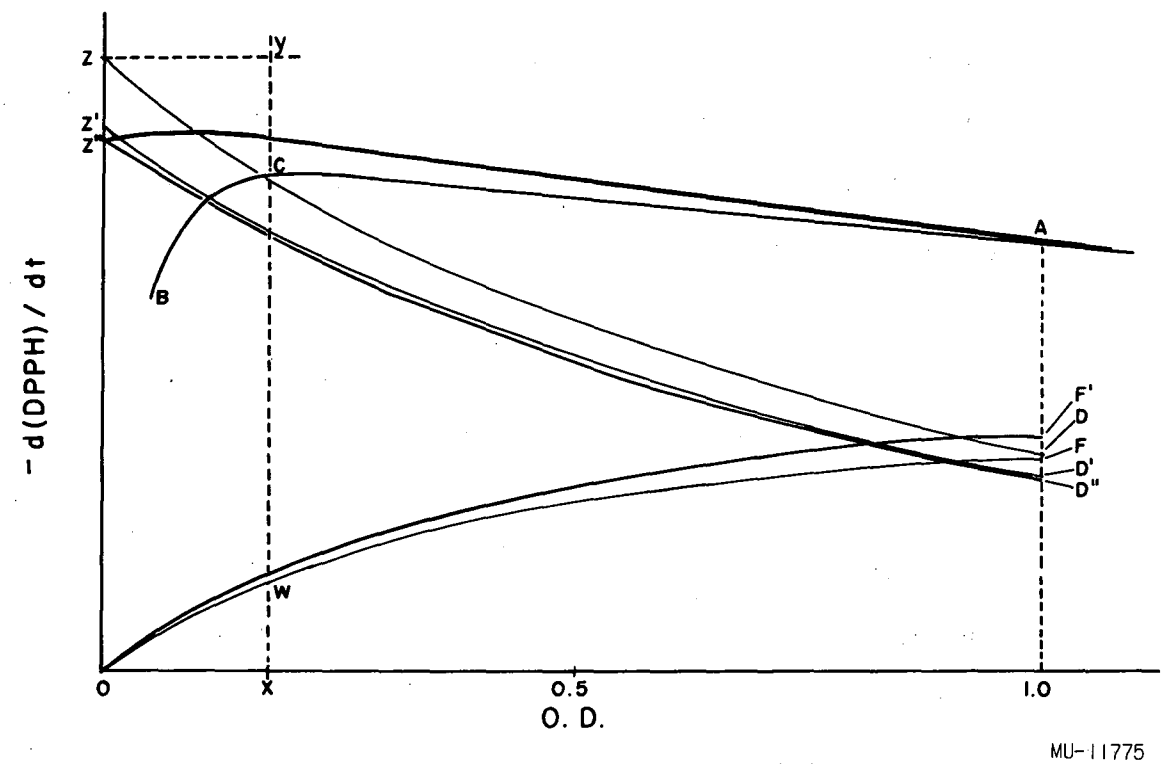

Fig. 30. The representation of the method for determining two curves describing reactions I-8 and I-12 from the original rate data.

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