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**PRELIMINARY INVESTIGATION OF SENSITIZED PHOTOLYSIS AS
A METHOD FOR THE DESTRUCTION OF HERBICIDES DERIVED
FROM 2,4-DICHLOROPHENOXYACETIC ACID**

Morris T. Reagan, Ph.D.
William H. Dennis, Jr.
David H. Rosenblatt, Ph.D.

**US ARMY MEDICAL BIOENGINEERING RESEARCH and DEVELOPMENT LABORATORY
Fort Detrick
Frederick, Md. 21701**

December 1974

FINAL COMPREHENSIVE REPORT FOR PERIOD JUNE 1973 - AUGUST 1974

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Herbicides	Propiophenone	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Photosensitized decomposition in aqueous solution was studied as a possible means of disposal of excess stocks of 2,4-dichlorophenoxyacetic acid (2,4-D). Under the conditions used, photodecomposition of 2,4-D was more than threefold faster with uranyl ion than with riboflavin. Photolysis of 2,4-D could be effected with ferric ion as a catalyst, but only under heterogeneous conditions. In methanol solution, 2,4-D octyl ester was quickly saponified by addition of a small excess of aqueous potassium hydroxide; appropriate dilution of the		

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20. Abstract (Continued)

reaction mixture and addition of riboflavin sensitizer permitted photodecomposition of the 2,4-D thus produced. Attempts to photosensitize the decomposition of 2,4-D octyl ester in isopropyl alcohol with triphenylamine, with riboflavin, with Michler's ketone, and with propiophenone were uniformly unsuccessful.

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TABLE OF CONTENTS

LIST OF FIGURES	2
LIST OF TABLES	3
INTRODUCTION	5
OBJECTIVE	6
MATERIALS AND METHODS	6
RESULTS AND DISCUSSION	16
CONCLUSIONS	27
SUGGESTIONS FOR FUTURE WORK	27
LITERATURE CITED	32
DISTRIBUTION LIST	35

LIST OF FIGURES

FIGURE 1	Crosby-Tutass Mechanism of 2,4-DH Photodecomposition . . .	7
FIGURE 2	Photolysis of 2,4-DH. Initial Molarity 4.99×10^{-3} . . .	17
FIGURE 3	Spectrum of Uranyl Nitrate, 0.00481 M, in the Presence of Various Ligands	20
FIGURE 4	Spectrum of Uranyl Nitrate, 0.0588 M, in Water	21
FIGURE 5	Photolysis of 2,4-DH at pH 7.0. Initial Molarity 4.99×10^{-3}	26
FIGURE 6	Photochemical Irradiation Vessel	29

LIST OF TABLES

TABLE 1	Dependence of Rate of Photolysis of 0.00250 M 2,4-DH on Concentration of Uranyl Nitrate (45 Min Irradiation) . . .	12
TABLE 2	Dependence of Rate of Uranyl-Sensitized Photolysis on 2,4-DH Concentration	13
TABLE 3	Effect of Various Ligands on Visible Absorption Maxima of Uranyl Nitrate	15
TABLE 4	Initial Rates of Disappearance of 2,4-DH with 4.2×10^{-3} M Sensitizer. (Initial 2,4-DH Molarity, 4.99×10^{-3})	18
TABLE 5	Irradiation of 2,4-DH in Presence and Absence of Riboflavin .	18
TABLE 6	Two Trials of Irradiation of 2,4-DH with Uranyl Nitrate . . .	19
TABLE 7	Average Rate of Disappearance of 2,4-DH (Initially 2.50×10^{-3} M) During 45 Min of Irradiation with Different Concentrations of Uranyl Nitrate	22
TABLE 8	Effect of 2,4-DH Concentration on the Rate of Uranyl Ion-Sensitized Photolysis. (Uranyl Ion Concentration, 0.01364 M)	23
TABLE 9	Irradiation of 4.99×10^{-3} M 2,4-DH Containing 2.21×10^{-2} M Ferric Nitrate	25

INTRODUCTION

A report by Miller (1972)¹ has defined the problem of disposal of two general categories of military pesticides: relatively large, consolidated stockpiles of military standard pesticide formulations (primarily organochlorine); and lesser quantities of various types of wastes (primarily organophosphate and carbamate) generated by the use of military standard pesticide formulations in worldwide Department of the Army pest management programs. That report recommended the investigation of thermal and microbiological methods for the destruction of large pesticide stockpiles, and the investigation of chemical methods for the destruction of pesticide wastes generated by routine pest management operations. In a subsequent report, Dennis (1972)² identified hydrolysis, dechlorination, oxidation, and photolysis as potential methods for the chemical destruction of relatively small quantities of routinely generated pesticide wastes, and recommended investigation of these types of chemical reactions to determine their suitability for use in an operational setting.

Since that time, considerable effort has been expended in investigating the hydrolysis of various organophosphate insecticides, catalyzed dechlorination of various organochlorine pesticides, and photolysis of phenoxyacetic acid herbicides. This report is related to the latter type of chemical destruction, namely, sensitized photolysis of 2,4-dichlorophenoxyacetic acid derivatives.

The problem of artificially harnessing the sun's energy has been discussed broadly by Daniels (1964)³. The rate at which solar energy reaches the earth's surface depends on a number of variables, but a reasonable average is $900 \text{ cal min}^{-1} \text{ft}^{-2}$ under a cloudless sky (Daniels, 1964)³. Comparison of this value with typical chemical activation energies shows that solar photodecomposition rates of the order of one mole per square foot of irradiation surface per hour might easily be expected if the energy could be efficiently trapped. With the probable exception of some chain processes, most sun-driven reactions are much slower than might be hoped on the basis of these data. The reasons are that (1) most compounds absorb only a small fraction of the wave-lengths reaching the earth's surface, (2) some of a compound's absorption bands may be chemically inactive, (3) a certain fraction of electronically excited molecules undergoes thermal decay rather than conversion to products, and (4) reaction products and intermediates may act as "inner filters" and protect the reactant from further degradation. The photolysis of 2,4-D has been reported by a number of authors (Crosby and Tutass, 1966⁴; Bell, 1965⁵; Payne and Fults, 1947⁶).

Crosby and Tutass (1966)⁴ conducted a very thorough product study of the photolysis of 2,4-D. Their proposed mechanism is shown in Figure 1. Components of their scheme not shown in the figure are molecular oxygen as a reactant, and glycolic acid and hydrogen chloride as products.

The use of riboflavin as a photosensitizer of the decomposition of 2,4-D has been reported (Crosby and Tutass, 1966⁴; Hansen and Buchholtz, 1952⁷). On the basis of a review by Plimmer (1970)⁸ it seems that no other sensitizers have been employed.

To provide continuity with previous studies, riboflavin was used as a sensitizer in the present work. The use of ferric ion and of uranyl ion as sensitizers in actinometry with oxalic acid (Parker, 1953⁹) prompted an investigation of these cations as sensitizers in 2,4-D photolysis. Representative organic triplet sensitizers (Michler's ketone, propiophenone and triphenylamine) (Lamola, 1969¹⁰) were also tried for the same purpose.

OBJECTIVE

The objective of this study was to investigate the feasibility of using a selected group of photosensitizers for sensitized decomposition with sunlight, as a means of disposal of excess quantities of herbicides derived from 2,4-dichlorophenoxyacetic acid.

MATERIALS AND METHODS

Materials. The substances used were free 2,4-dichlorophenoxyacetic acid and octyl 2,4-dichlorophenoxyacetate (hereafter, respectively, 2,4-DH and 2,4-DE). Solvents were reagent grade. Ferric nitrate nonahydrate and uranyl nitrate hexahydrate were Baker "Analyzed" reagent. Aqueous potassium hydroxide solution (0.4878 molar) was freshly prepared from Baker "Analyzed" reagent, and was standardized by triplicate titration of dried, weighed potassium hydrogen phthalate (primary standard grade) in water containing alcoholic phenolphthalein (1 drop) to a faint pink endpoint. The solution, kept tightly stoppered, was used over a period of seven weeks.

A stock solution of 2,4-DH (Aldrich; hereafter "solution I") was prepared by dissolving an analytically weighed quantity of the compound (approximately 4.41 grams, 0.02 mole) and an accurately measured equivalent amount of potassium hydroxide (approximately 41.0 ml 0.4878 M solution) in enough water to form 2 liters of solution. The solution was stored tightly stoppered in the dark for up to 5 weeks. For analysis an aliquot (25 ml) of solution I, acidified with hydrochloric acid (6 M), was extracted with

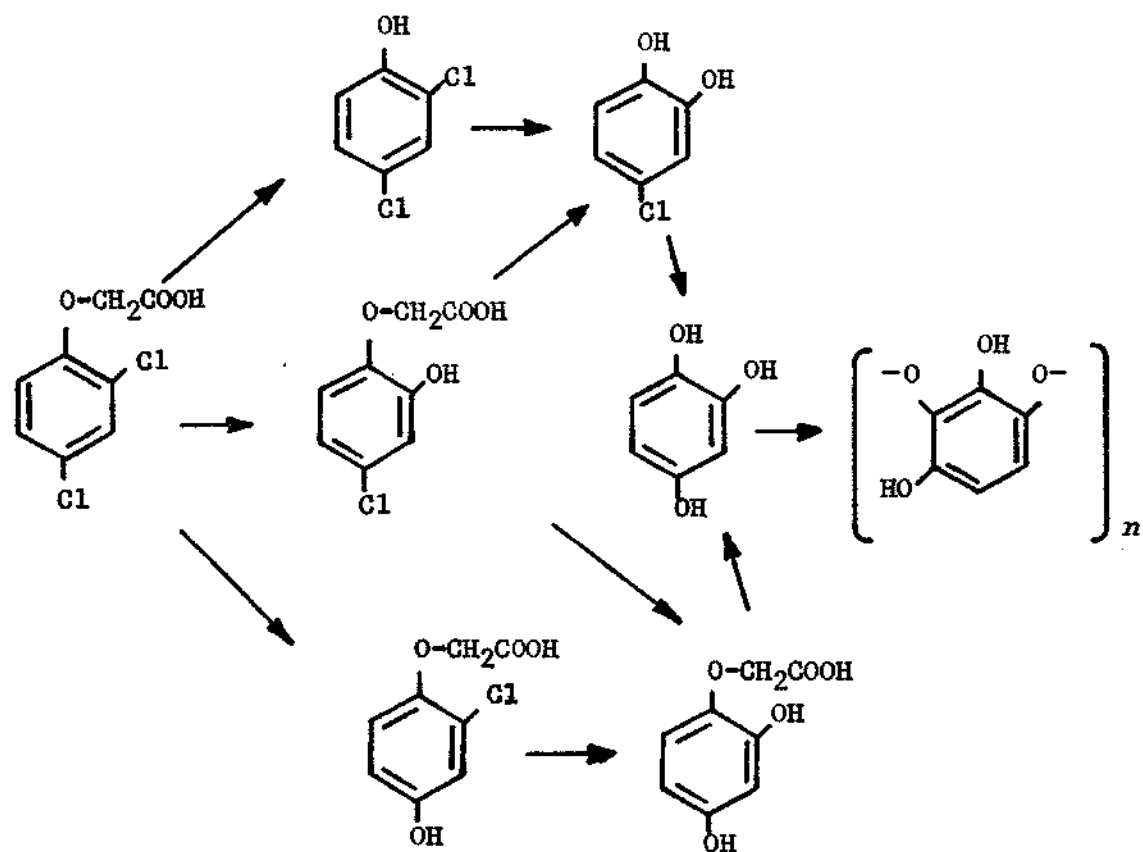


FIGURE 1. Crosby-Tutass Mechanism of 2,4-DH Photodecomposition.

ether (5 ml) and the ether extract was treated with an excess* of diazomethane solution (3 ml). Gas chromatographic examination of the ether layer showed that Solution I was stable during the storage period.

Riboflavin was stored in a refrigerator. Because of its low solubility in water, 0.3 gram per 100 ml (Lange, 1961¹¹), it was handled as a saturated aqueous solution. Saturated solutions were prepared by overnight magnetic stirring of a large excess of finely divided solid with water, followed by filtration. Michler's ketone and triphenylamine were only slightly soluble in aqueous isopropyl alcohol, and saturated solutions of these substances were prepared by a method similar to that used for riboflavin.

The 2,4-DE was a military standard formulation of the herbicide**. The material was dark brown-black, and was distilled *in vacuo* (bp 157-158°). The distillate was colorless but faintly cloudy, and gas chromatographic analysis (230°) revealed the presence of impurities in significant quantities.

Gas Chromatography. All analyses reported here were conducted with a Hewlett-Packard Model 5700A gas chromatograph; the column contained 3% OV 1 on 80/100 mesh Chromosorb W. The internal standard used for analysis of 2,4-D methyl ester was nonadecane (Aldrich, 97%).

Electronic spectra were recorded in quartz 1-cm cells with a Beckman Acta V visible-ultraviolet recording spectrophotometer, and pH was measured with an Orion "Ionalyzer" Model 801 pH meter.

General Photochemical Method. Unless otherwise stated, the following procedure was used. The solution in a 120 x 40 mm crystallizing dish was submerged to a depth of about 30 mm in a Forma water bath at 2°, and the contents were irradiated with a General Electric 275 watt sunlamp placed 3 inches above the solution with the beam perpendicular to the surface. The temperature of the solution during irradiation was near 15°. An aliquot

*If the yellow color of diazomethane remained for several minutes after the diazomethane solution was added, the reagent was considered to be in excess.

**FSN:6840-577-4194, manufactured by Rhodia, Inc., Chipman Division, New Brunswick, N.J.

was taken for gas chromatographic analysis before the irradiation was begun, and the concentration of unchanged 2,4-DH in each aliquot taken during the irradiation was determined by chromatographic comparison with the initial aliquot. Before each aliquot was withdrawn, the crystallizing dish was removed from the bath, and its contents were made up to the weight recorded after removal of the preceding aliquot by addition of reaction solvent. The stated irradiation times do not include the intervals during which reaction vessels were removed from the light source for analysis.

Rotary Irradiation Method. A means of simultaneously exposing up to eight solutions to identical conditions of irradiation for a fixed period of time was devised with a Bogen phonographic turntable. A circular sheet of thick cardboard (diameter, 12 inches) was fixed flat on the turntable, secured by attachment to the spindle. Eight circular holes, equidistant from the center of rotation, were made near the periphery of the sheet. Beakers (100 ml) could be secured to the turntable by the snug fit of their bases into the holes. The turntable was operated through a Variac transformer to permit control of the rotation speed. Two General Electric 275-watt sunlamps were positioned above the turntable so that during rotation the contents of the beakers would be exposed to periodic doses of radiation directed perpendicular to the solution surfaces. The rotation speed was approximately 15-20 rpm. Each beaker contained a small glass rod, with which its contents were periodically stirred during rotation.

From each solution in the set to be irradiated an aliquot was removed before irradiation was begun. At the end of the irradiation, the content of each beaker was made up with water to the weight recorded for it before irradiation. A second aliquot was removed, and the aliquots of each solution obtained before and after irradiation were analyzed by gas chromatography. The temperature of the solutions rose to *ca.* 40° during the irradiation.

Effect of Riboflavin in Photolysis of 2,4-DH. A mixture of solution I (100 ml) and water or saturated aqueous riboflavin (100 ml) was irradiated by the general photochemical method and periodically sampled for analysis. For analysis a 25-ml aliquot was made faintly acidic (as shown by Hydrion test paper) with a few drops of 6 M hydrochloric acid, then was extracted with ether (5 ml). Excess diazomethane solution (3 ml) was added, followed by 0.5 ml of an internal standard solution (15.3757 grams of nonadecane diluted to 250 ml with heptane). After being allowed to stand for several minutes, the mixture was shaken, and duplicate samples of the ether layer were analyzed by gas chromatography. The peak heights of the 2,4-D methyl ester and the internal standard were used to calculate the concentrations of unchanged 2,4-DH in the reaction solutions.

Ferric Nitrate-Sensitized Photolysis of 2,4-DH. Ferric nitrate nonahydrate (1.7811 gram, 0.00441 mole) was mixed with solution I (100 ml) and water (100 ml). A fine, milky precipitate formed. The mixture was treated by the general photochemical method. For analysis, the reaction mixture was well stirred, and a 25-ml aliquot was treated with 1 drop of 6 M hydrochloric acid, then extracted with ether. Excess diazomethane solution (3 ml), then 0.5 ml internal standard solution (15.3757 grams of nonadecane diluted to 250 ml with heptane) was added. After being allowed to stand for several minutes and shaken, the ether layer was analyzed in duplicate by gas chromatography (210°). The concentrations of unchanged 2,4-DH were calculated from peak heights of 2,4-D methyl ester and the internal standard.

After 21 hours of irradiation, the remainder of the mixture, which contained a brown-black precipitate, was extracted with ether (ca 5 ml). The clear yellow-brown ether extract was analyzed by chromatography using the program 100° (4 min) → 16 deg/min → 200°. There was no evidence of any substance except the ether solvent. The procedure would have shown the presence of 2,4-dichlorophenol or substance B (see p. 19)

Ferric Nitrate-EDTA Photolysis of 2,4-DH. Ethylenediaminetetracetic acid (EDTA), ferric nitrate nonahydrate, and 2,4-DH were dissolved in water to form a solution 5.0×10^{-3} M in each of the three reagents. It was irradiated for 72 hrs along with a second solution, identical to the first except that it contained no ferric nitrate or EDTA. Samples were periodically withdrawn from both solutions for gas chromatographic analysis.

Uranyl Nitrate-Sensitized Photolysis of 2,4-DH.

Trial 1. Uranyl nitrate hexahydrate (1.4496 grams, 0.002887 mole) in water (100 ml) was mixed with solution I (100 ml) and treated by the general photochemical method. The solution was initially pale yellow and clear, but about 20 min after irradiation was begun it acquired a milky white turbidity and a pungent odor similar to that of 2,4-dichlorophenol. Within 2 hrs a considerable quantity of white precipitate (substance A, p. 19) appeared, much of it adhering to the sides of the crystallizing dish. For analysis, a 25-ml aliquot was extracted with ether (5 ml). Excess diazomethane solution (3 ml) was added, followed by 0.5 ml internal standard solution (15.3757 g nonadecane diluted to 250 ml with heptane). After being allowed to stand for several minutes, the ether aliquots were analyzed in duplicate by gas chromatography (210°). The concentrations of unchanged 2,4-DH in the reaction solution were calculated from the peak heights of 2,4-D methyl ester and the internal standard.

Trial 2. The reaction solution consisted of a mixture of equal volumes of uranyl nitrate hexahydrate reagent (0.429 gram, 0.000846 mole in 100 ml of water) and solution I. The general photochemical method was used. The pH was 4.1 at the beginning and at the end of the irradiation. The analytical method was that used in Trial 1, except that the internal standard used with each aliquot was 1 ml of a solution prepared by dilution of nonadecane (1.2410 gram) to 100 ml with heptane. In the chromatographic analysis, concentrations of 2,4-D methyl ester and of the internal standard were taken to be proportional to the peak areas.

Trial 3. The reaction solution was solution I (100 ml) mixed with water (105 ml) and uranyl nitrate hexahydrate (0.7194 gram, .001433 mole). The solution was irradiated for 60 min, and an aliquot (25 ml) was treated with 1 drop of 6 M hydrochloric acid, then extracted with ether (5 ml). Chromatographic analysis (180°) of the ether extract showed a sharp peak (retention time, 0.3 min) identical to the peak produced by chromatography of an authentic sample of 2,4-dichlorophenol in ether, and a much smaller sharp peak (substance B, p. 19) with 0.4 min retention time.

Dependence of Rate of Photolysis of 0.00250 M 2,4-DH on the Concentration of Uranyl Nitrate. The rotary irradiation method was used. The concentrations of uranyl nitrate hexahydrate used are shown in Table 1. The solutions were irradiated 45 min. Turbidity appeared during the irradiation, first in Solution 4, last in Solution 2, and not at all in Solution 1. For analysis, a 25-ml aliquot was extracted with ether (5 ml). Excess diazomethane solution (3 ml), and internal standard solution (1 ml of 1.2410 grams nonadecane per 100 ml heptane solution) were added, and after being allowed to stand for several minutes, the ether layer was analyzed in duplicate by gas chromatography (210°). The molarities of 2,4-DH in the reaction mixtures at the end of the irradiation are given in Table 1. These values were calculated from the peak areas of 2,4-D methyl ester and internal standard.

Chromatograms of the ether extracts of the irradiated portion of all four solutions had, in addition to the 2,4-D methyl ester peak, a small, sharp peak identical to one produced by authentic 2,4-dichlorophenol. The 2,4-dichlorophenol was eluted only about 10 sec later than the solvent, and in earlier experiments its peak was often obscured. The reason for its sharp appearance in this experiment was probably that the chromatographic column had been freshly repacked.

TABLE 1. Dependence of Rate of Photolysis of 0.00250 M 2,4-DH on Concentration of Uranyl Nitrate (45 Min Irradiation).

Solution	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ grams	(M x 10 ³)	2,4-DH Molarities at End of Irradiation x 10 ³
1	0.3593	3.58	2.04
2	0.7967	7.93	1.85
3	1.1222	11.18	1.75
4	2.6371	26.26	1.40

Dependence of Rate of Uranyl-Sensitized Photolysis on the Concentration of 2,4-DH. The rotary irradiation method was used. Dilutions of Solution 1 were prepared and the volume of each (200 ml) was brought to 210 ml by addition of 10 ml of 0.2865 molar uranyl nitrate solution, so that the initial molarity of uranyl ion in each reaction solution was 0.01364 (see Table 2). A sample of each solution was irradiated for 50 min. A 25-ml aliquot of each solution was analyzed in the usual manner, with nonadecane (1.2410 g) diluted to volume (100 ml) as the chromatographic standard.

As explained on p. 18, Solution 3 of Table 2 did not follow the trend of the other three solutions. In the triplicate analysis of the unirradiated sample of Solution 3 there was an average deviation from the mean of $\pm 23\%$ in area of the 2,4-D methyl ester peak relative to the area of the internal standard peak. In the other seven analyses presented in the last two columns of Table 2, the average deviation from the mean in the relative area measurement ranged from $\pm 0.5\%$ to $\pm 10.4\%$, with an average of $\pm 4.5\%$.

Behavior of 2,4-Dichlorophenol Under Conditions of Uranyl Ion-Sensitized Photolysis of 2,4-DH. Potassium hydroxide (0.4878 molar solution, 2.05 ml; 0.000999 mole) and 2,4-dichlorophenol (0.1663 gram, 0.00102 mole) were mixed with uranyl nitrate hexahydrate (0.4508 gram, 0.000398 mole) and water (100 ml). The pH of the clear solution was 3.4; the yellow color was much deeper than the pale yellow typical of aqueous solutions containing similar

TABLE 2. Dependence of Rate of Uranyl-Sensitized Photolysis on 2,4-DH Concentration.*

Solution	2,4-DH Concentration $\times 10^3$ (M)	
	Before Irradiation	After Irradiation
1	4.99	3.55
2	2.50	1.11
3	1.25	0.99
4	0.749	0.243

*0.01364 M in uranyl nitrate; time 50 min.

concentrations of uranyl ion. An aliquot (20 ml) was extracted with ether (5 ml), and gas chromatographic analysis (110°) of the extract showed a diffuse peak with a retention time of about 0.9 min. A second aliquot (20 ml) was extracted with ether (5 ml), and excess diazomethane solution (3 ml) was added. The yellow diazomethane color of the ether layer faded over a period of several minutes. Gas chromatographic analysis of the ether layer showed diminution of the 2,4-dichlorophenol peak, and the appearance of a new peak (retention time, ca. 1.7 minutes) attributable to 2,4-dichloroanisole. Addition of more diazomethane solution (3 ml) caused further diminution of the 2,4-dichlorophenol peak and growth of the 2,4-dichloroanisole peak.

The remaining portion of the aqueous solution of 2,4-dichlorophenol and uranyl ion in a crystallizing dish positioned in a 2° water bath was irradiated with a General Electric 275-watt sunlamp. Aliquots (20 ml each) were periodically removed and extracted with ether (5 ml). The ether extract was analyzed by gas chromatography. The aliquots analyzed at the ends of the first and second hours of irradiation appeared qualitatively the same as the unirradiated solution; after 19 hours, however, the ether extract of the aliquot gave a blank gas chromatogram. Furthermore, the reaction solution became appreciably darker during the irradiation, although no precipitate formed during the first four hours. After 19 hours, a dark precipitate was present.

Spectrum of Uranyl Nitrate in the Presence of Various Ligands. To assist in interpreting the spectra of reaction mixtures, five aqueous solutions, each 4.214×10^{-3} molar in uranyl nitrate hexahydrate, were prepared by appropriate admixture and dilution of stock solutions in volumetric flasks. Four of the solutions contained additional solutes. The concentrations of these were:

Solution 1. No additional solute.

Solution 2. 2,4-dichlorophenol ($5.083 \times 10^{-3} M$).

Solution 3. 2,4-dichlorophenol ($5.083 \times 10^{-3} M$) and potassium hydroxide ($4.974 \times 10^{-3} M$).

Solution 4. 2,4-DH ($4.992 \times 10^{-3} M$) and potassium hydroxide ($5.000 \times 10^{-3} M$).

Solution 5. Potassium hydroxide ($4.974 \times 10^{-3} M$).

The spectrum of each solution was recorded between 600 and 200 nm. The cells were 1 cm, and water was in the reference cell. The results are shown in Figure 3 and summarized in Table 3. The spectrum of a more concentrated solution ($5.883 \times 10^{-2} M$) of aqueous uranyl nitrate is shown in Figure 4.

Saponification of 2,4-DE. Saponification of 2,4-DE was required to make this material water-soluble and thus susceptible to decomposition by sensitizers in aqueous solution. To a solution of 2,4-DE (0.1074 gram, 0.000322 mole) in methanol (10 ml) was added 1 ml of 0.4878 molar aqueous potassium hydroxide. The initially cloudy mixture became clear on being swirled. After 10 minutes, a portion of the solution was made just acidic (Hydrion paper) with a few drops of 6 M H_2SO_4 . A chromatogram (230°) of the solution prior to the addition of the potassium hydroxide showed a strong 2,4-DE peak. The chromatogram obtained 10 minutes after addition of potassium hydroxide showed only the solvent peak. The chromatogram obtained after the acidification step showed only the solvent peak and a very small impurity shoulder also seen in 2,4-DE solution before it was treated with potassium hydroxide.

Destruction of 2,4-DE Utilizing Saponification Followed by Riboflavin-Sensitized Photolysis. 2,4-DE (0.5890 gram, 0.00177 mole) in methanol (100 ml) was mixed with 0.4878 M aqueous potassium hydroxide (10 ml). After 15 minutes, an aliquot (25 ml) was added to a saturated aqueous solution of riboflavin.

TABLE 3. Effect of Various Ligands on Visible Absorption Maxima of Uranyl Nitrate.

Source of Data	$\lambda_{\max}(\text{nm})^*$
Figure 4	484(0.7), 468(1.4), 426(7.1), 414(8.5), 402(7.8), 369(3.4), 359(3.7)
Figure 3	
Solution 2	412(22.8), 401(23.6)
Solution 3	492(7.3), 476(8.5), 425(39.5)
Solution 4	419(16.6)
Solution 5	495(20.8), 422(68.6)

*Molar absorptivities are in parentheses.

The solution, in a crystallizing dish supported in a 2° water bath, was irradiated with a General Electric 275-watt sunlamp. Initial molarities in the irradiated solution were 0.00354 for 2,4-DH and about 0.004 for riboflavin. For analysis, an aliquot (25 ml) was extracted with ether (5 ml) and excess diazomethane solution (3 ml) was added. After *ca.* 3 hours of irradiation, the yellow color of riboflavin was noticeably paler. After 4 hours, roughly half the 2,4-DH was destroyed. A significant amount remained even after 18 hours.

Comparison of Prospective Organic Sensitizers of the Photolysis of 2,4-DE in Aqueous Isopropyl Alcohol. Three solutions were prepared, each containing 0.173 mole/liter 2,4-DE, and a prospective organic sensitizer. In each case the solvent was 7:3 (v/v) isopropyl alcohol:water, and the volume of each solution was 2 ml. One solution contained 0.591 M propiophenone (Eastman White Label). The second solution was half-saturated with riboflavin, and the third was half-saturated with triphenylamine. A fourth solution, used as a blank, was identical to the other three except that it contained no prospective sensitizer. The four solutions, each standing vertically in an open shell vial, were equivalently placed approximately 3 inches below a Mineralight Model R52 short wave ultraviolet lamp and irradiated for 40 hours. A 1-ml sample of each solution was analyzed by gas chromatography (230°) just prior to, near the mid-point, and at the end of the irradiation period. Before being sampled, each solution was diluted to its premarked original volume

with 7:3 (v/v) isopropyl alcohol:water. No change in 2,4-DE concentration appeared in any of the samples, and no new peaks were seen in the chromatograms. The only sensitizer chromatographically observable under the conditions used, triphenylamine, underwent no apparent change.

A second experiment was qualitatively and quantitatively identical to the one just described, except as follows. In addition to four solutions like those described above, a fifth solution (2 ml) in 7:3 (v/v) isopropyl alcohol:water, 0.173 M in 2,4-DE and half-saturated with Michler's ketone (kindly donated by Dr. D. O. Cowan), was irradiated. The vials containing the solutions were stoppered, and were exposed in horizontal position to direct outdoor sunlight for the daylight hours of six consecutive days. As in the experiment described above, gas chromatograms (230°) showed no diminution in the 2,4-DE peak of any of the solutions. The initial yellow color of the solution containing riboflavin faded completely.

RESULTS AND DISCUSSION

It was found that the sunlamp photolysis of 2,4-DH in aqueous solution is strongly promoted by uranyl ion, and also by ferric ion. Most of the present effort went into the study of uranyl ion sensitization. Figure 2 shows a comparison of the rates of disappearance of 2,4-DH from solutions irradiated with a sunlamp in the absence of a sensitizer, and in the presence of 4.23×10^{-3} M uranyl ion or of $\alpha. 4.2 \times 10^{-3}$ M riboflavin. Under the conditions applicable to the figure, the initial rates of disappearance of 2,4-DH had the values shown in Table 4. It is seen that uranyl ion promotes a significantly more rapid decomposition of 2,4-DH than does riboflavin. Furthermore, uranyl nitrate is, on a molar basis, 425 times more soluble in water than is riboflavin (Lange, 1961)¹¹, so the rate of decomposition of 2,4-DH can be further increased by raising the concentration of uranyl ion.

Riboflavin-Sensitized Photolysis of 2,4-DH. Data in Table 5 show that half saturated riboflavin (4.2×10^{-3} M) induces a two-fold initial acceleration in the photodecomposition rate of 2,4-DH (4.99×10^{-3} M).

Uranyl Nitrate Sensitized Photolysis of Aqueous 2,4-DH. In all trials a creamy precipitate ("Substance A", p. 19) formed within minutes, but was replaced by a dark, tarry material if the solution was irradiated overnight. Evidence of tarry decomposition began to appear before all the 2,4-DH was consumed. The data in Table 6 are from two typical trials. The uranyl ion molarity in trial 2 was the same as that of riboflavin in experiments where the latter was used as a sensitizer.

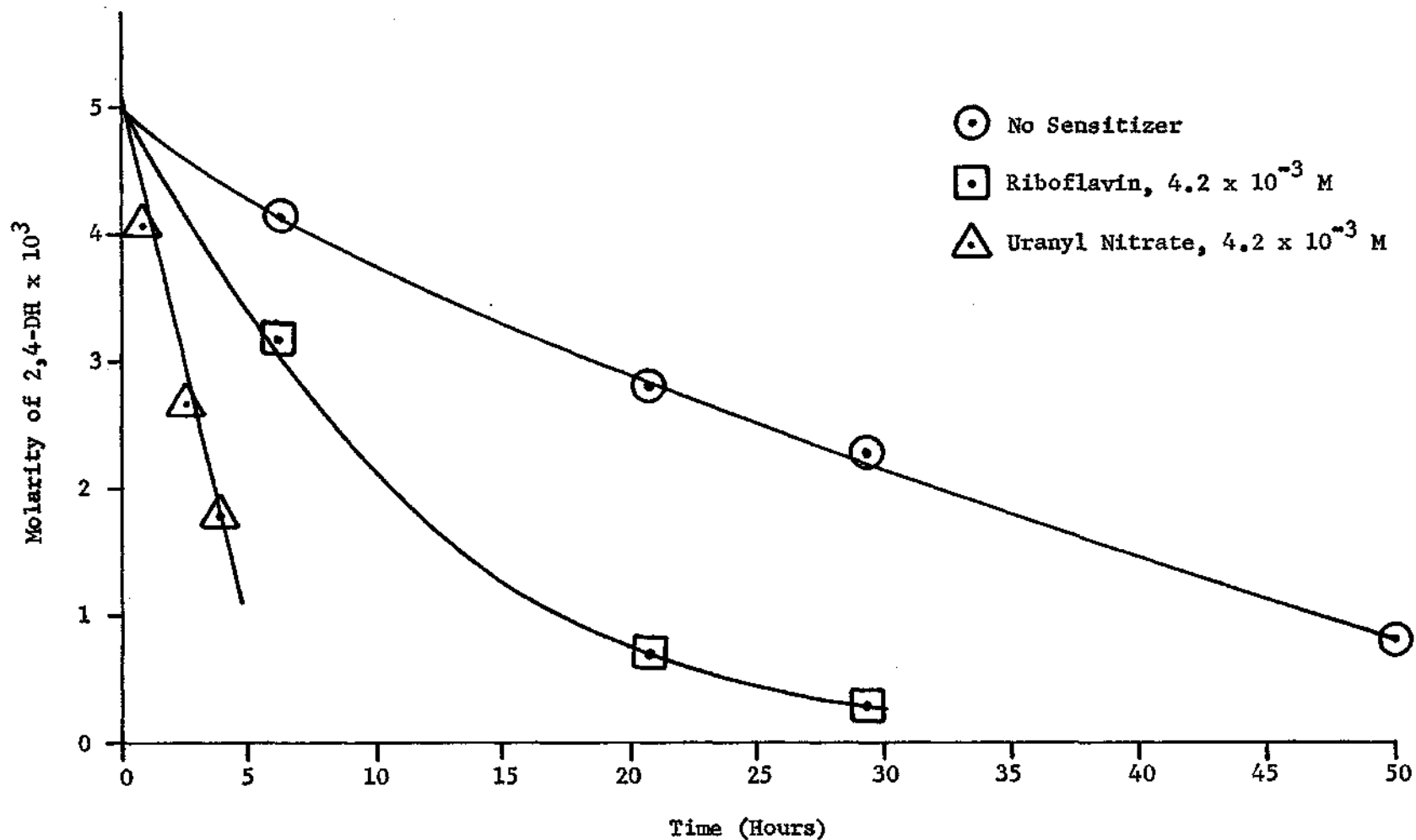


FIGURE 2. Photolysis of 2, 4-DH . Initial Molarity 4.99×10^{-3} .

TABLE 4. Initial Rates of Disappearance of 2,4-DH with 4.2×10^{-3} M Sensitizer. (Initial 2,4-DH Molarity, 4.99×10^{-3}).

Sensitizer Present	Rate of Disappearance of 2,4-DH ($M \text{ sec}^{-1} \times 10^8$)
None	4.27
Riboflavin	9.36
Uranyl nitrate	32.3

TABLE 5. Irradiation of 2,4-DH in Presence and Absence of Riboflavin.

Hours of Irradiation	Concentration of 2,4-DH, ($M \times 10^3$)	
	Riboflavin Present	Riboflavin Absent
0	4.99	4.99
5.25	3.22	4.13
21.50	0.71	2.73
28.50	0.23	2.28
50.50	0	0.84

TABLE 6. Two Trials of Irradiation of 2,4-DH With Uranyl Nitrate

Hours of Irradiation	Concentration of 2,4-DH (moles/l $\times 10^3$)	
	Trial 1 [UO ₂ ⁺⁺] = $1.44 \times 10^{-2} M$	Trial 2 [UO ₂ ⁺⁺] = $4.23 \times 10^{-3} M$
0	4.99	4.99
1	1.36	4.10
2	0.41	2.70

The data in Table 7 are from an experiment in which four 2,4-DH solutions differing only in uranyl nitrate concentration were subjected to identical conditions of irradiation. Table 7 gives the average rate of disappearance of 2,4-DH during the initial 45 minutes of irradiation of each solution. It is seen that a 7.3-fold increase in uranyl ion concentration caused the average reaction rate to increase by a factor of only 2.4. This observation has limited kinetic significance, since the rates are average rather than instantaneous values, and since the weak absorption of visible light by uranyl ion (Figures 3 and 4) indicates that the rate of photon absorption by the solutions must be a significant but unknown function of the uranyl ion concentration. However, if the average rates of Table 7 do not differ too greatly from the initial instantaneous rates, we may conclude that the apparent kinetic order in uranyl ion is less than one-half and that the true order* is less than the apparent order. Thus, the reaction may be of the most common type, in which the true order with respect to the absorbing species is zero. This result would be expected if the only uranyl ion involved in the mechanism during, or prior to, the rate determining step is the one that absorbs the photon in the primary process.

* The *true* order with respect to the light-absorbing species expresses the rate dependence on its concentration in solutions where changes in its concentration do not affect the rate of light absorption. Even if a reaction is truly zero-order in a sensitizer, an increase in the sensitizer concentration, if it causes an increase in rate of photon absorption, will cause an increase in reaction rate so that the "apparent" order in sensitizer exceeds zero.

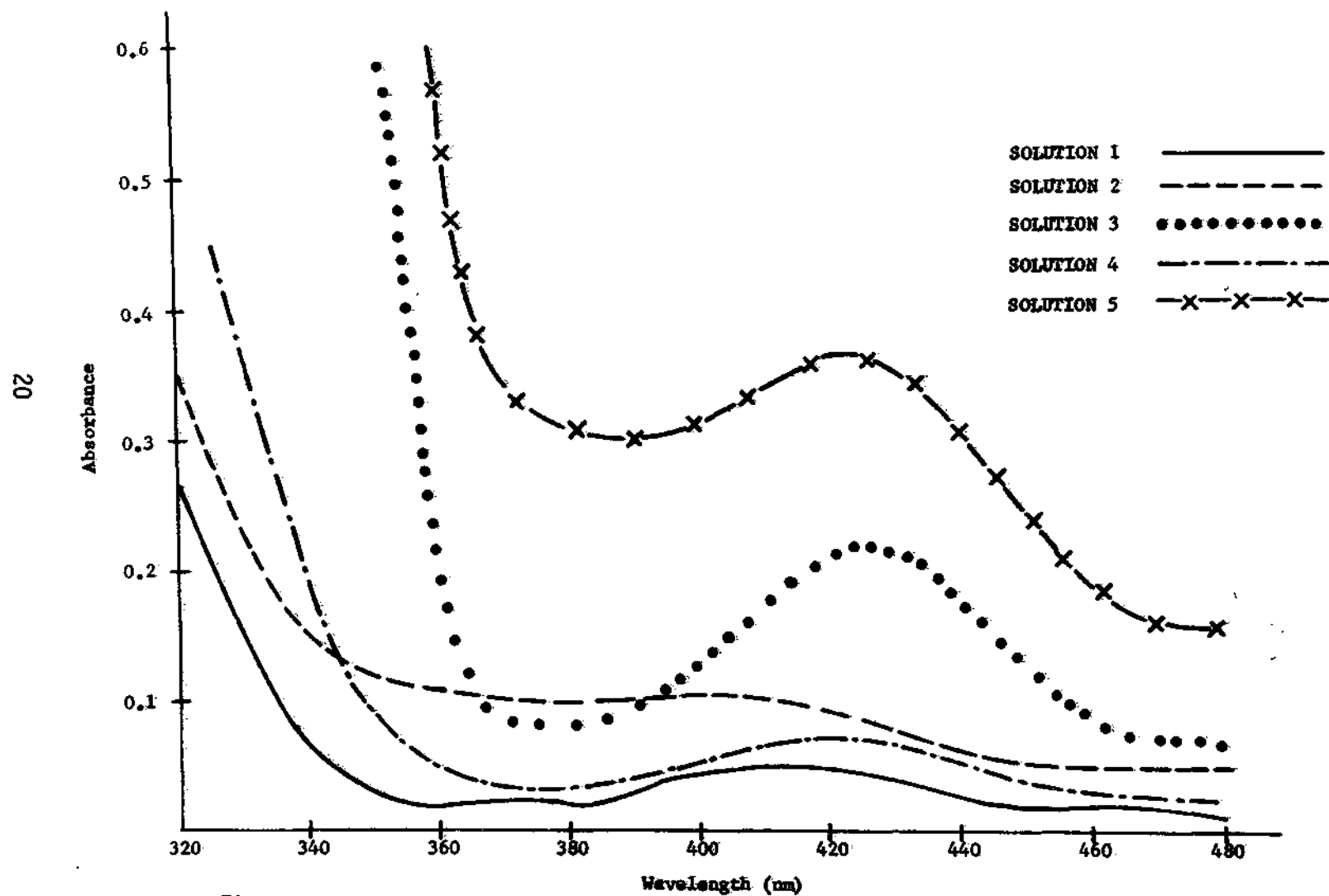


FIGURE 3. Spectrum of Uranyl Nitrate, 0.00481M, in the Presence of Various Ligands.

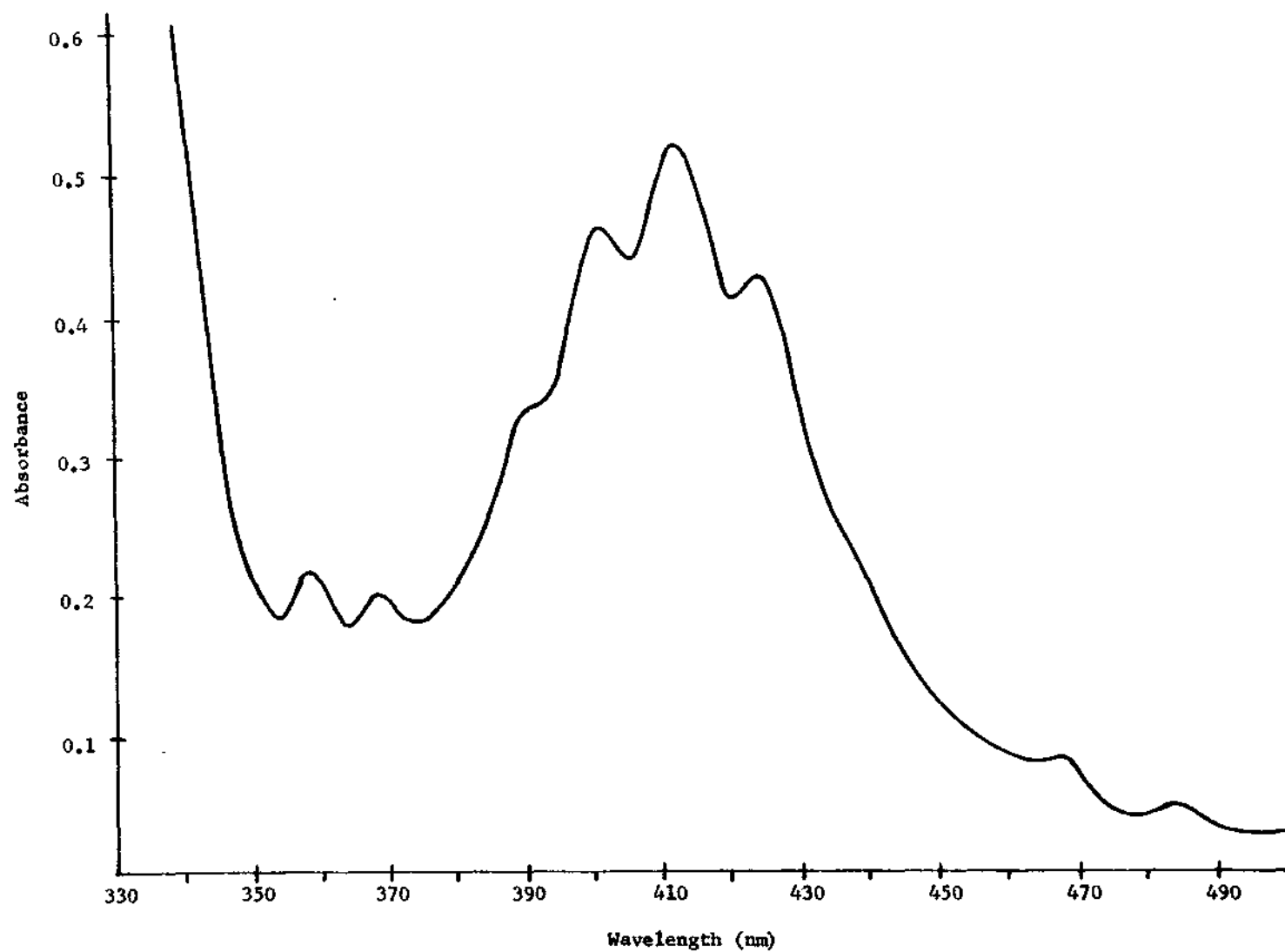


FIGURE 4. Spectrum of Uranyl Nitrate, 0.0588 *M*, in Water.

TABLE 7. Average Rate of Disappearance of 2,4-DH (Initially $2.50 \times 10^{-3} M$) During 45 Min of Irradiation with Different Concentrations of Uranyl Nitrate*

Uranyl Nitrate Concentration ($M \times 10^3$)	Rate of Disappearance of 2,4-DH ($M \text{ sec}^{-1} \times 10^7$)
3.58	1.70
7.93	2.41
11.18	2.78
26.26	4.07

*The data in this table should not be compared with those in Table 4, since both the initial 2,4-DH molarities and effective light intensities were lower in this experiment than in that shown in Table 4.

A study was also made of the dependence of the rate of the uranyl sensitized photolysis on the concentration of 2,4-DH. The data in Table 2 were obtained from an experiment (p. 8) in which four solutions that differed initially only in 2,4-DH concentration were identically irradiated for 50 min. A comparison of the ratios of the molarity of 2,4-DH at the end to that at the beginning of the irradiation period (fifth column of the table) shows that solution 3 did not follow the trend of the other three solutions. This is likely due to experimental error (p. 9). The data from solutions 1 and 2 suggest that the reaction is zero-order in 2,4-DH, since these solutions experienced nearly identical decreases in 2,4-DH molarity. The results with solutions 3 and 4 do not seem to support this suggestion. It should be realized however, that photochemical reactions are very likely to depart from "expected" kinetic behavior when the conversion of reactant to products approaches completion. One reason is that product molecules may quench the electronically excited state of either the reactant or the sensitizer or both. Or the product or an intermediate may be an inner filter that absorbs the same wave lengths as the sensitizer. For these reasons, when a set of solutions like those of Table 8 is irradiated under fixed conditions, the solutions with the lowest initial concentrations of reactant are the most likely to show complex kinetic behavior. Elucidation of the kinetic order in 2,4-DH obviously requires more study.

TABLE 8. Effect of 2,4-DH Concentration on the Rate of Uranyl Ion-Sensitized Photolysis. (Uranyl Ion Concentration, 0.01364 M.)

Solution	2,4-DH Concentration, (M x 10 ³)		Δ [2,4-DH] (M x 10 ³)	$\frac{[2,4-DH]_t}{[2,4-DH]_0}$
	Before Irradiation	After Irradiation		
1	4.99	3.55	1.44	0.711
2	2.50	1.11	1.39	0.444
3	1.25	0.99	0.26	0.792
4	0.749	0.248	0.501	0.331

As shown in Figure 1, direct photolysis of aqueous 2,4-DH leads to polymeric humic acids *via* a complex array of intermediates. It seems likely that the uranyl ion-sensitized photolysis is similarly complex. In the experiments described here, dark tarry material began to appear after about 4 to 3 hrs of irradiation. The most conspicuous substances initially formed were 2,4-dichlorophenol (identified by gas chromatographic comparison with an authentic sample) and an unidentified substance (substance A) that appeared as a fine creamy precipitate 15 to 30 minutes after the onset of irradiation. Chromatographic analysis of partially photolyzed solutions showed, in addition to 2,4-dichlorophenol, an apparently minor amount of another substance (substance B) with a retention time, at 180°, 1.33 times greater than that of 2,4-dichlorophenol. The possibility that substances A and B are identical cannot be excluded.

Conclusive evidence was obtained that substance A is neither identical to, nor formed from, 2,4-dichlorophenol. This was shown by a solution containing 1.00×10^{-2} mole/l each of 2,4-dichlorophenol and potassium hydroxide, and 8.80×10^{-3} mole/l of uranyl nitrate. Irradiation of aqueous solutions of 2,4-DH containing as much as 8.8×10^{-3} mole/l uranyl ion resulted in the prompt precipitation of substance A, even when the initial 2,4-DH molarity was one-fourth that of the 2,4-dichlorophenol in the solution mentioned above. The intensely yellow 2,4-dichlorophenol solution was absolutely clear, and careful inspection revealed no trace of a precipitate. Irradiation of the solution under the conditions used in uranyl-sensitized photolysis of 2,4-DH caused destruction of the 2,4-dichlorophenol, and after more than 4 hrs,

a dark precipitate began to appear. This is in contrast to the light precipitate of substance A formed in 30 min in the uranyl-sensitized photolysis of 2,4-DH.

The solution of 2,4-dichlorophenol and potassium hydroxide in aqueous uranyl nitrate described above had a pH of 3.4 so that the phenol ($pK_a=7.85$, Kortüm *et al.*, 1961¹²) was in its acidic form. Thus uranyl ion is a Lewis acid, and one would anticipate that its electronic absorption spectrum would be influenced by basic species in the medium. The effect of several hydroxylic compounds on the spectrum of uranyl ion was studied, and the results are summarized in Figure 3. The visible absorption of uranyl ion is influenced only slightly by 2,4-DH or by 2,4-dichlorophenol, but is markedly intensified by hydroxide ion.

Ferric Nitrate-Sensitized Photolysis of Aqueous 2,4-DH. The study was hampered by the fact that 2,4-DH and ferric ion are not soluble in water under the same conditions. Ferric ion is precipitated by base and 2,4-DH by acid. It is possible that a narrow pH range might be found in which significant quantities of both substances dissolve. This was not investigated. Only two trials of the ferric ion-sensitized reaction were performed (Table 9). A fine precipitate, presumably containing an iron compound, was present throughout the irradiation. After 2 hrs, only 43.3% of the 2,4-DH remained, but 9.0% still remained after 21 hrs.

The other trial differed significantly from the one just described only in that the reaction mixture contained 3.79×10^{-2} mole/l hydrogen chloride instead of potassium hydroxide. The hydrogen chloride caused formation of large clumps of white precipitate, presumably 2,4-DH, which made it impossible to collect meaningful samples for analysis. Followed chromatographically, the reaction seemed to proceed rapidly, but the small change in the appearance of the mixture adds still more doubt to the quantitative significance of the results.

Ferric Nitrate-EDTA Photolysis of Aqueous 2,4-DH. To overcome the precipitation of ferric ion under the pH 7.0 reaction condition, EDTA (ethylenediaminetetraacetic acid) was added in concentration equal to that of ferric nitrate (4.99×10^{-3} M at pH 7.0). Half of the initial concentration of 2,4-DH was still present at 72 hours of irradiation. Figure 5 shows the data for the ferric-EDTA irradiation, compared to irradiation of a 5×10^{-3} M solution of 2,4-DH (pH 7.0) without a sensitizer. One must conclude that ferric ion in presence of EDTA does not affect the rate of 2,4-DH degradation.

TABLE 9. Irradiation of $4.99 \times 10^{-3} M$ 2,4-DH containing $2.21 \times 10^{-2} M$ Ferric Nitrate*

Hours of Irradiation	Concentration of 2,4-DH ($M \times 10^3$)
0	4.99
2	2.16
4	1.38
21	0.45

*The solution contained $4.99 \times 10^{-3} M$ potassium hydroxide.

Reactions Beginning with 2,4-DE. In the early part of this work, the form of 2,4-D used was the octyl ester. The 2,4-DE was treated by saponification of the ester in methanol, following which a large volume of water and a sensitizer were added and the solution was irradiated. Thus, these photolyses differed significantly from those of 2,4-DH only in that the solutions contained octyl alcohol in an amount equivalent to the 2,4-DE used, and about 20 volume percent of methanol. The use of 2,4-DE was abandoned in favor of 2,4-DH for several reasons. (1) Gas chromatography revealed that available samples of 2,4-DE were markedly impure, even after distillation. Available 2,4-DH was chromatographically pure. (2) It was found that methanolic solutions of 2,4-DE underwent rapid saponification on addition of a small excess of aqueous potassium hydroxide (Brown and Newsome, 1962)¹³. (3) The presence of methanol in reaction mixtures to be analyzed hampered analytical extractions with nonpolar solvents.

Trials With Organic Sensitizers in Isopropyl Alcohol. Early in this work it was attempted to use organic substances as sensitizers of the decomposition of 2,4-DE in 3:7 (v:v) water-isopropyl alcohol. The substances tried were riboflavin, Michler's ketone, propiophenone and triphenylamine. Of these, the last three are triplet sensitizers. No information seems to be available on the electronic nature of photoexcited riboflavin. Propiophenone was chosen because of its high triplet energy of 74.6 kcal/mole

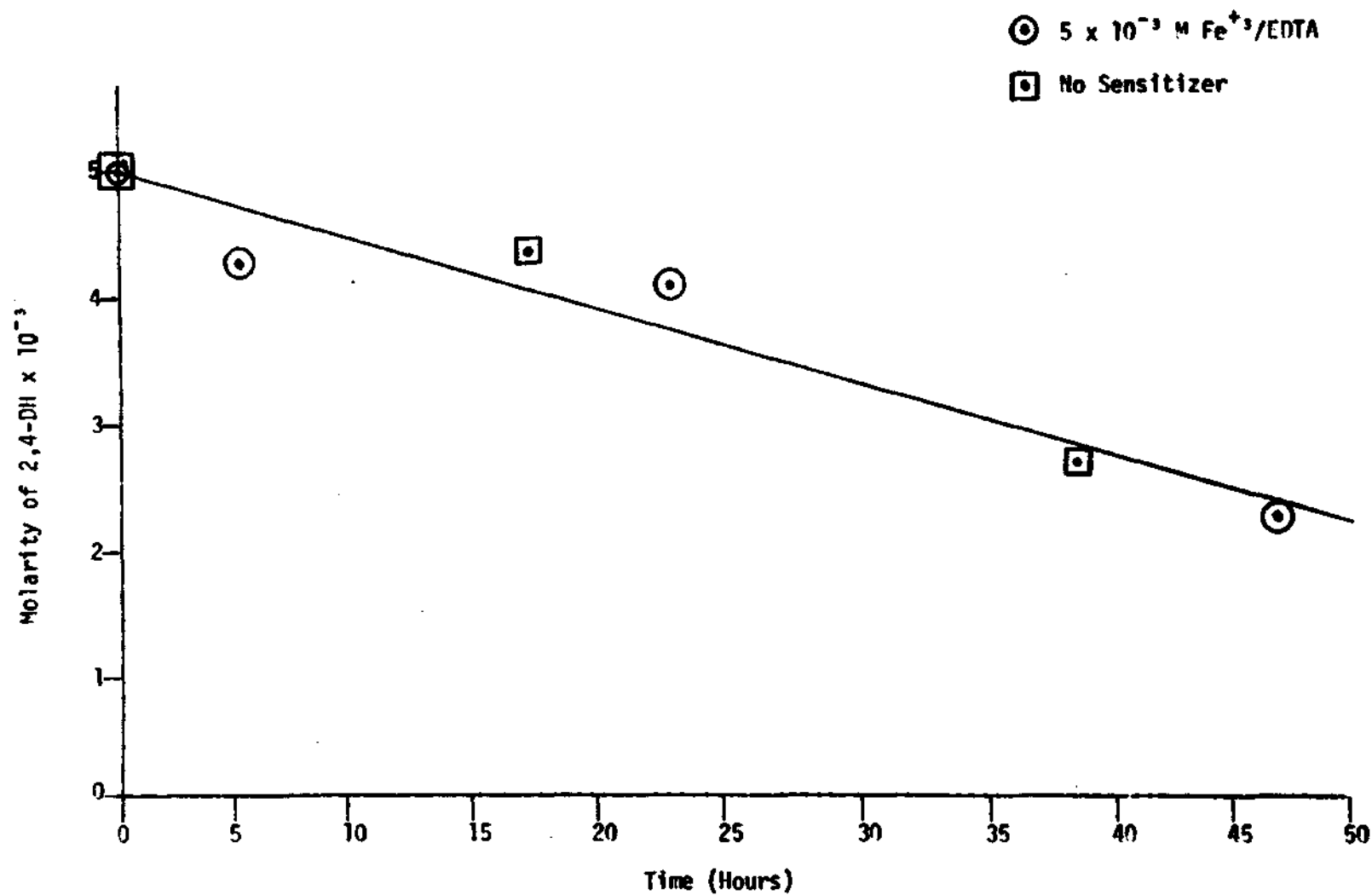


FIGURE 5. Photolysis of 2,4-D at pH 7.0. Initial Molarity 4.99×10^{-5} .

(Lamola, 1969¹²). Triphenylamine (triplet energy, 66.6 kcal/mole (Lamola, 1969¹²) was selected because it seemed less likely than the ketones to be photoreduced by isopropyl alcohol. The results were uniformly negative.

CONCLUSIONS

1. Sunlamp photolysis of aqueous 2,4-dichlorophenoxyacetic acid (2,4-DH) occurs in the absence of a sensitizer, but is accelerated by the addition of riboflavin, of uranyl ion, or of ferric ion.
2. The kinetic order of the uranyl ion-sensitized destruction of 2,4-D is most probably zero in both uranyl ion and 2,4-D, but firm conclusions on these points must await further study. The dependence of the reaction rate on light intensity was not investigated.
3. There are probably several products formed in the uranyl-sensitized decomposition of 2,4-DH. However, the present study demonstrated only two distinct substances, one of which was 2,4-dichlorophenol. The other substance was shown not to be a degradation product of 2,4-dichlorophenol.
4. The photolysis of 2,4-DH with ferric ion could be studied only in a heterogeneous mixture. An attempt to solubilize the ferric ion by addition of ethylenediaminetetraacetic acid caused total inhibition of sensitization by ferric ion.
5. A direct photodecomposition of 2,4-D octyl ester (2,4-DE) with the sensitizers used was not feasible. However, the rapid saponification of this ester permitted an indirect procedure to be used, since the hydrolysate could be decomposed photochemically.

SUGGESTIONS FOR FUTURE WORK

A good understanding of the uranyl ion promoted photolysis will probably require considerable work. It seems that the next step should be a thorough study of the initially formed products. In the present study, 2,4-dichlorophenol was identified, but essentially no information was acquired about the nature of substances A and B. The possible identity of these two substances could be determined by gas chromatographic analysis (180°) of ether solutions.

Surprisingly, there seems to be no report of the photolysis of 2,4-D in the absence of oxygen. Since molecular oxygen may be involved at some point in the photodecomposition (humic acid formation), it is possible that

exclusion of oxygen might allow the reaction to be separated into oxygen-dependent and oxygen-independent stages. This would facilitate an understanding of the overall process.

A Pyrex reaction vessel, specially constructed for photolysis of oxygen-free solutions, is available in our laboratory. It is diagrammed in Figure 6. It consists of an outer tube (A in the figure) with a standard taper joint (34/45) into which is fitted a unit with an inner tube. The inner tube extends nearly to the bottom of the outer one and is concentric with it. The temperature of the solution in the reaction vessel can be controlled by circulation of a coolant through the inner tube. The coolant enters the system through inlet C and leaves *via* outlet D. The solution in the reaction vessel can be purged of oxygen by passage of purified nitrogen through inlet E. The nitrogen enters the solution through a coarse sintered glass disc (F) sealed into the bottom of the inner tube, and leaves through outlet G.

Kinetic and quantum yield measurements would contribute greatly to an understanding of the mechanism. Certain special precautions need to be observed in kinetic work when the reaction is photochemical¹⁴. Perhaps most important, the dimensions of the reaction vessel and concentration of the absorbing species should be such that practically all (at least 97-98%) of the incident beam is absorbed by the solution before it passes through a vessel wall. The reasons for this are twofold: (1) It facilitates actinometric determination of the rate of photon absorption by the solution. (2) It allows the concentration of the absorbing species to be varied while the rate of photon absorption is held constant. The light beam may be collimated with lenses in the interest of increasing the path length available to the beam in the solution. However, an uncollimated beam is easier to acquire, and it allows the light energy incident on the solution to be varied by simply changing the distance between the lamp and the solution.

The requirement of total light absorption by the solution necessitates the selection of a light source emitting only wavelengths that are strongly absorbed by the sensitizer. Failure to observe this point would result in registration by the actinometer of photons that are inactive in the reaction being studied. The standard means of ensuring total light absorption is to use essentially monochromatic light from a spectral lamp. These lamps, manufactured by Osram and by Philips, and marketed by the Ealing Corporation (2225 Massachusetts Ave., Cambridge, MA 02140), emit several spectral lines, and the one of the desired wavelength can be isolated with filters. A wide selection of lamps, each with a different combination of wavelengths is available. The spectral lamps most often used in actinometry are low- or medium-pressure mercury arcs (Calvert and Pitts, 1966)¹⁵.

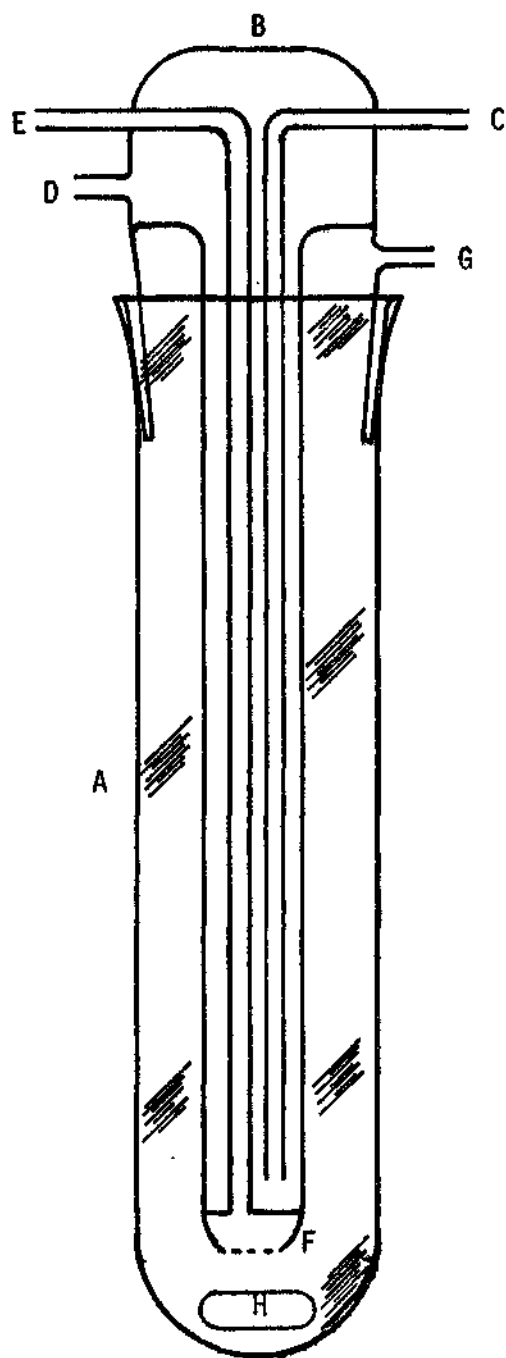


FIGURE 6. Photochemical Irradiation Vessel. A. Outer Tube.
 B. Lid with Inner Tube. C. Coolant Inlet.
 D. Coolant Outlet. E. Nitrogen Inlet.
 F. Sintered Glass Disc. G. Nitrogen Outlet.
 H. Stirrer.

The spectral characteristics of each lamp are displayed on a chart available from Ealing. Ealing also supplies lamp housings and power supplies. The lamp should be operated through a Sola constant voltage transformer to ensure constant intensity within an experiment. The lamp should be actinometrically recalibrated in every experiment in which the intensity must be known, since the effective intensity depends on the age of the lamp and the experimental geometry as well as the voltage. Experiments should be planned with the realization that many, if not all, spectral lamps must be operated base down. This could cause difficulties in the rotary irradiation method described previously.

It means that solutions would have to be irradiated through the sides of beakers or, if from above, with the aid of a mirror. Choice of the proper irradiation wavelength should obviously be guided by the absorption spectrum of the sensitizer. Calvert and Pitts (1966)¹⁵ detailed descriptions of a number of solution filters to be used with mercury lamps, and of glass filters available from Corning Glass Works.

It would appear that the spectral lamps available from Ealing have rather low intensities, and that it is sometimes difficult to obtain enough energy to drive the reaction at a convenient rate. The strongest lines available from mercury lamps are the ones at 2537 Å (low pressure lamp), and 3600 Å (medium pressure lamp) (Calvert and Pitts)¹⁵. Unfortunately the molar absorptivity of uranyl ion is not higher than 4.0 at 3600 Å. The 2537 Å line might be suitable for kinetic and actinometric work, provided that the concentration ratio uranyl ion/2,4-DH can be made high enough that the sensitizer absorbs virtually 100% of the light. To work at 2537 Å would, of course, require reaction vessels of quartz or Vycor.

Medium pressure mercury lamps have a fairly intense line at 3130 Å. Uranyl ion absorbs strongly at this wavelength. The 3130 Å line seems the most promising possibility. However, it might be necessary to use a battery of several lamps. There is a question as to the transmission characteristics of Pyrex at 3130 Å. Unless it is quite transparent, Vycor vessels might be needed.

For many years, uranyl oxalate was the accepted chemical actinometer, but it has been supplanted by the ferrioxalate system (Hatchard and Parker, 1956¹⁴, Parker, 1953¹⁵, Lee and Seliger, 1964¹⁶). The chief advantage of ferrioxalate is that it uses spectrophotometric assay (phenanthroline determination of ferrous ion) rather than titration. The ferrioxalate system is exceedingly sensitive, and great precaution must be taken to protect it from light. It is convenient to store solutions in blackened flasks and to work in a dark room illuminated by a red 15-watt lamp.

Crystalline potassium ferrioxalate may be prepared for use as the standard substance, or the actinometer solution may be prepared before use by mixture of standard solutions of ferric and oxalate ions (Baxendale and Bridge, 1955)¹⁷.

It is important, of course, that the solution being actinometrically analyzed and the ferrioxalate solution be identically exposed to the light source. Equivalent irradiation can be conveniently effected by a rotary irradiation device which places one or several samples of each of the two solutions alternately in the light path. A less convenient and less accurate procedure is to irradiate the two solutions serially in the same geometrical position relative to the lamp.

The common organic sensitizers, such as benzophenone, do not seem especially promising as prospective photodestructive agents of 2,4-D. The well-known organic sensitizers are all triplet sensitizers. Molecular oxygen quenches excited triplets (Calvert and Pitts, 1966)¹⁸, and the necessity of excluding oxygen would render a disposal procedure impracticable.

It seems that the most promising candidate substance for promotion of photodecomposition of 2,4-D may be ferric ion. Unlike riboflavin, ferric salts are chemically stable, and unlike uranium, iron as an inexpensive, common, and relatively harmless component of the environment. It would be desirable, though perhaps not mandatory, to overcome the solubility incompatibility of ferric ion with 2,4-DH. This might be possible with a substance that would chelate either ferric ion or 2,4-D.

Alternatively, the use of an alcohol solvent with a miscible form of ferric iron such as ferric chloride might be successful. Recent work by Grestorex and Kemp (1971)^{19,20} suggests that ceric ion might be a suitable sensitizer.

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