THE PHOTOCHEMICAL DECOMPOSITION OF POLYNITRATES

by

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ABSTRACT

The photolysis of nitrate esters in solution or in thin solid films occurred readily in the 2650 to 3340 A spectral region. In the presence of diphenylamine, phloroglucinol or hydroquinone, the photoreaction yielded colored products that gave a measure of the extent of the reaction. The most effective wavelength for formation of yellow products from diphenylamine was at 2890 A. Irradiation of ethanol or benzene solutions 0.02 M in diphenylamine and 1,4;3,6-dianhydro-D-glucitol-2,5-dinitrate (isosorbide dinitrate), followed by chromatographic separation, gave six organic compounds, two of which were isolated in pure form by adsorption chromatography and identified as 2- and 4-nitrodiphenylamine. Two other colored products were tentatively identified as N-nitroso- and p-nitrosodiphenylamine; no trace of the unreacted nitrate ester could be detected.

Photolysis of isosorbide dinitrate alone in ethanol solution caused a weight loss of 17.7% in 21 hours and the formation of an unidentified hydrophilic, colorless sirup. A similar product was obtained on irradiation of an anhydrous benzene solution of the dinitrate. Possible mechanisms of the photolysis are discussed.

HISTORICAL INTRODUCTION

ULTRAVIOLET IRRADIATIONS OF NITRATE ESTERS

The photochemical decomposition of nitrate esters has been studied in the condensed state, usually in thin films, and in the vapor state. Only three reports of photochemical reactions of nitrate esters in solution could be found in the literature.

When cellulose nitrate (13.5% nitrogen) was irradiated with ultraviolet light, a constant-rate decomposition occurred (1); the effects of the irradiation were followed by determining the decrease in the nitrogen content of the nitrate ester (2). The reaction was carried out in air and in nitrogen (3) and degradation was found to be much more severe in air, evidently taking place by cleavage of the cellulose chain.

A comparison of the effect of ultraviolet light on glycerin trinitrate, penta-erythritol tetranitrate, cellulose nitrate (13.5% nitrogen) and mannitol hexanitrate (1) indicated that the smaller the molecular weight of the nitrate ester, the higher the rate of decomposition and that the more nitrate ester groups there are in the molecule, the greater the rate of decomposition.

The decomposition of liquid glycerin trinitrate by ultraviolet irradiation (4) was found to vary exponentially, rather than linearly, with the irradiation exposure time, and to

continue spontaneously at a gradually decreasing rate after the light source was removed. It was also found that the photochemical decomposition of the glycerin trinitrate could be followed by the liberation of iodine from a potassium iodide solution (5).

After nitrate esters had been developed on paper chromatograms and sprayed with an alcoholic solution of diphenylamine, short-wave ultraviolet irradiation was found to produce a yellow-colored spot (6) (7) which provided a permanent record on the chromatogram.

Under the influence of short-wave ultraviolet light, reactions of nitrate ion and diphenylamine have been carried out both in solution and in the solid state (8) (9), producing, in both cases, a yellow-colored product. Analysis of this yellow-colored material yielded 2-nitrodiphenylamine and 4-nitrodiphenylamine (9) but no nitroso derivatives of diphenylamine were identified.

The reaction between diphenylamine and nitrate esters or nitrate ion, under the influence of short-wave ultraviolet light, was recently developed by Coldwell into a spot test for various explosives (10).

Acetone solutions of cellulose nitrate (13.5% nitrogen) were found to decrease in viscosity with time of ultraviolet irradiation (11), the decrease being more pronounced for

concentrated solutions.

An unusual decomposition reaction of primary, aliphatic nitrates dissolved in trifluoroacetic acid was discovered (12), in which the main products were nitric oxide and a carboxylic acid having the same number of carbon atoms as the ester. The reaction proceeded in the dark and was catalyzed by ultraviolet light. This latter observation, coupled with the nature of the products, suggested that, initially, a homolytic cleavage of the nitrate ester occurred.

The vapor phase photochemical reactions of simple alkyl nitrate esters have been investigated in greater detail than the condensed phase reactions. The photolysis of ethyl nitrate vapor (13) was considered to involve a number of reactions, the initial step being,

$C_2H_5O\text{-}NO_2 \longrightarrow C_2H_5O\cdot + NO_2$, followed by the decomposition of the ethoxyl radical,

$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O$, or

$C_2H_5O\cdot \longrightarrow H\cdot + CH_3CHO$. The methyl radical appeared to react preferentially with nitrogen dioxide to form nitromethane, and the hydrogen atom with ethyl nitrate to form ethyl alcohol and nitrogen dioxide.

The spontaneous (explosive) ignition of gaseous methyl nitrate was investigated (14), as well as both slow decomposition

and spontaneous decomposition induced by ultraviolet light. The nitrate ester decomposition was found to be extremely complicated, the products of the explosion being carbon monoxide, carbon dioxide, hydrogen, water, nitric oxide and nitrogen.

The Stereochemistry of the Isohexides and Their Dinitrates

The 1,4;3,6-dianhydrides of D-mannitol, D-glucitol and L-iditol, namely, isomannide (I), isosorbide (II) and isoidide (III), are a very interesting group of compounds in that they comprise a set of configurational isomers in which the conformation of each member is known and fixed. They, therefore, offer a unique opportunity for study of steric effects in reactions (15). These compounds have two fused five-membered rings with a cis arrangement at the ring junction. The rings are inclined to one another at an angle of about 120° and the substituents on carbon atoms 2 and 5 can either be on the inside of the V formed by the rings and, thus, called endo (R_1, R_3), or on the outside and called exo (R_2, R_4). The structures of the isohexides as well as the isohexide dinitrates (IV - VI) are shown in Figure 1.

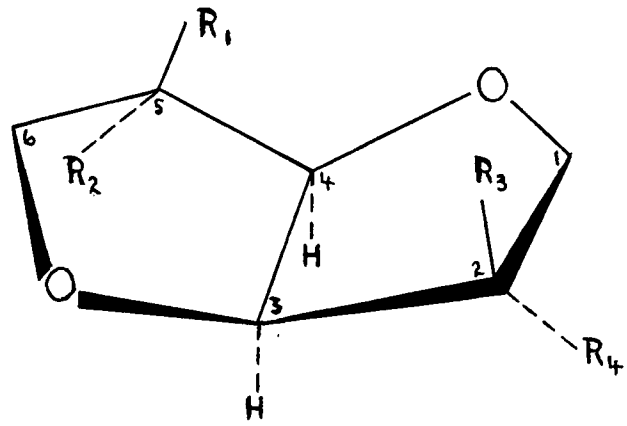


Fig. 1. 1,4;3,6 - Dianhydrohexitols and Their 2,5 - Dinitrates

I	R_1= OH	R_2= H	R_3= OH	R_4= H	Isomannide
II	R_1= OH	R_2= H	R_3= H	R_4= OH	Isosorbide
III	R_1= H	R_2= OH	R_3= H	R_4= OH	Isoidide
IV	R_1= ONO_2	R_2= H	R_3= ONO_2	R_4= H	Isomannide dinitrate
V	R_1= ONO_2	R_2= H	R_3= H	R_4= ONO_2	Isosorbide dinitrate
VI	R_1= H	R_2= ONO_2	R_3= H	R_4= ONO_2	Isoidide dinitrate

The fused ring system of these stereoisomers cannot undergo inversion as occurs with cyclohexane, therefore, the shape and dimensions of the molecules are quite well known (15).

Aromatic Nitrations by Free Radicals

Years of experimental work have indicated that aromatic nitration follows an ionic mechanism, in fact, this was considered to be the principal difference between aromatic and aliphatic nitrations, the former reaction being ionic, the latter, free radical (16). In recent years, however, studies have indicated that such a sharp distinction between the nitration mechanisms for the two groups of compounds may not be justified; there is

evidence that, under certain conditions, aromatic nitration may take place by a free radical mechanism. A review of the known aromatic and aliphatic nitration processes was recently published by Topchiev (17) in which was discussed a number of aromatic nitration processes which appeared to involve free radical mechanisms. Most of the work was concerned with the nitration of aromatic hydrocarbons (18) (19) (20) (21), halogenated aromatic hydrocarbons (22) and aromatic heterocyclics (23) by the free radical nitrogen dioxide. In these cases, mixtures of the aromatic compound and nitrogen dioxide gave a nitro derivative product but whether the free radical nitration was a single step or a multi-step process was not determined.

More detailed experimental work was performed using pernitrous acid and simple organic compounds (24) (25) (26), in which the postulated mechanism involved a homolytic cleavage of the unstable pernitrous acid, followed by an attack of the hydroxy radical onto the aromatic nucleus almost exclusively in the ortho and para positions, which in turn, was followed by an attack of the nitrogen dioxide. The unstable addition compounds, so formed, broke down with the elimination of water, of nitrous acid or of hydrogen.

Chromatography of the Nitrate Esters

Relatively little is known about the chromatographic

behavior of the nitrate esters. A paper chromatographic technique for separating diastereoisomeric nitrate esters was recently reported by Jackson and Hayward (6), who also discussed the detection of the nitrate esters by the use of an ethanolic diphenylamine spray reagent, followed by irradiation with short-wave ultraviolet light. The photochemical reaction of diphenylamine with the nitrate esters produced yellow spots on a white background.

Less work has been done on the column chromatographic behavior of the nitrate esters. In this laboratory, purification of the crude reaction products obtained from a number of nitrate ester syntheses (27) (28) (29) was accomplished by chromatography on alumina columns, as had been previously used by Honeyman and co-workers with sugar nitrates (30).

A frontal analysis technique was employed by Öhman (31) for the separation of the ethyl and butyl nitrates and the glycol mono- and dinitrates obtained from the nitration of olefins.

The analysis of several propellants and explosives containing nitrate esters was also successfully accomplished (32) (33), using column chromatography involving Celite-silicic acid adsorbent mixtures.

Nitrate Ester - Diphenylamine Reactions

It has been established for some time that the presence of diphenylamine in various explosive powders prevents a self-catalyzing decomposition of the powder (34, Vol.I, p.272; Vol.III, p.210) (35, Vol.II, p.470), which without diphenylamine results in an explosion. In the process of acting as stabilizer, diphenylamine was converted to its nitroso and nitro derivatives (34, Vol.III, p.219) (35, Vol.II, p.311), the exact mechanism of the product formation being as yet unknown.

Using double base powders, which contained cellulose nitrate (12.24% nitrogen), glycerin trinitrate and a small percentage of diphenylamine, accelerated aging experiments were carried out and the products separated by chromatography (36). Several schemes were postulated for the conversion of diphenylamine to its nitroso and nitro derivatives but the actual mechanism was not determined.

The accelerated aging of cellulose nitrate (12.6% nitrogen) was conducted in the presence of diphenylamine, with the result that diphenylamine derivatives ranging from N-nitroso diphenylamine to 2,4,2'-trinitrodiphenylamine was isolated (37), each derivative formed corresponded to a particular degree of decomposition of the smokeless powder.

Although diphenylamine is not the only stabilizer used for

the nitrate ester explosives, it is the most used and has been shown to react readily with the nitrous and nitric acids produced in the decomposition of cellulose nitrate (38).

EXPERIMENTAL

(A) MATERIALS

1. 1,4;3,6-Dianhydro-D-glucitol-2,5-dinitrate(Isosorbide Dinitrate)

A mixture of isosorbide and isoidide, prepared from D-sorbose by hydrogenation and dehydration (15), was twice distilled *in vacuo* and a fraction boiling at 161-163° C. at 0.15-0.17 mm. was recrystallized from ethyl acetate. Colorless, extremely hygroscopic crystals of m.p. 61.0-62.5° C. and specific rotation at 25° C. of +45.0° (c,2.09 in water) were obtained. The reported melting points and specific rotations were 62.0-63.5° C., $[\alpha]_D$ + 44.6 (c,1.78 in water) (39), 61.9-64.0° C., $[\alpha]_D^{22}$ + 44.8 (c,2.22 in water) (40) (41), 62.0-63.0° C., $[\alpha]_D^{23}$ + 45.2 (c, 2.22 in water) (28).

Using the method of Jackson and Hayward (15), 1 g. of isosorbide was nitrated and produced 1.2 g. (75.5%) of crude dinitrate, which on recrystallization from methanol gave 0.91 g. of colorless crystals, m.p. 69.2-70.0° C. and specific rotation at 25° C. + 141° (c, 1.01 in 95% ethanol). The reported melting points and specific rotation were 50.5-51.5° C. (15), 52° C. (61), 70° C. (62), 71° C. (63) and + 141° (15). The C, H, N contents were determined (Mr. A. Bernhardt, Mikroanalytisthes Laboratorium, Kaiser Wilhelm Platz 1, Mulheim (Ruhr), Germany) and compared to the calculated values:

Found:	C:30.96%,	H:3.44%,	N:10.89%
Calculated:	C:30.52%,	H:3.41%,	N:11.86%

The infrared spectrum of the isosorbide dinitrate was determined (see Appendix 1) and compared to previous spectra obtained by Dr. M. Jackson, with good agreement. This, however, was not conclusive evidence for two crystal structures, therefore, a number of Dr. M. Jackson's samples of isosorbide dinitrate (samples A to F) were used for melting point determinations. These samples had all been stored at room temperature for approximately one year. The observed melting point values are listed in Table I.

Sample	Observed Melting Points[a] °C.	Sample	Observed Melting Points[b] °C.
A.	69.2-70.0	A.	68.5-69.9
B.	69.2-70.0	B.	68.2-70.0
C.	67.0-68.0	C.	66.8-68.0
D.	69.3-70.0	D.	69.2-70.0
E.	67.0-68.0	E.	65.0-67.0
F.	66.5-68.0	F.	63.0-65.0

Table I. Melting Points of Isosorbide Dinitrate Samples
a. Cylindrical copper block apparatus.
b. Wetzlar microscope melting point apparatus.

A portion of sample D was dissolved in 95% ethanol and at 25° C. the specific rotation was found to be + 141° (c,1.01). This value was identical to that previously found by Jackson and Hayward (15), and indicated that isosorbide dinitrate has two crystal structures, the more prevalent and stable form melting at 69-70° C.

These samples all gave single spots on chromatograms.

2. Phloroglucinol

Phloroglucinol (Brothers Chemical Co., Orange, New Jersey) was purified by dissolving it in an excess of water, heating the solution to near boiling, adding activated charcoal and boiling for two or three minutes. The solution was then saturated with sulphur dioxide by bubbling the gas through the solution for five minutes. Filtration was carried out with suction, using a prewarmed Buchner funnel and filter flask containing a little boiling water and an excess of sodium chloride. The filtrate was shaken to dissolve the salt and crystallized in the refrigerator in the absence of light. Colorless crystals melting at 218.5-219.5° C. were obtained; the reported m.p. was 216-219° C. with rapid heating (42). The ultraviolet and infrared spectra of the purified phloroglucinol were determined (Appendix 1); both spectra agreed with those reported by Dubiel and Zuffanti (43). Their ultraviolet maximum was 268-269 mu, the observed was 268-269 mu.

On a paper chromatogram developed with solvent A and sprayed with reagent I (see Chromatography), the compound gave a single spot of R_f 0.65-0.67.

3. Diphenylamine

Diphenylamine (Eastman Organic Chemicals, Rochester, N.Y.) was purified by dissolving it in an excess of 95% ethanol, decolorizing with charcoal, filtering and adding water until

turbidity resulted. The mixture was then put in the refrigerator until crystallization was complete. This process was repeated four times for each crop of diphenylamine and resulted in colorless crystals of m.p. 52.7-53.5° C. The reported m.p. was 53° C. (36).

Diphenylamine was also purified by column chromatography using a prewashed silicic acid-Celite mixture and solvent E as irrigant (see Chromatography) and resulted in colorless crystals of m.p. 53.0-53.6° C. The ultraviolet and infrared spectra of both crystalline materials were determined (Appendix 1) and agreed with the reported ultraviolet (44) and infrared spectra (45). The reported and observed ultraviolet maxima were both 285 mu.

The purified diphenylamine was chromatographed by the chromatoplate technique to give a single developed spot. R_f values are quoted in Tables XII, XIII and XIV.

4. Hydroquinone

Hydroquinone (Nichols Chemical Co., Montreal, Canada) was purified by refluxing in benzene; the benzene extract was removed periodically and immediately put into an ice-cold beaker, producing a crop of colorless crystals. The crystals were filtered off and the benzene transferred back to the reflux apparatus. Each crop of hydroquinone was recrystallized three times using this procedure, to give crystals melting at

170.5-171.2° C.; the reported m.p. was 170.5° C. (46). The ultraviolet spectrum was determined. The reported ultraviolet maxima were 223 and 292 mu (47), the observed were 223 and 291 mu.

On paper chromatograms developed with solvent A and detected with spray reagent I, the purified compound gave a single spot of R_f 0.80-0.82.

5. Nitro- and Nitrosodiphenylamine Derivatives

Samples of N-nitrosodiphenylamine, p-nitrosodiphenylamine, 2-nitrodiphenylamine and 4-nitrodiphenylamine (Brickman and Co., Montreal, Canada) were crystallized to constant melting point according to procedures described by Schroeder et al (36). Portions of these purified materials were dissolved in anhydrous ethanol, ether or acetone and examined on chromatograms.

Using the recrystallized materials, 200-300 mg. samples were further purified on silicic acid-plaster of paris chromatographic columns (chromatobars), which were irrigated with solvent F and the central portions of the developed bands isolated. For N-nitrosodiphenylamine the developed material was practically colorless and the impurity, diphenylamine, was colorless. In this case, the bands were located by streaking the bar with spray reagent IV. The isolated portion from each bar was powdered and poured into a glass column and eluted with acetone. The acetone extracts were evaporated in the absence of

light at room temperature under reduced pressure. This procedure yielded pure, crystalline N-nitroso-, 2-nitro-, and 4-nitro-diphenylamine.

This purification technique was unsuccessfully applied four times to p-nitrosodiphenylamine. Eventually, the compound was purified by a vacuum sublimation (initial pressure 0.03 mm.) in the absence of light. Table II shows the purification techniques and weights recovered for the diphenylamine derivatives.

Compound	Initial Weight (mg.)	Purification Method	Weight Recovered (mg.)
Diphenylamine	300.3	2:1($^{w}/_{w}$)Silicic acid-Celite column	137.8
2-nitro diphenylamine	201.0	Chromatobar	122.1
4-nitro diphenylamine	200.0	Chromatobar	121.0
N-nitroso diphenylamine	206.3	Chromatobar	21.8
p-nitroso diphenylamine	200.0	Vacuum sublimation	102.5

Table II. Purification of Diphenylamine and Derivatives.

Table III lists the observed and reported melting points and ultraviolet spectra. The infrared spectra of the purified compounds were also recorded in Figures 14-19 (Appendix 1).

(B) SPECTRA

1. Ultraviolet Spectra

The ultraviolet spectra were determined on a recording spectrophotometer (Cary, Model 14) in either absolute ethanol, 95% ethanol or cyclohexane, using the same solvent as blank in the reference beam. When the molar extinction coefficient was

Compound	m.p. (°C.)	Reported m.p. (°C.)	Ultraviolet Spectra Observed max. (mu)	Observed min. (mu)	Reported max. (mu)	Reported min. (mu)
diphenylamine	52.7-53.5	53(36)	285	247-249	285	249(44)
N-nitrosodiphenylamine	66.5-66.9	67.2-67.6(48) 66.2-66.8(36)	286-296 212	259-260	295-296	259-260(44)
p-nitrosodiphenylamine	146.0-146.5	145.4-146.6(36) 143.0(49)(50) 144.6(51)	401-403[a] 260	271-277[a]	405-407[a] 258-260	279-281[a] 237-240(44)
2-nitrodiphenylamine	72.5-73.3	74.9-76.0(36) 75.0-75.5(52)	423-424 254-258 223-224	324-330 243-244	422-423 257-259 221-222	323-327 238-239 214-215(44)
4-nitrodiphenylamine	133.5-134.3	135.0-135.5(36) 132.0-133.0(52) 132.0-132.5(9)	390 255-257	300-310	390 257	305-306(44)

Table III. Melting Points and Ultraviolet Bands of Diphenylamine and Derivatives.
ä. Two drops of 6N hydrochloric acid were added to 100 ml. of the spectral solution.

known, the concentration was calculated for a particular peak height. If this peak height was not obtained, a base line was determined with two solvent blanks and the spectrum was cofrected for the observed differences.

2. Infrared Spectra

All the infrared spectra were determined on a Perkin-Elmer Model 21 Infrared Spectrophotometer in the solid state as either a potassium bromide pellet or a Nujol-hexachlorobutadiene mull. The weight of the material was usually between 0.5-1.5 mg.

The following specifications apply to all spectra; prism: sodium chloride, resolution:927, response:1, gain:6, speed:4, suppression:2.

(C) ANALYSIS

1. Melting Points

The melting points were determined using capillary tubes and a copper block apparatus. The thermometer was calibrated with recrystallized samples having small melting point ranges and was found to be accurate within $\pm$ 0.8° C. up to 200° C.

2. Chromatography

Adsorbents and Supporting Media

Whatman No. 1 chromatography paper was used without pretreatment or was impregnated with silicic acid as recently described by Marinetti, Erbland and Kochen (53).

Column chromatography on a preparative scale involved the use of (a), acid washed alumina (Alcoa, grade F-20, 80-200 mesh) (27) (28) (29), or (b), silicic acid (Mallinckrodt, 100 mesh, chromatography grade)-Celite (Analytical filter aid, Johns-Manville) (2:1, w/w), prewashed with a mixture of anhydrous ether-ligroin (65-110°) (1:2 $^{v}/_{v}$) (32).

Chromatoplates and chromatobars were prepared from the silicic acid and plaster of paris (Gypsum, Lime and Alabastine Limited, quick set) according to the procedures of Allentoff and Wright (54) and Miller and Kirchner (55), respectively.

Solvent Systems

Developing solvents are listed in Table IV.

Designation	Solvent Systems
A	n-butyl alcohol-glacial acetic acid-water (4:1:5, v/v) (top layer)
B	n-butyl alcohol-25% acetic acid (1:1, v/v)
C	n-hexane saturated with methanol
D	phenol-water (1:1, v/v) (bottom layer)
E	anhydrous ether-ligroin (65-110°) (1:13.3, v/v)
F	anhydrous benzene-ligroin (85-105°) (1:1, v/v)
G	anhydrous ethanol-anhydrous ether (1:19, v/v)
H	anhydrous benzene
I	anhydrous benzene-ligroin (85-105°) (2:1, v/v)
J	anhydrous ethanol-anhydrous benzene (1:19, v/v)
K	anhydrous ether-anhydrous benzene (1:19, v/v)
L	anhydrous benzene-ligroin (65-110°) (1:1, v/v)
M	petroleum ether (30-60°)-ethyl acetate (3:7, v/v)
N	ethyl acetate-petroleum ether (65-110°) (1:20, v/v)
O	petroleum ether (65-110°)

Table IV. Solvent Systems Used in Developing Chromatograms.

Spray Reagents

I. Diazotized Sulfanilic Acid

Sulfanilic acid was converted to its diazo derivative following a procedure described by Cramer (56). Approximately 0.1 g. of this diazotized salt in 20 ml. of 10% sodium carbonate solution formed a useful spray reagent for hydroxylated compounds developed on paper.

II. Diphenylamine

A 1% alcohol solution of diphenylamine sprayed on chromatograms, followed by exposure to short-wave ultraviolet light, was a useful method for detecting nitrate esters (6).

III. Calcium Nitrate

A 5% alcohol solution of calcium nitrate sprayed on chromatograms, followed by exposure to short-wave ultraviolet light, was found to be a useful method for detecting diphenylamine and its derivatives.

IV. Fuming Nitric Acid in Concentrated Sulphuric Acid

A spray reagent consisting of fuming nitric acid in concentrated sulphuric acid (1:19) (54) was found to produce distinctive colors with diphenylamine, p-nitrosodiphenylamine, 2-, and 4-nitrodiphenylamine and would detect all organic compounds on chromatoplates as carbon spots after heating on a metal plate in a fume hood.

V. Nitrous Acid

A 1% solution of sodium nitrite in concentrated sulphuric acid (36) was used as a streak reagent for detecting diphenylamine and diphenylamine derivatives. The colors produced, however, were not distinctive and this reagent was useful only when applied in conjunction with spray reagent IV.

VI. Potassium Periodatocuprate

A spray reagent consisting of an alkaline solution of potassium periodatocuprate was found to be useful in detecting certain polyhydroxy compounds on paper chromatograms. Permanent records of the chromatograms were obtained by a further spraying with an acidic rosaline base solution (57).

VII. Vanillin-Perchloric Acid

A spray reagent consisting of a 1% alcoholic solution of vanillin and a 3% aqueous perchloric acid solution (1:1) (58) was found to be useful in the detection of certain polyol compounds.

VIII. Sodium Metaperiodate-Potassium Permanganate

A spray reagent composed of a 1% potassium permanganate in 2% aqueous sodium carbonate solution and a 2% aqueous sodium metaperiodate solution (1:4) (59) was found to detect certain polyhydroxy compounds on paper chromatograms.

IX. Carbon Disulfide

An alkaline solution of carbon disulfide (60) sprayed on paper chromatograms, followed by iodine vapor treatment, was found to be reasonably effective as a means of detecting certain polyhydroxy compounds.

(D) IRRADIATION TECHNIQUES

1. Irradiation of Solutions

For irradiation of solutions the apparatus consisted of a quartz test tube mounted vertically at a distance of 20 cm. from a Mineralite ultraviolet lamp (Ultraviolet Products Inc., Los Angeles, Calif.) with filter removed. The tube contained a thin glass capillary through which nitrogen gas was introduced for stirring and purging of air. The tube was kept at a constant temperature (14.5-15.5° C.) by a cold water stream impinging on the outer surface.

A known weight of material dissolved in anhydrous ethanol or anhydrous benzene was placed in the quartz tube, the nitrogen gas was started and a steady, slow stream of bubbles was maintained. The cold water was turned on until an envelope of water completely surrounded the quartz tube. The lamp was warmed up for 10 min. while the solution was protected by a piece of aluminum foil.

2. Determination of the Effective Wavelengths for Nitrate Ester Photolysis

Three solutions in anhydrous ethanol were prepared: diphenylamine (0.402 M.), isosorbide dinitrate (0.0405 M.) and anthracene (Scintillation grade, Reilly Tar and Chemical Corp., New York) (0.0397 M.).

Using 7 cm. Whatman No. 1 filter paper, 36 papers were spotted with 5 λ of the isosorbide dinitrate solution on a central spot. After drying, two further 5 λ spots of the diphenylamine solution were applied on either side of the central spot, so that partial overlap occurred. Papers were also spotted with 5 λ of the anthracene solution on each of the three centers. A sample paper is shown in Figure 2.

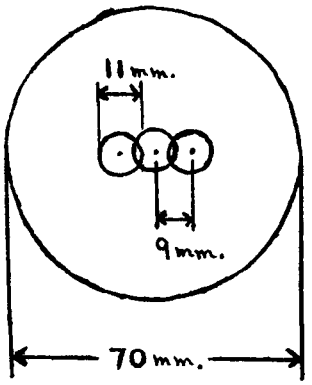


Fig. 2.

Spotted Filter Paper Circles.

The irradiation apparatus consisted of a Bausch and Lomb grating monochromator with an achromatic quartz-fluorite condenser and a medium pressure mercury arc lamp. The lamp was warmed up at least one-half hour before using; the filter paper was clamped vertically on a plastic-covered ring in front of the condenser lens and the exit slit was opened, allowing

radiation to pass through the condenser. All irradiation times were determined with a stop-watch.

Using the anthracene spotted papers, the focal length of the condenser was found to be approximately 285 mm. This distance was subsequently used in all irradiations.

The wavelength intensities for the emission spectra of a mercury arc were tabulated (46) and new wavelength intensities were calculated using a table of transmission efficiencies supplied by the manufacturer of the monochromator. All irradiation times were calculated with respect to the most intense line, 2537A, so that equal numbers of radiation quanta were used in all cases.

RESULTS AND DISCUSSION

A. EFFECT OF ULTRAVIOLET LIGHT ON ISOSORBIDE DINITRATE

The effect of ultraviolet radiation on an ethanolic solution of isosorbide dinitrate was investigated by irradiating a solution, 0.042 M in isosorbide dinitrate, in an open beaker with the Mineralite lamp (unfiltered) for 21 hours. The still colorless solution was evaporated to ~~dryness~~ an oil and the weight loss was determined, as recorded in Table V.

Compound	Initial Weight	Final Weight	Weight Loss
Isosorbide dinitrate	100.4 mg.	82.6 mg.	17.8 mg.

% Loss in Weight	% Loss in Weight if NO_2 removed
17.70%	19.02%

Table V. Effect of Ultraviolet Radiation on Isosorbide Dinitrate.

The yellow oil obtained was seeded with isosorbide mononitrate (28), but the crystal did not grow and further crystallization attempts were unsuccessful.

A 3-hour irradiation of a 0.04 M isosorbide dinitrate solution in absolute ethanol produced an extremely pale yellow coloration, whereas, a 3-hour irradiation of a solution of equal concentration in anhydrous benzene was colorless. These two solutions, as well as 0.04 M solutions of isosorbide and isosorbide dinitrate, were examined on a chromatoplate (Figure 3). The developed plate indicated that although undecomposed isosorbide dinitrate remained in both the benzene and ethanol solutions after irradiation, another compound was formed which,

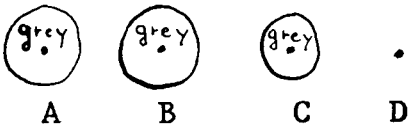


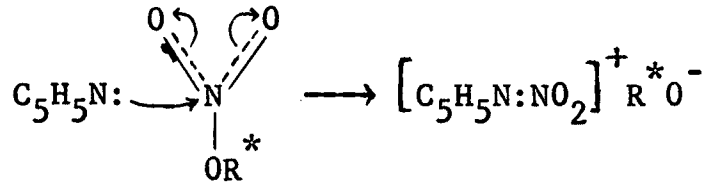
Fig. 3. Irradiated Benzene and Ethanol Solutions of Isosorbide Dinitrate Developed on a Chromatoplate.

A: 0.04 M isosorbide, B: Absolute ethanol solution, 0.04 M in isosorbide dinitrate, irradiated for 3 hours, C: Anhydrous benzene solution, 0.04 M in isosorbide dinitrate, irradiated for 3 hours, D: 0.04 M isosorbide dinitrate.
The plate was irrigated with solvent L, sprayed with reagent IV and heated.

like isosorbide, did not move from the original spotting position on irrigation.

B. PHOTOLYSIS OF NITRATE ESTERS IN THE PRESENCE OF PHLOROGLUCINOL

The work of Hayward and coworkers (15) (27) (28) (29) on the pyridine decomposition of nitrate esters indicated that the decomposition occurred by the nucleophilic attack of pyridine at the nitrogen of the nitroxy group and resulted in the heterolytic cleavage of the low energy $O\text{-}NO_2$ bond.



It was assumed that a photochemical decomposition of nitrate esters might occur by a similar mechanism, in which case, the presence of a compound having an electron-rich center would greatly enhance the possibility of product detection. Phloroglucinol was selected for this purpose, the three hydroxy groups producing a strong activating effect on the aromatic system.

Five 2 ml. absolute ethanol solutions, each 0.021 M in both isosorbide dinitrate and phloroglucinol, were prepared, as well as, two blank solutions, the first, 0.042 M in isosorbide dinitrate, the second, 0.042 M in phloroglucinol. The solutions

were transferred to quartz test tubes and irradiated with the unfiltered Mineralite lamp as shown in Table VI.

Solution No.	Solution Content[a]	Irradiation Time	Result
1	IsoS diN and Phl	5 minutes	light yellow coloration
2	IsoS diN and Phl	10 minutes	yellow coloration
3	IsoS diN and Phl	15 minutes	yellow coloration
4	IsoS diN and Phl	20 minutes	light orangish-yellow coloration
5	IsoS diN and Phl	25 minutes	orangish-yellow coloration
6	Phl	23 hours	bright yellow coloration
7	IsoS diN[b]	21 hours	colorless

Table VI. Irradiation of Isosorbide Dinitrate-Phloroglucinol Solutions.

a. IsoS diN: Isosorbide dinitrate, Phl: Phloroglucinol
b. See Table V.

Solutions 1-5 were combined, transferred to an acid-washed alumina column and eluted with solvent N. The adsorptives separated into two light yellow components; the colored material in the bottom band was extractable with ether, whereas, the only solvent which would partially extract the top band was methyl ethyl ketone. Both extracts were evaporated to light yellow oils.

The oil of the bottom band was subjected to a micro-boiling point determination, which indicated that the boiling point was in the region 295-319° C.

Tests for nitrogen, hydroxyl and carbonyl compounds, as well as solubility tests, were carried out on the oils following

standard procedures (64).

The results indicated that the oil from the top band was (1) probably not aromatic, (2) probably not an ether, (3) probably a carbonyl compound, (4) probably a hydroxylated compound, and, (5) did not contain nitrogen.

A structure of the type $R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}-R_1$, where R and R_1 combined contained 9 or more carbon atoms appeared to be consistent with the results, however, such a structure could only result from the reaction of two molecules of phloroglucinol or two molecules of isosorbide dinitrate or one molecule of each.

The tests on the oil from the bottom band indicated that it was (1) probably not aromatic, (2) probably a carbonyl compound, (3) probably not a hydroxylated compound, and, (4) did not contain nitrogen.

A possible structure was $R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_1$, where R and R_1 combined did not contain more than 9 carbon atoms. This structure, however, was not consistent with the extremely high boiling point, unless R or R_1 were groups with high molecular weights or which were highly polar.

Attempts to prepare the semicarbazone and 2,4-dinitrophenylhydrazone derivatives of both oils were not successful, the products decomposed at 240+° C. The only exception was a semicarbazone prepared from the oil from the top band which melted at 230.0-230.5° C.

The lack of satisfactory derivatives made it impossible to

Polynitrate Compound[a]	Solution No.	Concentration of Poly-nitrate	Concentration of Phloro-glucinol	Conditions	Results
isosorbide dinitrate	1	0.021M	0.021M	Dark (6°C.)	Colorless after 209 hours 15 minutes
isosorbide dinitrate	2	0.021M	0.021M	Laboratory light (25°C.)	Very pale yellow after 121 hours 30 minutes
isosorbide dinitrate	3	0.021M	0.021M	Laboratory light (78°C.)	Dark yellow-orange coloration after 41 hours 30 minutes
--------	4	----	0.042M	Laboratory light (78°C.)	Dark yellow-orange coloration after 41 hours 30 minutes
isosorbide dinitrate	5	0.042M	----	Laboratory light (78°C.)	Pale yellow after 41 hours 30 minutes
isosorbide dinitrate	6	0.021M	0.021M	Dark (25°C.)	Extremely pale yellow coloration after 408 hours
--------	7	----	0.042M	Dark (78°C.)	Yellow coloration after 71 hours 30 minutes
isosorbide dinitrate	8	0.042M	----	Dark (78°C.)	Pale yellow coloration after 71 hours 30 minutes
trans-cyclohexane-1,2-diol dinitrate	9	0.019M	0.024M	20 hours irradiation[b]	Dark yellow
trans-acenaphthene-1,2-diol dinitrate	10	0.015M	0.024M	20 hours irradiation[b]	Dark yellow
mannitol hexanitrate	11	0.009M	0.024M	20 hours irradiation[b]	Fairly dark yellow
dulcitol hexanitrate	12	0.009M	0.024M	20 hours irradiation[b]	Fairly dark yellow
methyl-β-D-glucopyranoside tetranitrate	13	0.011M	0.024M	20 hours irradiation[b]	Fairly dark yellow
mannitol pentanitrate	14	0.010M	0.024M	20 hours irradiation[b]	Yellow

Table VII. The Effect of Light and Heat on Phloroglucinol-Polynitrate Solutions (Continued)

Polynitrate Compound[a]	Solution No.	Concentration of Poly-nitrate	Phloro-glucinol	Conditions	Results
L-aribitol pentanitrate	15	0.010M	0.024M	20 hours irradiation[b]	Yellow
dulcitol pentanitrate	16	0.010M	0.024M	20 hours irradiation[b]	Light yellow
cellobiose octanitrate	17	0.006M	0.024M	20 hours irradiation[b]	Light yellow
xylitol pentanitrate	18	0.011M	0.024M	20 hours irradiation[b]	Light yellow
allitol hexanitrate	19	0.009M	0.024M	20 hours irradiation[b]	Pale yellow
adonitol pentanitrate	20	0.011M	0.024M	20 hours irradiation[b]	Pale yellow
maltose octanitrate	21	0.006M	0.024M	20 hours irradiation[b]	Pale yellow

Table VII. The Effect of Light and Heat on Phloroglucinol-Polynitrate Solutions.

a. Compounds prepared by Dr. L. D. Hayward and his students in earlier work.
b. Mineralite ultraviolet lamp, with filter in place, at a distance of 17 cm.

determine the composition of the oils; the classification and solubility tests gave only approximate structures. The most significant information obtained from these experiments was that neither the phloroglucinol nor the isosorbide dinitrate remained unaffected by the photochemical reaction and that nitrogen was not present in either of the oils isolated.

Ethanol solutions containing phloroglucinol and a series of polynitrate esters were exposed to different light and temperature conditions; the effects of these conditions are recorded in Table VII.

A comparison of the colorations formed in solutions 3 and 4, the first containing both phloroglucinol and isosorbide dinitrate, the second, only phloroglucinol, on a Bausch and Lomb colorimeter indicated that the solution which contained both compounds produced a greater coloration than the solution containing only phloroglucinol, moreover, the former solution was twice the volume of the latter. The optical density values are reproduced in Table VIII.

Solution Number[a]	Average Optical Density Readings at			
	360 mu	375 mu	400 mu	425 mu
3	0.212	0.160	0.107	0.080
4	0.150	0.118	0.080	0.070

Table VIII. Optical Density of Phloroglucinol and Phloroglucinol-Isosorbide Dinitrate Solutions after Heating at 78° C.

a. See Table VII.

A very slow thermal decomposition of isosorbide dinitrate occurred on extended heating, as indicated by the formation of a yellow coloration. Thermal decomposition of phloroglucinol also occurred and was much more extensive than in the case of the isosorbide dinitrate. Mixtures of the two compounds, on heating, produced an extreme yellow coloration, indicating that the presence of the dinitrate probably catalyzed the decomposition of phloroglucinol.

Decompositions also occurred in mixtures of the 2 compounds maintained at room temperature and in room light, but were not as extensive as the thermal decompositions, possibly because of the lack of a light wavelength of sufficient energy to cause reaction. Whether or not the products and mechanism of the thermal decomposition were identical to those of the ultraviolet irradiation was not established.

The irradiation of various phloroglucinol-polynitrate solutions in which the number of nitrate ester groups ranged from 2 to 8 produced yellow colorations (Table VII) and again indicated that decomposition had occurred. No definite conclusions could be drawn about the intensity of the yellow coloration versus the number of nitrate ester groups because of the qualitative nature of these experiments.

The effect of sunlight on equimolar aqueous and ethanol solutions of phloroglucinol in open beakers was investigated.

On exposure to sunlight for equal times, the aqueous solution of phloroglucinol was found to be more intensely colored than the ethanol solution, indicating a greater degree of decomposition with the former solution. These colored products were compared with those obtained from an ethanol solution, 0.16 M in both isosorbide dinitrate and phloroglucinol, irradiated for 10 minutes with filtered and for 25 minutes with unfiltered ultraviolet light (Mineralite lamp). The solutions, chromatographed on paper with solvent A, and spray reagent I, developed spots of, approximately, R_f 0.7 on all the papers, indicating that the breakdown product of phloroglucinol was more than likely identical in the 3 solutions (Table IX). Thus, under the influence of ultraviolet irradiation, phloroglucinol decomposed both with and without isosorbide dinitrate present to give the same product. This evidence was favorable to a homolytic cleavage of the $O\text{-}NO_2$ bond because if heterolytic cleavage had occurred nitro-derivatives of phloroglucinol would have been formed.

Solution	Treatment of Solution	R_f Values Volume of Solution Spotted 0.005 ml.	0.01 ml.	0.02 ml.	0.04 ml.
Aqueous Phloroglucinol (0.16 M)	Placed in sunlight to develope color	0.747	0.740	0.720	-----
Ethanolic Phloroglucinol (0.16 M)	Placed in sunlight to develope color	0.741	0.752	0.736	0.759
Ethanolic phloroglucinol-isosorbide dinitrate (each 0.16 M)	Irradiated for 10 minutes with the filter in place and 25 minutes without	0.750	0.700	0.715	0.726

Table IX. R_f Values Obtained in Paper Chromatography of Irradiated Phloroglucinol and Phloroglucinol-Isosorbide Dinitrate Solutions.

It was assumed that the breakdown products of phloroglucinol resulted from the oxidation of the compound and not from a decomposition caused directly by ultraviolet light. Without the presence of isosorbide dinitrate, this oxidation could be initiated by the effect of ultraviolet irradiation on the solvent, ethanol. Hydrogen atom loss from the solvent could result in peroxide formation, either by the alkoxy radicals reacting intramolecularly or by reacting with absorbed oxygen, followed by reaction with the hydrogen atom. The relative instability of aliphatic alcohols with atmospheric oxygen has been investigated by Brown *et al* (65), who discussed the rapid autoxidation of cyclohexanol.

To determine if an absolute ethanol solution of phloroglucinol was oxidized upon irradiation, a solution, 0.042 M in

phloroglucinol, was irradiated for 23 hours with the unfiltered Mineralite ultraviolet lamp. The bright yellow solution was concentrated, transferred to an acid-washed alumina column and eluted with solvent O. No separation occurred and the adsorbent was extruded and extracted with ethanol. The extract was evaporated to dryness and produced a crop of colorless and yellow crystals, upon which tests for hydroxyl and carbonyl compounds (64) were carried out.

The results indicated a non-hydroxylated diketo structure, of 4 or less carbon atoms. Thus, it appeared that on continued irradiation of ethanolic phloroglucinol solutions, the aromatic ring of the compound is broken down, most likely by oxidation.

The irradiation of isosorbide dinitrate, which caused a weight loss corresponding to one nitrate group, as well as, the lack of nitrogen in the products from the phloroglucinol-isosorbide dinitrate irradiation seemed to indicate that the photochemical decomposition of isosorbide dinitrate may not involve a heterolytic cleavage of the $O\text{-}NO_2$ bond. Instead, a homolytic cleavage would have produced nitrogen dioxide, a strong oxidizing agent. Thus, the presence of isosorbide dinitrate in the phloroglucinol irradiation mixture would enhance the oxidative decomposition of phloroglucinol.

C. PHOTOLYSIS OF NITRATE ESTERS IN THE PRESENCE OF HYDROQUINONE

Six sample solutions were prepared with absolute ethanol and irradiated in quartz test tubes, as shown in Table X.

Compound Concentration[a]	Irradiation Time	Result
0.021 M hydroquinone 0.021 M IsoS diN	10 minutes	Very light yellow coloration
0.021 M hydroquinone 0.021 M IsoS diN	20 minutes	Light yellow coloration
0.021 M hydroquinone 0.021 M IsoS diN	30 minutes	Yellow coloration
0.021 M hydroquinone 0.021 M IsoS diN	40 minutes	Dark yellow coloration
0.042 M hydroquinone	40 minutes	Colorless
0.042 M IsoS diN	21 hours[b]	Colorless

Table X. Irradiation of Isosorbide Dinitrate-Hydroquinone Solutions.

a. IsoS diN: Isosorbide dinitrate.
b. See Table V.

The colorations formed after irradiation of the isosorbide dinitrate-hydroquinone solutions indicated that, as in the case of phloroglucinol, the longer the irradiation time, the greater the intensity of the yellow coloration. The lack of coloration in the irradiated hydroquinone solution indicated that the presence of isosorbide dinitrate was necessary and responsible for the decomposition or reaction of hydroquinone.

D. PHOTOLYSIS OF NITRATE ESTERS IN THE PRESENCE OF DIPHENYLAMINE

The use of silicic acid-Celite or silicic acid-plaster of paris mixtures in columns and chromatobars, respectively, provided excellent techniques for the purification of diphenylamine

and its derivatives.

Paper chromatography of diphenylamine and the diphenylamine derivatives was attempted using silicic acid impregnated papers (53), but was unsuccessful since the compounds all ran on, or very close to, the solvent front, with the exception of p-nitroso-diphenylamine which did not move from the start line. It was not known whether this failure to chromatograph was due to insufficient adsorbent on the paper or whether the cellulose was "esterified" by the adsorbent, which blocked the free hydroxyl groups of the silicic acid that normally act as adsorption sites (66) (67).

Paper chromatography of diphenylamine was attempted using chromatography paper without pretreatment and solvents A, B, C and D. In all cases the hydrophobic diphenylamine was detected on the solvent front.

The paper chromatography of a number of nitrate ester compounds was investigated using non-pretreated chromatography paper and solvent system C. The chromatograms were sprayed with reagent II and irradiated with the Mineralite lamp. The observed R_f values are reproduced in Table XI.

A series of chromatoplates were prepared on which some of the materials were irradiated <u>in situ</u> after spotting and before developing. The results are shown in Table XII.

It was noted that on all the plates in which both irradiated

Compound[a]	R_f Values[b]
isomannide mononitrate	Did not chromatograph
isosorbide mononitrate	Did not chromatograph
isoidide mononitrate	Did not chromatograph
mannitol hexanitrate	Tailed
dulcitol hexanitrate	Tailed
allitol hexanitrate	0.20 - 0.22
L-aribitol pentanitrate	0.16 - 0.20
xylitol pentanitrate	0.12 - 0.15
adonitol pentanitrate	0.23 - 0.28
Methyl-β-D-glucopyranoside tetranitrate	Tailed
cellobiose octanitrate	Did not chromatograph
maltose octanitrate	Did not chromatograph
D-mannitol-1,2,3,5,6-pentanitrate	0.05 - 0.06
D-dulcitol-1,2,4,5,6-pentanitrate	0.04 - 0.06
cis-cyclohexane-1,2-diol dinitrate	On solvent front
trans-cyclohexane-1,2-diol dinitrate	On solvent front
trans-acenaphthene-1,2-diol dinitrate	On solvent front

Table XI. R_f Values Obtained in Paper Chromatography of Polynitrate Compounds.

a. Prepared by Dr. Hayward and his students in earlier work.
b. All papers were irrigated with solvent C, sprayed with reagent II and irradiated for 5 minutes with short-wave ultraviolet light.

Solvent System Designation	Solutions Spotted: N-nitroso-diphenylamine	p-nitroso-diphenylamine	2-nitro-diphenylamine	Mixture[a]	4-nitro-diphenylamine	Isosorbide dinitrate	Isosorbide	Diphenylamine	Irradiation Conditions[b,c]	R_f Values[b,c] Non-irradiated	Irradiated
E				✓ Spotted twice		✓ Spotted twice		✓ Spotted twice	One mixture, one IsoS diN and one DPA spot were irradiated for 2 minutes (filter removed)	IsoS diN 0.229, DPA 0.583, Mixture 0.257, 0.565	IsoS diN 0.222, DPA 0.580, Mixture 0.266, 0.659
E			✓	✓	✓		✓	✓	The mixture spot was irradiated for 2 minutes (filter removed)	Isosorbide 0.000, 4-nitro DPA 0.107, 2-nitro DPA 0.586, DPA 0.532	Mixture 0.131, 0.544
E	✓	✓		✓		✓		✓	None of the spots was irradiated	N-nitroso DPA 0.364, p-nitroso DPA 0.000, Mixture 0.115, 0.435, DPA 0.426, IsoS diN 0.157	----
E				✓ Spotted four times		✓		✓	First mixture spot not irradiated, second, third & fourth were irradiated for 2,4 & 8 minutes, resp. (filter in place)	DPA 0.615, IsoS diN 0.103, Mixture 0.095, 0.522	Mixture (2 min) 0.101, 0.552 (4 min) 0.106, 0.567 (8 min) 0.118, 0.615

Table XII. R_f Values of Materials Irradiated *in situ* on Chromatoplates. (Continued)

Solvent System Designation	Solutions Spotted: N-nitroso-diphenylamine	p-nitroso-diphenylamine	2-nitro-diphenylamine	Mixture [a]	4-nitro-diphenylamine	Isosorbide dinitrate	Isosorbide	Diphenylamine	Irradiation Conditions[b,c]	R_f Values[b,c] Non-irradiated	R_f Values[b,c] Irradiated
E				✓ Spotted four times		✓		✓	First mixture spot not irradiated, second, third & fourth were irradiated for 2, 4 & 16 minutes, resp. (filter removed)	DPA 0.533, IsoS diN 0.099, Mixture 0.095, 0.488	Mixture (2 min.) 0.080, 0.480 (4 min.) 0.073, 0.478 (16 min.) 0.090, 0.496

Table XII. R_f Values of Materials Irradiated *in situ* on Chromatoplates.

a. The mixture solution was 0.02 M in both isosorbide dinitrate and diphenylamine.
b. Mineralite lamp at 20 cm., sprayed with reagent IV and heated.
c. IsoS diN: Isosorbide dinitrate, DPA: diphenylamine.

and non-irradiated mixture spots were originally present, only 2 developed spots appeared, and that the R_f values of these spots corresponded with the R_f values of diphenylamine and isosorbide dinitrate. Thus, it appeared that the isosorbide dinitrate and diphenylamine were either not reacting under the influence of ultraviolet light, or, more probably, they were reacting, but only on the surface of the plate and the products were in too low a concentration for detection. It was concluded, therefore, that plate irradiations were ineffective and that irradiated solutions must be prepared and then spotted.

This supposition was tested by irradiating an absolute ethanol solution 0.02 M in both isosorbide dinitrate and diphenylamine for 6 hours. During this time, aliquots were removed periodically from the reaction solution and examined on chromatoplates, which were developed with solvent E and spray reagent IV and heated in the usual manner. The R_f values of these plates are listed in Table XIII.

The results showed that two developed spots were present up to 30 minutes' irradiation time, but that after one hour three developed spots appeared. Thus, a minimum irradiation time of one hour was required for the concentration of the third spot to be high enough for detection.

Solutions Spotted	Irradiation Time (minutes)	R_f Values[b]		
Mixture[a]	2	0.048		0.449
Mixture[a]	5	0.044		0.423
Mixture[a]	10	0.040		0.397
Diphenylamine	None		0.368	
Isosorbide dinitrate	None	0.036		
Mixture[a]	30	0.041		0.401
Mixture[a]	60	0.055	0.478	0.550
Mixture[a]	120	0.059	0.475	0.541
Mixture[a]	240	0.060	0.454	0.526
Diphenylamine	None		0.450	
Isosorbide dinitrate	None	0.056		
Mixture[a]	360	0.064	0.508	0.560

Table XIII. Determination of Irradiation Time for Maximum Product Formation.

a. The original mixture solution was 0.02 M in both isosorbide dinitrate and diphenylamine.
b. The plates were irrigated with solvent E, sprayed with reagent IV and heated.

Another portion of the solution containing isosorbide dinitrate and diphenylamine was irradiated for 2 hours and used in the determination of a suitable solvent system for the separation of the irradiation mixtures. The results, quoted in Table XIV, indicated that the most suitable solvent system was 1:1 anhydrous benzene-ligroin, 85-105° (solvent F) because it produced the greatest spot separation and, thus, easiest identification.

A plate spotted with a 2-hour irradiated mixture solution and irrigated with solvent system E produced either 2 or 3 spots, whereas, a similarly spotted plate irrigated with solvent F produced 5 developed spots. A chromatoplate spotted with a 2-hour irradiated mixture solution and developed 2

Solvent System	Color of Spots After Irrigation[b]							R_f Values[c]						
	N-nitroso-diphenylamine	p-nitroso-diphenylamine	2-nitro-diphenylamine	a Mixture	4-nitro-diphenylamine	Isosorbide dinitrate	Diphenylamine	N-nitroso-diphenylamine	p-nitroso diphenylamine	2-nitro-diphenylamine	a Mixture	4-nitro-diphenylamine	Isosorbide dinitrate	Diphenylamine
F	—	Dark orange	Orange	Light mauve Yellow Light orange	Yellow-orange	Colorless	—	0.288 0.522	0.126	0.458	0.117 0.169 0.306 0.454 0.525	0.185	0.249	—
G	—	—	—	—	—	—	—	All spots ran with the solvent front						
H	Grey	Dark orange	Orange	Mauve Yellow Light orange	Dark Yellow	Colorless	Colorless	0.775	0.269	0.868	0.232 0.298 0.352 0.555 0.748 0.880	0.555	0.554	0.884

Table XIV. Determination of a Suitable Solvent System for the Separation of Irradiated Solution Products..... (Continued)

Solvent System	Color of Spots After Irrigation[b]							R_f Values[c]						
	N-nitroso-diphenylamine	p-nitroso-diphenylamine	2-nitro diphenylamine	Mixture a	4-nitro-diphenylamine	Isosorbide dinitrate	Diphenylamine	N-nitroso-diphenylamine	p-nitroso-diphenylamine	2-nitro-diphenylamine	Mixture a	4-nitro-diphenylamine	Isosorbide dinitrate	Diphenylamine
I	—	Dark orange	Orange	Very light Yellow Light Yellow Light orange	Yellow	Colorless	Colorless	0.450 0.713	0.118	0.636	0.1195 0.231 0.446 0.638 0.694	0.242	—	0.714
J	—	Dark orange	Orange	Light Yellow Light orange	Yellow	Colorless	Colorless	0.910	0.737	0.895	0.792 0.898	0.822	0.915	0.897
K	Charcoal grey	Dark orange	Orange	Pale Yellow Pale orange	Yellow	Colorless	Colorless	0.852	0.346	0.888	0.606 0.868	0.606	0.608	0.873

Table XIV. Determination of a Suitable Solvent System for the Separation of Irradiated Solution Products.

a. An absolute ethanol solution, 0.02 M in both isosorbide dinitrate and diphenylamine, was irradiated for 2 hours.
b. The colors are listed from the lowest to highest R_f value.
c. All plates were sprayed with reagent IV and heated.

dimensionally was used to determine the number of components in each of the E developed spots, as shown in Figure 4.

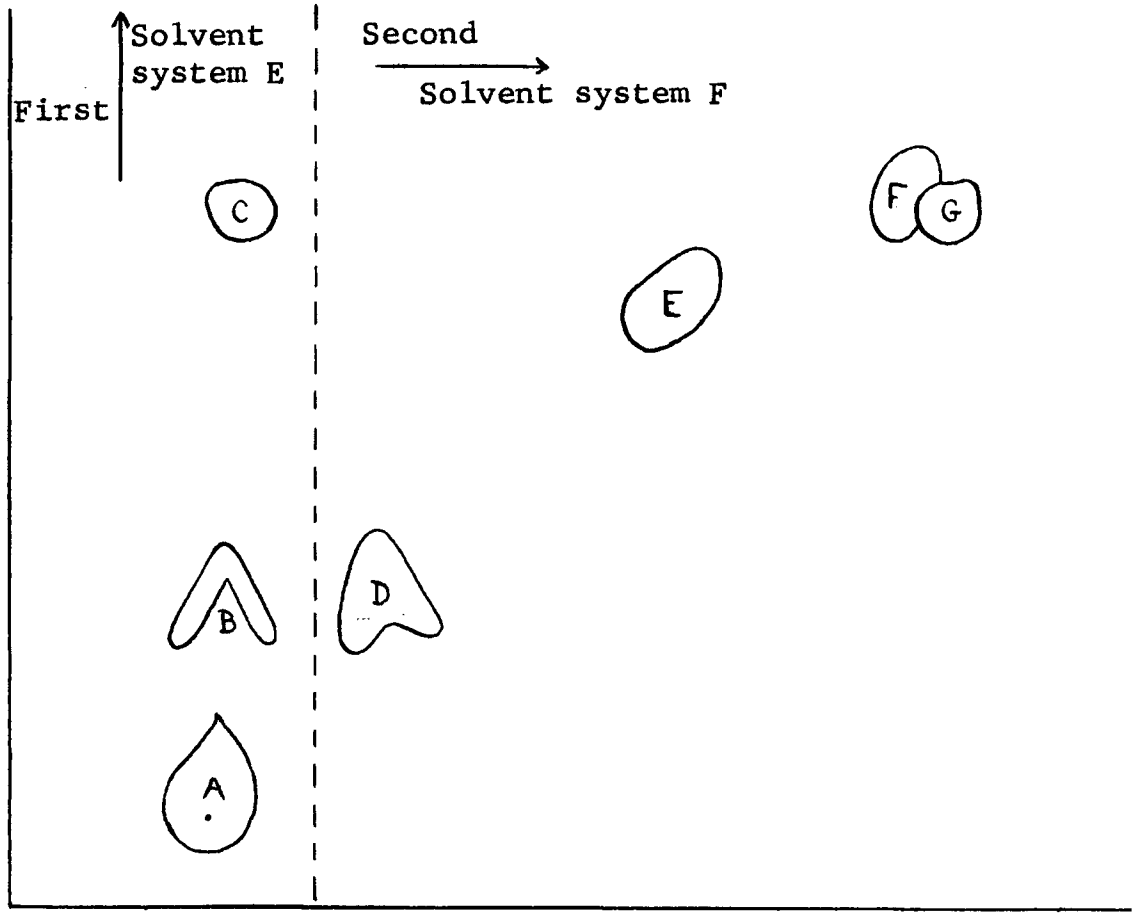


Fig. 4. Chromatoplate Spotted with an Irradiated Mixture Solution and Developed Two-Dimensionally.

Developed spots A, B, C, D, F, and G were visible immediately after irrigation; spot E appeared after spraying with reagent IV. The original mixture solution was 0.02 M in both isosorbide dinitrate and diphenylamine.
A: pink, B: yellow, C: orange, D: yellow, E: light blue, F: light orange, G: light blue.

It was concluded from this plate that the upper developed spot in solvent E consisted of 2 or 3 components and the lower, of 1 or 2.

When the pure diphenylamine and diphenylamine derivatives

were spotted and developed on a chromatoplate, only one spot appeared for each compound. On the original spotting positions, however, there were extremely light blue peripheral colorations apparent, which for N-nitrosodiphenylamine was almost invisible. It was supposed that these colorations were either due to ester formation between the solvent, ethanol, and the silicic acid adsorbent or to strong polyol adsorption, as in the case of isosorbide.

To test this supposition, a chromatoplate was spotted with 50λ, 100λ and 150λ of anhydrous ethanol. After irrigating with solvent L, spraying with reagent IV and heating to develop spots, three grey peripheral spots appeared on the original spotting positions, the color intensity increasing from the 50λ to the 100λ to the 150λ position. Because the grey colorations did not extend over the whole spot, it was concluded that neither ester formation or strong alcohol adsorption occurred. The coloration, however, could have been caused by the alcohol extracting some material from the plaster of paris and carrying it to the outer portions of the spots or, perhaps less likely, by the basic diphenylamine derivatives reacting with the silicic acid adsorbent to give a slightly colored salt. This would not explain the faint coloring observed for N-nitrosodiphenylamine unless a fraction of the compound underwent a Fischer-Hepp rearrangement, in which certain aromatic nitrosomines rearrange

to p-nitroso derivatives in the presence of acids (68).

The irradiations of isosorbide dinitrate and diphenylamine films on filter paper circles with a grating monochromator indicated that the greatest yellow coloration occurred on the overlap positions at approximately 290 mu, the most effective wavelength region being from 265 to 334 mu.

A General Electric lamp of wavelengths 3600-3800 A (H 100 BL 4) and the filtered Mineralite lamp of wavelength 2540 A and shorter, produced only light yellow colorations on the filter papers, whereas, the unfiltered Mineralite with radiation from 2350 to 5800 A produced a strong yellow coloration. This confirmed the irradiation work with the grating monochromator and indicated that the most useful wavelength region for the photochemical reaction was 254-360 A.

An important fact which emerged from these irradiations was that the crystalline isosorbide dinitrates of m.p. 69.2-70.0° C. and 50.5-51.5° C. behaved similarly when in the presence of diphenylamine and short-wave ultraviolet light. Thus, it appeared that the crystal structure of the dinitrate has no effect on the photochemical decomposition of the compound.

A comparison of the R_f values obtained from a "synthetic irradiation mixture" and an irradiated mixture on a chromatoplate developed in two dimensions was carried out as follows: an absolute ethanol solution, 0.02 M in both diphenylamine and

isosorbide dinitrate was irradiated for 2 hours, and 200 λ of this solution was spotted on a chromatoplate.

Another chromatoplate was spotted with 200 λ of a "synthetic irradiation mixture" solution which contained 1.35 mg. of diphenylamine and 1.35 mg. of each of its four derivatives and 3.78 mg. of isosorbide in 2 ml. of absolute ethanol.

Both plates were simultaneously introduced into the same tank and irrigated with solvent L. After sufficient development, the plates were removed, thoroughly dried in the absence of light, simultaneously introduced into another tank containing solvent M and irrigated in a direction at right angles to the previous case. Tracings of the plates are reproduced as Figures 5 and 6.

It was found that there was no correlation of the developed spots on the 2 plates (see Figures 5 and 6). This was unusual, because previous irradiation solutions spotted and developed on chromatoplates indicated that the irradiated mixture solution contained 2- and 4-nitrodiphenylamine, unreacted diphenylamine and, perhaps, N- and p-nitrosodiphenylamine (see Figure 7). It was thought that the differences between these plates may have been caused by variations in the adsorbent thickness, especially since both plates were prepared at the same time, with the same procedures and materials, and spotted and irrigated simultaneously.

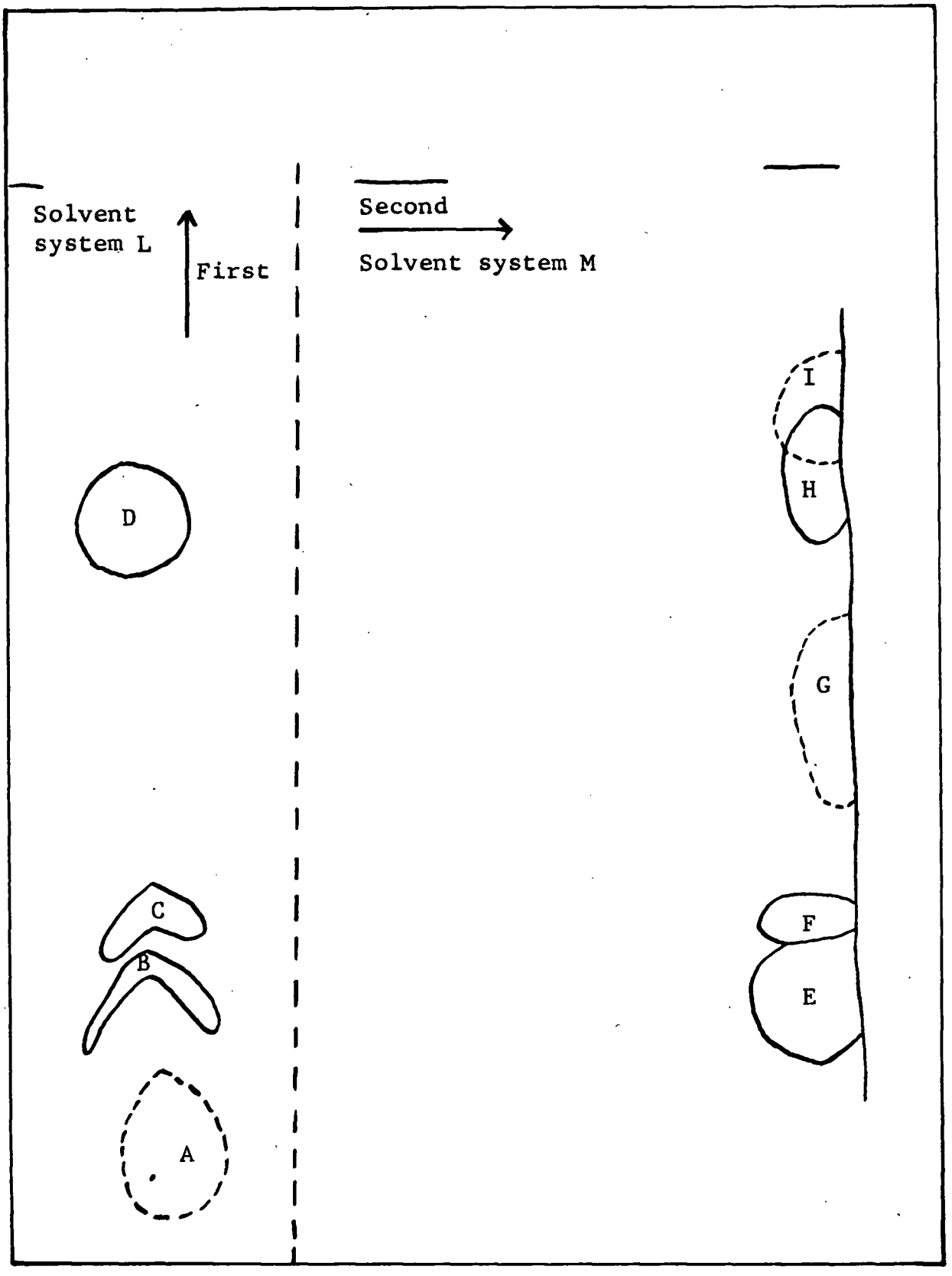


Fig.5."Synthetic Irradiation Mixture" Developed Two-Dimensionally. Developed spots B, C, D, E, F, H were visible immediately after irrigation; spots G and I appeared after spraying with reagent IV, spot A appeared after strong heating.
A: grey, B: dark orange, C: yellow, D: orange, E: dark yellow, F: yellow, G: dark blue, H: ~~mauve~~ orange, I: dark blue.

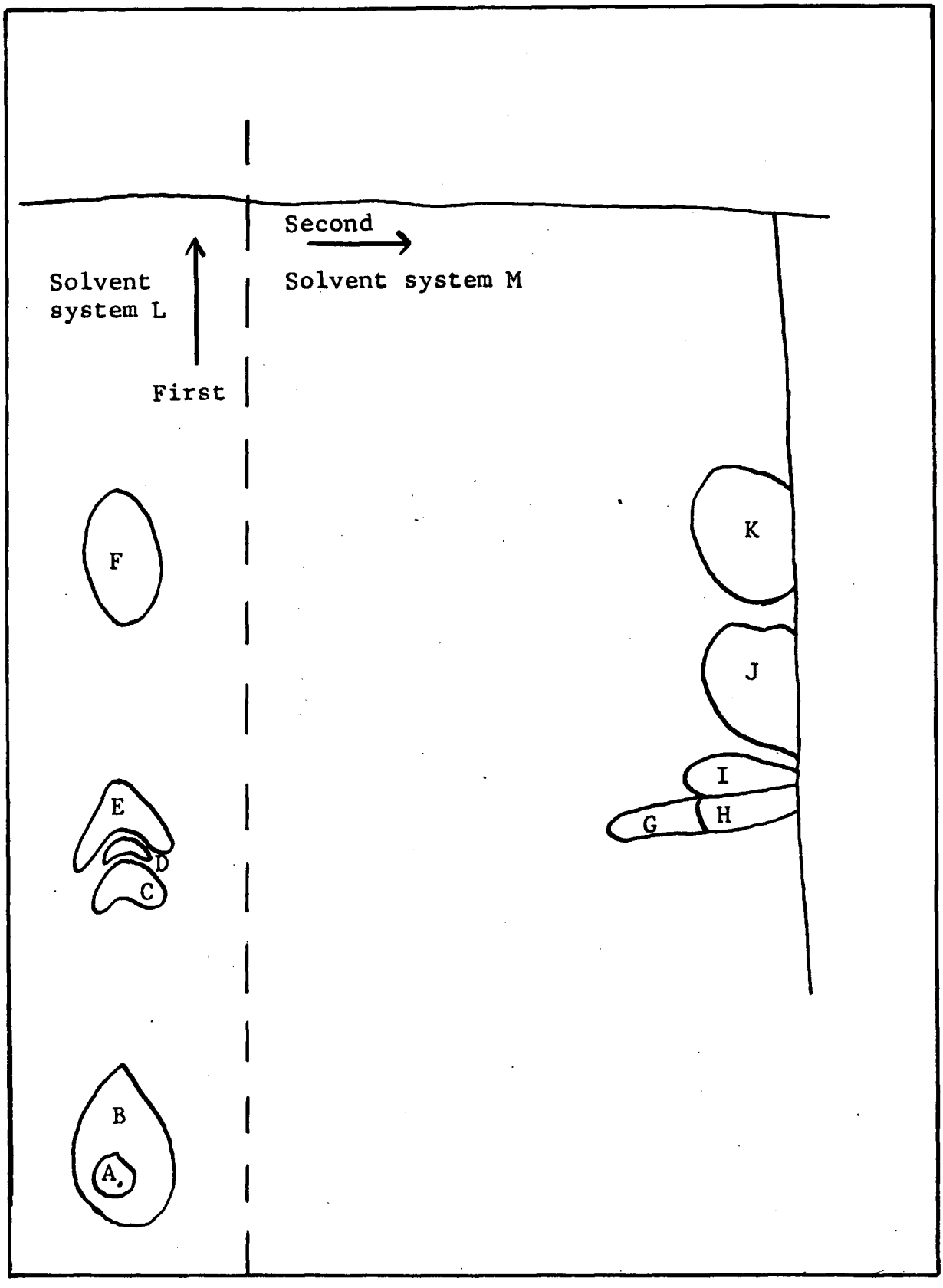


Fig. 6. Irradiation Mixture Developed Two-Dimensionally. Spots A, B, C, D, E, F, G, H, I and K were visible immediately after irrigation, spot J appeared after spraying with reagent IV. A: light purple, B: grey, C: light grey, D: light red, E: yellow, F: orange, G: pale pink, H: light brownish-orange, I: pale yellow, J: blue, K: ~~dark blue~~ orange.

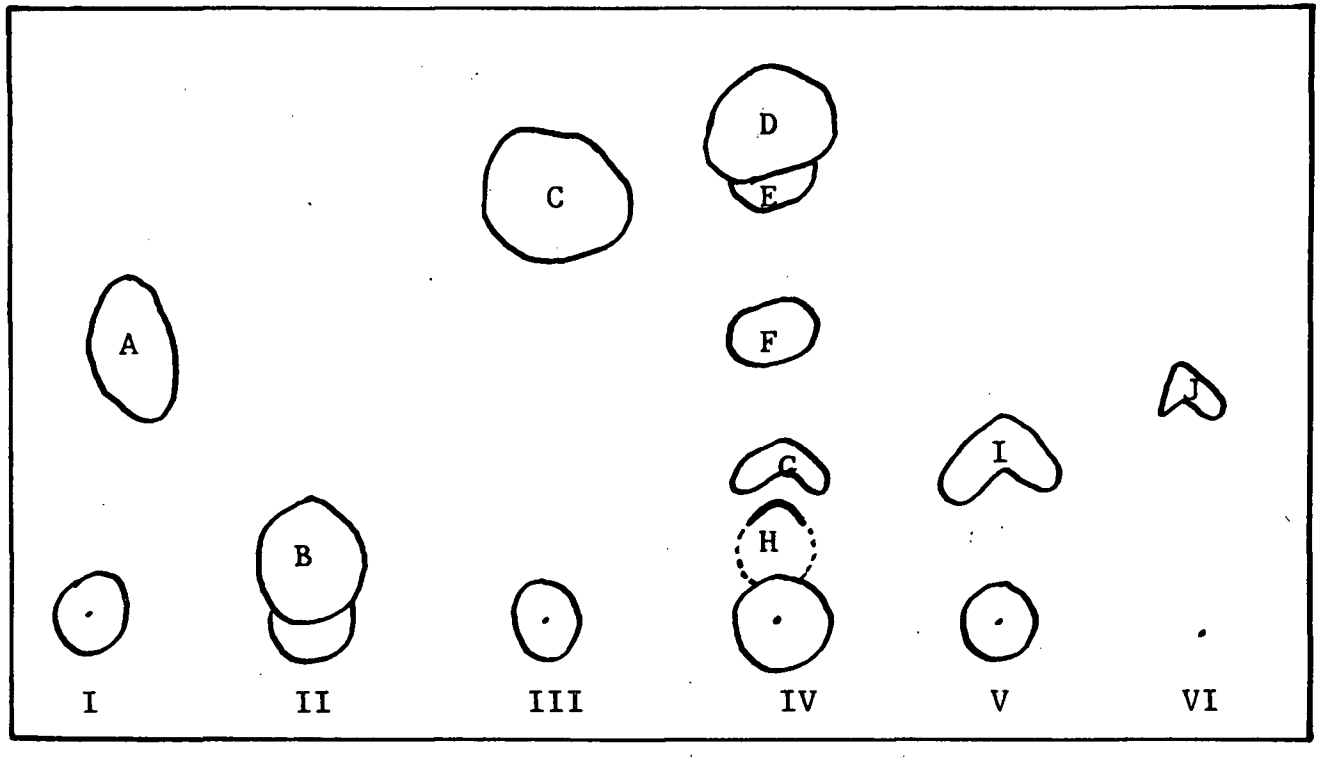


Fig. 7. Relative Positions of the Diphenylamine Derivatives on a Developed Chromatoplate. I: N-nitrosodiphenylamine, II: p-nitrosodiphenylamine, III: 2-nitrodiphenylamine, IV: An absolute ethanol solution, 0.02 M in both isosorbide dinitrate and diphenylamine, irradiated for 2 hours, V: 4-nitrodiphenylamine, VI: isosorbide dinitrate. The plate was irrigated with solvent F. Spots A, B, C, D, E, F, G, H and I appeared after spraying with reagent IV, spot J appeared on strong heating.
A: dark blue, B: dark green, C: mauve, D: dark blue, E: mauve, F: blue, G: purplish-blue, H: purple, I: purple, J: grey.

Another chromatoplate spotted with the irradiated mixture solution, the "synthetic irradiation mixture" and the diphenylamine derivative standards, and developed in one dimension, indicated that this supposition was correct. Fairly good agreement was observed between the R_f values of the spots from the irradiation and standard solutions in this case (Figure 8).

The most effective qualitative experiment for determining the composition of the irradiated mixture solutions was with a chromatoplate employing an "enrichment" principle. Using the five absolute ethanol solutions of diphenylamine and its derivatives, and the irradiated mixture solution, a plate was spotted with seven 50 λ spots of the irradiated solution. On top of each alternate spot, 20 λ of one of the five diphenylamine derivative solutions was applied, thus, providing an enrichment in one of the components of the irradiation mixture. The developed plate is reproduced in Figure 9.

After plate development, a greater color intensity was noted for the developed spots which corresponded to the enriched component in the irradiated mixture (Figure 9). This simple experiment indicated that the irradiation solution, initially containing isosorbide dinitrate and diphenylamine, now contained N-nitrosodiphenylamine, p-nitrosodiphenylamine, 2-nitrodiphenylamine, 4-nitrodiphenylamine and unreacted diphenylamine.

Although these experiments were not conclusive in determining

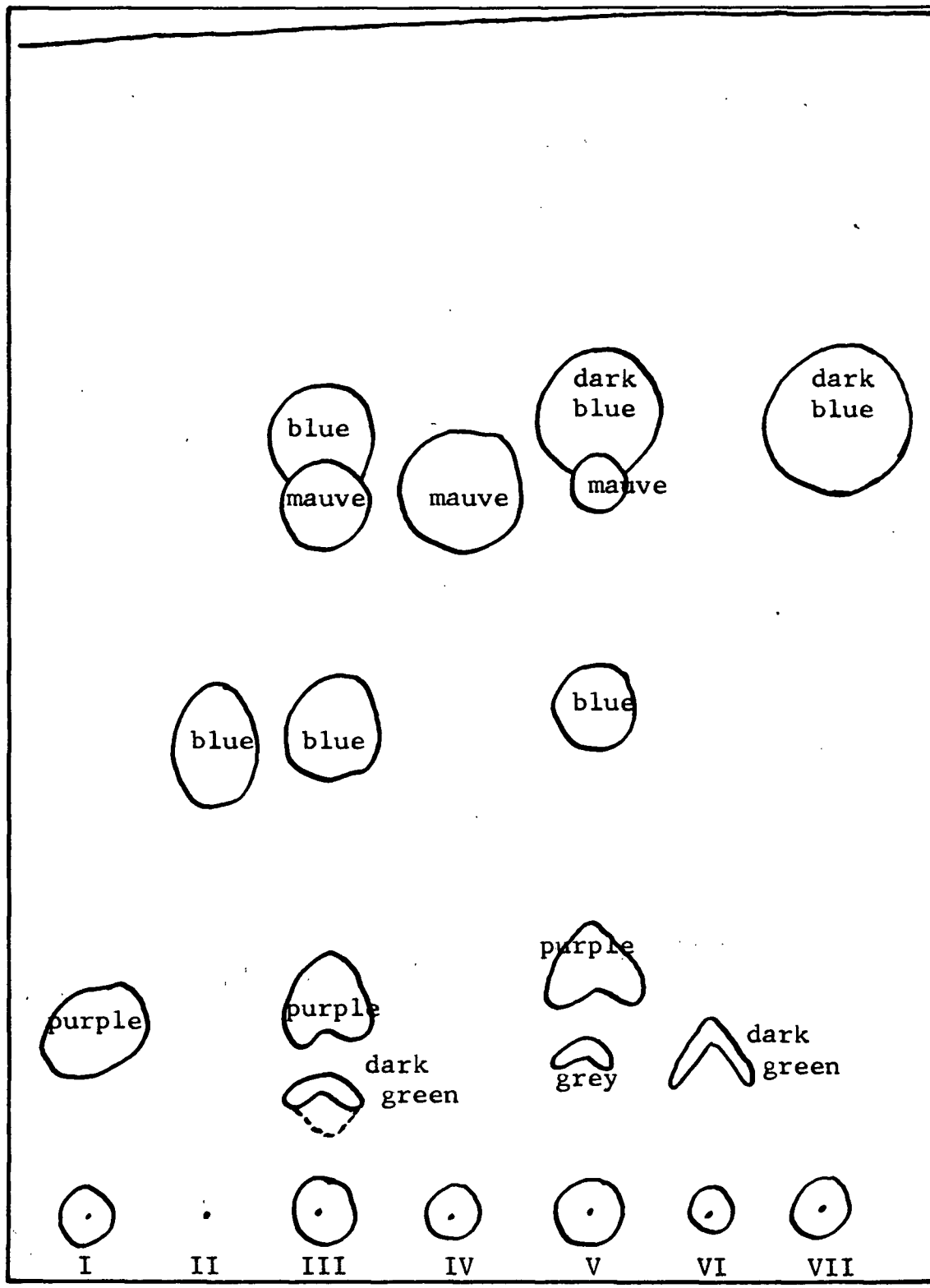


Fig. 8. Irradiated Solution, "Synthetic Irradiation Solution" and Standard Solutions Developed One-Dimensionally.
I: 4-nitrodiphenylamine, II: N-nitrosodiphenylamine, IV: 2-nitrodiphenylamine, VI: p-nitrosodiphenylamine, VII: diphenylamine, III: Synthetic irradiation mixture containing 1.35 mg. of diphenylamine and each of its derivatives and 3.78 mg. of isosorbide made up to a total volume of 2 ml. with anhydrous ethanol, V: An anhydrous ethanol solution, 0.02 M in both isosorbide dinitrate and diphenylamine, irradiated for 2 hours.
The plate was irrigated with solvent L and sprayed with reagent IV.

Irradiated solution: An anhydrous ethanol solution, 0.02 M in both isosorbide dinitrate and diphenylamine was irradiated for 2 hours.

A, C, F: Irradiated solution
B: Irradiated solution plus N-nitrosodiphenylamine
D: Irradiated solution plus p-nitrosodiphenylamine
E: Irradiated solution plus 2-nitrodiphenylamine
G: Irradiated solution plus 4-nitrodiphenylamine

The plate was irrigated with solvent L and sprayed with reagent IV.

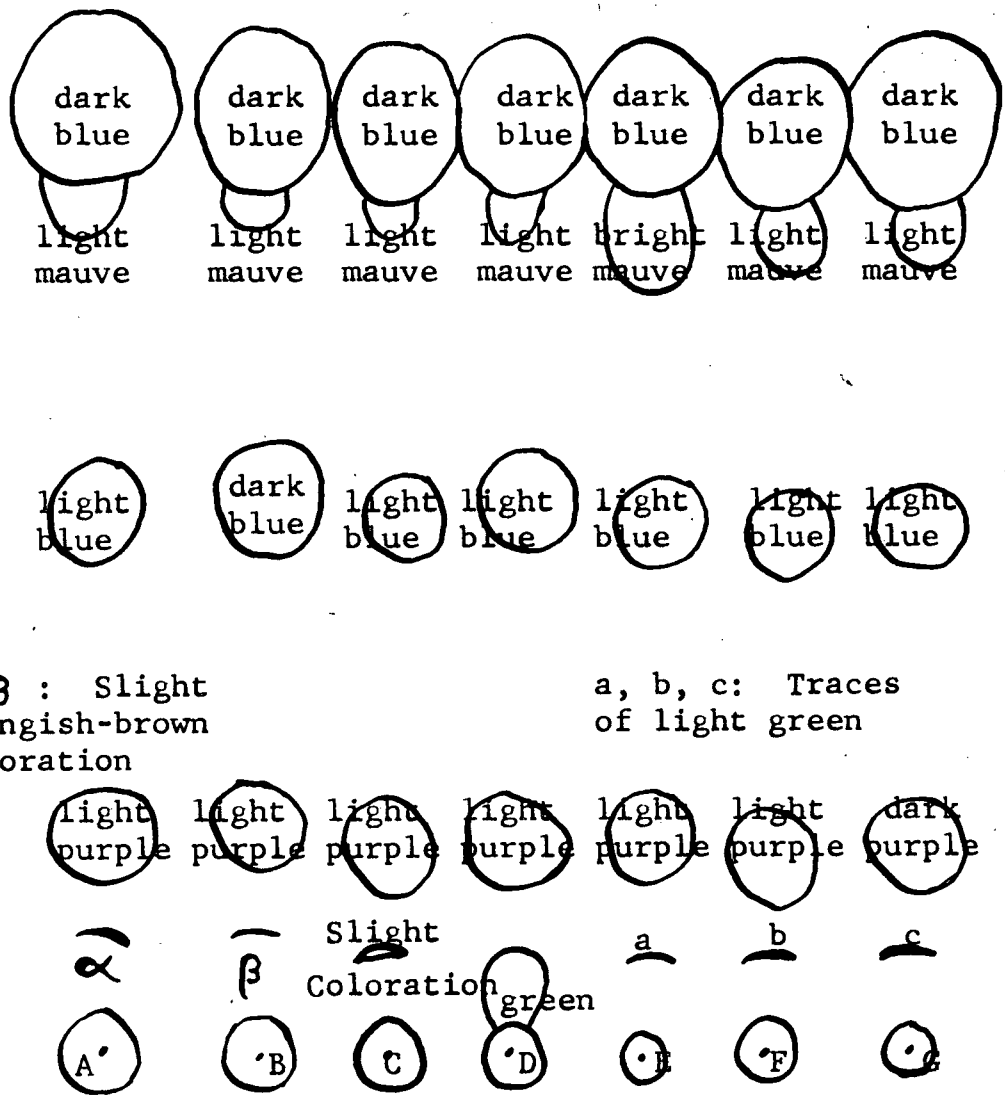


Fig. 9. Chromatoplate Spotted with an Irradiation Solution and Enriched in Diphenylamine Derivatives.

the composition of the irradiation solutions, they were close to being so, especially with the enriched chromatoplate. The spots of the irradiated solution agreed with those of the standard solutions in position, in color after irrigation and after spraying, the color of each diphenylamine derivative being different and distinctive.

A final quantitative irradiation experiment was performed in order to confirm thepresence of the diphenylamine derivatives in the irradiation products. Isosorbide dinitrate (169.99 mg.) was mixed with diphenylamine (121.84 mg.) and the total volume made up to 16 ml. with absolute ethanol. This solution was irradiated for 2 hours; the solution was then concentrated by evaporation in the absence of light and quantitatively transferred to a 1 x 1 x 18-inch chromatobar. The bar was irrigated with solvent L for 9.5 hours, removed from the tank and thoroughly dried with a cold air stream.

The adsorptives, which had separated into bands on the bar, were removed and each fraction was powdered, poured into glass columns and eluted with A.R. acetone in the absence of light. When elution was complete, the fractions were evaporated to dryness in the absence of light and dried over phosphorus pentoxide in a desiccator. The weights of the fractions obtained are quoted in Table XV.

Fraction	Suspected Material	Weight of Crude Materials (mg.)
1	Diphenylamine	5.11
2	2-nitrodiphenylamine	89.19
3	N-nitrosodiphenylamine	4.97
4	4-nitrodiphenylamine	26.51
5	p-nitrosodiphenylamine	2.59
6	Unknown material with a R_f lower than p-nitrosodiphenylamine	13.96

Table XV. Weights of Crude Fractions Obtained from the Quantitative Separation.

Only 49% of the weight of the original materials was isolated. This poor recovery was caused by the overlap of the various fractions on the bar; no attempt was made to separate these overlap mixtures.

Two fractions (2 and 4, Table XV) suspected to be 2- and 4-nitrodiphenylamine, were separately dissolved in a small volume of acetone and each solution was quantitatively rechromatographed on a chromatobar, 1 x 1 x 10 inches, as described above, yielding 6.95 mg. of 4-nitrodiphenylamine, m.p. 132.5-133.2° C., and 21.04 mg. of 2-nitrodiphenylamine, m.p. 72.0-73.0° C. The reported melting points are shown in Table III. The ultraviolet and infrared spectra of the reaction products which confirmed their identities are reproduced in Appendices 1 and 2.

The other fractions were each dissolved in absolute ethanol and the ultraviolet spectra determined. The values are quoted in Table XVI. The ethanolic spectral solutions were transferred back to their respective crude materials and the combined fractions were streaked on a chromatoplate, which, in this case,

was used as a micro-purification technique. The plate was irrigated with solvent L until separation had occurred. The adsorbents containing the materials having the R_f values of the suspected fractions were removed from the plate, powdered, and eluted as before. A material which had a lower R_f than p-nitrosodiphenylamine did not chromatograph on the plate and no further work was done on it.

The dried materials were dissolved in absolute ethanol and the ultraviolet spectra determined, as recorded in Table XVII.

One crystal of each of the irradiation produced 2- and 4-nitrodiphenylamine samples were dissolved in a few drops of absolute ethanol and these solutions, as well as the ethanol spectra solutions, were spotted on 2 chromatoplates with suitable standard spots. These plates are reproduced in Figure 10.

The quantitative irradiation experiment confirmed the formation of 2-nitrodiphenylamine and 4-nitrodiphenylamine from the irradiation of an ethanolic solution of diphenylamine and isosorbide dinitrate. The presence of p-nitrosodiphenylamine, N-nitrosodiphenylamine and the decomposition products of isosorbide dinitrate were not detected and, thus, only a tentative identification may be claimed for N- and p-nitrosodiphenylamine. When 2 chromatoplates were spotted and developed with the various purified fractions (see Figure 10), there was some evidence that N-nitrosodiphenylamine was present but the ultraviolet spectral

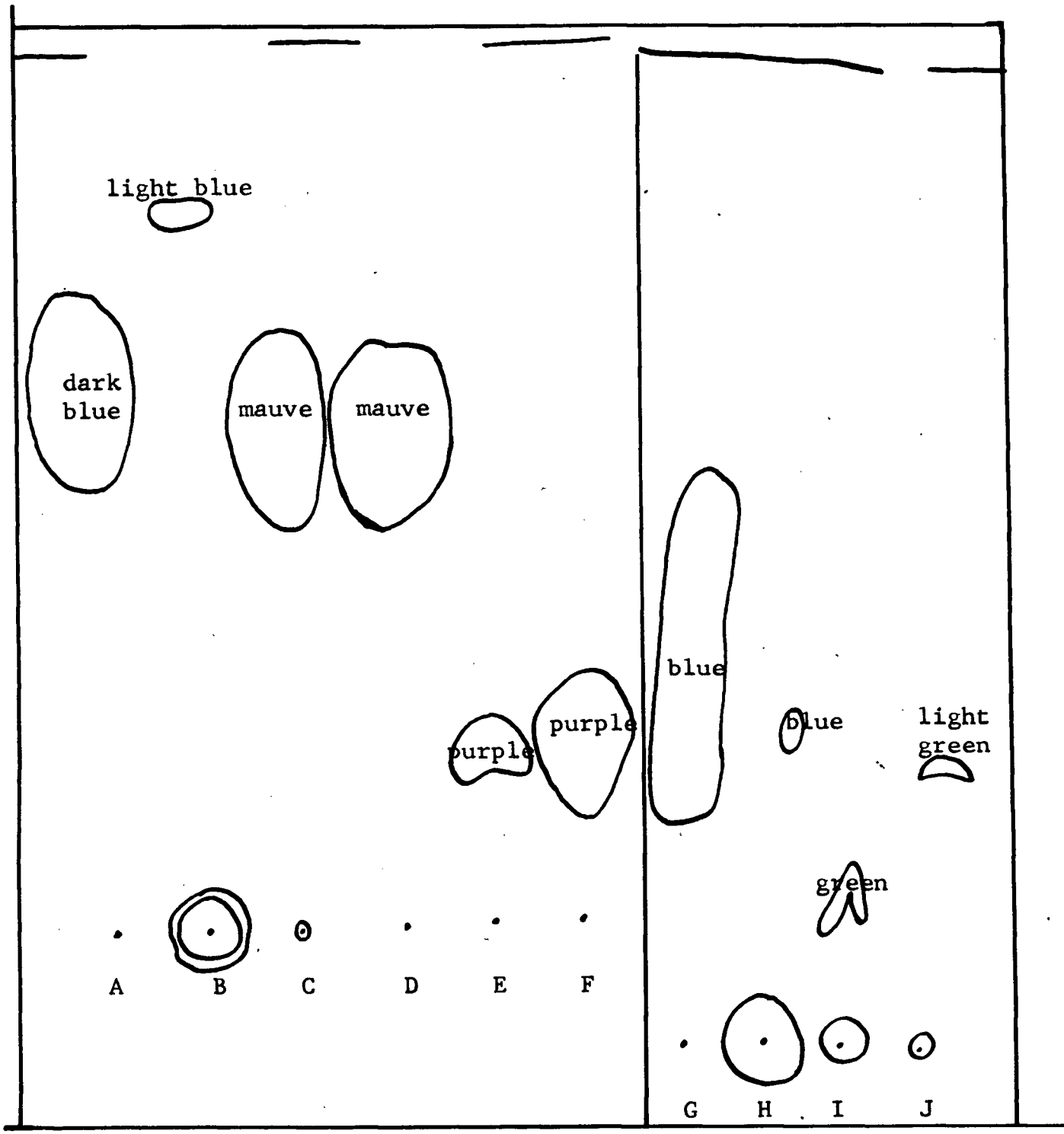


Fig. 10. Irradiation Products Separated on Chromatoplates. A: diphenylamine, C: 2-nitrodiphenylamine, E: 4-nitrodiphenylamine, B: Fraction 1, D: Fraction 2, F: Fraction 4, G: N-nitrosodiphenylamine, H: Fraction 3, I: p-nitrosodiphenylamine, J: Fraction 5. Both plates were irrigated with solvent L and sprayed with reagent IV.

values for this fraction did not confirm it (see Tables XVI and XVII).

Suspected Compound	Reference Peaks (44) max.(mu)	Reference Peaks (44) min.(mu)	Observed Peaks[b] max.(mu)	Observed Peaks[b] min.(mu)
Diphenylamine	285	249	285-287	249 and 264
p-nitrosodiphenylamine[a]	405-407 258-260	279-281 237-240	395 320-330	265
N-nitrosodiphenylamine	295-296	259-260	410-420 283 224	375 265-268
Material with a lower R_f than p-nitrosodiphenylamine			Absorbed strongly in ultraviolet and visible regions.	

Table XVI. Observed Ultraviolet Peaks for the Crude Irradiation Products.

a. One drop of 6N hydrochloric acid was added to the ethanolic solution.
b. The concentrations of the suspected materials in the absolute ethanol spectral solutions are unknown.

Suspected Compound	Reference Peaks (44) max.(mu)	Reference Peaks (44) min.(mu)	Observed Peaks[b] max.(mu)	Observed Peaks[b] min.(mu)
Diphenylamine	285	249	285 225	262
p-nitrosodiphenylamine[a]	405-407 258-260	279-281 237-240	285-289 218-219	255
N-nitrosodiphenylamine	295-296	259-260	328-333 282 220	290-295 270

Table XVII. Observed Ultraviolet Peaks for the Purified Irradiation Products

a. One drop of 6N hydrochloric acid was added to the ethanolic solution.
b. The concentrations of the suspected materials in the absolute ethanol spectral solutions are unknown.

E. THE MECHANISM OF THE PHOTOLYSIS

Ethanolic solutions of diphenylamine and isosorbide dinitrate, and a solution containing both compounds, were irradiated for a

few minutes with the Mineralite lamp, filter in place, and then rapidly transferred to an electron-spin resonance machine and the spectra determined (see Figure 24, Appendix 3). Resonance signals were not detected for the diphenylamine or the isosorbide dinitrate solutions, however, an extremely weak signal was apparent for the solution containing both compounds. Whether or not this signal signified the presence of a free radical or was only background noise could not be determined at this degree of resolution.

If radical formation did occur, it would most likely be formed from the isosorbide dinitrate and involve a homolytic cleavage of the $O\text{-}NO_2$ bond.

$$RO — NO_2 \xrightarrow{h\nu} RO\cdot + NO_2$$

$$RO\cdot + \text{solvent} \xrightarrow{h\nu} ROH$$

Both the homolytic cleavage of the $O\text{-}NO_2$ bond and the hydrogen atom cleavage from the ethanol are energetically possible using the non-filtered Mineralite lamp. The filtered lamp's main wavelength is 2540 A, which is equivalent to a bond dissociation energy of 113 kcals/mole. The bond dissociation energies of $CH_3O\text{-}NO_2$ and $CH_3O\text{-}H$ are quoted (69) as 40 and 100 kcals/mole, respectively.

The expected decomposition product of the photochemical breakdown of isosorbide dinitrate was isosorbide. It was thought that if a characteristic color reaction could be developed on

paper for isosorbide it might also be applicable to chromatoplates.

Spray reagents such as reagents VI, VII, VIII and IX were dispersed onto papers spotted with isosorbide, but in all cases, the isosorbide spot did not develop, although standard spots of cis- and trans-acenaphthenediol and d,l-hydrobenzoin were developed under these conditions. Isosorbide was readily detected on chromatoplates by spraying with reagent IV (5% fuming nitric acid in concentrated sulphuric acid) and heating the plate strongly (see Figure 11), but this reaction did not distinguish it from other organic compounds.

If a homolytic cleavage of the $O-NO_2$ bond occurred, the nitrogen dioxide produced could react with a hydrogen atom from the solvent, ethanol, or with an expelled hydrogen atom from the RO· radical to give nitrous acid. To determine whether or not this occurred an ethanol and two benzene solutions, 0.02 M., in both isosorbide dinitrate and diphenylamine, were irradiated for 2 hours, and aliquots from the reaction mixtures were tested for nitrous acid by the method of Carboni (70). Negative tests were obtained in all cases, although the reagent did give the required blue coloration with acidified sodium nitrite.

When benzene solutions containing isosorbide dinitrate and diphenylamine were irradiated, yellow colorations were formed. This behavior was unexpected because it was assumed that hydrogen

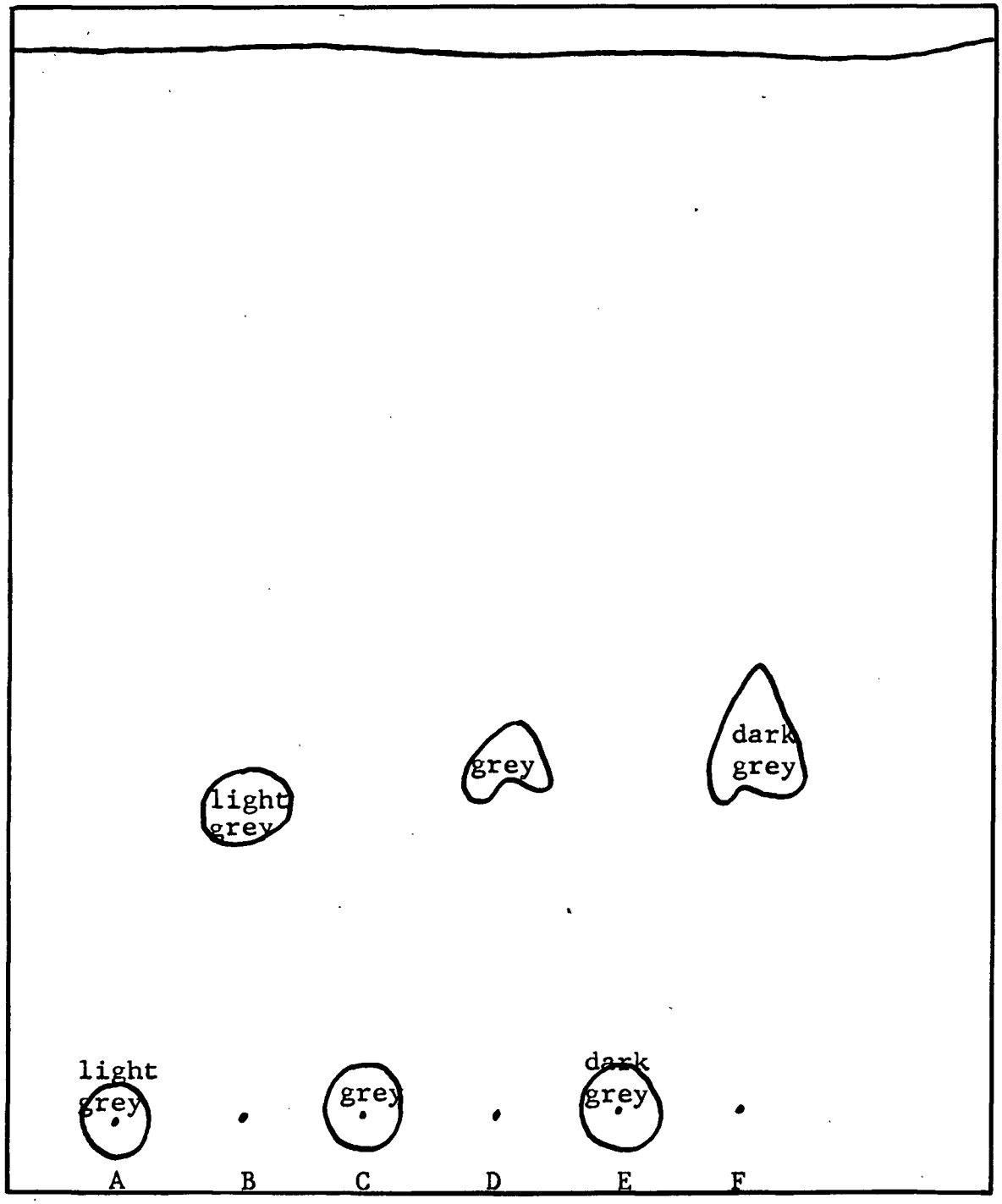


Fig. 11. Chromatoplate to Determine the Developed Position of Isosorbide and Isosorbide Dinitrate.

A, C and E: 50λ, 100λ and 150λ of a 0.04M isosorbide solution, respectively.

B, D and F: 50λ, 100λ and 150λ of a 0.04M isosorbide dinitrate solution, respectively.

The plate was irrigated with solvent F, sprayed with reagent IV and heated strongly.

atom cleavage occurred with the alcoholic solvent but would not occur with benzene. The yellow colorations in the benzene solutions, however, were much less intense than for the ethanolic solution. When the solutions, as well as suitable standards, were spotted on two chromatoplates having plaster of paris samples differing in their "hardness" after drying, and developed, the R_f values (see Tables XVIII and XIX) were found to be slightly higher on both plates for the ethanol solution. The values, however, for all the solutions were sufficiently close to indicate that the same materials were present in the three solutions.

Solutions Spotted	R_f Values				
Irradiated ethanolic mixture solution	0.115	0.244	0.495	0.690	0.715
Irradiated benzene mixture solution	0.091	0.226	0.461	0.660	0.687
Irradiated benzene mixture solution	0.084	0.212	0.455	0.655	0.671
2-nitrodiphenylamine				0.673	
4-nitrodiphenylamine		0.273			
p-nitrosodiphenylamine	0.182				
N-nitrosodiphenylamine			0.574		

Table XVIII. "Hard Set" Chromatoplate Spotted with Irradiated and Standard Solutions.
The ethanolic and benzene solutions, 0.02 M in both isosorbide dinitrate and diphenylamine, were irradiated for 2 hours. The plate was irrigated with solvent F, sprayed with reagent IV and heated.

Solutions Spotted	R_f Values				
	(top of spot)				
Irradiated ethanolic mixture solution	0.083	0.135	0.288	0.516	0.559
Irradiated benzene mixture solution	0.041	0.101	0.266	0.486	0.544
Irradiated benzene mixture solution	0.047	0.111	0.279	0.491	0.548
2-nitrodiphenylamine				0.520	
4-nitrodiphenylamine		0.155			
p-nitrosodiphenylamine	0.042				
N-nitrosodiphenylamine			0.359		

Table XIX. "Soft Set" Chromatoplate Spotted with Irradiated and Standard Solutions.

The ethanolic and benzene solutions, 0.02 M in both isosorbide dinitrate and diphenylamine, were irradiated for 2 hours. The plate was irrigated with solvent F, sprayed with reagent IV and heated.

Reference to tables of bond energies (71) indicated that hydrogen atom cleavage in benzene was as energetically favored as hydrogen atom cleavage in ethanol, the C-H bond energy being 100.7 kcals/mole. Thus, the production of isosorbide from isosorbide dinitrate appears likely in both benzene and ethanol irradiation solutions. The important point to consider, however, is not the possibility of hydrogen atom loss from the benzene but the fate of the phenyl radical so formed. Considerable work has been done with phenyl radicals (72) (73) (74) and in all cases one of the products formed from the reactions was diphenyl or a diphenyl derivative, usually in low concentration. If diphenyl were formed in the irradiation reactions and the solutions were spotted, the diphenyl would be carried with the

solvent front by either of the two most commonly used solvents (F and L) and quite possibly would not be detected by the nitric-sulphuric acid spray reagent.

Because of the lack of conclusive evidence for the mechanism of the isosorbide dinitrate photolytic decomposition, spot tests were carried out for nitrite and nitrate ions on aliquots of a 2-hour irradiated ethanolic solution, originally 0.02 M in both diphenylamine and isosorbide dinitrate. These tests involved nitron salts (75), diphenylamine oxidations (76) and diazotizations and couplings (77). The tests were inconclusive, however, because whenever a positive test was obtained for the irradiated diphenylamine-isosorbide dinitrate solution, a positive test was also obtained for a non-irradiated diphenylamine-isosorbide dinitrate solution.

The fact that diphenylamine and ionic nitrate (8) (9) (10) and diphenylamine and covalent nitrate, under the influence of short-wave ultraviolet light, both yield 2-nitro- and 4-nitro-diphenylamine is somewhat surprising. If the process is a free-radical one, as suspected from the phloroglucinol- and diphenylamine-isosorbide dinitrate work, it is difficult to see how ionic nitrate can be dissociated into nitrogen dioxide. Nitrate ion, however, can be reduced to nitrite ion by ultraviolet light of wavelengths below 2650 A and about 3000 A (9), perhaps under these same conditions nitrite ion can be converted

into nitrogen dioxide.

The actual mechanism whereby the two derivatives of diphenylamine are formed is unknown, although several pathways are suggested:

(a) N-nitrosation of diphenylamine, followed by a Fischer-Hepp rearrangement to a C-nitroso-derivative (68) and oxidation to C-nitro compounds,

(b) direct N-nitration of diphenylamine (78) (79), followed by rearrangement to the o- and p- derivatives (80), as has been observed for nitro derivatives of aniline,

(c) direct ring nitration of diphenylamine as has been observed for diphenylamine (81), benzene (82) and anthracene derivatives (83).

SUGGESTIONS FOR FURTHER WORK

1. Repeat the quantitative irradiation experiments discussed in this thesis, with aromatic compounds and isosorbide dinitrate, on a larger scale so as to obtain a sufficient quantity of product for analysis.
2. Investigate the photolytic cleavage of the ONO_2 group and establish unconditionally whether or not the cleavage is homolytic.
3. Determine the decomposition product of irradiated isosorbide dinitrate.
4. Determine whether or not a Fischer-Hepp rearrangement will occur on silicic acid, using N-nitrosodiphenylamine as substrate.

Appendix 1

INFRARED SPECTRA

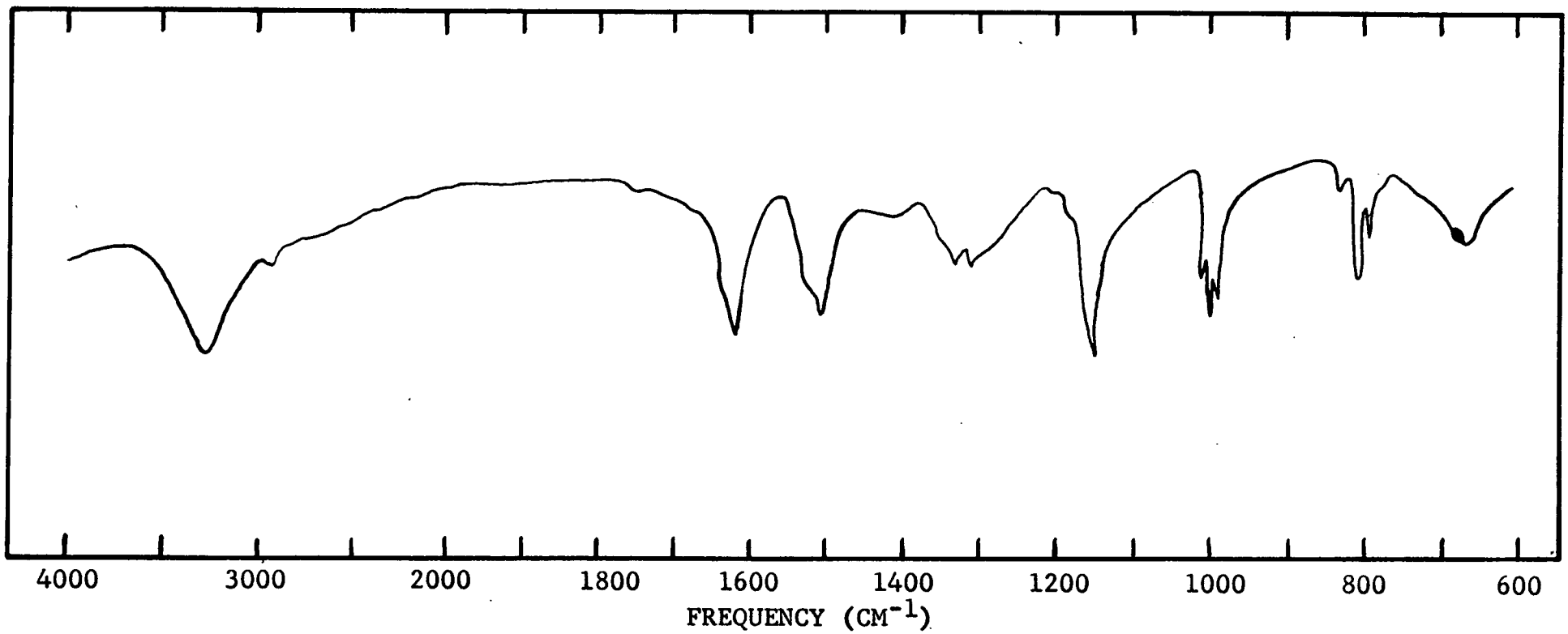


Fig. 12. Infrared Spectrum of Phloroglucinol.

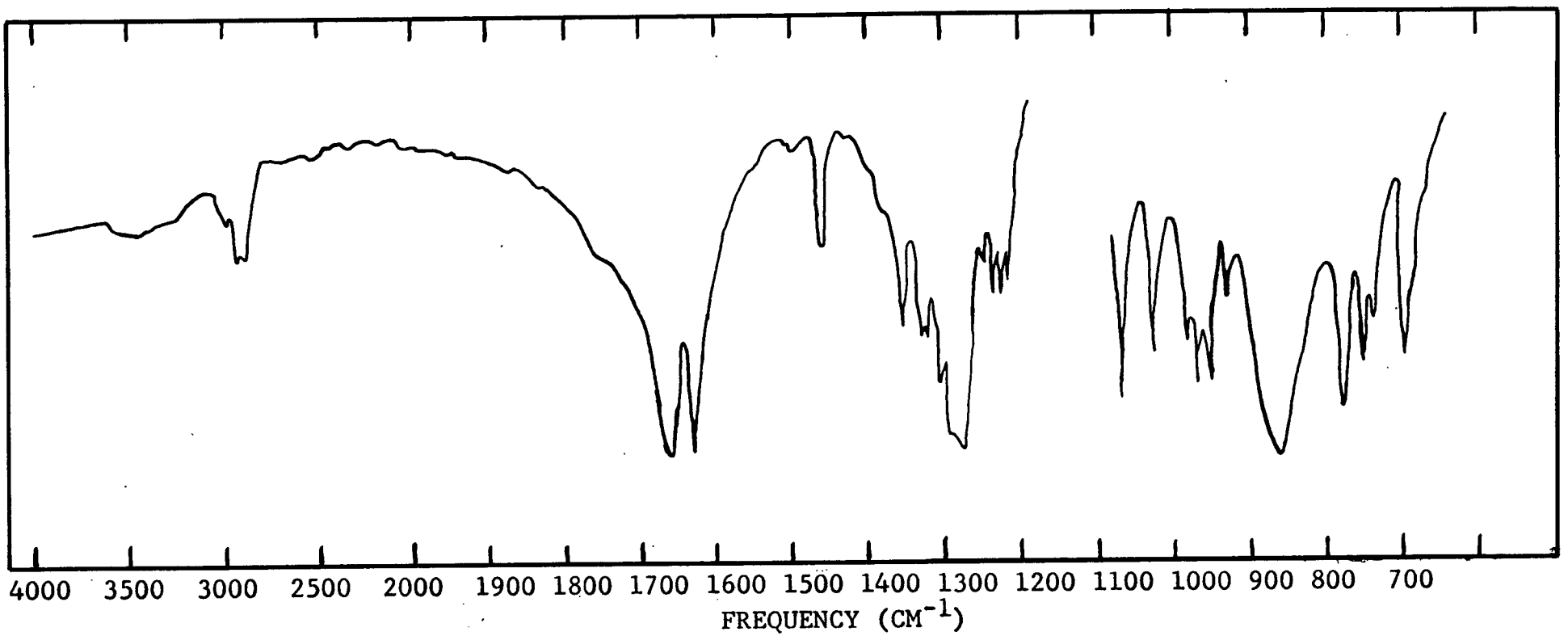


Fig. 13. Infrared Spectrum of Isosorbide Dinitrate.

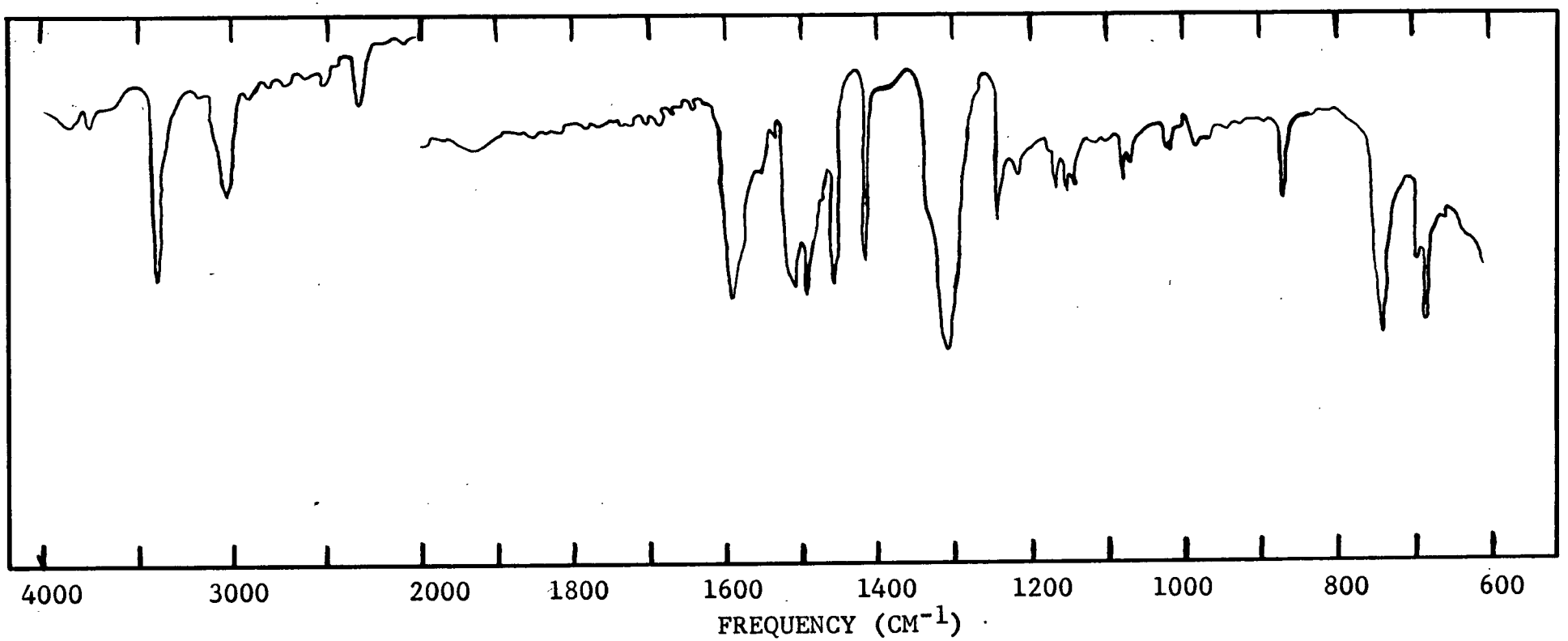


Fig. 14. Infrared Spectrum of Diphenylamine.

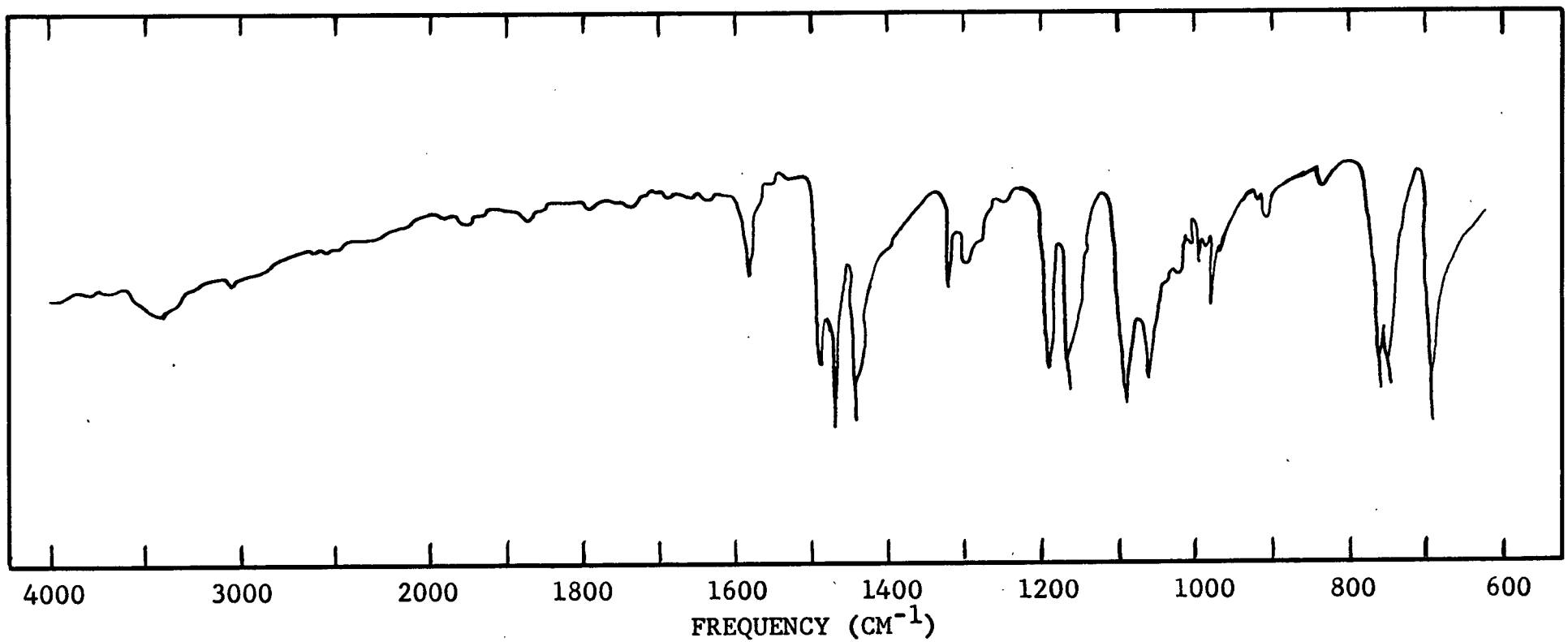


Fig. 15. Infrared Spectrum of N-nitrosodiphenylamine (chromatobar purification).

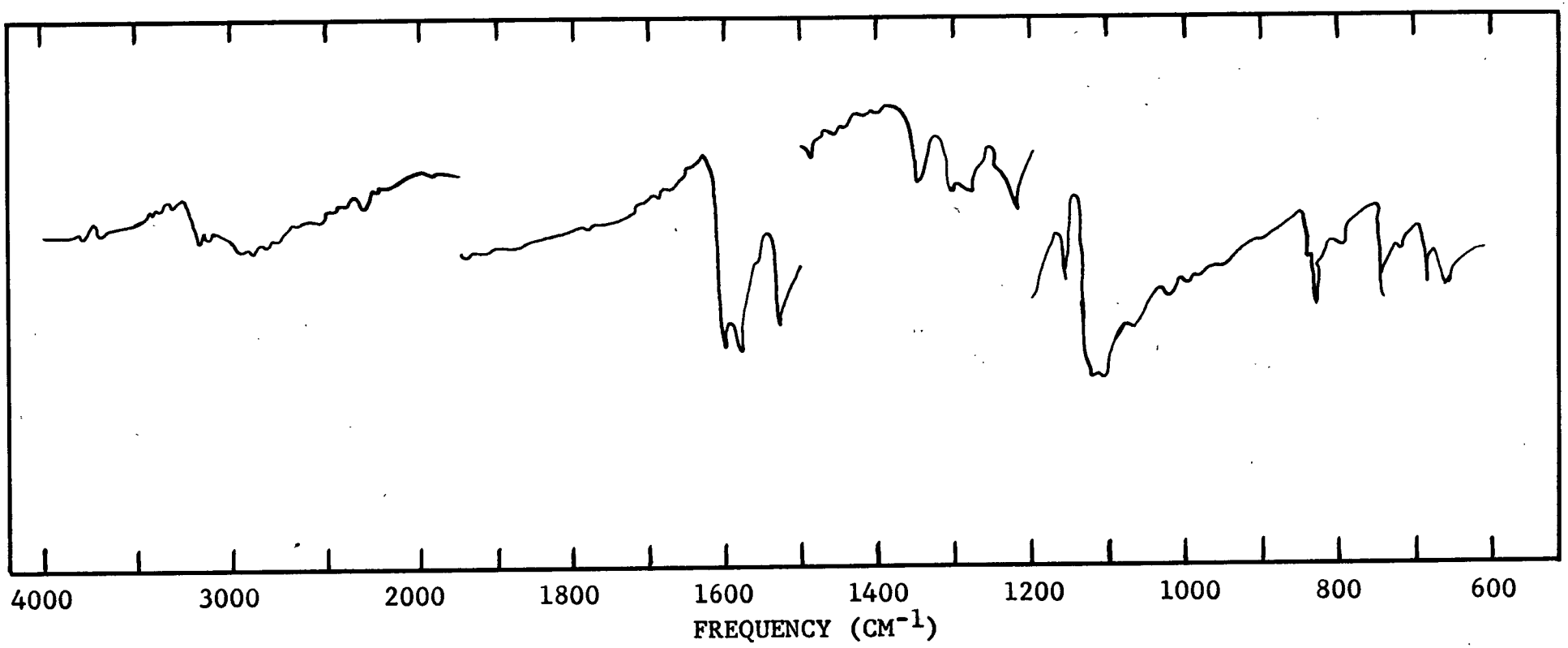


Fig. 16. Infrared Spectrum of p-nitrosodiphenylamine (vacuum sublimation purification).

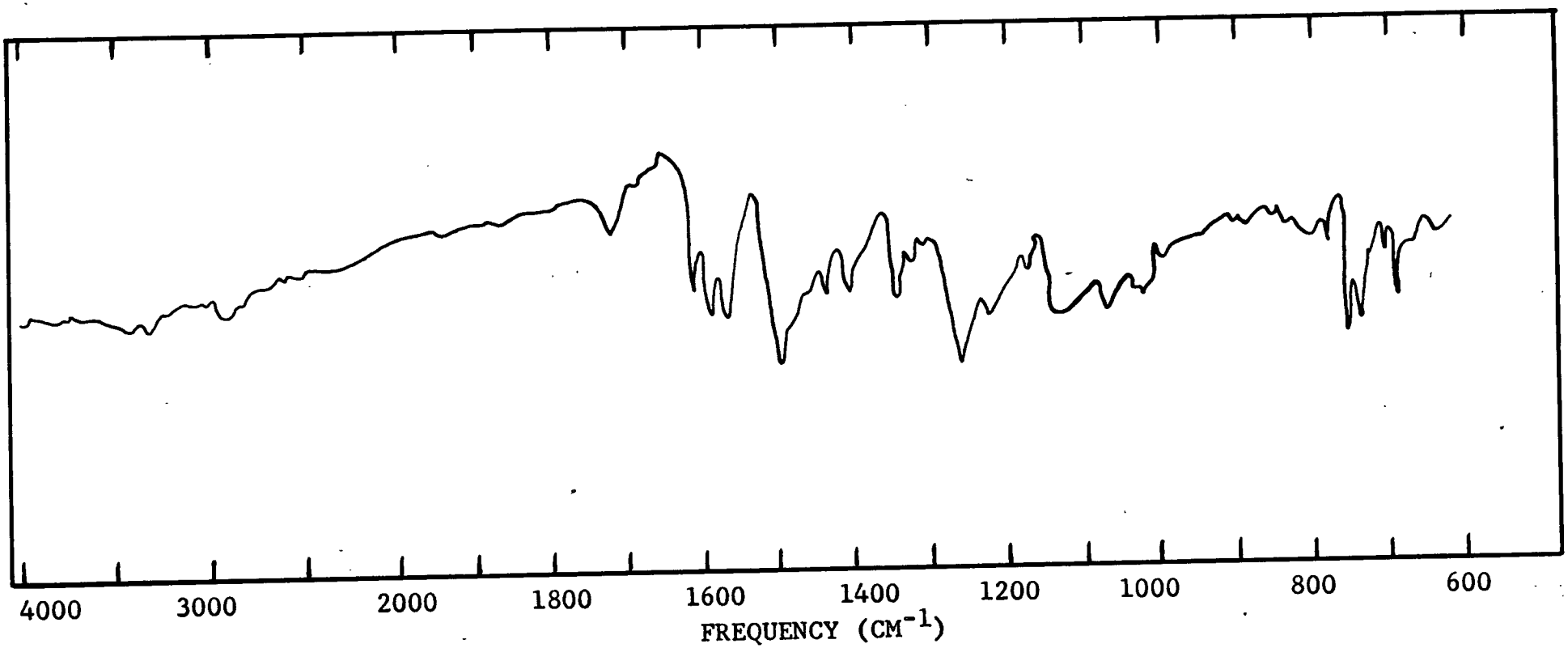


Fig. 17. Infrared Spectrum of 2-nitrodiphenylamine (chromatobar purification).

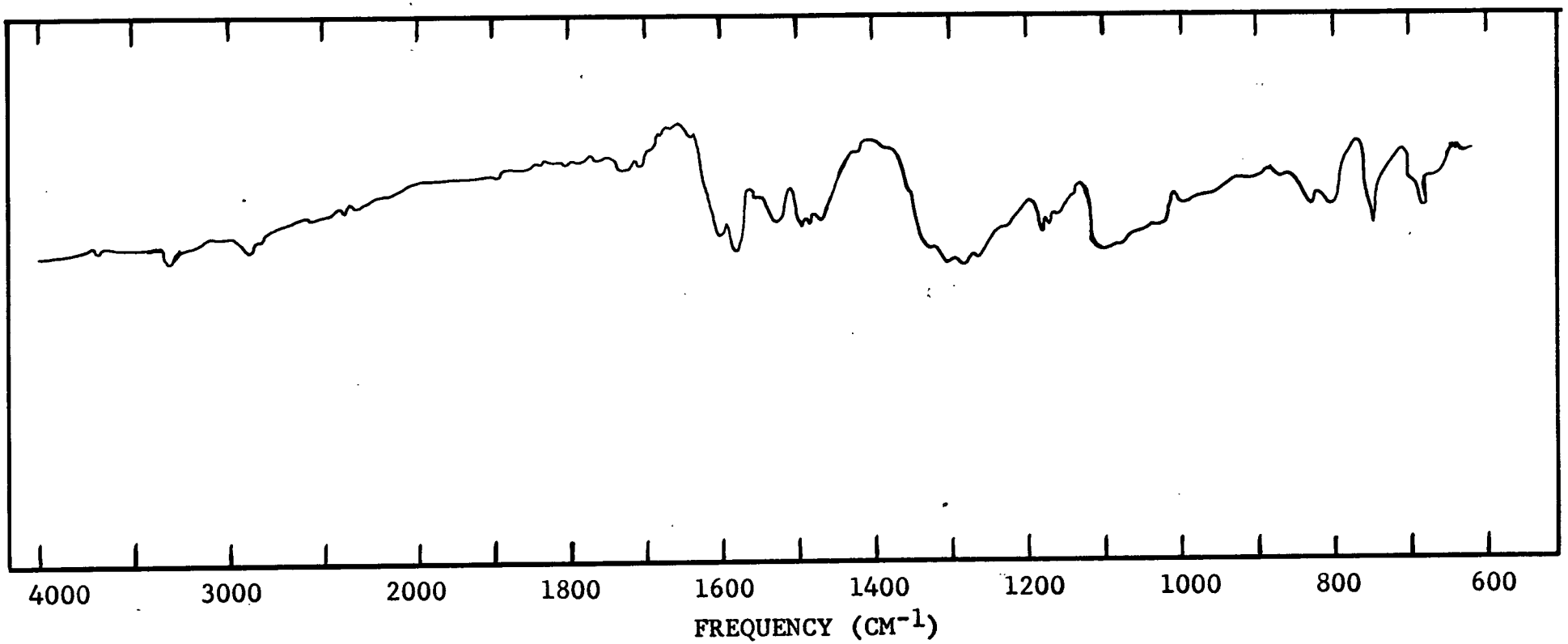


Fig. 18. Infrared Spectrum of 4-nitrodiphenylamine (chromatobar purification).

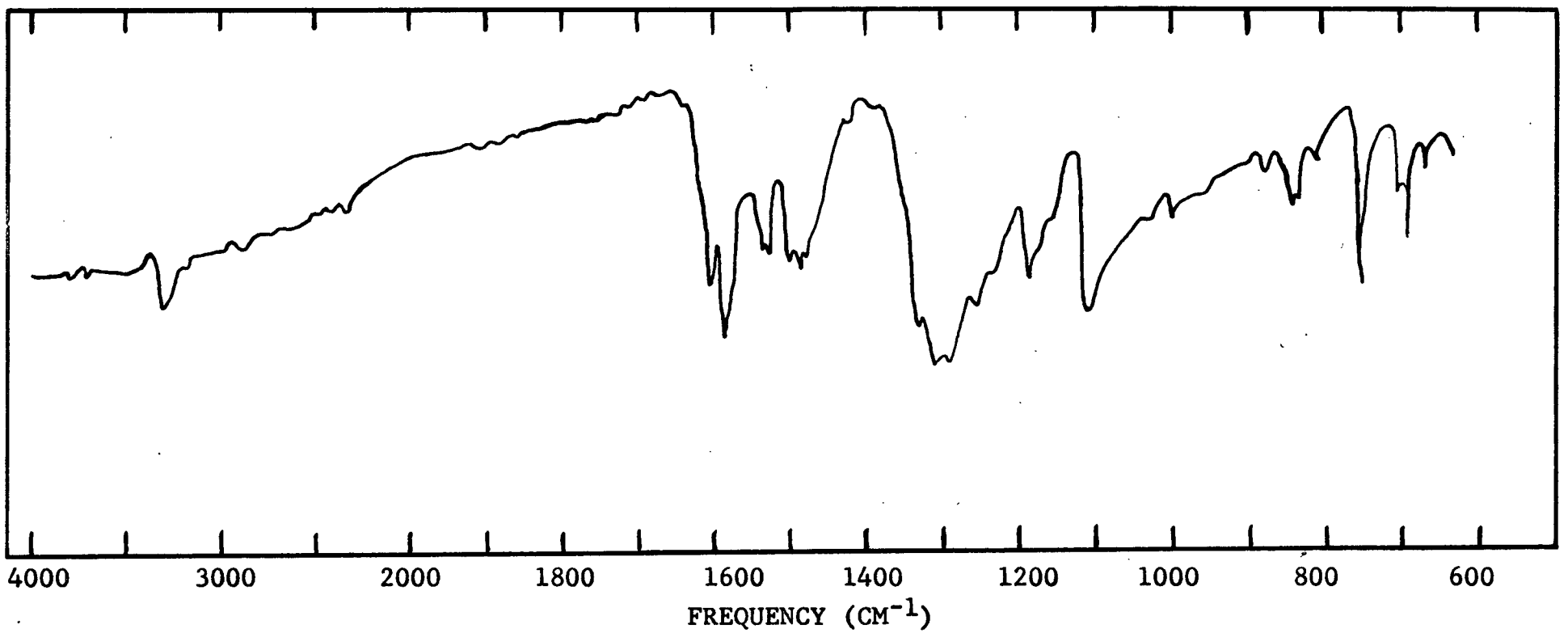


Fig. 19. Infrared Spectrum of 4-nitrodiphenylamine (recrystallized from glacial acetic acid).

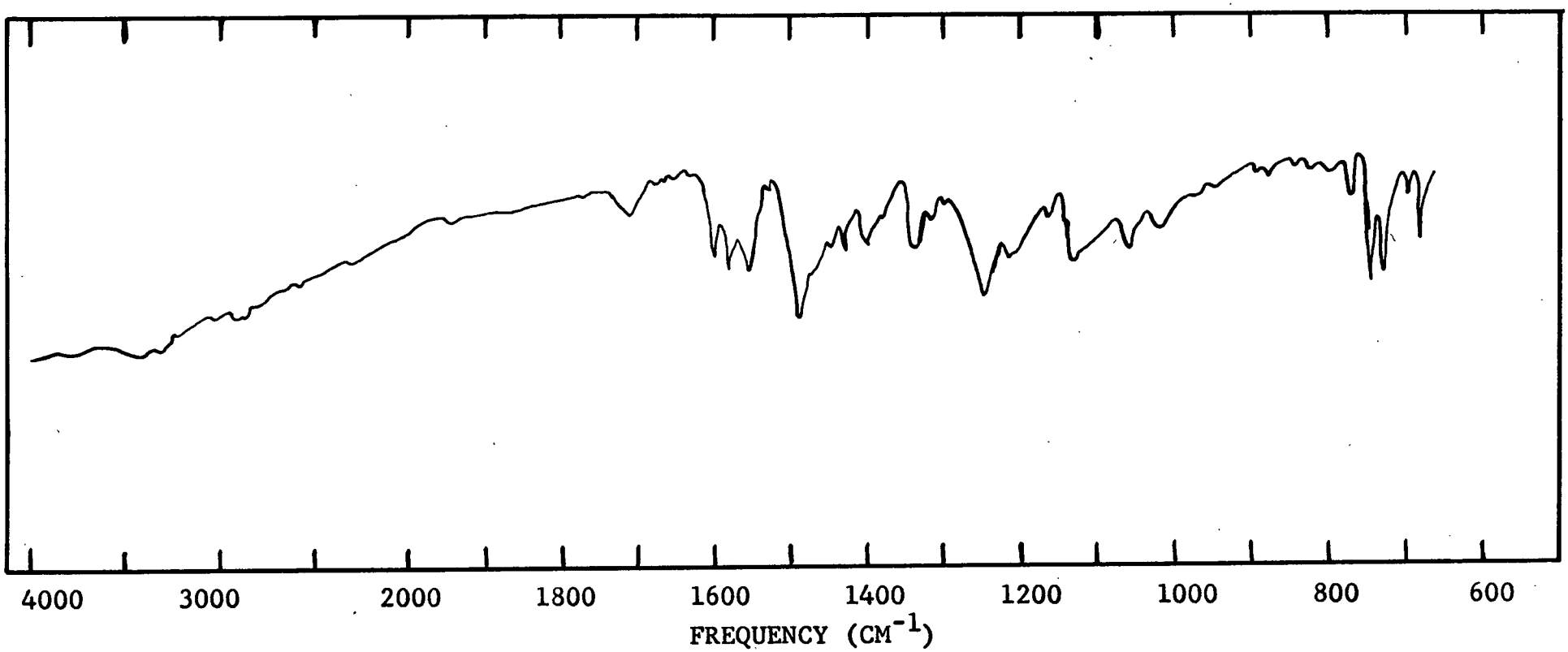


Fig. 20. Infrared Spectrum of the 2-nitrodiphenylamine Product from the Photolysis.

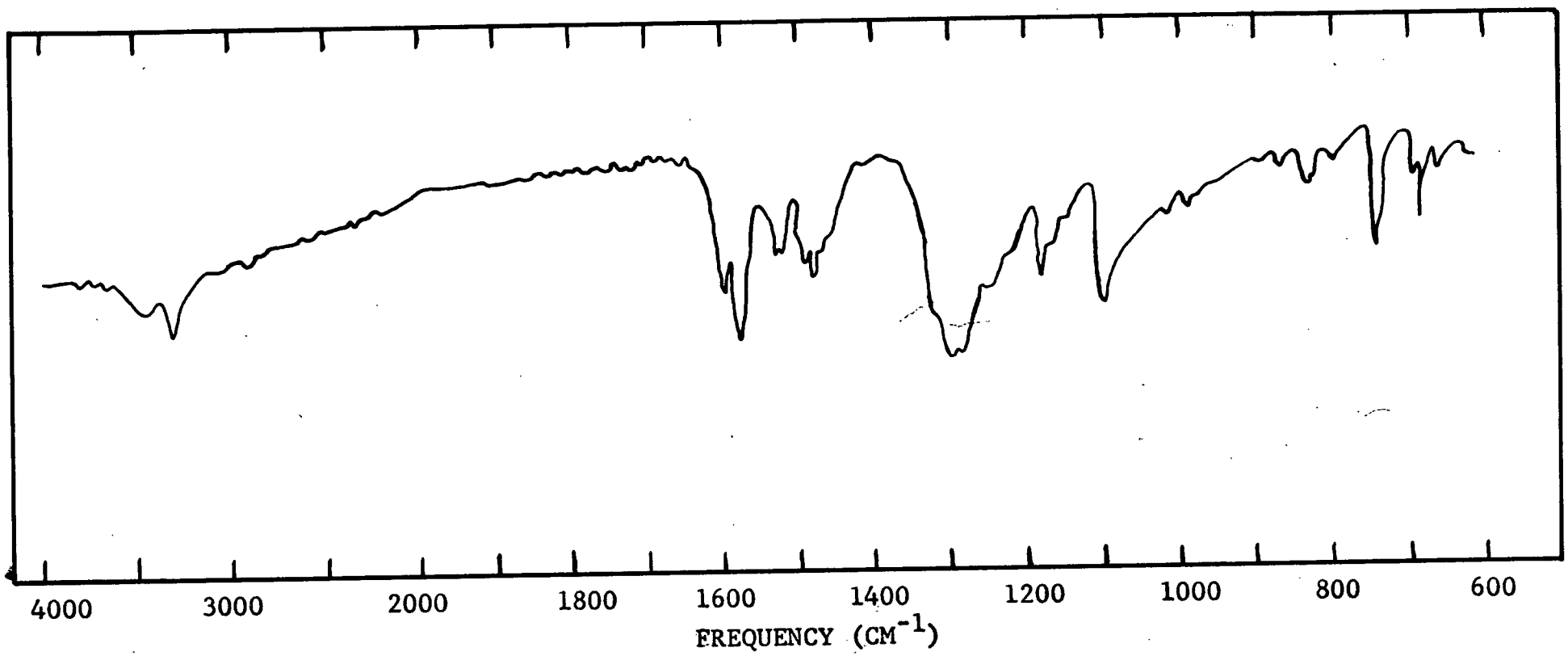


Fig. 21. Infrared Spectrum of the 4-nitrodiphenylamine Product from the Photolysis.

Appendix 2

ULTRAVIOLET SPECTRA

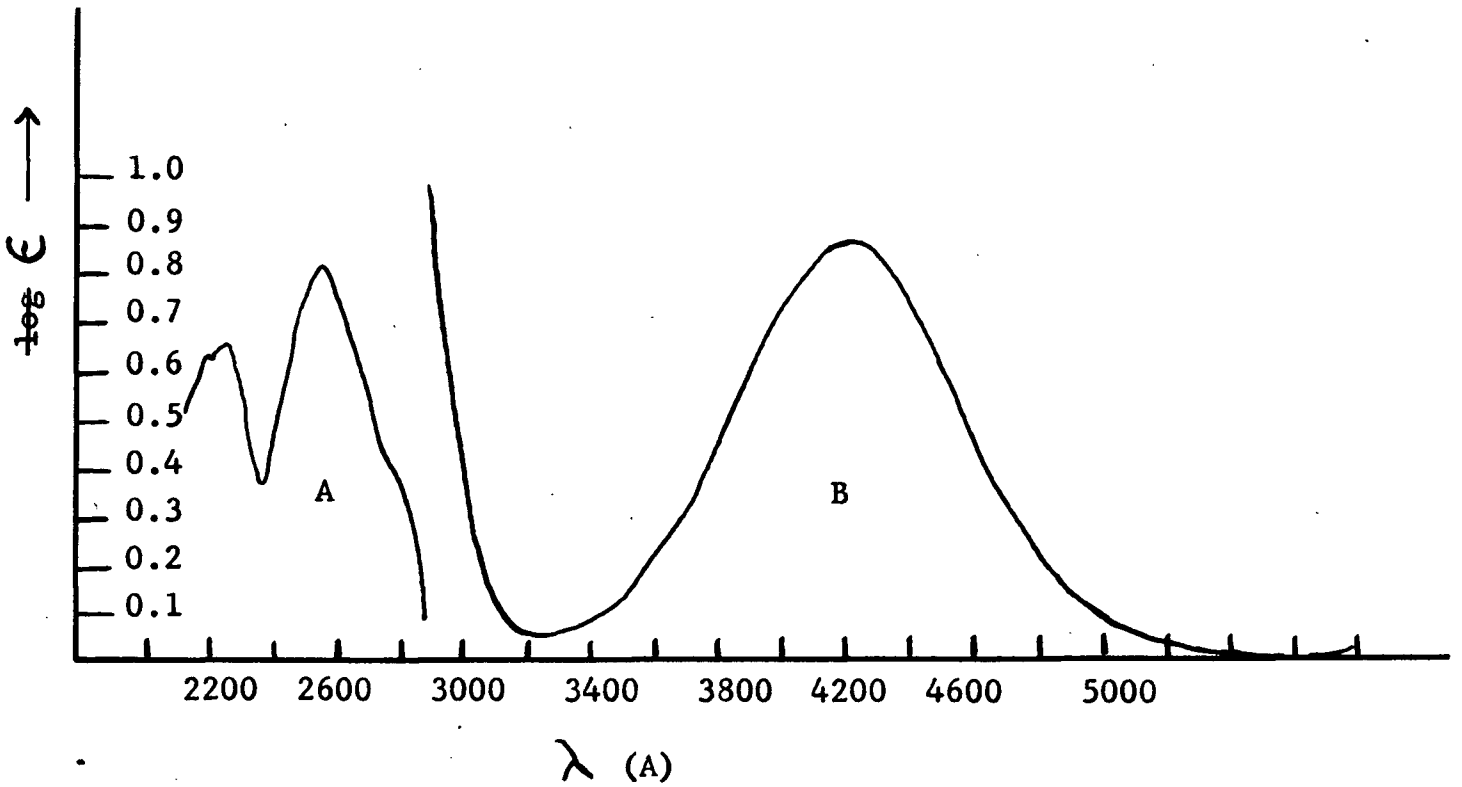


Fig. 22. Ultraviolet Spectrum of the 2-nitrodiphenylamine Product from the Photolysis.

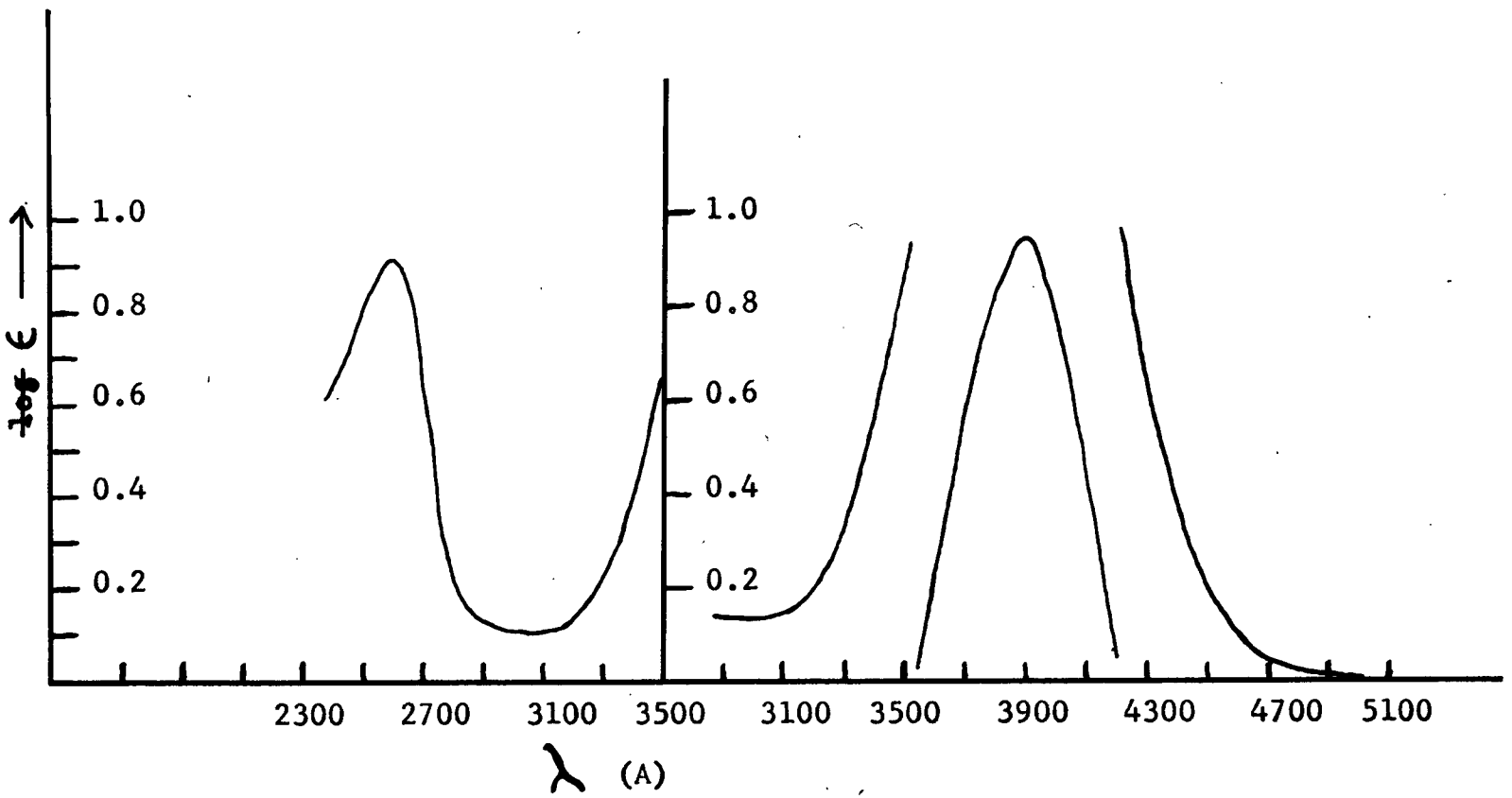


Fig. 23. Ultraviolet Spectrum of the 4-nitrodiphenylamine Product from the Photolysis.

Appendix 3

ELECTRON-SPIN RESONANCE SPECTRA

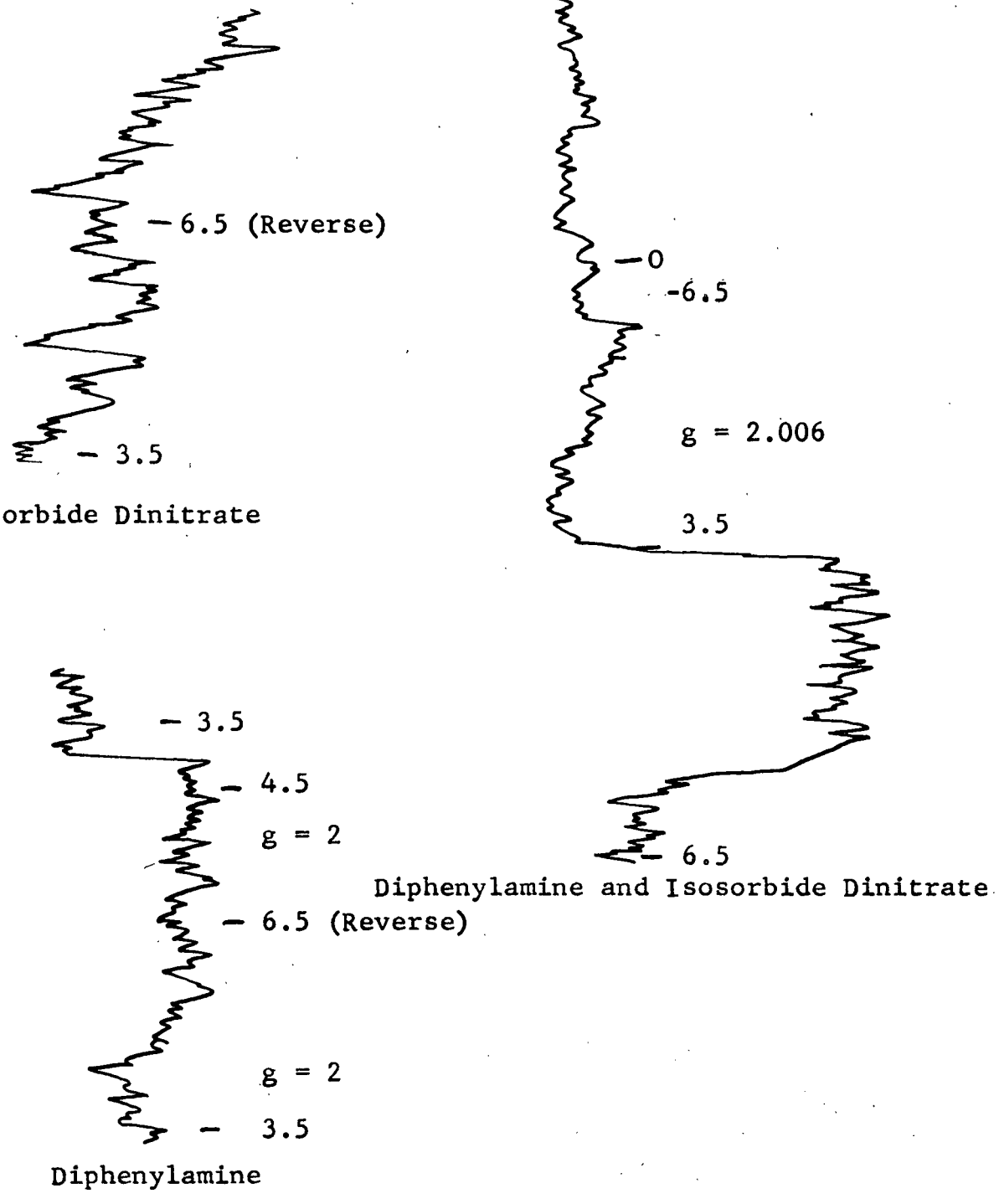


Fig. 24. Electron-Spin Resonance Spectra of Irradiated Diphenylamine, Isosorbide Dinitrate and Diphenylamine-Isosorbide Dinitrate Solutions.

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