

THE IDENTIFICATION OF POLY-NITRO AROMATIC COMPOUNDS BY
THEIR NAPHTHALENE ADDITION COMPOUNDS

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THE IDENTIFICATION OF POLYNITRO AROMATIC COMPOUNDS BY
THEIR NAPHTHALENE ADDITION COMPOUNDS

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TABLE OF CONTENTS

	Page
Introduction	1
Historical Review	3
Experimental	9
Discussion of Results	19
Summary	23
Bibliography	24
Autobiography	29

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INTRODUCTION

The identification of polynitro compounds generally involves a special treatment of the individual compound. Ordinarily the preparation of a derivative includes; reduction of a nitro group to an amino group, further nitration of the compound, or oxidation of a side-chain to form an acid derivative. In the process of reduction it is difficult to predict which nitro group will be reduced and to be certain that no polyamines are formed, which are not satisfactory as derivatives without further treatment. With fully nitrated compounds, obviously further nitration is not possible; while in the case of compounds which may be nitrated further, considerable difficulty is often encountered in separation and crystallization of their derivatives. When a compound possessing a side-chain is oxidized, the acid formed does not distinguish the nature of the side-chain present in the original compound.

Since a considerable number of polynitro aromatic compounds have been found to form addition compounds with naphthalene, and since picric acid, styphnic acid, and *symm.*-trinitrobenzene have been so valuable in the separation and identification of the condensed ring hydrocarbons of coal-tar, it seemed worthwhile to use naphthalene as a means of forming derivatives for polynitro aromatic compounds. This method has the unusual advantages that the compound can usually be recovered by removing naphthalene by steam distillation or by recrystallization after the derivative is prepared. The method is extraordinarily simple and requires little time, it yields a derivative of extra high purity because side reactions are exceedingly rare, and no costly reagents are necessary for its manipulation. Indeed, naphthalene is one of the commonest and most nearly pure reagents among organic chemicals.

Such polynitro compounds were chosen for study as are commercially available and therefore presumable in need of derivatives, or of importance in application to the theories of the structure of molecular compounds.

HISTORICAL

The formation of molecular compounds is quite common among certain types of organic compounds. The familiar types of compounds giving molecular addition are: nitro compounds, phenols, amines, quinones, and hydrocarbons.

Probably the most familiar are the picrates, the first of which were prepared by Fritzsche in 1859 (35), at which time he prepared the addition compound naphthalene-picric acid. Since Fritzsche's work many workers have attempted to prepare addition compounds of naphthalene and aromatic polynitro compounds, many of the nitro compounds giving addition complexes.

The literature dealing with the molecular complexes formed from aromatic nitro compounds and aromatic hydrocarbons may be divided into two classes. The great majority of investigators have followed Fritzsche's original example in which he described merely the preparation and properties of naphthalene "picrate"; in this way information has accumulated on the colors and melting points of a considerable number of such derivatives, with a few references to the failure of certain substances to enter combination. Since Fritzsche's original work, various methods have been used for proving compound formation. These methods have been described by Rheinboldt (66). The two most common methods used have been the isolation from solution and thermal analysis. Other less common procedures have been based on studies of: heat of combustion, viscosity, optical activity, magnetic susceptibility, and vapor pressure.

Tables I and II include the results of compiling data on the behavior of naphthalene in these respects; Table I shows the properties of

addition compounds of naphthalene with aromatic nitro compounds, while Table II lists the nitro compounds which have failed to give addition compounds with naphthalene.

TABLE I

Aromatic Polynitro Cpd.	M. P. (F.P. method) °C.	M. P. (Isolation) °C.
Dinitroabietic acid	110-17 (1)	
2,4,6-Trinitroaniline	168.8 (3)	168-9 (2)
symm.-Trichlorotrinitrobenzene	130 (50)	
2,4,6,2',4',6'-Hexanitroazobenzene		165.4 (4)
p-Dinitrobenzene		118-9 (5) (6) (7), 110-17 (8) (9)
m-Dinitrobenzene	51.2 (10) (11) (12) (13), 50.8 (15)	52-3 (5) (6), 50.7-51.6 (14)
"4,5-Dinitroso-1,3-dinitrobenzene"		172 (16)
1,3,5-Trinitrobenzene	152.5 (17)	152 (5) (6) (8) (9), 152.5 (18)
2,4,6-Trinitroethylbenzene		58 (19)
1-tert.-Butyl-2,4,6-trinitrobenzene		89-90 (20)
1-Bromo-2,4-dinitrobenzene		72 (21)
1-Chloro-2,4-dinitrobenzene		78 (22), 76.8 (21)
1-Chloro-2,3-dinitrobenzene		51 (23)
4,6-Dichloro-1,3-dinitrobenzene	68 (24)	

TABLE I Continued

Aromatic Polynitro Cpd.	M. P. (F.P. method) °C.	M. P. (Isolation) °C.
1-Chloro-2,3,4-trinitrobenzene		112-3 (23)
1-Chloro-2,3,5-trinitrobenzene		95-6 (23)
1-Chloro-3,4,6-trinitrobenzene		108 (23)
1-Chloro-3,4,5-trinitrobenzene		110 (23)
3,5-Dinitrobenzoic acid		77-80 (25)
3,5-Dinitro-p-hydroxybenzoic acid		214-7 (26) (Closed tube)
3,5-Dinitrobenzotrile		123 (25)
3,5-Dinitrobenzoyl chloride		127 (25)
4,5,6-Trinitro-o-cresol		106 (27)
2,4,6-Trinitro-m-cresol	124.5 (29) (30)	126-7 (28)
1,3,6,8-Tetranitronaphthalene		191-2 (31) (32)
2,4,6-Trinitroorcinol		120 (28)
2,4-Dinitrophenol	91.7 (29) (30)	94.7-95 (5)
2,3,5-Trinitrophenol		100-1 (33)
2,4,5-Trinitrophenol		72-3 (33)
2,3,6-Trinitrophenol		100 (33)

TABLE I Continued

Aromatic Polynitro Cpd.	M. P. (F.P. method) °C.	M. P. (Isolation) °C.
Picric acid	147-149.5 (3)	149 (34) (35) (36) (37), 149.5 (30) (38) (39), 151.5 (40)
Picryl chloride	91.2 (41), 91-2 (3)	95-6 (2), 94 (23)
Styphnic acid	165.5 (3)	163.5 (28) (42), 168-9 (43)
5-Nitrobenzene-1,3-disulfonyl chloride		102-3 (44)
Tetryl	86.4 (45)	
2,5-Dinitrothiophene		50 (46)
2,4-Dinitrotoluene	60-1 (7), 59 (15)	60-1 (5) (6) (48), 60.1-60.9 (14)
3,5-Dinitrotoluene	63.2 (7)	
2,4,6-Trinitrotoluene	96.5 (15)	97-8 (5)
2,4,5-Trinitrotoluene		88-9 (5)
2,3,4-Trinitrotoluene		100 (5) (6)

TABLE II

Aromatic Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.
m-Nitroaniline	No cpd. (51)	
2,4-Dinitroaniline		No cpd. (21)
2,3,4,6-Tetranitroaniline		No cpd. (52)
Trinitromesitylene	No cpd. (50)	
o-Nitrophenol	No cpd. (29)	
2,4-Dinitrobenzotrile		No cpd. (25)
m-Nitrotoluene	No cpd. (53)	
p-Nitrotoluene	No cpd. (53)	
2,4,6-Trinitro-m-xylene	No cpd. (54)	

HISTORICAL Continued

The other type of research has dealt with the theory of molecular compound formation, particularly as to structure and stability. Only those compounds are discussed here which have been concerned with the theory of compound formation.

It is well known that these addition complexes are generally unstable. From studies of their solubilities, Dimroth (55) concluded that the chief factor controlling the possibility of isolating them from solution is the solubility ratio of the two components making up such compounds. Dimroth and Bamberger (55) tested these conclusions, and, through studies of the behavior of a series of hydrocarbons with picric acid, found the following relative order of increasing stability of the picrate: benzene, fluorene, anthracene, indene, phenanthrene, naphthalene, acenaphthene, 1-methylnaphthalene, 2-methylnaphthalene.

Behrend (56) showed that the solubility of anthracene in alcohol is increased by picric acid and found a dissociation constant for the complex of 4.7-5.7 at 25 °C, a value confirmed by Bamberger and Dimroth.

Moore, Shepherd, and Goodall (57) measured the effect of the presence of a number of substituted aromatic hydrocarbons and bases on the partition of picric acid between chloroform and water. In all cases an increase of the solubility of the picric acid in the chloroform was observed. These authors conclude that the increased solubility of the picric acid caused by the presence of aromatic substances is mainly due to chemical combination in the liquid phase and derive a series of equilibrium constants that give a stability series agreeing with that of Bamberger and Dimroth.

By means of calorimetric studies, Kremann and Grasser (58) found the following degrees of dissociation of the fused complexes of several nitro compounds with naphthalene: m-dinitrobenzene .93, p-dinitrobenzene .87, dinitrotoluene .86, dinitrophenol .58.

Vanzetti (59) determined the heat of formation of naphthalene "picrate" calorimetrically in ethyl alcohol and found a value of 1450 calories.

By means of E. M. F. studies of the system naphthalene-picric acid-KCl-HCl-H₂O, Bronsted (60) found the heat of formation of naphthalene "picrate" to be 2,050 calories. He also found that the compound becomes more stable with rising temperature.

Brown (61) found that the depression of the freezing-point of nitrobenzene by mixtures of naphthalene and picric acid could be interpreted to give a dissociation constant of 0.23 and a heat of formation of 2,080 calories, in good agreement with the value obtained by Bronsted.

Halban and Zimpelmann (62) used a photoelectric method to determine the degree of dissociation for several compounds, by measuring the extinction coefficients at various concentrations. They found the following dissociation constants: acenaphthene-trinitrobenzene in tetrachloroethane 0.497, acenaphthene-dinitrobenzene in tetrachloroethane 3.51, acenaphthene-picric acid in tetrachloroethane 0.524, anthracene-picric acid in chloroform 0.219.

Briegleb and Schachowski (63) employed a similar method to that of Halban and Zimpelmann and calculated the heats of dissociation from their results for trinitrobenzene-naphthalene in various solvents: in carbon tetrachloride 3.45, in ether 0.99, in benzene 1.90 Calories. According to these authors, in these compounds, one or more moments of

one molecule link to another by polarizing a susceptible group. They conclude that all the nitro groups take part in the linkage, and that the stability of the compound depends on the mean polarizability of the hydrocarbon.

Bennett and Willis (44) have made a series of structure studies and from that have arrived at certain generalizations concerning the stability of nitro compound-hydrocarbon complexes. They propose that attachment takes place at one nitro group and that any others present tend to reinforce the attached group. Thus, two electron attracting nitro groups increase the stability of the addition compound over that given by one nitro group. They further propose that any group which attracts electrons (any "electron sink"), such as the carbomethoxy or sulfonyl chloride groups, should be able to contribute to the stability of such complexes.

McDonald, Bennett, and Wain (25), after studying a series of substituted dinitrobenzenes with certain amines and hydrocarbons, outline three series of substituents, showing comparative tendencies to form complexes and arranged in order of diminishing tendency: (a) COCl , COOCH_3 , CONH_2 (b) SO_2Cl , SO_2CH_3 , SOCH_3 (c) NO_2 , CN , COOCH_3 .

Hammick and Hellicar (50) found from studying the freezing-point curves of naphthalene with trinitromesitylene and trinitrochlorobenzene that the methyl group hinders compound formation, while the chlorine atom tends to increase the stability of the nitro compound.

Buehler, Hisey, and Wood (21) studied a series of monosubstituted *m*-dinitrobenzenes in relation to compound formation with amines and hydrocarbons. From these studies they found the following relative order of influence on compound formation, the series being arranged in

order of decreasing ability to form molecular compounds: Cl, Br, OH, H, CH₃, NH₂.

Several theories have been proposed for explaining the manner of linkage in molecular compounds. Pfeiffer (64) contended that the constituents of the complex were held together by means of fields of residual valency of either molecules or groups of atoms; the linkage in polynitro complexes thus involves a nitro group and the entire aromatic ring.

According to Bennett and Willis (44) the fact that in practically every case the constituents of molecular complexes unite in stoichiometric proportions is evidence that no such indefinite theory as that of Pfeiffer's holds. These authors propose that compound formation between nitro compounds and hydrocarbons occurs between a single nitro group and one of the conjugated ethylene bonds in the hydrocarbon, and that the linkage is brought about by induced polarization of the hydrocarbon by the nitro compound.

Hammick and Sixsmith (65) observed that the compound of dimethyl-2,4,2',4'-tetranitrodiphenate with indene does not react readily with bromine, and concluded that in the complex the ethylenic bond in the hydrocarbon no longer exists in its ordinary form.

EXPERIMENTAL

The chemicals used are listed below together with their source, reference to method of preparation, and purity. All temperature readings are in degrees Centigrade.

AROMATIC POLY-NITRO COMPOUNDS

- 2,4-Dinitroacetanilide - Made by the author. (67)
- Acetanilide was nitrated with sulfuric acid-nitric acid mixture with cooling.
- M. P. 119-120°.
- 2,4-Dinitrodiethylaniline - Made by the author. (68)
- Diethylaniline was dissolved in two volumes of sulfuric acid and slowly added to three volumes of fuming nitric acid with cooling. After 1-2 hours, the mixture was poured into water, filtered, and recrystallized.
- M. P. 80°.
- 2,4-Dinitroanisole - Made by the author. (69)
- Made by dissolving anisole in sulfuric acid, adding to a well-cooled mixture of sulfuric acid and nitric acid, warming gently after two hours, and finally pouring into cold water.
- M. P. 87-88°.
- 3,5-Dinitroanisole - Made by Dr. O. C. Dermer. (98)
- M. P. 105-105.5°.

- 2,4,6-Trinitroanisole - Made by the author. (70)
Made by heating 2,4-dinitroanisole for a short time with sulfuric acid and nitric acid.
M. P. 53-55°.
- 2,4-Dinitrobenzaldehyde - Chem. 620, student preparation. (71)
M. P. 68-69°.
- 2,4,6-Trinitrobenzaldehyde - Eastman Kodak Company product.
M. P. 119°.
- 3,5-Dichloronitrobenzene - Made by the author. (72)
Made from p-nitroaniline in two steps.
1. p-Nitroaniline was chlorinated, using HCl and KClO₃.
2. This product was suspended in ethyl alcohol and diazotized with sulfuric acid and sodium nitrite. This step removed the amino group. The temperature was kept below 50° during the diazotization.
M. P. 65°.
- o-Dinitrobenzene - Eastman Kodak Company product.
M. P. 117-118°.
- m-Dinitrobenzene - Eastman Kodak Company product.
M. P. 89.5°.
- m-Nitronitrosobenzene - Made by the author. (73)
Prepared by reducing m-dinitrobenzene with zinc dust in ethyl alcohol,

oxidizing the reduced group back to the nitroso group with ferric chloride, and finally steam distilling out the product.

M. P. 85°.

- 1-tert-Butyl-3,5-dimethyl-
2,4,6-trinitrobenzene - Eastman Kodak Company product.
M. P. 105-107°.
- 1-Chloro-2,4-dinitrobenzene - Eastman Kodak Company product.
M. P. 51°.
- 1-Iodo-2,4-dinitrobenzene - Made by Dr. O. G. Dermer. (99)
87-88°.
- 3,5-Dinitrobenzoic acid - Eastman Kodak Company product.
M. P. 204-205°.
- Isoamyl-3,5-dinitrobenzoate - Chem. 620, student preparation. (100)
M. P. 62°.
- 2,4,6-Trinitrobenzoic acid - Eastman Kodak Company product.
M. P. 220° (decomp.)
- 2,4,2',4'-Tetranitrobibenzyl - Made by the author. (74)
Made by adding bibenzyl to 10 times its weight of fuming nitric acid at 15°, allowing to stand at room temp. for one hour, and finally pouring into ice-water.
M. P. 170-171°.
- 2,2'-Dinitrobiphenyl - Chem 620, student preparation. (75)
M. P. 123-124°.

- 3,3'-Dinitrobiphenyl - Chem. 620, student preparation. (76)
M. P. 197-198°.
- 4,4'-Dinitrobiphenyl - Chem. 620, student preparation. (77)
M. P. 232-233°.
- 2,4,2',4'-Tetranitrobiphenyl - Made by the author. (78)
Prepared by allowing biphenyl to react with 90 percent nitric acid in the presence of an equal volume of sulfuric acid.
M. P. 165-166°.
- 4,6-Dinitro-o-cresol - Made by the author. (79)
Warmed o-cresol with 1.5 times its weight of sulfuric acid, diluted with water, added 2.5 times its weight of nitric acid, gradually brought to boiling and poured into water.
M. P. 85-86°.
- 2,4-Dinitrodiphenylamine - Chem. 620, student preparation. (80)
M. P. 156-157°.
- 2,4,6,2',4',6'-Hexanitrodiphenylamine - Eastman Kodak Company product.
M. P. 244-246°.
- 2,4-Dinitrodiphenyl ether - Chem. 620, student preparation. (81)
M. P. 70°.

- 2,4,2',4'-Tetranitro-
diphenylmethane - Made by Dr. O. C. Dermer. (83)
M. P. 171-172°.
- 3,5-Dinitroguaiacol - Made by the author. (84)
A mixture of nitric acid and acetic acid (1:4) was added to guaiacol dissolved in chloroform (1:10). The chloroform was evaporated off and the remaining mixture poured into water.
M. P. 122°.
- 2,6-Dinitrohydroquinone - Made by Dr. O. C. Dermer. (101)
M. P. 135°.
- 2,6-Dinitrohydroquinone-
4-acetate - Chem. 620, student preparation. (85)
M. P. 95-96°.
- 2,4-Dinitromesitylene - Made by the author. (86)
Mesitylene was dropped into conc. nitric acid and heated persistently. The mixture was poured into water.
M. P. 85-86°.
- 1,8-Dinitronaphthalene - Made by the author. (87)
Made by nitrating 1-nitronaphthalene with a mixture of nitric acid and sulfuric acid with heating. By cooling the mixture, fractional precipitation occurred. The 1,5 product

- separated out and the 1,3 product was obtained by pouring into water and filtering.
- M. P. 170-172^o.
- 1,3,8-Trinitronaphthalene - Eastman Kodak Company product.
- M. P. 218-219^o.
- 2,4-Dinitro-1-naphthol - Made by the author. (68)
- Made by nitrosating 1-naphthol with sulfuric acid and sodium nitrite, finally heating the mixture with nitric acid and potassium nitrate.
- M. P. 137-138^o.
- 2,4-Dinitroorcinol - Chem. 620, student preparation. (69)
- M. P. 164-165^o.
- 2,4-Dinitrophenetole - Made by the author. (69)
- Made by using the same procedure as in the preparation of 2,4-dinitroanisole.
- M. P. 87-88^o.
- 2,6-Dinitrophenol - Eastman Kodak Company product.
- M. P. 64^o.
- 2,4,6-Trinitrophenetole - Made by the author. (70)
- Made by using the same procedure as in the preparation of 2,4,6-trinitroanisole.
- M. P. 78-79^o.

- 2,4-Dinitro-6-cyclohexyl-phenol - Made by the author. (69)
Prepared from o-cyclohexylphenol with the same procedure as in the preparation of 2,4-dinitroanisole.
M. P. 105-106°.
- 3-Chloro-2,4,6-Trinitrophenol - Made by Dr. O. C. Dermer. (102)
M. P. 114°.
- 2,3,4,6-Tetranitrophenol - Made by Dr. O. C. Dermer. (90)
M. P. 139-140°.
- 2,4-Dinitrophenylacetic acid - Made by the author. (91)
Prepared by treating phenylacetic acid with a mixture of conc. sulfuric acid and fuming nitric acid.
M. P. 179-80°.
- 2,4-Dinitrophenylhydrazine - Eastman Kodak Company product.
M. P. 197-198°.
- Picramic acid - Chem. 620, student preparation. (92)
M. P. 168-169°.
- 2,4-Dinitroresorcinol - Made by the author. (93)
Prepared by treating 2,4-dinitrosoresorcinol with four-fold conc. nitric acid.
M. P. 147-148°.
- 2,4-Dinitrosoresorcinol - Chem. 620, student preparation. (93)
M. P. 162°.

- 3,5-Dinitrosalicylic acid - Made by the author. (94)
 Made by stirring salicylic acid for
 some time in cooled fuming nitric
 acid, pouring in water after 24 hrs.
 and filtering.
 M. P. 172-173°.
- 3,5-Dinitromethylsalicylate - Made by Dr. O. C. Dermer. (103)
 M. P. 127.5°.
- 2,4-Dinitro-1-naphthol-
 7-sulfonic acid - Eastman Kodak Company product.
 M. P. 148-150°.
- m-Nitrobenzene sulfonyl
 chloride - Chem. 620, student preparation. (95)
 M. P. 63°.
- 3,4,5-Trinitroveratrole - Made by Dr. O. C. Dermer. (No refer.)
 Made by straight nitration of
 veratrole.
 M. P. 144-145°.

OTHER REAGENTS

- Naphthalene - Resublimed and recrystallized. M. P. 80.2°.
- Ethyl alcohol - Absolute, commercial product.
- Methyl alcohol - Absolute, commercial product.
- Acetone - Commercial product.

APPARATUS

Apparatus used in the determination of cooling curves was a modification of that of Washburn (96). In place of a Dewar flask, three test tubes (1 cm. by 8 cm., 2 cm. by 11 cm., and 4 cm. by 14 cm.) were used. Each tube was fitted into the next larger with an ordinary cork stopper in such a way that a dead-air space separated each pair. The fusion mixture to be studied was placed in the inner tube. The thermometer was fitted with a cork of the proper size to fit the inner tube. Heat was furnished by a Fisher burner, the fusion bath resting upon an ordinary asbestos-centered wire gauze.

PROCEDURE

The procedure for the determination of freezing-point was a modification of that used by Baril and Hauber (97). Ten millimols each of naphthalene and the polynitro aromatic compound were weighed out into a porcelain crucible, in which the mixture was fused over a low flame until homogeneous. The cooled and crushed mass was then placed in the innermost of the three test tubes described above. The thermometer was inserted and the mass fused again, to a temperature 10 to 15 degrees above the fusion-point of the mixture, which had been approximately determined previously. Care was taken that the thermometer was kept completely immersed in the melt. The flame was now adjusted so that the melt cooled at a rate of about one and one-half to two degrees per minute for temperatures above 100°C ., or one degree per minute for temperatures below 100° . By means of a stop-watch the temperature was read at intervals of one minute, care being taken that the melt was thoroughly stirred between each pair of readings. The stirring was accomplished by means of the thermometer, which was rotated with a

swirling motion against the sides of the test tube, without removing the soft cork stopper. Each set of cooling-curve data was checked at least twice. In most cases supercooling was not a problem; in some, however, it was necessary to keep a small amount of the melt sticking to the sides of the tube just above the liquid. When the freezing-point was reached, this small portion solidified before the main portion. By agitating the main portion of the melt with the thermometer, crystallization was induced by the solidified portion above the melt. The freezing-point data were plotted on graph paper, temperature as the ordinate and time as the abscissa. In the case of compound formation, the curve exhibits a horizontal flat portion persisting for several minutes parallel to the temperature axis. The thermometer was calibrated in the apparatus used with compounds of known purity: naphthalene, benzoic acid, picric acid, and diphenylamine. Capillary tube melting points were also run on several of the crushed and fused compounds with naphthalene. The values check very well with those obtained by other methods.

The method used for isolating the nitro compound-naphthalene complexes was the same as that employed by most workers before. The solid mass from the cooling curve method was dissolved in the least possible amount of absolute alcohol or other solvent by heating on the water bath. The compound was allowed to crystallize and was filtered out and allowed to dry in the air. The crystals were examined under the microscope for homogeneity and the melting point determined by the capillary method. Table III gives the results of the above methods applied to the compounds studied in this work. All temperature values shown in the table are corrected.

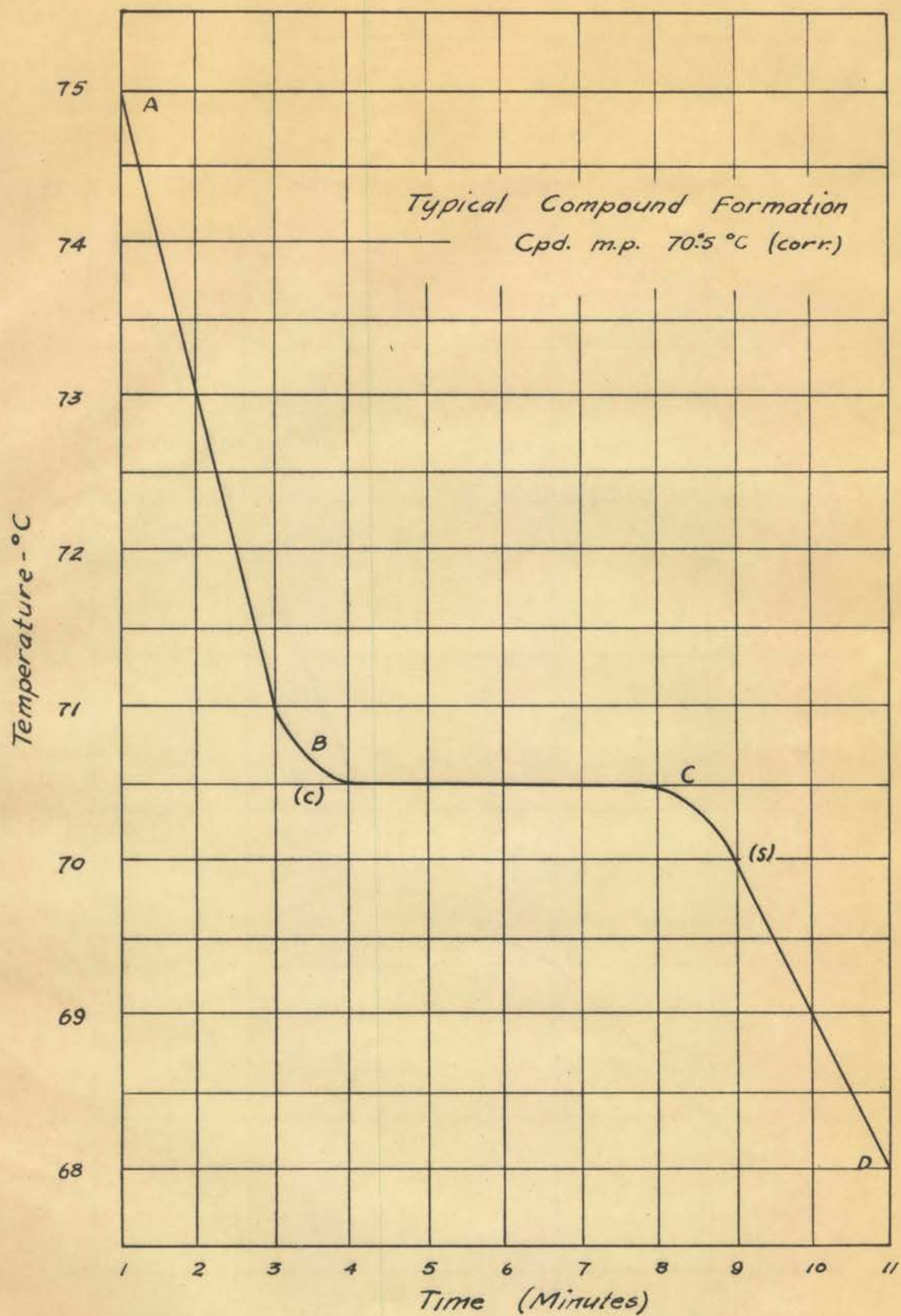


Figure I
 Freezing Point Curve
 2,4-Dinitro-6-cyclohexylphenol + Naphthalene (1-1)

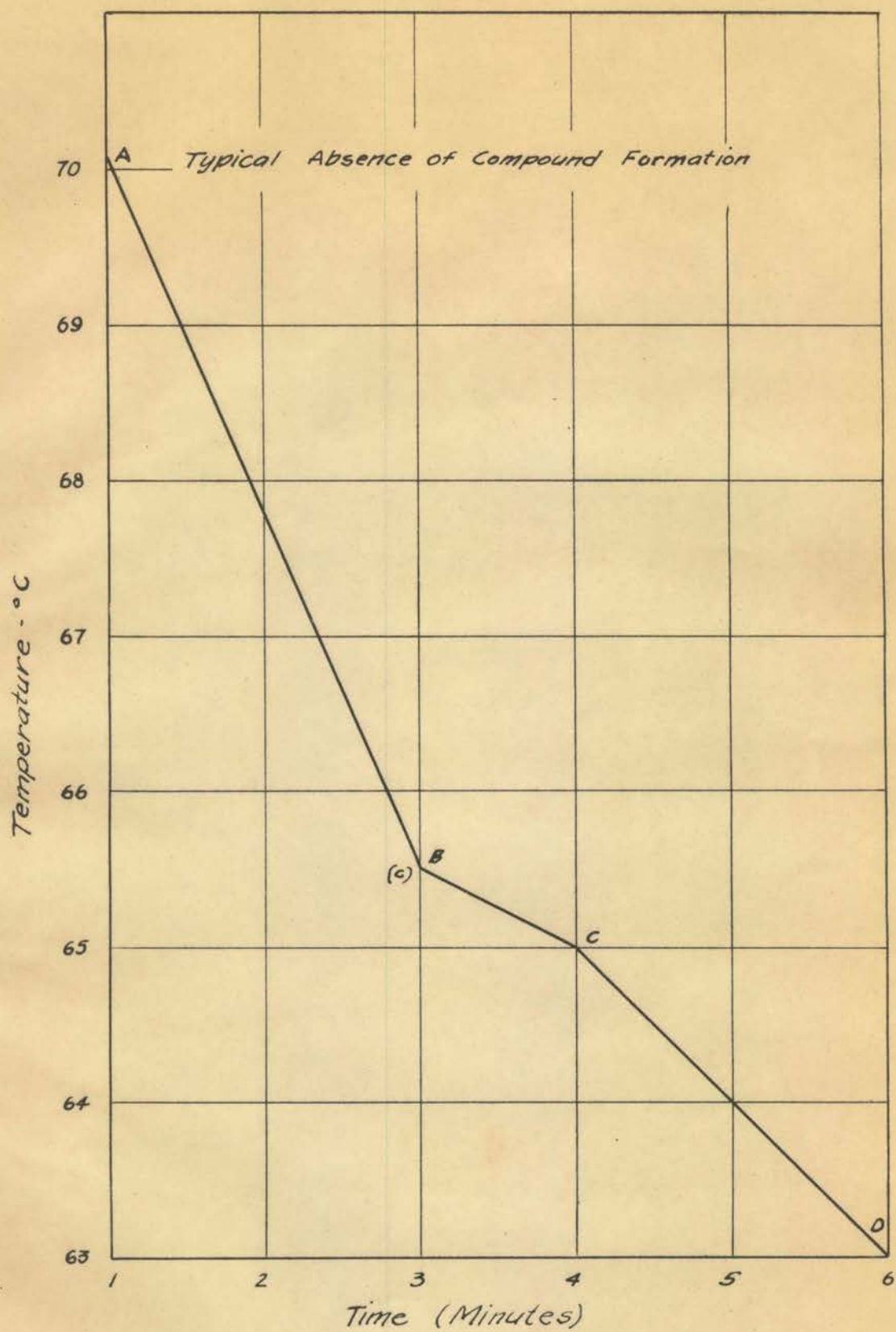


Figure II
Freezing Point Curve
2,6-Dinitrohydroquinone-4-Acetate + Naphthalene (1-1)

TABLE III

Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
2,4-Dinitroanisole	47	50	Color change slight with fusing.
3,5-Dinitroanisole	69	Not isolated	Color deepened with fusion.
2,4,6-Trinitroanisole	66.5	69-70	Color deepened in solution with naphthalene.
o-Dinitrobenzene	83.5	Compound not isolated	Yellow fused mass reverts to colorless mass with cooling.
2,4,6-Trinitrobenzaldehyde	135.5	136.5	Isolated compound has deeper color than original nitro compound.
m-Dinitrobenzene	51	51	Checks literature. (Table I)
1-Chloro-2,4-dinitrobenzene	75	77	Checks literature. (Table I)
1-Iodo-2,4-dinitrobenzene	66.5	Not tried	Color deepened with fusion.
2,2',4,4'-Tetranitrobibenzyl	134.5 (1:2 C ₁₀ H ₈)	Compound not isolated	No cpd. formed with 1:1 ratio. Solvents used were: acetone, acetone-methyl alcohol, dioxane.
3,5-Dinitrobenzoic acid	Not run	77	Checks literature. (Table I)

TABLE III Continued

Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
Isoamyl-3,5-dinitrobenzoate	46.5	Not run	Color deepened slightly with fusion.
2,2',4,4'-Tetranitrobiphenyl	103.5 (1:2 C ₁₀ H ₈)	Compound not isolated	No compound formed with 1:1 ratio. Solvents used were: acetone, acetone-methyl alcohol, dioxane.
3,5-Dinitro-o-cresol	92	94	Isolated compound deeper in color than original nitro compound.
2,2',4,4'-Tetranitro- diphenyl ether	127.5 (1:2 C ₁₀ H ₈)	Compound not isolated	No compound formed with 1:1 ratio. Solvents used were: acetone, acetone-methyl alcohol, dioxane.
2,2',4,4'-Tetranitro- diphenyl methane	111.5 (1:2 C ₁₀ H ₈)	Compound not isolated	No compound formed with 1:1 ratio. Solvents used were: acetone, acetone-methyl alcohol.
3,5-Dinitroguaiacol	91	94	Nitro compound deepened in solution with naphthalene.

TABLE III Continued

Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
2,4-Dinitroresorcinol	98.5	104-5	Forms red solution.
2,4-Dinitrophenetole	41	None isolated	Solution slightly deeper in color than original nitro compound in solution.
2,4,6-Trinitrophenetole	37	39	Characteristics similar to the dinitro compound.
2,4-Dinitro-6-cyclohexyl-phenol	70.5	73.5-74	Color of fused mass was deeper than original mix.
3-Chloro-2,4,6-Trinitro-phenol	128.5	Not run	Color deepened with fusion.
2,6-Dinitrophenol	56.5	58	Fused mass was deeper in color than original.
Picric acid	149.5	150.5	Checks literature. (Table I)
2,4-Dinitroresorcinol	165	165	Compound greenish yellow.
2,4-Dinitroacetanilide	No cpd.	No cpd.	No color change on fusing.
2,4-Dinitrodiphenylamine	No cpd.	No cpd.	No color change on fusing.

TABLE III Continued

Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
2,4,6,2',4',6'-Hexanitro- diphenylamine	No cpd. indicated	None isolated	Color deepened slightly with fusion.
2,4-Dinitrodiethylaniline	No cpd. indicated	None isolated	No color change.
2,4-Dinitrobenzaldehyde	No cpd. indicated	None isolated	No color change.
3,5-Dichloronitrobenzene	No cpd. indicated	Not run	No color change.
m-Nitronitrosobenzene	No cpd. indicated	None isolated	Decomposes when fused with naphthalene.
1-tert-Butyl-3,5-dimethyl- 2,4,6-trinitrobenzene	No cpd. indicated	None isolated	No color change.
m-Nitrobenzene sulfonyl chloride	No cpd. indicated	Not run	No color change.
2,4,6-Trinitrobenzoic acid	No cpd. indicated	None isolated	No color change.
2,2'-Dinitrobiphenyl	No cpd. indicated	None isolated	No color change.
3,3'-Dinitrobiphenyl	No cpd. indicated	None isolated	No color change.
4,4'-Dinitrobiphenyl	No cpd. indicated	None isolated	No color change.
2,4-Dinitrodiphenyl ether	No cpd. indicated	None isolated	Slight color change on fusing.

TABLE III Continued

Nitro Compound	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
2,6-Dinitrohydroquinone- 4-acetate	No cpd. indicated	None isolated	No color change.
2,6-Dinitrohydroquinone	No cpd. indicated	Not run	Fused mass deep red.
2,4-Dinitromesitylene	No cpd. indicated	None isolated	No color change.
1,8-Dinitronaphthalene	No cpd. indicated	None isolated	No color change.
1,3,8-Trinitronaphthalene	No cpd. indicated	None isolated	Color slightly deeper with fusion.
2,4-Dinitro-1-naphthol	No cpd. indicated	None isolated	Decomposition occurs with fusion.
2,4-Dinitro-1-naphthol-7- sulfonic acid	No cpd. indicated	None isolated	Decomposition occurs with fusion.
2,3,4,6-Tetranitrophenol	Not determined	None isolated	Decomposed with fusion.
2,4-Dinitrophenylacetic acid	No cpd. indicated	None isolated	No color change.
2,4-Dinitrophenylhydrazine	No cpd. indicated	None isolated	No color change.
Picramic acid	No cpd. indicated	None isolated	Color in solution deeper red with naphthalene.

TABLE III Continued

Nitro Compounds	M. P. (F.P. method) °C.	M. P. (Isolation) °C.	Remarks
2,4-Dinitrosoresorcinol	No cpd. indicated	None isolated	No color change.
3,5-Dinitrosalicylic acid	No cpd. indicated	None isolated	No color change.
3,5-Dinitromethylsalicylate	No cpd. indicated	Not run	No color change.
3,4,5-Trinitroveratrole	No cpd. indicated	Not run	No color change.

DISCUSSION OF RESULTS

From the standpoint of qualitative organic analysis, this work has yielded satisfactory results. Of the 45 compounds studied here for the first time, 20 yielded complexes with naphthalene, 10 of which were isolated. Many of the 45 compounds were studied because of theoretical aspects as well as for qualitative analytical purposes, which accounts for the apparently low percentage of derivatives secured. From the literature studies, 41 nitro compounds have been found to give complexes with naphthalene, which, together with those obtained in this work, gives a total of 61 nitro compounds known to form addition compounds with naphthalene. Most of the common polynitro compounds and those important commercially fall within this group. From results of this work and from the literature, many more compounds seem certain to give derivatives with naphthalene. Those classes of compounds which are most apt to give addition complexes with naphthalene are: polynitrophenols, nitrated aromatic hydrocarbons, and nitrated aromatic halides.

Consideration of the methods used shows that the isolation procedure has an advantage in that it is unnecessary to weigh the components accurately. However, polynitro compounds which form weak addition complexes with naphthalene often cannot be recrystallized from any solvent. The freezing-point method offers the advantage that even weak complexes can be detected, although, with this method, it is necessary to know the probable identity of the compound in question in order to assure equimolecular proportions. In this respect, the freezing-point method is of value as confirmatory proof, as in the preparation of secondary derivatives of polynitro derivatives.

It is suggested that in the identification of small amounts of

polynitro compounds which produce naphthalene complexes of doubtful stability, the analyst should first fuse equimolecular proportions of the nitro compound and naphthalene and then determine the melting point of the cooled mass by means of the capillary tube method. In the case of the polynitrophenols, the isolation method probably can be used to advantage.

From the standpoint of structural relations and in consideration of the theory of molecular compound formation, it seems evident that much work is necessary before definite generalizations can be established, although in this work several salient points were brought to the attention of the author.

The fact that 2,4-dinitromesitylene and 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene did not form compounds further confirms the work of previous investigators (50) (54) in which methyl groups on an aromatic ring were shown to hinder compound formation.

In no case did an amine or substituted amine form a complex, except where the compound was so fully nitrated as to overcome the effect of the amino group. Even then, hexanitrodiphenylamine apparently did not form a compound, a fact not easily explainable. It is possible that its high melting point and consequent low solubility may play an important part in its refusal to form an addition compound.

Hammick and Hellicar (50) say that chlorine atoms on the benzene ring are electron attracting and that they therefore act in the same way as other electron attracting groups in reinforcing the nitro group. The fact that 3,5-dichloronitrobenzene does not form a compound indicates that even if chlorine atoms are electron attracting they are not sufficiently so to reinforce a single nitro group enough to form molec-

ular compounds with naphthalene.

Polynitrophenols seem to form the most stable addition compounds with naphthalene and the derivatives are most easily isolated from solvents. The study of 2,6-dinitrophenol shows that a hydroxyl group between two nitro groups does not hinder compound formation. However, in the case of 2,6-dinitrohydroquinone, no complex was formed apparently. This compound gives peculiar color reactions when fused or when dissolved in water which probably can be explained by a tautomeric interference with compound formation since possibly both nitro groups have been converted into acid groups by the two hydroxyl hydrogen atoms.

From a comparison of nitrated hydrocarbons containing two phenyl groups, it was found that each phenyl group acts independently in complex formation, since these complexes are composed of one molecule of nitro compound and two molecules of naphthalene. 2,4-dinitrodiphenyl ether does not give a compound, possibly owing to the added molecular weight of the phenoxy group attached to the dinitrobenzene, since 2,4-dinitrotoluene itself does not form a very stable compound.

It was found from the results of the study of o-nitronitrosobenzene and 2,4-dinitrosoresorcinol that the nitroso group is incapable of causing compound formation, nor does the nitroso group reinforce a nitro group sufficiently to permit an addition compound to form.

Since 3,5-dinitrosalicylic acid did not give compound formation, it was first thought that this might be due to the strongly ionic carboxyl group. The methyl ester of this acid was prepared and studied and also was found to give no addition complex. This eliminated the carboxyl group as the hindering group.

It seems pertinent that more work should be done along the lines of

physical measurement, especially solubility and polarity. Finally, much should be gained from studies of structural relations concerning substitution positions on the benzene ring and their relation to compound formation.

SUMMARY

The formation of addition compounds with naphthalene was studied for 45 polynitro compounds. Of these compounds, 20 were found to give addition complexes, 10 of which were isolated. Several of the complexes listed in the literature were studied and were found to check with the literature value. The 41 derivatives in the literature together with those found in this work give a total of 61 polynitro compounds which form addition complexes with naphthalene, most of which are of 1:1 ratio.

Simplified procedures have been outlined for the identification of addition complexes of varying degrees of stability.

From a study of the literature and from this work certain general conclusions have been drawn as to the stability of these complexes. The observation that a methyl group on the benzene ring hinders compound formation has been further confirmed. The polynitrophenols seem to form the most stable addition compounds. The amino group hinders compound formation, but the carboxyl group itself is not a direct hindrance to the formation of complexes.

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