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J.W. Marlow.*

THE INVESTIGATION OF TECHNICAL
ORTHOCHLORONITROBENZENE

by

Porter Merle Waldron, A. B.

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P. F. Howledge
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INTRODUCTION.

When para-chloronitrobenzene was prepared by the nitration of chlorobenzene, there was found to be a liquid left after the para had been crystallized out. At first this was looked on as a sort of mother liquor containing impurities, by-products of the nitration. Later it was considered to be the ortho derivative with a little para. More careful investigation disclosed the fact that this liquid was not a simple mixture but a compound of the ortho and para chloronitrobenzenes in a definite proportion. It consisted of 21 parts ortho to 10 parts para and is called a eutechtic mixture.

In order to study the properties of this eutechtic mixture, spoken of as technical o-chloronitrobenzene, (as it is a by-product of manufacturing concerns), it was necessary to prepare the pure ortho and para derivatives. The first was obtained by fractional distillation and crystallization of some of the technical mixture and the latter by recrystallization of some of the impure para compound.

There is very little in the literature concerning the separation of the ortho from the para chloronitrobenzene

in the eutechtic mixture. The object of this research is to review and investigate the few and impractical methods which are given and to determine a practical method of separation. There is no doubt that a method of this kind will be of great practical value since both of the compounds are valuable in the synthesis of many important and necessary products. The experiments have been carefully carried out and while some did not work according to expectations others were very satisfactory.

HISTORICAL

It will probably be of interest to know how the ortho- and para- chloronitrobenzenes were first prepared, and how the earlier chemists looked upon these compounds, and upon the eutectic mixture which the earlier men regarded as a simple compound.

In 1862, A. Riche (25) added strong nitric acid to chlorobenzene and noticed that there was a vigorous reaction. When the mixture was boiled for a short time, a nitrated oil was formed, which on cooling, crystallized into long needles. "These crystals are a new substance; benzene in which 2 atoms of hydrogen are replaced by 1 atom of chlorine and 1 nitrate radicle. The formula of this substance is $C_{12}H_4ClNO_4$, and its properties indicate that it is truly chloronitrobenzene". (Note. At that time the atomic weight of Oxygen was considered as 8 and that of Carbon as 6). It is evident that he thought he had only one compound, for in giving its properties he makes no note of the fact that there might probably be two different nitro compounds formed. He determined several physical properties of his derivative and they may be interesting enough to record. He found that it melts at 78° and softens at 74° . It does not dissolve noticeably in water even on boiling, but is quite soluble in both boiling alcohol and ether. IT is only a little affected by acids; it is dissolved by nitric acid and reprecipitated by the addition of water".

When he took his "new substance" and added Sodium or Potassium hydroxid, dissolved either in alcohol or water, he obtained a brown solution similar to that obtained when nitrobenzene is put thru the same process. He does not name the new liquid which was probably nitrophenol. What he urges as a proof that this compound is chloronitrobenzene, in fact says it proves the structure beyond a doubt, is the way it acts with reducing agents; "it makes a fixed base, which has the smell of aniline, and its melting point and reactions with iron and copper salts show that it is chloraniline; so now this base, which has hitherto been obtained indirectly from indigo can now be obtained in a more direct manner from the bodies of this type."

A. Riche, then was the first man to prepare the chloronitrobenzene. To prove that he did not have a single derivative was left for the men who followed him and who had the benefit of the more modern theories. However, in the light of the knowledge of the day, of molecular structure and theories, it is almost marvelous to observe what advances the early men made in the science of organic chemistry.

It might be noted here that in 1862, Griess (10) did some work with iodinitrobenzene with the assistance of Schutzenburger and Segenwald. If the conclusion were drawn that he did experiment with the chloro derivative at this time it would probably not be wrong as it is well known that he did work with it in later years, 1866, (11). A review of the

literature obtainable does not reveal such information however.

In 1871 V. von Richter (26) records that he has experimented with the chloronitrobenzenes and has found that there are two derivatives, which are isomeric forms; one of these compounds was crystallized from alcohol in long prisms with a melting point of 84°. He said that the other derivative was a liquid. The first had been previously prepared by Griess (11) from nitraniline giving the pure para form while the second had been prepared (6) by the action of phosphorus pentachlorid upon o-nitrophenol. Von Richter claims to have separated the two derivatives by means of steam distillation. It can easily be seen by this and by some of his previous statements that he considered the fluid compound a single derivative. He had, however, recognized the fact that there were two derivatives and has made note of the fact that the third compound had been prepared by Griess. Griess(11) had done some work on the chloronitrobenzenes in 1866 and it was probably then that he obtained the three derivatives.

'This shows how he prepared the meta compound. The platinum salt of the diazo compound from paranitraniline is heated with sodium and the resulting compound recrystallized from alcohol.

In 1875, A. Laubenheimer (20) attempted to obtain the chloronitrobenzene, previously prepared by several men.

' Refers to an abstract from a Zeitschrift which is not obtainable.

Noting that chlorine gas had no effect on nitrobenzene he tried several catalytic agents. The one with he had the most success was iodine. When 10% of iodine was added to nitrobenzene he observed that the chlorine gas was then readily absorbed, and hydrochloric acid was evolved. When the requisite amount of chlorine had passed in to form the monochloronitrobenzene and iodine trichloride and the liquid left to itself, the product solidified to a crystalline mass. When agitated with alcohol, washed, and distilled in steam, a yellow liquid was obtained "which became almost a solid at 0°". When pressed and recrystallized from alcohol, it formed pure monochloronitrobenzene, $C_6H_4ClNO_2$, melting at 45°. It was identical with that obtained by Griess, and so was the meta derivative and neither the ortho or para form.

It is to be observed that some work had been done on the composition of benzene and the atomic weights of carbon and oxygen by this time. The formula was now written $C_6H_4ClNO_2$ and not as previously, $C_{12}H_4ClNO_4$.

In 1876 F. Beilstein and A. Kurbatow (1) continued the work of A. Laubenheimer with respect to catalytic agents when chlorinating nitrobenzene. They found that when antimony trichloride was used instead of iodine, the action of the chlorine was much more rapid and the yield of monochloronitrobenzene far more abundant. They observed that their product was the same as that obtained by Laubenheimer,

accompanied, however, by more highly chlorinated bodies up to C₆ Cl₆.

Later on in the same year, 1876, F. Beilstein and A. Kurbatow (2) experimenting in the preparation of chloronitrobenzene, prepared one that was different than any other hitherto obtained. For the first time the composition of the liquid left after the crystallizing out of the para-chloronitrobenzene, prepared by the action of nitric acid upon nitrobenzene, was questioned.

When they mixed para-nitro-meta-chloraniline with nitrous acid and alcohol a chloronitrobenzene was obtained which crystallized in needles melting at 32° and boiling at 243°. The theory was that orthonitrochlorobenzene would have been formed which indeed boiled at close to the same temperature but which crystallized at 15°. These men were so convinced about their results that they carefully repeated their experiments. Before doing this they prepared and purified their materials so there could be no cause of error there. When they obtained their chloronitrobenzene this time they did not hesitate to assert that heretofore pure ortho-chloronitrobenzene had not been prepared. In order to further prove their point they made mixtures of the ortho- and para-derivatives and observed that the "product kept after the nitrating of chlorobenzene stubbornly retains both products which lowers the melting point considerably". They analyzed their ortho derivative for purity. The theoretical amount of chlorine was 22.83% and they obtained 22.64%.

They went even further and reduced some of the ortho-chloronitrobenzene with tin and hydrochloric acid and obtained reddish liquid chloraniline but which was mixed with a stable higher boiling point substance. To determine what this was they added sulfuric acid and distilled in steam and found that there was a little dichloraniline there as an impurity.

In 1882 C. Willgerodt(30) made some careful determinations of the action of alcoholic potash upon para-chloronitrobenzene, the results of which are very interesting. Different conditions and concentrations brought the following results:

"1. Potash dissolved in absolute or high percentage alcohol, at a temperature of 100°-130°, reduces para-chloronitrobenzene to dichlorazoxybenzene, and at a higher temperature 150°-200° to dichlorazobenzene.

2. The reducing power of the alcoholic solution varies with the alcohol used; thus ethyl alcohol forms dichlorazoxybenzene at once, without assisting the reaction by the application of heat, while methyl alcohol has only a moderate reducing action, a considerable quantity of para-nitranisole being formed in the reaction besides the dichlorazobenzene.

3. On diluting the alcohol with water, the reducing power is considerably modified; para-nitrophenetole being obtained on heating para-chloronitrobenzene with dilute alcoholic potash, thus:

In order to separate the phenetol from the unaltered chloro-nitrobenzene and from any dichlorazobenzene which may be formed the crude product is distilled in a current of steam, when the nitro-phenetol passes over. Similarly on substituting methyl for ethyl alcohol, para-nitranisole is obtained.

4. Finally, by the action of more dilute alcoholic potash on para-chloronitrobenzene, potassium nitrophenate is formed, either by the replacement of the chlorine atom by the OK group or by the saponification of the intermediate phenetol, or more probably by both of these reactions".

Dr. Hermann Kolbe's *Organische Chemie* (18), 1884, gives a brief resume of the work done on the three isomerides up to that time. "The three known modifications are crystalline; ortho-needles; para-rhomboidal leaves; meta-rhomboidal crystals". The methods for the preparation of the three forms are those previously described in this paper and therefore need not be repeated here. "In their chemical properties the three derivatives show many differences. On heating the ortho-form with NaOH to 130° it is converted into ortho-nitrophenol; the para derivative is with difficulty converted to the nitrophenol, and the meta derivative undergoes no change at all. In the same manner with alcoholic ammonia act on the ortho and para derivatives substituting the amide group for the chlorine. By treating with alcoholic ammonium sulfide all three of the isomers are changed into the corresponding chloranilines. Fuming nitric acid forms chlorodinitrobenzenes. Potassium cyanide reacts in alcoholic solution at 250° - 270°

upon the meta and para forms but not upon the ortho derivative".

Dr. Kolbe's text shows that an advance had been made in organic chemistry both in theory and structure. It reads like a modern text book and shows clearly that some careful and accurate work had been done on the chloronitrobenzenes. From this period on the literature is written in a form such that there is no difficulty in its being easily understood.

In 1890, Ludwig Gatterman (9) made a quantitative determination of the percentage yield of para-chloronitrobenzene when prepared from pure para-nitraniline. 46 grams of para-nitraniline, 225 grams of HCl, 23 grams of sodium nitrite, and 40 grams of powdered copper were mixed together and on distilling in steam, 27 grams of crystalline para-chloronitrobenzene were obtained. This is 70% of the theoretical yield.

A. A. Noyes and John Dorrance (22) reduced some para-chloronitrobenzene electrolytically in the presence of sulfuric acid; they proved their product to be the sulfonic acid of amido phenol, $C_6H_3NH_2OH SO_3H$.

F. Ullmann (27) did considerable work in 1896 on the ortho-halogen derivatives of nitrobenzene. He prepared ortho-chloronitrobenzene in several ways, and noted that it was "best prepared by means of Sandmeyer's reaction, "bronze powder" washed with ether being used instead of precipitated copper; a yield of 65% is obtained".

William Oechner de Coninck (3) had shown that isomerides in the benzene series arrange themselves in pairs with respect to solubilities and to some of their chemical properties. In 1897 he noted that this held good also for their boiling and melting points.

Walter Lob (21) added metallic sodium to chloronitrobenzene in ethereal solution and formed a product the composition of which he did not definitely determine. Probably the Sodium entered the nitro group (von Hoffmann and Geyger (15)). The compound from para-chloronitrobenzene, a black, unstable substance, has the composition $(C_6H_4ClNNa)_2O$.

In 1900 Arnold F. Holleman and B. R. de Bruyn (16) studied the isomeric substitution products of benzene. They analyzed the products that were simultaneously produced to determine the percentage of ortho, meta, and para derivatives present, and found that when chlorobenzene was nitrated 0° , the amounts were 30.1% orthochloronitrobenzene, 69.9% para, while at 30° , the proportions were 26.9% and 73.1% respectively. Holleman did more and better work (13), and in 1905 gave the percentage 29.8% ortho, .3% meta, and 69.9% para for the nitration of chlorobenzene at 0° .

A. Hantzsch and J. W. Blagden (17) prepared para-chloronitrobenzene from para-chlordiazoniumsulfate. 4 grams of pure para-chlordiazoniumsulfate were dissolved in water and poured into a freshly prepared mixture of 5 grams of cupric cuprosulfite and a concentrated water solution of 15-20 grams

of potassium or sodium nitrite. The reaction went so violently at ordinary temperature that the evolution of nitrogen gas was ended after about a quarter of an hour. The solution was then made alkaline and distilled with steam. The product that came over was pure para-chloronitrobenzene, m.p. 82° - 83° . He obtained a 63% theoretical yield by this process.

Paul Cohn (4) mixed chloronitrobenzene dissolved in alcohol with a number of zinc sticks and NaOH. Heat was generated and important red azo bodies were formed.

C. Haeussermann and August Müller (14) working with the aromatic halogen derivatives confirmed the observations of P. Julius; namely, that in those benzene compounds "which have a nitro group ortho to the halogen are more able to react in all cases than the analogous para derivative". Ortho-chloronitrobenzene reacted much quicker with potassium phenolate than the para derivative. It is not recorded whether or not these men did any work with the chloronitrobenzenes and alcoholic KCN. Kolbe's (18) observation in this case seems to be an exception to the above mentioned rule of Julius.

F. Ullmann and Pasdumadjian (28) used ortho-chloronitrobenzene in the preparation of 2-nitro-diphenyl sulfonic acid, $C_6H_5SO_2C_6H_4NO_2$.

F. Ullmann (29) working in 1901 with Jean Bieleki, prepared 2,2'-dinitrodiphenyl by heating ortho-chloronitrobenzene in a closed in the presence of copper. On extracting with

alcohol, or benzene, he found his yield to be 60% theoretical.

2 2' dinitrodiphenyl

F. Kehrman and G. Steiner (19) prepared 2-nitro-3-amido diphenylamine from ortho-chloronitrobenzene and meta-phenylenediamine.

2-nitro-3-amido diphenylamine

They prepared 2-nitro-2-amido diphenylamine from ortho-chloronitrobenzene and ortho-phenylenediamine.

2-nitro-2-amido diphenylamine

In 1902 Alfred Ekbohm (5) proved that para-chloronitrobenzene was one of the splitting products of para-nitrophenyldiazo-para-nitrophenylsulfonic acid, when it was heated to 135° with HCl. The other products were para-nitrobenzene sulfonic acid and para-dinitrobenzene sulfonic acid.

The 3 splitting products are :

1. para-chloronitrobenzene
2. nitrobenzene sulfonic acid
3. para-dinitrobenzene sulfonic acid

It will be observed that the work of the men so far recorded has had to do either with the preparation of the chloronitrobenzenes or their use in the synthesis of compounds. From the time that Beilstein and Kurbatow (2) proved that after para-chloronitrobenzene had been crystallized from nitrated chlorobenzene, ortho did not remain alone, but formed a eutectic mixture with para, the separation of this so-called technical mixture into its two isomerides has been the object of many researches. Few attempts were even in a minor degree successful, while those used even in manufacturing concerns were far too expensive and impractical to be of much importance. Before the work of this paper is outlined the analysis and attempts at separation of the mixture will be discussed briefly.

P. Fischer(8) in 1891 described a method for the separation of the two derivatives by means of fuming sulfuric acid. He found that the ortho was acted upon to some extent but that the para was not. The para could be separated by pouring into water, in which it would be crystallized. No further data was obtained; evidently, tho, he had a small amount of the para; and did not succeed in converting the ortho chloronitrobenzene sulfonic acid into the ortho-chloronitrobenzene. Had he been successful in procuring an almost theoretical yield of para and converting the sulfonic acid into

ortho-chloronitrobenzene the literature would probably have made mention of the fact, and the problem of this paper would have been solved before this research was undertaken.

In 1900, A. F. Holleman and B. R. de Bruyn (12) made some studies of the isomeric substitution products of benzene. For determining the proportion of compound in which there are two isomers they employ a method used in Holleman's previous researches. The solidification point of the mass is determined and its composition deduced from a previously prepared curve of the points of solidification of the mixtures of the isomers.

A series of mixtures containing known amounts of the two isomers was made. The mixtures were melted and the point of solidification was observed with a thermometer graduated to $1/10^{\circ}$. These solidification points furnish the means for making a finished curve by means of which an analysis of any mixture of ortho and para isomers may be made.

The ortho and para chloronitrobenzenes used in Holleman and de Bruyn's experiments were obtained from the factory of Kahlbaum. The specimens were analyzed and Holleman said that "the purity of the specimens left nothing to be desired".

The specific gravities of the compounds were determined after the method of M. Eykman(7). The temperature chosen 80.05° because it was easily kept constant with boil-

ing benzene.

Sp.Gr.	Ortho	80.05	1.3052
"	meta	"	1.3112
"	para	"	1.3092

Holleman asserts that "these determinations exact to one unit in the fourth decimal".

Below is given the table of the points of solidification (melting points) of mixtures of ortho and para chloronitrobenzene.

%para	M.P.	%para	M.P.
0.00	32.09°C	35.43	18.43°C
1.05	31.06	37.53	21.9
4.60	29.92	39.96	26.1
6.54	29.	41.67	28.5
8.89	27.89	45.86	33.98
12.61	26.10	48.94	37.65
16.26	24.19	60.18	50.1
19.22	22.65	64.66	54.32
22.91	20.75	68.54	57.83
26.89	18.30	70.02	59.22
30.26	16.29	71.93	60.80
32.39	15.35	75.48	63.97
32.71	14.94	81.93	69.10
32.90	14.85	86.70	72.77
33.07	14.77	90.30	75.40
33.1	14.65	95.57	79.13
34.09	16.73	100.00	82.15

"The eutechtic point of these mixtures is found to be 14.65° according to this table. The composition of the mixture at that point is 33.1% para and 66.9 ortho. With agraphic representation one sees that the curve is very regular. See the following figure.

SOLIDIFICATION POINTS OF MIXTURES OF ORTHO
AND PARANITROCHLORBENZENE.

Holleman found that there were impurities in the nitration products of chlorobenzene which probably accounted for some of the mistakes in boiling and melting point determinations of the earlier chemists. They (impurities) are unattacked chlorobenzene, dinitrobenzene, and meta-chlorobenzene; and all traces cannot be removed by ordinary purification methods.

Dr. Leo Markwald (24) in his patent mentions the fact that the method of Jungfleisch for the separation of ortho and para chloronitrobenzene was not practical and its value is overestimated. Jungfleisch's procedure applied to the treatment of the solid technical mixture with alcohol and Markwald says "by this method pure ortho chloronitrobenzene cannot be obtained".

The melting point of the eutectic mixture containing 66.9% ortho and 33.1% para chloronitrobenzene 14.7° . Markwald asserts that this or any other mixture of similar composition may be separated into its component parts by extracting with a quantity of dilute ethyl or methyl alcohol insufficient for complete solution at a temperature above the melting point of the mixture. More ortho is extracted than corresponds to the eutectic mixture; on cooling the residual mixture to 16° a further quantity of para separates out; and by distilling off the alcohol from the extract and cooling, crystals of ortho separate out.

He carried out the experiment as follows:

" 100 kg. chloronitrobenzene are stirred in with 50 liters of alcohol, of 80% by volume at 33°. After settling well the remaining liquid mixture of ortho and para chloronitrobenzene is drained off, evaporated and cooled, to 16°. Whereupon .9 kg parachloronitrobenzene (m.p. 83°) crystallized out and is collected by filtering. The the alcohol is distilled off by fractional distillation and the ortho and para mixture remaining behind is separated from water by precipitation and after cooling to 16° by filtration 1.8kg ortho-chloronitrobenzene (m.p. 32.5°) is obtained. The liquids from both crystallizations can now be put back into the process". This represents a total 2.7% yield.

SUMMARY OF HISTORICAL DATA

1. A. Riche in 1862 obtained the nitration products of chlorobenzene but did not realize that he had two derivatives. He knew that he had a "new substance".

2. In 1871 V. von Richter discovered that there two derivatives when chlorobenzene is nitrated which are isomer

3. Beilstein and Kurbatow prepared pure orthochlorobenzene and proved that the liquid left after para chloronitrobenzene had been crystallized out was not a single derivative.

4. In 1891, Paul Fischer, and in 1901 Leo Markwald had a slight degree of success in separating the eutechtic mixture of ortho and para chloronitrobenzenes.

5. Holleman and de Bruyn made a table in 1900 whereby an analysis of ortho and para mixtures could be made by determining the melting points.

6. Properties of the chloronitrobenzenes according to Beilstein:

<u>Isomer</u>	<u>M. P.</u>	<u>B. P.</u>	<u>Sp. Gr. at 22°.</u>
ortho	32.50° C	243° C	1.368
meta	44.40°	235.6	1.534
para	83.00°	242.0	1.380

The boiling points were later corrected and found to be ortho-245° and para-239.5°(23).

The eutechtic mixture m.p.14° consists of 21 parts ortho and 10 parts para.

EXPERIMENTAL

A. Preparation of Pure Para-chloronitrobenzene.

It was necessary to prepare the pure chloronitrobenzenes and to ascertain their properties before attempting to separate the technical mixture into the two isomers.

Technical para was procured which had a m.p. of 80°-81°. This was recrystallized from alcohol to a constant melting point of 82.8°. Three recrystallizations were necessary to bring this degree of purity.

PROCEDURE: 200gm of the technical para were dissolved in 500cc. of redistilled ethyl alcohol(95%). The para went into solution easily on being warmed. When cooled to 20° the recrystallized substance was freed of the alcohol by means of a suction filter, (Büchner funnel fitted to a filter flask). The crystals were again dissolved in alcohol and the process repeated to constant m. p. A sample of each fraction was saved and dried in a vacuum dessicator over KOH, so that the m. p. might be determined. The results obtained are given below:

200 grams of Technical para	
- M.P. 81.2 (dry)	
Dissolved in 500 cc warm alcohol	
-----	-----
Cooled with tap water (20°)	Cooled with ice water
-----	-----
160 gm (5gm for sample)	(not used)
I _f - M.P. 82.6°	A 10 gm
dissolved in 425 cc EtOH	
-----	-----
145 gm (5gm for sample)	
II _f - M.P. 82.7°	B 7 gm
250 cc EtOH	
-----	-----

123 gm (5gm for sample)		
III _f - M.P. 82.8°	C	4.5 gm
200 cc EtOH		

108 gm		
IV _f - M.P. 82.8°	D	2.7 gm

By this method a sufficiently large quantity of para chloronitrobenzene was prepared to determine its solubilities and to study other necessary chemical and physical properties.

B. Solubility Determinations of Para-chloronitrobenzene.

It was known that para-chloronitrobenzene was very volatile. So tests were made to determine whether the amount lost was proportional to the time. When allowed to stand in a draught the time loss curve was not regular; when standing out of a draught the time loss line was approximately straight. The graphs of the determinations are shown (Fig. 1 and 2).

Four .2 gm amounts of para chloronitrobenzene were weighed in evaporating dishes and duplicate determinations were run in a draught and out of a draught. The time of the weighings was recorded and the loss per hour determined. (See tables I and II and Fig. 1 and 2). The results were that out of a draught the loss was approximately 1mm per hour; in a draught it was too irregular for this work.

CONCLUSION: a. Solubility determinations must be carried on out of a draught. b. As loss in weight by evaporation is constant, correct weighings can be computed altho not made right on the hour.

GENERAL METHOD for the solubility determinations of the para derivative in the several solvents: A large constant temperature bath regulated to $1/10^{\circ}$ total variation was used. Bottles containing the chloronitrobenzenes were left in this bath for at least a day and agitated several times during this period. A certain amount of the liquid was then withdrawn by means of a pipette prepared for the purpose (see drawing). The liquid was then allowed to evaporate from glass evaporating dishes spontaneously, out of a draught.

Table I. Evaporation of a Solution of Para- in Ether.

(.2 gm para in 10 gm ether, out of draught)

<u>Time</u>	<u>Hours</u>	<u>Weight</u>	<u>Sample</u>
10:30 A.M.		.2000	#1
		.2000	#2
1:00 P.M.	2 hr 30 min	.	#1
	2 " 30 "	.1995	#2
2:15 P.M.	1 " 15 "	.1990	#1
	1 " 15 "	.1984	#2
3:30 P.M.	1 " 15 "	.1975	#1
	1 " 15 "	.1973	#2
5:30 P.M.	2 " 00 "	.1971 (error)	#1
	2 " 00 "	.1959	#2
8:30 P.M.	3 " 00 "	.1933	#1
	3 " 00 "	.1933	#2
8:30 A.M.	12 " 00 "	.1857	#1
	12 " 00 "	.1880	#2

Table II. Evaporation of a Solution of Para- in Alcohol.

(.2 gm para in 10 gm alcohol in draught)

11:30 A.M.		.2000	#3
		.2000	#4
3:30 P.M.	4 hr 00 min	.	#3
	4 " 00 "	.1941	#4
5:30 P.M.	2 " 00 "	.1931	#3
	2 " 00 "	.1881	#4
8:45 P.M.	3 " 15 "	.1910	#3
	3 " 15 "	.1843	#4
8:30 A.M.	11 " 45 "	.1824	#3
	11 " 45 "	.1749	#4

GRAPH FOR TABLE I.

Sample 1.

Sample 2.

Shows loss of weight of paranitrochlorobenzene when standing out of a draught.

GRAPH FOR TABLE II.

Shows loss in weight of paranitrochlor-
benzene standing in a draught.

Sample 3.
Sample 4.

The solubilities of pure para are given below:

<u>Solvent</u>	<u>% of Solvent by Wt</u>	<u>-Sp. Grav.</u>	<u>- Temp</u>	<u>- Gm per 100 gm Solv</u>	
Ethyl-OH	92.44	.8331	0°C	1.48	
"	"	.8423	14	6.40	
"	"	.8411	25	10.25	
"	"	.8443	35	14.01	Graph 1
"	78.32	.8648	0	1.88	
"	"	.8659	14	3.07	
"	"	.8621	25	5.41	
"	"	.8594	35	7.30	" 2
"	68.46	.8871	0	.90	
"	"	.8953	14	1.14	
"	"	.8791	25	3.27	
"	"	.8788	35	3.68	" 3
Methyl-OH	100.00	.8714	0	1.17 ?	
"	"	.	14	1.07	
"	"	.	25	3.73	
"	"	.8562	35	5.32	" 4
"	84.2	.8709	0	.95	
"	"	.8731	14	1.93	
"	"	.8691	25	2.95	
"	"	.8623	35	4.11	" 5
"	73.77	.8774	0	.97	
"	"	.8742	14	1.76	
"	"	.8701	25	2.88	
"	"	.8647	35	3.87	" 6
Ether	100.00	.8230	0	27.43	
"	"	.8567	14	41.09	
"	"	.8861	25	57.19	" 7
Petrol.Ether	100.00	.6606	0	2.13	
"	"	.6634	14	3.86	
"	"	.6593	25	5.86	" 8
CHCl ₃	100.00	.	0	39.32	
"	"	.	14	58.09	
"	"	.	25	76.22	" 9
Acetone	100.00	.	0	56.94	
"	"	.	14	87.01	
"	"	.	25	231.26	" 10

CURVES SHOWING THE SOLUBILITIES
OF PURE PARA IN DIFFERENT SOLVENTS.

G
r
a
m
s

p
e
r

1
0
0

g
r
a
m
s

s
o
l
v
e
n
t
.

Graph 1.

Graph 2.

Graph 3.

Graph 5.

Graph 6.

GRAPHS (continued).

G
r
a
m
s

Graph 7.

Graph 8.

GRAPHS (continued).

Graph 9.

GRAPHS (continued).

Graph 10.

C. Preparation of Pure Ortho-chloronitrobenzene.

1. Ortho-nitrophenol and PCl_5 were used to prepare orthochloronitrobenzene without much success. The byproducts, which are the phosphorus derivatives (see Norris' Organic Chemistry) are so greatly in excess of the o-chloronitrobenzene that the method is not at all a practical one.

2. The diazotization of o-nitraniline was tried without much success the first time. There was no second attempt made as no more o-nitraniline could be procured.

3. The o-chloronitrobenzene was prepared from the technical mixture by fractional distillation and crystallization, the method of which will be described in detail further on in this paper. When purified it had a m.p. of 32.2° .

The technical mixture with which the experiments for the separation were carried out was reddish brown in color. This coloration was due to impurities either from the containers in which the chlorobenzene was nitrated or from the impurities of the nitration, (dinitrobenzene, m-chloronitrobenzene, etc.,) or may be both. This eutectic mixture can be purified by steam distillation; but this method is slow and unnecessary as the coloring matter can be easily removed in subsequent crystallizations. The mixture has a melting point of about 14.1° .

A rough determination for Cl present in the para chloronitro benzene was made by mixing the compound with lime

' Technical mixture furnished by a manufacturing concern.

and sodium carbonate in a hard glass tube. As the p-chloronitrobenzene is very volatile a 2in layer of the fusion mixture was placed above to prevent a loss of the compound on warming. After heating to dull redness 5-10 minutes, the tube was allowed to cool and its contents were washed into a beaker, and then filtered. Silver nitrate was added and the chlorine is determined from the insoluble silver chloride.

92.3 % of the theoretical Cl was obtained.

An analysis for the Cl in the technical mixture was run in the same way. 93.4% of the theoretical Cl was obtained.

D. The Solubility Determinations of o-Chloronitrobenzene

METHOD: 1 gram of the ortho chloronitrobenzene was weighed out in a tube and alcohol added, drop by drop, at a little above the desired temperature, until all was dissolved but a few minute crystals. The mixture was then cooled till there was a noticeable separation of solid and the temperature noted. The tube was again weighed and the amount of alcohol obtained by difference. From this the number of grams of o-chloronitrobenzene in 100 grams alcohol was ascertained.

Due to the lack of time these solubilities were not determined with quite the same accuracy as those of the para-derivative. However, the approximate curves were needed to compare with those of the para and ascertain, if possible, whether or not the technical mixture might be separated by means of solvents. (see following tables and graphs).

By comparing the curves of solubility of orthochlore nitrobenzene in 68.46% alcohol with that of the para derivative it may be readily seen why there cannot be a technical separation. In the 92.64% alcohol, however, the ortho is much more soluble than the para, and it would seem that a separation could be brought about with this solvent. Such is not the case, though. There is one explanation for this phenomenon and that is that the ortho and para chloronitrobenzenes in the technical mixture are not free to act as they would separately; they evidently form a compound whose solubility curve is somewhere between that of the ortho and para forms.

Table I (see curve 1)

Solubility of the Ortho isomer at 25° in different alcoholic concentrations.

<u>% of Alcohol</u>	<u>Gm Ortho per 100 gm Solvent</u>
92.44	120.64
68.46	22.77
25.00	trace

Table II (see curve 2)

Solubility of Ortho in 92.44% alcohol at various temperatures.

<u>Temperature</u>	<u>Gm Ortho per 100 gm Solvent</u>
35° C	practically completely miscible.
25	120.64
15	30
5	15

Table III (see curve 3)

Solubility of Ortho in 68.46% alcohol at various temperatures.

Temperature

Gm Ortho per 100 gm Solvent

35° C
25
15
5

35
22
12
5

Curve I.

G
r
a
m
s

p
e
r

1
0
0

g.

a
l
c
o
h
o
l

Per cent Alcohol.

Curve II.

Curve III.

METHODS OF SEPARATION

I. Sulfonation of the Technical Mixture.

The first method of separation attempted was that undertaken by P. Fischer(8). It is also spoken of as the "oleum" method.

Following the methods in the literature the technical mixture (100gm) was heated with 200gm of fuming sulfuric acid, on the water bath for an hour. The mass is poured into a liter of cold water. The p-chloronitrobenzene crystallizes out and is filtered off. The yield of para is about ¹² per cent of the theoretical. The first time the experiment was performed the acid was neutralized by addition of calcium carbonate. This formed the soluble calcium o-chloronitrobenzene sulfonate, which is soluble in hot water, and the insoluble calcium sulfate. The hot solution was filtered and sodium carbonate added. In this manner the sodium sulfonate was formed and the calcium carbonate filtered off. The solution was concentrated until the sodium sulfonate began to crystallize. It was then set aside. On cooling a mass of sodium o-chloronitrobenzene sulfonate crystallized out.

This separation was too long and impractical for technical use. So the next time, after the para was removed, the solution was saturated with sodium chloride; whereupon the sodium chloronitrobenzene sulfonate crystallized out. On contrating to get a larger yield of the sodium salt, the NaCl commenced to crystallize out. This was unsatisfactory

and work was begun to improve the method of obtaining a purer sulfonic derivative.

Previous to this, tho, it had been noticed that in concentrating the solution after the para had been removed, drops of an oily substance continually collected in the bottom of the evaporating dish. On examination this proved to be the technical mixture. By following the directions in the literature the compound had not been completely sulfonated. Various attempts were made to completely sulfonate the ortho in the technical mixture.

It was found that if 50gm of the technical mixture and 100gm of fuming sulfuric acid were heated in an oil bath in a pressure bottle, 150° for an hour, a complete sulfonation was brought about. A small quantity of an undesirable material was present, probably due to decomposition. This, then, was not satisfactory either. The most satisfactory results were obtained when the technical mixture and fuming sulfuric acid in the above amounts were heated in a pressure bottle for three hours in a water bath.

When the contents of the pressure bottle were poured on ice (sulfonation brought about by the last process given above), the p-chloronitrobenzene crystallizes out readily and this time the yield of para was from 70%-80% of the theoretical. Part of this weight was due to moisture as the weighing was made after allowing it to remain in a suction filter for 10-20 minutes and was of course not completely dry.

To work out a better method for obtaining the ortho-chloronitrobenzene sulfonic acid was the next problem. It was known that the sulfonic acid was not readily soluble in water nor in ether. If then, a water-ether solution of the right strength could be procured, the sulfonated technical mixture could be diluted with the correct amount of cold water; the para would separate out, and the sulfonic acid solution could be mixed with ether. The sulfonic acid would then form a third layer, in the separatory funnel. After several trials it was found that when sulfonated technical mixture was poured into three times its volume of ice water, the para could be precipitated and removed by the suction filter. When ether is added to the filtrate a third layer of ortho-chloronitrobenzene sulfonic acid will form between, the ether and water-sulfuric acid. The sulfonic acid can now be separated with separatory funnel and washed (a) with water to remove excess sulfuric acid (b) with ether to remove any unsulfonated material. This when dry proved to be fairly pure.

When the solution is not diluted sufficiently the sulfuric acid keeps the sulfonic acid in solution and the ether cannot aid in its extraction; on the other hand when too much water is added the separation is not brought about either. The strength of the sulfuric acid must be approximately 20%.

Having obtained the para chloronitrobenzene from the eutectic mixture and obtained pure ortho chloronitro

benzene sulfonic acid, the next step in the procedure is the splitting off of the sulfonic group thereby obtaining ortho chloronitrobenzene. This was attempted in several ways, none of which was found to be satisfactory.

Outline of the Methods Used for Splitting
off the Sulfonic Acid (HSO_3) Group.

The general methods were to boil with reagents (given below) both under ordinary conditions and under pressure. The sulfonic acid was treated with steam at room conditions and under pressure. At no time was there any evidence that the sulfonic group had been affected.

1. Boiling with $\text{Ba}(\text{OH})_2$ at atmospheric pressure.
2. " " " under pressure, 160° - 170° in an autoclave
3. Boiling in HCl in a pressure tube, 130° .
4. " " " " " bottle in autoclave, 150° - 160° .
5. " " H_2SO_4 in a " tube, 150° .
6. " " " " " bottle in an autoclave, 150° - 160° , $3\frac{1}{2}$ hours.
7. " " Ba Cl_2 in a pressure bottle to 140° .
8. Steam with reflux condenser.
9. Superheated steam.
10. Steam distillation. Sulfonate heated to 200° and dry steam passed in.

II. Solubility Method.

It will be noticed that after preparing the pure para-chloronitrobenzene its solubility in several solvents was determined with great care. The principal object of these determinations was to see if it would not be possible to separate the technical mixture by means of its solubility in one or other of the solvents. The literature mentioned the fact that Markwald had made a separation with methyl and ethyl alcohols above the melting point of the eutectic mixture. A photo copy of his patent was sent for. In the meantime several attempts were made with very little practical success. A few crystals of ortho were obtained when the solvents in some cases were allowed to evaporate spontaneously. The yield was so small that no determination of amounts was made. This method of separation was then given up till Markwald's patent (24) should arrive.

His process is outlined under "Historical" (p.18) of this paper. It was far too inefficient to be of technical value. From 100 kg of the technical mixture he obtained only .9 kg of para and 1.8 kg of ortho-chloronitrobenzene, a yield of only 2.7% of the theoretical.

It has probably been noticed the solubility determinations of the ortho derivative are by no means as complete as those of the para. The inefficiency of the Markwald separation and of others made during this research is the explanation. The time was limited and a method of separation was

Curves showing the comparative solubilities of the ortho and para isomers in 92.44 per cent ethyl alcohol.

Ortho.

Para.

120

110

100

90

80

70

60

50

40

30

20

10

0

0°

5°

10°

15°

20°

25°

30°

35°

Curves showing the comparative solubilities
of the ortho and para isomers in 68.4 per cent
ethyl alcohol.

Ortho.

Para.

preferred to the very exact solubility determinations.

III. Fractional Distillation and Crystallization.

There was a reference in the December "Color Trade Journal" to a German Patent (23) in which the separation of the technical mixture into its isomers was brought about by fractional crystallization and distillation. The boiling points of the pure ortho and para chloronitrobenzenes are given as 243° and 242° respectively, in Beilstein. Some one, no reference to whom could be found, had again determined the boiling points and found that for ortho to be 245.5° C at 750 mm pressure and that for para to be 238.5° C at the same pressure. Under reduced pressure the boiling points are 119° ortho and 113° para. The assertion was made that "although the difference is not great it allows them to be separated by fractional distillation and crystallization". No further data could be procured; so with the idea of bringing about a technical separation by reduced pressure, fractional distillation and crystallization, the next experiments were carried out.

Three different types of stills and still-heads were used. There were several experiments performed with each, but a description of the work done with each kind will suffice here.

Below is a drawing of the first type.

A. An Ordinary Distillation Apparatus (see above fig.)

An ordinary 500 cc side-neck distillation flask was fitted to a condenser, the receiver of which was attached to the suction pump. A paraffin bath was used to heat the flask. 200 gm of the technical mixture were used in this trial. For a while the liquid boiled nicely at 113° and 12 mm pressure and a yellow liquid came over. This crystallized on cooling. The liquid in the flask began to "bump" and some of it bubbled over into the receiver. For this reason it was obvious that a change would have to be made in the apparatus. The experiment was continued, however, till there were about 100 gm in the receiver. Distillation was discontinued; the two portions crystallized. That in the receiver, which should have contained most of the para, was cooled to 16° , and the other was cooled to between 15° and 16° . In both cases the crystals were gathered on a suction filter and recrystallized. A fairly good grade of para was obtained by this method. The ortho contained a quantity of the technical mixture and had to be recrystallized 4-5 times. The yield for the para should have been 66 gm approximately, but was really just a little over three grams or 5% theoretical. The amount of ortho should have been theoretically 132 gm but was in reality about

5 gm or a little less than 4%.

However, some of both isomers had been obtained and it had been proved that some of the mixture could be separated. Then the next problem was to get a better and more efficient apparatus.

B. Large Flask with Still-head. (see fig. below)

The operation in this case was essentially the same as in the first. There were some changes in the still, however, that will be described. The flask this time was large and pear-shaped, about $2\frac{1}{2}$ liters in size. The three-hole stopper was equipped with a thermometer, a Kjeldahl still-head, and a tube the capillary point of which dipped under the liquid to keep down excessive bubbling. The upper end of it was fitted with a rubber tube closed by a screw clip. This let in a small stream of air, which, with the glass beads, lessened the bubbling and bumping so that none of the mixture was forced over.

A 1000 gm of the technical mixture was used and at 110° and 10 mm pressure a yellow liquid distilled steadily. After about 500 gm had been collected, the process of crystallization and recrystallization was repeated as described in process A. (Note: after each crystallization the mother

liquor is preserved for the next distillation).

The yields for this experiment are :

<u>Isomer</u>	<u>Theoretical yield</u>	<u>Experimental</u>	<u>Efficiency</u>
Ortho	666 gm	60 gm	10%
Para	333 gm	50 gm	15%

This was such an improvement over the previous experiment that another attempt was made with a still that was thought might yield better results.

C. Still-head Made in Laboratory. (see fig. below)

A still-head such as is shown in the drawing was made from T-tubes. A large flask with a tubulature in the side was fitted with the head, the condensed liquids from which were allowed to flow back into the flask thru the opening. The end of the tube, which was of capillary size, dipped under the surface of the boiling mixture.

In to the flask was poured 1200 gm of the technical mixture. The first came over this time at a temperature of 112° and a pressure of 10-12 mm.

Crystallization and recrystallization this time brought the following results:

<u>Isomer</u>	<u>Theoretical Yield</u>	<u>Practical Yield</u>	<u>Efficiency</u>
Ortho	800 gm	160 gm	20%
Para	400 gm	120 gm	30%

This was 160 gm Ortho-chloronitrobenzene after recrystallization from alcohol in which there was some wastage.

INDICES OF REFRACTION OF ORTHO AND PARA MIXTURES.

Holleman has compiled a very complete table to determine the percent of ortho and para-chloronitrobenzenes present in a mixture of the two. His method is that of the determination of the melting point and is very accurate and rapid.

The indices of refraction of several mixtures was made with a view of making a table from which the percentage composition could be ascertained. The method is not at all practical because with the purest compounds the variation was only one point in the third place to the right of the decimal. Should there be even the slightest impurity present, the method would not be a very reliable one.

CONCLUSION

I.

Pure para- and pure ortho-chloronitrobenzenes have been prepared.

II.

The melting point of pure para chloronitrobenzene was found to be 82.8° .

The melting point of pure ortho-chloronitrobenzene was found to be 32.2° .

III.

The indices of refraction were determined but were found to be of doubtful importance.

IV.

The sulfonation process is by far the most efficient for effecting the separation of the ortho and para chloronitrobenzenes in the technical mixture as far as obtaining a nearly theoretical yield of para is concerned. But, as yet the valuable ortho cannot be recovered from the orthochloronitrobenzene sulfonic acid. However, the sulfonic acid may eventually prove to be of importance, for, if it can be converted into the 2-amino-1-hydroxy-5-sulfonic acid derivative of benzene, it will be a valuable compound in the synthesis of dyes and other useful products. Some experiments have been undertaken to produce this compound by boiling with KOH and reducing with tin and HCl. As yet it is too early to give the results of these experiments.

V.

Markwald's method is far too inefficient to be considered a commercial process; not only are the yields by no means near theoretical, but the cost of the solvents, even though they might be recovered, makes the process prohibitive.

VI.

Of the three processes, that of fractional distillation and crystallization is the most satisfactory for separation of the technical mixture into its two constituents. Not only are the pure para and pure ortho-chloronitrobenzenes obtained but the method is not too complicated or expensive to be of technical value. With such apparatus as was at hand the yield was 20% theoretical. With a good still, copper or otherwise, and a more efficient still-head there should be no trouble at all in obtaining at least a 30% yield. It might be even possible to secure a more nearly theoretical yield.

VII.

One method, which was not investigated, was that of converting the ortho and para chloronitrobenzenes into dihydroxy phenols and separating by distillation in steam. The ortho is readily volatile in steam while the para derivative is only so with great difficulty.

VIII.

Another method, which was planned after reading Kolbe, was not undertaken in this research, but might be of value. If the technical mixture was heated 2-3 hours at 250°-270° with alcoholic KCN the para would probably form the

chlorobenzene cyanide which could be readily hydrolyzed to the acid by boiling in water. The ortho is not affected by the cyanide. Whether this would be a method of separation or not remains to be worked out.

IX.

It might be stated further that the method suggested by A.A. Noyes and others for the electrolysis of the para - chloronitrobenzene to the corresponding amino phenol sulfonic acid is being tried on the ortho-chloronitrobenzene sulfonic acid. The object is to obtain the amino phenol of the ortho compound. This would make the sulfonation process of separation a very valuable^{one} from the commercial point of view as the amino-phenol-sulfonic acid is used for making dyes and other things.

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ABBREVIATIONS

Ann. Chem. Pharm. - Liebig's Annalen der Chemie und Pharacie.

Ber. - Berichte der Deutschen Chemischen Gesellschaft.

Z.- Zeitschrift für Chemie von Beilstein, Fittig, und Hübner.

A. - Abstracts of the Chemical Society.

Jahresber. d. Chem. - Jahresberichte über die Fortschritte der
Chemie.

Rec. P.B.- Recueil des Travaux chimiques des Pays - Bas.

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