
Theses and Dissertations

1919

A study of paradichlorobenzene

Joyce Homer Crowell
State University of Iowa



This work has been identified with a [Creative Commons Public Domain Mark 1.0](#). Material in the public domain. No restrictions on use.

This thesis is available at Iowa Research Online: <http://ir.uiowa.edu/etd/4108>

Recommended Citation

Crowell, Joyce Homer. "A study of paradichlorobenzene." MS (Master of Science) thesis, State University of Iowa, 1919.
<http://ir.uiowa.edu/etd/4108>.

Follow this and additional works at: <http://ir.uiowa.edu/etd>

UNIVERSITY OF IOWA
LIBRARY

A STUDY OF PARADICHLOROBENZENE.

XXXXXXXXXXXXXXXX

18031
19
847

A Thesis
Presented to the Faculty of the Graduate College
of the
State University of Iowa
in Partial fulfilment of the Requirements
for the Degree of
Master of Science.

-by-

Joyce Homer Crowell.

July, 1919.

Archives
T1919
C953

A STUDY OF PARADICHLOROBENZENE.

Historical. The formation of a dichlorobenzene was first observed in 1862 by Müller (Soc., xv, 41, 1862.), who obtained it along with other products, by passing chlorine into a benzene solution of iodine; but there is nothing in the papers cited to indicate that he gained, through this work, any insight into the structure of the compound in question beyond the fact that it was a substitution product. In 1865, Jungfleisch (Bull., ii, 241, 1865,) confirmed Müller's observations on the dichlorobenzene melting at 53°, and added a statement indicating the analysis, the crystalline form and several important properties of the compound. Kekule' had meanwhile formulated his theory of the benzene ring in several papers (Bull., i, 99, 1865; ii, 40, 1866; Ann., 137, 129, 1866.) and in one of these (Bull., i, 99, 1865.) he predicted ^{the} existence of three isomeric modifications of dichlorobenzene. Next, he obtained evidence (Bull., ii, 200, 1867.) which led to the view that three isomeric dihydroxy-derivatives of benzene might be obtained from the disulfonic acids, which tended to support the prediction mentioned above. These relationships, however, were still more clearly indicated by work done by Barbaglia and Kekule' (Ber., 5, 876, 1872.) who found that paraphenolsulfonic acid reacted with phosphorus pentachloride to give, among

Chlorine
112011815HERTZ
1.85

other products, a dichlorobenzene identical with Müller's product; while Petersen (Ber., 6, 373, 1873.) pointed out that this compound corresponded in general properties (melting point, etc.,) with, and must belong in the same series as, the 1,4-dibromobenzene which V. Meyer (Ber., 3, 753, 1870.) had converted into terephthalic acid. Kekule' next noted (Ber., 6, 943, 1873.) that the dichlorobenzene under consideration could be prepared by the action of phosphorus pentachloride on parachlorophenol and that the structure of the latter was fixed by the fact that upon being melted with potassium hydroxide *it* gave hydroquinone (Ber., 7, 61, 1874.; Ann., 157, 127, 1871.). Evidence summarized by Petersen (Ber., 6, 377, 1873; 7, 58, 1874.) led to the same view. Further study of the action of chlorine on benzene showed that when the amount of chlorine used is that required to form a disubstituted compound, the product always represents a mixture. Thus, Beilstein and Kurbatow (Ber., 7, 1395, 1874.) found that by chlorinating a large quantity of benzene they obtained a small quantity of a liquid dichloro-compound which they at first thought was the ortho isomer, but which they subsequently recognized (Ber., 7, 1760, 1874.) as a mixture, through its action with nitric acid, and in which

they were finally able to identify both ortho and para dichlorobenzene by the differences in behavior of these isomers towards sulfuric acid. Later, Thomas (Compt. rend., 126, 1212, 1898.) obtained paradichlorobenzene by heating monochlorobenzene with ferric chloride, while Mouneyrat and Pouret (Compt. rend., 127, 1025, 1898.) found that the action of chlorine on monochlorobenzene, or on benzene, gave a mixture of the three isomeric dichlorobenzenes, along with other products. Other catalysts, such as iron or ferric oxide have been used, but all lead to a mixture of products.

Paradichlorobenzene as a By-product. The extended study of the action of chlorine on benzene has been stimulated, in large measure, by the technical importance of the monochlorinated product, which, as is well known, is used in the preparation of picric acid. Some idea of the extent to which the dichlorinated products are formed at the same time, even when the reaction is carried out in accord with the best technical practice, is obtained from Ullman's figures. (Enzyklopädie der technischen Chemie, vol. II, p.370.). A mixture of 300 kg. of benzene, 1 kg. iron, 1 kg. ferric chloride and 156 kg. of chlorine give a mixture of 335 kg. of mono-

chlorobenzene, 24 kg. of pure paradichlorobenzene and 3 kg. of dichlorobenzene mixture, the nature of which is not further specified. From this, which is supported by similar data from other sources, it is seen that paradichlorobenzene is a plentiful by-product and that the finding of an application for it, as such, or the development of a process by which it could readily be converted into products of technical importance would be an interesting piece of work. Apart from the fact that it can be converted into paraphenylenediamine on a semi-technical scale (C.,ii,122,1908.), it has practically no industrial value. It seemed, therefore, a matter of interest to investigate more closely than had been done heretofore some of the chemical characteristics of this substance, with the hope of finding, perhaps, some reaction that might lead to a technical application.

Among the reactions that suggested themselves in this connection were the following:

- a) The removal of one or both chlorine atoms and their replacement by hydroxy¹ or other groups.
- b) The introduction of the nitro group and the study of the derivatives obtainable therefrom.

(c) The introduction of the sulfonic acid group and the study of the resulting derivatives.

(d) The preparation of some of the nitrosulfonic acids with some of their derivatives.

The attempts to replace halogen with hydroxyl were made in accordance with the method employed by Meyer and Bergius (Ber., 47, 3155, 1914.) in studying the behavior of monochlorobenzene. A number of experiments were carried out, but the high pressure that developed prevented a satisfactory test of the method by use of the apparatus then available. ** The introduction of the nitro group seemed especially desirable for two reasons. First, the nitro compounds can be easily reduced to the corresponding amino compounds which are quite reactive. In the second place, the presence of a nitro group in an aromatic compound often "activates" or has a loosening effect on other substituents, especially halogen atoms. (Ber., 37, 3892, 1904; Ullman, Enzy. der tech. Chemie, vol. II, p. 379.).

** Note. Since that time, a specially designed autoclave has been secured and it is hoped to repeat the experiments mentioned above.

Nitration of Paradichlorobenzene. In this work, the mononitro compound, 2,5-dichloromononitrobenzene, was obtained in good yield ^{the} by use of Morgan's method (Soc., 81, 1382, 1902.). Several experiments were made in order to determine the optimum conditions for nitration and special care was taken to avoid the formation of isomers through the introduction of more than one nitro group. The further identification of my product with that described by Morgan was secured by a repetition of Laubenheimer's work (Ber., 7, 1600, 1874.) on the reduction of the nitro compound in alkaline solution, with the formation of the azoxy compound accompanied by portions of the corresponding phenol and aniline. Alkaline reduction of my product by means of zinc dust and alcoholic sodium hydroxide in an effort to obtain the analogous hydrazo compound was unsuccessful. German investigators report that by electrolytic reduction even the corresponding benzidine is formed, but no details of the method, isolation or properties of the hydrazo or benzidine compounds are given. (Zeit., fur Elek., 4, 606, 1898.). Alcoholic ammonium sulfide was found after several days to have formed slightly yellow crystals melting at 149° , probably the $(C_6H_3Cl(SH)_2N_2S)$ compound noted by Beilstein

and Kurbatow (Ber., 11, 2056, 1878; C., 67, 1879.)

2,5-Dichloraniline and Derivatives. The reduction of 2,5-dichloronitrobenzene in acid solution was next considered, because the corresponding aniline has some interest as a starting material in the preparation of azo dyes (Ullman. Enzy. der tech. Chemie. vol I, p. 439.). Noelting and Kopp (Ber., 38, 3505, 1905.) have studied this aniline and its derivatives in considerable detail, and have described certain azo dyes made from it. In my work, it was found to give, in addition, a dye similar to aniline black, and also one having the general characteristics of the nigrosines. The aniline was next sulfonated and the structure of the resulting sulfanilic acid determined by oxidation with chromic acid mixture to ^{the} corresponding quinone (M.P. 160° uncorr.) Ber., 13, 1426, 1880; Soc., 61, 558, 1892.) and the reduction of the latter to 2,5-dichlorohydroquinone melting at 168° (uncorr.) (Ann. 210, 148, 1881.); all of which confirms the work of Noelting and Kopp.

2,5-Dichlorobenzenesulfonic Acid. Lesimple (Bull., ii, 266, 1868.) studied the action of sulfuric acid on a dichlorobenzene, evidently the para compound, as early

as 1868 and described a dichlorobenzenesulfonic acid and several of its salts. During the sulfonation he noted the formation of an insoluble body, which he thought was probably the sulfobenzid. Beilstein and Kurbatow (Ber., 7, 1760, 1874) found later that paradichlorobenzene reacts with sulfuric acid with much difficulty and then only incompletely even after long heating in a sealed tube at 230° , using massy, fuming acid, while on the other hand, the ortho compound was easily attacked on warming. Friedel and Crafts (A. 52, ii, 1101, 1887.)** used this difference in reactivity of the ortho and para compounds as a means of purification of the ortho isomer. Holleman and Van der Linden (Rec. trav. chim. 30, 305, 1911; C., i, 219, 1912, ; A., i, 20, 1912.) made this behavior the basis of a quantitative separation of the components of the mixtures obtained when they chlorinated benzene. They treated such mixtures with 95.2% sulfuric acid with the result that the monochlorobenzene was sulfonated and the three dichlorobenzenes were not attacked. They also found that a sulfuric acid containing 0.3 % of free sulfur trioxide sulfonated the ortho and meta isomers but not the para; however, if the free sulfur trioxide exceeded the above amount the para com-

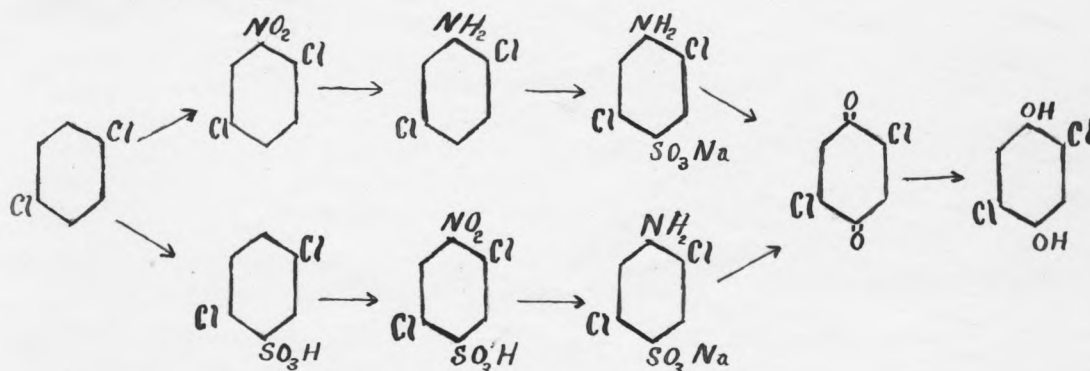
** Note. The original article (Ann. chim. Phys. (6), 10, 411.) was not available.

pound was sulfonated. They also sulfonated the para compound alone and identified their product by the preparation of the chloride, amide and barium salt. My work confirmed their results and my acid was identified by the preparation from it of the sodium salt, which was separated by Langmuir's method (Ber., 28, 91, 1895.). The free acid had the characteristics ascribed to it by Lesimple (loc. cit.).

2,5-Dichloro-4-nitrobenzenesulfonic Acid. So far as I am aware, no mononitro sulfonic acid derived from paradichlorobenzene has been reported in the literature, although similar derivatives of the ortho and meta isomers are known (C., ii, 750, 1904; ii, 1537, 1906.) Certain important uses of the latter, both as synthetic reagents or as technical intermediate products, are dependent upon the "loosening" effect mentioned above. This effect is well exemplified by the comparative ease with which aqueous ammonia replaces both of the halogen atoms in 2,4. dichloro-5-nitrobenzenesulfonic acid (C., ii, 752, 1900.) forming a substituted metaphenylenediaminesulfonic acid which was used in the pre-

paration of some dyes belonging to the Primulin type. It was therefore, a matter of considerable interest to investigate the action of fuming nitric acid upon the acid derived from paradichlorobenzene by sulfonation. It may be noted here, at once, that this is probably the only method by which this acid can be obtained; for all attempts to sulfonate the 2,5-dichloronitrobenzene were unsuccessful. Many experiments with varying concentrations of acid showed that no sulfonation took place below 150° , but above that temperature, complete decomposition with violent carbonization occurredⁿ. The action of fuming nitric acid on the sulfonic acid, alone or in the presence of sulfuric acid, gave a mono nitrated product. The constitution of this acid was determined by the reduction of its sodium salt, and the preparation and study of several of its derivatives. The amino compound was shown to be identical with the sodium salt of the paradichlorosulfanilic acid described by Noelting and Kopp (loc.cit.), by oxidation to the corresponding quinone, the structure of which is known, and also by the reduction of the latter to its corresponding hydroquinone. The acid was further characterized by the preparation and analysis of several of its salts, a description

of which is found in the experimental part of this paper. These changes may be briefly summarized by the following steps:



Sodium Salt of 2,2'-5,5'-Tetrachloro-4,4'-Azobenzene disulfonic Acid. Alkaline reduction of the sodium salt, by use of alcoholic sodium hydroxide gave a dark red solution, very likely a mixture of the azo and azoxy compounds. Zinc dust, sodium hydroxide and water, after passing through the red stage, led to an almost colorless solution, probably the hydrazo compound. However, on attempting to isolate this compound it began to oxidize and turn dark and soon became red. This change was accelerated by shaking or heating. The red substance was isolated and analyzed and the results of the analysis were consistent with those calculated for the azo compound.

EXPERIMENTAL PORTION

Paradichlorobenzene, $C_6H_4Cl_2$. The material used in this research was obtained from the Dow Chemical Co., and consisted of white, massy transparent crystals, melting sharply at 53° (uncorr.). It was free from the ortho and meta compounds, which are liquids at ordinary temperatures and was used without further purification.

2,5-Dichloronitrobenzene, $C_6H_3Cl_2NO_2$. Two parts by volume of nitric acid varying in specific gravity from 1.46 to 1.55 and three parts by volume of sulfuric acid (1.84) were mixed and, after cooling, a volume of this mixture equal to one and one-half times the number of grams of the dichlorobenzene were taken for the nitration. The mixed acid was added in four or five portions, the last portion causing little or no evolution of heat. The end of the reaction was reached in about half an hour and the flask was well shaken throughout the operation. The reaction mixture was then placed upon the water bath for an hour or so in order to complete the action. The recovery of the product was quite simple; the mixture being poured, with much stirr-

ing, into cold water where it solidified into a yellow mass. Then, after being ground finely in a mortar and well washed with water and dilute alkali, it was oven dried at a temperature of about 40° and finally recrystallized from alcohol. The yield was very nearly theoretical. 2,5-dichloronitrobenzene crystallizes in thick plates with a pale yellow color and a faint, sweetish odor resembling that of nitrobenzene, M.P. 54.5° (uncorr.). This agrees with Morgan's work (loc. cit.). It is insoluble in water but is quite soluble in hot organic solvents.

2,5-Dichlorobenzenesulfonic Acid, $C_6H_3Cl_2SO_3H$.

One hundred and fifty grams of the pure dichlorobenzene were placed in an Erlenmeyer flask and mixed with 225 grams of fuming sulfuric acid containing 10-12 % of free sulfur trioxide and having a density of 1.88. ** The mixture was then heated to $140-150^{\circ}$ and

** Note. Holleman and Van der Linden [loc.cit.] used seven and one-half parts of an acid containing 10% sulfur trioxide at ordinary temperatures and acting for twenty-four hours time.

thoroughly stirred by means of a mechanical stirrer. After about 45 minutes the two layers had disappeared and the mixture, which was quite dark, was, after cooling somewhat, slowly poured into a large amount of cold water, which separated out the unchanged material together with some of the tetrachlorodiphenylsulfone. About 30-35 gms. of these substances were filtered off and the filtrate concentrated, whereupon the acid separated out in long, rhombic colorless needles. Recrystallization from water removed practically all of the sulfuric acid. A yield of about 85-90% was obtained. A portion of the acid solution was poured into saturated salt solution and the sodium salt precipitated. On recrystallization from hot water, this separated out in glittering hexagonal plates or in long silky needles. The plates contained one molecule of water of crystallization and had a tendency towards efflorescence. A sample heated to constant weight at 110° , gave the following results:

.5233 gm. gave .0338 gm. H_2O .

Calc. for $C_6H_3Cl_2SO_3Na, H_2O$: H_2O 6.74.

Found: H_2O 6.46.

2,2'-5,5'-Tetrachlorodiphenylsulfone, $(C_6H_2Cl_2)_2SO_2$.

About 25 or 30 grams of this substance were formed in the above sulfonation. It is not very soluble in cold alcohol, but is more soluble in the hot liquid, out of which on cooling, it crystallizes, in colorless, small, thick, diamond-shaped crystals, whose sides are parallelograms. It is quite soluble in hot benzene but is insoluble in water. M. P. 179° (uncorr.). Since it has not been reported in the literature, it was analyzed for chlorine.

.5262 gm. gave. 8438 gm. AgCl (Carius).

Calc. for $(C_6H_2Cl_2)_2SO_2$: Cl 39.84.

Found : Cl 39.67.

2,5-Dichloro-4-nitrobenzenesulfonic Acid, $C_6H_2Cl_2NO_2SO_3H$.

This acid was prepared by treating 75 grams of the paradichlorobenzenesulfonic acid with a mixture of 54 cc. of nitric acid (1.6) and 32 cc. of sulfuric acid (1.84). Such a mixture approximates that one found by Saposchinikoff (J. Russ. Phys. Chem. Soc. 36, 518, 1904; A., ii, 558, 1904.) to have the maximum pressure which, according to his results, contains nitric acid, sulfuric acid and water very nearly as represented by the

formula $5 \text{HNO}_3 + 2 \text{H}_2\text{SO}_4 + 3 \text{H}_2\text{O}$. The mixture was then boiled down until it crystallized out on cooling. This acid was also prepared by treating 35 grams of the sulfonic acid with 50 cc. of nitric acid (1.6), which mixture was then boiled down to a syrupy state. On standing for a day or two, bushy, burr-like crystals composed of flat yellow needles appeared. Successive recrystallization from water was used as a means of purification. The acid is quite hygroscopic and apparently has a melting point near 150° . It is not soluble in organic solvents to any noticeable extent. On account of these properties, it has not yet been possible to prepare a perfectly pure sample of the acid; therefore, analysis can not be given at this time. However, as several of its salts and derivatives were prepared and analyzed, its composition and structure are fixed without doubt.

The Salts of 2,5-Dichloro-4-nitrobenzenesulfonic Acid. $\text{C}_6\text{H}_2\text{Cl}_2\text{NO}_2\text{SO}_3\text{Me}$.

The Sodium Salt., $\text{C}_6\text{H}_2\text{Cl}_2\text{NO}_2\text{SO}_3\text{Na}$. This compound was prepared by salting out the free nitro acid from the nitration mixture and also by nitration of the

sodium salt of the sulfonic acid. 50 gms. of the sodium salt were treated with 50cc. of fuming nitric acid (1.6) and heated for several hours under a return condenser, after which, 40cc, more of the acid were added and the heating continued. On evaporation of the excess nitric acid, the sodium nitro sulfonate was left as a pale yellow, amorphous powder. It was purified by recrystallization from water. About 90% of the salt was nitrated. It crystallizes in thin, wing-like scales or leaflets with a tendency towards clumping together. It is easily soluble in hot water, from which it crystallizes with one molecule of water of hydration. It is not easily soluble in organic solvents. Analyses for water of crystallization, for halogen and for sodium were made with the following results:

** 1) 2.5005 gm. gave. 1386 gm. of H_2O .

2) .8124 gm. gave. 0455 gm. of H_2O .

Calc. for $C_6H_2Cl_2NO_2SO_3Na, H_2O$.: H_2O 5.77.

Found : H_2O 1) 5.54 2) 5.61

** Note. With the exception of 1), the analyses given were made upon portions of the same sample.

.5464 gm. gave .5434 gm. AgCl (Carius).

Calc. for $C_6H_2Cl_2NO_2SO_3Na$: Cl 24.12.

Found : Cl 24.57.

.8273 gm. gave .2013 gm. Na_2SO_4 .

Calc. for $C_6H_2Cl_2NO_2SO_3Na$: 7.82.

Found : Na 7.87.

The Potassium Salt, $C_6H_2Cl_2NO_2SO_3K$. This substance was prepared by salting it out from a saturated potassium chloride solution with the free nitro acid in the manner used to obtain the sodium salt. It has practically the same solubilities as the sodium salt, crystallizing out of water in faint yellow, flat, bushy needles that tend to cluster in the form of nodules and separating with one molecule of water of hydration. Analyses for water and for potassium gave the following results:

1.0454 gm. gave .0553 gm. H_2O .

Calc. for $C_6H_2Cl_2NO_2SO_3K, H_2O$: H_2O 5.47.

Found : H_2O 5.29.

.7354 gm. gave .2081 gm. K_2SO_4 .

Calc. for $C_6H_2Cl_2NO_2SO_3K$: K 12.61.

Found : K 12.69

The Ammonium Salt. $C_6H_2Cl_2NO_2SO_3NH_4$. This salt was prepared by the addition of aqueous ammonia in excess to the solution of the free nitro acid and followed by concentration of the solution. It crystallized out of the aqueous solution in lemon-yellow tufts of flat, grass-like needles, sometimes clustering together to form hard balls. It is easily soluble in water. It was analyzed for the ammonium radical.

.7552 gm. gave. 0446 gm. NH_3 .

Calc. for $C_6H_2Cl_2NO_2SO_3NH_4$: NH_3 5.88.

Found : NH_3 5.91.

The Barium salt. $(C_6H_2Cl_2NO_2SO_3)_2Ba$. This compound was made by the action of barium nitrate upon the sodium salt and obtained as a precipitate by mixing the solutions of these salts. It is sparingly soluble in water out of the hot solution of which it separates in thin, sharp-pointed leaflets looking like peach leaves and clustering together in rosette-like forms. It was analyzed for barium with the following results.

.2553 gm. gave. 0882 gm $Ba SO_4$.

Calc. for $(C_6H_2Cl_2NO_2SO_3)_2Ba$: Ba 20.22.

Found : Ba 20.32.

Proof of the Constitution of the Acid, $C_6H_2Cl_2NO_2$
 SO_3H .

Some of the sodium salt was reduced with tin and hydrochloric acid in the usual manner and the resulting sodium dichlorosulfanilate was recrystallized out of the mixture from which it separated in the form of white, shining leaflets. Its solution slowly turned red on standing exposed to the air. Analysis for halogen gave results consistent with formula below.

.4230 gm. gave .4600 gm AgCl (Carius).

Calc. for $C_6H_2Cl_2NH_2SO_3Na$: Cl 26.85.

Found : Cl 26.89.

This salt was further identified by the preparation of its acetyl derivative, which was carried out by heating it with acetic anhydride in the usual way. The product is easily soluble in hot water, from which it was crystallized in the form of colorless masses made up of long, thin needles, having the appearance of cotton. It was analyzed for nitrogen by ^{the} Kjeldahl method.

.2985 gm. required 6.95 cc. of .1427 N. HCl
 for neutralization of the NH_2 .

Calc. for $C_6H_2Cl_2SO_3NaNHCOCH_3$: N 4.58.

Found : N 4.65.

Five grams of the sodium salt, prepared as described above were mixed with a solution containing 9 gms. of sodium dichromate dissolved in 35 cc. of water and 14 cc. of concentrated sulfuric acid dissolved in 80 cc. of water. The temperature was kept below 10° , while the mixture was constantly agitated by means of a mechanical stirrer. The 2,5-dichloroquinone was formed in yellow needles and after recrystallization from alcohol, melted sharply at 160° . To show that this product was identical with that prepared by Noeltling and Kopp (loc. cit.), a sample of the latter was prepared by the method described by these chemists. This product also melted at 160° , and a mixture of this with the quinone obtained from my acid melted at the same temperature as either of them separately, which indicates their identity. The conclusion, therefore, is, that the nitro and sulfonic acid groups are in the para position to each other.

Sodium Salt of 2,2'-5,5'-Tetrachloro-4,4'-azobenzenedisulfonic Acid, ($\text{SO}_3\text{Na C}_6\text{H}_2\text{Cl}_2$) 2N_2 .

This was formed by the alkaline reduction of the sodium salt of the nitrosulfonic acid and also by re-

duction in weakly acid solution. 10 gm. of the recrystallized sodium salt were treated with 15 gm. of zinc dust (added in three portions), 1 gm. of sodium hydroxide and 10 cc. of water. The mixture was warmed and the reaction completed by boiling until it became faint brown or nearly colorless. On filtering, it rapidly became red and dark brownish red on boiling. When the solution seemed to have become as dark as it would get to be, it was allowed to crystallize out. On recrystallization from 95 % alcohol it formed long, double wedge-shaped yellowish red crystals with thin, pointed ends. It contains some water of crystallization, the amount of which was not determined, and on complete dehydration, it forms a dark, grayish-brown, amorphous powder. This powder is quite soluble in water, giving a deep red solution. Analysis of the dehydrated product for sodium gave figures that agree with the formula given below.

.2970 gm. gave .0800 gm Na_2SO_4 .

Calc. for $(\text{C}_6\text{H}_2\text{Cl}_2\text{SO}_3\text{Na})_2\text{N}_2$: Na 8.77.

Found : Na 8.72.

SUMMARY.

1. The details of a method of obtaining practically a quantitative yield of paradichloronitrobenzene have been worked out on a laboratory scale.

2. The results of Holleman and Van der Linden in the sulfonation of paradichlorobenzene were confirmed and the details of the method of preparation and isolation of the sodium salt described.

3. A new tetrachlorodiphenylsulfone, occurring as a by-product in the sulfonation of paradichlorobenzene was isolated and analyzed.

4. One of the nitrosulfonic acids of paradichlorobenzene, the 2,5-dichloro-4-nitrobenzenesulfonic acid was prepared and its structure determined.

XXXXXXXXXXXXXXXXXXXXXXX

-ACKNOWLEDGEMENTS-

The author wishes to take this opportunity to express his appreciation for the assistance and suggestions so generously given by Dr. L. Chas. Raiford, under whose supervision, the major portion of this research was done. Acknowledgements are also made to Dr. W.J. Karslake at whose suggestion this work was undertaken and under whose direction, a portion of it was completed.

BIOGRAPHY.

Joyce Homer Crowell was born in Monroe County, Iowa, and received his early education in the high school at Albia in the same county and also in the high school at Ottumwa, Wapello County, Iowa. After graduation in 1910 from the latter school, he taught the next two years in the public schools in and around Wapello County. He entered the State University of Iowa in the fall of 1912 and received the degree of Bachelor of Arts in the year of 1916. The year 1916-17 was spent as an assistant instructor in the chemistry department of the State University of Iowa. He held the position of Instructor in Chemistry during the years of 1917-18 and 1918-19 in the above University. He is a member of Sigma Xi and Phi Beta Kappa fraternities and also of the American Chemical Society.