Summary

A survey has been made of all existing data on the vapor density of formic acid. There is complete agreement between the measurements made by Coolidge and those of Ramsperger and Porter. Traces of impurities were probably responsible for the discordant results of the earlier investigators.

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SOME PROPERTIES AND TRANSFORMATIONS OF ORTHO-DICHLORO-4-NITROBENZENE[1,2]

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Introduction

Beilstein and Kurbatow[3] found that 4-nitro-*o*-dichlorobenzene formed in two modifications when *o*-dichlorobenzene was treated with fuming nitric acid. They describe a semi-fluid mixture from which the solid part settles out and can be crystallized from alcohol in long needles of m. p. 43° and b. p. of 255–256°. Holleman[4] has studied the nitration of the dichlorobenzenes and found that when the ortho compound is dropped into nitric acid cooled to 0 or 30° the 1,2-dichloro-4-nitrobenzene is the principal product along with small amounts of isomers. His work on its physical constants agrees with those of Beilstein and Kurbatoff but he makes no mention of a liquid form.

In connection with some work to prepare *o*-chloro-*p*-nitraniline, we found that the nitration of *o*-dichlorobenzene always gave us a mixture of the liquid and solid forms of *o*-chloro-4-nitrobenzene. Since Beilstein and Kurbatoff give no information regarding any changes of the one form into the other and since the literature records no other nitro-*o*-dichlorobenzenes as liquids we decided to make a study of some of the properties and transformations of *o*-dichloro-4-nitrobenzene.

Experimental

Purification and Nitration of *o*-Dichlorobenzene.—The *o*-dichlorobenzene used in this work was prepared from the commercial material supplied us by the Monsanto Chemical Works. It was first distilled to remove any mono- and trichlorobenzene, the fraction between 165 and 200° being retained. One liter of this fraction was then cooled to −15° so that any of the para compound present would crystallize out and could be

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[1] In memory of Ira Remsen.

[2] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis Meeting, April, 1928.

[3] Beilstein and Kurbatow, *Ann.*, **176**, 41 (1875).

[4] Holleman, *Rec. trav. chim.*, **23**, 357 (1904).

filtered off. The filtrate was distilled, the fraction boiling between 174 and 180° being collected and cooled to −15°. This procedure was repeated and the fraction boiling between 177 and 180° was found to be free from the para isomer[5] by sulfonating a portion of the liquid with fuming sulfuric acid and pouring the mixture into water. By this process the ortho only is sulfonated. Any *p*-dichlorobenzene present would be unchanged and separate out in the water. If the aqueous solution of the *o*-dichlorobenzenesulfonic acid is then steam distilled, the *o*-dichlorobenzene will pass over. After drying and distilling, it was water white and had a sp. gr. of 1.299 at 20°.

In order to purify the material further it was nitrated and distilled with steam. *p*-Dichlorobenzene does not readily nitrate and, if present, can be blown out with steam. The nitro compound was then reduced with tin and hydrochloric acid. The reduced product was not removed from the mixture but was diazotized at once and boiled with water and an excess of caustic soda. The *o*-dichlorobenzene separated out, was drawn off, dried and distilled. In order to replace the diazo group by hydrogen we found that alcohol and other reducing agents were not necessary. The crystallizing point of the compound was found to be −17.5°. The "International Critical Tables" give it as −17.6°, whereas the Monsanto Chemical Works[6] have recently found it to be −16.7° on a sample prepared by a different method than just described.

One hundred and twenty-five cc. of the pure *o*-dichlorobenzene was nitrated, using 200 cc. of sulfuric acid of sp. gr. 1.84 and 175 cc. of nitric acid of sp. gr. 1.42. Nitration at 60° was easily effected in two hours with stirring. The nitro compound was separated, washed a number of times with water, dried over calcium chloride and distilled, the fraction between 254 and 257° being collected; yield, 95% of the theoretical. Nitration of 125 cc. of the *o*-dichlorobenzene was also accomplished in two hours at 60° by using 370 cc. of commercial mixed acid containing 57.3% of sulfuric acid and 33% of nitric acid; yield, 94% of the theoretical. A mixture of the liquid and solid forms was obtained.

Some Properties of *o*-Dichloro-4-Nitrobenzene.—The solid portion obtained above, when crystallized from alcohol or carbon tetrachloride, melts at 43°. When *o*-dichloro-4-nitrobenzene is kept at 15° the liquid form changes entirely to the solid form as long yellow needles of m. p. 43°. This would seem to indicate that no other isomer is present in the liquid form. We recognized the fact that a small amount of the *o*-dichloro-3-nitrobenzene (m. p. 62°) might be present. If, however, the material is kept at 25°, all of it changes to the liquid modification mentioned by Beilstein, the solid phase disappearing. Twenty g. portions of the material were kept for periods of eight hours each at various temperatures between 15 and 25°. It was found that an appreciable amount of the liquid was present at 17°. At 22° the material appeared to be half liquid and half solid. At 24° a very small quantity of the solid remained. The portion at 22° was rapidly filtered and the solid weighed. The crystals obtained weighed 10.1 g. Apparently the solid and liquid are present in equal quantities at this temperature. When the crystals were allowed to stand at 22° they gradually changed until about 50% of liquid was present. When the liquid was allowed to stand at this same temperature about 50%

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[5] The b. p. of the *o*-compound is 179–180° and that of the para 172°.

[6] Carswell, *Ind. Eng. Chem.*, **20**, 728 (1928).

of crystals formed. Of course the solubility of the solid form in the liquid is to be considered, but a number of experiments gave the same results. When the solid material was crystallized from alcohol or carbon tetrachloride, the crystals obtained did not change to the liquid modification. If some of the other *o*-dichloronitrobenzenes were liquids, it is quite possible that the liquid form of the 4-nitro compound would be a mixture of the solid form and the liquid dichloronitrobenzene, but such is not the case.

Action of Alcoholic Potash on *o*-Dichloro-4-Nitrobenzene.—There is no mention in the literature of the action of alcoholic potash on *o*-dichloro-4-nitrobenzene. Twenty g. of the liquid-solid mixture was refluxed with 40 g. of potassium hydroxide in 200 cc. of ethyl alcohol. When the reaction mixture reached 80°, a vigorous reaction set in and within five minutes was complete. The solution turned red and a dark red solid precipitated out. The solid, which proved to be 3,3′,4,4′-tetrachloro-azoxybenzene, was filtered off and recrystallized from carbon disulfide; 14 g. of crystals of m. p. 139° was obtained. The filtrate was poured into water and acidified with hydrochloric acid. A black, tarry mass formed. This was filtered off, warmed with caustic soda to dissolve the phenol and again filtered. The filtrate, when acidified with hydrochloric acid, had a very pronounced phenol odor. The liquid was extracted with ether and 0.5 g. of 2-chloro-4-nitrophenol, melting at 110°, was obtained. The residue obtained by heating the tarry mass with caustic soda was extracted with ether, from which was obtained 1.8 g. of 3,4-dichloro-aniline of m. p. 72°. The literature records 71.5°.

3,3′,4,4′-Tetrachloro-azoxybenzene was prepared by G. M. Kraay[7] by the oxidation in air of 3,4-dichloro-phenylhydroxylamine. He found the melting point to be 139–139.5°.

Action of *o*-Dichloro-4-Nitrobenzene with Sodium Alcoholates.—When *o*-dichloro-4-nitrobenzene is treated with solutions of various sodium alcoholates in the corresponding alcohol, ethers are formed, a chlorine group being replaced by O–R. In each case given in the adjoining table, 10 g. of *o*-dichloro-4-nitrobenzene was refluxed for two hours with the alcoholate, the mixture cooled and the solid which formed filtered off and washed with the corresponding cold alcohol. The solubility of the resulting ether in methyl alcohol, ethyl alcohol, benzene, ether and acetone was determined, as was also the melting point. A determination of the percentage of nitrogen in the compound also was made. Five g. of each nitro-ether was reduced with tin and hydrochloric acid. The resulting amine in most of the cases was diazotized and coupled with an alcoholic solution of β-naphthol, giving a dye.

We can find in the literature none of the ethers described except the

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[7] G. M. Kraay, "Dissertation," Amsterdam, 1926.

2-chloro-4-nitro-anisole which was prepared by Griess[8] by replacing the amino group of 2-amino-4-nitrophenyl methyl ether with chlorine. He records its m. p. to be 93–94°.

TABLE I

DATA ON THE ETHERS

Ether, 2-chloro-4-nitro-	Color and cryst. form	Yield, g.	Nitrogen, Calcd.	% Found	M. p., °C.	Color of amine dye
Anisole	Cream flakes	9.0	7.46	7.44	94	Purple
Phenetole	Dark brown cryst.	4.0	6.94	7.00	142	...
*Iso*propyl ether	Light brown flakes	4.5	6.49	6.45	128	Dark red
Phenyl-*n*-butyl ether	Brown flakes	8.4	6.10	6.10	136	Purple-red

The first of the above ethers is insoluble in cold or hot water, slightly soluble in ethyl alcohol and acetone and very soluble in these latter solvents when hot. It is also soluble in ether and benzene. The second ether is insoluble in water, cold ethyl alcohol and acetone but soluble in the last two when hot. The third ether is insoluble in water and slightly soluble in cold ethyl and *iso*propyl alcohols and acetone. It is also soluble in ether, benzene, hot ethyl alcohol and acetone. The last one is slightly soluble in acetone, soluble in ether and benzene and very much so in hot methyl and ethyl alcohols.

Summary

1. *o*-Dichloro-4-nitrobenzene was found to exist in a liquid and a solid modification, the two existing in approximately equal quantities at 22°.

2. Alcoholic potash on the compound gives mainly 3,3′,4,4′-tetrachloro-azoxybenzene and small quantities of 3,4-dichloro-aniline and 2-chloro-4-nitrophenol.

3. Four ethers of the compound were prepared, three of them for the first time. The 2-chloro-4-nitro-anisole had been previously prepared by a different method. Some of their properties are described. Three of these were reduced, diazotized and coupled with β-naphthol, giving red and purple dyes.

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[8] Griess, *Jahresber. Fortschritte Chem.*, **1866**, 459.