

방향족 디아민의 Tetrazo 화에 관한 연구 (제1보).
염산 및 과염소산 중에서 *p*-Phenylenediamine의 Tetrazo 화

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The Studies on The Tetrazotization of Aromatic Diamines (I).
Tetrazotization of *p*-Phenylenediamine in
Hydrochloric Acid and Perchloric Acid

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요 약. *p*-Phenylenediamine 을 과량의 진한 염산 및 과염소산을 매질로하여 거의 완전히 tetrazo 화 하였다. Tetrazonium 염의 두 diazo 기를 할로젠으로 치환하여 생긴 dihalobenzene 의 수량으로 반응의 정도를 알아 보았다.

이 반응의 성패는 tetrazonium 염의 안정도에 의하여 좌우되었으며, 그 안정도는 매질의 종류, 산도(농도) 및 그 양과 밀접한 관계가 있음을 알았다. 즉 산매질의 농도가 너무 묽으면 tetrazonium 염은 불안정하여 완전히 분해되었으며, 매질의 농도가 너무 진하면 tetrazonium 염은 안정한 반면에 tetrazo 화 반응이 방해되었다. 이 상반되는 두 경향을 조화시키기 위해서는 tetrazonium 염이 안정하게 존재할 수 있는 가장 낮은 농도의 산을 매질로 써야함을 알 수 있었다. *p*-Phenylenediamine 의 tetrazo 화에서는 약 40~45%의 산매질이 적당하였다.

H⁺이온이 부족매로 작용하는 것으로 보아 diazo 화 반응이 아민의 염의 상태에서 일어나는 것이아 아니고 유리상태의 아민과 nitroso group 사이에서 일어난다는 설이 타당함을 알 수 있었다. Tetrazo 화 반응을 diazo 화 반응의 kinetics 및 mechanism 과 관련시켜서 설명하였다.

Abstract. *p*-Phenylenediamine was tetrazotized with sodium nitrite in an excess amount of concentrated hydrochloric acid media at -10°C . It was also tetrazotized almost completely in 45% perchloric acid media. The two diazo groups in the tetrazonium salt were substituted by halogen, and the degree of tetrazotization reaction was observed by dihalobenzene yielded.

The result of the tetrazotization was dependent upon the stability of the tetrazonium salt, and the stability was determined by concentration and quantity of the acid media. In dilute acid media the tetrazonium salt was unstable and completely decomposed. In concentrated acid media, though the tetrazonium salt was stable, tetrazotization reaction was retarded. To harmonize the two opposing tendencies it was advisable to find the optimum acidity of media at which the salt

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was fairly stable. About 40-45% of the acid media was suitable.

The fact that the H^+ ion behaved as a negative catalyst supported the assumption that the diazotization reaction is primarily a reaction between the free amine and a nitroso group. The reaction of tetrazotization is expressed with respect to the kinetics and mechanism of diazotization.

Introduction

Although the properties of diazonium salts and the mechanism of diazotization were extensively investigated by many workers, the tetrazotization of aromatic diamines has been in a difficult situation. In previous communications, there were many trials on the tetrazotization of *p*-phenylenediamine and substituted ones. The efforts, however, failed in the diazotization of the both amino groups. Griess¹ found that it was impossible to convert *p*-phenylenediaminobenzoic acid into the tetrazonium compound. It has also been observed that nitrous acid converts only one of the amino groups of *p*-phenylenediaminosulfonic acid². Similar examples were shown by *o*-nitro-*p*-phenylenediamine³ and *p*-phenylenediaminoarsenic acid⁴. Cain⁵ and Morgan⁶ have failed to give a satisfactory explanation for the partial diazotization of *p*-phenylenediamines.

The earlier authors, including Schoutissen, have explained the failure of tetrazotization by normal method by saying that the basicity of these substituted aromatic diamines are remarkably reduced by the introduction of a extremely electronegative group, thus they do not have sufficiently high electron density to form an ammonium salt which, they thought, contributes to the diazotization.

p-Phenylenediamine also has not been tetrazotized by normal method though it has no substituents in the ring. Whereas the diazotization of one of the amino groups will not be troublesome and proceed in dilute mineral acid

in consequence of the relatively strong basic property of *p*-phenylenediamine. This was also interpreted by Schoutissen to mean that the first diazonium group being strongly electronegative, it will reduce the basicity of the second amino group in para position to a great extent, therefore diazotization of the second amino group will not be expected. Then, he emphasized to use high concentration of mineral acid media to form a sufficient amine salt which contributes to the diazotization.

The authors found that the above explanation was not correct and the failure was due to the stability of the tetrazonium salt, which was stable only in the high acidity. Although tetrazonium salt was stable at high acidity of the media, the formation of the salt was retarded rather than accelerated.

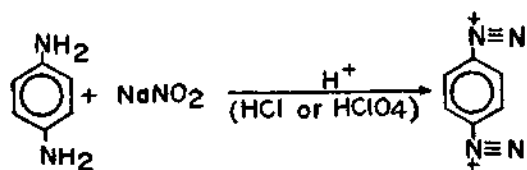
Schoutissen succeeded in the "diazotization of very weakly basic amines"⁷ and the "tetrazotization of *p*-phenylenediamines"⁸ in the media of concentrated phosphoric acid, using nitrosyl sulfuric acid as diazotizing agent. However, he could not tetrazotize *p*-phenylenediamine in strong mineral acid which he recommended to use. We found that his method was inconvenient by high viscosity of concentrated phosphoric acid and that the yield was not so excellent as he reported.

Tetrazotization of *p*-phenylenediamine was also tried by Belov and Kozlov⁹ in the media of organic acids, including formic, acetic, trichloroacetic, tartaric, and oxalic acid. They found from the experiments that tetrazotization of *p*-phenylenediamine in dilute RCOOH led to

monodiaz compound, and in concentrated solutions bis (diaz) compound was formed; however, in the latter cases quinone formation interfered with the reaction and this effect increased with weakening of the acid strength of the RCOOH used.

Since the works of Schoutissen, the tetrazotization of *p*-phenylenediamine has hardly been investigated and overlooked and long-forgotten. It is well-known fact that the aromatic monoamines are usually diazotized in strong mineral acid. Nevertheless, *p*-phenylenediamine has never been tetrazotized in strong mineral acids. Karl Schnitz-Spahn¹⁰ found that the tetrazotization of *p*-phenylenediamine was effected in concentrated sulfuric acid, and he was able to separate a small amount of solid tetrazonium sulfate at a temperature below 0°C, though the yield was disregarded. But the method is inconvenient because high viscosity of concentrated sulfuric acid gives a trouble in filtering procedure of product and the exothermic property of concentrated sulfuric acid on dilution gives a difficulty in regulating the temperature in overall procedures of experiments.

Now, the authors' efforts were crowned with success in the tetrazotization of *p*-phenylenediamine in strong acids media. We found that *p*-phenylenediamine was tetrazotized with a good result in an excess amount of concentrated hydrochloric acid, whereas it was not possible in a dilute media of the acid. We found also it was possible to tetrazotize *p*-phenylenediamine almost completely in 40-45% perchloric acid media, though it was somewhat explosive.



Experimental

1. Tetrazotization in Concentrated Hydrochloric Acid. (1) In a three-necked round-bottomed flask fitted with a mechanical stirrer, 3.62 gr (0.02 mole) of *p*-phenylenediamine dihydrochloride was dissolved in 20 ml of water. To this solution 200 ml of concentrated hydrochloric acid was added and cooled in an ice-salt mixture, then white suspension was formed. To this suspension, with stirring, an aqueous solution of 3 gr of sodium nitrite was added drop by drop from a separatory funnel during 30 minutes. After the addition of nitrite, stirring was continued for 2 hours at -10°C. To remove the excess nitrite, 1 gr of urea was added and stirred for 20 minutes. The tetrazonium salt solution colored pale yellow suspending some white precipitates.

(2) Same experiments were tried with 3.62 gr of *p*-phenylenediamine dihydrochloride in the media of concentrated hydrochloric acid less than 100 ml. After the addition of about 2/3 of the nitrite solution, the reaction mixture suddenly began to hydrolyse evolving nitrogen violently. In a few minutes the reaction mixture was thoroughly decomposed, the flask was overflowed with foam, and the mixture changed to dark brown.

Similar behavior was also observed in the experiments where various concentrations of dilute hydrochloric acids were used as media. These facts showed that the tetrazonium salt was unstable in dilute acid and in a small amount of concentrated acid media.

(3) A solution of 6 gr of freshly prepared cuprous chloride in concentrated hydrochloric acid was slowly poured with stirring into the tetrazonium salt solution prepared from (1). Nitrogen gas evolved violently and the mixture darkened to brown. Stirring was continued for

3 hours. After standing overnight the reaction mixture was transferred into a round-bottomed flask and steam-distilled carefully. A white crystalline solid, *p*-dichlorobenzene, was obtained. The yield was about 85%. It was recrystallized from dilute ethanol. m. p. 53°C.

(4) The tetrazonium salt solution prepared from (1) was poured with stirring into an aqueous solution of 10 gr of potassium iodide. Nitrogen gas evolved and reaction mixture changed to dark brown. Stirring was continued for 2 hours. After being kept overnight, the crude product was filtered off by suction and washed three times with water. It was washed again several times with sodium thiosulfate or potassium iodide solution to remove the free iodine separated. The product was recrystallized from dilute ethanol treating with Norit. The colorless leaflet of *p*-diiodobenzene melted at 129°C. The yield was about 70%.

(5) A solution of 8 gr of freshly prepared cuprous bromide in concentrated hydrochloric acid was poured with stirring into the tetrazonium salt solution obtained from (1). The reaction mixture was quickly darkened with evolution of gas. Stirring was continued for 2 hours. After standing overnight the precipitate was filtered off and extracted several times with a small quantity of ethanol. On diluting the solution with cold water a white product was separated, which was recrystallized from ethanol as colorless needles of *p*-dibromobenzene. m. p. 87-88°C. The yield was about 60%. The crude product was also purified by steam distillation.

2. Tetrazotization in Perchloric Acid. (6)

In a three-necked round-bottomed flask fitted with a mechanical stirrer, 3.24 gr (0.03 mole) of finely powdered *p*-phenylenediamine was dissolved in a small amount of water by adding a few drops of perchloric acid. To this solution 200 ml of 45% perchloric acid was

slowly added and cooled in an ice-salt mixture to -5~10°C, then a white suspension was formed. An aqueous solution of 5 gr of sodium nitrite was added drop by drop, with stirring, into the suspension during 30~40 minutes. Tetrazotization was continued for 3 hours by stirring the mixture at a temperature below -5°C. A bright yellow suspension of tetrazonium salt was formed at the end of the reaction. To remove the excess nitrite 2 gr of urea was added and stirred for 20 minutes. The tetrazonium salt was so stable that it was hardly hydrolysed, and the solubility being low, most of them are separated to form a suspension. The tetrazonium salt being explosive, care must be taken.

(7) The tetrazonium salt solution prepared from (6) was poured with vigorous stirring into a solution of 10 gr of freshly prepared cuprous chloride in concentrated hydrochloric acid. Nitrogen gas evolved and the reaction mixture was darkened. Stirring was continued for 2 hours and the mixture was kept overnight. The mixture was steam-distilled, collecting the product in a receiver immersed in an ice bath. The yield was about 90%. The *p*-dichlorobenzene was recrystallized from dilute ethanol, m. p. 53°C.

(8) An aqueous solution of 10 gr of potassium iodide was poured stirring vigorously into the tetrazonium salt solution obtained from (6). The mixture colored promptly to dark brown evolving nitrogen. Stirring was continued for 2 hours and kept overnight. The crude product was filtered off by suction and washed twice with water and several times with sodium thiosulfate or potassium iodide solution. The yield was about 60%. On recrystallization from ethanol colorless leaflet of *p*-diiodobenzene was obtained. m. p. 129°C.

(9) A cold solution of 12 gr of freshly pre-

pared cuprous bromide in concentrated hydrochloric acid was poured with stirring into the reaction mixture obtained from (6). The reaction mixture changed promptly to purple evolving gas. After stirring for 2 hours, the mixture was kept overnight. The crude mixture was transferred into a round-bottomed flask and *p*-dibromobenzene formed was passed over steam distillation. The yield was about 65%. On recrystallization from ethanol beautiful colorless needles were precipitated. m. p. 87°C.

The crude product could also be purified by filtering the mixture, washing the crude product with water, extracting with ethanol, decolorizing with Norit, filtering the solution, and diluting the filtrate with cold water.

(10) Same experiments were carried out in various concentration of perchloric acid media; 3.24 gr(0.03mole) of *p*-phenylenediamine was tetrazotized in perchloric acid media with sodium nitrite for 3 hours at $-5\sim-10^{\circ}\text{C}$, two diazo groups were substituted with halogen by Sandmeyer reaction, and the degree of tetrazotization was observed by the dihalobenzene yielded.

In dilute perchloric acid media less than 30%, the yield was negligible. In 35% of the acid media the yield was about 10%. The yield gradually increased with increasing the acidity of the media and reached a maximum(about 90%) at 45% of the acid media.

At higher acidities more than 45% of the acid media, the yield was gradually decreased with increasing the concentration. The yields were about 70% and 60% at the concentrations of 55% and 70% of the perchloric acid media respectively.

Results and Discussions

The authors found from the experiments that *p*-phenylenediamine was nicely tetrazotized in

a large amount of concentrated hydrochloric acid(38–40%). However it was never tetrazotized in a small amount of concentrated hydrochloric acid or in a dilute one, because the reaction mixture was thoroughly decomposed evolving nitrogen during the reaction. This shows that the tetrazonium salt is very unstable in a small amount of concentrated hydrochloric acid or in dilute one. We found also that *p*-phenylenediamine was tetrazotized almost completely in the media of 40–45% perchloric acid. However, very or considerably low concentration of the media was not suitable; at high concentration of media the yield was low, and at low concentrations the reaction mixture was decomposed.

Let us now discuss the reaction of tetrazotization with respect to the kinetics and mechanism of diazotization investigated by many workers.

The first kinetic study of diazotization was carried out by Hantzsch and Schumann¹¹ in 1899. Until fairly recently, a great number of other workers, including Schoutissen¹², Dusenbury and Powell¹³, Morgan¹⁴, and Saunders¹⁵, have supported Hantzsch's conclusion, and stated that the diazotization occurs primarily between amine salt and undissociated nitrous acid.

According to this assumption, it may be said that the tetrazotization of *p*-phenylenediamine proceeds more rapidly at high concentration of acid media than at low one, and more rapidly in strong acid than in weak. Nevertheless, the tetrazotization of *p*-phenylenediamine has little been performed in concentrated strong acid media. In spite of failures of earlier workers, the authors could tetrazotize the *p*-phenylenediamine in concentrated strong mineral acid media. We found, however, that high concentration of perchloric acid retarded the reaction,

although the reaction proceeded to completion in high concentration of hydrochloric acid. This is contradictory to the assumption. This may be explained, in consideration of Vernikovskaya's work¹⁶, by saying that the chloride ion is a positive catalyst and the hydrogen ion is a negative catalyst.

In light of the modern electronic theory, Hantzsch's assumption seems hardly possible. Recently, most of the worker in this field, including Hughes, Ingold^{17,18}, Porai-Koshits¹⁹, et al. interpreted their results to mean that the diazotization primarily occurs between the free base and a number of Lewis acids such as NO^+ , $\text{NO}\cdot\text{NO}_2$, NOCl , $\text{NO}\cdot\text{OH}$ and $\text{NO}^+\cdot\text{OH}_2$. The mechanism was considered to be aldol-type addition to the polarized $\text{N}::\text{O}$ double bond.

On this assumption, it is expected that the diazotization proceeds fast at a low concentration of acid at which the hydrolysis of amine salt is accelerated and appreciable free base is formed, and the diazotization proceeds more slowly at high concentration of acid at which the hydrolysis is largely retarded and little free base is formed.

Even if the theory was true, it could not be applied in the tetrazotization, because the tetrazonium salt was very unstable in the dilute acid media. On the contrary, the authors succeeded the tetrazotization in a large amount of concentrated hydrochloric acid media. This may be interpreted by saying that the primarily formed diazo group is so electronegative that it reduce the basicity of the second amino group to a great extent, thus the hydrolysis of the salt of the second amino group is accelerated forming appreciable amount of free base which contribute to aldol-type addition.

The authors may now interpret conclusively for the tetrazotization of aromatic diamines:

(1) Strong mineral acids may also serve as

useful media in the tetrazotization of aromatic diamines, as they considerably stabilize the tetrazonium salt. *p*-Phenylenediamine was tetrazotized in a large amount of concentrated hydrochloric acid and in 45% perchloric acid media at a temperature below -5°C .

(2) The tetrazotization of *p*-phenylenediamine was largely affected by the stability of tetrazonium salt, and the stability was dependent upon the acidity and the quantity of media.

The tetrazonium salt was unstable in a low concentration of acid media and decomposed completely, while it was fairly stable in high concentration of acid media. However, the tetrazotization reaction was retarded at high acidity of media. The difficulty of the tetrazotization of aromatic diamine has been attributed by the two mutually opposing tendencies. So that it is necessary to choose an appropriately high concentration of acid media at which not only the amine salt hydrolyse to form appreciable free base, but also the tetrazonium salt is stable. About 40~45% of acid media was suitable in the tetrazotization of *p*-phenylenediamine.

(3) The fact that the tetrazotization of *p*-phenylenediamine was carried out in concentrated hydrochloric acid (38-40%, 12*N*) and 45% perchloric acid media, whereas it was retarded in high concentration (60-70%) of perchloric acid, was explained by saying that the H^+ ion behaved as negative catalyst. This supports the assumption that the diazotization reaction occurs primarily between free base and nitroso group.

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