Kinetics of the Rearrangement of β-4-Nitroazoxy-benzene in Strongly Acidic Solution

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强酸性 溶液中에서의 β-4-Nitroazoxybenzene 의 轉位反應에 關한 反應速度論的 研究

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要 約

强酸性溶液 中에서 β-4- Nitroazoxybenzene 이 4-Hydroxy-4′-Nitroazobenzene 으로 轉位하는 反應을 UV 分光光度法에 의하여 確認하였다. 20 Vol. %의 알코올과 80 Vol. %의 여러 가지 농도의 황산수용액에서의 이 轉位反應의 反應速度를 究明하였으며, 그 結果 이 反應이 酸觸媒에 의한 擬1次反應임을 알았으며, 또한 이 轉位反應의 機構도 考察하였다.

Abstract

The rearrangement of β-4-nitroazoxybenzene into 4-hydroxy-4′-nitroazobenzene in strongly acidic solutions has been as certained by UV spectrophotometry. The kinetics of the rearrangement in 20 vol. % ethanol and 80 vol. % of aqueous sulfuric acid-water solutions has been studied, and the rearrangement was found to be acidcatalyzed pseudo-frst-order reaction. The mechanism of the rearrangement is also discussed.

Introduction

A study of the rearrangement of 4-nitroazoxybenzenes into 4-hydroxy-4′-nitroazobenzene in the presence of strong acid was done by Angeli and Valori, [1] who separated α-and β-isomers of 4-nitroazoxybenzene. Thereafter, Gore [2] pointed out that the β-isomer rearranges extensively into α-isomer with acid, while Shemyakin and co-workers [3] reported rearrangement of the α-and β-isomers. Sill, the mechanism of the rearrangement based upon chemical kinetics has not yet been studied.

Recently, one of the authors has been reported [4] that the rearrangement of azoxybenzene, 4-bromo- and 4-methyl substituted azoxybenzenes into the corresponding hydroxyazobenzenes, the Wallach rearrangement, is an acid-catalyzed pseudo-first-order reaction, and the existence of a second conjugate acid [1] has been suggested. Futhermore, it has also been proposed that the rearrangement proceeds via a symmetric triangular hydrated intermediate. (I—c)

Continuing their previous investigation [4] the authors

from to the conjugate acid of authentic 4-hydroxy-4'-nitroazobenzene in 100% sulfuric acid These show that β-4-nitroazoxybenzene rearranges into 4-hydroxy-4'-nitroazobenzene in strongly acidic solution. It is concluded that the spectra (2—4) and(2—5) are due to the conjugate acid of the rearranged product, 4-hydroxy-4'-nitroazobenzene, and the result coincides with the authors' previous report[6] that the azoxy oxygen atom in the presence of strong acid migrates to the para position of the unsubstituted ring just as in the case of bromo-and methoxy substituted azoxybenzene. This also accords with the Angeli's work of β-4-nitroazoxybenzene.

Kinetics. The spectra in Figure 3 indicate the exent of completion of the rearrangement; that is, the intensity at absorption maximum of the rearranged product is increased as the rearrangement proceeds. This made possible a kinetic study of to the rearrangement, and the rate of the rearrangement was measured at the absorption maximum, 480mμ. The kinetic runs were carried out with 85, 90 and 100% sulfuric acid

temperatures table are listed in Table I,and a pseudo-first -order plot for the rearrangement of β-4-nitroazoxybenzene is given in Figures 4 and 5. Activation parameters were estimated table 2 from the measurement of the rates at two temperatures, and are presented in table 3. The dependence of the rates on acidity is plotted in Figure 6, from which it can be seen that the logarithm of all the rates is linear with Ho.

Mechanism. From the above data it can be concluded that the rearrangement of β-4-nitroazoxybenzene in the presence of strong sulfuric acid is an acid-catalyzed pseudo-first-order reaction as in previous by reported, 4) cases it is probable that the path for the rearrangement consists of several steps. The first is a fast acid-base equilibrium controlled step, the formation of conjugate acid, which is followed by a second protonation. The second protonation may be explained as follows. Since the conjugate acid has other proton accepting sites, and the concentration of sulfuric acid used for the rearrangement ranges from 85% to 100%, it can be speculated that there might
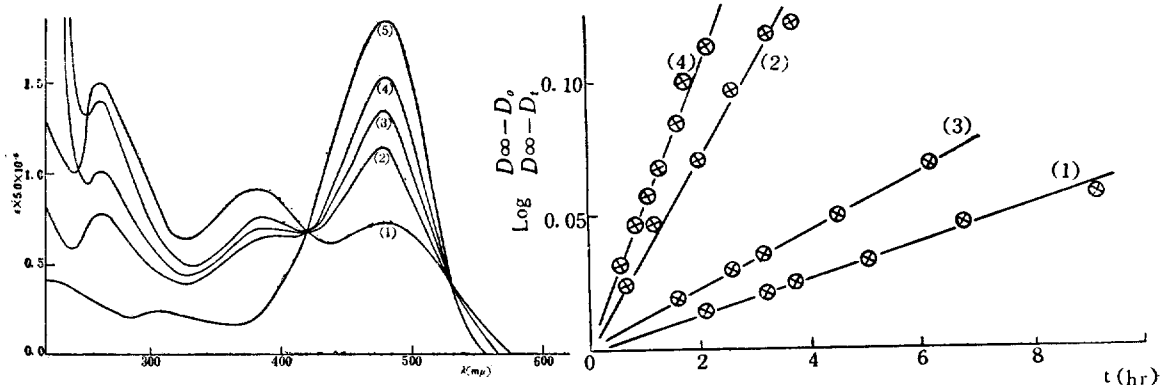

Figure 3. Absorption Spectra of β-4-Nitroazoxybenzene

(1) in 90% H$_2$SO$_4$ (after 30 min; at 100°);

(2) in 90% H$_2$SO$_4$ (after 1 hr. at 100°);

(3) in 100% H$_2$SO$_4$ (after 30 min. at 100°);

(4) in 100% H$_2$SO$_4$ (after 1hr. at 100°);

(5) authentic 4-hydroxy-4'-nitroazobenzene in 100% H$_2$SO$_4$ (room temp.).

at 65° and 80°, respectively. The result of one of these runs, using 80% sulfuric acid at 65°, is tabulated in table 1. The pseudo-first-order rate constants for the rearrangement in a series of sulfuric acid solutions at two

Figure 4. Pseudo-First-Order Rate Plot for the Rearrangement of β-4-Nitroazoxybenzene

(1) in 80% H$_2$SO$_4$ at 65°; (2) in 85% H$_2$SO$_4$ at 80°;
(3) in 90% H$_2$SO$_4$ at 65°; (4) in 90% H$_2$SO$_4$ at 80°.

also be a diprotonated species the conjugate acid of β-4-nitroazoxybenzene, even at room temperature. Since, however, the fraction of the conjugate acid must be increased as the concentration of sulfuric acid increases, it is conceivable that the fraction of the monoprotonated species be large under kinetic conditions. Neverthless, this by no means says that there

have examined, in the first place, the orientation of the migrating oxygen atom in azoxy group of β-4-nitroazoxybenzene, and, secondly, the kinetics of the rearrangement of β-4-nitroazoxybenzene in order to shed further light on the mechanism of the Wallach rearangement.
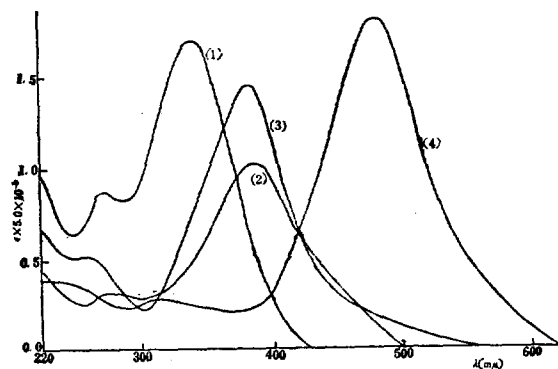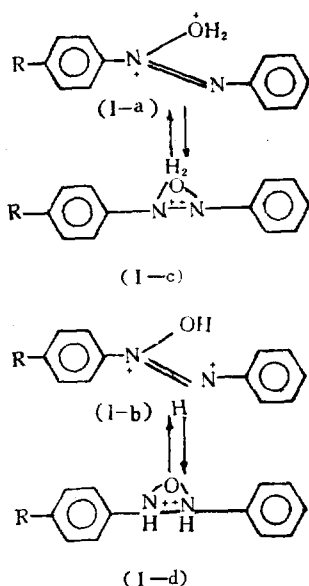

(l—c)

(l—d)

Figure 1. Absorption Spectra of

1. β-4-nitroazoxybenzene in EtOH(5.0×10⁻⁵M);

2. ibid. in 20vol.% EtOH-80 vol.% of 100% H₂SO₄;

3. 4-hydroxy-4′-nitroazobenzene in EtOH (5.0×10⁻⁵M);

4. ibid. in 20 vol.% EtOH-80 vol.% of 100% H₂SO₄.

Results and Discussion

Spectroscopic Observation   The spectra 1 and 2 in Figure 1(1—1, 1—2) having absorption maxima at

340 mμ and 385 mμ are π→π* transition band 5) of β-4-nitroazoxybenzene in 100% ethanol and 20 vol. % ethanol-80 vol. % of 100% sulfuric acid, respectively (only the concentration of sulfuric acid will be indi-cated hereafter). The spectrum(1—2)was taken imme-diately after the solution was prepared, and it seems likely to be due to the conjugate acid of β-4-nitroa-zoxybenzene. The spectra (1—3) and (1—4) having absorption maxima at 380 mμ and 480mμ are due respectively to the free base and the conjugate acid of 4-hydroxy-4′-nitroazobenzene and are also attributed to π→π* transition.

These show that β-4-nitroazoxybenzene in strong acid converts to its conjugate acid in a short time and the same is true of 4-hydroxy-4′-nitroazobenzene.

The spectra in Figure 2 show that the free base of β-4-nitroazoxybenzene initially forms its conjugate acid and then converts into some other species in the presence of strong acid. Spectrum (2—1) shifted to the spectra (2—2) and (2—3) in 90% and 100% sulfuric acid solution, respectively. After I hour, the spectra of the same solution shifted farther to the spectra (2—4) and (2—5). It should be noted that the spectra (2—4) and (2—5) of the new species have the same absorption maxima (480 mμ)as spectrum (2—6)
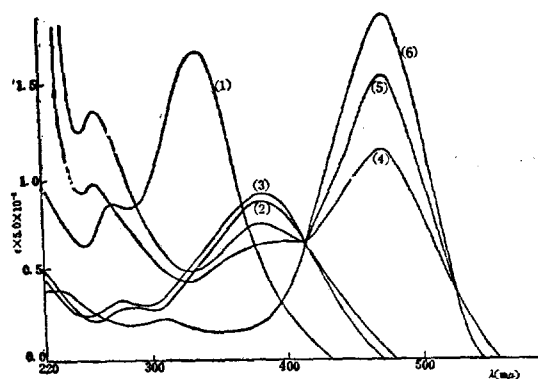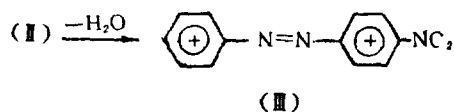

Figure 2. Absortion Spectra of β-4-Nitroazoxybenzene

1. in EtOH;

2. in 90% H₂SO₄ } right after;
3. in 100% H₂SO₄

4. in 90% H₂SO₄ } 1hr. at 100°C;
5. in 100% H₂SO₄

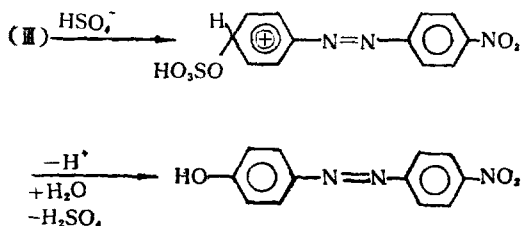6. authentic 4-hydroxoy-4-nitroazobenzene in 100% H₂SO₄ at room temp.

rearrangement. Buncel and his coworker 7)have shown that the rate of rearrangement greatly increases with increasing acid concentration, in spite of the fact tha the fraction of monoprotonated species remained substantially constant in such concentrated acid solutions, and they have also called for second proton transfer. These facts lead us to postulate the first two steps of the mechanism as follows:

Based upon the above, it seems likely that a diprotonated species might function as an intermediate, though the exact structure of the intermediate cannot be shown from the present investigation. Yet, the relatively large negative value of activation entropy in Table 3 is significant enough to suggest that the transition state in the rate-determining step must be complex and structured to some extent. In addition to this, considering that large negative entropy in a reaction involving water can usually be refered to the decrease of motional freedom of water molecules, [8] the two hydrated forms out of the above four intermediates seem to be the most favorable choice.

It now remains to speculate about the rate-determing step. In the first place, it can readily be recognized that neither of the above protonations could be the rate-determining step from the fact that the half-lives of most acid-base reactions are as fast as the order of 10^{-8} sec, while the rate constants of the Wallach rearrangement are of the order of 10^{-5} sec^{-1}. Next for an azoxy group convert to an azo group bond cleavage is required between nitrogen and oxygen atoms in use azoxy group, that is, the following step is essential for the rearrangement.

All steps leading to the final rearranged product, after the dicationic species (II) is formed, are similar to the routes proposed previously[4]; i.e.

Since all these steps are ionic in nature, it appears reasonable that the rate-determining step of this acid-catalyzed rearrangement of β-4-nitroazoxybenzene is the formation of the dicationic species that is the dehydartion product of the hydrated intermediate [1]. The dicationic species must then be attacked by a nucleophile. It is difficult to choose between sulfate and bisulfate ions as the nucleophile at this point. Finally, assuming as above, the authors propose that substitution by hydroxy group is intermolecular, agreeing with Shemyakin's conslusions [9] which were demonstrated by isotope labeling studies..

Experimental Section

Materials. All chemieals used were Wako (Japanese) special grade except absolute alcohol and sulfuric acid (Merck special grade) and were used without further purification.

4-Nitroazobenzene. Coupling p-nitroaniline with nitrosobenzene in glacial acetic acid solution at 40°, reddish brown crystals were obtained. Recrystallized from 50% aq. EtOH three times: mp 133°.

Oxidation of 4-Nitroazobenzene. 4-Nitroazobenzene obtained above was oxidized with 30% hydrogen peroxide solution in glacial acetic acid. The reaction mixture was refluxed for 5 hours.. Yellowish crystals obtained by pouring the mixture into ice-water were washed until no longer acidic (checked with pH paper). These are presumed to be a mixture of 4α and β-isomers of 4-nitroazoxybenzenes.

Separation of β-4-Nitroazoxybenzene. The β-isomer was separated by liquid column chromatography. alumina (Merck reagent grade) was used and eluting solvent was benzene. The mixture was developed into 3 fractions and the β-isomer was separated from the first (bottom) yellow band. Recrystallization from MeOH gave pale yellow crystals: mp 147° (1) 148°).

4-Hydroxy-4/-Nitroazobenzene According to the general method, [10] this compound was prepared by coupling of diazonium salt of 4-nitroaniline with phenol in alkaline solution. Recrystallization from 20% aq. EtOH gave yellowish brown crystals: mp 212° (lit. 213°).

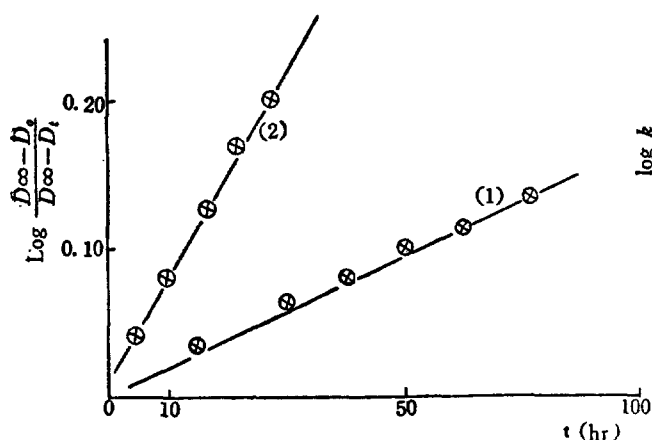**Kinetics.** The preparation of solutions and the method of kinetic measurements for the present inves-

Figure 5. Pseudo-First-Order Rate Plot for the Rearrangement of β-4-Nitroazoxybenzene in 20 vol. % EtOH—100% H_2SO_4 at (1) 65°; (2) 80°.

must be only the monoprotonated species. Accordingly, the authors suspect that the diprotonated species might function as an intermediate at some stage in the

Table 1. Rates of the Rearrangement of β-4-nitroazoxybenzene in 20 vol. % EtOH 85% H_2SO_4 at 65°C

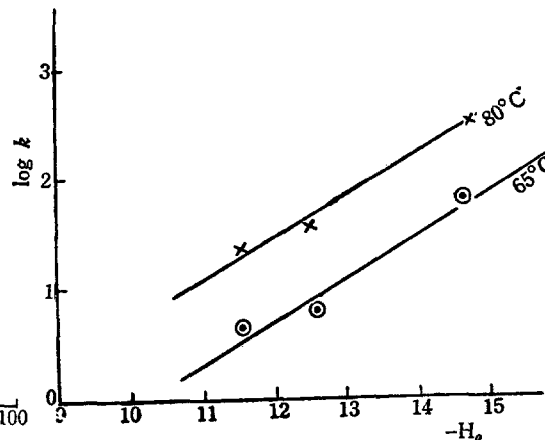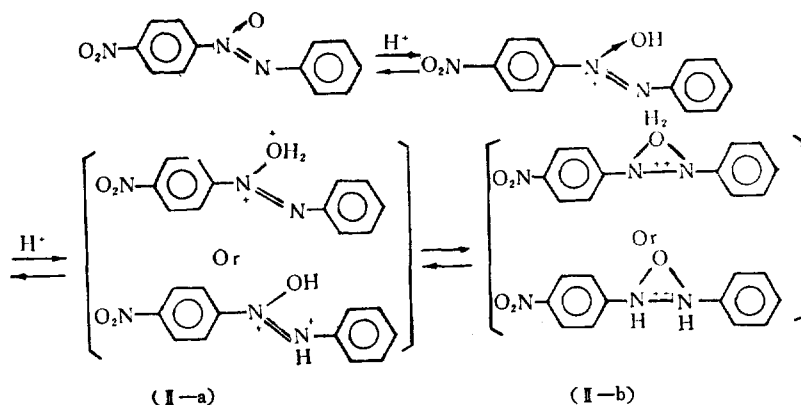| Time (min)	O.D. at 480mμ	$Log\frac{D_\infty - D_o}{D_\infty - D_t}$	$k \times 10^6$ sec^{-1}
0	0.047		
120	0.087	0.0122	3.86
180	0.109	0.0190	3.80
210	0.122	0.0230	3.83
300	0.152	0.0326	3.80
400	0.190	0.0450	3.75
540	0.219	0.548	3.65

$k = 3.78 \pm 0.06$

Figure 6. The Dependence of Rates on Acidity.

Table 2. Pseudo-First-Order Rate Constants for the Rearrangement of β-4-Ntroazoxybenzene (5.0×10^{-5}M)

	β-4-Nitroazoxybenzene	
Vol. %	At 65° $k \times 10^5 \times$ sec^{-1}	At 80° $k \times 10^5 \times$ sec^{-1}
85	0.378	2.35
90	0.644	3.59
100	7.13	31.7

Table 3. Activation Parameter for the Rearrangement of β-4-Nitroazoybenzene

Vol. % H_2SO_4	Ea (Kcal/mole)	Ss (e. u.)
85	28.5	0.48
90	26.7	−3.83
100	23.1	−9.76

(I —a)   (I —b)

tigation are described in previous paper.[4]

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