THE WALLACH REARRANGEMENT

PART II.[1] KINETICS AND MECHANISM OF THE ACID-CATALYZED REARRANGEMENT OF AZOXYBENZENE

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ABSTRACT

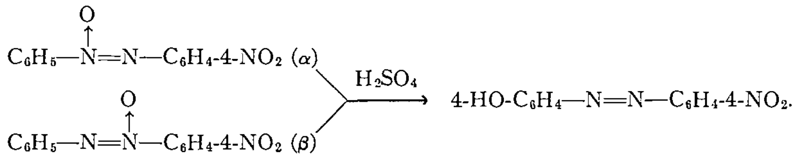
The rate of rearrangement of azoxybenzene to *p*-hydroxyazobenzene has been measured in 75.3–96.4% sulfuric acid at 25° and in 65.0–90.4% sulfuric acid at 75.5° by spectrophotometric methods. The pK_a of azoxybenzene in aqueous sulfuric acid has also been determined. It is found that although azoxybenzene is almost completely protonated over the entire range of acid concentration studied, the rate increases by more than 1 000-fold. A two-proton process is therefore indicated and mechanisms are proposed involving a dication (II) as the key intermediate. The rate data do not allow differentiation between two proposed mechanisms, one involving two equilibrium protonations, and the other a single equilibrium protonation followed by rate-determining proton transfer. Past mechanisms of the Wallach rearrangement are discussed.

INTRODUCTION

In 1880, Wallach and Belli (2) discovered that azoxybenzene on treatment with concentrated sulfuric acid isomerized to *p*-hydroxyazobenzene. This reaction is known as the Wallach rearrangement. Since then numerous studies have been made to elucidate the nature of this reaction but up to the present time (1) no kinetic study of the Wallach rearrangement has been reported. As an introduction to the present work the more recent studies on this topic will be reviewed.

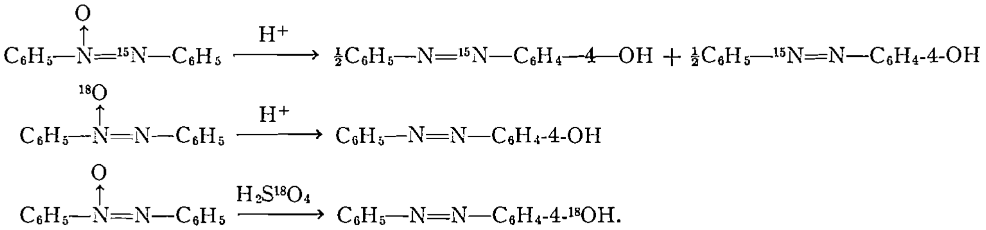
Of particular interest to the early investigators was to determine whether the rearrangement is intramolecular or intermolecular, and the direction of migration of the oxygen function in the case of substituted azoxybenzenes. Angelli (3), who was the first to isolate two position isomers of a mono-substituted azoxybenzene, observed that both isomers of 4-nitroazoxybenzene gave the same rearranged product, 4-nitro-4′-hydroxyazobenzene (eq. 1). When both para positions are substituted, the oxygen enters one of the ortho positions (4*b*).

[1]



$$\left.\begin{array}{l} C_6H_5-\overset{\overset{O}{\uparrow}}{N}=N-C_6H_4\text{-4-}NO_2\ (\alpha) \\ C_6H_5-N=\overset{\overset{O}{\uparrow}}{N}-C_6H_4\text{-4-}NO_2\ (\beta) \end{array}\right\rangle \xrightarrow{H_2SO_4} \text{4-HO-}C_6H_4-N=N-C_6H_4\text{-4-}NO_2.$$

The most revealing studies on the mechanism of the acid-catalyzed para rearrangement have been the N-15 and O-18 tracer investigations of Shemyakin *et al.* (5, 6). Their main observations can be summarized by the following equations:



$$C_6H_5-\overset{\overset{O}{\uparrow}}{N}={}^{15}N-C_6H_5 \xrightarrow{H^+} \tfrac{1}{2}C_6H_5-N={}^{15}N-C_6H_4-4-OH + \tfrac{1}{2}C_6H_5-{}^{15}N=N-C_6H_4\text{-4-}OH$$

$$C_6H_5-\overset{\overset{^{18}O}{\uparrow}}{N}=N-C_6H_5 \xrightarrow{H^+} C_6H_5-N=N-C_6H_4\text{-4-}OH$$

$$C_6H_5-\overset{\overset{O}{\uparrow}}{N}=N-C_6H_5 \xrightarrow{H_2S^{18}O_4} C_6H_5-N=N-C_6H_4\text{-4-}^{18}OH.$$

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[1] *A preliminary communication on part of this work has appeared (ref. 1).*

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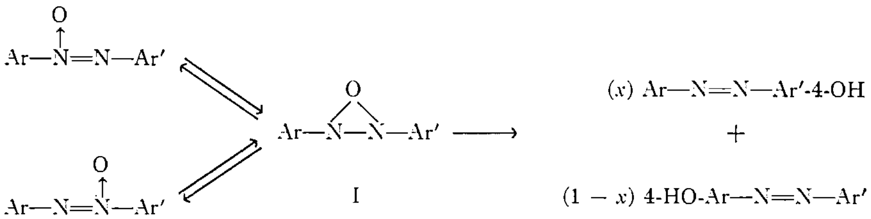
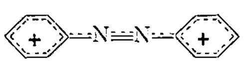
In addition, azoxybenzene recovered from partial reaction in all three types of experiments contained the original label undisturbed. On the basis of the equalization of the nitrogen label during the rearrangement but not prior to it, Shemyakin *et al.* deduced that a symmetrical intermediate must be formed. They proposed that the symmetrical intermediate was the N,N-oxide (I) and suggested Scheme 1 for the mechanism of the Wallach rearrangement.

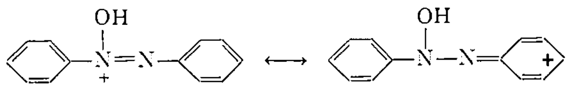


Scheme 1.

The α and β isomerization was included in the scheme for the following reasons. Although azoxybenzene itself does not undergo this isomerization under the conditions of the rearrangement, as shown by the N-15 tracer experiments, Gore (7) found that β-4-nitroazoxybenzene underwent extensive conversion to the more stable α-isomer under rearrangement conditions.[2] Now the isomerization of β-4-nitroazoxybenzene in $H_2S^{18}O_4$ resulted in no O-18 enrichment in the recovered α-isomer (6). Shemyakin hence concluded that the N,N-oxide was a common intermediate in isomerization and rearrangement. Gore (7) suggested that the dicationic species (II) is also a possible intermediate in the Wallach rearrangement. He considered that II represents the major reaction route, with a minor route proceeding via the monocationic species (III).



II



III

Oxygen-18 tracer studies on the azoxybenzene rearrangement have also been carried out, independently, by Oae *et al.* (9); the results are very similar to those of the Russian workers. The mechanism proposed by Oae *et al.* is shown in Scheme 2.

The value of kinetic data in the interpretation of the mechanism of acid-catalyzed reactions is well known (10). It was with the expectation that kinetic data would shed further light on the mechanism of the Wallach rearrangement that the present study was initiated.

RESULTS

Kinetic Data

Before a kinetic study of the acid-catalyzed rearrangement of azoxybenzene could be undertaken it was important to determine to what extent the reaction was quantitative and what was the nature of side products, if any, under the kinetic conditions. Previous work had shown that azobenzene, an azo-sulfonic acid, aniline, and polymer may all be formed as side products of reaction (4*a*). However, in the single reported study (11*a*) where the conditions were comparable to those planned for the kinetic work, i.e. low azoxybenzene concentrations (ca. 10^{-3} *M*), the yield of *p*-hydroxyazobenzene was found

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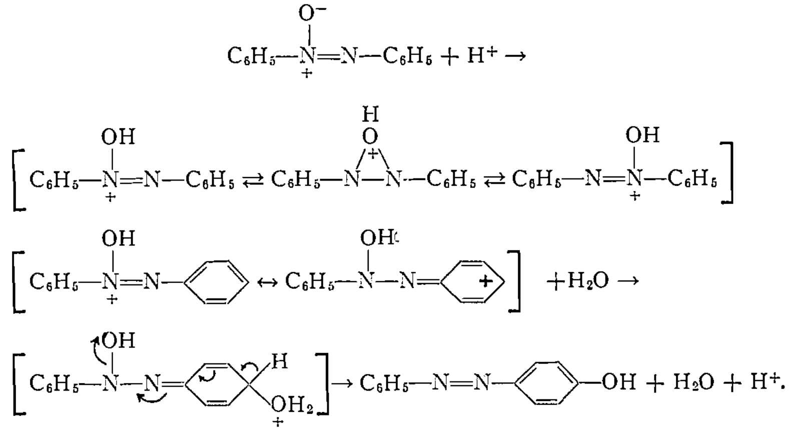
[2] *The only other report of α–β isomerization under rearrangement conditions is due to Angelli (8) who found that a bisazoxybenzene isomerized as well as rearranged in cold sulfuric acid.*



SCHEME 2.

to be quantitative by spectrophotometry and no side products were apparent. In contrast, the earlier work was carried out at much higher azoxybenzene concentrations, from 0.5 *M* to 3 *M*, and often at high temperatures and for long reaction times. Since it thus appeared that the formation of side products may be connected with the reactant concentration and the vigor of the reaction conditions, it was decided to carry out a trial run under favorable reaction conditions.

The data for the run ($1.87 \times 10^{-3} M$ azoxybenzene in 88.22% H_2SO_4 at 25° C) are shown in Table I. The rate of reaction was followed spectrophotometrically (12). Aliquots were removed periodically and quenched in ethanolic aqueous alkali, thus taking advantage of the long-wavelength absorption of the anion of *p*-hydroxyazobenzene (λ_{max} = 435 mμ) compared with azoxybenzene (λ_{max} = 323 mμ), as shown in Fig. 1 and Fig. 2. The spectra of the quenched solutions were both qualitatively and quantitatively identical with that of *p*-hydroxyazobenzene. After eight half-lives the spectra remained constant for several more half-lives. The pseudo-first-order rate constant, calculated from the linear plot of log ($\mathrm{O.D.}_{\infty} - \mathrm{O.D.}_t$) at 435 m$\mu$ against time, is $5.20 \times 10^{-5}\ \mathrm{s}^{-1}$. These results showed that under the kinetic conditions *p*-hydroxyazobenzene is produced quantitatively. However, as the acid concentration was increased it was observed that the absorbance of the "infinity solutions" was greater by a few percent than the calculated value and the absorption maximum was shifted slightly. This result was shown to be due to decomposition of *p*-hydroxyazobenzene. In 96.4% sulfuric acid this decomposition amounted to about 1.5% per half-life of the azoxybenzene reaction. Runs in over 92% sulfuric acid were corrected for this decomposition of *p*-hydroxyazobenzene.

In order to confirm the soundness of the rate data a check was made by another method. Instead of following the rate by a sampling procedure and spectrophotometric measurement of the quenched alkaline solutions, the rate was followed by direct spectrophotometric measurement of the acid solutions in a thermostatted cell of a spectrophotometer. Spectral sweeps were taken at various time intervals over the regions of protonated azoxybenzene (λ_{max} = 390 mμ) and protonated *p*-hydroxyazobenzene (λ_{max} = 463 mμ). The curves exhibited a regular decrease of the 390 mμ absorption and corresponding increase of the 463 mμ absorption, with a single well-defined isosbestic point. Rate constants were calculated both from the disappearance of the azoxybenzene absorption and the development of the *p*-hydroxyazobenzene absorption. The rate constants so obtained

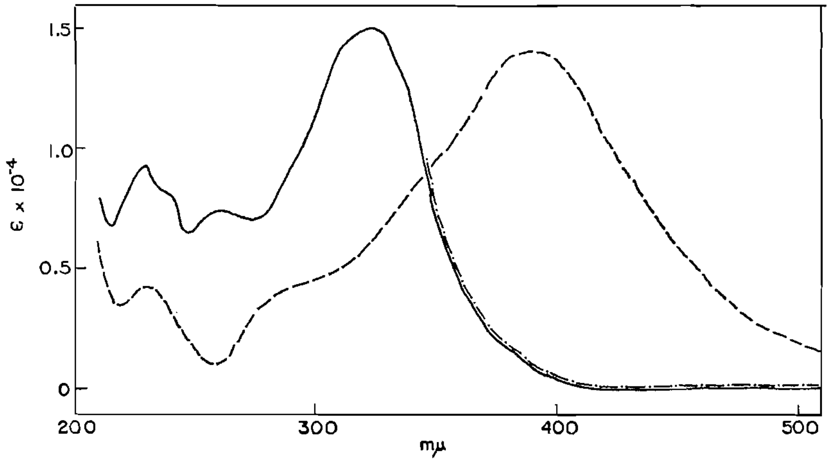


FIG. 1. Spectrum of azoxybenzene in 95% ethanol (—); 90% sulfuric acid (---); aqueous ethanolic alkali (1 *M*) (-···).

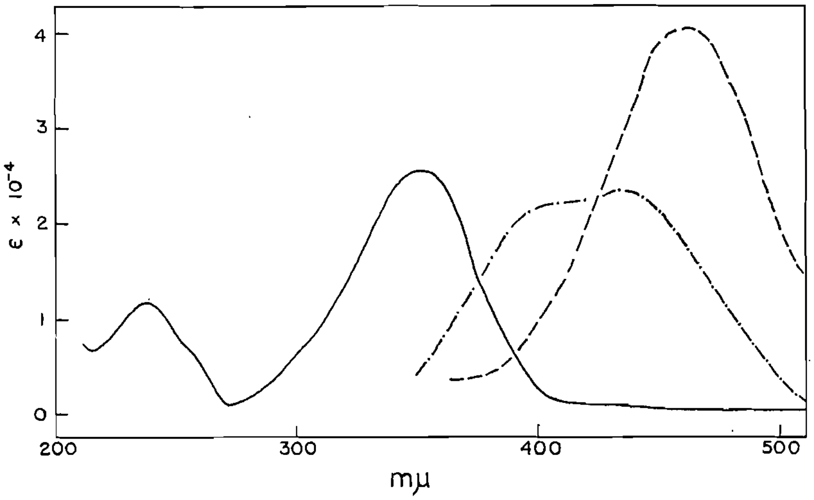


FIG. 2. Spectrum of *p*-hydroxyazobenzene in 95% ethanol (—); 90% sulfuric acid (---); aqueous ethanolic alkali (1 *M*) (-···).

were equal within experimental error and also agreed with the value obtained by the quenching method. These results are shown in Fig. 3.

The rate data at 25° and 75° and at various acid concentrations are recorded in Table II. The usual method of measurement was the dilution method. At 75°, some of the rates were determined by a sealed-tube method. The reproducibility of the rate data was about 2% when the same stock solution of sulfuric acid was used and about 10% between two different stock solutions of acid. The larger error in the latter case is evidently caused by the very steep rise in rate constant with acid concentration and the difficulty of reproducing exactly a given acid concentration by ordinary analytical techniques; thus at 95% H_2SO_4 the rate increases by 9% for an increment of 0.1% H_2SO_4 while at 80% H_2SO_4 the corresponding increase in rate constant is 30%.

TABLE I

Rearrangement of azoxybenzene in 88.22% H_2SO_4 at 25.0° by dilution method

Time (h)	O.D. at 435 mμ	$O.D._\infty - O.D._t$	$\log (O.D._\infty - O.D._t) + 2$
0	0.007	0.774	1.889
0.25	0.042	0.739	1.869
0.50	0.076	0.705	1.848
0.75	0.111	0.670	1.826
1.00	0.134	0.647	1.808
1.25	0.171	0.610	1.785
1.50	0.197	0.584	1.766
2.00	0.250	0.531	1.725
2.50	0.297	0.484	1.685
3.00	0.343	0.438	1.641
4.00	0.416	0.365	1.562
5.00	0.476	0.305	1.484
6.00	0.529	0.252	1.401
7.50	0.590	0.191	1.281
9.50	0.642	0.139	1.143
12.00	0.693	0.088	0.944
24.00	0.774	0.007	
48.00	0.781	0.000	

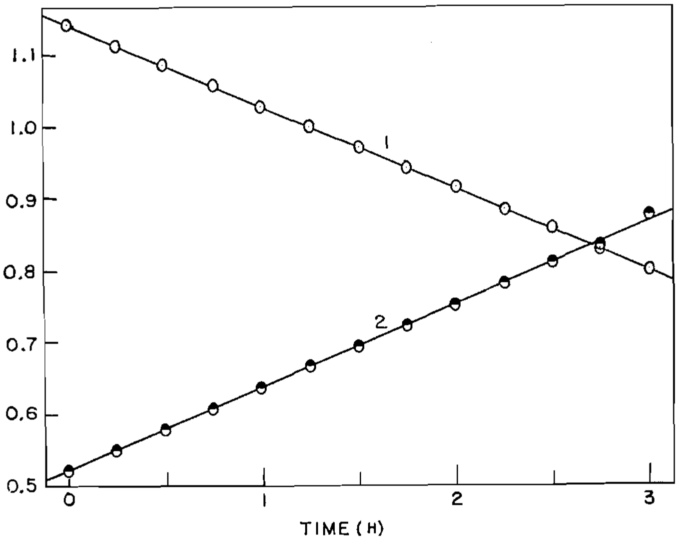


FIG. 3. First-order plots for rearrangement of $3.93 \times 10^{-5}M$ azoxybenzene in 90.37% H_2SO_4 by the "direct" method: (1) $1 + \log (O.D._\infty - O.D._t)$ vs. time, absorbances at 463mμ; (2) $-\log (O.D._t - O.D._\infty)$ vs. time, absorbances at 390 mμ. Rate constant from plot (1), $7.24 \times 10^{-5}\ s^{-1}$, from plot (2), $7.35 \times 10^{-5}\ s^{-1}$.

Product analysis was also carried out, at two acid concentrations, 90.4% H_2SO_4 and 77.5% H_2SO_4, in order to cover most of the range of the kinetic study. The azoxybenzene concentration was about 3×10^{-2} *M*. Unexpectedly it was found that the quantity of side products, mainly azobenzene, depended not only on the reaction time, as anticipated from the kinetic work, but also on the manner of isolation of products. The most satisfactory method was slow addition of the acidic reaction mixture to cooled aqueous sodium hydroxide, keeping the temperature below 0°. If during the neutralization the temperature was allowed to reach 50°, the side products increased by several percent. Also the exclusion of light was found to be necessary, both during reaction and work-up.

TABLE II

Kinetic data for azoxybenzene rearrangement*

T = 25.0°			T = 75.5°		
Stock solution	Wt. % H_2SO_4	10^5k, s^{-1}	Stock solution	Wt. % H_2SO_4	10^5k, s^{-1}
2	75.30	0.016	4	65.00	0.0854
2	77.45	0.048	4	65.00	0.0800‡
2	80.15	0.208	4	70.00	0.916
3	80.15	0.245	4	70.00	1.08
3	80.15	0.236	4	70.00	1.03‡
2	82.87	0.778	4	75.30	11.5
2	85.61	2.17	4	75.30	11.1
3	85.61	2.43	4	80.15	95.2
3	85.61	2.41	4	80.15	97.5
2	87.57	3.68	4	85.61	611
1	88.22	5.20	4	85.61	601
2	90.37	7.23	4	90.37	1 670
3	90.37	7.69	4	90.37	1 680
3	90.37	7.69			
3	90.37	7.35†			
3	90.37	7.24†			
2	92.81	11.6			
2	95.19	20.2			
3	95.19	21.2			
3	95.19	21.1			
2	96.40	26.1			

*Data were obtained by the dilution method unless otherwise stated.
†Direct method.
‡Sealed tube method.

When this precaution was not taken, small amounts of *o*-hydroxyazobenzene were obtained. The reaction at 90.4% H_2SO_4 after 5 half-lives yielded 3% of unchanged azoxybenzene, 1.5% of other neutral material, and 95% of *p*-hydroxyazobenzene. At 77.5% H_2SO_4 after 2.5 half-lives, the corresponding values were 17, 2, and 81% respectively. The product analyses were hence in full agreement with the kinetic data.

pK Determinations

Knowledge of the pK_a of azoxybenzene is essential for the interpretation of the kinetic data, since azoxybenzene is expected to be appreciably protonated in the acid concentrations employed. The pK_a of azoxybenzene in 20% ethanol and 80% sulfuric acid – water mixture was found to be −6.45 by Jaffé and Hahn (11*b*), based on the H_0 scale appropriate for this ethanolic aqueous acid medium (13*a*). Since the present study was carried out in aqueous medium, in which interpretation of rate data is less ambiguous than in mixed solvents (14*a*), determination of the pK_a of azoxybenzene in aqueous sulfuric acid was deemed necessary.

Spectra of azoxybenzene solutions of various sulfuric acid concentrations, covering the complete range of protonation, were recorded. The data, shown in Table III, were treated by the methods of Davis and Geissman (15) and Katritzky, Waring and Yates (16). The two methods gave pK_a values of −5.15 and −5.14 ± 0.05, respectively, rounded off to −5.15.

The Katritzky–Yates procedure also allows one to test whether or not a given substrate undergoes equilibrium protonation in the manner of a true Hammett base (understood to mean a primary aromatic amine (17)). Thus, since $H_0 = \mathrm{p}K_a - \log\,[\mathrm{BH}^+]/[\mathrm{B}]$, a plot of log $[\mathrm{BH}^+]/[\mathrm{B}]$ against H_0 should be linear of unit slope, if in fact protonation of the base is governed by H_0. For azoxybenzene the value of this slope, calculated from the

ϵ_{383} and ϵ_{323} plots is 0.92 ± 0.10 and 1.01 ± 0.05 respectively. (The error depends directly on the gradient at the inflection point of the sigmoid curves.) It is therefore concluded that, within the error of the present measurements, the protonation of azoxybenzene is in fact governed by the Hammett acidity function H_0.

TABLE III

Data for determination of pK_a of azoxybenzene

% H_2SO_4	$-H_0$	O.D. at 383 mμ	O.D. at 323 mμ	(O.D.$_{383}$ − O.D.$_{323}$)
41.07	2.50	0.081	0.904	−0.823
50.77	3.48	0.100	0.905	−0.805
54.70	3.88	0.127	0.893	−0.766
60.31	4.50	0.264	0.847	−0.583
64.49	5.01	0.524	0.725	−0.201
67.24	5.38	0.760	0.619	+0.141
70.16	5.83	0.921	0.518	+0.403
71.07	5.97	0.953	0.490	+0.463
73.82	6.38	1.015	0.447	+0.568
76.18	6.75	1.040	0.434	+0.606
77.93	7.01	1.048	0.424	+0.624
85.17	8.16	1.060	0.385	+0.675
90.49	9.02	1.070	0.392	+0.678
96.54	10.12	0.956	0.353	+0.603

TABLE IV

Protonation and rate data for azoxybenzene rearrangement

% H_2SO_4	log C_{H^+}	$-H_0$	$\frac{C_{SH^+}}{C_S + C_{SH^+}}$	$\frac{C_S}{C_S + C_{SH^+}}$	$-\log a_{H_2O}$	log k + 7
T = 25.0°						
75.30	1.108	6.61	0.967	0.0335	1.77	0.20
77.45	1.126	6.95	0.984	0.0156	1.97	0.68
80.15	1.149	7.37	0.994	0.00599	2.28	1.36
82.87	1.170	7.80	0.998	0.00223	2.69	1.89
85.61	1.191	8.22	0.999	0.000850	3.04	2.37
87.57	1.205	8.55	1.000	0.000399	3.28	2.57
88.22	1.210	8.64	1.000	0.000324	3.35	2.72
90.37	1.223	9.00	1.000	0.000141	3.66	2.87
92.81	1.237	9.45	1.000	0.000050	4.01	3.06
95.19	1.249	9.89	1.000	0.000018	4.44	3.32
96.40	1.256	10.10	1.000	0.000011	4.88	3.42
T = 75.5°						
65.00	0.999	5.07	0.454	0.546	1.05	0.82
70.00	1.060	5.80	0.817	0.183	1.35	2.00
75.30	1.096	6.61	0.966	0.0335	1.77	3.05
80.15	1.136	7.37	0.994	0.00599	2.28	3.98
85.61	1.178	8.22	1.000	0.000850	3.04	4.78
90.37	1.210	9.00	1.000	0.000141	3.66	5.22

DISCUSSION

Proposed Mechanism for Wallach Rearrangement

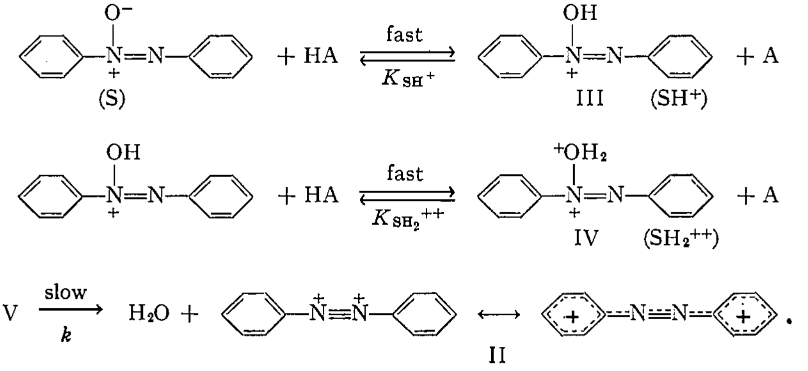
The kinetic data coupled with the pK measurement allow an interpretation of the mechanism of the rearrangement of azoxybenzene. The first deduction, that the reaction is acid catalyzed, is evident from the rapid increase in rate with acid concentration. Further insight on the manner of the acid catalysis is obtained by calculating the extent of monoprotonation of azoxybenzene ($C_{SH^+}/C_S + C_{SH^+}$) in the acid solutions used, from the relationship $\log C_{SH^+}/C_S = pK_a - H_0$. The unexpected result then becomes apparent that azoxybenzene is present almost entirely in the protonated form even in the lowest acid concentrations used, and yet there is a great increase in the rate of reaction with increasing concentration. Thus the data of Table IV show that on increasing the sulfuric acid concentration from 75.3% to 85.6% the protonation changes only from 96.7% to 99.9%, yet the rate constant increases by 140-fold. From 85.6% to 96.4% sulfuric acid the extent of protonation remains virtually constant, but the rate constant increases by another 12-fold over this range.[3] This striking increase in rate constant with acidity while the amount of monoprotonated species remains virtually unchanged can only be explained on the basis that a second proton transfer is involved at some stage of the reaction.

With the knowledge that the transfer of two protons is a necessary feature in the reaction path of the conversion of azoxybenzene to *p*-hydroxyazobenzene (VIII), it is possible to formulate mechanisms which may then be tested by the experimental data. The proposed reaction paths are given in Schemes 3 and 4.

[2]

[3]

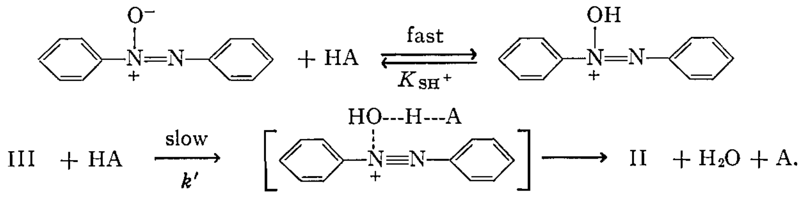
[4]



Scheme 3.

[5]

[6]



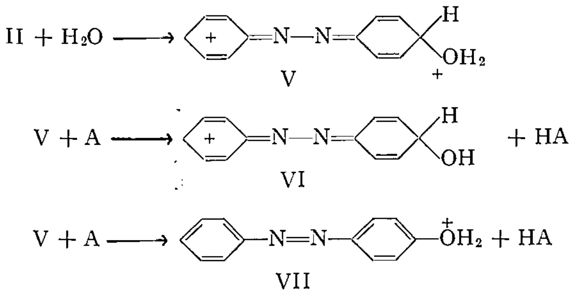
Scheme 4.

Steps [4] and [6] are followed by [7], [8] or [8*a*], and [9] or [9*a*].

[7]

[8]

[8*a*]



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[3] *The degrees of protonation given in Table IV are slightly different from those reported in (1) due to the replacement of the H_0 values compiled by Paul and Long (14a) by the recently measured Jorgenson–Hartter H_0 scale (17). Use of the new H_0 scale has also changed the pK_a of azoxybenzene from −5.10 to −5.15.*

$$\text{VI} + \text{A} \longrightarrow \text{VIII} + \text{HA} \tag{9}$$

$$\text{VII} + \text{A} \longrightarrow \text{VIII} + \text{HA}. \tag{9a}$$

Scheme 3 begins with a rapid equilibrium protonation of azoxybenzene; the site for the proton has been shown to be the coordinated oxygen (11*b*). (The acid is depicted as HA in order to include all possible species present in the relatively concentrated acid, viz. H_3O^+, H_2SO_4; A is then the conjugate base of HA, which is also depicted without charge.) Next follows a second fast equilibrium protonation, again on the oxygen. The rate-determining step is the loss of a water molecule from the oxonium ion to give the dication (II). Steps [3] and [4] are analogous to the formation of a carbonium ion from an alcohol. Scheme 4 also begins with a rapid equilibrium protonation, but is followed directly by a rate-determining proton transfer to oxygen with simultaneous heterolysis of the nitrogen–oxygen bond. Thus step [6] of Scheme 4 combines step [3] and [4] of Scheme 3. The dication (II), formed by either of the two schemes, would then undergo further reactions as outlined in eq. [7]–[9], which for the present are assumed to be fast steps. According to the classical interpretation of acid-catalyzed reactions, Scheme 3 is the two-proton analogue of the A-1 case while Scheme 4 is similar to the A-S_E2 mechanistic case (14*b*). The following discussion on the correlation of the kinetic data with theoretical derivations will consider both these schemes.

Rate Expressions for Scheme 3

The rate of reaction is given by the Brönsted eq. [10], in which the symbols have their usual significance. Substitution for a_{H^+} is made in terms of h_+ since the second equilibrium protonation is governed by the h_+ acidity function ($h_+ = a_{H^+}f_{C^+}/f_{CH^{++}}$ where C^+ is the reference charged base and CH^{++} its conjugate acid), the resulting expression [11] can then be equated with $k_{obs}\cdot(C_S + C_{SH^+})$ where k_{obs} is the pseudo-first-order rate constant, assuming that there is negligible diprotonation ($C_{SH_2^{++}} \ll C_{SH^+}$) and yields the final rate expression [12].

$$\text{Rate} = \frac{ka_{SH_2^{++}}}{f_\ddagger} = \frac{kC_{SH^+}f_{SH^+}a_{H^+}}{K_{SH_2^{++}}f_\ddagger} \tag{10}$$

$$= \frac{kC_{SH^+}h_+f_{SH^+}f_{CH^{++}}}{K_{SH_2^{++}}f_\ddagger f_{C^+}} \tag{11}$$

$$\log k_{obs} - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} = -H_+ + \log \frac{k}{K_{SH_2^{++}}} + \log \frac{f_{SH^+}f_{CH^{++}}}{f_\ddagger f_{C^+}}. \tag{12}$$

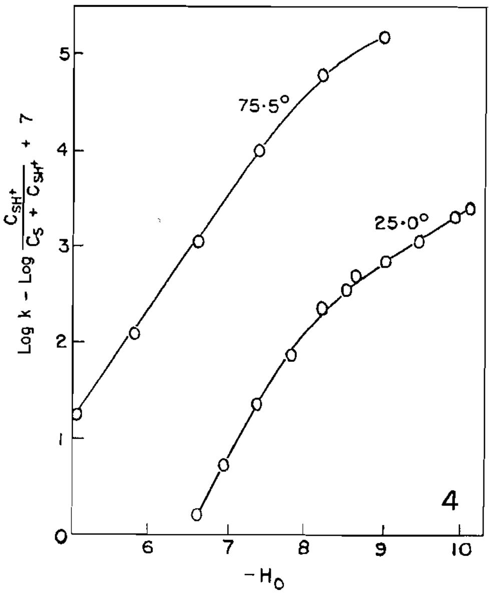
An alternative rate expression can be derived by substitution for a_{H^+} in the expressions for K_{SH^+} and $K_{SH_2^{++}}$ in terms of h_0 and h_+, respectively, followed, as previously, by equating the Brönsted equation with $k_{obs}(C_S + C_{SH^+})$:

$$a_{SH^+} = \frac{a_S h_0 f_{BH^+}}{K_{SH^+}f_B}\,; \quad a_{SH_2^{++}} = \frac{a_{SH^+}h_+f_{CH^{++}}}{K_{SH_2^{++}}f_{C^+}}$$

$$\text{rate} = \frac{ka_{SH_2^{++}}}{f_\ddagger} = \frac{kC_S h_0 h_+ f_S f_{BH^+} f_{CH^{++}}}{K_{SH^+}K_{SH_2^{++}}f_\ddagger f_B f_{C^+}}$$

$$\log k_{obs} - \log \frac{C_S}{C_S + C_{SH^+}} = -H_0 - H_+ + \log \frac{k}{K_{SH^+}K_{SH_2^{++}}} + \log \frac{f_S f_{BH^+} f_{CH^{++}}}{f_\ddagger f_B f_{C^+}}. \tag{13}$$

In order to test the experimental rate and equilibrium data according to eqs. [12] and [13], knowledge of the acidity function H_+ is required. The presently available measurements show that for the indicator 4-aminoacetophenone over the acid range 75–95%



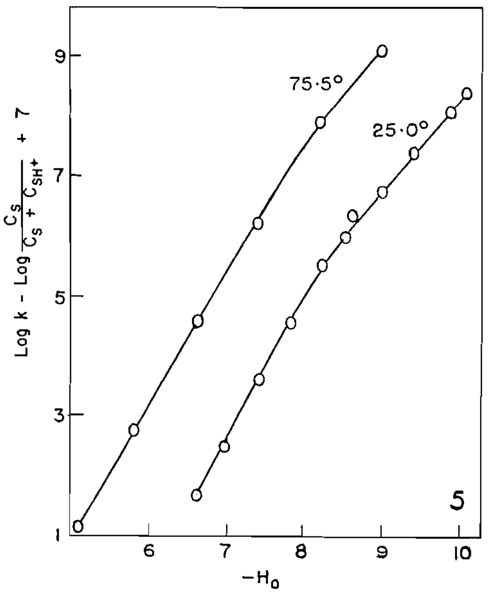


FIG. 4. Plot showing rate dependence based on rate expression [12].
FIG. 5. Plot showing rate dependence based on rate expression [13].

H_2SO_4 H_+ is a parallel function of H_0 (18). Although the generality of this relationship has not been proved, as has not the applicability to this particular system, it has, however, been found to hold in some other studies (19), and hence H_0 will be substituted for H_+ in these tests.[4] Hence the plots of the left sides of eqs. [12] and [13] against H_0 should be linear with slopes of 1 and 2 respectively if the activity coefficient terms are zero or constant. The plots are shown in Figs. 4 and 5 and the appropriate data are contained in Table IV. All the plots are curved downwards and the initial slopes are slightly in excess of the predicted values. Thus the 25° and 75° curves of Fig. 4 have initial slopes of 1.30 and 1.19, while the corresponding curves of Fig. 5 have slopes of 2.32 and 2.17.[5] The assumptions behind these plots must be critically examined. The pairs $C^+ - CH^{++}$ and SH^+ — T.S. have the same charge characteristics and both differ by one proton. The ratios of the activity coefficients should then vary in a parallel manner with acid concentration, i.e. $f_{C^+}/f_{CH^{++}} = f_{SH^+}/f_{\ddagger}$. In the case of eq. [13], however, the argument concerning cancellation of activity coefficients cannot be made, so that this term would not be expected to cancel, unless fortuitously. Therefore the plot of Fig. 4 according to eq. [12] is considered to be the more sound one theoretically. A possible reason for the deviation from linearity at the higher acid concentrations will be considered later.

Rate Expressions for Scheme 4

Since all acid species present can fulfill the function of HA one should have general acid catalysis. In practice this is difficult to demonstrate in strongly acid solutions (14*b*)

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[4] *The parallelism of H_+ and H_0 refers to H_0 values compiled by Long and Paul (14a) and will not be strictly correct when the recently measured Jorgenson–Hartter (17) values are used. However, in view of the scarcity of data on the H_+ function it seems to be desirable to continue assuming this parallelism with the new H_0 function (17) also, even though an error may be introduced. It is also noteworthy that for the medium 20% ethanol – 80% aqueous sulfuric acid H_0 and H_+ are equivalent functions (13b).*

[5] *If the H_0 values at 25° (17) are corrected to 75° using the data of Gelbstein et al. (20) then the 75° slopes become 1.25 and 2.44 respectively. Similarly, if the other plots involving H_0 are so corrected, the slopes of the 75° plots assume values closer to the 25° plots. This would indicate that there is no change in mechanism over this temperature range.*

and hence acidity function correlations are sought. The problem now arises whether to assign the H_2O of H_3O^+ a structural role in the transition state (14*b*). If a transition state free of H_2O is considered then the rate expressions [14] and [15] may be derived.

$$[14] \qquad \log k_{\mathrm{obs}} - \log \frac{C_{\mathrm{SH^+}}}{C_{\mathrm{S}} + C_{\mathrm{SH^+}}} = -H_0 + \log k' + \log \frac{f_{\mathrm{SH^+}} f_{\mathrm{BH^+}}}{f_{\ddagger}' f_{\mathrm{B}}}$$

$$[15] \qquad \log k_{\mathrm{obs}} - \log \frac{C_{\mathrm{S}}}{C_{\mathrm{S}} + C_{\mathrm{SH^+}}} = -2H_0 + \log \frac{k'}{K_{\mathrm{SH^+}}} + \log \frac{f_{\mathrm{S}} f_{\mathrm{BH^+}}^{\;2}}{f_{\ddagger}' f_{\mathrm{B}}^{\;2}} .$$

Except for the activity coefficient terms, these equations are similar to [12] and [13], derived for Scheme 3, and in practice cannot be differentiated from them.

When water is considered to be present in the transition state one may derive eq. [16] and [17] for consideration.

$$[16] \qquad \log k_{\mathrm{obs}} - \log \frac{C_{\mathrm{SH^+}}}{C_{\mathrm{S}} + C_{\mathrm{SH^+}}} = \log C_{\mathrm{HA}} + \log k' + \log \frac{f_{\mathrm{SH^+}} f_{\mathrm{HA}}}{f_{\ddagger}''}$$

$$[17] \qquad \log k_{\mathrm{obs}} - \log \frac{C_{\mathrm{S}}}{C_{\mathrm{S}} + C_{\mathrm{SH^+}}} = -H_0 + \log C_{\mathrm{HA}} + \log \frac{k'}{K_{\mathrm{SH^+}}} + \log \frac{f_{\mathrm{S}} f_{\mathrm{HA}} f_{\mathrm{BH^+}}}{f_{\ddagger}'' f_{\mathrm{B}}} .$$

The activity coefficient term in [16] is likely to change uniformly with acid concentration. In fact the $\log k_{\mathrm{obs}} - \log (C_{\mathrm{SH^+}}/C_{\mathrm{S}} + C_{\mathrm{SH^+}})$ vs. $\log C_{\mathrm{H^+}}$ plots at 25° and 75° are curved with initial slopes of 27 and 25! No obvious assumption can be made concerning the activity coefficient term in [17]. A plot of $\log k_{\mathrm{obs}} - \log (C_{\mathrm{S}}/C_{\mathrm{S}} + C_{\mathrm{SH^+}})$ vs. $\log C_{\mathrm{H^+}} - H_0$ is closely similar to that in Fig. 5, with initial slopes at 25° and 75° of 2.30 and 2.13 respectively.

In evaluation of the above tests of Schemes 3 and 4 it is apparent that the rate data do not fit exactly any of the derived rate expressions. Hence differentiation between the proposed schemes cannot be made. Also, yet other mechanisms cannot be excluded. In this regard the curvature of the plots provides a clue, since the break in most of the curves occurs very close to the monohydrate composition. A plausible explanation would appear to be that step [7] of the proposed scheme may become rate determining as the water activity decreases, which will become particularly crucial above the monohydrate composition. Alternatively, the curvature could be considered to lend support to Scheme 3. If, as is likely, catalysis by H_2SO_4 is less effective than by H_3O^+, then this decreasing dependence of rate on acidity would be expected, particularly above the monohydrate composition.

The Bunnett Criteria

According to the proposals of Bunnett (21, 22) $\log k_{\mathrm{obs}} - \log (C_{\mathrm{SH^+}}/C_{\mathrm{S}} + C_{\mathrm{SH^+}})$ was plotted (*i*) against $\log a_{\mathrm{H_2O}}$ and (*ii*) against $\log C_{\mathrm{H^+}} + H_0$. Plot (*i*) is curved; at 25° the initial slope is -2.1 decreasing to -0.5 while at 75° the slopes are -2.8 and -0.8. Plot (*ii*) is also curved; the corresponding slopes at 25° are -1.8 and -0.4 and at 75°, -1.5 and -0.5. Negative slopes in the Bunnett-type plots indicate that water is not involved in the rate-determining transition state, either as nucleophile or as proton-transfer agent. The Bunnett criteria are thus in accord with Scheme 3 but are subject to the qualification that they have not been extensively tested in the high acid regions used in this study and neither is it known whether they would apply to two proton processes. It has also been suggested (22) that curvature in these plots is indicative of more than one competing mechanism.

Activation Parameters

The activation parameters calculated from the rate data at 25° and 75° for the common acid concentrations from 75% to 90% H_2SO_4 are given in Table V. Long *et al.* (23) have proposed that entropies of activation may be used as criteria of mechanism in acid-catalyzed hydrolyses; thus reactions proceeding by the A-1 mechanism have in general $\Delta S^{\ddagger}$ values between 0 and +20, while A-2 reactions have $\Delta S^{\ddagger}$ values between −10 and −30. The $\Delta S^{\ddagger}$ values for azoxybenzene rearrangement fall somewhere in between the two ranges. However, most of the literature data refer to very dilute acid solutions, in contrast to the present work. The data (Table V) show a trend, that $\Delta S^{\ddagger}$ becomes more positive as the acid concentration decreases, so that a positive $\Delta S^{\ddagger}$ might well result in dilute acid solution. This would then be in accord with the A-1 mechanism of Scheme 3, though it is not known whether the entropy criterion would apply to two-proton processes.

TABLE V

Activation parameters for azoxybenzene rearrangement

% H_2SO_4	90.37	85.61	80.15	75.30
E_a(kcal)	22.1±0.2	22.7±0.2	24.7±0.3	26.8±0.5
Log A	12.08	12.03	12.47	12.86
$\Delta S^{\ddagger}$ (e.u.)	−5.3±0.5	−5.5±0.5	−3.5±0.9	−1.7±1.5

It was also hoped that the high temperature data might provide an indication of a competing mechanism proposed in the past (7, 9). The close similarity of the various curves at the two temperatures suggest that there is no change in reaction mechanism on increasing the temperature from 25° to 75°.[5]

Discussion of Previous Mechanisms of the Wallach Rearrangement

Shemyakin *et al.* (5) proposed that the Wallach rearrangement proceeds by way of the N,N-oxide intermediate as a means of explaining the equalization of the nitrogen label on rearrangement. As evidence of this intermediate, the Russian workers cited the formation of 50%–60% azobenzene when the rearrangement was carried out in chlorosulfonic acid in presence of potassium iodide (6). However, that chlorosulfonic acid may act in an anomalous manner is indicated by the finding that 4,4′-dichloro- and 4,4′-dibromoazoxybenzene in chlorosulfonic acid yielded only the corresponding azobenzenes (24), whereas in sulfuric acid the former yielded some 2-hydroxy-4,4′-dichloroazobenzene in addition to the azobenzene (4*b*). In view of the complex situation with respect to side products (4) under usual preparative conditions, a more extensive study of the effect of added iodide on the rearrangement of a number of azoxybenzenes, both in sulfuric acid and in chlorosulfonic acid, is required for such evidence to be decisive. It is doubtful that the role of the α-β isomerization in the scheme of the Wallach rearrangement can be considered as known in the absence of further tracer as well as kinetic studies.

The interpretation of Shemyakin *et al.* (5, 6) suffers from the disadvantage that it does not consider the participation of acid, even though the reaction is clearly acid catalyzed. The basic difficulty with the N,N-oxide intermediate is that it appears not to provide a path for further reaction on the basis of the theories of acid catalysis. Oae *et al.* (9) consider the protonated N,N-oxide to be intermediate in the interconversion of α- and β-isomers but not in the Wallach rearrangement. The difficulty now becomes that in order to explain the lack of equalization of label in the recovered azoxybenzene one has to postulate that protonation of azoxybenzene is not reversible, as shown in Scheme 2, a situation which is not likely to obtain in view of the present equilibrium (pK) studies. Further, our data show that monoprotonated azoxybenzene is not the rate-limiting species, as is suggested by Scheme 2.

In conclusion it should be stated that the present work has not provided proof of the dication intermediate (II), although it is fully in accord with this intermediate. Definitive evidence may perhaps be found through kinetic and other physical studies, now in progress, in anhydrous acids where it is possible that (II) might become stabilized.

EXPERIMENTAL

Materials

Recrystallizations were carried out in the dark to exclude the possibility of *cis–trans* isomerization, and in the case of azoxybenzene the occurrence of the ortho-Wallach rearrangement. Ultraviolet and visible spectra were determined on a Beckmann DK1 recording spectrophotometer using 1 cm quartz cells. Commercial 95% ethanol was fractionally distilled using a Dufton column and the fraction boiling at 78.2 °C was collected. The following compounds were recrystallized at least twice from aqueous ethanol and their ultraviolet and visible spectra in 95% ethanol determined: *trans*-azoxybenzene, m.p. 35–36° (lit. (11*a*) m.p. 35°), log $\epsilon_{\max}$ 4.17 (322 mμ), 3.87 (260 mμ), 3.95 (232 mμ) (lit. (25) log $\epsilon_{\max}$ 4.16 (323 mμ), 3.85 (260 mμ), 3.92 (231 mμ)); *p*-hydroxyazobenzene; m p. 153–154° (lit. (26) m.p. 155–156°) log $\epsilon_{\max}$ 4.40 (349 mμ) (lit. (27) log $\epsilon_{\max}$ 4.39 (348 mμ)); *trans*-azobenzene; m.p. 67.5–68.5° (lit. (28) m.p. 68–69.5°); *o*-Hydroxyazobenzene was prepared by irradiating a 4% solution of azoxybenzene in 95% ethanol for 3 h using a Hanovia high pressure mercury lamp with a quartz insert. The product had m.p. 83–84° (lit. (29*a*) m.p. 82.5–83.5°), log $\epsilon_{\max}$ 4.26 (323 mμ) (lit. (29*b*) log $\epsilon_{\max}$ 4.26 (323 mμ).

Fisher C.P. Reagent grade sulfuric acid was used throughout this study. Concentrations were determined by titrating weighed samples with standard sodium hydroxide. The aqueous sulfuric acid solutions used for both the kinetic measurements and the pK studies were prepared by dilution by weight of a stock solution of known concentration. All concentrations of sulfuric acid are percent by weight.

Product Analysis

Azoxybenzene (1.2 g) was dissolved in 200 ml of 77.5% sulfuric acid contained in a stoppered, aluminium foil covered flask. The reaction was carried out for 1 000 h at room temperature, equivalent to 2.5–3.0 half-lives. The reaction mixture was then added slowly to a solution of 250 g of sodium hydroxide in 250 g of water cooled in ice–methanol. The temperature of the neutralization process was never allowed to rise above 0 °C. By a series of ether extractions from acidic and basic solutions, the products of the rearrangement and unreacted azoxybenzene were separated into neutral, basic, and acidic fractions which were then analyzed qualitatively by thin-layer chromatography, using 35–60° petroleum ether and benzene–methanol (10:1) as developers, and quantitatively by ultraviolet and visible spectroscopy.

A second rearrangement was similarly carried out by dissolving 1 g of azoxybenzene in 200 ml of 90.4% sulfuric acid. After 12.5 h at 25 °C, equivalent to 5 half-lives the reaction mixture was worked up as previously.

Kinetic Procedures

Dilution Method

The reaction solution was prepared by adding a 0.01 g accurately weighed sample of azoxybenzene to 25 ml of aqueous sulfuric acid of known concentration in a 50 ml round bottom glass stoppered flask wrapped in aluminium foil and immersed in the thermostatted bath. Samples were removed at regular intervals using a 1 ml fast delivery calibrated pipette and run into 40 ml of quenching solution, which had been precooled in ice–water, in a 50 ml graduated flask. The flasks were stored in the dark and after attaining room temperature were made up to mark with quenching solution and analyzed spectrophotometrically. Rate constants were calculated from absorbances at 435 mμ, the wavelength corresponding to maximum absorption of *p*-hydroxyazobenzene in the quenching solution, 1 M NaOH in 80% aqueous ethanol (ϵ = 22 830).

Sealed Tube Method at 75.5°

The reaction solution was prepared as for the dilution method except that 0.005 g of azoxybenzene was used. Two milliliter samples were pipetted into small tubes which were sealed, wrapped in foil, and placed in the thermostatted oil bath at 75.5 °C. The tubes were removed at intervals, cooled, and stored in a refrigerator. On completion of the run the contents were added to quenching solution, made up to 50 ml, and analyzed as previously. Studies on the decomposition of *p*-hydroxyazobenzene in aqueous sulfuric acid, where required, were carried out under the same conditions as the kinetic measurements.

Direct Method at 25 °*C*

The reaction solution was prepared by successive dilution: a 1 ml portion of a solution of 0.01 g azoxybenzene in 50 ml sulfuric acid was further diluted to 50 ml using sulfuric acid of the same concentration. This solution was placed in the thermostatted sample cell. Aqueous sulfuric acid of the same concentration as the reaction solution was used in the reference cell. The spectrum of the reaction solution was recorded at regular time intervals from 500 mμ to 375 mμ.

pK Determination

A 1 ml sample of a 2×10^{-3} M solution of azoxybenzene in 95% ethanol was pipetted into a 50 ml flask and the solvent evaporated with a slow stream of dry nitrogen. Aqueous sulfuric acid (25 ml) of known concentration was added and the flask was agitated vigorously to ensure dissolution of the azoxybenzene. The spectrum of each solution was recorded over the range 300–500 mμ. For the 85, 90, and 95% sulfuric acid solutions, in which the rearrangement is relatively fast, the spectra were recorded at regular time intervals and extrapolated to zero time. In the case of the 85 and 90% sulfuric acid solutions, the extrapolated values did not differ by more than 5% from the first recorded values. In the case of the 95% sulfuric acid the difference was 12%. The results are shown in Table III.

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