L. J. Andrews during his stay there as a Fulbright–Hays Research Scholar (1967–1968). Two of the authors are further indebted to the National Science Foundation for fellowships which they held while the research was conducted (M. J. S. for a Predoctoral Cooperative Fellowship, and A. D. M. for support under the terms of the Undergraduate Research Participation Program).

Mechanisms of Oxidation of Aniline and Related Compounds in Basic Solution

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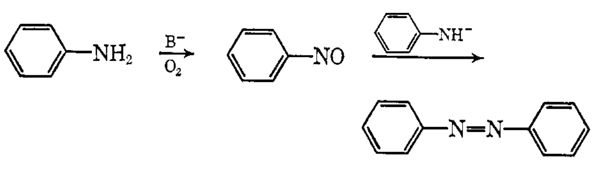
Abstract: The formation of azobenzene by oxidation of aniline in basic solution is explicable in terms of condensation involving nitrosobenzene rather than coupling of anilino radicals. This view is supported by the experimental results of a study of the oxidation of hydrazobenzene and condensation of nitrosobenzene with aniline. In the condensation reaction, the different results observed in the presence and in the absence of oxygen depend on the behavior of nitrosobenzene radical anion. In the oxidation of nitrosobenzene itself, azoxybenzene is possibly formed from the condensation of nitrosobenzene radical anion with nitrosobenzene rather than coupling of nitrosobenzene radical anions; this view is supported by the experimental rate of decay of the nitrosobenzene radical anion by esr as compared to the oxygen absorption rate and by the comparison of the behavior of nitrosobenzene in the presence of excess base with deficient base.

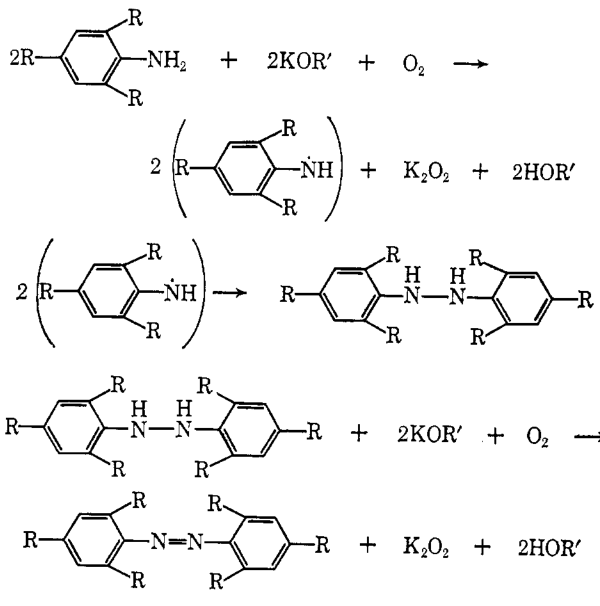
It is well known that primary arylamines react with molecular oxygen to yield azobenzene derivatives in the presence of base.[1-4] Russell[5a,6] suggested that azobenzene is formed from a base-catalyzed condensation involving the nitroso compound as shown in eq 1.



(1)

Alternatively, Horner[4] proposed that azobenzene derivatives may result from the dehydrogenation of the hydrazobenzenes arising from the coupling of anilino radicals as shown in eq 2–4.

In the present paper, we discuss these mechanisms in view of results of a study of a base-catalyzed oxidation of hydrazobenzene and a base-catalyzed condensation of nitrosobenzene with aniline in the presence of molecular oxygen or nitrogen. This condensation reaction sequence accompanying the azoxybenzene formation is also discussed based on its reaction rate and esr spectroscopy.



(2)

(3)

(4)

$R = CH_3, R' = C(CH_3)_3$

Reactions 2–4 relate to the base-catalyzed oxidation of nitrosobenzene, which produces mainly azoxybenzene and nitrobenzene.[7] However, the effect of oxygen and the oxidation mechanism have not been investigated yet. Consequently, the base-catalyzed oxidation of nitrosobenzene was examined by product analysis, oxygen absorption rate, and esr spectroscopy. A novel mechanism of azoxybenzene formation has been proposed.

Experimental Section

Reagents. Dimethyl sulfoxide (Crown Zellerbach Corp.) was distilled under reduced pressure from molecular sieves. Commercial *t*-butyl alcohol was distilled from calcium hydride. Potassium *t*-butoxide was commercial material (K & K Laboratories, Inc.). Aniline was purified as follows. Commercial aniline was

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(1) R. Anschütz and G. Schulz, *Ber.*, **10**, 1803 (1877).

(2) A. Bacovescu, *ibid.*, **42**, 2938 (1909).

(3) G. A. Russell, E. G. Janzen, H-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

(4) L. Horner and J. Dehnert, *Ber.*, **96**, 786 (1963).

(5) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965: (a) p 150; (b) p 120.

(6) After this manuscript was submitted, Russell reported the mechanism of oxidation of aniline in basic solution (G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Am. Chem. Soc.*, **89**, 3821 (1967)).

(7) E. Bamberger, *Ber.*, **33**, 1939 (1900); **35**, 732 (1902).

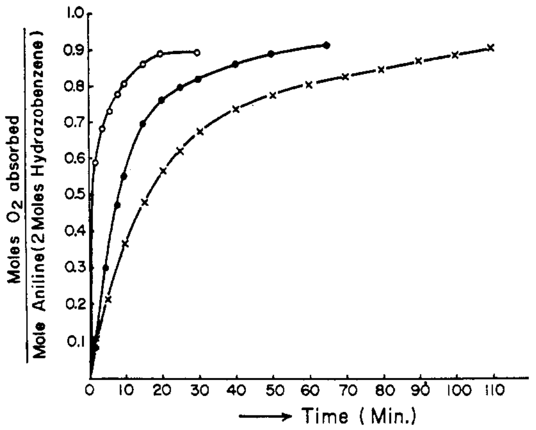

Figure 1. Oxygen absorption rate of aniline and hydrazobenzene in 80:20 DMSO–*t*-BuOH (25 ml) at 25°: ●, Ph–NH$_2$: 3 mmol, *t*-BuOK: 6 mmol; ×, Ph–NH$_2$: 3 mmol, *t*-BuOK: 3 mmol; ○, Ph–NHNH–Ph: 1.5 mmol, *t*-BuOK: 3 mmol.

acidified with hydrochloric acid, followed by steam distillation. The alkalized residue was again steam distilled. The distillate was extracted with ether and dried over calcium chloride, and the solution was distilled with a rectifying column to yield pure aniline.

Commercial hydrazobenzene was purified by a catalytic hydrogenation technique using palladium–charcoal to give a white crystalline material according to the method of Brand,[8] mp 126° (lit.[8] mp 126°). Thin layer chromatography showed only one spot.

Nitrosobenzene was prepared from aniline according to the method of Gattermann,[9] mp 67° (lit.[9] mp 68°). Pentadeuterionitrobenzene was prepared from commercial hexadeuteriobenzene (Merck's reagent) according to the method of Fieser.[10] The nmr spectrum and the infrared spectrum of this compound showed it to be pure pentadeuterionitrobenzene.

General Oxidation Procedure. The oxidations were performed at 25 ± 1° (*ca.* 760 mm) in a 50–100-ml creased, three-necked flask, equipped with an addition funnel, a paddle stirrer, and an oxygen introduction tube. This tube was connected to a manifold containing an oxygen inlet valve, a pressure relief by-pass, a gas buret with a mercury leveling bulb, and a mercury manometer. Solutions containing a substrate were placed in the creased flask, followed by introduction of oxygen to purge air prior to the start of a reaction. After air was purged completely, solutions of base were added to the creased flask at 25° under vigorous stirring (800 rpm). Oxygen absorption was recorded as a function of reaction time. When oxygen absorption had ceased, the contents of the flask were poured into water. The solutions were extracted with ether, dried over calcium chloride, evaporated to remove ether, and then analyzed by glpc.

Glpc Analysis. The reaction mixtures were analyzed with a Shimazu GC-1B type gas chromatograph using a 5% SE-30 column. Aniline and nitrobenzene were analyzed at 130° using naphthalene as a reference. Azobenzene and azoxybenzene were analyzed at 180°; in the former case hexamethylbenzene, in the latter case azobenzene were used as references, respectively.

Electron Spin Resonance Technique. The esr spectra were recorded with a Varian V-4502 spectrometer having a 12-in. magnet with 100-kcps field modulation. Cells similar to the type proposed by Russell[11] were used for all experiments and esr spectra measured according to their method. The esr spectrum of nitrosobenzene in an 80:20 DMSO–*t*-BuOH solution containing potassium *t*-butoxide was analyzed, and identified with nitrosobenzene radical anion having hfsc as follows: $a^{\mathrm{N}} = 8.08$, $a_p{}^{\mathrm{H}} = 4.04$, $a_{o_1}{}^{\mathrm{H}} = 4.04$, $a_{o_2}{}^{\mathrm{H}} = 2.93$, $a_m{}^{\mathrm{H}} = 1.11$. This signal disappeared immediately on exposure of the solution to oxygen.

Determinations of the radical concentrations were made compared to a standard solution of diphenylpicrylhydrazyl by using a Varian V-4532 dual sample cavity. For the purpose of examination of the behavior of nitrosobenzene radical anion, an 80:20 DMSO–*t*-BuOH solution of known concentration of nitrosobenzene was mixed with a potassium *t*-butoxide solution in a nitrogen box followed by sampling into an esr flat cell. On the one hand an esr decay curve was recorded, on the other, the reaction mixture was quenched with water containing no oxygen and analyzed. Figure 2a shows a decay curve of nitrosobenzene radical anion generated in an 80:20 DMSO–*t*-BuOH solution, at an initial concentration of 2×10^{-2} *M* nitrosobenzene and 3×10^{-1} *M* potassium *t*-butoxide. The reaction mixture was quenched at the 9-min point, where the concentration of nitrosobenzene radical anion was 1.32×10^{-2} *M* (66% yield), to give 77.8% yield of azoxybenzene, 6% yield of azobenzene, and 2.6% yield of nitrobenzene. In another experiment, after 27 hr under the same conditions, the solution containing 7.28×10^{-4} *M* (3.6% yield) nitrosobenzene radical anion gave 76% yield of azoxybenzene, 16% yield of azobenzene, and a trace of nitrobenzene. A high yield of nitrosobenzene radical anion (86%) was obtained after 6 min from a more dilute solution (5×10^{-3} *M* nitrosobenzene, 5×10^{-2} *M* potassium *t*-butoxide).

Oxidation of Aniline and Hydrazobenzene. According to the general oxidation procedure, aniline and hydrazobenzene, respectively, were oxidized in basic solution.

In some cases, prior to pouring of a reaction mixture into water, some excess water was added in the closed system, the mixture was warmed in a water bath and cooled to 25°, and the amount of oxygen generated was measured. As one method for the analysis of the products, thin layer chromatography was applied. From the oxidation of aniline, five small spots were obtained in addition to those corresponding to azobenzene and nitrobenzene, and on the oxidation of hydrazobenzene one spot which was not found in the former was recognized.

Condensation of Aniline and Nitrosobenzene. In the Presence of Oxygen. According to the general oxidation procedure, in which a four-necked, creased flask was used instead of a three-necked flask, an 80:20 DMSO–*t*-BuOH solution (2 ml) of aniline (0.5 mmol), a solution (2 ml) of nitrosobenzene (0.5 mmol), and a solution (4 ml) of potassium *t*-butoxide (1.0 mmol) were mixed under stirring (800 rpm). At reaction times of 20 sec, 2 min, and 8 min, each run was quenched by water and analyzed by glpc.

In the Absence of Oxygen. In a nitrogen box, to a mixture of 0.5 mmol of aniline and 0.5 mmol of nitrosobenzene in 4 ml of 80:20 DMSO–*t*-BuOH was added a solution of 1.0 mmol of potassium *t*-butoxide in 4 ml of 80:20 DMSO–*t*-BuOH. At reaction times of 6 min, 15 min, and 25 min, each run was quenched by water containing no oxygen, and then analyzed by glpc.

Oxidation of Nitrosobenzene. According to the general oxidation procedure, nitrosobenzene was oxidized in 80:20 DMSO–*t*-BuOH solution containing potassium *t*-butoxide with variations in the concentration of nitrosobenzene, the stirring rate, and the molar ratio of nitrosobenzene to potassium *t*-butoxide. In this case the reaction was quenched by acetic acid, because it was noted that by quenching with water a small amount of azoxybenzene was produced from nitrosobenzene itself; azoxybenzene was not produced by quenching with acetic acid.

Reaction of Nitrosobenzene with Pentadeuterionitrobenzene. A mixture of nitrosobenzene and pentadeuterionitrobenzene was oxidized using the general oxidation apparatus under the same conditions as for the oxidation of nitrosobenzene alone. From the reaction mixture azoxybenzene was isolated by alumina column chromatography and recrystallized from petroleum ether (bp 30–60°), mp 35.5° (lit.[9] mp 36°). The nmr spectrum of this compound was the same as that of authentic azoxybenzene.

Results

Oxidation of Aniline and Hydrazobenzene. As Russell[3] reported previously, aniline absorbs oxygen, in 80:20 DMSO–*t*-BuOH solution containing potassium *t*-butoxide, to yield azobenzene. Oxygen absorption rates at 25° are demonstrated in Figure 1. At the end points of these curves, the reaction mixtures were quenched with water and analyzed by glpc. Yields of products are listed in Table I.

Hydrazobenzene was oxidized under the same condition to give azobenzene as shown in Table I. During the reaction time, the reaction mixture changed color from dark brown to orange. The brown color suggests

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(8) K. Brand and J. Streiner, *Ber.*, **55**, 886 (1922).

(9) L. Gattermann, "Die Praxis des organischen Chemikers," Walter De Gruyter & Co., Berlin, Germany, 1940, p 184.

(10) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 1957, p 148.

(11) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

Table I. Oxidation of Aniline and Related Compounds in Basic Solution[a]

Run	Compound	Amount, mmol	*t*-BuOK, mmol	Stirring rate, rpm	Yield, %[b]			
					Azobenzene	Azoxybenzene	Nitrobenzene	Aniline
1	Aniline	3	6	800	86.0	0	6	0[c]
2	Aniline	3	3	800	63.0	0	9	1.8[c]
3	Aniline	3	6	800	64.6	0	Trace	18.1[d]
4	Hydrazobenzene	1.5	3	800	95.3	0	0	0[e]
5	Hydrazobenzene	1.5	6	800	88.9	0	0	0[e]
6	Nitrosobenzene	0.5	6	800	Trace	40.0	38.0	0
7	Nitrosobenzene	1.5	6	800	Trace	41.3	32.7	0
8	Nitrosobenzene	3	6	800	Trace	41.3	31.3	0
9	Nitrosobenzene	3	6	600	Trace	47.3	29.7	0
10	Nitrosobenzene	3	6	200	Trace	47.6	26.2	0
11	Nitrosobenzene	3	6	1000	Trace	41.3	29.7	0
12	Nitrosobenzene	3	1.5	800	Trace	48.0	26.0	0
13	Nitrosobenzene	0.5	7.5	...	6.0	77.8	2.6	0[f]
14	Nitrosobenzene	0.5	0.25	...	Trace	78.4	Trace	0[f]

[a] 25 ml of 80:20 DMSO–*t*-BuOH at 25°. [b] After oxygen absorption ceased, quenched and analyzed by glpc. [c] No phenazine from glpc and tlc. [d] Quenched at absorbed O_2: 1.5 mmol. [e] Another spot from tlc. [f] Absence of oxygen.

the presence of azobenzene radical anion. It was surprising, however, to find that hydrazobenzene rapidly absorbed 2 mol of oxygen/mol of hydrazobenzene (Figure 1). It should be noted that azobenzene in 80:20 DMSO–*t*-BuOH did not absorb oxygen in the presence of potassium *t*-butoxide. After oxygen absorption stopped, an excess of water was added to generate oxygen corresponding in amount to about 0.75 equiv of absorbed oxygen. With toluene as a solvent instead of 80:20 DMSO–*t*-BuOH, the same result was obtained.

Reaction of Aniline with Nitrosobenzene. The condensation reaction between aniline and nitrosobenzene was examined in the presence or absence of oxygen. The reaction rates are summarized in Table II.

Table II. Reaction of Nitrosobenzene with Aniline in Basic Solution in the Presence or Absence of Oxygen[a]

	Yield, %[b]							
				In the absence of O_2				
	In the presence of O_2			Run 1			Run 2[c]	
	20 sec	2 min	8 min	6 min	15 min	25 min	6 min	15 min
Aniline	21.0	14.0	6.0	30.8	30.8	30.8	5.0	7.0
Azobenzene	65.0	69.0	70.0	56.9	58.8	59.8	85.0	88.0
Azoxybenzene	15.6	20.0	20.0	27.4	27.4	27.4	56.0	50.0
Nitrobenzene	12.0	12.0	14.0	4.0	4.6	5.2	1.0	1.0
Absorbed O_2[d]	16.0	32.8	49.0	...	...	...	...	...

[a] Initial concentration: Ph—NH_2 0.5 mmol, Ph—NO 0.5 mmol, *t*-BuOK 2.0 mmol in 8 ml of 80:20 DMSO–*t*-BuOH at 25°. [b] Yields were calculated based on the following reactions: Ph—NH_2 + Ph—NO → Ph—N=N—Ph, 2Ph-NO → Ph—N(O)=N—Ph, Ph—NO → Ph—NO_2. [c] Initial concentration: Ph—NH_2 0.5 mmol, Ph—NO 1.0 mmol, *t*-BuOK 2.0 mmol in 8 ml of 80:20 DMSO–*t*-BuOH. [d] Molar per cent based on aniline.

The yield of azobenzene in Table II is calculated based on the condensation of aniline with nitrosobenzene, because if it is based on the formation from aniline alone, an unreasonably high yield is obtained. In both the presence and absence of oxygen, the reactions for all practical purposes stopped within 6 min. There is some difference in the product distribution with and without oxygen although the formation of nitrobenzene may suggest the presence of a trace of oxygen in the latter runs. As shown in runs 1 and 2 of Table II, increasing the molar ratio of nitrosobenzene to aniline increases the conversion of aniline. The behavior of nitrosobenzene in the absence and presence of oxygen in basic solution was examined as follows.

Electron Spin Resonance of Nitrosobenzene in Basic Solution. Recently, by using the esr technique Russell[12] reported that the reaction of nitrosobenzene and phenylhydroxylamine in basic solution produces a quantitative yield of nitrosobenzene radical anion, and suggested that the formation of azoxybenzene is due to a coupling of this radical anion.

In the present study, it was found that nitrosobenzene alone in 80:20 DMSO–*t*-BuOH containing potassium *t*-butoxide gave rise to the nitrosobenzene radical anion from the esr spectrum which is similar to that reported previously.[12–14] Figure 2 demonstrates two of the decay curves of nitrosobenzene radical anion which follow second-order kinetics.

From the decay curve a in the presence of excess base and another esr experiment (Experimental Section) we learn that the formation rate of this radical anion is rapid while the decay is slow. On the other hand, it was found that by quenching with water containing no oxygen at the 9-min point in a of Figure 2, azoxybenzene was produced in 78% yield. This result is similar to the result of the self-condensation of nitrosobenzene with potassium hydroxide by Oae.[15]

In the case of the deficient base solution (nitrosobenzene 0.02 *M*, potassium *t*-butoxide 0.01 *M*), the decay curve follows b of Figure 2. The maximum point of the concentration of nitrosobenzene radical anion will not exceed 0.01 *M*, and the decay rate is faster than a (rate constants: a, 2.85×10^{-2} l./mol sec; b, 5.75×10^{-1} l./mol sec). It was noteworthy to find that azoxybenzene was produced in 78.4% yield by quenching with acetic acid containing no oxygen at the 10-min point of curve b.

Oxidation of Nitrosobenzene in Basic Solution. For the purpose of explaining the formation of azoxybenzene under the oxygen atmosphere in the condensation reaction of nitrosobenzene with aniline, oxidation of nitro-

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(12) G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, **87**, 122 (1965).

(13) F. J. Smentowski, *ibid.*, **85**, 3036 (1963).

(14) E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, 13 (1965).

(15) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Japan*, **36**, 728 (1963).

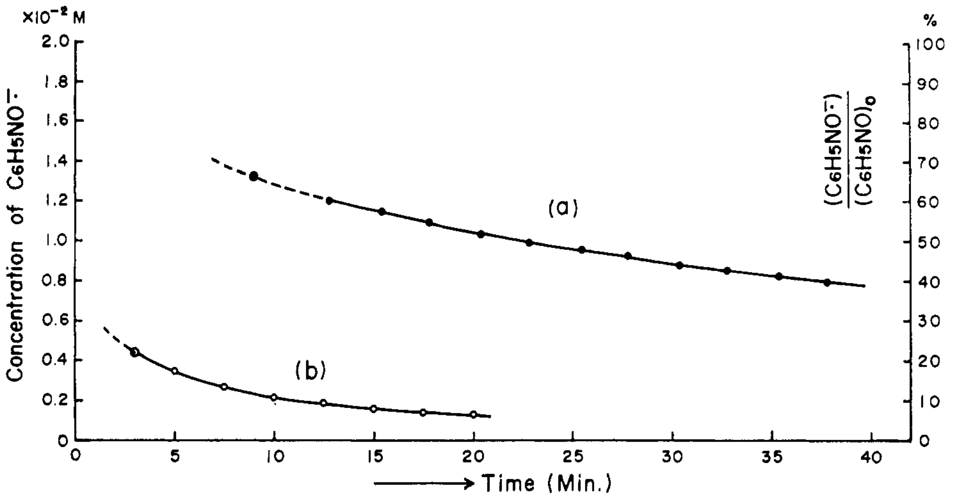

Figure 2. Decay curve of nitrosobenzene radical anion in 80:20 DMSO-*t*-BuOH from esr spectrum at 25°: (a) initial concentration: Ph-NO 0.02 *M*, *t*-BuOK 0.3 *M*; (b) initial concentration: Ph-NO 0.02 *M*, *t*-BuOK 0.01 *M*.

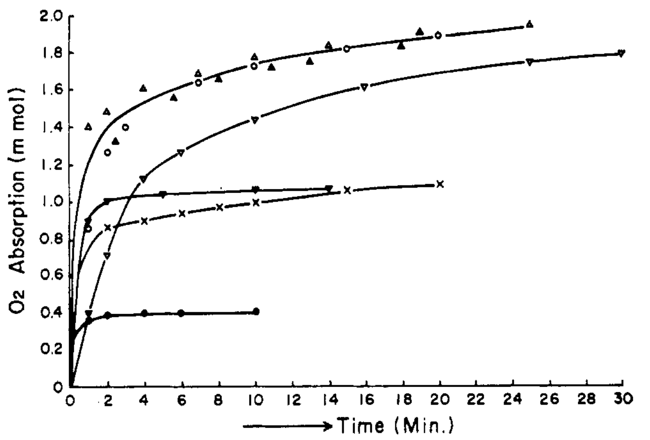

Figure 3. Oxygen absorption rate of nitrosobenzene in 80:20 DMSO-*t*-BuOH (25 ml) containing *t*-BuOK (6 mmol) at 25°: ●, 6; ×, 7; ○, 8; ▲, 9; ▽, 10; △, 11; ▼, 12. Numbers refer to the runs in Table I.

sobenzene itself in basic solution was carried out. After oxygen absorption had nearly ceased, the reaction mixtures were analyzed by glpc. Oxygen absorption rates and yields of azoxybenzene and nitrobenzene are shown in Figure 3 and Table I, respectively. It was somewhat surprising to find in Table I that a considerable amount of azoxybenzene was formed even in the presence of oxygen.

Discussion

The following reaction sequence on the oxidation of hydrazobenzene in basic solution is proposed to rationalize the experimental results.

$$C_6H_5NHNHC_6H_5 + B^- \rightleftharpoons [C_6H_5NHNC_6H_5]^- + BH \quad (5)$$

$$[C_6H_5NHNC_6H_5]^- + B^- \rightleftharpoons [C_6H_5N{-}NC_6H_5]^{2-} + BH \quad (6)$$

$$[C_6H_5N{-}NC_6H_5]^{2-} + O_2 \longrightarrow [C_6H_5N{=}NC_6H_5]\cdot^- + O_2\cdot^- \quad (7)$$

$$[C_6H_5N{=}NC_6H_5]\cdot^- + O_2 \longrightarrow C_6H_5N{=}NC_6H_5 + O_2\cdot^- \quad (8)$$

$$2O_2\cdot^- + 2K^+ \longrightarrow K_2O_4 \quad (9)$$

On adding water

$$K_2O_4 + H_2O \longrightarrow 2KOH + {}^3/_2O_2 \quad (10)$$

Hinshelwood[16] studied the kinetics of the oxidation of hydrazobenzene in basic solution and concluded that the rate-determining step in this process is the second ionization of hydrazobenzene to give a doubly charged negative ion (eq 6), but no comment was given about stoichiometry in this reaction. Previously, Russell[17,18] reported that significant concentration of the radical anion was detected by esr in the reaction of a trace of oxygen with hydrazobenzene (eq 7).

The fact that on adding an excess of water in the reaction mixture about 0.75 equiv of the absorbed oxygen was generated shows the existence of K_2O_4[19] and reactions 7, 8, 9, and 10. Manchot[20] reported that hydrazobenzene absorbed equimolar oxygen in 90% alcohol containing sodium. This difference may be explained by the reaction[19]

$$K_2O_4 + aq \longrightarrow K_2O_2aq + O_2$$

The fact that the oxidation of aniline consumes only 1 mol of oxygen/mol of aniline while hydrazobenzene requires 2 mol of oxygen to produce azobenzene excludes the possibility of the coupling of two anilino radicals, which mechanism was proposed by Horner for the autoxidation of aniline derivatives (eq 2, 3, and 4). Furthermore, another spot found in the thin layer chromatography of the oxidation products from hydrazobenzene was not observed at all in the oxidation of aniline. Although this by-product has not been characterized, its presence does not support Horner's mechanism.

The formation of azobenzene from aniline can be explained by the following scheme (S = solvent).

$$C_6H_5NH_2 + B^- \rightleftharpoons C_6H_5NH^- + BH \quad (11)$$

$$C_6H_5NH^- + O_2 \longrightarrow C_6H_5NH\cdot + O_2\cdot^- \quad (12)$$

$$C_6H_5NH\cdot + O_2 \longrightarrow C_6H_5NHOO\cdot \quad (13)$$

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[16] D. A. Blackadder and C. Hinshelwood, *J. Chem. Soc.*, 2898 (1957).

[17] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

[18] E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965).

[19] C. A. Kraus and E. F. Parmenter, *J. Am. Chem. Soc.*, **56**, 2385 (1934).

[20] W. Manchot and J. Herzog, *Ann.*, **316**, 331 (1901).

$$C_6H_5NHOO\cdot + C_6H_5NH_2 \text{ (or S)} \longrightarrow C_6H_5NHOOH + C_6H_5NH\cdot \text{ (or S}\cdot\text{)} \quad (14)$$

or

$$\left[\begin{array}{l} C_6H_5NHOO\cdot + C_6H_5NH^- \text{ (or S}^-\text{)} \longrightarrow C_6H_5NHOO^- + C_6H_5NH\cdot \text{ (or S}\cdot\text{)} \\ C_6H_5NHOO^- + C_6H_5NH_2 \text{ (or S)} \longrightarrow C_6H_5NHOOH + C_6H_5NH^- \text{ (or S}^-\text{)} \end{array}\right] \quad (15)$$

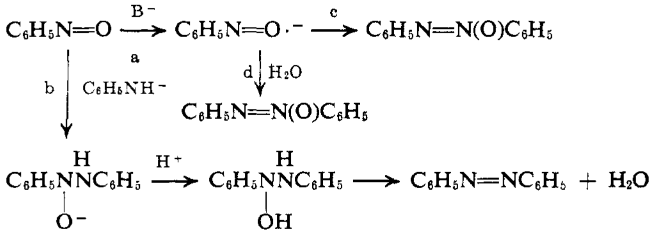
$$C_6H_5NHOOH \longrightarrow C_6H_5N{=}O + H_2O \quad (16)$$

$$C_6H_5N{=}O + C_6H_5NH^- \longrightarrow C_6H_5N{=}NC_6H_5 \quad (17)$$

If the kinetic chain length is long (*i.e.*, reactions 13 and 14 or 13 and 15), one would expect aniline to absorb theoretically only 0.5 mol of oxygen/mol of aniline. If this reaction is not a chain reaction, aniline will absorb theoretically 1 mol of oxygen/mol of aniline. However, after the absorption of 0.5 mol of oxygen, about 20% of the aniline remains unchanged. After absorption of about 0.9 mol of oxygen, no aniline was found. Also, on addition of water to a reaction mixture which no longer absorbed oxygen, about one-sixth of the absorbed oxygen was generated. This result presumably may suggest a short kinetic chain in this reaction.[21] Furthermore, the fact that, by using equimolar amounts of potassium *t*-butoxide and aniline, aniline was almost completely consumed although the reaction rate decreased (run 2, Table I; Figure 1), also suggests that azobenzene is formed by condensation (eq 1) rather than by the coupling of radicals (eq 2, 3, and 4).

The oxidation mechanism mentioned above is confirmed by the base-catalyzed condensation of nitrosobenzene with aniline. The facts that the condensation reaction of 0.5 mmol of aniline with 0.5 mmol of nitrosobenzene gives 0.35 mmol of azobenzene (corresponds to 70% yield based on $C_6H_5NH_2 + C_6H_5NO \rightarrow C_6H_5N{=}NC_6H_5$) after 8 min (Table II) and that the rate of azobenzene formation is extremely rapid compared to the oxygen absorption show that azobenzene is mostly formed from the condensation of aniline with nitrosobenzene under the conditions of the oxidation of aniline. Consequently these results satisfy a prerequisite for the condensation mechanism in the oxidation of aniline to azobenzene.

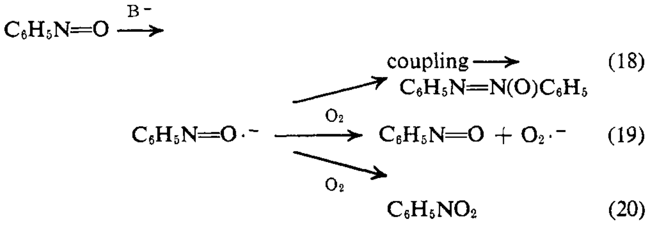
In connection with eq 17 on the oxidation path of aniline, a plausible mechanism of the reaction of aniline with nitrosobenzene is shown in the following scheme, deduced from the results in Table II and from the esr of nitrosobenzene in basic solution.



The fact that the yields of azobenzene in the presence and absence of oxygen are almost the same[22] (Table II) excludes the reaction of the nitrosobenzene radical anion with aniline from the path of azobenzene formation, since this radical anion is unstable to oxygen as indicated by its esr[12] (Experimental Section).

It is evident from the publication by Russell[12] and from the data presented here (esr data in Experimental Section) that the nitrosobenzene radical anion is related to the formation of azoxybenzene. Thus, azoxybenzene formation in the absence of oxygen comes from the slow coupling of nitrosobenzene radical anions in the reaction mixture (path c) and quick formation by quenching of the radical anion with water (path d). In the case of run 1 in Table II, paths a and b occur competitively until about 70% aniline was consumed. It may support this mechanism that the amount of unchanged aniline decreased when an excess of nitrosobenzene was used in this reaction (run 2, Table II). In the presence of oxygen the yield of azoxybenzene seems to be somewhat high (Table II) in view of the instability of nitrosobenzene radical anion to oxygen. This problem will be discussed in the following in detail.

In the absence of oxygen, nitrosobenzene itself in 80:20 DMSO–*t*-BuOH solution containing potassium *t*-butoxide produces above 70% yield of azoxybenzene (Experimental Section), while in the presence of oxygen it gives mainly azoxybenzene and nitrobenzene (Table I).[23] The products can be superficially explained by eq 18–20. Reaction 19 may be supported by the results



of Russell[5b] according to which nitrobenzene radical anion reacts with oxygen similarly to eq 19. However, since the oxygen absorption rate is extremely rapid (Figure 3) compared to the decay rate for nitrosobenzene radical anion (a, Figure 2), the high yield of azoxybenzene cannot be attributed only to eq 18. The possibility of the formation of azoxybenzene from the reaction of nitrobenzene with nitrosobenzene was excluded by an experiment in which the oxidation of a mixture of pentadeuterionitrobenzene and nitrosobenzene did not produce deuterated azoxybenzene under the same conditions. Therefore, it appears that azoxybenzene is possibly formed by some other sequences than eq 18. The base-catalyzed oxidation of nitrosobenzene can be rationalized by the series of reactions in Scheme I, although a little uncertainty still remains about the formation of nitrobenzene. Regarding the formation of azoxybenzene the sequences in Scheme II also may be conceivable.

However, nitrosobenzene in the deficient base solution in the absence of oxygen produces much more

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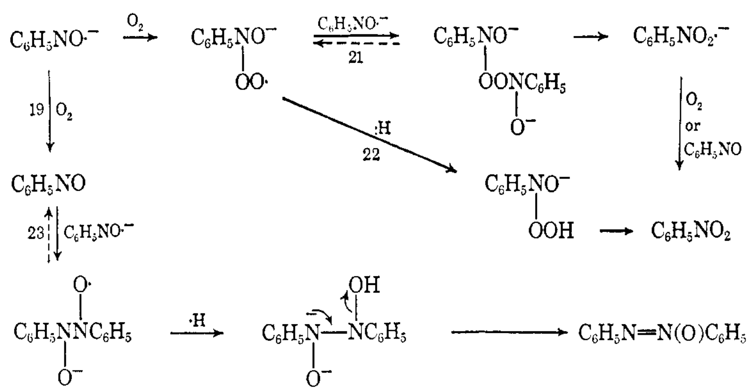
[21] Assuming that oxygen generated by water is only from eq 12, oxygen consumed by eq 12 is $0.9/6 \times 4/3 = 0.2$ mol, while oxygen consumed by eq 13 is $0.86/2 = 0.43$ mol. Accordingly the chain length of this reaction is $(0.43 - 0.2)/0.2 \approx 1$. If the above assumption is contradicted, a long kinetic chain reaction accompanying the consumption of oxygen in a side reaction may occur.

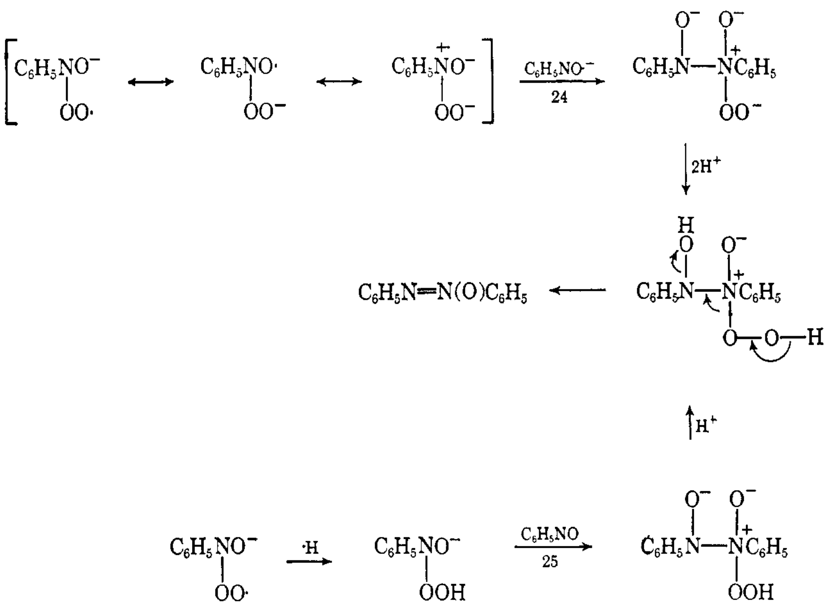
[22] In the presence of oxygen, azobenzene may be formed partly from aniline alone by oxidation.

[23] It was reported that minor products were *o*-, *p*-aminophenol, *o*-, *p*-oxyazoxybenzene, *o*-oxyazobenzene, and aniline in a NaOH aqueous solution.[7]

Scheme I



Scheme II



azoxybenzene (run 14, Table I) than the theoretical amount (50%) based on eq 18. Besides, the decay rate of nitrosobenzene radical anion in the deficient base solution is faster than that in the excess base solution (Figure 2). These results exclude eq 24, and favor eq 23 rather than eq 25.

Furthermore, in view of the product distribution in the various concentrations of nitrosobenzene and stirring rates, eq 25 is excluded as for the formation of azoxybenzene,[24] and it seems likely that the formation of nitrobenzene mainly would follow eq 21.[25]

In the oxidation of nitrosobenzene in the deficient base solution, the ratio of azoxybenzene to nitrobenzene is somewhat higher than that in the excess base solution (runs 8 and 12, Table I). This also probably supports eq 21 and 23.

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[24] If the reaction sequence 25 accompanying 21 or 22 is the case, increasing the concentration of nitrosobenzene to six times will decrease the ratio of nitrobenzene to azoxybenzene by a factor of 6 (eq 22 and 25) or about 6 (eq 21 and 25), and decreasing the stirring rate will increase the ratio of nitrobenzene to azoxybenzene. As shown in Table I (runs 6, 8, and 10), increasing the concentration of nitrosobenzene and decreasing the stirring rate increase somewhat the ratio of azoxybenzene to nitrobenzene. These results can be explained by the slight concurrence of the coupling of nitrosobenzene radical anions (eq 18) due to a little accumulation of the radical anion. The authors thank a referee for the suggestions about the effects of concentration of nitrosobenzene and stirring rate.

[25] In the presence of a better hydrogen donor, reaction sequence 22 might occur.