A Mechanistic Study of the Decomposition of Phenylhydroxylamine to Azoxybenzene and Aniline and its Catalysis by Iron(II) and Iron(III) Ions stabilised by Ethylenediaminetetra-acetic Acid

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The catalysis by Fe^{II} and Fe^{III} of the slow decomposition $3PhNHOH \longrightarrow PhN_2OPh + PhNH_2$ has been investigated kinetically under nitrogen by quantitative u.v. and e.s.r. spectroscopy and by potentiometric measurements at pH 6—8 in aqueous 30% t-butyl alcohol containing EDTA. The reactions of nitrosobenzene with (a) phenylhydroxylamine and (b) Fe^{II} have been examined similarly and a mechanism for all these reactions is put forward. Small percentages of nitrosobenzene and of phenylnitroxide radicals are formed during all these reactions and the rapidly attained equilibria (i) and (ii) appear to control their concentrations, the much slower formation of azoxybenzene being due to the dimerisation (iii). Aniline formation is due to reaction (iv)

$$PhNO + 2Fe^{II} + 2H^+ \rightleftharpoons PhNHOH + 2Fe^{III} \qquad (i)$$

$$PhNO + PhNHOH \rightleftharpoons 2\,PhNHO\cdot \qquad (ii)$$

$$2\,PhNHO\cdot \longrightarrow PhN_2OPh + H_2O \qquad (iii)$$

of which the first stage must be (v) and becomes dominant when high percentages of Fe^{II} are used. Reaction

$$2\,Fe^{II} + PhNHOH + 2H^+ \longrightarrow PhNH_2 + 2Fe^{III} + H_2O \qquad (iv)$$

$$Fe^{II} + PhNHOH \longrightarrow PhNH\cdot + Fe^{III} + (OH)^- \qquad (v)$$

(iv) does not appear to be pH dependent. Azoxybenzene formation, initiated by reaction (vi), occurs more rapidly the higher the pH, this being due to the effect of base on the [PhNO]:[PhNHOH] ratio controlled by equilibrium (i). With low percentages of Fe^{II} or Fe^{III} catalysts, the reaction velocities approximately depend

$$Fe^{III} + PhNHOH \longrightarrow PhNHO\cdot + Fe^{II} + H^+ \qquad (vi)$$

on the total iron salt concentration. Under these conditions the transient PhNO concentrations change so slowly with time that both the decomposition of PhNHOH and the formation of azoxybenzene become pseudo-unimolecular processes. The noteworthy feature of this transition metal catalysed decomposition is the kinetic control of a sequence of one-electron transfer reactions by the formation of a molecular intermediate (PhNO).

HYDROXYLAMINES are known to be thermodynamically metastable with respect to their oxidation and reduction products but the mechanisms of their disproportionation reactions have not thoroughly been investigated. In 1900 Bamberger and Brady[1] showed that under hydrogen the slow decomposition of *N*-phenylhydroxylamine in water was alkali-catalysed and yielded aniline

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[1] E. Bamberger and F. Brady, *Ber.*, 1900, **33**, 271.

and azoxybenzene in reasonable accord with equation (1), but reported that in ethanolic alkali azobenzene was

$$3PhNHOH = PhN_2OPh + PhNH_2 + 2H_2O \quad (1)$$

the main reaction product. We have confirmed these observations (see Table 1).

Following the discovery [2] that sodium aquapentacyanoiron(II), $Na_3[Fe^{II}(CN)_5,H_2O]$ effects the disproportion of hydroxylamines RNHOH (R = alkyl or aryl) to amines RNH_2, and Baudisch complexes, $Na_3[Fe^{II}(CN)_5,RNO]$ by one-electron transfer reactions in which nitroxide radicals RNHO• are involved, we have investigated the catalysis of the decomposition under nitrogen of *N*-phenylhydroxylamine by the ethylenediaminetetra-acetate (EDTA) complexes formed from both iron(II) and iron(III) ammonium sulphates in aqueous 30% t-butyl alcohol solutions of controlled pH (6—8), this solvent mixture being chosen to minimise the slow reduction of nitrosobenzene (a reaction intermediate) which occurs in alkaline solutions of primary or secondary alcohols.[3] Subsequently the reactions of nitrosobenzene with phenylhydroxylamine and with iron(II) ions were also investigated in the same solvent.

METHODS

1. On the preparative scale representative catalysed and uncatalysed decompositions of phenylhydroxylamine were allowed to proceed to completion under nitrogen. Then the solutions were made strongly alkaline and extracted with ether. The ether solutions were then extracted with dilute sulphuric acid to remove aniline which was collected and estimated gravimetrically as benzanilide. The neutral products were separated chromatographically on alumina and crystallised from aqueous methanol before weighing.

2. In kinetic studies analyses were made by adding portions (10 ml) of reaction mixtures under nitrogen to oxygen-free distilled water and benzene (40 ml of each) and shaking. The water, which then contained the catalyst and buffer, was removed and the benzene layer was washed with N-sulphuric acid (2 × 20 ml), diluted to standard volume (50 ml), and dried ($MgSO_4$). In these solutions azoxybenzene and nitrosobenzene were determined spectrographically from their extinction coefficients at 323 and 284 nm, these being their respective $\lambda_{max.}$ values in the u.v. region. No allowance was made for the presence of a very small amount ($\ll 1\%$, see Table 1) of azobenzene which has an absorption similar to that of azoxybenzene. The error of the analytical method is estimated as $\pm 0.5 \times 10^{-4}$M for product concentrations below 10^{-3}M and ±5% at higher concentrations.

3. E.s.r. measurements showed that low concentrations of phenylnitroxide radicals were always present in catalysed decompositions of phenylhydroxylamine in oxygen-free aqueous t-butyl alcohol. No other free radical (*e.g.* PhNH•) was ever observed. By operating the spectrometer continuously at constant instrument settings the change with time of the concentration of the PhNHO• radicals could be monitored from peak height measurements [4,5] though the assessment of radical molarities and accurate temperature control of the reaction mixture within the spectrometer were both impracticable.

4. Potentiometric measurements using bright platinum and saturated calomel electrodes were made under nitrogen. (i) With mixtures of iron(II) and iron(III) ammonium sulphates (*ca.* 10^{-2} molar) in 0.05—0.1 molar EDTA buffers in aqueous 30% t-butyl alcohol equilibration at the electrode was attained in under 1 min. From measurements over a wide range of $[Fe^{III}] : [Fe^{II}]$ ratios the redox potentials *v.* s.c.e. for this system at 19 °C were found to be −0.141 V at pH 6 or 7 and −0.150 V at pH 8 (±1 mV).

(ii) Mixtures of nitrosobenzene and phenylhydroxylamine in the same solvent took 5—8 min for voltage equilibration at the platinum electrode. Except when equimolar mixtures were taken the equilibrated voltages changed linearly with time owing to the occurrence of reaction (2) which is discussed below.

$$PhNO + PhNHOH \longrightarrow PhN_2OPh + H_2O \quad (2)$$

By extrapolation of the voltage measurements to the time of admixture the redox potentials at 19 °C for the [PhNO]-[PhNHOH] system were found to be −0.035 V at pH 6.3, −0.083 V at pH 7.1, and −0.137 V at pH 8.05 (*versus* s.c.e.) which accord to ±3 mV with the equation $E_0' = +0.33 - 0.06$ pH given for the same equilibrium at 25° in aqueous 10% ethanol by Smith and Walker,[6] taking into account the high temperature coefficient previously noted by Lutz and Lytton.[7] Figure 1 gives the reference voltage–composition curves for computing concentration ratios for both the Fe^{III}–Fe^{II} and PhNO–PhNHOH systems.

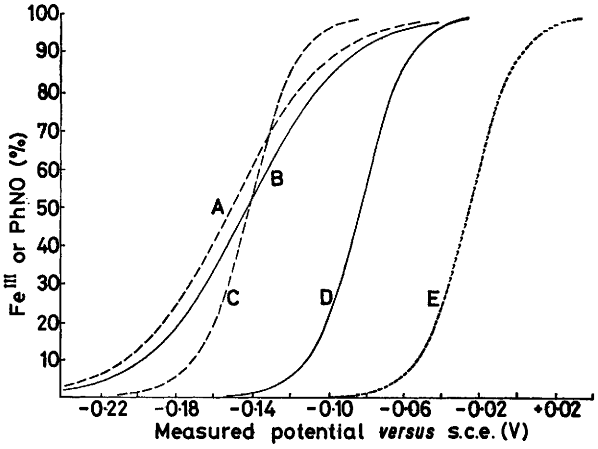

FIGURE 1 Potential curves *versus* s.c.e. for the Fe^{III}–Fe^{II} and PhNO–PhNHOH systems at 19 °C: Fe^{III}–Fe^{II}, A pH 8, B pH 7 and pH 6; PhNO–PhNHOH, C pH 8.1, D pH 7.1, E pH 6.1

(iii) In the first 5 min the voltages of mixtures of phenylhydroxylamine (up to 10^{-2} molar) and buffered iron salt catalysts changed rapidly, but thereafter their changes were much slower and were reproducible to *ca.* 2 mV. As time passed these observed voltages, starting with either Fe^{II} or Fe^{III}, became less negative. In view of the consistency of these voltage changes over a long time period it was concluded that they could be used to calculate both

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[2] W. A. Waters, *J.C.S. Perkin II*, 1976, 732.

[3] J. Hutton and W. A. Waters, *J. Chem. Soc. B*, 1968, 191.

[4] D. J. Cowley, M. H. Millen, and W. A. Waters, *J. Chem. Soc. B*, 1971, 2393.

[5] D. J. Cowley and W. A. Waters, *J. Chem. Soc. B*, 1970, 96.

[6] J. W. Smith and J. S. Walker, *Trans. Faraday Soc.*, 1950, **46**, 290.

[7] F. E. Lutz and M. R. Lytton, *J. Org. Chem.*, 1937, **2**, 68.

$[\mathrm{Fe^{III}}]:[\mathrm{Fe^{II}}]$ and $[\mathrm{PhNO}]:[\mathrm{PhNHOH}]$ ratios in the catalysed reactions of phenylhydroxylamine.

(iv) Reactions between nitrosobenzene and iron(II) ions which took *ca.* 5 min for pseudo-equilibration could be used for similar calculations.

TABLE 1

Preparative scale reactions of phenylhydroxylamine under nitrogen at room temperature

Reaction conditions		Duration	Products isolated (mol%)			
(A) Uncatalysed reactions		months	PhN_2OPh	$PhNH_2$	PhN_2Ph	Total recovery
0.2M-PhNHOH in aqueous M-NaOH		5	32.6	31.6	0.02	97
0.4M-PhNHOH in 10% ethanolic KOH		5	15.5	Trace	33.9	96
(B) * Catalysed reactions in aqueous 30% t-butyl alcohol		days				
pH	Catalyst					
6.8	$\mathrm{Fe^{II}}$; 2×10^{-2} moles	5	16.2	67.0	Trace	95
7.2	$\mathrm{Fe^{II}}$; 1×10^{-2} moles	7	23.5	50.2	1.2	98
7.3	$\mathrm{Fe^{III}}$; 2×10^{-2} moles	2	32.0	31.8	0.02	96
6.9	$\mathrm{Fe^{III}}$; 1×10^{-2} moles	7	31.8	30.2	Trace	94
8.2	$\mathrm{Fe^{II}}$; 2×10^{-2} moles	7	17.4	63.5	0.0	98
8.2	$\mathrm{Fe^{III}}$; 2×10^{-2} moles	11 †	31.3	32.6	0.5	96

* 2×10^{-2} moles PhNHOH taken in 5×10^{-2} molar solution. † A similar mixture contained some nitrosobenzene after 7 days.

RESULTS

We have found that at room temperature and pH 8 in aqueous 30% t-butyl alcohol under nitrogen the uncatalysed rate of formation of azoxybenzene from 10^{-2} molar solutions of phenylhydroxylamine is *ca.* 6×10^{-5} mol h^{-1} and that the addition of only 1 mol % of either iron(II) or iron(III) ions, stabilised by EDTA, enhances the rate *ca.* 10-fold.

The product yields for completed decompositions of phenylhydroxylamine on the preparative scale under nitrogen are summarised in Table 1. The trace of azobenzene ($<1\%$) formed in the reactions in water or aqueous t-butyl alcohol may possibly be formed by the known acid-catalysed reaction between nitrosobenzene (an intermediate product) and aniline. No trace of hydrazobenzene was ever detected. However tests showed that though hydrazobenzene is not reduced by iron(II) ions in EDTA at pH 8, it is slowly oxidised under nitrogen to azobenzene by high concentrations of iron(III) ions in EDTA at pH 6 or 8; even if the detected azobenzene is formed in this way it is clear that the dimerisation of phenylamino-radicals [reaction (12) below] is negligible.

When iron(II) ions were used as catalyst they predominated at the end of the reaction and the product mixture closely had the composition predictable from equation (1) but some nitrosobenzene formed early in the reaction and took a long time to disappear.

When iron(II) ions were used they were oxidised by reaction (3) with formation of more aniline but less azoxybenzene. Thus Table 1 shows that when 1 mole of an iron(II) salt is taken per mole of phenylhydroxylamine the

$$2\mathrm{Fe^{II}} + \mathrm{PhNHOH} + 2\mathrm{H^+} = 2\mathrm{Fe^{III}} + \mathrm{PhNH_2} + \mathrm{H_2O} \quad (3)$$

reaction product finally contains nearly 0.5 moles of aniline by reaction (3) plus a further 0.5/3 moles each of aniline and azoxybenzene by equation (1), *i.e.* in all 0.67 moles of aniline and 0.16 moles of azoxybenzene. With 0.5 moles of iron(II) salt per mole of phenylhydroxylamine the predicted yields of 0.5 moles of aniline and 0.25 moles of azoxybenzene are approximately obtained.

Now throughout all reactions proceeding under an inert atmosphere oxidations must balance reductions and since aniline, azoxybenzene, and nitrosobenzene comprise over 95% of the organic components of all the iron-salt catalysed decompositions of phenylhydroxylamine in aqueous t-butyl alcohol it is possible to calculate both the amounts of aniline formed and of the phenylhydroxylamine remaining at the sampling times of any reaction from the values of $[\mathrm{PhNO}]$ and $[\mathrm{PhN_2OPh}]$ determined spectrographically and the $[\mathrm{Fe^{III}}]:[\mathrm{Fe^{II}}]$ ratios found potentiometrically in corresponding reaction mixtures by using relationship (A). This relationship can also be used for product calculations in reactions between nitrosobenzene and iron(II) ions.

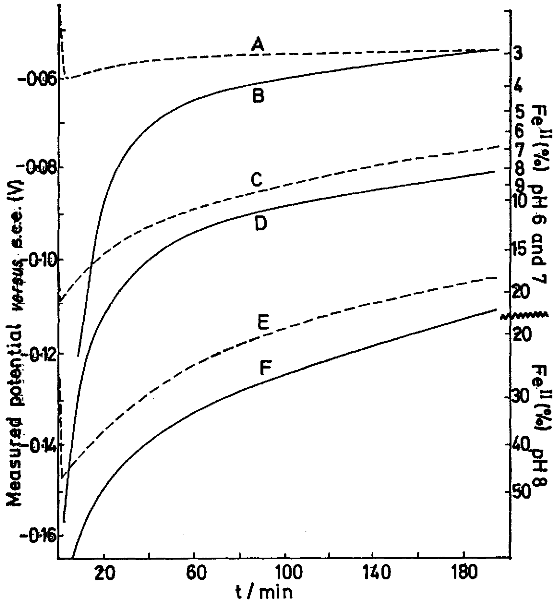

FIGURE 2 Measured potential changes (*versus* s.c.e.) for mixtures 5×10^{-3}M in PhNHOH and iron at 19 °C: dashed lines $\mathrm{Fe^{III}}$; full lines $\mathrm{Fe^{II}}$; curves A and B pH 6; curves C and D pH 7; curves E and F pH 8

$$2(\Delta[\mathrm{PhNO}] + \Delta[\mathrm{PhN_2OPh}]) - \Delta[\mathrm{Fe^{II}}] = 2\Delta[\mathrm{PhNH_2}] \quad (A)$$

Figure 2 shows the voltage changes at pH values 6, 7, and 8 in reactions between 1 mole of phenylhydroxylamine and 1 mole of iron(II) or iron(III) ions while Figures 3 and 4 show the rates of formation of the organic reaction products.

Figure 2 shows that in 1 h the conversion of $\mathrm{Fe^{II}}$ to $\mathrm{Fe^{III}}$

is much more complete at pH 6 than at pH 7 or 8; in contrast the initial reduction of Fe^{III} is very substantial at pH 8 and very slight at pH 6. Figure 3 shows that Fe^{III} effects the rapid formation of nitrosobenzene and that the concentrations of this product then decline slowly as phenylhydroxylamine is consumed. In contrast azoxybenzene concentrations rise progressively towards the limit predicted from equation (1) and necessarily aniline concentrations exceed azoxybenzene concentrations so long as nitrosobenzene is present. Nitrosobenzene is the dominant initial product at pH 8 but only reaches a low concentration at pH 6 when the reactions of Fe^{III} with phenylhydroxylamine are evidently slower than they are in more alkaline solution.

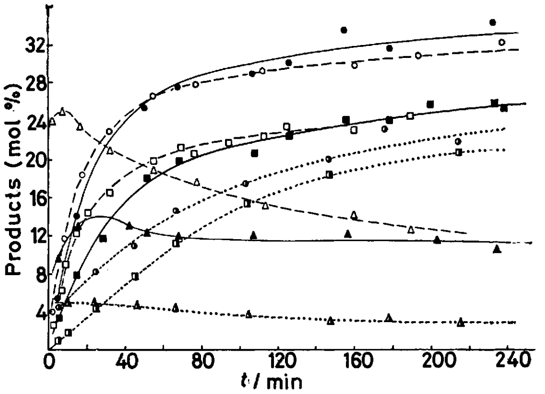

FIGURE 3 Production of azoxybenzene, nitrosobenzene, and aniline at pH 6, 7, and 8 and 19° from 5 × 10^{-3}M mixtures in PhNHOH and Fe^{III}: circles $PhNH_2$; squares PhN_2OPh; triangles PhNO; dashed lines and open symbols pH 8; full lines and filled symbols pH 7; dotted lines and half-filled symbols pH 6

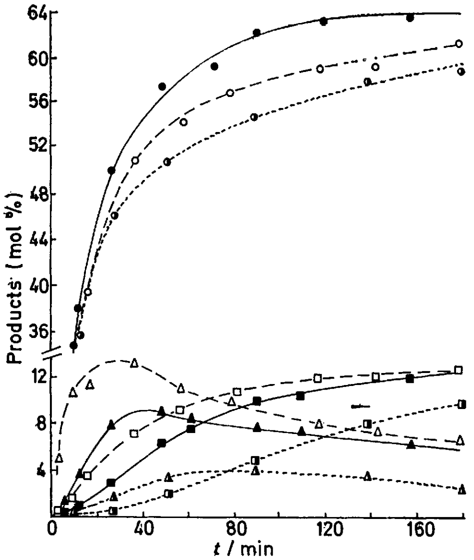

FIGURE 4 Production of azoxybenzene, nitrosobenzene, and aniline at 19 °C from mixtures 5 × 10^{-3}M in PhNHOH and Fe^{II}. Key as Figure 3

Figure 4 shows, in sharp contrast, that with Fe^{II} aniline formation corresponding to equation (3) is the dominant initial reaction; 50% of its production is complete within 10 min and this amount is not noticeably pH dependent. As would be expected the yields of nitrosobenzene and azoxybenzene are both much lower than in the corresponding reactions with Fe^{III}. Nitrosobenzene formation is again pH dependent and azoxybenzene formation is as first very slow but accelerates for a time after the nitrosobenzene concentrations have reached their maxima.

Examples of the voltage changes in the first 100 min of reactions of phenylhydroxylamine with different percentages of Fe^{II} and Fe^{III} are given in Figure 5. These voltage–time curves have similar overall features to those of Figure 2 in that after rapid initial voltage changes, potentials of pseudo-equilibrium are reached which slowly become less negative as time progresses. For reactions initiated by low corresponding concentrations of either Fe^{II} or Fe^{III} ions similar potentials are soon attained. The higher the percentage of the initial catalyst the less negative is the potential.

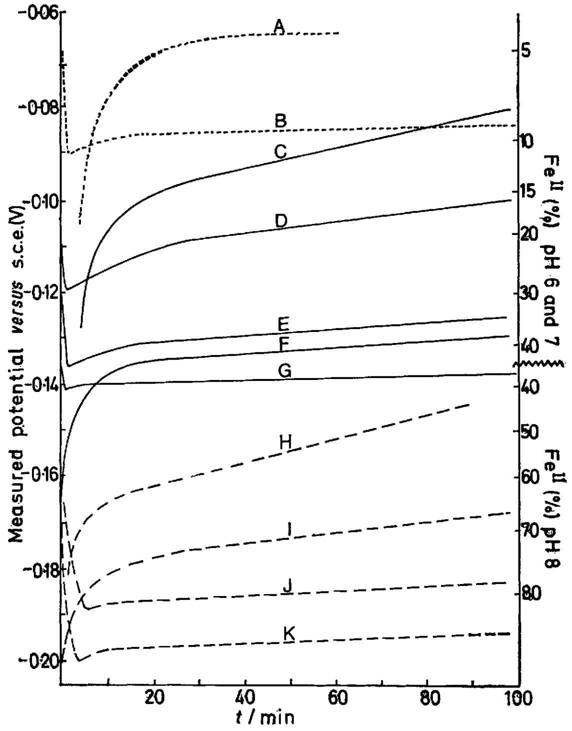

FIGURE 5 Potential changes for catalysed decompositions of 10^{-2}M-phenylhydroxylamine: pH 6, A Fe^{II} 4.6 × 10^{-3}M, B Fe^{III} 6.0 × 10^{-4}M; pH 7 C Fe^{II} 5.2 × 10^{-3}M, D Fe^{III} 1.2 × 10^{-3}M, E Fe^{III} 5.1 × 10^{-4}M, F Fe^{II} 3.7 × 10^{-4}M, G Fe^{III} 2.0 × 10^{-4}M; pH 8 H Fe^{II} 8.1 × 10^{-4}M, I Fe^{II} 3.6 × 10^{-4}M, J Fe^{III} 1.5 × 10^{-4}M, K Fe^{III} 9.0 × 10^{-5}M

At pH 8 the $[Fe^{III}]$: $[Fe^{II}]$ ratio remains below unity for a long time; at pH 7 it exceeds unity after the initial fast phases of the catalysed reactions and at pH 6 the reaction mixtures from a very early stage contain a large excess of Fe^{III} over Fe^{II}.

At low catalyst concentrations only a small amount of nitrosobenzene is formed. By neglecting this and assuming from equation (1) that $3[Ph\cdot N_2O\cdot Ph]_t = [PhNHOH]_0 - [PhNHOH]_t$ or by compensating for nitrosobenzene formation, which soon reaches a fairly steady value, and using relationship (A) rates of consumption of phenylhydroxylamine can be calculated from analytical measurements. With up to 10% of catalyst at pH 6, or 6% at pH 7, these calculations can, for the formation of 10—70% of the expected eventual yield of azoxybenzene, be fitted, to ±5%, to the logarithmic equation of a first-order reaction, but at pH 8 even with only 4% of catalyst the deviations from this equation may be as much as 10% and are indicative of a reaction order slightly greater than unity.

With higher percentages of catalyst than those mentioned above, 10^{-2} molar solutions of phenylhydroxylamine produce over 2.5 × 10^{-4}M-nitrosobenzene and evidently this should not be neglected in attempts to deduce kinetic formulae.

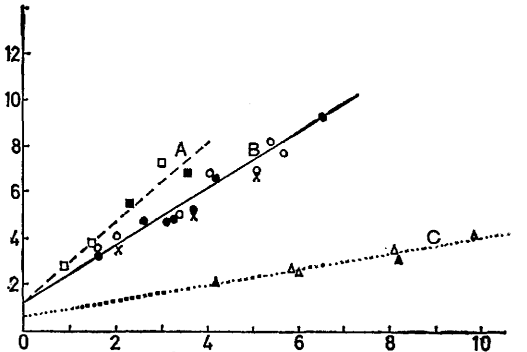

FIGURE 6 Observed first order rate constants *versus* total iron concentration at 19 °C and [PhNHOH]10^{-2}M; A pH 8 (squares) from loss of PhNHOH; B pH 7 (circles) from loss of PhNHOH, × from e.s.r.; C pH 6 (triangles) from loss of PhNHOH. Open symbols denote Fe^{III} as the initial catalyst and filled symbols Fe^{II} as the initial catalyst

Figure 6 which gives the mean points of calculated first-order rate constants shows (i) that Fe^{II} and Fe^{III} are almost equally effective as catalysts of azoxybenzene formation, (ii) that the reaction rate rises steadily as [Total Fe] increases, and (iii) that the rate of azoxybenzene formation increases with pH.

From the e.s.r. measurements with buffered solutions of phenylhydroxylamine containing small percentages of Fe^{II} or Fe^{III} it was found that the peak heights of the e.s.r. signals decreased logarithmically with time, indicating that $-d[PhNHO\cdot]/dt = kt$ (see Figure 7). The rate constants were found to be approximately the same as those for the consumption of phenylhydroxylamine in corresponding mixtures (see Figure 6).

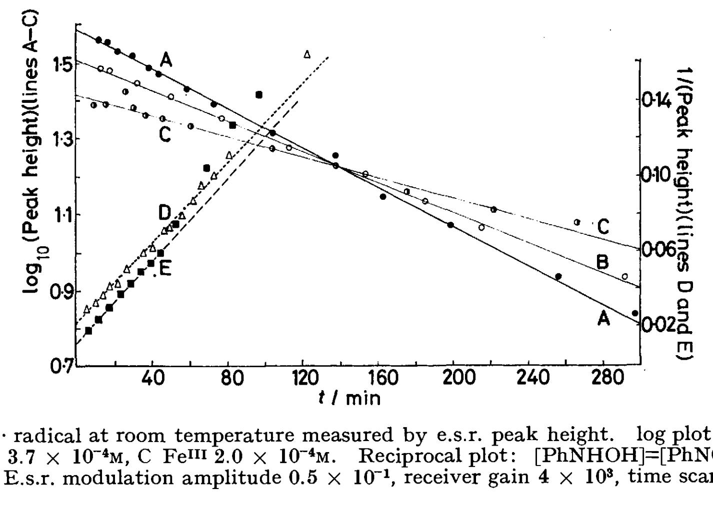

FIGURE 7 Decay of PhNHO· radical at room temperature measured by e.s.r. peak height. log plot: [PhNHOH]10^{-2}M; pH 7; A Fe^{III} 5.1 × 10^{-4}M; B Fe^{II} 3.7 × 10^{-4}M, C Fe^{III} 2.0 × 10^{-4}M. Reciprocal plot: [PhNHOH]=[PhNO]: D pH 6.3 2.14 × 10^{-3}M; E pH 8.1 3.15 × 10^{-4}M. E.s.r. modulation amplitude 0.5 × 10^{-1}, receiver gain 4 × 10^3, time scan 8 min

When the decay of the [PhNHO·] spectrum was followed with equimolar mixtures of phenylhydroxylamine and nitrosobenzene in the absence of a catalyst it was found to be a second-order process, *i.e.* $-d[PhNHO\cdot]^2/dt = kt$.

DISCUSSION

(a) *The Reaction Mechanism.*—As in the reactions[2] between hydroxylamines and sodium aquapentacyanoiron(II) it is evident that the EDTA-complexed ions of Fe^{II} and Fe^{III} react concurrently with phenylhydroxylamine according to equations (4) and (5). Aniline can then be produced by reactions (6) and (7) and azoxybenzene by the dimerisation (8). However the production of phenylnitroxide radicals by reaction (5) inevitably leads to the reversible formation of nitrosobenzene and consequently reactions (9)—(11) as well as (2) also have to be considered.

$$Fe^{II} + PhNHOH \longrightarrow Fe^{III} + PhNH + OH^- \quad (4)$$

$$Fe^{III} + PhNHOH \longrightarrow Fe^{II} + PhNHO\cdot + H^+ \quad (5)$$

$$PhNH\cdot + PhNHOH \longrightarrow PhNH_2 + PhNHO\cdot \quad (6)$$

$$PhNH\cdot + Fe^{II} + H^+ \longrightarrow PhNH_2 + Fe^{III} \quad (7)$$

$$2PhNHO\cdot \longrightarrow PhN_2OPh + H_2O \quad (8)$$

$$PhNHO\cdot + Fe^{III} \longrightarrow PhNO + Fe^{II} + H^+ \quad (9)$$

$$PhNO + Fe^{II} + H^+ \longrightarrow PhNHO\cdot + Fe^{III} \quad (10)$$

$$PhNHO\cdot + Fe^{II} + H^+ \longrightarrow PhNHOH + Fe^{III} \quad (11)$$

$$2PhNH\cdot \not\longrightarrow PhNHNHPh \quad (12)$$

At high alkalinities a very slow uncatalysed decomposition of phenylhydroxylamine occurs. This may be due to electron transfer from the anion of phenylhydroxylamine (13) followed thereafter by reactions (6) and (8). Many such electron transfers to π electron systems from their anions are known.[8,9]

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[8] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.

[9] G. A. Russell, 'Essays on Free Radical Chemistry,' *Chem. Soc. Special Publication*, 1970, **24**, 271.

(b) *The Reaction between Nitrosobenzene and Phenylhydroxylamine.*—The uncatalysed reaction (2) between

$$PhNHO^- + PhNHOH \longrightarrow PhNHO\cdot + PhNH\cdot + OH^- \quad (13)$$

nitrosobenzene and phenylhydroxylamine is not slow. Its rate can be measured potentiometrically since, putting $[PhNO]_0 = a$, $[PhNHOH]_t = b$, and $[PhN_2OPh]_t = x$, the integrated form of the bimolecular rate equation corresponding to (2) is

$$k_2t(a - b)/2.303 = \log_{10}(a - x)/(b - x) + \log b/a$$

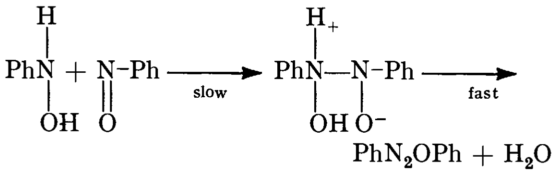
and the Nernst equation for the change of the voltage which measures [PhNO] : [PhNHOH] is

$$V_t = E_0' + 0.03\log_{10}(a - x)/(b - x)$$

so that $k_2t(a - b)/2.303 = (V_t - V_0)/0.03$. Values of the bimolecular rate constant k_2 at 19° calculated in this way are 15 mol^{-1} min^{-1} at pH 8.0, 16 mol^{-1} min^{-1} at pH 7.1, and 17 mol^{-1} min^{-1} at pH 6.3. Less accurate values of 16 ± 1 mol^{-1} min^{-1} at both pH 6 and 8 have been obtained by spectroscopic measurements of the disappearance of nitrosobenzene from equimolar mixtures of both 2.1 and 3.3×10^{-3} molar phenylhydroxylamine and nitrosobenzene in aqueous 30% t-butyl alcohol (0.07M-EDTA). With these two initial concentrations the half-lives of the reactants are *ca.* 30 and 18 min, respectively and consequently the times required for satisfactory admixtures of the reactants (0.5—1 min) lead to significant errors in the calculated values of k_2.

These rates have the same order of magnitude as those published by Ogata *et al.*[10] for reactions at pH 4 or less in methanol or slightly aqueous methanol.

Now reaction (2) is not a direct nitrogen–nitrogen coupling [equation (2′)] but involves a rapid homolytic



$$\underset{OH}{\overset{H}{PhN}} + \underset{O}{N}\text{-}Ph \xrightarrow[\text{slow}]{} \underset{OH\ O^-}{\overset{H_+}{PhN\text{—}N\text{-}Ph}} \xrightarrow[\text{fast}]{} PhN_2OPh + H_2O \quad (2')$$

equilibration (14) followed by the slower combination

$$Ar^1NHOH + Ar^2NO \overset{K_{14}}{\rightleftharpoons} Ar^1NHO\cdot + Ar^2NHO\cdot \quad (14)$$

of two arylnitroxide radicals [reaction (8)] since (i) admixture of one arylhydroxylamine with a different aromatic nitroso-compound leads to the formation of all three possible aromatic azoxy-compounds[10,11] and (ii) our e.s.r. measurements have shown that admixture of phenylhydroxylamine with nitrosobenzene at once leads to the formation of phenylnitroxide radicals which decay bimolecularly. The half-life of this decay is comparable with the times reported above for similar initial concentrations of the reactants in the uncatalysed reaction (2). Consequently for reaction (2) one can write $k_2 = k_8K_{14}$.

Ingold and his colleagues[12] who have used a very different system for producing phenylnitroxide radicals from phenylhydroxylamine in benzene also found that nitrosobenzene was a major initial oxidation product. They have studied equilibrium (14) and reported that at room temperature K_{14} was of the order of 10^{-5}. All our results are in theoretical accord with their findings but since we have used buffered aqueous t-butyl alcohol as solvent our velocity constants for azoxybenzene formation cannot be correlated with their figures.

(c) *The Iron Salt Catalysed Decomposition of Phenylhydroxylamine.*—It is evident from our potentiometric work that with low concentrations of iron(II) or iron(III) salts reaction mixtures fairly soon come to pseudo-equilibria with respect to both the ratios $[Fe^{III}] : [Fe^{II}]$ and [PhNO] : [PhNHOH] in the reacting mixtures. Now in the absence of the radical dimerisation (8) reactions (5), (9), (10), and (11) should reach an equilibrium such that relation (B) holds, K being equal to $k_5k_9/k_{10}k_{11}$.

$$[PhNO] : [PhNHOH] = K[Fe^{III}]^2/[Fe^{II}]^2[H^+]^2 \quad (B)$$

The calculated values of $K/[H^+]^2$ at 19° from our voltage measurements are 9×10^{-5} at pH 6, 9.3×10^{-3} at pH 7, and 0.45 at pH 8. The low figure at pH 8 arises because the redox potential of the EDTA complexed $[Fe^{III}]/[Fe^{II}]$ system at pH 8 is different from that at pH 6 or 7.

Again, assuming that reaction (8) is rate determining, it can be shown that equations (C) and (D) should hold approximately. Both these theoretical equations are

$$[PhNHO\cdot]^2 = [PhNO][PhNHOH](k_5k_{10}/k_9k_{11}) \quad (C)$$

$$d[Ph\cdot N_2O\cdot Ph]dt = k_8[PhNO][PhNHOH](k_5k_{10}/k_9k_{11}) \quad (D)$$

independent of pH and of the concentrations of the iron salt catalysts, though the velocity constants k_5, k_9, k_{10}, and k_{11} are those for reactions involving Fe^{II} or Fe^{III} and [PhNO] and [PhNHOH] are directly related by equation (B) which involves $[Fe^{III}]^2/[Fe^{II}]^2$ and $[H^+]^2$.

Since truly equilibrated systems reach the same final concentrations of reactants and reaction products irrespective of the natures or concentrations of the catalyst, one can infer that K_{14} has nearly the same value as (k_5k_{10}/k_9k_{11}).

Therefore, if approximately equilibrated concentrations of nitrosobenzene are formed in iron salt catalysed decompositions of phenylhydroxylamine, nitrosobenzene formation and consumption should play a dominant controlling role in the production of azoxybenzene at all catalyst concentrations.

Now we have found that in our catalysed reactions

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[10] Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Amer. Chem. Soc.*, 1957, **79**, 3397.

[11] E. Bamberger and E. Renauld, *Ber.*, 1897, **30**, 2278.

[12] D. F. Bowman, J. L. Brokenshire, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 6551.

when $[Fe^{II}]$ or $[Fe^{III}]$ are small in comparison with $[PhNHOH]_o$ (i) the measured nitrosobenzene concentrations change very slowly indeed until up to 70% of the phenylhydroxylamine has been decomposed and the error involved in determining a small amount of nitrosobenzene in the presence of a much larger amount of azoxybenzene has become considerable, (ii) the rate of decomposition of phenylhydroxylamine calculated from relationship (A) is approximately of the first order, and (iii) the disappearance of PhNHO· radical, as measured from the peak heights of their e.s.r. spectra (see Figure 7), is also a first-order process with approximately the same rate constant. Thus two independent kinetic measurements support equation (D) and the conclusion that [PhNO] is nearly constant throughout reactions effected by low percentages of catalysts.

Table 2 which gives mean values of nitrosobenzene concentrations and of first-order rate constants for the consumption of phenylhydroxylamine shows that the values found for $k/[PhNO]$ are at most 50% greater than the values cited in section (b) for the bimolecular rate constant $k_2 = k_8K_{14}$. This gives added support for equation (D). In particular it shows that $k/[PhNO]$ is not significantly pH dependent, whereas $k/[\text{Total Fe}]$ is undoubtedly pH dependent (Figure 6).

TABLE 2

Relationship between the rate of phenylhydroxylamine consumption and the nitrosobenzene concentration

pH	Catalyst and concentration		Nitrosobenzene	10^3k/ min^{-1}	$k[PhNO]^{-1}$/ l^{-1} mol^{-1} min^{-1}
		10^4 + Molarity			
6.0	Fe^{II}	4.2	0.9 ± 0.4	2.1 ± 0.1	23
6.1	Fe^{III}	6.0	1.1 ± 0.1	2.5 ± 0.1	23
5.8	Fe^{III}	5.8	1.2 ± 0.3	2.6 ± 0.1	22
6.0	Fe^{III}	8.1	1.8 ± 0.7	3.6 ± 0.2	20
6.1	Fe^{III}	9.9	2.0 ± 0.7	4.2 ± 0.4	21
7.2	Fe^{III}	2.0	1.2 ± 0.2	3.8 ± 0.4	31
7.1	Fe^{II}	3.3	1.9 ± 0.3	4.8 ± 0.3	25
7.1	Fe^{III}	3.4	2.1 ± 0.4	4.9 ± 0.3	23
7.2	Fe^{II}	3.7	1.8 ± 0.3	5.0 ± 0.3	28
7.2	Fe^{III}	5.1	2.3 ± 0.3	6.9 ± 0.3	30
7.2	Fe^{II}	6.6	3.7 ± 0.6	9.3 ± 0.5	25
7.0	Fe^{III}	12.1	4.7 ± 0.4	10.5 ± 0.5	22
8.0	Fe^{III}	0.89	1.1 ± 0.05	2.7 ± 0.2	25
8.0	Fe^{III}	1.5	1.6 ± 0.2	3.7 ± 0.4	23
8.1	Fe^{II}	2.3	2.6 ± 0.2	5.5 ± 0.5	21
8.1	Fe^{II}	3.6	2.6 ± 0.2	6.8 ± 0.6	26

An alternative approach however merits brief consideration. If at low catalyst concentrations it is presumed that nearly all the phenylnitroxide radicals produced by reaction (5) dimerise promptly to azoxybenzene then the formation of a small and fairly constant amount (say <2%) of nitrosobenzene may not significantly alter the rates of formation of much greater amounts of azoxybenzene and aniline. Then the overall decomposition of phenylhydroxylamine should mainly be due to reactions (4)—(8). Assuming this, then reacting systems should soon reach potentiometric equilibria such that $[Fe^{III}]/[Fe^{II}] = k_4/k_5$ if the destruction of PhNH· radicals proceeds by reaction (6) or $2k_4/k_5$ if equation (7) is concerned. The former case leads to the rate equation

$$-d[PhNHOH]/dt = [PhNHOH][\text{Total Fe}]3k_4k_5/(k_4 + k_5)$$

and the latter to

$$-d[PhNHOH]/dt = [PhNHOH][\text{Total Fe}]3k_4k_5/(2k_4 + k_5)$$

in which the reaction velocities are dominated by the slower rates of reactions (4) or (5). As noted in the Results section these rate equations accord with reaction velocity measurements at low catalyst concentrations. However the prediction that in catalysed reactions $[Fe^{III}] : [Fe^{II}]$ ratios should become constant irrespective of the initial concentration of the catalyst is not true as Figure 5 shows quite decisively.

The potentiometric measurements of Figure 5 show that after the initial phase the changes of voltage with time become almost linear. This is in accord with the view that these voltages then measure both [PhNO] : [PhNHOH] and $[Fe^{III}] : [Fe^{II}]$ ratios, and that equation (D) satisfactorily represents the overall reactions with [PhNO] remaining constant and [PhNHOH] decreasing logarithmically with time [compare the use of voltage measurements in section (b)].

(d) *The Rate of Aniline Formation.*—Reaction (3) giving one mole of aniline for two equivalents of Fe^{II} involves the consecutive bimolecular reactions (4) and (7) which must proceed at equal rates if all the PhNH· radicals are converted to aniline. For conditions in which $[Fe^{II}] \gg [Fe^{III}]$ one can therefore write $-d[Fe^{II}]/dt = k_4(a - x)(b - x)/2]$ where $a = [Fe^{II}]_o$, $b = [PhNHOH]_o$, and $x = [Fe^{III}]_t$ which in its integrated form can be used to calculate the rate constant k_4 since values of x can be obtained from voltage measurements of the initial stages of reactions such as those displayed in Figures 2 and 4.

TABLE 3

Reduction of phenylhydroxylamine by Fe^{II} in EDTA at 19 °C

pH	$[Fe^{II}]_o$ (10^{-3}M)	$[PhNHOH]_o$ (10^{-3}M)	Δt for half reaction */ min	k_4/mol^{-1} min^{-1}
6.1	2.47	4.78	5	32 ± 0.4 over 8 min
6.3	4.92	5.15	5	30 ± 0.3 over 10 min
7.0	2.43	5.11	6	24.5 ± 0.4 over 6 min
7.3	5.08	5.11	6	29 ± 0.5 over 5 min
7.3	4.88	5.19	5.5	26 ± 0.4 over 5 min
8.0	4.91	5.18	11	18 ± 0.5 over 4 min
8.1	5.07	4.95	19	18 ± 1.5 over 3 min

* When $[Fe^{III}] = [Fe^{II}]$.

Fortunately the production of a little more Fe^{II} by the onset of reaction (5) is partly offset by the consumption of more phenylhydroxylamine and it has been found that the bimolecular equation given above gives values of k_4 which at pH 7 drop by <10% during consumption of half the original Fe^{II} or as much as 70% of it at pH 6 but are less constant at pH 8 when much less

Fe^{II} is eventually consumed. Table 3 which gives values of k_4 which have been calculated in this way supports the inference from Figure 4 that reaction (4) is not significantly pH dependent.

(e) *The Reduction of Nitrosobenzene by Iron*(II) *Ions.*—Potentiometric and analytical measurements of the reduction of nitrosobenzene by iron(II) ions (Table 4) have shown that both the reactions which correspond to equation (15) and the further reduction of phenylhydroxylamine to aniline [equation (3)] are rapid while

$$PhNO + 2Fe^{II} + 2H^{+} \rightleftharpoons PhNHOH + 2Fe^{III} \quad (15)$$

the formation of azoxybenzene is slow. With equimolar solutions at pH 7 or 8, aniline formation is virtually complete within 5 min and the slower combination of the phenylhydroxylamine then formed with the residual nitrosobenzene accounts for the formation of most of the azoxybenzene. As in the direct reaction between nitrosobenzene and phenylhydroxylamine the voltage–time curves for the PhNO–Fe^{II} reaction then become linear.

TABLE 4

Reactions between nitrosobenzene and iron(II) ions at 19 °C in 30% aqueous t-butyl alcohol

pH 7 Equimolar reactants
Products (10^{-4} molar)

t/min	Fe^{III}	PhNO left	$PhNH_2$	PhNHOH	$\begin{array}{l}Ph{-}\overset{+}{N}{-}\overset{-}{O}\\ \quad\ \| \\ \quad\ N{-}Ph\end{array}$
0	[10.2] *	9.7	0	0	0
3	9.2	5.8	1.0	2.6	0.15
6	9.2	5.6	0.9	2.8	0.25
10	9.2	5.4	0.8	2.7	0.35
43	9.3	4.8	0.8	2.2	0.95
62	9.4	4.5	0.9	1.7	1.3
132	9.6	3.8	1.0	0.9	2.0
190	9.7	3.4	0.9	0.8	2.3
271	9.8	2.9	0.9	0.7	2.6

pH 8 Equimolar reactants
Products (10^{-4} molar)

t/min	Fe^{III}	PhNO	$PhNH_2$	PhNHOH	$\begin{array}{l}Ph{-}\overset{+}{N}{-}\overset{-}{O}\\ \quad\ \| \\ \quad\ N{-}Ph\end{array}$
0	[10.2] *	9.7	0	0	0
3	7.0	6.2	0.1	3.2	0.1
10	7.5	7.1	1.4	0.6	0.3
38	7.8	6.5	1.3	0.6	0.65
77	8.3	5.7	1.2	0.8	1.0
132	8.4	5.1	1.0	0.8	1.4
195	8.9	4.7	1.2	0.6	1.6
235	9.1	4.6	1.3	0.2	1.8

* $[Fe^{III}] = [Fe^{II}]$ taken. Analytical error $\pm 0.1 \times 10^{-4}$ molar. $[PhNH_2]$ and [PhNHOH] are calculated from equation (A).

Conclusions and their Significance.—The main conclusion of this study of the catalysis of the formation of azoxybenzene from phenylhydroxylamine by iron(II) and iron(III) ions is that although azoxybenzene formation is due to the dimerisation of PhNHO· radicals, the rate of formation of these radicals [equation (5)] does not control the reaction kinetics. Instead the controlling factor is the reversible formation of nitrosobenzene which acts as a ' kinetic buffer ' to regulate PhNHO· radical concentrations. Very few cases of the kinetic control of free radical reactions by a stable molecular intermediate have as yet been established,* possibly because potentiometric measurements have seldom been used to monitor them. However biochemical studies of metabolic process have frequently shown that the participating enzyme reactions operate within well defined redox potential ranges and the present work could be viewed as a model for the interpretation of such reactions. Nitroso-compounds in general are known to be biologically active molecules but little attention has been paid to kinetic features of their interactions with transition metal ions of variable valency.

EXPERIMENTAL

All reagents were made up freshly by weight in nitrogen-blown solvents. Crystallised phenylhydroxylamine [13] and nitrosobenzene were made up in 50% aqueous t-butyl alcohol (v/v) and the AnalaR iron(II) or iron(III) ammonium sulphates in air-free water containing a few drops of dilute sulphuric acid before dilution into air-free EDTA–NaOH (0.1—0.15M) of the desired pH. A final pH adjustment, checked by a meter to 0.1 pH unit, was made after dilution. In the nitrogen-flushed reaction vessels the solutions of the organic reactants and catalyst were further diluted with 50% t-butyl alcohol or EDTA buffer to give final mixtures containing 30% t-butyl alcohol by volume. Early reactions were carried out at room temperature, but later this was kept to 19 ± 0.1°. Conventional apparatus was used for the potentiometric measurements and a Varian E4 spectrometer for the e.s.r. work.

On testing the analytical procedure outlined in the Methods section it was found (i) that immediate quenching of samples in benzene and dilute sulphuric acid tended to give high values of [PhNO] since acidic solutions of Fe^{III} soon oxidise PhNHOH. Towards the end of reactions the aqueous extracts were milky and a second benzene extraction was then used. (ii) Continuous passage of nitrogen through reaction mixtures caused loss of PhNO by evaporation (as much as 10% in 3 h from a 10^{-3}M solution). Nitrogen flushing was therefore used only during the abstraction of samples for analysis and only initially in the potentiometric cells.

Since the estimation of nitrosobenzene largely depends on calculations based on the small difference between the extinction coefficients of PhNO and PhN_2OPh at 284 nm (8.6 and 7.0 × 10^3 respectively) the error in calculations of [PhNO] is considerable and can be over 50% when $[PhN_2OPh]$ has risen so much that 5- or 10-fold dilution of the benzene extracts is required for measurement in 1 cm spectrometric cells.

We consider that these limitations to the accurate estimation of *ca.* 10^{-4}M-nitrosobenzene and losses of organic

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* Hydroperoxide molecules, RO_2H, formed in autoxidations are of course regenerators of RO· and RO_2· radicals in transition metal catalysed systems, but this is not quite an analogous case since hydroperoxides are major reaction products and themselves thermal catalysts in the absence of metal ions.

[13] A. I. Vogel, A Text-book of Practical Organic Chemistry, Longman, Green, London, 1948.

products during the extractions into benzene are responsible for the major analytical errors in this research.

In the large scale experiments traces of highly polar red or purple products were formed. These may be decomposition products of nitrosobenzene[3] or oxidation products of aniline (with Fe^{III}). Benzoylation of aniline was effected in pyridine, thorough alkali washing was needed to remove any residual phenylhydroxylamine.

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