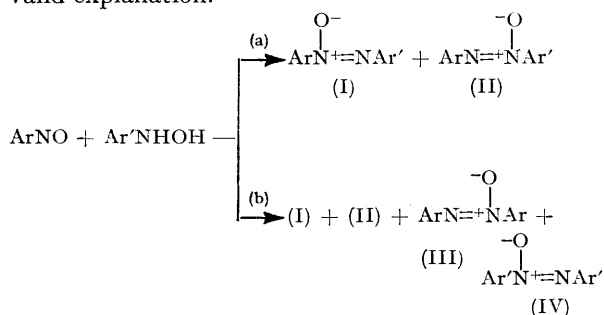


Hydrogen Transfer from *N*-Arylhydroxylamines to Nitrosoarenes: an Accompaniment to Azoxyarene Formation

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The discovery of a ready reversible transfer of molecules of hydrogen from *N*-arylhydroxylamines to nitrosoarenes in ethanolic media may necessitate a refinement of prevailing views on azoxyarene formation from these components.

THE fact originally reported by Bamberger¹ that a given nitrosoarene reacts with a differently substituted *N*-arylhydroxylamine to yield not only the expected cross condensation products (I) and (II) [Scheme (a)] but rather a mixture of all the possible disproportionated azoxyarenes (I)—(IV) [Scheme (b)] has as yet received no valid explanation.



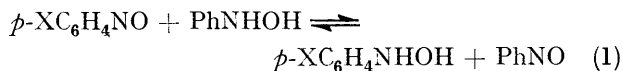
Recent investigations^{2,3} have confirmed Bamberger's findings and several authors have attempted to give them some rationale. The stoichiometry and kinetics of the

¹ E. Bamberger, *Ber.*, 1900, **33**, 1941, 1953.

² B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1954, 3340.

³ K. Ueno and S. Akiyoshi, *J. Amer. Chem. Soc.*, 1954, **76**, 3670.

condensation of nitrosobenzene and *N*-phenylhydroxylamine were recorded by Ogata *et al.*⁴ who showed the reaction to be first order in both components and to be subject to acid catalysis. They further showed that the condensations of *p*-chloronitrosobenzene with *N*-phenylhydroxylamine or of nitrosobenzene with *N*-*p*-chlorophenylhydroxylamine led in both cases to the occurrence of four azoxy-compounds whose relative ratios were the same from either reactant pair. They accounted for this observation by suggesting, without direct experimental evidence, that a rapid preliminary equilibrium (1) was



set-up and that condensations of all possible reactant pairs led to the observed azoxy-products.

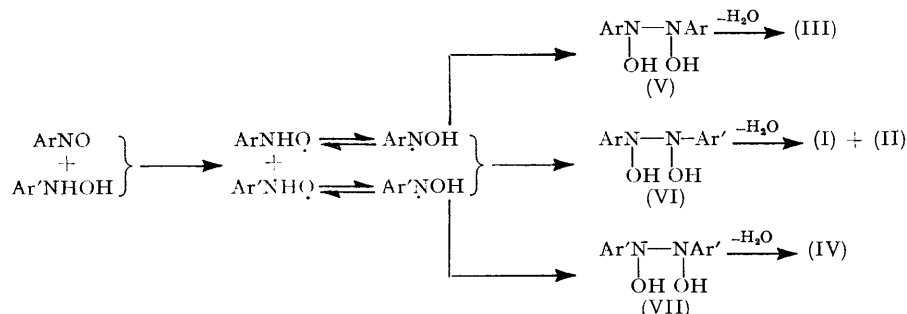
E.s.r. studies of the nitrosobenzene-*N*-phenylhydroxylamine reaction by Russell and his co-workers⁵ have shown that in basic solution an essentially quantitative yield of the nitrosobenzene anion radical is rapidly produced which subsequently decays with the production of azoxybenzene. Russell suggests the combination of

⁴ Y. Ogata, M. Tsuchide, and J. Takagi, *J. Amer. Chem. Soc.*, 1957, **79**, 3397.

⁵ G. A. Russell, E. J. Geels, F. J. Smetowski, K. H. Chang, J. Reynolds, and G. Knapp, *J. Amer. Chem. Soc.*, 1967, **89**, 3821.

two anion radicals to give the symmetrical bisdianion as intermediate. In neutral solution the part of the anion radical is taken by the phenylnitroxyl radical (PhNHO•), although in this latter case the production of radical is not quantitative, the stationary concentration being of the order of 2% of the reactant concentrations.

When applied to the reaction of variously substituted pairs of reactants this scheme provides intermediates (V)–(VII) which of necessity lead to the occurrence of all the possible azoxyarene types (I)–(IV).



Support for a symmetrical intermediate and/or rapid pre-equilibrium was given by the work of Shemyakin *et al.*⁶ who showed from ¹⁵N studies that the reaction proceeded *via* an intermediate with chemically equivalent nitrogen atoms, and later work by the same authors⁷ with ¹⁸O-labelled *N*-phenylhydroxylamine showed isotopic levelling to have taken place.

The present work has obtained kinetic parameters for all the possible condensations from unsubstituted, *p*-chloro-, and *p*-methyl-phenylhydroxylamines and the corresponding *p*-substituted nitrosobenzenes, and has further demonstrated that a rapid pre-equilibrium as suggested by Ogata⁴ does occur.

Initially, and for other purposes, a kinetic investigation of the uncatalysed reaction of nitrosobenzene with *N*-phenylhydroxylamine at 30 °C in ethanol was undertaken. The reactions were monitored by loss of nitrosobenzenes with reference to the $n \rightarrow \pi^*$ visible absorption at *ca.* 750 nm. The reaction was found to obey the simple second-order expression (2) where *a* and *b* are the initial concentration of *N*-phenylhydroxylamine and

$$kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} \quad (2)$$

nitrosobenzene, and moreover gave a quantitative yield of azoxybenzene. The second-order rate constants calculated from expression (2) for various initial reactant concentrations are given in Table 1 as further confirmation of this second-order kinetic behaviour.

Determination of the second-order rate constants for the reaction over the temperature range 12.5–55 °C (Table 2), allowed for the determination of the activation parameters as $\Delta F^\ddagger_{302} = 19.0$ kcal mol⁻¹, $\Delta H^\ddagger = 13.2$ kcal mol⁻¹, and $\Delta S^\ddagger_{302} = 19.4$ cal mol⁻¹ K⁻¹. These re-

sults are *not* consistent with those previously reported by Ogata,⁴ but recalculation of the data in that paper shows the actual parameters for methanol solvent, as recorded by Ogata should be $\Delta F^\ddagger_{313} = 19.1$ kcal mol⁻¹, $\Delta H^\ddagger = 13.1$ kcal mol⁻¹, and $\Delta S^\ddagger_{313} = 19.5$ cal mol⁻¹ K⁻¹, and not those quoted.

The variations of reaction rate with changes in solvent were found to be modest, with a 16-fold rate increase between benzene and ethanol (Table 3). This magnitude of solvent effect would not be inconsistent with the radical

mechanism postulated by Russell,⁵ if electron transfer between neutral molecules is rate determining.

TABLE 1

Second-order rate constants for the reaction of nitrosobenzene with *N*-phenylhydroxylamine at 30 °C in ethanol

10 ³ [Nitrosobenzene]/M	10 ³ [<i>N</i> -Phenylhydroxylamine]/M	10 ² <i>k</i> ₂ /l mol ⁻¹ s ⁻¹
19.3	17.3	11.1
19.3	54.5	10.9
7.2	17.3	11.2

TABLE 2

Variation of second-order rate constants with temperature for the reaction of nitrosobenzene with *N*-phenylhydroxylamine in ethanol

<i>t</i> /°C ^a	10 ² <i>k</i> ₂ /l mol ⁻¹ s ⁻¹
12.5	2.80
30.0	10.9
43.5	28.1
55.0	68.5

^a ± 0.5 °C.

TABLE 3

Second-order rate constants for the reaction of nitrosobenzene with *N*-phenylhydroxylamine at 30 °C in various solvents

Solvent	10 ² <i>k</i> ₂ /l mol ⁻¹ s ⁻¹
Ethanol	10.9
Dimethylformamide	6.6
Tetrahydrofuran	3.4
Carbon tetrachloride	2.2
Benzene	0.68

When this study was extended to examine the effects of *para*-substituents on the rates of reaction we found that the second-order rate constants as calculated from

⁷ L. A. Neiman, V. I. Maimind, and M. M. Shemyakin, *Tetrahedron Letters*, 1965, 3157.

⁶ M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite, *Izvest. Akad. Nauk. S.S.S.R.*, 1957, 1260.

the apparent loss of the *para*-substituted nitroso-benzenes,* in reactions with near equimolar quantities of variously *para*-substituted *N*-phenylhydroxylamines in ethanol at 30 °C, showed certain combinations of reactants to be *isokinetic* with others (Table 4). The

TABLE 4

Isokinetic relationships for condensations of *para*-substituted nitrosobenzenes and phenylhydroxylamines

Hydroxylamine substituent	Nitrosobenzene substituent		
	Cl	H	Me
Cl	93	33	1.8
H	27	11	9.7
Me	1.5	9.0	8.6

isokinetic combinations are connected by broken lines in Table 4 and, for example it may be seen that nitrosobenzene apparently condenses with *N*-*p*-chlorophenylhydroxylamine at the same rate (within experimental error) as *p*-chloronitrosobenzene condenses with *N*-phenylhydroxylamine.

The existence of three coincidences of this kind seemed to be beyond the bounds of statistics, and we were forced to conclude either (i) that the reactant pairs form a large stationary concentration of intermediate radicals which then undergo a rate-determining colligation (an unlikely suggestion bearing in mind the reactivity of such nitroxyl radicals) or, (ii) that the isokinetic combinations of reactants rapidly become identical prior to the measured loss of nitroso-compound. That the latter was indeed the case was proved by a detailed spectroscopic examination of the various isokinetic combinations at dilutions where the azoxyarene-forming condensations would proceed with half-lives in the order of years (Table 5). T.l.c. of the solutions confirmed the spectral results.

TABLE 5

Results of a spectroscopic examination of *para*-substituted nitrosobenzenes and phenylhydroxylamines as reactant pairs (2×10^{-4} M) in ethanol at 30 °C

Original equimolar components of mixture	Observed components of mixture after 1 h
PhNO + MeC ₆ H ₄ NHOH	PhNHOH + MeC ₆ H ₄ NO
MeC ₆ H ₄ NO + PhNHOH	PhNHOH + MeC ₆ H ₄ NO
PhNO + ClC ₆ H ₄ NHOH	PhNO + ClC ₆ H ₄ NHOH
ClC ₆ H ₄ NO + PhNHOH	PhNO + ClC ₆ H ₄ NHOH
ClC ₆ H ₄ NO + MeC ₆ H ₄ NHOH	MeC ₆ H ₄ NO + ClC ₆ H ₄ NHOH
MeC ₆ H ₄ NO + ClC ₆ H ₄ NHOH	MeC ₆ H ₄ NO + ClC ₆ H ₄ NHOH

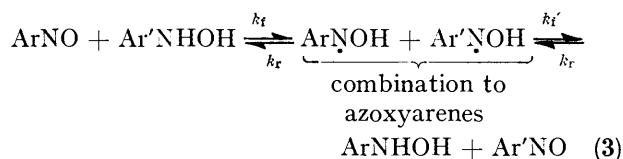
Thus it is clearly shown that for each isokinetic pair of Table 4 there is rapidly established a high preferred actual combination of nitrosoarene and *N*-arylhydroxylamine, with the more electron-attracting *para*-substituent ending up on the hydroxylamine whilst the more electron-releasing substituent appears on the nitroso-

* Kinetics were monitored by observation of the $n \rightarrow \pi^*$ transition in the visible spectrum; the frequency and intensity of this nitroso-band are not very sensitive to aryl substituents.

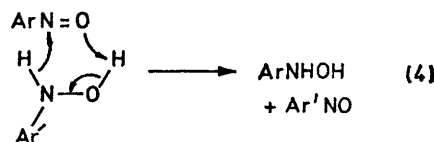
arene, in line presumably with the maximization of resonance stabilization. This substituent effect is also in agreement with the reductive potential of the *para*-substituted nitrosoarenes as measured potentiometrically as the half-wave potentials by Holmes⁸ and by Lutz and Lytton.⁹

These results give direct evidence for Ogata's hydrogen transfer postulate. Evidently a very rapid equilibrium is established well in advance of conversions into azoxyarene.

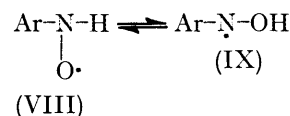
The hydrogen transfer is in itself interesting and one may speculate that it arises by an extension of Russell's original mechanism to include the nitroxyl radical disproportionation steps labelled k_r , k_r' [equation (3)],



although the alternative of direct thermal hydrogen transfer (4) which would be analogous to the reduction of olefins by di-imide,¹⁰ cannot be excluded at this time as a possible route.



The occurrence of a radical mechanism similar to that proposed by Russell, coupled with the observations that the disproportionation step is much faster than the combination to azoxyarene, suggests that the nitroxyl radical intermediates [which are known to exist predominantly as the oxygen-centred radical (VIII) rather than (IX)¹¹], undergo hydrogen exchange if reaction



occurs with the statistically more likely form (VIII), whereas combination to azoxyarene can occur only by the colligation of two nitrogen spin centred radicals (IX). The rate of overall azoxyarene formation will thus depend not only on the rate of the various independent reaction steps but also on the position of the tautomeric equilibrium between the possible radical intermediates (VIII) and (IX), about which little is known.

EXPERIMENTAL

U.v. spectra was recorded with a Perkin-Elmer 402 spectrophotometer. M.p.s were determined on a Mettler F.P.2 thermal investigator. Elemental analyses were

⁸ J. Holmes, *J. Org. Chem.*, 1964, **29**, 3076.

⁹ R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, 1937, **2**, 73.

¹⁰ R. G. Pearson, *Chem. Eng. News*, 1970, **48**, (41), 66.

¹¹ J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, 1961, **35**, 1507.

obtained using a Perkin-Elmer 240 automatic analyser. T.l.c. was carried out on silica gel coated glass plates.

Materials.—All solvents were distilled and dried before use. Nitrosobenzene, m.p. 65–66 °C, was a commercial sample which was purified before use by steam distillation. *p*-Chloronitrosobenzene, m.p. 88–89 °C, and *p*-nitrosotoluene, m.p. 42–43.1 °C, were prepared by ferric chloride oxidation⁹ of the corresponding hydroxylamines and were purified by steam distillation. *N*-Phenylhydroxylamine, m.p. 82–84 °C, *N*-(*p*-chlorophenyl)hydroxylamine, m.p. 89–89.2 °C, and *N*-*p*-tolylhydroxylamine, m.p. 89–91 °C, were all prepared by reduction of the corresponding nitro-compounds according to the method of Utzinger.¹² All these compounds gave correct elemental analyses, were single components as judged by t.l.c., and all the m.p.s agreed well with the literature values.¹³

Kinetic Studies of the Reaction of para-Substituted Nitrosoarenes with para-Substituted *N*-Arylhydroxylamines.—The reactions were monitored by following the decay of the nitrosoarene with reference to the $n \rightarrow \pi^*$ transition occurring in the visible spectrum (*ca.* 750 nm). The reactions were carried out in the cavity of the spectrophotometer in a 1 cm quartz-faced cell with integral condenser. The cell was maintained at constant temperature throughout by passing heating or cooling fluids from an external thermostatted bath through the condenser, the cell temperature being measured by a precise thermocouple. Separate solutions of the hydroxylamine and the nitroso-compound in ethanol were allowed to equilibrate in the thermostatted bath to the required temperature prior to mixing. Calibration curves were constructed for the concentration of the various nitrosoarenes by measurement of the absorbance of the $n \rightarrow \pi^*$ transition occurring at *ca.* 750 nm, the graphs being linear for concentrations up to 3×10^{-2} M. The reactant concentrations were normally

¹² G. E. Utzinger, *Annalen*, 1944, **50**, 556.

¹³ I. M. Heilbron, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1934.

of the order of 1.5×10^{-2} M which gave half-lives of under 1 h.

Spectroscopic Examination of Reactions at High Dilutions.—These were carried out by examination of the distinctive u.v. finger-print patterns of the reactants (Table 6).

TABLE 6
U.v. spectra of reactants

Entry	Compound	Peak positions (nm)
1	<i>N</i> -(<i>p</i> -Chlorophenyl)hydroxylamine	250, 296
2	<i>p</i> -Chloronitrosobenzene	290, 314
3	<i>N</i> -Phenylhydroxylamine	242, 285
4	Nitrosobenzene	283, 307
5	<i>N</i> - <i>p</i> -Tolylhydroxylamine	243, 289
6	<i>p</i> -Nitrosotoluene	289, 317

Equal volumes of equimolar reactant solutions (2×10^{-4} M) in ethanol were mixed at room temperature in a 1 cm cell located in the cavity of the spectrometer. The spectra of the mixture was immediately recorded, the solutions were left for 1 h, and the spectra were re-recorded. The results are shown in Table 7.

TABLE 7

U.v. spectroscopic examination of reaction solutions

Mixtures ^a	Initial peak positions (nm)	Peak positions after 1 h at 30 °C (nm)
1 + 4	252, 284, 308	251, 284, 309 ^b
2 + 3	240, 288, 314	249, 283, 308 ^c
1 + 6	250, 290, 318	248, 290, 318 ^b
5 + 2	244, 290, 313	248, 289, 317 ^c
5 + 4	244, 285, 306	244, 287, 316 ^c
6 + 3	243, 288, 317	241, 287, 317 ^b

^a See Table 6 for key. ^b Spectra unchanged. ^c Spectra agree in intensity and peak position with their isokinetic pair.

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