Formation of Baudisch Complexes $[Fe^{II}(CN)_5,RNO]^{3-}$ from Alkyl- and Aryl-hydroxylamines and Aquapentacyanoferrate(3−) Anions, $[Fe^{II}(CN)_5,H_2O]^{3-}$

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Aqueous sodium aquapentacyanoferrate(3−) reacts with phenylhydroxylamine at pH 7—10 under nitrogen to give the purple complex of Baudisch in approximate accord with equation (i). The free radicals PhNHO• and PhNH•

$$[Fe(CN)_5,H_2O]^{3-} + 2PhNHOH = [Fe(CN)_5,PhNO]^{3-} + PhNH_2 + 2H_2O \qquad (i)$$

participate in the reaction process. Aliphatic hydroxylamines react similarly at pH 5—8 to give pink solutions containing analogous anions, of a type hitherto unknown except for the Legal complexes of aliphatic aldehydes and ketones. The reactions with aliphatic hydroxylamines are slower and more complex, rearrangements of alkylaminyl radicals being involved. Spectrographic and e.s.r. studies have been used to elucidate the mechanisms of these reactions.

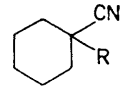
FREE nitroxide radical-anions of cobalt(III) $[(NC)_5Co^{III}\text{-}NRO\cdot]^{3-}$ have proved to be stable for some hours in alkaline aqueous solution at room temperature [1,2] and consequently the existence of the corresponding d^6 radical-ions of iron(II) (I) has been envisaged. Though

$[(NC)_5Fe^{II}NRO\cdot]^{4-}$ (I)

$[(NC)_5Fe^{II}NR{=}O]^{3-}$ (II)

$Na_3[Fe^{II}(CN)_5H_2O]^{3-}$ (III)

$[Fe^{II}(CN)_5,RNHOH]^{3-}$ (IV)



(V) R = NHOH

(VI) R = NO

an e.s.r. spectrum claimed to be that of type (I; R = Ph) [3] has been obtained by γ-ray bombardment of a frozen solid containing the purple Baudisch complex (II; R = Ph) [4] formed from nitrosobenzene and sodium aquapentacyanoferrate(3—) (III), attempts in this laboratory to obtain distinctive e.s.r. spectra by reducing aqueous solutions of (II; R = Ph) which had been extracted thoroughly with ether to remove free nitrosobenzene have failed. Solutions before such extraction easily gave e.s.r. spectra of the phenyl nitroxide radical, PhNHO•, or, at high alkalinities, of its anion $(PhNO\cdot)^-$.[5]

Since the hydroxylaminopentacyanoferrate(3—) anion $[Fe^{II}(CN)_5,NH_2OH]^{3-}$ appears to be autoxidisable in strong alkali to give a free radical, possibly (I; R = H) [6] it was thought that another route to the formation of radical-anions (I) in solutions might be to react organic hydroxylamines, RNHOH, with aqueous solutions of (III) and then oxidise the postulated complexes (IV).

However even when effected carefully under nitrogen the reaction of (III) with *N*-phenylhydroxylamine in aqueous alcohol at pH 5—10 rapidly gives the purple complex (II; R = Ph) of Baudisch ($\lambda_{max.}$ 528 nm) the structure of which has been established conclusively by later work.[7] Other *N*-arylhydroxylamines also react with (III) to give deeply coloured solutions with absorption spectra identical with those given by the reactions of (III) with the corresponding nitrosobenzenes. Pink solutions are slowly formed from (III) and *N*-alkylhydroxylamines in the same range of concentration and pH and evidently must contain the aliphatic analogues of Baudisch complexes, *i.e.* (II; R = alkyl). In confirmation of this conclusion it was found that identical visible spectra were given by admixture of solutions of (III) with 1-cyano-1-hydroxylaminocyclohexane (V) or with 1-cyano-1-nitrosocyclohexane (VI), but whilst (VI) reacted rapidly with (III) the colour development with (V) was slow (see below). Again both 2-methyl-2-nitrosopropane and monomeric 2-acetyl-2-nitrosopropane immediately gave pink colours with (III).

The existence of aliphatic Baudisch complexes (II) has not been reported hitherto, but structures of this type must undoubtedly be assigned to the unstable Legal complexes [8] obtainable from aqueous solutions of sodium

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[1] M. G. Swanwick and W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 1059.

[2] D. Mulvey and W. A. Waters, *J.C.S. Perkin II*, 1974, 666.

[3] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 243.

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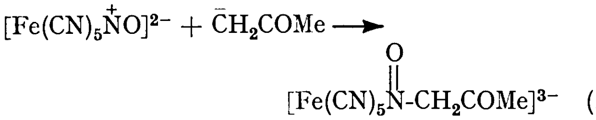
[5] C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, 1964, 230.

[6] D. Mulvey and W. A. Waters, *J.C.S. Dalton*, 1975, 951.

[7] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32; I. Dezsi, B. Molnar, J. Szalay, and I. Jaszberenyi, *Chem. Phys. Letters*, 1973, **18**, 598.

[8] N. V. Sidgwick ' Chemical Elements and their Compounds,' Clarendon, Oxford, 1950, vol. 2, p. 1345.

nitroprusside and the carbanions of aliphatic aldehydes or ketones [equation (1)] in view of the similarity of their absorption spectra (Table 1). Strongly alkaline solutions



$$[Fe(CN)_5\overset{+}{N}O]^{2-} + \bar{C}H_2COMe \longrightarrow [Fe(CN)_5\overset{\overset{O}{\|}}{N}\text{-}CH_2COMe]^{3-} \quad (1)$$

(pH *ca.* 11) are normally required for the preparation of Legal complexes which usually have lifetimes of only a few minutes. The coloured complexes obtainable from aliphatic hydroxylamines appear to be more stable, but since they are obtainable in solutions of pH 5—8 in which they persist for some hours the extra stability is probably due to the lower pH of their environment, alkaline hydrolysis being the route of decay in all cases. The aromatic Baudisch complexes (II; R = Ar) are much more stable again for at pH < 10 they persist in aqueous solution for several days, but this may be due to the fact that they are formed from stable nitrosobenzenes and not from nitrosoalkanes which, if primary or secondary, have only a transitory existence in alkaline solution.

TABLE 1

Absorption maxima (nm) of Baudisch and Legal complexes

Baudisch complex from	λ	Legal complex from	λ	Legal complex from	λ
$Me_3C{\cdot}NO$	518	MeCHO [a]	510	Cyclopentanone	485
$MeCOCMe_2{\cdot}NO$	500	MeCOMe	470	Cyclohexanone	485
$C_6H_{10}CN{\cdot}NO$ [and (V)]	500	MeCOEt	472	$(PhCH_2)_2CO$	492
Me·NHOH	484	$MeCOCHMe_2$	480	PhCOMe [b]	534
$MeCH_2{\cdot}NHOH$	482	EtCOEt	472	Acetylacetone [a]	478
$Me_2CH{\cdot}NHOH$	480	$EtCOC_4H_9$	483		

Average error in $\lambda_{max.}$ ±2 nm

[a] Using sodium carbonate as base. [b] Colour stable for a few hours.

The reactions which lead to the formation of Baudisch complexes (II) from organic hydroxylamines, RNHOH and aquapentacyanoferrate(3—) anions (III) have been elucidated by spectrographic measurements, supported by e.s.r. studies.

Spectrographic Studies.—Curves A of Figures 1 and 2 show that the fast reaction between (III) and nitrosobenzene at pH 8 fairly closely accords with the stoicheiometric equation (2). Within the limits of experimental

$$[Fe^{II}(CN)_5,H_2O]^{3-} + PhNO = [Fe^{II}(CN)_5,PhNO]^{3-} + H_2O \quad (2)$$

error the same curves have resulted from measurements at both pH 6.8 and 10. The curvature around the equivalent point may in part be due to photochemical decomposition of (II) (see line A′ on Figure 2) but reaction (2) is slightly reversible since some nitrosobenzene slowly distils off in the steam when aqueous solutions of (II; R = Ph) are boiled.

Curves B of these Figures show that in the reaction between phenylhydroxylamine and (III) nearly all the latter is converted into (II) if at least two moles of phenylhydroxylamine are used per mole of (III), but when (III) is used in excess the yields of (II) are apt to be variable even when carried out with nitrogen-flushed solutions. This variability has been traced to concurrent autoxidation of phenylhydroxylamine to azoxybenzene by residual traces of oxygen, a reaction which has been shown by Ogata and Morimoto [9] to be facilitated by alkali and strongly catalysed by salts of iron. Exactly similar results to those of curves A and B of both Figures have been obtained by the use of *p*-chloronitrosobenzene and *p*-chlorophenylhydroxylamine, which give a complex (II) with $\lambda_{max.}$ 535 nm.

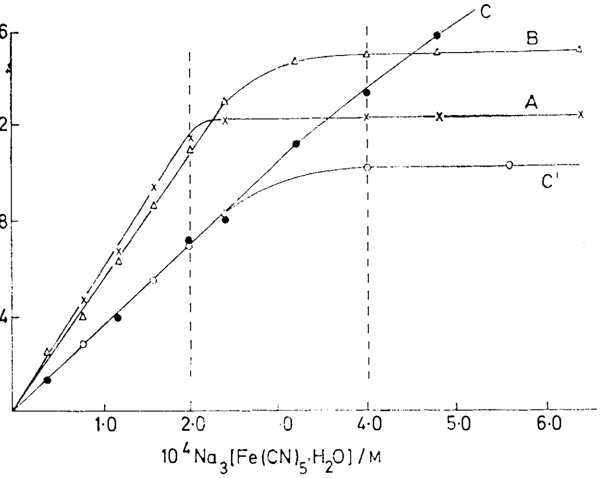


FIGURE 1 Absorbance of Baudisch complexes at pH 8 with differing concentrations of $[Fe(CN)_5,H_2O]^{3-}$: A, nitrosobenzene (2×10^{-4}M) ×; B, phenylhydroxylamine (4×10^{-4}M) △; C, 1-cyano-1-hydroxylaminecyclohexane (4×10^{-4}M) ●; C′, 1-cyano-1-hydroxylaminocyclohexane (2×10^{-4}M) ○

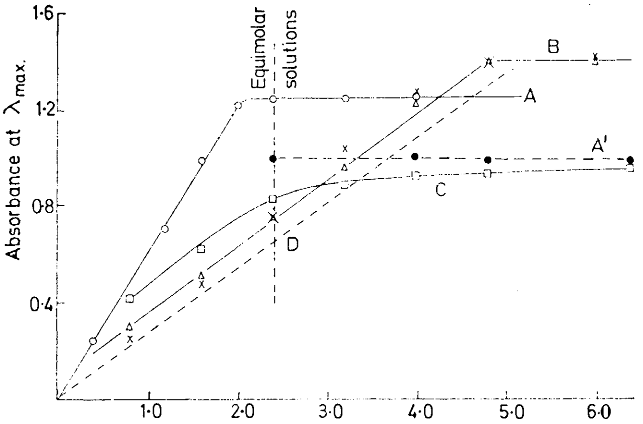


FIGURE 2 Absorbance of Baudisch complexes using 2.4×10^{-4}M-$[Fe(CN)_5H_2O]^{3-}$ and varying concentrations of the organic compounds; A, nitrosobenzene, pH 8.0 ○; A′, after 1 h exposure to daylight ●; B, phenylhydroxylamine, △ pH 8.0; × pH 6.8; C, 1-cyano-1-hydroxylaminocyclohexane, □ pH 8.0. The dashed line D has half the slope of that of line A [compare equation (3) in text]

Both sets of spectrographic measurements approximately accord with the stoicheiometry of equation (3). From phenylhydroxylamine aniline has been detected as

$$[Fe(CN)_5,H_2O]^{3-} + 2ArNHOH = [Fe(CN)_5,ArNO]^{3-} + ArNH_2 + 2\ H_2O \quad (3)$$

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[9] Y. Ogata and T. Morimoto, *J. Org. Chem.*, 1965, **30**, 597.

another major reaction product, accompanied however by some azoxybenzene and the corresponding two products have been obtained from *p*-chlorophenylhydroxylamine (see Experimental section).

Curves C of Figure 1 represent the maximum absorption at $\lambda_{max.}$ (500 nm) from dilute solutions of (III) and of the tertiary aliphatic hydroxylamine (V). As with other *N*-alkylhydroxylamines the coloured product (II) from (V) forms slowly and then gradually decomposes, but its rate of formation is much greater than that of its decay since with 10^{-3}—10^{-4}M solutions at pH 6—10 and 20 °C the colour maximum is attained in 2—4 h and the reactant solutions are still distinctly coloured after 24 h. Figure 1 indicates that nearly two moles of (III) per mole of (V) are needed for maximum colour production and that the complex has an extinction coefficient ($>5 \times 10^3$) similar to that of (II; R = Ph). Curve C of Figure 2 again shows that the stoicheiometry of equation (3) does not hold in the aliphatic series and accords with the absorption trend of curves C in Figure 1.

With methyl-, ethyl-, and isopropyl-hydroxylamines plots of the development of pink colours in solutions of pH between 5 and 8 follow the trend of curves C of Figure 1, but the decay of the colour is evidently more rapid than with (V), though the colour maxima are of a similar order of magnitude ($\varepsilon > 10^{-3}$). The rates of these reactions with aliphatic hydroxylamines were pH dependent, maximum colour formation being faster at the lower pH values.

E.s.r. Studies.—At pH 7—10 nitrogen-flushed solutions (10^{-2}M) of phenylhydroxylamine in aqueous ethanol themselves gave weak e.s.r. spectra of the radical PhNHO·[5] and the addition under nitrogen of 0.01—0.05 equivalents of aqueous (III) immediately enhanced the signal intensities 5—6-fold; these stronger signals gradually decayed as the colour of the Baudisch complex developed. Subsequent addition of more (III) led to no further signal enhancement and with over 0.1 equivalents the e.s.r. signal was destroyed completely. With *p*-chlorophenylhydroxylamine a 5-fold enhancement of the signal of $ClC_6H_4{\cdot}NHO{\cdot}$ was achieved with 0.03—0.05 equivalents of (III). This decreased to 30% of its original intensity in 15 min and was at once destroyed by further addition of (III).

The aliphatic hydroxylamines behaved similarly. The stable hydroxylamine (V) in 5×10^{-2}M solution in aqueous ethanol at pH 8 under nitrogen gave no e.s.r. signal but on the addition of 0.2—0.3 equivalents of (III) a 4-line spectrum (intensities 1 : 2 : 2 : 1) corresponding to the radical $(C_6H_{10}CN)NHO{\cdot}$ at once appeared (Found: $a_N = a_{N-H} = 1.31 \pm 0.005$ mT; *g* 2.005 8) and no other signal was detectable over a 1 000 G field sweep. Methyl-, ethyl-, and isopropyl-hydroxylamines in buffered solutions of pH 7—8 under nitrogen also gave weak, wide-lined spectra of the corresponding radicals RNHO· when treated with a similar proportion of (III). These disappeared in *ca.* 10 min, but from methyl- and ethyl-hydroxylamines were soon replaced by somewhat more persistent signals of secondary radicals. The primary e.s.r. spectra were also obtainable as transient signals by oxidising the hydroxylamines at pH 6—7 with dilute aqueous potassium ferricyanide. As Table 2 shows, our splitting constants accord with those of Anderson and Norman[10] who have made a thorough study of the reduction of alkylhydroxylamines by titanium(III). Compound (V) was not oxidised by ferricyanide at alkalinities less than pH 10 but then gave the 3-line spectrum of the radical-anion $(C_6H_{10}CN)\dot{N}\bar{O}$ having a_N 1.56 ± 0.005 mT.

TABLE 2

E.s.r. spectra of hydroxylaminyl radicals RNHO· (hyperfine splitting constants in mT; maximum errors ±0.02 mT)

	$a_N = a_{N-H}$			a_{C-H}		
Group R	A	B	C	A	B	C
Me	1.49	1.48	1.48	1.49	1.48	1.48
Et	1.45	1.42	1.415	1.42	1.415	1.415
Pr^i	1.425	1.425	1.425	1.35	1.34	1.335

A = Reaction of RNHOH with $[Fe^{II}(CN)_5H_2O]^{3-}$. B = Reaction of RNHOH with $[Fe^{III}(CN)_6]^{3-}$. C = Measurements of Anderson and Norman.[10]

By analogy with the work of Anderson and Norman we infer that the secondary e.s.r. spectra are those of β-amino nitroxides. That from methylhydroxylamine clearly shows the presence of two nitrogen atoms and corresponds to $H_2N{\cdot}CH_2{\cdot}NMeO{\cdot}$ [Found: $a_N(1)$ 1.64, a_{CH_3} 1.45, a_{CH_2} 0.97, $a_N(2)$ 0.22 mT, with maximum error 0.01] whilst that from ethylhydroxylamine could be due to $H_2N{\cdot}CHMe{\cdot}NEtO{\cdot}$ [Found: $a_N(1)$ 1.63, a_{CH_2} 1.3, a_{CH} 0.4 mT] but here the line width of 0.1—0.2 mT obscures splitting due to a second nitrogen and in *ca.* 5 min the signal decays to insignificance.

DISCUSSION

The spectrographic measurements with the aromatic hydroxylamines, qualitatively summarised by equation (3), could be taken to indicate that aquapentacyanoferrate(II) anions (III) catalyse the disproportionation (4)

$$2\ RNHOH \longrightarrow RNO + RNH_2 + H_2O \quad (4)$$

and that the nitroso-compounds so formed react rapidly with (III) to give Baudisch complexes (II; R = aryl). However this is an over-simplification of the reaction mechanism since the e.s.r. studies indicate that there is some participation of ArNHO· free radicals in the reaction sequence; again their dimers, the azoxybenzenes have been isolated as minor reaction products.

With the *N*-alkylhydroxylamines the participation of primary nitroxide radicals has been established more conclusively, but though the formation of nitrosoalkanes may be inferred from the appearance of pink colours indicative of Baudisch complexes (II; R = alkyl) other competing reactions must be involved since the curves C of Figures 1 and 2 differ significantly from the curves B.

One-electron transfers are to be expected of reactions involving complexes of iron(II) and iron(III). Consequently, since hydroxylamine and its *N*-alkyl derivatives

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[10] N. H. Anderson and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1971, 993.

have been shown to be reducible by one-electron transfer to aminyl radicals $RNH\cdot$ (or, in acid, $R\dot{N}H_2^+$) the reaction scheme of equations (5)—(10) can rationally be postulated.

$$Fe^{II} + RNHOH \xrightarrow{\text{slow}} Fe^{III} + RNH\cdot + OH^- \tag{5}$$

$$Fe^{III} + RNHOH \xrightarrow{\text{fast}} Fe^{II} + RNHO\cdot + H^+ \tag{6}$$

$$Fe^{III} + RNHO\cdot \xrightarrow{\text{fast}} Fe^{II} + RNO \xrightarrow[\text{(2)}]{\text{reaction}} \text{(II)} \tag{7}$$

$$Fe^{II} + RNH\cdot + H_2O \longrightarrow Fe^{III} + RNH_2 + OH^- \tag{8}$$

$$RNH\cdot + RNHOH \longrightarrow RNH_2 + RNHO\cdot \tag{9}$$

$$2RNHO\cdot \longrightarrow R(N_2O)R + H_2O \tag{10}$$

Here Fe^{II} represents the iron(II) complex (III) and Fe^{III} the anion $[Fe^{III}(CN)_5H_2O]^{2-}$ which is known to be a stronger oxidising agent[11] than ferricyanide, $[Fe^{III}(CN)_6]^{3-}$. Since the latter rapidly oxidises hydroxylamines, equations (6) and (7) should also be fast reactions. With *N*-alkylhydroxylamines the occurrence of reaction (9) has been substantiated by Anderson and Norman[10] who also found that *N*-alkylaminyl radicals $R_2CH\cdot NH\cdot$ rapidly rearrange to α-aminoalkyl radicals, $R_2\dot{C}\cdot NH_2$, which then, with nitrosoalkanes, R'NO, give secondary nitroxides $H_2N\cdot CR_2\cdot NR'O\cdot$. The secondary e.s.r. spectra obtained in this investigation from *N*-methyl- and *N*-ethyl-hydroxylamine (see previous section) can be those of the nitroxides formed respectively from $\cdot CH_2NH_2$ and MeNO and from $Me\dot{C}H\cdot NH_2$ and EtNO.

The degree to which amine formation is due to reaction (8) or (9) must be a function of the redox potentials of the Fe^{II} ion and of the various $RNH\cdot$ radicals and might be pH dependent, but the overall stoicheiometry [equation (3)] does not discriminate between these two reactions. The absence of possible rearrangement of radicals $ArNH\cdot$ suffices to explain the differences between curves B and C of Figures 1 and 2. The formation of azoxy-compounds [reaction (10)] has been included in the reaction scheme given above. Since curves A and B of Figure 1 so closely coincide for phenylhydroxylamine (10) must be a much slower reaction than (7) and much of the azoxybenzene obtained in the large scale reaction between phenylhydroxylamine and (III) may be due to concurrent autoxidation.

EXPERIMENTAL

Materials.—The arylhydroxylamines and the corresponding nitrosobenzenes were crystallised from dry light petroleum–benzene until quite colourless and were stored in a refrigerator. Samples of the hydroxylamines which did not give colourless solutions in nitrogen-flushed ethanol were discarded. The hydrochlorides of the alkylhydroxylamines were made from the corresponding nitroparaffins by the method of Meisenheimer and Chou,[12] keeping the temperature below 40° throughout. Compound (V) was prepared as described by Neelakantan and Hartung;[13] it had the required analysis and m.p.

Sodium amminepentacyanoferrate(3−), $Na_3[Fe(CN)_5NH_3],6H_2O$ prepared from sodium nitroprusside[14] was reprecipitated from concentrated aqueous ammonia with methanol and air-dried. It gave satisfactory analyses when titrated electrometrically with permanganate and its solutions in strong aqueous ammonia had the literature values $\lambda_{max.}$ 402 nm (ε 450).[15] 10^{-2}M * Solutions were prepared by weight in distilled water and had $\lambda_{max.}$ 394 nm indicative of complete conversion to the aqua-anion (III), but they were further diluted over 10-fold with nitrogen-flushed water or aqueous buffer solutions for all spectrographic work. The optical absorption at 402 nm of such solutions after 5-fold dilution with concentrated ammonia was regularly used for calibration of molarities.

Spectrographic Work.—Solutions of (III) were nitrogen-flushed and used within 2 h of preparation. Solutions (1 or 2×10^{-3}M) of the hydroxylamines were freshly prepared by weight in ethanol. The two reactants were diluted under nitrogen with a much larger volume of the desired borate buffer (*m*/20; Clark and Lubs formulation) and finally mixed in a nitrogen-flushed flask. Optical densities were recorded in a Unicam 825 spectrometer using stoppered 1 cm cells thermostatted at 20°. Table 3 illustrates a typical reaction. Absorption maxima only are illustrated in the Figures.

TABLE 3

Reaction between (V) and (III) at pH 8.0

The stated amounts of (III) were added to 10 ml samples of 1.0×10^{-3}M-(V) in ethanol under nitrogen together with 5×10^{-2}M-buffer, pH 8.0, to give a total volume of 25 ml in each reaction mixture. The mixtures were stored in the dark at 20°; the absorptions recorded at the stated reaction times were those at the $\lambda_{max.}$ for the solutions (500 nm)

Volume of (III) per sample	Absorption at reaction time (h)				
ml of 1.0×10^{-3}M	1	2	4	5	24
1	0.10	0.13	0.13	0.13	0.09
3	0.29	0.37	0.39	0.39	0.30
5[a]	0.54	0.67	0.71	0.71	0.54
ml of 2.0×10^{-3}M					
1	0.19	0.21	0.22	0.21	0.16
2	0.45	0.49	0.48	0.49	0.39
3	0.71	0.77	0.78	0.79	0.73
4	1.04	1.10	1.12	1.13	0.99
5[b]	1.20	1.28	1.32	1.34	1.19
6	1.39	1.49	1.55	1.57	1.39
8	1.58	1.68	1.77	1.80	1.68

[a] 0.5 Equivalents. [b] 1.0 Equivalents.

E.s.r. Measurements.—10^{-2}M Solutions of the reactants were prepared and mixed under nitrogen then transferred immediately to a Varian E4 spectrometer. The reported measurements (*e.g.* Table 2) have been calibrated by the use of Frémy's salt.

Preparative Reactions.—Sodium amminepentacyanoferrate(3−) (0.03 mol) in water (200 ml) containing sodium hydrogen carbonate (5 g) was brought to pH 8 by addition of dilute acetic acid and then nitrogen flushed. Pure phenylhydroxylamine (5 g, 0.045 mol) in methanol (50 ml) and water (150 ml) was also nitrogen flushed and the two solutions were mixed in a stoppered flask. After 1.5 h the mixture was extracted with ether and this extract was

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* 1M = 1 mol dm^{-3}.

[11] R. Stasiu and R. G. Wilkins, *Inorg. Chem.*, 1968, **8**, 157.

[12] J. Meisenheimer and L.-H. Chou, *Annalen*, 1939, **539**, 78.

[13] L. Neelakantan and W. H. Hartung, *J. Org. Chem.*, 1958, **23**, 964.

[14] K. A. Hofmann, *Annalen*, 1900, **312**, 1.

[15] F. J. Baran and A. Muller, *Z. anorg. Chem.*, 1969, **368**, 144: A. D. James, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 1273.

extracted with dilute hydrochloric acid. The residual ether on evaporation yielded azoxybenzene (0.62 g, 12.5%), m.p. 36° (from aqueous methanol), and the acid extract after basifying gave aniline, which was recovered as benzanilide (3.2 g), m.p. 163°, equivalent to 70% of the yield calculated from equation (3).

On boiling, a portion of the purple aqueous solution from the first extraction yielded some nitrosobenzene. Neither electrolytic reduction of the purple extracted solution in the cavity of the e.s.r. spectrometer nor sodium dithionite reduction gave evidence of free radical formation. Sodium tetrahydroborate did not reduce (II; R = Ph).

A similar experiment with *p*-chlorophenylhydroxylamine gave 50% *p*-chloroaniline calculated from equation (3) and 15% of 4,4′-dichloroazoxybenzene, m.p. 153°. From the hydroxylamine (V) only cyclohexanone could be isolated by a similar solution, but a solution of the pink complex gave a trace of the blue nitroso-compound (VI) when boiled.

Legal Complexes.—The compounds of Table 1 (0.5 ml) in ethanol (10 ml) were basified with 0.1M-sodium hydroxide (0.1—0.5 ml) or sodium carbonate. Portions were then transferred to spectrometer cells, rapidly mixed with 2—3 drops of dilute aqueous sodium nitroprusside, and their visible absorption spectra recorded in under 1 min. The colours of the solutions soon change from pink to yellow, especially if the mixtures are too alkaline, but do not form at $<$ pH 10. Table 1 records $\lambda_{max.}$ only for mixtures which by this procedure gave repeatedly an absorption peak in the 450—550 nm region. The Legal complex from isopropyl methyl ketone had a very low stability; Table 1 indicates that it is evidently a derivative of $Me_2CH{\cdot}CO{\cdot}CH_2NO$ and not of $MeCOCMe_2NO$ which gives a stable Baudisch complex.

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