Reduction of Alkaline Aqueous Disodium Pentacyanonitrosylferrate(2−) (Sodium Nitroprusside) and Kinetic Features of its Colour Reaction with Thiols

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The products of each one-electron step in the reduction of the anion $[(NC)_5Fe^{II}NO]^{2-}$, (I), to pentacyano(hydroxylamine)ferrate(3−) ion, $[(NC)_5Fe^{II}(NH_2OH)]^{3-}$, have been characterised spectroscopically. The anions $[(NC)_5Fe{-}\dot{N}{=}O]^{3-}$ and $[(NC)_5Fe{-}N(H)\dot{O}]^{4-}$ have characteristic e.s.r. spectra; the anions $[(NC)_5Fe{-}\dot{N}{=}O]^{4-}$ and $[(NC)_5Fe(NH_2OH)]^{3-}$ have broadish optical absorption maxima at 347 and 436 nm respectively and hydrolyse slowly to the aquapentacyanoferrate(3−) anion, $[(NC)_5Fe^{II}OH_2]^{3-}$. The reduction processes resemble those of the stepwise reversible reduction of nitrobenzene to phenylhydroxylamine in alkali. Reversible reactions between (I) and thiolate anions give pink products, $[(NC)_5Fe^{II}(NO)SR]^{3-}$, which decompose irreversibly yielding $[(NC)_5Fe{-}\dot{N}{=}O]^{3-}$ anions. The reactions (i) and (ii) may both be involved in these decompositions.

$$[(NC)_5Fe(NO)SR]^{3-} \longrightarrow [(NC)_5Fe{-}\dot{N}{=}O]^{3-} + RS\cdot \qquad (i)$$

$$[(NC)_5Fe(NO)SR]^{3-} + RS^- \longrightarrow [(NC)_5Fe{-}\dot{N}{=}O]^{4-} + RS{\cdot}SR \qquad (ii)$$

FOR several years it has been known that the reduction of the pentacyanonitrosylferrate(2−) anion, $[(NC)_5Fe^{II}NO]^{2-}$ (I), in solution can be effected in stages, the first of which leads to the formation of an anion of magnetic moment $\mu = 1{\cdot}4$—$1{\cdot}5$ B.M. to which Griffith *et al.*[1] assigned the formula $[(NC)_5FeNO]^{3-}$, (II).† The e.s.r. spectrum of an anion, considered to be (II), prepared electrolytically in *NN*-dimethylformamide (dmf) solution, was first observed by Bernal and Hockings[2] who illustrated the characteristic shape of its three lines [see Figure 6(a)] and stated that they are centred at g 2·0253. Later Raynor[3] and McNeil *et al.*,[4] who investigated the e.s.r. spectrum more fully after freezing the dmf solutions to −196 °C, reported g 2·026 and assigned a nitrogen splitting constant, a_N, of 14·8 G which is similar in value to that of the organic nitroxides $R_2NO\cdot$, including the complexes $[(NC)_5Co^{III}\{N(R)\dot{O}\}]^{3-}$ (R = alkyl[5] or aryl[6]). No physical characteristics of any other reduction product of (I) have yet been described.

We have studied the reduction of alkaline aqueous sodium pentacyanonitrosylferrate(2−) at room temperature more thoroughly and have been able to characterise spectroscopically each single stage in the reduction of the anion (I) to the pentacyano(hydroxylamine)ferrate anion, $[(NC)_5Fe^{II}(NH_2OH)]^{3-}$ (III). Particular attention has been paid to the reduction of (I) by thiols which has also been examined kinetically. Our findings lead to a consistent reinterpretation of earlier work and show that the reduction processes are physicochemically similar to the stepwise reduction of nitrobenzene in alkali to phenylhydroxylamine.

Historical Background.—Kolthoff and Toren[7,‡] in 1953 investigated the reduction of $Na_2[(NC)_5FeNO]$ polarographically in aqueous alkali (pH 7—14) and concluded that its first two stages were reversible one-electron reductions ($E_{\frac{1}{2}}$ −0·4 and −0·6 V *versus* a s.c.e.) whereas a third step, at −1·2 V, appeared to be irreversible. Since the polarographic diffusion current decreased abruptly at pH >10 they concluded that the observed reduction was that of the anion $[(NC)_5FeNO]^{2-}$, (I), and not that of pentacyanonitroferrate(4−), $[(NC)_5FeNO_2]^{4-}$ (IV), which is formed reversibly as shown in equation (1). A little later Zuman and Kabát[8,‡] who worked only at pH 8·1 confirmed that

$$[(NC)_5FeNO]^{2-} + 2\,OH^- \rightleftharpoons [(NC)_5FeNO_2]^{4-} + H_2O \qquad (1)$$

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† 1 B.M. ≈ $9{\cdot}27 \times 10^{-24}$ A m², 1M = 1 mol dm⁻³.

‡ A paper by J. Mašek and E. Mášlová (*Coll. Czech. Chem. Comm.*, 1974, **39**, 2141) has become available in England since our text was submitted for publication. It substantiates the polarographic work of refs. 7 and 8 but ascribes the absorption at $\lambda_{max.}$ 347 nm to (II) and not, as we deduce, to (V). These workers showed that a little CN^- is liberated during the electrolytic reduction of $[(NC)_5FeNO]^{2-}$. Since CN^- is a probable hydrolysis product of the unstable anions (V) and (VI), its detection does not vitiate our main conclusions.

[1] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1958, 3993.

[2] I. Bernal and E. F. Hockings, *Proc. Chem. Soc.*, 1962, 361; *J. Chem. Soc.*, 1964, 5029.

[3] J. B. Raynor, *Nature*, 1964, **201**, 1206.

[4] D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 410.

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

[6] M. G. Swanwick and W. A. Waters, *J. Chem. Soc. (B)*, 1971, 1087.

[7] I. M. Kolthoff and P. E. Toren, *J. Amer. Chem. Soc.*, 1953, **75**, 1197.

[8] P. Zuman and M. Kabát, *Coll. Czech. Chem. Comm.*, 1954, **19**, 873.

the first two stages were one-electron reductions, and deduced that the last stage was a two-electron reduction of an ion (V) to give (III) [equation (2)] but considered all three stages to be irreversible.

$$\underset{\text{(V)}}{[(NC)_5FeNO]^{4-}} + 2e^- + 3H^+ \longrightarrow \underset{\text{(III)}}{[(NC)_5Fe(NH_2OH)]^{3-}} \quad (2)$$

Krasna and Rittenberg,[9] who in 1955 found that $[(NC)_5FeNO]^{2-}$ inhibited the action of the hydrogenase enzyme from *Proteus vulgaris*, studied the uptake of hydrogen by (I) at pH 6·7 in the presence of this enzyme. Blue solutions resulting from uptake of $\frac{1}{2}$ mol H_2 per mol of (I) changed through green to brown for uptake of 1·0 mol H_2 per mol of (I), and for the complete reduction protons were liberated in accordance with equation (3).

$$[(NC)_5FeNO]^{2-} + H_2 \longrightarrow [(NC)_5Fe(NOH)]^{3-} + H^+ \quad (3)$$

Iodine titration under nitrogen supported this equation and indicated a formula (II) for the intermediate present in the blue solutions which were unstable and gradually precipitated Prussian Blue. Air bleached them to yellow-brown solutions containing nitrite anions. It was from similar blue solutions that Bernal and Hockings [2] later detected the three-line e.s.r. spectrum mentioned above.

Following the work of Bernal and Hockings [2] and of McNeil *et al.*,[4] van Voorst and Hemmerich [10] studied the reduction of aqueous $Na_2[(NC)_5FeNO]$ under nitrogen by sodium dithionite, sodium tetrahydroborate, and thiols. They investigated e.s.r. spectra only after freezing their solutions and measured optical spectra down to 400 nm. At pH 4 unstable blue solutions were obtained which gave e.s.r. spectra similar to those obtained previously [2] in dmf, but at pH 7—10 brown solutions were obtained which when frozen gave different spectra ($g_{\parallel}$ 1·92, $g_{\perp}$ 1·99); these broadened as the temperature rose and disappeared at 240 K. By correlating e.s.r. and optical studies they inferred the existence of equilibrium (4), with a pK of 6·0—6·5, the acid form (blue) being unstable. Raynor and Symons [11] disagreed

$$[(NC)_5Fe\dot{N}O]^{3-} + H^+ \rightleftharpoons [(NC)_5Fe(\dot{N}OH)]^{2-} \quad (4)$$

with this conclusion. Other e.s.r. spectra with low g values can be obtained by γ irradiation of both hydrated and anhydrous crystalline $Na_2[(NC)_5FeNO]$ at low temperatures [12] but as yet none of these has been observed in solutions at room temperature.

Our own work indicates that the unstable blue solutions obtainable at pH <8 probably contain colloidal Prussian Blue, which gradually deposits when these solutions are stored. In general we have studied reductions of (I) only in alkali when the three-line e.s.r. signal described by Bernal and Hockings [2] is persistent at room temperature.

Hydrolysis of Alkaline Aqueous (I) *and its Implications*.—The anion (I) is unstable in alkali; it changes first to the pentacyanonitroferrate(4−) anion, (IV), by the reversible reaction of equation (1) for which Swinehart and Rock [13] evaluated K as $1·5 \times 10^6$ at 25 °C, and then hydrolyses more slowly to aquapentacyanoferrate(3−), (VI), by the reversible reaction (5) which these workers showed to have $K = 3 \times 10^{-4}$ at 25 °C. Visible light

$$\underset{\text{(IV)}}{[(NC)_5Fe^{II}NO_2]^{4-}} + H_2O \rightleftharpoons \underset{\text{(VI)}}{[(NC)_5Fe^{II}OH_2]^{3-}} + NO_2^- \quad (5)$$

markedly accelerates decompositions of aqueous (I) and at room temperature (VI) gradually breaks down especially in the presence of air.[14] The nitro-anion (IV) gives deep yellow solutions having $\lambda_{max.}$ at 400 nm ($\varepsilon_{max.}$ $3·07 \times 10^3$ l mol^{-1} cm^{-1}) whereas (I) has less than 1% of this absorption.[13] For $Na_3[(NC)_5Fe^{II}OH_2]$ prepared by Hofmann's method [14] we find $\lambda_{max.} = 394$ nm ($\varepsilon_{max.}$ $2·6 \times 10^2$ l mol^{-1} cm^{-1}) at pH 10. A different spectrum has been reported for this ion in acid solution.[15] Consequently, alkaline solutions of (VI) are visually indistinguishable from, though at similar concentrations much paler than, those of (IV).

From the equilibrium constants evaluated by Swinehart and Rock, it follows that in solutions of pH $\leqslant$10 the formation of both (IV) and (VI) from aqueous (I) can be eliminated by adding an excess of sodium nitrite which has no significant absorption above 400 nm, but in solutions of pH $\geqslant$12 (IV) then predominates. We have found that aqueous $Na_2[(NC)_5FeNO]$ (*ca.* 5×10^{-3}M) containing sodium nitrite (2×10^{-2}M) can be stored in the dark under nitrogen for a month without change in its optical absorption. But though this simple procedure overcomes some of the errors which have vitiated the quantitative interpretation of earlier studies of reduction of (I), any hydrolyses [equation (6)] of reduction products $[(NC)_5Fe^{II}X]^{4-}$ can then lead through the back reaction (5) to reformation of (I) and so to

$$[(NC)_5Fe^{II}X]^{4-} + H_2O \rightleftharpoons [(NC)_5Fe^{II}OH_2]^{3-} + X^- \quad (6)$$

further consumption of the reducing agent. Equilibria (1), (5), and (6) have proved to be of importance in reactions between alkaline (I) and thiols (see below).

RESULTS

Reductions of Aqueous Disodium Pentacyanonitrosylferrate(2−) *under Nitrogen in Buffered Solutions containing*

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[9] A. I. Krasna and D. Rittenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 5295.

[10] J. D. W. van Voorst and P. Hemmerich, *J. Phys. Chem.*, 1966, **45**, 3914.

[11] J. B. Raynor and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 339.

[12] M. B. D. Bloom, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 3209; B. A. Goodman, D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *ibid.*, 1966, 1547.

[13] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 1966, **5**, 573.

[14] K. A. Hofmann, *Annalen*, 1900, **321**, 1.

[15] A. D. James, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 1273.

Sodium Nitrite.—(a) *Electrolysis*. The electrolytic cell, having a mercury cathode and platinum anode in a separate compartment, has been described previously.[16] Controlled potentials of 2—8 V were applied and from time to time samples were removed for examination of both e.s.r. and optical spectra.

At pH 10 the e.s.r. spectrum of (II) (g 2·024, a_N 1·491 mT) appeared almost immediately and after a short time the solutions became yellow showing an absorption maximum at 347 nm. As Figure 1 shows, the intensity of the e.s.r. spectrum reached a maximum and then declined slowly before the maximum at 347 nm was attained. With applied potentials of $\geqslant$5 V the solutions eventually turned brown and as the e.s.r. signal weakened a band with $\lambda_{max.}$ *ca.* 440 nm appeared. From other evidence (below p. 954) we ascribe this absorption to the ion $[(NC)_5Fe^{II}(NH_2OH)]^{3-}$, (III). At pH 8, as the Figure shows, the e.s.r. signal of (II) was relatively much stronger and the absorption at 347 nm weaker than at pH 10; evidently the product with $\lambda_{max.}$ at 347 nm is formed by reduction of (II) and could be anion (V). Using potentials of $\geqslant$5 V at pH 8 the solutions became yellowish green and darkened to olive green before eventually turning brown. No new absorption band was observed at wavelengths below 600 nm, but on termination of the electrolysis a deposit of Prussian Blue was noticed on the cathodic side of the diaphragm separating the two electrodes. On storage after electrolysis, at both pH values, the optical absorption at 347 nm decreased more rapidly than did the e.s.r. signal. Both the absorption at 347 nm and the e.s.r. signal disappeared when these solutions were exposed to oxygen (or air).

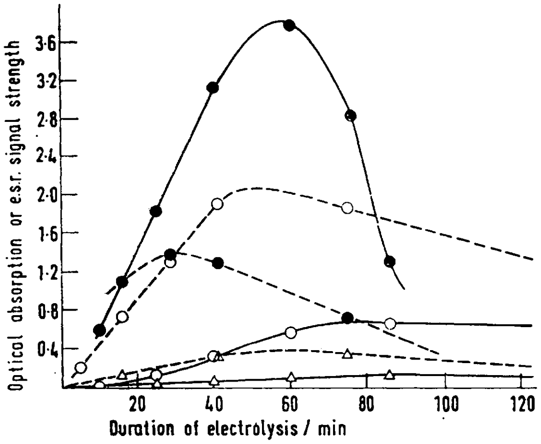

FIGURE 1 Electrolysis of aqueous $Na_2[(NC)_5FeNO]$ (10^{-3}M) at a potential of 7·6 V and pH 8 (——) and pH 10 (— — —): (●), e.s.r. spectra at a constant instrument setting (arbitrary units of signal strength); (○) and (△), optical absorptions at 347 and 440 nm

The electrolysis of aqueous sodium pentacyanonitroferrate(4—), (IV), containing nitrite was also examined at pH 12·5 using potentials of $\geqslant$4 V. The electrolysed solutions did not visibly change colour and did not give the e.s.r. spectrum of (II), but on storage in the e.s.r. cell yielded a weak five-line spectrum, (B) (Figure 2), which was never detected in reductions of $Na_2[(NC)_5FeNO]$ at pH $\leqslant$10·5. This spectrum had g 2·0230 ± 0·0001 and we suggest that it is indicative of a NH group having a_N 0·25, a_{N-H} 0·50 mT, and a linewidth of *ca.* 0·5 mT (*i.e.* overlapping lines of intensity ratio close to 1 : 1 : 2 : 1 : 1).

The admission of a trace of air increased the intensity of this spectrum. Other evidence (below, p. 954) indicates that (B) can probably be assigned to the radical anion $[(NC)_5Fe^{II}\{\dot{N}(H)O^-\}]^{4-}$, (VII). In support of this assignment it may be noted that other hydroxylamine radical anions observable in alkali give splittings with $a_{N-H} > a_N$.[17]

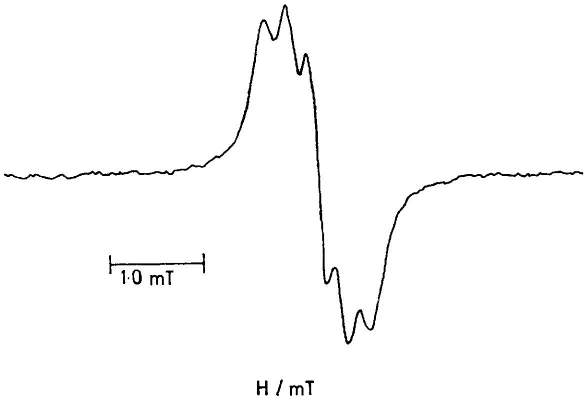

FIGURE 2 E.s.r. spectrum (B), probably due to $[(NC)_5Fe^{II}-\dot{N}(H)O^-]^{4-}$, obtained by exposure of aqueous $[(NC)_5Fe^{II}(NH_2OH)]^{3-}$ to a little air at pH 12

(b) *With sodium tetrahydroborate*. At pH 10 this was evidently effected by measurably slow reactions and, as Figure 3 shows, it had similar spectroscopic features to electrolytic reduction. In particular the e.s.r. signal decreased dramatically as the absorption at 440 nm increased and the optical spectra had an isosbestic point at 375 nm between the 347 and 440 nm absorption maxima, indicating the absence of any appreciable concentration of any other intermediate substance. On exposure of these solutions to the air both the 347 and 440 nm absorption maxima soon disappeared. Brown, more strongly alkaline, solutions (pH $>$12) gave the five-line e.s.r. spectrum (B) on storage, probably on account of a little access of air.

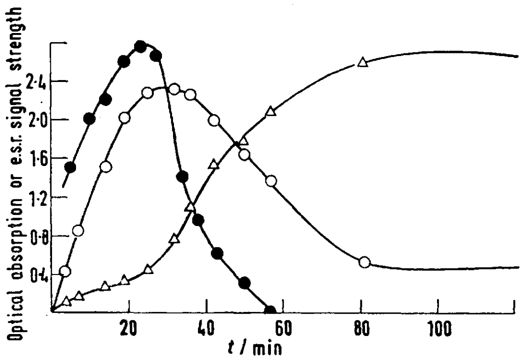

FIGURE 3 Tetrahydroborate reduction of 10^{-3}M-$Na_2[(NC)_5FeNO]$ at pH 10: (●), e.s.r. spectra at constant instrument setting (arbitrary units of signal strength); (○) and (△), optical absorptions at 347 and 442 nm (initial $Na_2[(NC)_5FeNO]$ and $NaBH_4$ both 10^{-3}M)

(c) *With dithionite*. At pH 10 this was rapid and was followed quantitatively by using solutions which had been

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[16] A. R. Metcalfe and W. A. Waters, *J. Chem. Soc.* (*B*), 1969, 918.

[17] C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751.

titrated against iodine [equation (7)]. With excess of

$$Na_2[S_2O_4] + 3I_2 + 4H_2O \longrightarrow 2NaHSO_4 + 6HI \quad (7)$$

dithionite the e.s.r. spectrum of the radical anion $\cdot SO_2^-$ (*g* 2·0057) appeared. Figure 4, which shows how the concentrations of the three reduction products vary with portionwise addition of dithionite, accords with both 1 and 3. At pH 8 the maximum concentration of the radical anion (II) was greater than at pH 10 but that of the product having $\lambda_{max.}$ at 347 nm was less, and on further reduction there was an isosbestic region at 376—378 nm between the 347 and 440 nm maxima. The radical anion (II) was easily formed over the pH range 7—10·6, but at pH 12·5 when the nitro-anion (IV) is the reactant dithionite failed to effect reduction (*cf.* ref. 7) and the solutions exhibited only the e.s.r. spectrum of $\cdot SO_2^-$. However, brown solutions obtained at pH 10 and then made more strongly alkaline, to pH 12·5, and thereafter given a slight exposure to air exhibited weakly the five-line spectrum (B).

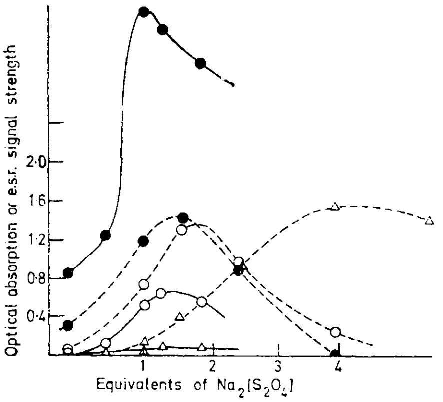

FIGURE 4 Dithionite reduction of 10^{-3}M-$Na_2[(NC)_5FeNO]$ at pH 8 (——) and pH 10 (– – –): (●), e.s.r. spectra at a constant instrument setting; (○) and (△), optical absorption at 347 and 440 nm

(d) *With ascorbic acid and quinol.* Both these reagents in 10^{-3}M aqueous solution under nitrogen reduced aqueous (I) of comparable concentration but only at pH > 9. With ascorbic acid at pH 10 the e.s.r. spectrum, (A), of (II) was much more intense than the doublet spectrum of the ascorbate radical ion, but with quinol spectrum (A) was weak and that of the semiquinone radical ion ($\cdot OC_6H_4O^-$) was very strong. Relatively stronger spectra (A) were obtained at pH 11 and signals could still be observed when these mixtures were basified to pH 13 where the semiquinone radical-ion signal also decreased in intensity. With ascorbic acid at pH 10 a slow build-up of optical absorption with $\lambda_{max.}$ at *ca.* 340—355 nm was observed, but from 340 to 430 nm the absorptions of alkaline solutions of quinol themselves masked further changes. These qualitative experiments place the redox equilibria (8) in the

$$\underset{\text{(I)}}{[(NC)_5FeNO]^{2-}} \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} \underset{\text{(II)}}{[(NC)_5Fe\dot{N}O]^{3-}} \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} \underset{\text{(V)}}{[(NC)_5Fe\ddot{N}O]^{4-}} \quad (8)$$

potential range of the *p*-benzosemiquinone system (9) and

$$\cdot OC_6H_4O^- \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} {}^-OC_6H_4O^- \quad (9)$$

are in reasonable accord with the polarographic measurements of Kolthoff and Toren [7] for equilibria (8).

Pentacyano(hydroxylamine)ferrate(3–), $[(NC)_5Fe(NH_2OH)]^{3-}$, (III).—The reduction of $Na_2[(NC)_5FeNO]$ at pH 8—11 by four or more equivalents of dithionite, sodium tetrahydroborate, or prolonged electrolysis yielded brown solutions showing a broad absorption band at $\lambda_{max.}$ 440 ± 2 nm ($\varepsilon_{max.}$ *ca.* 3×10^3 l mol^{-1} cm^{-1}). Stoicheiometrically this should correspond to (III). Similar brown solutions with $\lambda_{max.}$ at 436 nm ($\varepsilon > 2 \times 10^3$ l mol^{-1} cm^{-1}) could be made by adding hydroxylamine in very large excess to dilute aqueous aquapentacyanoferrate(3–), (VI).* Table 1 shows how $\lambda_{max.}$ for $[(NC)_5Fe^{II}X]^{n-}$ changes for a number of ligands X. Aliphatic amines, like water, yield complex ions with low values of both $\lambda_{max.}$ and $\varepsilon_{max.}$, but $\lambda_{max.}$ shifts to longer wavelengths and $\varepsilon_{max.}$ increases significantly for both the hydroxylamine and the *O*-methylhydroxylamine complexes.

TABLE 1

Absorption maxima for anions $[(NC)_5Fe^{II}X]^{n-}$

X	H_2O	NH_3	$BuNH_2$	NH_2OH	NH_2OMe
$\lambda_{max.}$/nm	394	400	394	440	434

Equilibrium (10) appears to be attained slowly, for after admixture of aqueous (VI) with hydroxylamine the absorption took over 1 h to reach its maximum. At pH 4

$$[(NC)_5FeOH_2]^{3-} + NH_2OH \rightleftharpoons [(NC)_5Fe(NH_2OH)]^{3-} + H_2O \quad (10)$$

(VI) did not react with hydroxylamine (then present in solution as $[NH_3OH]^+$), but reaction was apparent at pH 5·5 and $\lambda_{max.}$ for complex (III) remained constant up to pH 10. Evidently, therefore, it is the unchanged molecule NH_2OH which comprises the ligand X. At pH 12·5—13 the solutions were orange in colour and slowly evolved a gas (*cf.* the decomposition of strongly alkaline aqueous hydroxylamine, $3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$). When exposed to the air they gradually turned yellow and the gassing then ceased. Soon after the admission of air, these orange solutions gave strongly the five-line e.s.r. spectrum (B) to which we have assigned above the radical-anion structure (VII).

Reactions between $Na_2[(NC)_5FeNO]$ *and Thiols.*—(a) *With thioglycolic acid.* The acid reacted rapidly with alkaline (I) to give a pink solution ($\lambda_{max.}$ 522 nm) which, under nitrogen, faded rapidly during the first few minutes and then more slowly over several hours. The intensity of the colour was pH dependent, being weak at pH 8 and much stronger at pH 10, indicating that it is given by a compound formed by the addition of a thiolate anion to (I). Strongly alkaline solutions containing anion (IV) did not react with thiols to give pink solutions. Under nitrogen, but not in air, these pink solutions as they decayed exhibited a three-line e.s.r. signal of type (A) which persisted even after the disappearance of the colour. Gradually too the absorption at 347 nm rose and, as indicated in Figure 5, this was more pronounced when the thiol was used in excess. In air, neither the e.s.r. spectrum nor the 347 nm absorption were observable. To obtain reproducible kinetic data (to within 10% during the initial rapid reaction but thereafter

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* *Note added in proof.* Very recently S. Luňák and J. Vepŏek-Šiska, *Coll. Czech. Chem. Comm.*, **1974**, **39**, 2719 have described (III); they give $\lambda_{max.}$ 443 nm and $\varepsilon_{max.}$ 3·9 l mol^{-1} cm^{-1}.

with deviations of less than 5%) in experiments in which [(I)] and [Thiol] were varied independently it was necessary to add nitrite to prevent concurrent hydrolysis of the unchanged (I) (see p. 952), and to minimise exposure of the coloured solutions to light even in the spectrometer, for comparative tests indicated that there was some photochemical decomposition of the pink compound in addition to that due to reactions which can occur in the dark.

When, under nitrogen, the e.s.r. spectrum (A) first appeared, the shape of the central line was irregular as if another radical giving a much weaker signal (*g* 2·025—2·026) were also present (see Figure 6). However, this irregularity does not accord with the spectrum of the thioglycolate radical anion ($^-O{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}$) which should have a *g* value of *ca.* 2·01.[18] At corresponding times the strength of the e.s.r. signal could not be correlated with the absorption at 347 nm. The latter rose to a maximum and then decayed slowly; when the thiol was used in excess there was also a very slow slight rise of absorption in the whole region 400—460 nm probably due to the formation of a trace of (III). Tests showed that eventually, in the presence of nitrite, all the thioglycolic acid was consumed and (I) remained in the solution even when the former reagent had initially been used in large excess. With thiol in excess, the decay of the pink colour was very slow in air and the colour increased in intensity on addition of air to nitrogen-flushed reacting mixtures. Under these conditions the three-line e.s.r. spectrum (A) had a significantly lower a_N value than that of spectra obtained with (I) in excess, or by the use of other reducing agents, but the *g* value did not alter. Similar changes in a_N values occurred when other thiols were used in excess as reducing agents (see Table 2).

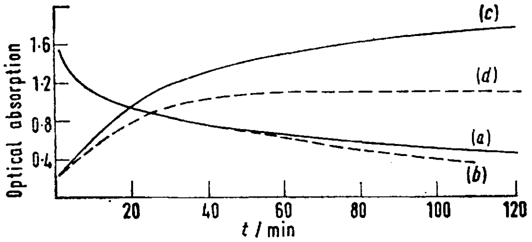

FIGURE 5 Reaction between $[(NC)_5FeNO]^{2-}$ and thioglycolate anions at pH 9·1 and 20 °C under nitrogen: (——), $1{\cdot}0 \times 10^{-3}$M-$[(NC)_5FeNO]^{2-}$ and $5{\cdot}0 \times 10^{-3}$M-thioglycolate; (— — —), $5{\cdot}0 \times 10^{-3}$M-$[(NC)_5FeNO]^{2-}$ and $1{\cdot}0 \times 10^{3}$M-thioglycolate: optical absorptions at 322 [(*a*),(*b*)] and 347 nm [(*c*),(*d*)]

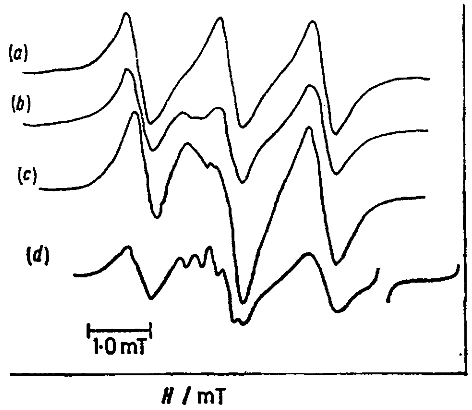

FIGURE 6 E.s.r. spectra (A) mainly due to $[(NC)_5Fe\dot{N}O]^{3-}$: (*a*), $[(NC)_5Fe\dot{N}O]^{3-}$ produced by electrolysis of aqueous $[(NC)_5FeNO]^{2-}$, (I); (*b*), initial spectrum from $HS{\cdot}CH_2{\cdot}CO_2H$ and excess of (I); (*c*), initial spectrum from excess of $HS{\cdot}CH_2{\cdot}CH_2OH$ and (I); (*d*), initial spectrum from Ph·SH and (I); the low-field line of Frémy's salt occurs at the gap shown. The right-hand ordinate marks *g* 2·0055, the central line of Frémy's salt

TABLE 2

Radicals of type (A). Apart from the figures for HS·Ph which was dissolved in aqueous alcohol, all the results refer to reductions effected in dilute aqueous solution

Reducing medium	pH	a_N/mT	*g*	Reducing medium	pH	a_N/mT
Electrolysis	8—13	1·491 ± 0·005	$2{\cdot}024_2$	$NaBH_4$	10—13	1·488 ± 0·006
$Na_2[S_2O_4]$	8—13	1·491 ± 0·008	$2{\cdot}024_2$			
Quinol	11—13	1·49 ± 0·01	$2{\cdot}024_2$	Ascorbic acid	10—12	1·490 ± 0·006

	a			*b*	
Thiol	pH	a_N/mT	*g*	a_N/mT	*g*
$HS{\cdot}CH_2{\cdot}CH_2OH$	9	1·480 ± 0·007	$2{\cdot}024_1$	1·411 ± 0·006,[c] 1·42 ± 0·01 [d]	$2{\cdot}024_2$
$HS{\cdot}CH_2CO_2^-$	10	1·48 ± 0·01		1·42 ± 0·01,[c] 1·454 ± 0·006 [d]	$2{\cdot}024_3$
HS·Ph	11			1·47 ± 0·01 [c]	$2{\cdot}024_2$
	9—10	1·487 ± 0·005			
$HS{\cdot}CH_2Ph$	12			1·394 ± 0·005 [c]	$2{\cdot}024_5$
Cysteine	9	1·49 ± 0·01	$2{\cdot}024_4$	1·46 ± 0·01,[c] 1·48 ± 0·01 [d]	$2{\cdot}024_5$
HS^-	8—10	1·487 ± 0·005	$2{\cdot}024_2$		

[a] $[(NC)_5FeNO]^{2-}$ was present in excess. [b] Thiol was present in excess. [c] Initial values with thiol in excess. [d] After reaction for 1—2 h.

(b) *With* β-*mercaptoethanol.* This compound also reacted in alkali to give a pink colour, with $\lambda_{max.}$ at 522 nm and pH-dependent intensity, which decayed rather more rapidly, under nitrogen, than that formed with thioglycolic acid. Figure 7 shows the changes with time in the intensities of the optical-absorption maxima and of the e.s.r. spectra in two reaction mixtures with contrasting relative concentrations of reagents. The slow rise in absorption at

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[18] J. C. Kertesz, W. Wolf, and H. Hayase, *J. Mag. Resonance*, 1973, **10**, 22.

ca. 440 nm is more evident than with thioglycolic acid. As with thioglycolic acid, when nitrite was added, the eventual solutions contained free (I) and no residual thiol. Again the e.s.r. spectrum initially showed central irregularity. In air, with either reagent in excess, the decay of the pink colour was much slower than under nitrogen: with thiol in excess the dissolved oxygen was soon exhausted and the decay of the 522 nm absorption then increased to the rate corresponding to that of similar reaction mixtures under nitrogen.

(c) *With cysteine.* Cysteine behaved very much like β-mercaptoethanol, but α-toluenethiol (prepared *in situ* from *S*-benzylthiouronium chloride) and benzenethiol gave very transient pink colours: their solutions very soon became turbid due to the separation of disulphide, RS·SR. Yet they produced under nitrogen spectra of type (A) which persisted long after the pink reaction products had been destroyed completely. Strong extra lines centred at *g* 2·025 (Figure 6) were observed in the initial e.s.r. spectrum obtained with benzenethiol; these decayed more rapidly than did spectrum (A).

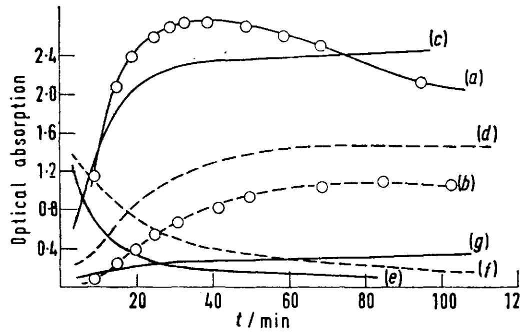


FIGURE 7 Reaction between $[(NC)_5FeNO]^{2-}$ and β-mercaptoethanol anions at pH 9·1 and 20 °C: (——), 0·89 × 10^{-3}M-$[(NC)_5FeNO]^{2-}$ and 6·4 × 10^{-3}M-mercaptoethanol; (— — —), 4·9 × 10^{-3}M-$[(NC)_5FeNO]^{2-}$ and 1·1 × 10^{-3}M-mercaptoethanol. E.s.r. spectral intensities at a constant instrument setting [(*a*),(*b*)] and optical absorptions at 347 [(*c*),(*d*)], 522 [(*e*),(*f*)], and 440 nm [(*g*)]

(d) *With sodium sulphide.* At pH values in which the HS^- anion is present, sodium sulphide gave a deep purple solution ($\lambda_{max.}$ 572 nm) and again, under nitrogen, the e.s.r. spectrum and absorption at 347 nm. The optical absorptions at 572 and 347 nm increased during the first few minutes and then decreased: the solutions soon became turbid due to the separation of sulphur. Scagliarini and Pratesi [19] studied the coloured product and by alcohol precipitation isolated the salt $K_4[Fe(CN)_5(NOS)]$.

DISCUSSION

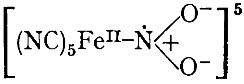
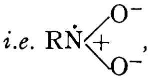
(a) *Structure of the Ions in Solution.*—Early workers [7,8] described three successive stages in the reduction of aqueous $[(NC)_5FeNO]^{2-}$ at pH 7—10 (see above).

$$\underset{(I)}{[(NC)_5Fe{-}\overset{+}{N}{=}O]^{2-}} \underset{}{\overset{e^-}{\rightleftharpoons}} \underset{(II)}{[(NC)_5Fe{-}\dot{N}{=}O]^{3-}} \overset{e^-}{\rightleftharpoons}$$

$$\underset{(V)}{[(NC)_5Fe{-}\ddot{N}{=}O]^{4-}} \xrightarrow{2e^-} \underset{(III)}{[(NC)_5Fe(NH_2OH)]^{3-}}$$

Since solid analysable salts of the ions (II), (V), and (III) have not been isolated their exact formulae but not their oxidation levels are questionable. Our experiments, summarised above, indicate that (II) gives the e.s.r. spectrum (A), with *g* 2·024 and a_N 1·49 mT, (V) gives yellow solutions with $\lambda_{max.}$ at 347 nm, and (III) gives the brown solutions with $\lambda_{max.}$ at 440 nm mentioned by all earlier workers. In agreement with Kolthoff and Toren [7] we conclude that the redox equilibria between (I), (II), and (V) are easily reversible. Since at pH 10 solutions containing (III) and (V) show an isosbestic point, we agree with Zuman and Kabát that in weak alkali the two-electron reduction of (V) is effected in a single stage. At pH 12·5, however, we have e.s.r. evidence [spectrum (B)] of the existence of the expected intermediate, $[(NC)_5Fe{-}\dot{N}(H)\bar{O}]^{4-} \leftrightarrow [(NC)_5Fe{-}\ddot{N}(H)\dot{O}]^{4-}$ (VII), though this is only formed by reoxidation of (III).

The reduction of (I) to (III) thus resembles both in oxidation levels and in redox potentials the reductions of aromatic nitro-compounds and of tertiary nitroparaffins to hydroxylamines, $RNO_2 \rightleftharpoons RNO_2^{\cdot -} \rightleftharpoons RNO \rightleftharpoons R\dot{N}{-}O^-$ and $RN(H)O\cdot \rightleftharpoons RN(H)OH$, in which each one-electron step has been characterised though at certain pH ranges some of the species are metastable [RNO for instance cannot be made directly from RNO_2 but is easily obtained by oxidising RN(H)OH]. The ion (V) resembles not only organic nitroso-compounds but also the pink Co^{III} ion $[(NC)_5Co{-}\dot{N}{=}O]^{3-}$.[5] We have recently described [5] the e.s.r. spectrum of $[(NC)_5Co{-}\dot{N}{-}O^-]^{4-}$, the equivalent of (VII). It is thus rational to ascribe all stages in the reduction of (I) to reactions in which electrons have been added stepwise to the original nitrosyl group ($\overset{+}{N}{=}O$) of a complex ion of iron(II). In our formulae the reduction stages have been indicated by placing dots at the nitrogen atom to indicate unshared electrons, without prejudice to the degree of delocalisation of these electrons onto adjacent atoms (Fe and O).

Though the nitroferrate ion $[(NC)_5Fe^{II}NO_2]^{4-}$, (IV), is extremely resistant to reduction, probably on account of its high negative charge, the possibility that the e.s.r. signal (A) is really that of  $\left[(NC)_5Fe^{II}{-}\dot{N}{\overset{+}{<}}\begin{matrix}O^-\\O^-\end{matrix}\right]^{5-}$,(VIII), structurally corresponding to $RNO_2^{\cdot -}$, *i.e.*  $R\dot{N}{\overset{+}{<}}\begin{matrix}O^-\\O^-\end{matrix}$, and not (II), merits consideration. Raynor and Symons [11] assigned structure (VIII) to an ion giving an e.s.r. spectrum with low *g* values (g_x 1·9993, g_y 1·9282, and g_z 2·0080) observed only after freezing to 77 K brown alkaline aqueous solutions of chemically reduced (I). This spectrum disappeared when the frozen solutions were warmed. Van Voorst and Hemmerich,[10] however, have suggested that this spectrum of low *g* value is really that of (II) and assigned a spectrum of type (A) having *g* 2·025, which they detected in unstable

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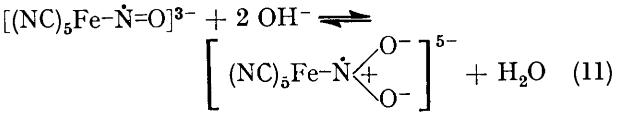
[19] G. Scagliarini and P. Pratesi, *Atti Accad. naz. Lincei*, 1928, [6], **8**, 75.

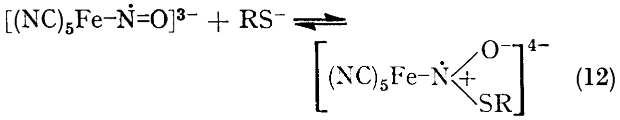
blue solutions at pH 4—7, to a protonated radical anion, $[(NC)_5Fe{-}\dot{N}{-}OH]^{2-}$. Since strong alkali is needed to convert (I) to (IV) [equation (1)], it is rational to expect that a similar equilibrium, (11), will need very concentrated alkali to produce (VIII) in view of its very high negative charge.



$$[(NC)_5Fe{-}\dot{N}{=}O]^{3-} + 2\,OH^- \rightleftharpoons \left[(NC)_5Fe{-}\dot{N}\overset{O^-}{\underset{O^-}{\lessdot}}\!+\right]^{5-} + H_2O \tag{11}$$

We have found that the e.s.r. spectrum (A) does not change its g or a_N values over the pH range 7—13 in water at room temperature and this is inconsistent with the views of van Voorst and Hemmerich. Since freezing of dilute solutions has the same dehydrating effect on solutes as intense freeze drying, it will move the equilibrium of equation (11) to the right and in this way one can rationalise the conclusions of Raynor and Symons, and since there is no evidence for the existence of a radical anion in solution with g less than 2·02 we conclude that spectrum (A) accords with structure (II).

Our measurements (Figures 1, 2, and 4), which indicate equilibration of radical anion (II) with (I) and (V), have all shown that formation of (II) is more pronounced at pH 8 than at 10, while that of (V) is more favoured at pH 10, but this finding gives no support for the view that spectrum (A) may be that of (VIII). The stability of (V) may perhaps be pH dependent and it is possible to write for more acid solutions a structure $[(NC)_5Fe{-}\overset{+}{N}H{=}O]^{3-}$, (IX), corresponding to that of the coloured complexes $[(NC)_5Fe{-}\overset{+}{N}Ar{=}O]^{3-}$ first obtained by Baudisch [20] from nitrosobenzenes and (VI). However, Table 2 shows that in reactions between (I) and thiols a radical anion, clearly of type (A) from its g value but with a lower a_N splitting, is formed when the thiolate anion is present in large excess. Equilibrium (12) can explain the production of a radical anion, (X),



$$[(NC)_5Fe{-}\dot{N}{=}O]^{3-} + RS^- \rightleftharpoons \left[(NC)_5Fe{-}\dot{N}\overset{O^-}{\underset{SR}{\lessdot}}\!+\right]^{4-} \tag{12}$$

(X)

with a different a_N value under these experimental conditions and (X) has some structural resemblance to (VIII). We suggest tentatively that the initial irregularities in the (A) type spectra illustrated in Figure 6 may possibly be due to the formation from (X) of unstable radicals $[(NC)_5Fe^{II}{-}\dot{N}H{-}SR]^{3-}$, (XI), analogous to (VII).

(b) *Stabilities of Reduction Products*.—The equilibria (8) between (I), (II), and (V) must be attained fairly rapidly. Our measurements have shown that under nitrogen the 347 nm absorption decays more rapidly in stored solutions than does the e.s.r. spectrum of (II), though the reverse is the case if reduction is still proceeding (Figures 1, 3, and 4). We ascribe the decay of (V) to the slow hydrolysis (13) which, by a shift of

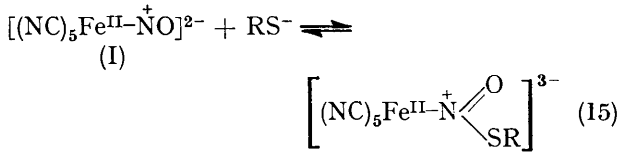
$$[(NC)_5Fe^{II}{-}\dot{N}{=}O]^{4-} + H_2O \longrightarrow [(NC)_5Fe^{II}OH_2]^{3-} + :\ddot{N}{=}O^- \longrightarrow N_2O \tag{13}$$

equilibria (8), will also lead to decay of the radical anion (II). In the presence of nitrite this will lead to the slow reformation of (I) which occurs in late stages of the reactions with thiols (p. 952).

Our study (above) of the hydroxylamineferrate anion, (III), indicates that it too is hydrolysable [equilibrium (10)]: this explains why stored brown solutions of reduced (I) containing nitrogen gradually turn yellow. Both (II) and (V) are destroyed by air and regenerate some (I). From the redox potentials of the reagents needed to form (II), reaction (14) is expected.

$$[(NC)_5Fe^{II}{-}\dot{N}{=}O]^{3-} + O_2 \longrightarrow [(NC)_5Fe^{II}{-}\overset{+}{N}{=}O]^{2-} + O_2\cdot \tag{14}$$

(c) *Kinetics of Reactions between* $[(NC)_5FeNO]^{2-}$ *and Thiols*.—The reversible addition (15) of thiolate anions to (I) to give pink products is fast, but not instantaneous;



$$\underset{\text{(I)}}{[(NC)_5Fe^{II}{-}\overset{+}{N}O]^{2-}} + RS^- \rightleftharpoons \left[(NC)_5Fe^{II}{-}\overset{+}{N}\overset{O}{\underset{SR}{\lessdot}}\right]^{3-} \tag{15}$$

(XII)

by a stopped-flow method it has already been shown [21] for HS^- anions to be first order in the concentration of each reactant. If the coloured product (XII) did not decompose irreversibly, expression (16) would be valid

$$c_0 = K(a - c_0)(b - c_0) \tag{16}$$

for equilibrium (15), where a and b are the initial concentrations of the reactants, c_0 is the theoretical maximum concentration of (XII), and K incorporates both the ionisation constant of the thiol, RSH, and the OH^- concentration of the buffer solution used. Actually slow decomposition of (XII) must start as the reagents are being mixed so that concentration c_0 is never reached. In a short time, which in our experiments we estimated to be *ca.* 3 min, the rate of decomposition of (XII) leading to formation of the radical anion (II) and of a disulphide, RS·SR, balances its rate of formation. Soon after this reaction (15) attains a pseudo-equilibrium and thereafter the slow decomposition of (XII) controls the measurable values of c_t, for which one can write equation (17) in which c_t corresponds to the intensity of

$$c_t = K(a - c_t - x_t)(b - c_t - y_t) \tag{17}$$

the pink colour of (XII), x_t is the consumption of

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[20] O. Baudisch, *Ber.*, 1921, **54**, 413.

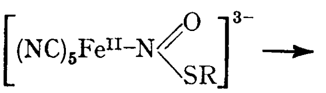
[21] P. A. Rock and J. H. Swinehart, *Inorg. Chem.*, 1966, **5**, 1078.

reagent a, and y_t that of reagent b. If $a \gg b$, since both c_t and y_t must be less than b, equation (18) is applicable

$$y_t = (c_0 - c_t)(1 + Ka)/Ka \qquad (18)$$

and hence, since $dy/dt = -[(1 + Ka)/Ka]dc/dt$, the decay of colour is proportional to but less than the rate of consumption of the minor reagent.

For reactions under nitrogen in which the radical anion (II) is formed two reaction schemes merit consideration: (*i*) unimolecular homolysis of the coloured



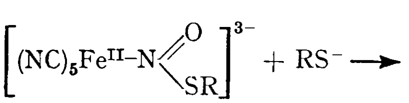
$$\left[(NC)_5Fe^{II}-N\begin{smallmatrix}O\\SR\end{smallmatrix}\right]^{3-} \longrightarrow$$

(XII)

$$[(NC)_5Fe^{II}-\dot{N}=O]^{3-} + RS\cdot \qquad (19)$$

(II)

ion (XII) followed by $2RS\cdot \longrightarrow RS\cdot SR$ (fast); and (*ii*) nucleophilic attack on (XII) by RS^- anions followed



$$\left[(NC)_5Fe^{II}-N\begin{smallmatrix}O\\SR\end{smallmatrix}\right]^{3-} + RS^- \longrightarrow$$

(XII)

$$[(NC)_5Fe^{II}-\ddot{N}=O]^{4-} + RS\cdot SR \qquad (20)$$

(V)

by equilibration of (V) with free (I) to give (II) [*i.e.* equilibria (8)]. For scheme (*i*), since the net loss of colour depends on the consumption of the reactants, one can write, when $a \gg b$, equation (21) and a similar

$$dc/dt = k_1c[Ka/(1 + Ka)]$$

$$\text{or} \quad \log c_0 - \log c_t = k_1t[Ka/(1 + Ka)] \qquad (21)$$

expression applies if $b \gg a$. For scheme (*ii*) equation (22) applies, where b is the initial concentration of the

$$-dc/dt = k_2c_t(b - c_t - y_t)$$
$$= k_2K(a - c_t - x_t)(b - c_t - y_t)^2 \qquad (22)$$

thiol and y_t the amount consumed in time t. If $a \gg b$, by using expressions (16) and (18) that of (23) follows,

$$-dc/dt = \frac{k_2c_t^2}{Ka} \text{ or } \frac{1}{c_t} - \frac{1}{c_0} = \frac{k_2t}{Ka} \qquad (23)$$

but if $b \gg a$ the logarithmic expression (21) is still applicable.

Figure 8 shows that for thioglycolic acid the logarithmic decay of colour required for the unimolecular decomposition (15) holds for at least an hour after the first 15 min of faster reaction, but Figure 9 shows that for the less persistent colour obtained with β-mercaptoethanol the reactions of scheme (*ii*) more satisfactorily explain the experimental observations. Possibly both reaction schemes are cogent but have different relative rate constants depending on the structure of the thiol involved; probably photochemical decompositions of the coloured complexes follow the homolytic path.

In air neither (II) nor (V) are reaction products and (I) will be regenerated rapidly [equation (14)], so that the overall process becomes a $[(NC)_5FeNO]^{2-}$-catalysed autoxidation of the thiol. If (I) is used in very large excess over the thiol the rate equations (21) and (23) will still be valid, but if the thiol is present in large excess nearly all (I) (*a*) is converted to the coloured product (XII) (*c*) which therefore decays very slowly as the two relevant kinetic expressions (24) both show.

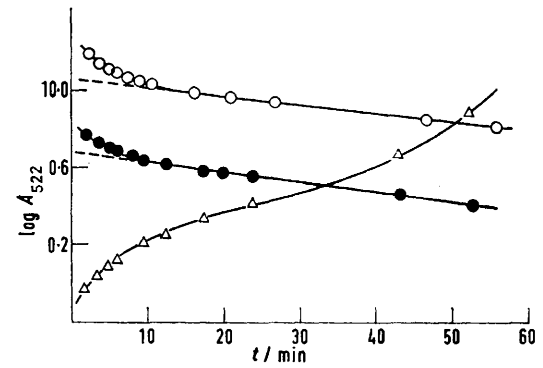


FIGURE 8 Logarithmic and reciprocal plots for the decay in absorption at 522 nm in the reaction between $[(NC)_5FeNO]^{2-}$ and thioglycolate anions at pH 9·1 and 20 °C: (○), 1·0 × 10^{-3}M-$[(NC)_5FeNO]^{2-}$ and 5·0 × 10^{-3}M-thioglycolate; (●), 5·0 × 10^{-3}M-$[(NC)_5FeNO]^{2-}$ and 1·0 × 10^{-3}M-thioglycolate; (△), reciprocal plot for the logarithmic plot (●). The scales for the two logarithmic plots are staggered

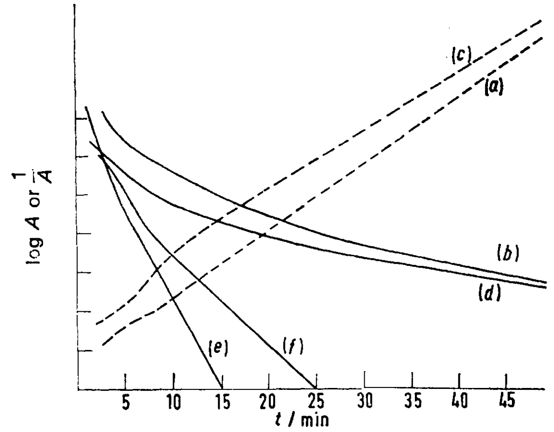


FIGURE 9 Logarithmic (——) and reciprocal plots (— — —) for the decay in absorption at 522 nm in the reaction between $[(NC)_5FeNO]^{2-}$ and β-mercaptoethanol anions at pH 9·1 and 20 °C under nitrogen: $[(NC)_5FeNO^{2-}]$ = 1·0 × 10^{-2} [(*a*),(*b*)], 5 × 10^{-3} [(*c*),(*d*)], and 1 × 10^{-3}M [(*e*),(*f*)]; [β-mercaptoethanol] = 1·0 × 10^{-3} [(*a*),(*b*),(*c*),(*d*)], 1·0 × 10^{-2} [(*e*)], and 5 × 10^{3}M [(*f*)]

$$-dc/dt = k_1K(a - c_t)(b - c_t - y_t) \text{ or}$$
$$k_2K(a - c_t)(b - c_t - y_t)^2 \qquad (24)$$

This conclusion accords with the experimental findings

(Figure 10), from which too it can be concluded that the coloured complexes (XII) are not directly attacked by oxygen.

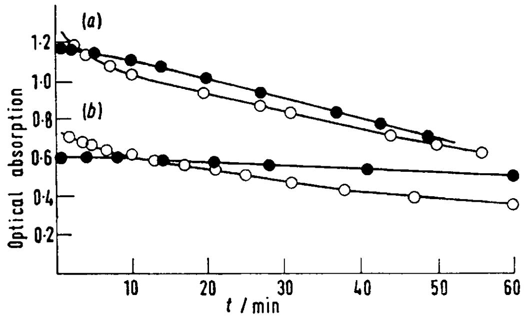


FIGURE 10 Plots of optical absorption at 522 nm in reactions between $[(NC)_5FeNO]^{2-}$ and thioglycolate ions at pH 10·1 and 20 °C in air (●) and under nitrogen (○). $[(NC)_5FeNO^{2-}]$ = 3·0 × 10^{-3} [(*a*)] and 0·3 × 10^{-3}M [(*b*)]; [thioglycolate] = 0·7 × 10^{-3} [(*a*)] and 3·4 × 10^{-3}M [(*b*)]

In view of the occurrence of secondary reactions [*e.g.* (13) and (5)] we consider that a more detailed analysis of our spectrographic data is not warranted.

EXPERIMENTAL

All solutions were prepared in nitrogen-blown distilled water from reagents of analytical quality and transferred under nitrogen by syringes for admixture or analysis. For alkalinity control $Na_2B_4O_7\cdot10H_2O-H_3BO_3$ buffers (20mM) were used for pH 8 and 9 and a $CO_3^{2-}-HCO_3^-$ buffer (50mM) for pH 10. The stock $Na_2[(NC)_5FeNO]$, (I), solutions (5mM) contained 20mM-sodium nitrite and were stored in the dark but discarded as soon as any change in optical absorption was detected. The thiols, which were dissolved directly in the requisite nitrogen-blown buffer solutions, were titrated iodometrically on the day of usage.

Optical spectra were recorded at 20 °C with a Unicam SP 825 spectrometer using 1 cm stoppered quartz cells which for filling were placed in a nitrogen atmosphere in a deep jar and flushed with nitrogen as reacting mixtures of initial concentrations (0·5—10mM) suitable for colour measurement during 1—4 h were added. The comparison cells contained buffered (I) of concentrations equal to those of the initial mixtures. E.s.r. measurements were made with a Varian E4 spectrometer calibrated by use of Frémy's salt. All electrolyses were carried out with nitrogen-flushed solutions.

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