An Electron Spin Resonance Study of Pentacyanocobalt(III) Nitroxide Radical-anions from *C*-Nitroso-compounds, Nitroparaffins, and Nitrolic Acids (α-Nitro-oximes)

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Aqueous potassium pentacyanocobalt(II), $K_3Co(CN)_5$, reacts immediately under nitrogen with α-substituted nitrosoparaffins and more slowly with nitro-olefins and α-halogenated nitroparaffins to give alkyl pentacyanocobalt(III) nitroxide radical-anions, $\{(NC)_5Co{-}NR{-}O{\cdot}\}^{3-}$, detectable by their e.s.r. spectra which are listed and discussed. These radical-anions are unstable: under nitrogen they disappear within a very few hours and rapidly on exposure to air. Simpler nitroparaffins give similar but transient spectra on treatment with $K_3Co(CN)_5$ plus $NaBH_4$. Aqueous $K_3Co(CN)_5$ reacts rapidly with alkyl nitrites and nitric oxide, and slowly with sodium nitrite, to give red, diamagnetic $\{(NC)_5Co{-}NO\}^{3-}$ which by reduction gives a radical-anion thought to be $\{(NC)_5Co{-}\dot{N}{-}\bar{O}\}^{4-}$. If cyanide ions are present in excess, or are added initially, alkyl nitrites and some *C*-nitroso-compounds yield a radical-anion thought, from its e.s.r. spectrum, to be $\{(NC)_5Co{-}N(CN){-}O{\cdot}\}^{3-}$, nitrosyl cyanide being the probable precursor. With excess of $K_3Co(CN)_5$ the α-halogenated α-nitroso- or nitro-paraffins slowly give secondary radical-anions which have larger a_{Co} hyperfine splittings than those first formed: these are stable in air. Two series of e.s.r. spectra have been obtained from nitrolic acids (α-nitro-oximes): both show splittings due to one ^{59}Co and two ^{14}N atoms. These radical-anions are stable in air. No e.s.r. spectra have been obtained from *N*-nitrosamines. E.s.r. spectra of the stable nitroxides, $R_2NO{\cdot}$, from the nitroso-compounds examined are listed.

PREVIOUS work has shown that the green, paramagnetic pentacyanocobaltate(II) anion, $\{Co(CN)_5\}^{3-}$ combines both with aromatic[1] and with tertiary aliphatic[2] nitroso-compounds to give free radicals which, from their e.s.r. splitting constants, are evidently[3] aryl or alkyl pentacyanocobalt(III) nitroxide radical-anions $\{(NC)_5Co{-}NR{-}O{\cdot}\}^{3-}$. The aryl nitroxide anions can also be obtained by the direct reduction of aromatic nitro-compounds by $\{Co(CN)_5\}^{3-}$ anions, but nitroparaffins cannot be reduced in a similar way unless they also contain strongly electrophilic groups (Cl, Br, or NO_2) as α-substituents. Consequently the detailed study of alkyl pentacyanocobalt(III) nitroxide radical-anions, which we now report, has also yielded fresh knowledge of the chemistry of both nitro- and nitroso-paraffins.

Radicals from Aliphatic C-*Nitroso-compounds*.—Relatively few monomeric aliphatic nitroso-compounds have as yet been described and most of these have limited stability. Primary and secondary nitroso-paraffins are, at best, only transient intermediates in the formation of oximes and most simple tertiary nitroso-paraffins, including even the pseudo-nitroles, $R^1R^2C(NO_2)NO$, tend to form colourless, unreactive dimers in solution at room temperature. A limited number of monomeric α-chloro-, α-bromo-, and α-cyano- nitroso-paraffins were prepared, many years ago,[4] and a few monomeric nitroso-acetates, $R_1R_2C(NO){-}OCOMe$, have been obtained more recently by oxidising ketoximes with lead tetra-acetate.[5]

The reactions of representative methanol-soluble compounds of these types with aqueous potassium pentacyanocobalt(II) have now been examined; the e.s.r. spectra of the radicals thus obtained are listed in Tables 1 and 2.

Since solutions of aliphatic nitroso-compounds are easily decomposed by visible light to give dialkyl nitroxides and other products [reactions (1) and (2)] the e.s.r. spectra obtained from stored materials must be analysed with caution. Reproducible results can however be obtained by using freshly prepared solutions in ether, drying them for a short time in the dark, then

TABLE 1

Group A radical-anions from nitroso-compounds $R^1R^2C(X)NO$

Alkyl groups R¹	R²	Splitting constants (mT) a_{Co}	a_N	Overall width (mT)	g	Other signals		
(i) X = Cl								
Me	Me	1·06	1·76	11·0	(2·0052) *	B	C	D
Me	Et	1·09	1·75	11·1	2·0053	B		D
Me	Pr^i	1·12	1·75	11·4	2·0048	B	C	D
Me	Bu^t	1·05	1·74	10·8				D
Et	Et	1·12	1·76	11·3	2·0048	B		D
$[CH_2]_5$		1·09	1·71	11·0				
(ii) X = Br								
Me	Me	1·06	1·76	10·9	2·0054	B		D
Me	Et	1·08	1·74	11·0		B	C	
Me	Pr^i	1·13	1·77	11·4	2·0050	B		
Me	Bu^t	1·06	1·73	10·9	2·0053	B		
Et	Et	1·12	1·76	11·3	2·0048	B		
$[CH_2]_5$		1·09	1·76	11·1				D
(iii) X = OCOMe								
Me	Me	1·05	1·75	10·8	2·0054	B	C	
Me	Pr^i	1·12	1·75	11·3	2·0049	B	C	
Me	Bu^t	1·06	1·75	10·9	2·0049			
$[CH_2]_5$		1·10	1·73	11·0	2·0050	B		
(iv) X = CN								
Me	Me	1·06	1·76	10·9	2·0052			
Me	Et	1·09	1·76	11·2	2·0054			
Et	Et	1·17	1·76	11·6	2·0050			
$[CH_2]_5$		1·07	1·76	11·0	2·0052			D
(v) X = NO_2								
Me	Me	1·06	1·76	10·9	2·0053	B		D?
Me	Et	1·09	1·75	11·1	2·0050	B	C	
Me	Pr^i	1·13	1·76	11·4		B	C	[a]
Et	Et	1·14	1·77	11·5		B	C	D?
$[CH_2]_4$		1·08	1·76	11·1	2·0057	B		
$[CH_2]_5$		1·09	1·73	11·1		B		

Errors in all Tables a_{Co}, a_N = ± 0·01 mT.

* From Table 5.

[a] Wider signal indicating two nitrogen atoms.

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

[2] W. A. Waters, *J.C.S. Chem. Comm.*, 1972, 1087.

[3] J. G. Wilkinson and M. C. R. Symons, *J. Chem. Soc. Faraday II*, 1972, 1265; *cf.* N. M. Atherton and D. Waldram, *ibid.*, p. 413.

[4] H. Metzger and H. Meier, 'Methoden der Organischen Chemie (Houben-Weyl),' Georg Thieme, Stuttgart, 1971, vol. X/1, pp. 946—956.

[5] D. C. Iffland and G. X. Criner, *Chem. and Ind.*, 1956, 176.

diluting portions under nitrogen with methanol and adding these to an excess of nitrogen-flushed aqueous potassium pentacyanocobalt(II). This procedure favours reaction (3) and gives strong, well-defined 24 line e.s.r. spectra which clearly belong to one consistent group of cobalt-containing nitroxide radicals (group A). The presence of an excess of cobalt(II) in such solutions can easily be checked by inspection of the e.s.r. spectrum in the lowfield region (2500—3300 G) in which a broad line due to the d^7 system of cobalt(II) appears.[6]

TABLE 2

Group A radical-anions from nitroso-compounds RABCNO

Groups			Splitting constants (mT)					Other signals	
R	A	B	a_{Co}	a_N	a_H	Overall width (mT)	g		
Me	Me	Me	1·11	1·87		11·5	2·0054		
Me	Me	CH_2CH_2CN	1·07	1·76		11·0	2·0055		
Me	H	Cl	1·32	1·75	0·05	12·7		B	C
Me	Cl	Cl	1·09	1·62		10·9	2·0055	B	C
Et (not	Cl Et H	Cl * Cl)	1·05	1·75		10·9	2·0053		C
Me	Cl	COMe	1·10	1·61		10·9	2·0056		C
Me	Cl	COPh *	1·05	1·76		10·9w			
Me	H	Cl	1·31	1·76	0·05?	12·7w			
Me	Me	COMe	1·19	1·78		11·9	2·0053		

* See text. w = Weak.

$$R\text{-}N{=}O \xrightarrow{h\nu} R\cdot + NO \qquad (1)$$

$$R\cdot + R\text{-}N{=}O \longrightarrow R_2N\text{-}O\cdot \qquad (2)$$

$$R\text{-}N{=}O + \{\cdot Co^{II}(CN)_5\}^{3-} \longrightarrow \{(NC)_5Co^{III}NR\text{-}O\cdot\}^{3-} \qquad (3)$$

$$R\text{-}N{=}O + \{\cdot Co^{II}(CN)_5\}^{3-} \longrightarrow R\text{-}\dot{N}\text{-}O^- + \{(NC)_5Co^{III}\}^{2-} \qquad (4)$$

$$\{(NC)_5Co^{III}NR\text{-}O\cdot\}^{3-} \longrightarrow \{(NC)_5Co^{III}\text{-}N{=}O\}^{3-} + R\cdot \qquad (5)$$

$$\{(NC)_5Co^{III}\text{-}NR\text{-}O\cdot\}^{3-} + \{\cdot Co^{II}(CN)_5\}^{3-} + H_2O \longrightarrow \{(NC)_5Co^{III}\text{-}NR\text{-}OH\}^{3-} + \{HOCo^{III}(CN)_5\}^{3-} \qquad (6)$$

The e.s.r. spectra of group A can usually be obtained when the reactants are mixed in the reverse order provided that the mixture remains alkaline, but when the nitroso-compound is present in excess some of them may yield three line spectra of nitroxide radicals [equations (2) and (4)][2] or other spectra (B, C) (see Tables 1 and 2) with splitting constants that do not depend on the structure of the organic nitroso-compound used.

All the spectra of group A slowly decay; their half-lives range from several minutes to a few hours. Moreover no spectra of this group can be obtained from reaction mixtures which have been exposed to the air. While the slow decay of the group A radicals can be ascribed either to their homolytic decomposition (5), which also accounts for the orange colours of these solutions (see below), or to further reduction to a hydroxylamine derivative [reaction (6)], still other reactions can occur, for with nitroso-compounds $R^1R^2C(X)NO$ in which X = Cl or Br the spectra of group A may, as they decay, gradually change to different 24 line spectra which, characteristically, have much larger a_{Co} hyperfine splitting constants (Table 6). These spectra (group D) do not disappear when the solutions which exhibit them are exposed to the air. Since spectra of group D can also be obtained from nitroparaffins $R^1R^2C(X)NO_2$ they are discussed separately.

The Spectra of Group A (*Tables* 1 *and* 2).—The radical-anions which give the spectra of group A are produced immediately solutions of *C*-nitroso-compounds are added to nitrogen-flushed aqueous potassium pentacyanocobalt(II) when greenish yellow or orange solutions result according to the amount of nitroso-compound used (see next section). In view of the closely similar hyperfine splitting constants (a_N *ca.* 1·8; a_{Co} *ca.* 1·1 mT) and g values (2·0050—2·0055) of all these spectra and the rapidity of the reactions we consider that they all correspond to the radical-anions $\{(NC)_5Co\text{-}NR\text{-}O\cdot\}^{3-}$ in which the three original substituent groups of the nitroso-compound are still present.

Comparison among data in Table 1 for radical-anions from $R^1R^2C(X)NO$, where R is alkyl and X is Cl, Br, CN, NO_2, or OCOMe, shows that the electron-attracting substituent X lowers the a_N splitting constant by 0·10—0·15 mT and the a_{Co} splitting constant by at most 0·05 mT from the values (a_N 1·87; a_{Co} 1·11) for the radical from 2-methyl-2-nitropropane. These decreases are less than those for the e.s.r. spectra of $\{(NC)_5Co\text{-}NAr\text{-}O\cdot\}^{3-}$ radical-anions (a_N 1·0—1·4; a_{Co} 0·9—1·05 mT)[1] with which electron spin density can spread into the aromatic ring, though the g values fall within the same range. We suggest that the groups X affect the splitting constants of the $\{(NC)_5Co\text{-}NR\text{-}O\cdot\}^{3-}$ radical-anions by inductively withdrawing electronic charge from the locus of the nitrogen nucleus.

The variations of a_N with the natures of the hydrocarbon groups R^1 and R^2 are only fractionally greater than the experimental errors of our measurements, but the variations of a_{Co} with R^1 and R^2 are definitely greater than this. Except for the pinacolone derivatives, $Bu^tCMe(X)NO$, a_{Co} falls in the sequence $Pr^i > Et > Me$ though it has no clear dependence on the precise nature of X. These variations of a_{Co} with the structures of R^1 and R^2 may have a stereochemical origin and be due to

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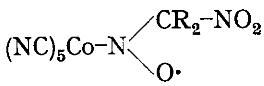
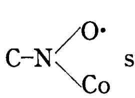
[6] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3356; F-D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 3760.

the proximity of R^1 and R^2 to the bulky rigid $\{Co(CN)_5\}^{3-}$ system, since changes in the bulks of R^1 and R^2 can alter the geometry of these nitroxide radical-anions, particularly with respect to the relative orientations of the two polarised bonds $N{-}Co^{III}$ and C–X.

One further structural feature merits comment. The radical-anions of group A from the ψ-nitroles, $R^1R^2C(NO_2)NO$, show hyperfine splitting due to one nitrogen atom only, yet splitting due to two nitrogens is found in radicals obtainable from nitrolic acids (see Table 7) and with the $\{(NC)_5Co{-}N(CN){-}O\cdot\}^{3-}$ nitroxide radical-anion (see below). A stereochemical model shows that to avoid steric hindrance the plane of the NO_2 group in  $(NC)_5Co{-}N\langle^{CR_2-NO_2}_{O\cdot}$ must be orthogonal to that of the  $C{-}N\langle^{O\cdot}_{Co}$ system containing the unpaired *p* electron. Consequently the latter does not hybridise sufficiently with the π electrons of the nitro-group to cause detectable hyperfine splitting from its nitrogen atom.

Other radical-anion spectra obtained immediately from monomeric aliphatic nitroso-compounds are collected in Table 2. Though they show much greater variations in their a_N and a_{Co} splitting constants their *g* values are still in the range of 2·0050—2·0055 and so we consider them to be spectra of group A.

The assignments for spectra obtained from the chlorination products of acetaldoxime and propionaldoxime are supported by measurements of the e.s.r. spectra obtained by the $K_3Co(CN)_5$ reduction of halogenated nitroparaffins (Table 5). The 1-chloro-1-nitrosoethane contained a little of the 1,1-dichloro-compound, which was also prepared separately by Piloty's method,[7] but chlorination of propionaldoxime must have yielded 1,1-dichloro-1-nitrosopropane directly. These spectra are discussed in a later section of this paper (p. 671).

The radical-anion obtained from 1-acetyl-1-chloro-1-nitrosoethane gave strong spectra showing no sign of hydrogen splitting. In contrast only one weak signal of a similar type was obtained from solutions thought to contain the 1-benzoyl compound. Stronger spectra from preparations of this substance show a distinct hydrogen splitting and are almost certainly due to the radical-anion of 1-chloro-1-nitrosoethane; this could result from hydrolysis of the benzoyl group by the alkaline, aqueous $K_3Co(CN)_5$.

Both polar and stereochemical effects could be operative in affecting the hyperfine splitting constants of the radical-anion spectra of Table 2.

The Radical-anion $\{(NC)_5Co{-}N(CN){-}O\cdot\}^{3-}$.—When the nitroso-compounds marked B in Tables 1 and 2 are treated in methanol with a deficiency of aqueous potassium pentacyanocobalt(II) containing free cyanide ions (initial ratio $[CN] : [Co^{2+}] > 6/1$) then an e.s.r. spectrum corresponding to a free radical containing two nitrogen atoms and one cobalt(III) nucleus regularly appears in the course of a few minutes. It has a_{Co} 0·997 ± 0·005, a_{N_1} 1·096 ± 0·005; a_{N_2} 0·213 ± 0·005 mT (overall width 9·60 ± 0·07 mT) and the high *g* value of 2·0072. There is no associated e.s.r. signal in the region 2500—3300 G indicative of the d^7 structure of a cobalt(II) atom. These splitting constants and *g* value are independent of the *C*-nitroso-compound being examined, for the slight variability indicated above can be associated with changes in the composition of the aqueous methanol used as solvent (compare ref. 2). This same signal, B, which is stable to air can also be obtained, at a much higher intensity, by treating ethyl or amyl nitrite in aqueous methanol with aqueous potassium cyanide and, after a few minutes, adding, under nitrogen, aqueous $K_3Co(CN)_5$. Tetranitromethane when similarly treated gives signal B strongly.

The action of aqueous potassium cyanide alone on the nitrite esters gives pale yellow solutions ($\lambda_{max.}$ 396 nm, shoulder from 420—520 nm) which gradually darken and the addition of $K_3Co(CN)_5$ immediately turns them bright red ($\lambda_{max.}$ 500 nm). Red solutions showing a pronounced $\lambda_{max.}$ at 500 nm are also formed when aqueous $K_3Co(CN)_5$ containing a slight excess of free cyanide ions is treated under nitrogen with nitric oxide, but the latter exhibit no e.s.r. spectrum over fields of 2500—4000 G. Similar pink or orange solutions (with $\lambda_{max.}$ 500 nm) which eventually fade to yellow are obtained when all the *C*-nitroso-compounds listed in Tables 1 and 2, or the *C*-nitro-compounds of Table 5 are treated with a deficiency of $K_3Co(CN)_5$ and also form slowly when aqueous sodium nitrite is treated under nitrogen with aqueous $K_3Co(CN)_5$. The eventual yellow solutions absorb radiation below 380 nm and are similar to the aqueous solutions of stable cyanocobalt(III) complexes [$K_3Co(CN)_6$ and $K_3Co(CN)_5OH$].[8] We therefore ascribe the pink colour not to the free radical giving signal B but to the diamagnetic anion $\{(NC)_5Co{-}N{=}O\}^{3-}$ which has occasionally been mentioned [9] though its $\lambda_{max.}$ has not been reported hitherto: the ion $\{(NH_3)_5Co{-}NO\}^{2+}$ has been well characterised.[10] Since we have confirmed that alkyl nitrites are easily reduced by aqueous iron(II) sulphate as in equation (7) we consider that the main reaction between nitrites and $\{\cdot Co^{II}(CN)_5\}^{3-}$ ions can be represented by (8) and (9) and that equation (5) explains the production of pink colours from the *C*-nitroso-compounds as well as the decay of the initial signal of type A.

$$RO{-}NO + Fe^{2+} \longrightarrow RO^- + NO + Fe^{3+} \tag{7}$$

$$RO{-}NO + \{\cdot Co(CN)_5\}^{3-} \longrightarrow RO^- + NO + \{Co^{III}(CN)_5\}^{2-} \tag{8}$$

$$NO + \{\cdot Co(CN)_5\}^{3-} \longrightarrow \{(NC)_5Co^{III}{-}N{=}O\}^{3-} \tag{9}$$

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[7] O. Piloty and H. Steinbock, *Ber.*, 1902, **35**, 3101.

[8] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1959, 2757; A. N. King and M. E. Winfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3366.

[9] A. A. Blanchard and F. S. Magnusson, *J. Amer. Chem. Soc.*, 1941, **63**, 2237; W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

[10] J. L. Milward, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1938, 233; J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32; C. C. Addison and J. Lewis, *Quart. Rev.*, 1955, **9**, 146.

Since the e.s.r. spectrum B is only formed in solutions containing free cyanide ions we suggest that its immediate precursor is nitrosyl cyanide, formed as in equation (10) from alkyl nitrites and as in equation (11) from the ψ-nitroles, and assign B to the radical-anion $\{(NC)_5Co{-}N(CN){-}O{\cdot}\}^{3-}$ formed as in equation (12).

$$RO{-}NO + CN^- \longrightarrow RO^- + ON{-}CN \qquad (10)$$

$$R_2C(NO_2){-}NO + CN^- \longrightarrow (R_2C{=}NO_2)^- + ON{-}CN \qquad (11)$$

$$ON{-}CN + \{{\cdot}Co(CN)_5\}^{3-} \longrightarrow \{(NC)_5Co{-}N(CN){-}O{\cdot}\}^{3-} \qquad (12)$$

Nitrosyl cyanide has recently been described by Kirby and his colleagues [11] as a reasonably stable blue substance with $\lambda_{max.}$ 738 nm. In our experiments no absorption maximum at this wavelength was detected, but we consider that reaction (10) proceeds to a slight extent only.

To account for the production of spectrum B from solutions of tetranitromethane we suggest that nitryl cyanide is the precursor of nitrosyl cyanide: equation (13) is rational for cyanide attack on tetranitromethane.

$$C(NO_2)_4 + CN^- \longrightarrow (O_2N)_2C{=}NO_2^- + O_2N{-}CN \qquad (13)$$

The formation of spectrum B from the α-chloro, α-bromo, or α-acetoxy-nitroso-compounds is not so easy to explain. One possibility is that a little cyanide attack, as in (10) or (11), yields a carbanion that could be stabilised as a carbene [*e.g.* reaction (14)]; this would not

$$R_2CCl{-}NO + CN^- \longrightarrow ON{-}CN + (R_2CCl)^- \longrightarrow R_2C\!: + Cl^- \qquad (14)$$

occur with either 2-methyl-2-nitrosopropane or with the α-cyano-nitroso-compounds which do not yield spectrum B. However the *C*-nitroso-compounds of Tables 1 and 2 yield only weak signals B and although the α-halogeno-nitroso-compounds are not rapidly attacked by dilute alkali their methanolic solutions turn acid on exposure to air and light [*cf.* equation (1)]. Alternatively, therefore, traces of nitrosyl chloride or of dinitrogen trioxide may be possible precursors of nitrosyl cyanide and thence of spectrum B from some of the solutions which we have examined.

The Radical-anion $\{(NC)_5Co{-}\dot{N}{-}O^-\}^{4-}$.—When aqueous methanolic solutions of ethyl or amyl nitrite are treated with less than an equivalent of aqueous $K_3Co(CN)_5$ not containing an appreciable concentration of free cyanide anions (initial $[CN^-] : [Co^{2+}] < 6/1$) a 24 line e.s.r. spectrum (C) appears instead of B. It has a_{Co} 1·01 ± 0·01, a_N 1·43 ± 0·01, overall width 9·92 ± 0·05 mT, $g = 2{\cdot}0053$. The same spectrum has been obtained, though at low intensity, from solutions of all the nitroso-compounds marked C in Tables 1 and 2. It is not destroyed when solutions of this radical are exposed to the air but is not found in solutions containing a significant amount of free $\{{\cdot}Co(CN)_5\}^{3-}$ [shown by the low-field signal of cobalt(II)] or in solutions which have been acidified to pH 4.

Much more intense spectra of C (10^2—10^3 times) can be obtained by treating any of the red or orange solutions which we believe to contain the nitrosopentacyanocobalt(III) anion, $\{(NC)_5Co{-}NO\}^{3-}$, including those obtainable from sodium nitrite, with aqueous sodium dithionite, provided that this reagent is not used in sufficient excess to cause complete decolourisation, but it cannot be obtained by sodium borohydride reduction. We therefore ascribe spectrum C to the anion $\{(NC)_5Co{-}\dot{N}{-}O^-\}^{4-}$ produced [equation (15)] by the one-electron reduction of red, diamagnetic $\{(NC)_5CO{-}N{=}O\}^{3-}$ and suggest that further reduction destroys it by producing the hydroxylaminopentacyanocobalt(III) anion [equation (16)]. In view of the observation that signal C is destroyed by acidification of solutions which exhibit it we suggest that the protonated radical-anion $\{(NC)_5Co^{III}{-}NH{-}O{\cdot}\}^{3-}$, structurally corresponding to those which give signal A, is unstable and, like the neutral nitrobenzene radical $(Ph\dot{N}O_2H)$, rapidly disproportionates.

$$\{(NC)_5Co^{III}{-}N{=}O\}^{3-} + e \longrightarrow \{(NC)_5Co^{III}{-}\dot{N}{-}O^-\}^{4-} \qquad (15)$$

$$\{(NC)_5Co{-}\dot{N}{-}O^-\}^{4-} + e + 2H^+ \longrightarrow \{(NC)_5Co{-}NH{-}OH\}^{3-} \qquad (16)$$

E.s.r. Spectra from Nitroparaffins and Nitro-olefins.—(i) *Nitroparaffins.* Nitroparaffins devoid of electrophilic substituents are not reduced by aqueous $K_3Co(CN)_5$, but e.s.r. signals which disappear in a few minutes can be obtained if sodium borohydride is added to such mixtures. When the nitroparaffin is in excess these spectra (Table 3) are clearly those of the radical-anions of the nitroparaffins $(RNO_2{\cdot})^-$ which have been obtained previously by electrolytic reduction [12] though in a different solvent.

TABLE 3

E.s.r. spectra of radical-anions of nitroparaffins

Compound	Splitting constants (mT) a_N	$a_{H\alpha}$	$a_{H\beta}$	g
Me_3CNO_2	2·67			2·0055
Me_2CHNO_2	2·65	0·49		2·0052
$MeCH_2NO_2$	2·55	1·01 (2)	0·06	
Cyclopentyl-NO_2	2·70	0·83		
$PhCH_2NO_2$	2·62	0·94 (2)		
$Me_2C(CH_2CH_2CN)NO_2$	2·61			2·0055

From consideration of a previous study of the borohydride reduction of nitrobenzenes [13] it was thought possible that by using this reducing mixture on nitroparaffins transient primary and secondary nitrosoparaffins might be trapped as $\{(NC)_5Co{-}NR{-}O{\cdot}\}^{3-}$ provided that there is a sufficient concentration of $\{{\cdot}Co^{II}(CN)_5\}^{3-}$ anions. Under these conditions 2-nitropropane did in fact give a 24 line e.s.r. signal [Table 4 (i)] which was detectable for up to 10 min provided that free cobalt(II) was still present. Each line was wide (*ca.* 0·27 mT)

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[11] P. Horsewood and G. W. Kirby, *Chem. Comm.*, 1971, 1139; R. Dickinson, G. W. Kirby, J. G. Sweeny, and J. K. Tyler, *J.C.S. Chem. Comm.*, 1973, 241.

[12] L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, 1962, **84**, 4214; A. K. Hoffmann, W. G. Hodgson, D. L. Mancle, and W. H. Jura, *ibid.*, 1964, **86**, 631.

[13] M. G. Swanwick and W. A. Waters, *Chem. Comm.*, 1970, 63.

and showed distinct signs of doublet splitting indicative of the single α-hydrogen in the radical-anion $\{(NC)_5Co{-}N(O\cdot){-}CHMe_2\}^{3-}$. The e.s.r. spectra taken rapidly after the addition of sodium borohydride to mixtures of aqueous $K_3Co(CN)_5$ to the other nitroparaffins listed in Table 4 also gave, at high receiver gain, initial signals having similar splitting constants but, with static solutions, these became too weak for definite characterisation when only a few lines had been recorded.

TABLE 4

E.s.r. spectra of $\{(NC)_5Co{-}NR{-}O\cdot\}$ radical-anions from nitroparaffins and nitro-olefins

Compound	Splitting constants (mT) a_{Co}	a_N	$a_{H\alpha}$	Overall width (mT)	g	Comments
(i) Nitroparaffins						
Me_3CNO_2	(1·11)	(1·87)		(11·5)	2·0054	Measured for Me_3CNO
Me_2CHNO_2	1·38	1·88	0·07	13·4	2·0049	With $NaBH_4$
Cyclopentyl-NO_2	$1{\cdot}3_6$	$1{\cdot}8_5$		(13·2)		With $NaBH_4$; 6 lines only
$PhCH_2NO_2$	$1{\cdot}3_2$	$1{\cdot}8_5$	0·1?	(12·9)		With $NaBH_4$; 6 lines only
(ii) Nitro-olefins						
$PhCH{=}CHNO_2$	1·24	1·59		11·9	2·0054	
$Me_2C{=}CHNO_2$	1·25	1·53		11·8	2·0055	
$PhCH{=}CMeNO_2$	1·03	1·69		10·5		Very weak signal
$Me_2CHCH{=}CMeNO_2$	1·29	1·80	+	12·7	2·0050	Evidently nitroparaffin signals
$PhCH{=}CBrNO_2$	1·31	1·72	0·17	12·8	2·0053	Same signal from $PhCHBrCHBrNO_2$
(iii) Secondary signals						
$Me_2C{=}CHNO_2$	1·44	1·81		13·7	2·0042	Assigned to group D
$PhCH{=}CMeNO_2$	1·38	1·86		13·4	2·0045	

The large increase in a_{Co} (0·27 mT) in passing from the spectrum of $\{(NC)_5Co{-}N(O\cdot){-}CMe_3\}^{3-}$ to that of $\{(NC)_5CO{-}N(O\cdot){-}CHMe_2\}^{3-}$ is noteworthy. A high value for a_N (*ca.* 1·87 mT) seems to be characteristic of radical-anions of this group.

(ii) *Nitro-olefins.* 1-Nitro-2-phenylethylene and 1-nitro-2-methylprop-1-ene can be reduced slowly by $K_3Co(CN)_5$ without the use of sodium borohydride to give yellow solutions exhibiting 24 line spectra [Table 4(ii)] in which further splitting due to the α-hydrogen cannot be detected, while 1-phenyl-2-nitroprop-1-ene gave a very weak signal which may also belong to this group: all decay in a few hours. These signals have similar g values but much lower a_N values than the radicals from the nitroparaffins and the a_{Co} values have decreased correspondingly. These changes in splitting constants are rational if, as with the $\{(NC)_5Co{-}NAr{-}O\cdot\}^{3-}$ radical-anions,[1] there is some hybridisation of the π electrons of the double bond with the p electron of the nitroxide group. The absence of detectable α-hydrogen splitting in the radicals obtained from nitro-olefins but not from nitroparaffins is also explicable since the nitro-olefins have rigidly planar structures and in their $\{(NC)_5Co{-}NR{-}O\cdot\}^{3-}$ radical-anions spin coupling between the nitroxide group and an α-hydrogen could only involve the s fraction of the sp^2 hybridised C–H bond.

The reduction of nitro-olefins by a large excess of $K_3Co(CN)_5$, or better by the combined use of $K_3Co(CN)_5$ and $NaBH_4$ in some cases produces radicals giving signals with higher a_{Co} and a_N values. Judging from their g values these appear to belong to two different groups of radical-anions. Both 2-nitro-4-methylpent-2-ene and 1-bromo-1-nitro-2-phenylethylene give short-lived spectra with g values indicative of radical-anions from nitroparaffins and show hyperfine splitting indicative of the presence of an α-hydrogen. In fact 1-bromo-1-nitro-2-phenylethylene gives a signal almost identical with that from 1,2-dibromo-1-nitro-2-phenylethane [Table 5(i)]. In these cases we consider that the double bond must have been hydrogenated, possibly before the $\{(NC)_5Co{\cdot}NR{-}O\cdot\}^{3-}$ is formed.

With 1-nitro-2-methylprop-1-ene and 1-phenyl-2-nitroprop-1-ene, both of which also gave narrower signals, the wider signals [Table 4(iii)] have low g values and a_N and a_{Co} splitting constants corresponding to the e.s.r. signals of group D which are discussed later. It is possible that in the formation of these radical-anions the hydridopentacyanocobalt anion $\{HCo(CN)_5\}^{3-}$ which is present in mixtures of potassium pentacyanocobalt(II) and sodium borohydride[8] has added on to the double bond of the olefin or of the olefinic nitroxide radical-anion. The wide signals from these two compounds show no sign of splitting due to an α-hydrogen atom and they are stable for some hours.

E.s.r. Spectra from Halogenated Nitroparaffins.—(i) *Tertiary compounds* $R^1R^2C(Hal)NO_2$. In contrast to 2-methyl-2-nitropropane, the nitroparaffins which contain a halogen atom attached to the same carbon atom as the nitro-group are reduced in a few minutes by aqueous potassium pentacyanocobalt(II) to give radical-anions containing cobalt. This is easily explicable since electron attraction by the halogen atom will facilitate reduction of the nitro-group. The initial e.s.r. signals evidently correspond to radical-anions of group A, and indeed for both 2-chloro- and 2-bromo-2-nitropropane, which have been studied in detail, are identical with the group A signals from the corresponding nitroso-compounds.

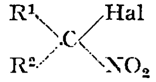
These signals persist for several minutes under nitrogen but, if cobalt(II) is present in excess, as the group A spectra decay others (group D) appear in which the splitting due to cobalt has increased from *ca.* 1·1 to *ca.*

1·4 mT though the nitrogen splitting has altered very little and g has decreased to 2·0045—2·0049. With the bromonitro-compounds the wide spectra (D) appear after a few minutes, but the change is slower with the chloronitro-compounds. It can be accelerated by the further addition of sodium hydroxide or sodium borohydride.

When 2-chloro- or 2-bromo-2-nitrosopropane are used these changes from group A to D spectra occur more slowly than with the corresponding nitro-compounds. This may be due to a difference in the reactivities of the halogen atoms in the two series of compounds.

TABLE 5

Initial spectra from halogenated nitroparaffins



Groups			Splitting constants (mT)		Overall width (mT)		Splitting constants (mT)			Overall width (mT)		Other spectra	Comments
R^1	R^2	Hal	a_{Co}	a_N		g	a_{Co}	a_N	a_H		g		
(i)													
Me	Me	Cl	1·06	1·75	10·9	2·0052						D	
Me	Me	Br	1·06	1·77	11·0	2·0055						D	
PhCHBr	Me	Br	1·05	1·76	10·9w							D	
(ii)													
Me	H	Br					1·32	1·75	0·06	12·8			
Et	H	Cl					1·32	1·76	0·13	12·9	2·0052		
Et	H	Br					1·32	1·76	0·18	12·9	2·0051		
PhCHBr	H	Br					1·31	1·72	0·15	12·8	2·0053		
(iii)													
Me	Br	Br	1·05	1·76	10·9	2·0054	1·33	1·78	+?	12·8w		Dw	Mostly dibromo
Et	Cl	Cl	1·05	1·78	10·9	2·0053	1·33	1·75	*ca.* 0·2	12·9w	2·0051		Mostly dichloro
Et	Br	Br					1·32	1·75	0·17	12·9	2·0053		Reduced to monbromo immediately

w = Weak.

Spectra of group D persist for many hours and are not destroyed by exposure of the reaction mixtures to the air. In fact air flushing of stored solutions helps in producing clear signals of group D free from admixture with those of group A or of cobalt(II). Secondary signals of group D have not been obtained from compounds $R^1R^2C(OCOMe)NO$, but weak signals, probably of this group, can be obtained from compounds $R^1R^2C(CN)NO$ if sodium borohydride is used in addition to $K_3Co(CN)_5$ as the reducing agent.

None of the halogenated nitroparaffins gave spectra B or C.

(ii) *Secondary compounds* $RCH(Hal)NO_2$. The 1-halogeno-1-nitroparaffins which we have examined are reduced fairly easily by potassium pentacyanocobalt(II). They do not give initial signals with a_{Co} *ca.* 1·1 mT, but wider signals with a_{Co} *ca.* 1·3 and a_N *ca.* 1·75 mT which show doublet splitting of 0·1—0·2 mT due to the α-hydrogen [Table 5(ii)], but their g values are also in the range 2·0050—2·0055. These signals disappear in a very few minutes and even when cobalt(II) is used in large excess they have not been observed to change to wider signals having lower g values. We consider therefore that they correspond to radical-anions $\{(NC)_5Co\text{-}N(O\cdot)\text{-}CHRHal\}^{3-}$.

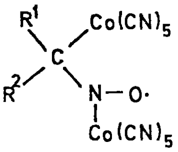
The solutions which exhibit these e.s.r. signals are orange indicating that homolysis (5) can occur.

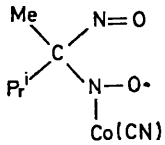
(iii) *Dihalogen compounds* $RC(Hal)_2NO_2$ [*Table* 5(iii)]. The 1,1-dihalogenated 1-nitroparaffins react with $K_3Co(CN)_5$ to give orange or brown solutions which give signals of group A with a_{Co} *ca.* 1·05 mT and g 2·0050—2·0055 together with wider signals with a_{Co} *ca.* 1·3 mT showing α-hydrogen splitting. These dihalogen compounds are not stable to alkali, degrading to olefins $R_2C{=}C(Hal)NO_2$, and evidently reduction to radical-anions $\{(NC)_5Co\text{-}N(O\cdot)\text{-}CHR\cdot Hal\}^{3-}$ can occur when $\{\cdot Co^{II}(CN)_5\}^{3-}$ anions are used in excess. Both groups of signals decay in a few minutes and are not observable in solutions which have been exposed to the air.

Discussion of Group A and Group D Spectra.—The transient spectra obtained from 2-nitropropane and nitrocyclopentane [Table 4(i)] indicate that in the $\{(NC)_5Co\text{-}NR\text{-}O\cdot\}^{3-}$ radical-anions obtainable from secondary nitroparaffins the replacement of one alkyl group by hydrogen increases the value of a_{Co} by 0·2—0·3 mT over that found for the radical from 2-methyl-2-nitrosopropane. This same enhancement of a_{Co} is evident if the values for the radical-anions derived from the halogenated 1-nitroparaffins [Table 5(ii)] are compared with the a_{Co} splitting for the spectra of Tables 1 and 5(i). Again the g values are similar for the radical-anions listed in both Tables and therefore both sets of signals can be assigned to radical-anions of group A.

Similarly the transient narrow signals (a_{Co} *ca.* 1·05 mT) from the 1,1-dihalogenated 1-nitro- and 1-nitrosoparaffins can be assigned to group A and the wider signals to monohalogen radical-anions of the same group showing α-hydrogen splitting.

The e.s.r. spectra of group D [Table 6(i) and (iii)] however which are formed when $K_3Co(CN)_5$ is used in excess must correspond to radical-anions with a different structure. They often have line-widths *ca.* 0·05 mT larger than the corresponding group A spectra from the same nitro- or nitroso-compounds but this is scarcely *enought to mask* the presence of an α-hydrogen. Again the a_{Co} values and especially the overall spectral widths are too high for them to correspond to olefinic compounds [*cf.* Table 4(ii)]. Since, to within the limits of experimental error, the same group D spectrum is obtainable from both 2-chloro- and 2-bromo-2-nitropropane as well as from 2-chloro- and 2-bromo-2-nitrosopropane we conclude that the change from the group A to the group D spectrum involves the replacement of the halogen atom. Because this change, which occurs in solutions initially containing an excess of cobalt(II), evidently does not comprise the replacement of halogen by hydrogen, or hydrogen halide elimination to give an olefin, and cannot be effected with the hydrolysable acetoxy-compounds, $R^1R^2C(OCOMe)NO$, and so is most unlikely to be derived from the unknown, unstable hydroxy-compounds $R^1R^2C(OH)NO$, we suggest that it may be due to the replacement of the halogen atom by another $\{Co^{III}(CN)_5\}^{3-}$ group to give a radical-anion (I)


(I)


(II)

in which the second cobalt atom is too far away from the nitroxide group to produce detectable hyperfine splitting, but yet is near enough to increase line widths.

Many alkyl halides have been shown to react, probably homolytically[14] with cobalt(II) complexes to give alkylcobalt(III), and α-halogenated nitroparaffins have been

$$\text{R-Hal} + \cdot\text{Co}^{\text{II}}\text{L}_5 \longrightarrow \text{R}\cdot + \text{Hal-Co}^{\text{III}}\text{L}_5 \qquad (17)$$

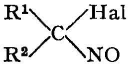
$$\text{R}\cdot + \cdot\text{Co}^{\text{II}}\text{L}_5 \xrightarrow{\text{very fast}} \text{R-Co}^{\text{III}}\text{L}_5 \qquad (18)$$

shown to be susceptible to homolytic carbon–halogen fission.[15] With the halogenated nitroparaffins at least we think that reactions (17) and (18) occur concurrently with, but more slowly than the $\{\cdot Co^{II}(CN)_5\}^{3-}$ reduction of the nitro-group so that with cobalt(II) present in excess the less stable e.s.r. signal of a group A radical initially predominates and that the group D signal slowly grows and persists as the group A signal decays. It has been suggested above that the decay of the group A signal is due to homolysis (5) which yields an unstable alkyl radical that would of course combine immediately with oxygen. The persistence for many hours of the group D signals indicates that the corresponding radical-anions (I) are not prone to such homolysis. Though they can be observed in pink or orange solutions containing $\{(NC)_5Co{-}NO\}^{3-}$ anions they can also be detected in yellow or even greenish solutions containing free $\{\cdot Co^{II}(CN)_5\}^{3-}$ anions and so their further reduction [reaction (6)] must be slow.

We have had some indications that the production of group D signals can be effected [*e.g.* with $Et_2C(CN)NO$] or enhanced [*e.g.* with $Me_2C(Cl)NO$] by the

TABLE 6

(i) Secondary spectra (group D) from halogenated nitrosoparaffins

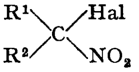


Groups			Splitting constants (mT)		Overall width (mT)	g	Comments
R^1	R^2	Hal	a_{Co}	a_N			
Me	Me	Cl	1·38	1·79	13·2		Also from nitro-compounds
Me	Me	Br	1·37	1·76	13·2		Only 1 value
Me	Et	Cl	1·36	1·77	13·1		
Me	Pr^i	Cl	1·38	1·81	13·3		With $NaBH_4$
Me	Bu^t	Cl	1·40	1·82	13·4w		With $NaBH_4$
Et	Et	Cl	1·39	1·79	13·3	2·0043	With $NaBH_4$
Et	Et	Br			13·2w		
Et	Et	CN	1·40	1·78	13·3	20·044	With $NaBH_4$
$[CH_2]_5$		Br	1·37	1·76	13·1w		
$[CH_2]_5$		CN	1·36	1·81	13·1w		With $NaBH_4$

(ii) Secondary spectra from ψ-nitroles

Groups			Splitting constants (mT)			Overall width (mT)	g	Comments
R^1	R^2		a_{Co}	a_N	a_{CH}			
Me	Me	NO_2	1·38	1·88	0·07?	13·5w		With $NaBH_4$
Et	Et	NO_2	1·37	1·88	+?	13·4	2·0046	With $NaBH_4$

(iii) Secondary spectra (group D) from halogenated nitroparaffins



Groups			Splitting constants (mT)		Overall width (mT)	g	Comments
R^1	R^2	Hal	a_{Co}	a_N			
Me	Me	Cl	1·37	1·77	13·2	2·0043	Also from nitrosoparaffins
Me	Me	Br	1·38	1·79	13·3	2·0045	Also from nitrosoparaffins
PhCHBr	Me	Br	1·39	1·87	13·5	2·0047	
Me	Br	Br	1·38	1·81	13·1w	2·0043	

w = Weak.

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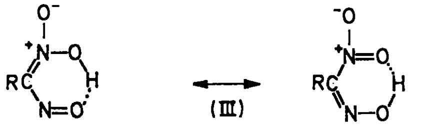
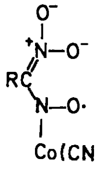
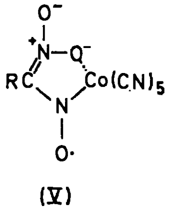
[14] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 1965, **87**, 5361; J. Kwiatek and J. K. Seyler, *J. Organometallic Chem.*, 1965, **3**, 421.

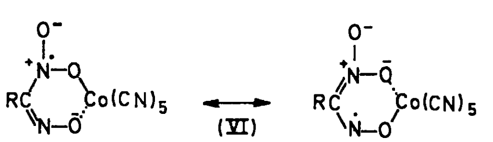
[15] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1947, 492.

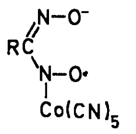
addition of sodium borohydride to reacting solutions. Though this reagent is essentially a hydride reductant it can re-form cobalt(II) complexes from cobalt(III) complexes [8] and so would certainly facilitate reactions (17) and (18) even if it does not effect the homolytic fission of substituents like CN.


(III)


(IV)


(V)


(VI)


(VII)

The ψ-nitroles do not give spectra of group D on treatment with an excess of $K_3Co(CN)_5$ but, with one compound, $Pr^iCMe(NO_2)NO$, a wider signal showing the presence of two nitrogen atoms was obtained (a_{Co} 1·36, a_{N_1} 0·67, a_{N_2} 1·04, overall width 13·0 mT, g 2·0044). In view of the similarity between this spectrum and the narrower of the two spectra obtained from nitrolic acids (Table 7) we think that in this case the nitro-group has been reduced to a nitroso-group yielding the radical-anion (II) in which the N=O and $>$N–O· bonds are co-planar.

TABLE 7

E.s.r. spectra of radicals from nitrolic acids (III)

			Excess of Co^{II} or pH >11						Deficiency of Co^{II} and pH <11				
	Overall width (mT)		Splitting constants (mT)					Overall width (mT)	Splitting constants (mT)				
R	Expt.	Calc.	a_{Co}	a_{N_1}	a_{N_2}	a_H	g	Expt.	a_{Co}	a_{N_1}	a_{N_2}	a_H	g
H	12·7	12·7	1·36	1·00	0·51		(2·0041)	17·4	2·09	0·88	0·67		2·0040
Me	14·0	14·0	1·39	1·04	0·65	0·28	2·0043	18·7	(2·1)	(1·0)	0·67	0·29	2·0039
Et	13·6	13·5	1·39	1·06	0·62	0·21	2·0042	18·2	(2·1)	(1·0)	0·65	0·30	2·0042
Ph	13·1	13·0	1·38	1·04	0·66		2·0041	17·6	2·04	0·97	0·66		2·0040

Values in parentheses are estimated by interpolation from the overall widths of the spectra.

If sodium borohydride is used together with $K_3Co(CN)_5$ wider, but short lived, signals can be obtained from ψ-nitroles [Table 6(ii)]. These have a_N values which are too high for classification as group D spectra and gave indications of hydrogen splitting; they may well be due to the radical-anions from the secondary nitroparaffins [*cf.* Table 4(i)] obtained by hydride replacement of the nitro-group.

{$(NC)_5Co$–NR–O·} *Radical-anions from Nitrolic Acids* (*α-Nitro-oximes*).—Nitrolic acids (III) are immediately reduced by aqueous $K_3Co(CN)_5$ under nitrogen to give deep wine-red solutions ($\lambda_{max.}$ 540 nm) which exhibit very complicated e.s.r. spectra showing hyperfine splitting due to one cobalt atom and two nitrogen atoms and having g values of *ca.* 2·0040 (Table 7).

When only a small amount of $K_3Co(CN)_5$ is added to the nitrolates the red solutions give, at pH 7—10, predominantly a wide spectrum (17—19 mT overall) with lines 0·1—0·2 mT wide that overlap, except at the edges of the spectra, so much that the larger hyperfine splitting constants often have to be estimated from knowledge of the overall spectral width. When the [Cobalt(II)] : [Nitrolic acid] ratio approaches 1 or the pH is >11, the middle of the spectrum grows more intense, and at higher [Cobalt(II)] : [Nitrolic acid] ratios the outer lines vanish leaving a sharper signal of overall width 13—14 mT. This signal persists when the ratio is as high as 4 but the colour then fades to an orange-yellow. Complete reduction, with cobalt(II) in excess and no remaining nitroxide signal, is achieved only slowly even when the ratio is at least 6. Both the wide and the narrow signals are stable for at least a day and persist strongly in solutions which have been exposed to the air. They disappear when the solutions are acidified (pH <6) but reappear when they are again made alkaline.

Table 7 shows that the main difference between the two groups of signals is due to a change in the magnitude of the a_{Co} splitting constant. Neither benzene- (III; R = Ph) or methane-nitrolic acid (III; R = H) show proton splitting in either signal but ethane- and propane-nitrolic acids (III; R = Me or Et) show small splittings assignable to CH_3 and CH_2 respectively. These acids have β-C–H bonds which do not lie in the plane of the ring of the nitrolic acid, unlike the α-C–H bond in methanenitrolic acid.

In both series of radicals the combined nitrogen splitting constants ($a_{N_1} + a_{N_2}$) are very close to 1·7 mT as found in the radical-anions from *C*-nitroso-compounds (Tables 1, 2, and 6). This supports the view that they are essentially cobalt(III) nitroxide signals from radical-anions in which there can be resonance hybridisation between the two nitrogens. In view of the stoicheiometry of the initial reaction the wide signals could come from radical-anions (IV) in which only the nitroso-group has been reduced; they could perhaps have five-membered (V), or six-membered (VI) chelated ring structures. The deep red colour of solutions which contain these radical-anions may possibly be due to a charge transfer complex between a cobalt(II) centre and a nitrolate anion, which would be spatially very similar to (VI) and would have high electron spin density associated with the cobalt atom.

The narrower, sharper lined signal which predominates at high [Cobalt(II)] : [Nitrolic acid] ratios of the components, can, we suggest, correspond to a reduced radical-anion (VII) in which the nitro-group has been reduced to an oxyimino-group.

Dialkyl Nitroxides, $R_2N{-}O$.—As the preliminary communication [2] explained, the e.s.r. signal obtained immediately after the addition of a little aqueous $K_3Co(CN)_5$ to 2-methyl-2-nitrosopropane in aqueous methanol is that of the t-butylhydroxylamino radical-anion, $(Me_3C{-}\bar{N}{-}\dot{O})$, which in a few minutes changes to the more persistent three line signal of di-t-butyl nitroxide $(Me_3C)_2N{-}O\cdot$. When this procedure has been used three line signals have been obtained from the majority of the *C*-nitroso-compounds which we have examined. Similar signals are often given by solutions of nitroso-compounds which have been exposed to light and in the case of the cyano-compounds $R^1R^2C(CN)NO$ have also been obtained by the oxidation of the hydroxylamines $R^1R^2C(CN)NHOH$ with iron(III) chloride or alkaline ferricyanide.

Reactions (1), (2), and (5) explain the origin of these signals and their appearance in pink solutions containing the nitrosopentacyanocobalt(III) anion, $\{(NC)_5Co{-}N{=}O\}^{3-}$, substantiates the occurrence of homolysis (5). These spectra, listed in Table 8, are stable in air and usually are detectable without change over 24 h. In some cases the initially observed signals have slightly lower a_N values (by *ca.* 0·05 mT) and are probably due to short-lived hydroxylamino radical-anions, $R{-}\dot{N}{-}\bar{O}$, but they reach the tabulated limit in a very few minutes. A few of the persistent signals, though undoubtedly being spectra of dialkyl nitroxides may, for two reasons, not contain just a pair of the substituents $R^1R^2C(X)$ of the original nitroso-compounds and so the figures of Table 8 must be viewed with caution.

TABLE 8

a_N Splittings of nitroxides $[R^1R^2C(X)]_2N{-}O\cdot$

R^1	R^2	X	a_N(mT)	R^1	R^2	X	a_N(mT)
Me	Me	Me	1·70	Me	Me	CH_2CH_2CN	1·52
Me	Me	Cl	1·54	Me	Et	Cl	1·51
Me	Me	Br	1·57	Me	Et	Br	1·48
Me	Me	CN	1·53	Me	Et	CN	1·48
Me	Me	NO_2	1·52	Me	Et	NO_2	1·50
Me	Me	OCOMe	1·54	Me	Me	COMe	1·57
Me	Pr^i	Cl	1·53	Me	Bu^t	Cl	1·43
Me	Pr^i	Br	1·46	Me	Bu^t	Br	1·50
Me	Pr^i	NO_2	1·50	Me	Bu^t	OCOMe	1·52
Me	Pr^i	OCOMe	1·52				
Et	Et	Cl	1·45	$[CH_2]_5$		Cl	1·48
Et	Et	Br	1·43	$[CH_2]_5$		Br	1·43
Et	Et	CN	1·46	$[CH_2]_5$		CN	1·50
$[CH_2]_4$		NO_2	1·40	$[CH_2]_5$		OCOMe	1·43

First, following homolysis (5) the alkyl radical so formed may decompose sufficiently rapidly that the dialkyl nitroxide produced by reaction (2) may not be symmetrical. For instance, on treatment with $K_3Co(CN)_5$, 2-acetyl-2-nitrosopropane gives a three line spectrum immediately (a_N 1·54 mT) but after a day the persisting spectrum is that of a triplet, also obtainable from stored solutions of the dimeric nitroso-compound, and presumably that of the symmetrical nitroxide (a_N 1·57 mT), admixed with another strong signal of *g* 2·0057 showing a triplet of four line splittings with the 1 : 3 : 3 : 1 intensity pattern indicative of a nitroxide, $MeCOCMe_2{-}N(Me){-}O\cdot$, containing an α-methyl group (*i.e.* a_N 1·62, $a_{H(3)}$ 1·37 mT). This is consistent with the occurrence of the radical decomposition (19).

$$MeCOCMe_2\cdot \longrightarrow MeCOMe + Me\cdot \qquad (19)$$

Secondly, it is possible that the alkali-sensitive nitroso-compounds (having X = Cl, Br, or OCOMe) or radicals derived therefrom may, after storage at the pH (*ca.* 10) of the reaction mixtures, break down to other products yielding nitroxides.

General Comments.—The addition of the pyramidal $\{\cdot Co(CN)_5\}^{3-}$ anion by way of its unpaired d_{z^2} electron [6] to N=O bonds of organic compounds and the general structure of the adducts have been discussed previously.[1,3] Only the true nitroso-compounds behave in this way for no reactions have been found with *N*-nitrosamines (the nitrosamines from methylaniline, diphenylamine, and piperidine have been examined). It is now evident that $\{(NC)_5Co\cdot NR{-}O\cdot\}^{3-}$ radical-anions are not as stable as their aryl analogues and tend to break down to air-sensitive alkyl radicals and diamagnetic nitrosopentacyanocobalt(III) anions. Our experiments indicate that further one-electron reduction to the anions $\{(NC)_5Co{-}NR{-}OH\}^{3-}$ can occur and in view of the known chemistry of hydroxylamines this should be a reversible process. Many metals form bonds to nitrogen and so the preparation of analogous nitroxides containing other metals can be envisaged.

Reduction by one-electron transfer to alkyl nitrites and nitroso-compounds has also been established [equations (8) and (4)]. The failure to effect such a reduction directly with simple nitroparaffins but its achievement with aromatic nitro-compounds, nitro-olefins, and α-halogenated nitroparaffins indicates that the redox potential of $\{\cdot Co(CN)_5\}^{3-}$ in alkaline solution cannot be much more negative than −0·2 V. Though the listed standard redox potential of this anion (*i.e.* in 1·0N-acid) is −0·83 V_a (British convention) it is rational to conclude that E'_0 cannot be more negative than −0·4 V_a under conditions in which one-electron transfer alone occurs. It follows that the cyanide, and probably several other, complexes of cobalt(II) can have redox potentials within the range (0·0 to −0·5 V) appropriate to selective biochemical oxidations and reductions.[16]

Again $\{\cdot Co(CN)_5\}^{3-}$ is an excellent trapping agent for

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[16] W. A. Waters, IUPAC Lecture, Boston, 1971; *Pure Appl. Chem. Suppl.*, 1971, Butterworths, London, vol. 4, p. 307.

nitric oxide and can reduce nitrite anions. In view of the known biochemical reactions of haemoglobin with these substances and of the established metabolic oxidation of some amines to carcinogenic hydroxylamines we think that the reactions described in this paper may be helpful in the elucidation of the functions of trace metals as biological catalysts or inhibitors.

EXPERIMENTAL

Preparations of C-*Nitroso-compounds*.—With the exception of the dimers of 2-nitro-2-nitrosopropane and of 2-acetyl-2-nitrosopropane [17] the nitroso-compounds were not isolated as solids on account of their unstability, but were prepared as required in ether solution, dried, and stored at 0—5° in the dark. Only simple aliphatic nitroso-compounds (C_6 or less) were sufficiently soluble in aqueous methanol for the study of their reactions with $K_3Co(CN)_5$.

2-Methyl-2-nitrosopropane was prepared by reducing the nitro-compound in aqueous alcoholic ammonium chloride with zinc powder [3,18] filtering, and then oxidising the filtrate at 0° with either iron(III) chloride or dilute chromic acid. The blue ether solution was then washed with dilute acid and dried (Na_2SO_4). The product from the latter oxidant was contaminated with a little di-t-butyl nitroxide. 4-Methyl-4-nitrosopentanenitrile was obtained similarly, in poor yield, from the corresponding nitro-compound.[19]

The monomeric α-chloronitroso-compounds were prepared by gradual addition of 10% aqueous sodium hypochlorite to ice-cold solutions of ketoximes in aqueous acetic acid (5—20%) containing sodium chloride under a layer of ether. When hypochlorite was present in slight excess a little dilute hydrochloric acid was added to extract unchanged oxime from the ether layer which was then separated and washed thoroughly with dilute acid, aqueous sodium hydrogen sulphite, and finally sodium hydrogen carbonate. The clear blue solutions were dried and stored in the dark: for immediate use portions were diluted with methanol and neutralised if necessary with sodium hydrogen carbonate. On exposure to air and light they gradually became acidic and turned greenish; a test with aqueous iron(II) sulphate then showed the presence of nitrous acid or nitric oxide. The blue solutions were not immediately attacked by cold dilute ($<0{\cdot}1$M) sodium hydroxide or potassium cyanide but after some minutes those which gave e.s.r. signal B (Tables 1 and 2) had turned yellow. Acidified silver nitrate reacted with all the solutions giving silver chloride in a few minutes.

Solutions of acet- and propion-aldehydes gave blue solutions only after treatment with a large excess of sodium hypochlorite. These were much less stable than the solutions obtained from ketoximes. 1,1-Dichloro-1-nitrosoethane was prepared in solution by further chlorination; [7] our e.s.r. studies (Table 2) showed that propionaldoxime had been dichlorinated directly.

2-Hydroxyiminobutan-3-one and α-hydroxyiminopropiophenone, PhCOC(NOH)Me, gave blue solutions only in poor yield. These became acidic much more rapidly than did those from simple aliphatic ketoximes, and were slowly decomposed by aqueous sodium hydrogen carbonate and rapidly by aqueous sodium hydroxide.

The α-bromonitroso-compounds were prepared similarly in ether from solutions of ketoximes in dilute aqueous acetic acid or aqueous pyridine [20] by cautious addition of bromine. The yields were low and no nitroso-compound could be obtained from the oximes of pinacolone or of the 1,2-diketones. Their stabilities and general reactions were similar to those of the chloro-compounds. The α-acetoxynitroso-compounds were prepared in methylene chloride from oximes and lead tetra-acetate by the general method of Iffland and Criner.[5] The solutions, after washing and drying, were evaporated under diminished pressure and the blue residues were dissolved in methanol and used without delay. These methanolic solutions were completely decomposed by dilute sodium hydroxide or potassium cyanide in <1 min.

The α-cyanonitroso-compounds were prepared in solution by aqueous chromic acid oxidation of α-cyanohydroxylamines. The latter were obtained either by treating ketoximes with concentrated buffered aqueous potassium cyanide [21] or from ketones by treatment with aqueous potassium cyanide and hydroxylamine hydrochloride.[22]

The α-nitronitroso-compounds (ψ-nitroles) corresponding to 2-nitropropane and nitrocyclopentane were made by treating these nitroparaffins with nitrous acid. The others listed in Table 1(v) were made in ether solution by treating the corresponding oximes with aqueous sodium nitrite and then acidifying gradually with dilute acetic or sulphuric acid.[23] The blue ether solutions were in each case washed with aqueous sodium hydroxide to remove contaminants.

The Nitroparaffins and their Halogenation Products.—Nitrocyclopentane was prepared from bromocyclopentane and sodium nitrite by the method of Kornblum and Powers; [24] phenylnitromethane was prepared from benzyl chloride and silver nitrite. The other nitroparaffins were commercial products. 1-Bromo-1-nitroethane and 1-bromo-1-nitropropane, made by dissolving the nitroparaffins in 20% sodium hydroxide and slowly adding one molecular equivalent of bromine, were distilled under reduced pressure; their n.m.r. spectra showed the presence of the hydrogen atom in the 1-position. The corresponding 1,1-dibromo-compounds were made by adding 2·5 mol equiv of bromine in portions to the nitroparaffins at 0° and then adding 20% sodium hydroxide solution with shaking until the aqueous solution became strongly alkaline and a dense, colourless oil remained undissolved. These oils were distilled under reduced pressure; their n.m.r. spectra confirmed their identities. 2-Bromo-2-nitropropane was prepared similarly. The chloronitro-paraffins were gifts from I.C.I. Ltd. The 1-chloro-1-nitropropane sample proved to be a mixture which on treatment with 20% sodium hydroxide was separated into 1-chloro-1-nitropropane (alkali soluble) and insoluble 1,1-dichloro-1-nitropropane, the separate identities of which were confirmed by n.m.r. spectroscopy.

The 1-nitro-2-phenylethylene, 1-phenyl-2-nitroprop-1-ene, and their dibromo-adducts were prepared by literature methods and crystallised to correct m.p.; their identities

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[21] C. C. Porter and L. Hellerman, *J. Amer. Chem. Soc.*, 1939, **61**, 754; 1944, **66**, 1654.

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

[23] R. Scholl, *Ber.*, 1888, **21**, 506; A. Schöfer, *ibid.*, 1901, **34**, 1911.

[24] N. Kornblum and J. W. Powers, *J. Org. Chem.*, 1957, **22**, 455.

were confirmed by n.m.r. 1-Bromo-1-nitro-2-phenylethylene, m.p. 65°, was obtained by warming ethanolic 1,2-dibromo-1-nitro-2-phenylethane with ethanolic sodium acetate.

The specimens of 1-nitro-2-methylprop-1-ene and 2-nitro-4-methylpent-2-ene had been prepared by Dr. J. D. Rose and were gifts from I.C.I. Ltd (Blackley).

Nitrolic Acids (*α-Nitro-oximes*).—Apart from methanenitrolic acid which is unstable these acids were prepared as crystalline solids from the corresponding nitroparaffins and nitrous acid. Methanenitrolic acid, prepared in water from nitromethane, was extracted from an acid solution into ether. This solution was washed with water and the acid was then extracted into sodium carbonate and used within a day.

Procedure (cf. *ref.* 1).—All operations were carried out under a slow stream of White Spot grade nitrogen. Transferences of solutions were made with syringes. Aqueous potassium pentacyanocobalt(II) was made by adding aqueous cobalt(II) sulphate or chloride (0·2M) to aqueous potassium cyanide (1·5M) usually in the ratio $[Co^{II}] : [CN^-]$ 1 : 6. Portions of the deep green solution thus obtained were transferred to another nitrogen-flushed flask, treated with the reactant in methanol, and transferred as rapidly as possible to a nitrogen-flushed e.s.r. cell for immediate measurement. If necessary a little air-free water was added to the mixture to dissolve any of the purple dimer [8, 25] of $K_3Co(CN)_5$ that had been precipitated by the methanol. To minimise possible reactions due to decomposition products of $K_3Co(CN)_5$ [8, 26] its solutions were not kept for more than 3 h.

The e.s.r. spectra were recorded on a Varian E4 spectrometer using a modulation amplitude of 0·5 G or less. The line widths of the spectra vary between 1·0 and 2·5 G (0·1—0·25 mT) depending upon the nature of the reactant. With the *C*-nitroso-compounds there is, in general, an increase in the line width with increase in size of the alkyl groups. Spectra in which hyperfine splitting due to hydrogen is suspected but not clearly evident (marked as ?+ in the Tables) have line widths of 0·25—0·3 mT. The Tables give averaged results of repeated experiments.

The visible spectra were recorded on a Unicam SP 825 spectrometer.

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