Alkylpentacyanocobalt Nitroxide and Primary Alkyl Nitroxide Radical-anions

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Summary Monomeric aliphatic nitroso-compounds react with $\{Co(CN)_5\}^{3-}$ in aqueous/alcoholic solutions to give radical-anions $\{(NC)_5Co{-}N(Alk){-}O\cdot\}^{3-}$ and/or $(Alk{-}\dot{N}{-}O^-)$ which can be characterised by e.s.r.; they have lifetimes of the order of minutes.

IN 1970 Swanwick and Waters[1] found that arylpentacyanocobalt nitroxides $\{(NC)_5Co{-}N(Ar){-}O\cdot\}^{3-}$ could be obtained by treating many aromatic nitro- or nitroso-compounds under nitrogen with aqueous sodium pentacyanocobalt(II), $Na_3Co(CN)_5$, and reported later[2] that a similar reaction did not occur with nitromethane.

I now report that monomeric nitroso-paraffins react with $\{Co(CN)_5\}^{3-}$ ions to give alkylpentacyanocobalt nitroxides, $\{(NC)_5Co{-}N(Alk){-}O\cdot\}^{3-}$ and/or the unstable radical-anions $(Alk{-}\dot{N}{-}O^-)$ of primary alkyl nitroxides.[3] These species are sufficiently stable for e.s.r. characterisation in static solutions but undergo further reactions within minutes or hours of their formation. Simple nitro-paraffins are not sufficiently reduced by $\{Co(CN)_5\}^{3-}$ ions (for example even in strong alkali 2-methyl-2-nitropropane gives only the nitro-radical-anion $(Me_3C{-}NO_2\cdot)^-$ having a_N 2·67 mT, g 2·0055 (previously obtained by electrolytic reduction in 1,2-dimethoxyethane[4]) but α-halogenated nitro-paraffins and α-dinitro-paraffins ($R^1R^2CX{\cdot}NO_2$, X = Cl, Br, NO_2) do react rapidly with $\{Co(CN)_5\}^{3-}$ ions to yield alkylpentacyanocobalt nitroxide, and other detectable radicals. Cobalt nitroxide radicals can also be formed from nitrolic acids and pseudo-nitroles [$R^1R^2C(NO)NO_2$, R^2 = H or Alk]. The e.s.r. spectra given by many of these compounds have not yet been interpreted fully and are often indicative of mixtures, but definite structural assignments can be given to the new radicals listed in the Table.

The form of the e.s.r. signal obtained from solutions made by treating nitroso-paraffins with aqueous $K_3Co(CN)_5$ may depend upon the experimental procedure as well as on the nature of the solvent and its pH. Thus the addition of a blue solution of 2-methyl-2-nitrosopropane in methanol–ether to aqueous $K_3Co(CN)_5$ under nitrogen gives a pink solution which shows the 24-line e.s.r. spectrum of $\{(NC)_5Co{-}N(CMe_3){-}O\cdot\}^{3-}$ on which is superimposed the 3-line spectrum of $(Me_3C{-}N{-}O\cdot)^-$. After storage for some minutes the solution turns yellow and concurrently with this the cobalt signal disappears. However, gradual addition of $K_3Co(CN)_5$ solution to one of the nitroso-compound gives only the 3-line signal of $(Me_3C{-}N{-}O\cdot)^-$ which on storage, exposure to air, or acidification soon widens to the well-known signal of di-t-butyl nitroxide, $(Me_3C)_2NO\cdot$ (a_N 1·70 mT). Again cobalt nitroxide signals from 2-methyl-2-nitrosobutan-3-one, advocated by Lagercrantz[5] as a good radical trapping agent, can only be obtained by the use of hot solutions containing some monomeric nitroso-compound. The tabulated cobalt nitroxide signals obtained immediately after admixture of $\{Co(CN)_5\}^{3-}$ with the α-halogenated nitro- or nitroso-paraffins change with time or exposure of solutions to the air to wider, more persistent signals having a_{Co} *ca.* 1·4 mT, a_N *ca.* 1·8 mT, and there are concurrent colour changes. Tests show that some of the secondary slow reactions involve removal of the halogen atoms as halide anions.

E.s.r. splitting constants of radical-anions (mT)

Nitroso-compound	$\{(NC)_5Co{-}N(Alk){-}O\cdot\}^{3-}$		$(Alk{-}\dot{N}{-}O^-)$
	a_{Co}	a_N	a_N
$Me_3C{-}N{=}O$	1·11	1·80	1·63
$MeCO{\cdot}CMe_2{-}N{=}O$	1·19	1·78	(1·6)
$MeCH(Cl){-}N{=}O$			1·31 (a_{C-H} 0·22)
$Me_2C(Cl){-}N{=}O$[a]	1·07	1·76	1·49
$Me_2C(Br){-}N{=}O$[a]	1·06	1·76	1·41
$Me_2C(NO_2){-}N{=}O$	1·06	1·75	1·49
$C_6H_{10}(Cl){-}N{=}O$[b]	1·09	1·68	1·41
$C_6H_{10}(Br){-}N{=}O$[b]	1·10	1·67	1·39

[a] Also the nitro-paraffin. [b] C_6H_{10} = Cyclohexylene.

The splitting constants were measurable to ±0·005 mT but can be up to 0·02 mT greater in water than in solutions of high (>30%) methanol content (compare ref. 3).

Confirmation that the 3-line signal immediately obtained by adding aqueous $K_3Co(CN)_5$ to alcoholic 2-methyl-2-

nitrosopropane is that of the radical anion $(Me_3C\text{–}N\text{–}O\cdot)^-$ resulting from 1-electron transfer has been obtained by producing the same signal (a) by partial reduction of the nitroso-compound at pH > 11 with sodium borohydride and (b) by admixture of the nitroso-compound at pH 7—9 with aqueous t-butylhydroxylamine, when the 3-line signal was observed together with the 6 or 4 line signal of $Me_3C\text{–}NHO\cdot$ described by Wajer, Mackor, and De Boer.[3] As these workers have explained, the a_N and a_{N-H} splitting constants of this radical are separable in solutions containing a high percentage of methanol, but merge to 1·38 mT as the water content of the mixed solvent increases. However, reduction of 2-methyl-2-nitrosopropane by alkaline dithionite does not give $(Me_3C\text{–}N\text{–}O\cdot)^-$ but a radical stable over the pH range 4—10 having a_N 1·47, $a(^{13}C)$ 0·4 mT, g 2·0055, which may be an adduct of $(\cdot SO_2)^-$ to the nitroso-compound, *i.e.* the radical $Me_3C\text{–}N(O\cdot)\text{–}SO_2^-$, the first example of another new group of nitroxides. Further support for the view that the hyperfine splitting constants now assigned to radical-anions $(Alk\text{–}N\text{–}O\cdot)^-$ are those of primary reduction products of Alk–N=O comes from the finding that the reaction with 1-chloro-1-nitrosoethane[6] shows the splitting due to the remaining α-hydrogen and hence the chlorine atom must still be present in this radical.

The procedure used was that of ref. 2; the e.s.r. spectra were observed in a Varian E-4 spectrometer calibrated by the use of Frémy's salt. The nitroso-compounds were prepared by published methods, though solutions of 2-methyl-2-nitrosopropane were very easily and safely made without the use of peroxides by reducing 2-methyl-2-nitropropane to t-butylhydroxylamine with zinc powder and aqueous ammonium chloride,[7] oxidising the resulting solution, as needed, with ferric chloride or chromic acid, and extracting the blue product into ether.

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