Aryl-pentacyanocobalt Nitroxides—a New Group of Stable Free Radicals

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Summary The reduction of aromatic nitro-compounds by $Na_3Co(CN)_5$ gives stable radical-anions $\{(NC)_5Co–N(Ar)–O\cdot\}^{3-}$ (identified by e.s.r.) which can also be made by addition of $\{Co(CN)_5\}^{3-}$ to $Ar\cdot N{=}O$.

E.S.R.,[1,2] radiolysis,[3] and potentiometric[2] studies have shown that in neutral or alkaline solution aromatic nitro-compounds can readily be reduced by the 1-electron transfer route of equations (1)—(4), 2-electron or hydride transfer reduction being more difficult to effect.[4]

$$Ar\cdot NO_2 + e \rightarrow (Ar\cdot NO_2\cdot)^- \text{ (I)} \tag{1}$$

$$2(Ar\cdot NO_2\cdot)^- + H^+ \rightarrow ArNO_2 + ArNO + OH^- \tag{2}$$

$$(ArNO_2\cdot)^- + ArNO \rightarrow ArNO_2 + (Ar\cdot NO\cdot)^- \text{ (II)} \tag{3}$$

$$2(ArNO\cdot)^- + H_2O \rightleftharpoons Ar(N_2O)Ar \text{ (III)} + 20H^- \tag{4}$$

The radical (I) has a fairly long life-time in alkali, but with strong reducing agents it gradually changes to (II), also detectable by e.s.r., and finally to an azoxybenzene (III), which can be isolated.

In a survey of the actions of reducing agents on nitrobenzene we have investigated the action in aqueous ethanol of the extremely powerful reducing agent sodium pentacyanocobalt(II), $Na_3Co(CN)_5$. When equimolar quantities were used azoxybenzene and nitrobenzene could be isolated after completion of the reaction. An e.s.r. study in aqueous methanol under nitrogen by the flow method did not yield the spectrum of either (I) or (II), but a strong and much more complicated signal extending over 12 mT was observed on stopping the flow. This still showed at its verges the (1,2,1) × (1,3,3,1) hyperfine splitting indicative of a phenyl group, and persisted for over 24 h.

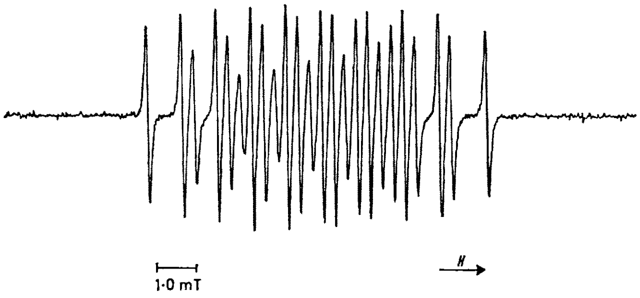
Substituted nitrobenzenes gave e.s.r. spectra of similar

E.s.r. data for radicals $\{(NC)_5Co–N(Ar)–O\cdot\}^{3-}$

Ar	g	$a(^{59}Co)$	$a(^{14}N)$	$a(o\text{-H})$	$a(m\text{-H})$	$a(p\text{-H})$
Ph	2·0051	1·06	1·38	0·32	0·11	0·32
p-$^-O_2C\cdot C_6H_4$	2·0055	1·02	1·30	0·31	0·10	—
p-$Cl\cdot C_6H_4$	2·0055	1·03	1·33	0·32	0·06	—
2,4,6-$Cl_3C_6H_2$	2·0052	1·67	1·25	—	0·07	—
2,3,5,6-Cl_4C_6H ..	2·0050	1·62	1·21	—	—	not detected

Splitting constants in millitesla: 1mT = 10 gauss.

stable radicals, and simplification of the pattern by the use of 2,3,5,6-tetrachloronitrobenzene, which in aqueous alcohol gives only a 3-line signal for (I; Ar = C_6Cl_4H),[5] gave the spectrum shown in the Figure. This has 24 lines in a 3 × 8 sequence and can only arise by spin-coupling of an odd electron with one ^{14}N ($I = 1$) and one ^{59}Co ($I = 7/2$) nucleus. Consequently our whole series of spectra, listed in the Table, can be assigned to radicals $(NC)_5Co–N(Ar)–O\cdot$ (IV) in which splitting due to nitrogen in the cyanide groups is not detectable.



FIGURE

A particularly strong spectrum of (IV; Ar = Ph) could be obtained by mixing, under nitrogen, equimolar solutions of $Na_3Co(CN)_5$ and of nitrosobenzene.

$$\{(NC)_5Co\cdot\}^{3-} + Ph\cdot N{=}O \rightarrow \{(NC)_5Co–N(Ph)–O\cdot\}^{3-} \quad (5)$$

This reaction (5) can be visualised as the direct addition of the cobalt atom to the nitrogen of a N=O group, and exactly parallels the ready acceptance by nitrosobenzene of free carbon radicals.

The radicals (IV) are evidently related structurally to the known pentacyanonitrosyl radical-anions $\{(NC)_5M\cdot NO\}^{n-}$ of iron and other transition metals.[6,7] However, another possible analogue, $\{(NC)_5Fe^{II}\cdot PhNO\}^{3-}$, the purple compound prepared from aquo-pentacyanoferroate and nitrosobenzene[8,9] is not a free radical: in solution it did not give an e.s.r. spectrum. This discovery of radicals (IV) has obvious implications in connection with the findings by Vlček and Rusina,[10] of the catalyses by cobalt complexes of the reduction of nitrobenzene by sodium borohydride, but we suggest that this catalysis is, in the main, due to the much easier reduction of nitrobenzene by one-electron donors than by hydride-transferring reagents.

Our e.s.r. measurements were made with a Varian E4 spectrometer.

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