Nitroxide Chemistry. Part XI.[1] Reaction of Trifluoronitrosomethane and Bis(trifluoromethyl)nitroxide with some Cobalt(II) Species

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Trifluoronitrosomethane reacts with alkaline solutions of the cobalt(II) species $[Co(CN)_5]^{3-}$ and $[Co(dmg)_2{\cdot}H_2O]$ to afford solutions of the relatively stable nitroxide radicals $[CF_3{\cdot}N(O{\cdot}){\cdot}Co(CN)_5]^{3-}$ and $[CF_3{\cdot}N(O{\cdot}){\cdot}Co(dmg)_2{\cdot}H_2O]$ respectively, the e.s.r. parameters of which are discussed. E.s.r. spectroscopic evidence suggests that under similar conditions the reaction between $[Co(CN)_5]^{3-}$ and bis(trifluoromethyl)nitroxide leads to the formation of the compound $[(CF_3)_2NO{\cdot}Co(CN)_5]^{3-}$; attempts to isolate this particular complex free from impurities were unsuccessful.

AROMATIC and aliphatic nitroso-compounds react with the pentacyanocobaltate(II) anion in aqueous solution to afford cobalt-substituted nitroxides (I) and (II) (R = aryl or tertiary alkyl) but these have only moderate stability;[2,3] thus (I; R = tertiary alkyl) is stable in solution for only a few minutes. The stability is slightly improved when the tertiary alkyl group contains

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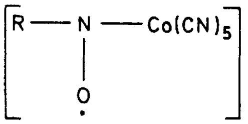
[1] Part X, R. N. Haszeldine, D. J. Rogers, and A. E. Tipping, *J.C.S. Dalton*, **1976**, 1056.

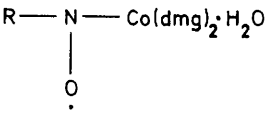
[2] M. G. Swanwick and W. A. Waters, *J. Chem. Soc.* (*B*), **1971**, 1059.

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

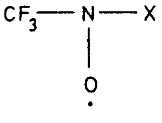
α-chlorine,[3] and where R = aryl the nitroxides are stable for up to 24 h. Since the presence of a trifluoromethyl group in other anionic nitroxides enhances stability, so much so that the pure nitroxides may be isolated,[4] we have investigated the stabilisation of cobalt-substituted nitroxides by incorporation of a trifluoromethyl group, and specifically have studied reactions between trifluoronitrosomethane and cobalt(II) species.


$[R\text{—}N(O^{\bullet})\text{—}Co(CN)_5]^{3-}$

(I)


$R\text{—}N(O^{\bullet})\text{—}Co(dmg)_2{\cdot}H_2O$

(II)


$CF_3\text{—}N(O^{\bullet})\text{—}X$

(III)

RESULTS AND DISCUSSION

(I; R = CF_3).—When trifluoronitrosomethane was bubbled through a freshly prepared aqueous solution of sodium pentacyanocobaltate(II) of pH $\geqslant$8, the e.s.r. spectrum of the resulting solution showed an intense signal having the parameters $a_{CF_3} = a_N = 13.92$ G, $a_{Co} = 10.25$ G, and $g = 2.0066$,* which was assigned to the nitroxide radical (I; R = CF_3). No asymmetric line broadening was observed in the spectrum in contrast to that for radical (I; R = aryl), ascribed to intramolecular anisotropy.[2,5] The spectrum of the new trifluoromethyl nitroxide radical persisted for several weeks when the solution was kept under nitrogen, and even when exposed to air the intensity of the spectrum decreased only slowly.

The electronic spectrum of a solution of this radical at pH $\geqslant$8 showed an intense absorption at 275 nm, and a less intense band at 375 nm, neither of which were present in the spectrum of $[Co(CN)_5]^{3-}$.[6] The bands at 275 and 375 nm decayed when the solution was kept, and a new band at 245 nm appeared; the first two absorptions, noted for other dialkyl [7a] and diaryl nitroxides,[7b] appear to be π–π^* and n–π^* transitions characteristic of the $>$N–O· group.[7c]

(II; R = CF_3).—Similar treatment of an aqueous methanol solution of bis(dimethylglyoximato)cobalt(II) at pH $\geqslant$7 with trifluoronitrosomethane gave an e.s.r. signal with the parameters $a_{CF_3} = a_N = 13.6$ G, $a_{Co} = 10.1$ G, and $g = 2.0065$, in agreement with the spectrum expected for the species (II; R = CF_3); the spectrum was less well resolved than that obtained from the ion (I; R = CF_3).

The ^{59}Co hyperfine coupling constants of radicals (I; R = CF_3) and (II; R = CF_3) are almost identical to those observed previously for other radicals of types (I) and (II).[2,3,5] The hyperfine splitting (h.f.s.) values obtained for the fluorine atoms of the CF_3 group and for the nitroxyl nitrogen atom are slightly higher (*ca.* 2—3 G) than those found for most nitroxides of the general type (III; X = CR_3 or NR_2).[8] Similarly, the nitrogen h.f.s. values in (I; R = aryl or tertiary alkyl) are somewhat higher than those in radicals of the type RR′NO· (R = R′ = aryl or alkyl; R = aryl, R′ = alkyl).[2,3] The *g* values of these new nitroxides are very similar to those obtained for other nitroxides of type (III).[8] There is some controversy regarding the origin of the ^{59}Co h.f.s. value. It has been suggested, on the basis of an analysis of the asymmetric linewidth effect, that the *d* orbitals on the cobalt are involved,[5] whereas analysis of the solid-state spectrum led to an alternative explanation by spin polarisation.[9] The results obtained in the present work tend to support the latter viewpoint. Nitroxides of type (III; X = CR_3 or NR_2) are believed to be less planar at the nitroxyl nitrogen than their non-fluorinated counterparts,[8,10] and, since deviation from planarity would be expected to change greatly the amount of *d* orbital overlap possible, the ^{59}Co h.f.s. value should change, whereas this value is virtually constant for all the organocobalt nitroxides so far observed.

The stabilities of the radicals (I; R = CF_3) and (II; R = CF_3) are markedly affected by the pH of the solution. The spectrum of the nitroxide (I; R = CF_3) is not observed below pH 8, but the radical is quite stable up to pH 12. Similarly, nitroxide (II; R = CF_3), which is somewhat less stable than (I; R = CF_3), is unstable below pH 7, but stable for several hours in solutions of up to pH 11. This contrasts with radicals of type (II; R = aryl or tertiary alkyl) which are stable in solution only over a narrower pH range (*ca.* 8—10), and decay to form the radical RNHO· up to pH 10, and the radical RNO$^{\cdot-}$ at higher pH.[2] There has been no indication of the formation of the species CF_3·NHO· or CF_3·NO$^{\cdot-}$ from radicals (I; R = CF_3) or (II; R = CF_3) under any conditions of pH. Another notable difference between these trifluoromethyl organocobalt nitroxides and their hydrocarbon analogues is that the e.s.r. spectrum of (I; R = tertiary alkyl) was always mixed with that of the cobalt(II) starting material, suggesting that the two species are in equilibrium.[3] The e.s.r. spectra obtained for the trifluoromethyl organocobalt nitroxides were free from cobalt(II) spectra, reflecting the enhanced stabilities of (I and II; R = CF_3).

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* 1 G = 10^{-4} T.

[4] R. E. Banks, D. J. Edge, J. Freear, and R. N. Haszeldine, *J.C.S. Perkin I*, 1974, 721.

[5] N. M. Atherton and D. Waldron, *J.C.S. Faraday II*, 1972, 413.

[6] N. Kelso King and M. E. Winfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3366.

[7] (*a*) R. M. Dupeyne, H. Lemaine, and A. Rassat, *Tetrahedron Letters*, 1964, 1781; (*b*) C. A. Kalashnikova, E. G. Rozantsev, and A. M. Chaikin, *Bull. Acad. Sci., U.S.S.R.*, 1965, **5**, 782; (*c*) A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, New York, 1968, p. 220.

[8] D. J. Edge, R. N. Haszeldine, and E. White, unpublished work.

[9] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Faraday II*, 1972, 1265.

[10] G. R. Underwood and N. L. Vogel, *Mol. Phys.*, 1971, **19**, 621.

Treatment of an aqueous solution of $Na_3[Co(CN)_5]$ with an excess of bis(trifluoromethyl) nitroxide caused complete disappearance of the spectrum due to the cobalt(II) species, without generation of any other radicals, suggesting the formation of the cobalt(III) complex $[(CF_3)_2NO\cdot Co(CN)_5]^{3-}$, although attempts to isolate this in a pure state have so far been unsuccessful.

The formation of the stable radicals reported in this work suggests that this nitroso-compound may be a useful 'spin probe' for the detection of transient cobalt(II) species in organometallic reactions, *e.g.* those related to the chemistry of Vitamin B_{12}.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E9 instrument and electronic spectra on a Perkin-Elmer SP 700 spectrometer. All the reactions were carried out under an atmosphere of oxygen-free nitrogen, with rigorously deoxygenated solvents.

Reactions of Sodium Pentacyanocobaltate(II).—(a) *With trifluoronitrosomethane.* A 0.05 mol dm^{-3} aqueous solution of sodium cyanide (4 cm^3) was added to a 0.01 mol dm^{-3} aqueous solution (4 cm^3) of cobalt(II) chloride, and the pH of the solution was adjusted to pH 9 with aqueous sodium hydrogencarbonate. An excess of trifluoronitrosomethane was passed through the solution for 5 min, and this was followed by the passage of nitrogen to remove the excess of trifluoronitrosomethane. The pH of the solution was recorded before transferring a sample of the solution to a solution cell for e.s.r. measurement.

A similar procedure, using a 10^{-4} mol dm^{-3} solution of $Na_3[Co(CN)_5]$, was employed for the determination of the electronic spectrum of the mixture.

(b) *With bis(trifluoromethyl) nitroxide.* A 0.01 mol dm^{-3} solution of $Na_3[Co(CN)_5]$ (lit.[11] e.s.r. spectrum) was prepared as described above, and bis(trifluoromethyl)nitroxide was bubbled through the solution (5 min) before recording the e.s.r. spectrum.

Reaction between Bis(dimethylglyoximato)cobalt(II) *and Trifluoronitrosomethane.*—An excess of trifluoronitrosomethane was passed for 5 min through a 0.01 mol dm^{-3} aqueous solution of bis(dimethylglyoximato)cobalt(II),[2] and the e.s.r. spectrum of an aliquot portion was recorded.

We thank the S.R.C. for a Research Studentship (to R. G. G. H.).

[5/1972 *Received, 9th October,* 1975]

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