Reactions of Oxygen with Tris(di-isopropylaminato)chromium(III)

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Summary Oxygen reacts rapidly with tris(di-isopropylaminatochromium(III); depending on the conditions, an unstable complex $Cr(O_2)(NPr^i_2)_3$ may be isolated and a chromium(IV) complex of di-isopropylnitroxide has been detected by e.s.r.

RECENTLY there has been an increased interest in the reactions of low-valent transition-metal compounds with oxygen[1] with emphasis on the understanding of the diversity of reactions pathways. Bradley and his co-workers[2,3] have shown that the use of bulky ligands produces reactive metal complexes containing co-ordinatively unsaturated metals. Of special interest is the highly reactive monomeric $Cr(NPr^i_2)_3$[2] which gave rise to a relatively stable mononitrosyl $Cr(NO)(NPr^i_2)_3$.[4] We now report some interesting results on the reactions of $Cr(NPr^i_2)_3$ with molecular oxygen.

A dilute solution (10^{-4}M in heptane or toluene) of $Cr(NPr^i_2)_3$ gave an e.s.r. signal (Figure, A) consisting of a single symmetrical line ($g = 1{\cdot}975$; width 10·8 gauss)[5] but like $V(NR_2)_4$[6] showed no nitrogen hyperfine splitting. Addition of small amounts (10 μl) of oxygen at low temperatures (*ca.* $-90°$) caused the disappearance of this signal which was replaced by a new one (Figure, B) which in turn was replaced by a third signal (Figure, C).

Species B ($g = 1{\cdot}971$; $a_N = 11{\cdot}46$; $a_H = 3{\cdot}34$ gauss) shows coupling with one nitrogen nucleus and two equivalent protons, whilst C which is clearly resolved ($g = 2{\cdot}0026$; $a_N = 15{\cdot}0$; $a_H = 3{\cdot}9$ gauss) may be identified as di-isopropylnitroxide.[7] Species B was unstable even at $-90°$ whereas C was reasonably stable at room temperature and was also obtained directly from A by a single addition of an excess of oxygen. Addition of an excess of oxygen to dilute solutions of $Cr(NPr^i_2)_3$ at room temperature caused loss of signal A without the formation of B or C. Small additions of oxygen to dilute solutions of $Cr(NPr^i_2)_3$ in tetrahydrofuran at low temperature caused the disappearance of A and the formation of C without the intervention of B.

At higher concentration (10^{-3}M) in heptane, the reaction gave broad signals whose g values could be related to those of B and C without resolvable hyperfine features. At 10^{-2}M, the reaction led simply to the loss of signal A.

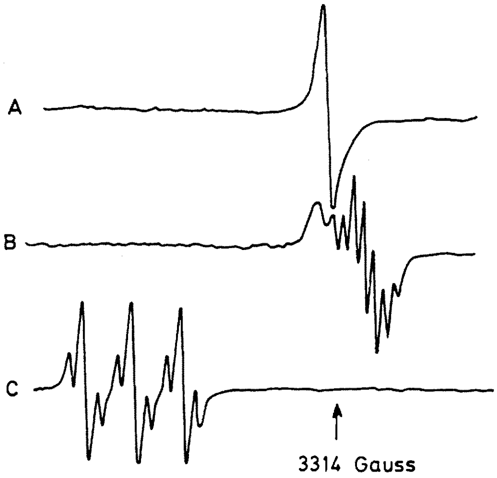

FIGURE. *E.s.r. spectra of reaction mixture of* $Cr(NPr^i_2)_3$ *and oxygen*

A reaction pathway consistent with these observations is as follows:

$$Cr^{III}(NPr^i_2)_3\ (A) + O_2 \rightarrow Cr^{IV}O(NPr^i_2)_2,(ONPr^i_2)\ (B) \quad (1)$$

$$B \rightleftharpoons Cr^{IV}O(NPr^i_2)_2 + ONPr^i_2\ (C) \quad (2)$$

$$2ONPr^i_2 \rightarrow \text{Products} \quad (3)$$

$$Cr(NPr^i_2)_3 + ONPr^i_2 \rightarrow Cr^{IV}O(NPr^i_2)_2 + \text{Products} \quad (4)$$

Species B is considered to be a nitroxide complex of the chromium(IV) compound for the following reasons. The spectral parameters are consistent with a nitroxide complex and are significantly different from those of the free nitroxide radical. Also dialkylnitroxide complexes with metal compounds are known and in $(R_2NO)AlCl_3$[8] the large value of a_N compared with the smaller value in B may well be due to the absence of *d*-electrons in aluminium and their presence in chromium.

When oxygen was added to more concentrated solutions (*ca.* 1M) of $Cr(NPr^i_2)_3$ in pentane or toluene at 0° the e.s.r. signal due to $Cr(NPr^i_2)_3$ ($g = 1{\cdot}977$) did not disappear but was considerably enhanced in intensity without changing its *g*-value. No nitroxide radicals or complexes were detected under these conditions. However, addition of oxygen to $Cr(NPr^i_2)_3$ in pentane at -10 to $+5°$ led to the isolation of a very volatile unstable blue crystalline compound D which gave a satisfactory chromium analysis for $Cr(O_2)(NPr^i)_3$ or $CrO(NPr^i_2)_2(ONPr^i_2)$. Its electronic spectrum (mull) gave bands at 30,100; 17,870; and 14,180 (sh) cm^{-1} whilst its magnetic susceptibility gave temperature and field-dependent values for μ_{eff} (2·03 at 0° to 1·58 at $-175°$). The mass spectrum gave a peak at *m/e* 284, corresponding to (D less NPr^i_2). In the i.r. spectrum a strong band at 980 cm^{-1} not present in $Cr(NPr^i_2)_3$ could well be due to a Cr=O stretching frequency. Further discussion of these results is deferred until full details and additional results are published later.

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