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Cobaloxime(II)-Catalysed Oxidation of Isocyanides to Isocyanates and Nitrosobenzene to Nitrobenzene with Dioxygen

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Catalytic oxygen insertion and dehydrogenation reactions mediated by transition metal complexes are relevant to biological oxidation processes. They may also provide new synthetic paths *via* homogeneous catalysis, utilising inexpensive atmospheric dioxygen [1, 2].

Recent reports reveal the ability of cobaloxime(II) complexes** to catalyse the selective oxidation of organic substrates, such as hydroquinone, hydrazobenzene and Ph_3P [3], with dioxygen under mild conditions. We now report the extension of these catalytic oxidations to isocyanides and nitrosobenzene. The oxidation of these substrates usually occurs much less readily than that of the compounds reported in Ref. [3]. To our knowledge there has been only a single report on catalytic isocyanide oxidation by dioxygen [4].

n-Butyl and n-octyl isocyanide were found to undergo catalytic oxidation to the corresponding isocyanates in the presence of the cobaloxime(II) complexes listed in Table I. The reaction occurs at room temperature in an atmosphere of dioxygen. GC and TLC analyses show a 100% selectivity in both cases. The yields are moderate to low but catalysis is clearly involved as witnessed by the blank experiment (entry 7, Table I). No oxidation is observed when the cobaloxime(II) catalysts are replaced by their cobaloxime(III) derivatives, *e.g.* $pyCo(Hdmg)_2OH$. Cobaloxime(III) complexes do not form adducts with O_2, as opposed to cobaloxime(II) whose dioxygen adducts have been characterised [5]. Consequently, cobaloxime(II)-dioxygen complexes are key intermediates in the catalytic process.

The initial rate of O_2-uptake from the gas phase and the UV-Vis spectra of the initial solution are independent of the axial ligand(s) in the catalyst complex. Both the initial rate and the spectra remain the same if independently prepared $(R\text{-}NC)_2Co(Hdmg)_2$ is used as catalyst. Apparently, the cobaloxime(II) catalysts used are immediately converted to this species upon dissolution in the presence of excess R-NC. The situation resembles the oxidation of $(Bu\text{-}NC)_4Ni$ by O_2 or other oxidants [4].

Nitrosylcobaloxime(II) reacts with dioxygen to form nitro- and nitratocobaloximes [6, 7]. The catalytic oxidation of nitrosobenzene yields nitrobenzene as the only product, as shown by GC and IR spectroscopy (Table II). The reaction is very slow but the presence of cobaloxime is absolutely necessary (cf. blank, Table II). The cobaloxime(III) complex $(Ph_3P)Co(Hdmg)_2OH$ is a less active catalyst (entry 3, Table II), probably requiring reduction by Ph-NO to cobaloxime(II).

Work is in progress to elucidate mechanistic details of the catalytic oxygen insertions.

TABLE I. Catalytic Oxidation of Isocyanides (R-NC) (T = 23 °C; O_2 pressure 1 bar; solvent acetone; 2×10^{-2} *M* catalyst; 0.1 *M* isocyanide; reaction time 16 h).

Catalyst[a]	R	R-NCO yield[b] (%)
$(Ph_3P)_2Co(Hdmg)_2$	Butyl	46
$(Ph_3P)_2Co(Hdmg)_2$	Butyl	28[c]
$pyCo(Hdmg)_2$	Butyl	42
$pyCo(Hdmg)_2$	Octyl	42
$(Ph_3P)_2Co(Hdmg)_2$	Octyl	44
$(NEt_3)Co(Hdmg)_2$	Octyl	43
None	Octyl	<1 (24 h)

[a]Catalysts were prepared as in Ref. 5. [b]Selectivity to R-NCO is 100% in all cases. [c]Catalyst concentration 1×10^{-2} *M*; reaction time 26 h.

TABLE II. Catalytic Oxidation of Nitrosobenzene (T = 23 °C; O_2 pressure 1 bar; solvent acetone; 2×10^{-2} *M* catalyst; 0.1 *M* nitrosobenzene; reaction time 72 h).

Catalyst[a]	Nitrobenzene yield (%)[b]
$(Ph_3P)_2Co(Hdmg)_2$	28
$(Ph_3P)_2Co(Hdmg)_2$	12[c]
$(Ph_3P)Co(Hdmg)_2OH$	8
$pyCo(Hdmg)_2$	22
None	1 (72 h)

[a]Catalysts were prepared as in Ref. 5. [b]Selectivity to $PhNO_2$ is 100% in all cases. [c]1×10^{-2} *M* catalyst.

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**Cobaloxime(II) is the square-planar $Co(Hdmg)_2$ complex, where Hdmg is the monoanion of dimethylglyoxime. It binds ligands such as amines or phosphines in its axial position(s).

References

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