Catalytic Oxidation of Isocyanides: a Nickel–Oxygen Complex

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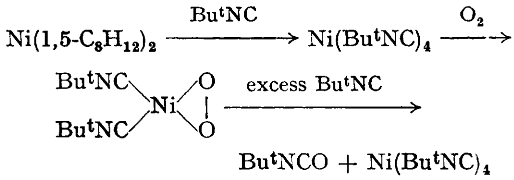
DURING studies on the catalytic oxidation of t-alkyl isocyanides available in our laboratory[1] a new catalytically active nickel–oxygen complex has been isolated. Recent reports on discrete oxygen complexes[2–5] prompted us to publish our results.

A pale yellow solution of $Ni(Bu^tNC)_4$ in diethyl ether absorbed approximately one mole of oxygen at −20°, when a pale green crystalline precipitate formed. The product was filtered at that temperature, washed with dry ether, and dried *in vacuo*. Elemental analysis conformed to a composition, $Ni(Bu^tNC)_2O_2$. (Found: C,46·0; H, 7·0; O, 12·9. Calc. for $C_{10}H_{18}N_2O_2Ni$, C, 46·7; H, 7·0; O, 12·5%). The complex in the crystalline state exhibits considerable thermal stability, decomposing slowly at room temperature and rapidly at 95°. It is apparently more stable than $Ni(PPh_3)_2O_2$.[3] However, the complex when dissolved in benzene or chloroform deteriorates immediately at room temperature. The infrared spectrum (Nujol mull) showed strong absorptions at 895 and 2180 cm.$^{-1}$, assignable to the peroxy (–O–O–) and –N≡C stretching vibrations, respectively, and no band in the region 2200—2400 cm.$^{-1}$, which indicates absence of –N=C=O group. The n.m.r. spectrum (chloroform) at −10° showed a singlet at τ 8·55 due to a t-butyl group, implying that the complex is diamagnetic. The successful preparation of this oxygen complex constitutes the first reported example of a discrete compound involving a peroxy-ligand and an unsaturated system subject to oxidation.

When oxygen was introduced at ambient temperature into a 1-molar solution of Bu^tNC in ether to which bis(cyclo-octa-1,5-diene)nickel (2 mole % based on the isocyanide) had been added, oxygen up-take ensued smoothly under atmospheric pressure, homogeneity being apparently kept. Distillation of the reaction solution produced colourless Bu^tNCO, b.p. 85·5°, in 60—70% yield, which was identified by converting it into di-t-butylurea. The yield of the isocyanate corresponded to the amount of oxygen absorption. Oxidation of Bu^tNC using $Ni(Bu^tNC)_4$ or $Ni(Bu^tNC)_2O_2$ gave the isocyanate in comparable yields.

The oxidation may be formulated as follows:



The oxidation of Bu^tNC with molecular oxygen was much faster with bis(cyclo-octa-1,5-diene)cobalt than with the corresponding nickel complexes. Chlorotris(triphenylphosphine)rhodium which was reported to give an oxygen complex[5] was also found to be effective catalytically for the oxidation of isocyanides.

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