Catalytic Reduction of Nitric Oxide to Nitrous Oxide by Alcohols mediated by Copper(I) Complexes

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In a reaction relevant to environmentally important processes carried out by copper-containing enzymes and heterogeneous catalysts, copper(I) complexes of 1,4,7-triisopropyl-1,4,7-triazacyclononane dissolved in alcohols (*e.g.* benzyl alcohol) efficiently promote the reduction of NO to N_2O by the solvent at room temperature, yielding the respective carbonyl compounds (*e.g.* benzaldehyde).

Interconversions of nitrogen oxides such as nitrate (NO_3^-), nitrite (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O) comprise key aspects of the global nitrogen cycle that are promoted by metal ions in both biological and heterogeneous catalytic systems.[1] Important examples of such reactions involve copper, such as (i) the sequential reduction of NO_2^- to NO, N_2O, and ultimately N_2 by copper-containing enzymes in denitrifying bacteria[2] and (ii) the decomposition of NO to N_2O and/or N_2 (plus O_2) by copper-exchanged zeolites that have attracted attention due to their potential utility in pollution control.[3] We,[4,5] and others,[6,7] have taken a synthetic modelling approach toward understanding the pathways by which these complex transformations are effected, with specific emphasis to date on the characterization of structural and spectroscopic analogues of active site species. More recent attention toward functional modelling has led to the discovery of stoichiometric formation of N_2O from NO and/or NO_2^- at mono- and di-nuclear copper centres in synthetic compounds.[5,7] Here we report catalysis of the NO → N_2O conversion by discrete copper complexes in solution using simple alcohols as the reducing agents.[8]

Solutions of [LCu(CH_3CN)]PF_6[4] or [LCuCl]† (L = 1,4,7-triisopropyl-1,4,7-triazacyclononane)[9] in alcohols [MeOH, EtOH, $(Me)_2CHOH$, or $PhCH_2OH$] were exposed to excess NO in a sealed vessel at ambient temperature and the headspace gas was monitored by gas chromatography.‡ Evolution of N_2O was observed until the NO was consumed; subsequent readdition of NO allowed continuation of N_2O production at the original rate of *ca.* ten turnover per h (Fig. 1).§ This cycle was repeated more than four times without significant diminution of the rate of N_2O production when precautions were taken to prevent exposure of the system to air (which oxidises the copper species and irreversibly arrests catalytic activity), indicating that the active copper-containing catalyst is quite stable. Concomitant generation of carbonyl compounds during the reaction was confirmed for the cases where isopropanol or benzyl alcohol were used as solvents *via* ^1H NMR and GCMS analysis of the volatile products after a typical catalytic run; benzaldehyde production in the latter instance was further verified by preparation and isolation of its semicarbazone (87% yield based on amount of N_2O formed). Water was also identified as a reaction product by ^1H NMR spectroscopy. The combined evidence thus supports the overall transformation shown in eqn. (1).

$$2NO + RCH_2OH \xrightarrow[\text{(R = H, Me or Ph; for isopropanol the product was acetone)}]{\text{catalyst (0.1 mol \%)}} N_2O + H_2O + RCHO \quad (1)$$

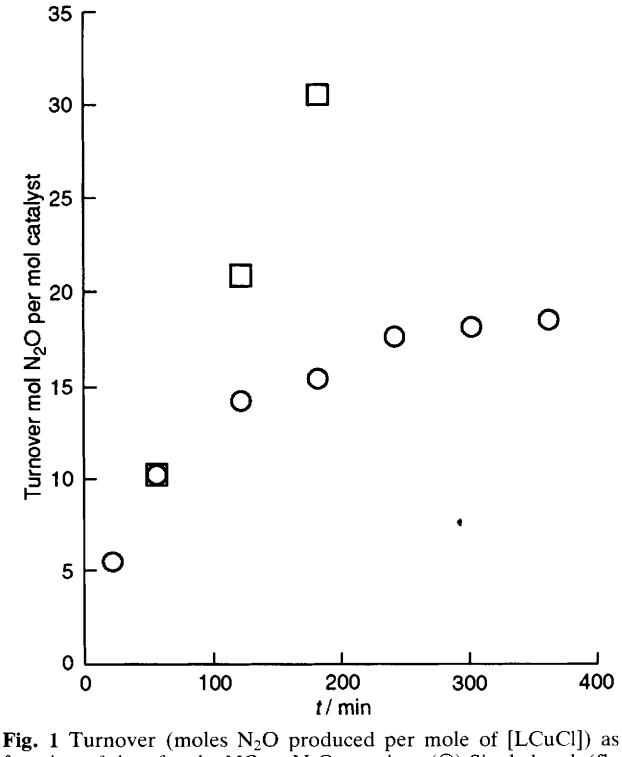

Fig. 1 Turnover (moles N_2O produced per mole of [LCuCl]) as a function of time for the NO → N_2O reaction. (○) Single batch (flask filled with NO only at the beginning of the experiment). (□) Repeat batches (flask evacuated and then filled with NO every hour). Under these latter conditions of constant NO pressure, the rate of N_2O production was 0.06 mmol h^{-1}.

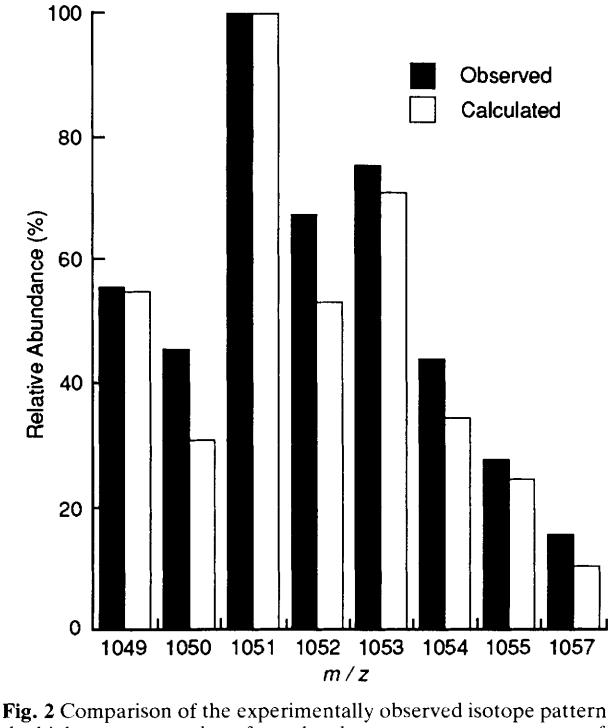

Fig. 2 Comparison of the experimentally observed isotope pattern for the highest mass envelope from the electrospray mass spectrum of the green solution obtained upon treatment of [LCuCl] in MeOH with NO at −78 °C with that calculated for the ion $[(LCu)_3(N_2O_2)Cl]^+$

Although mechanistic details for this reaction are currently sparse, we have obtained initial evidence which suggests that multicopper species may be involved. When a solution of the precatalyst [LCuCl] in MeOH was treated with NO (1 atm) at −78 °C a deep green colour developed (λ_{max} = 670 nm) but no N_2O evolved. An electrospray mass spectrum of this cold solution contained an envelope of peaks consistent with a trimer of formula $[(LCu)_3(N_2O_2)Cl]^+$ (Fig. 2). It is unclear from these data alone whether the species contains two nitrosyl (NO) ligands or an N–N coupled $N_2O_2^{n-}$ (n = 0, 1, or 2) group. Warming of the solution to room temperature induced N_2O evolution, suggesting—but certainly not proving—that the complex is a reaction intermediate. Future work will focus on testing this idea and on more complete characterization of the green compound.

The catalytic reduction of NO to N_2O by alcohols described herein complements other NO → N_2O reactions promoted by copper complexes, in which reductive NO coupling is linked to oxidation of a dicopper(I) unit (to an oxo-dicopper(II) compound),[7] of NO (to NO_2 in an overall disproportionation),[5] or of an electrode (in an electrocatalytic process).[8] The multiplicity of pathways followed attests to the effects of differences in complex nuclearities and in ligand environments on copper-mediated nitrogen oxide reduction, the deconvolution of which continues to stimulate research.

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Footnotes

† The complex was prepared in 90% yield by mixing equimolar amounts of 1,4,7-triisopropyl-1,4,7-triazacyclononane and CuCl in THF. ^{1}H NMR (C_6D_6, 300 MHz) δ 2.95 (septet, J 6.6 Hz, 3H), 2.34–2.20 (m, 6H), 1.76–1.62 (m, 6H), 1.15 (d, J 6.6 Hz, 18H) ppm; ^{13}C {^{1}H} NMR (C_6D_6, 75 MHz): δ 57.5, 50.2, 19.4 ppm; FABMS (*m*-nitrobenzylalcohol) *m/z* 353 (M^+), 318 (M^+ − Cl); satisfactory elemental analysis (C, H, N) was obtained.

‡ The reaction was carried out in a 140 ml Schlenk flask containing 1 ml of alcohol and 5.56×10^{-5}–2.82×10^{-4} mol of complex; the flask and its contents were degassed by three successive freeze-pump-thaw cycles, and the internal pressure was adjusted to 1 atm of NO.

§ The simple copper(I) complexes $[Cu(CH_3CN)_4]PF_6$ or CuCl in the absence of ligand L did not catalyse N_2O formation.

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