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

**Samiran Mahapatra, Jason A. Halfen and William B. Tolman***

*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA*

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).

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

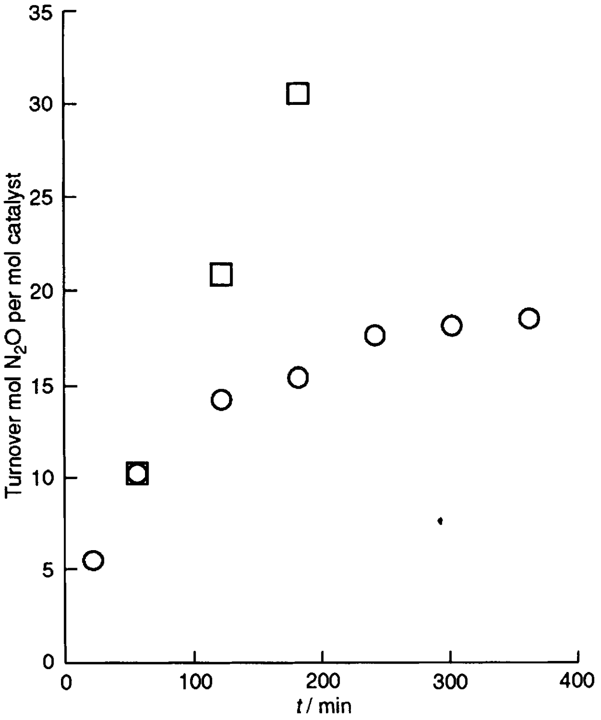

**Fig. 1** Turnover (moles $N_2O$ produced per mole of [LCuCl]) as a function of time for the NO → $N_2O$ reaction. (○) Single batch (flask filled with NO only at the beginning of the experiment). (□) Repeat batches (flask evacuated and then filled with NO every hour). Under these latter conditions of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

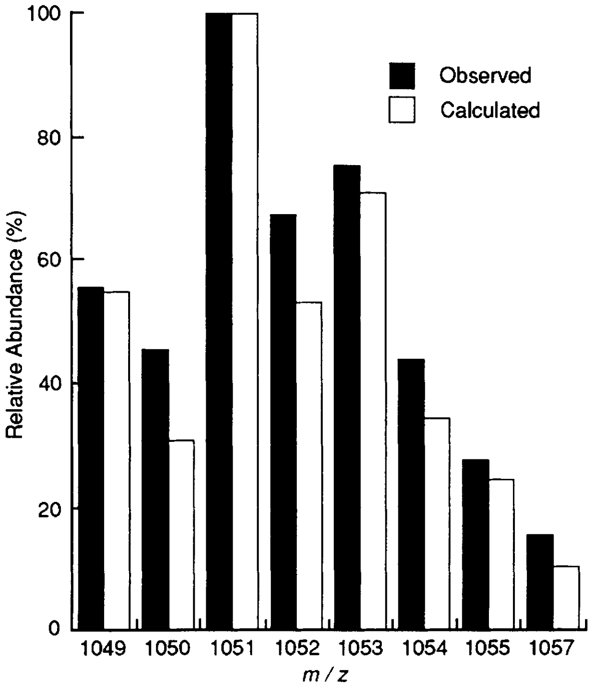

**Fig. 2** Comparison of the experimentally observed isotope pattern for the highest mass envelope from the electrospray mass spectrum of the green solution obtained upon treatment of [LCuCl] in MeOH with NO at −78 °C with that calculated for the ion $[(LCu)_3(N_2O_2)Cl]^+$

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 ($\lambda_{max}$ = 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.

This research was supported by the National Institutes of Health (GM47365), the Searle Scholars Program/Chicago Community Trust, and the National Science Foundation (National Young Investigator Award).

*Received, 5th April 1994; Com. 4/02027H*

---

## 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. $^1H$ 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; $^{13}C$ {$^1H$} 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 $5.56 \times 10^{-5}$–$2.82 \times 10^{-4}$ 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.

## References

1 V. Smil, *Carbon Nitrogen Sulfur: Human Interference in Grand Biospheric Cycles*, Plenum Press, New York, 1985, pp. 115–250; J. N. Armour, *Appl. Catal.*, 1991, **78**, 141.

2 P. M. H. Kroneck, J. Beuerle and W. Schumacher, in *Degradation of Environmental Pollutants by Microorganisms and their Metalloenzymes*, ed. H. Sigel and A. Sigel, Marcel Dekker, New York, 1992, vol. 28, pp. 455–505; E. Libby and B. A. Averill, *Biochem. Biophys. Res. Commun.*, 1992, **187**, 1529; R. W. Ye, I. Toro-Suarez, J. M. Tiedje and B. A. Averill, *J. Biol. Chem.*, 1991, **266**, 12848; C. L. Hulse; B. A. Averill and J. M. Tiedje, *J. Am. Chem. Soc.*, 1989, **111**, 2322; M. A. Jackson, J. M. Tiedje and B. A. Averill, *FEBS Letters*, 1991, **291**, 41; Z. H. L. Abraham, D. J. Lowe and B. E. Smith, *Biochem. J.*, 1993, **295**, 587.

3 Recent exemplary references: E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, *J. Catal.*, 1992, **136**, 510; Y. Li and W. K. Hall, *J. Catal.*, 1991, **129**, 202; M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, *J. Phys. Chem.*, 1992, **96**, 9360.

4 J. A. Halfen, S. Mahapatra, M. M. Olmstead and W. B. Tolman, *J. Am. Chem. Soc.*, 1994, **116**, 2173; C. E. Ruggiero, S. M. Carrier, W. E. Antholine, J. W. Whittaker, C. J. Cramer and W. B. Tolman, *J. Am. Chem. Soc.*, 1993, **115**, 11285 and references therein; J. A. Halfen and W. B. Tolman, *J. Am. Chem. Soc.*, 1994, **116**, in the press.

5 C. E. Ruggiero, S. M. Carrier and W. B. Tolman, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 895.

6 P. P. Paul, Z. Tyeklár, A. Farooq, K. D. Karlin, S. Liu and J. Zubieta, *J. Am. Chem. Soc.*, 1990, **112**, 2430.

7 P. P. Paul and K. D. Karlin, *J. Am. Chem. Soc.*, 1991, **113**, 6331.

8 Electrocatalytic reduction of NO to $N_2$ by a copper complex in aqueous solution has been reported: N. Komeda, H. Nagao, G. Adachi, M. Suzuki, A. Uehara and K. Tanaka, *Chem. Lett.*, 1993, 1521.

9 G. Haselhorst, S. Stoetzel, A. Strassburger, W. Walz, K. Wieghardt and B. Nuber, *J. Chem. Soc., Dalton Trans.*, 1993, 83.