

Homogeneous Catalytic Reduction of Nitrous and Nitric Oxides to Dinitrogen by Carbon Monoxide

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Catalytic reductions of N_2O and NO by CO to N_2 can be achieved at 100°C in solutions containing $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and a base: the highest rate for the N_2O reduction of 25.2 turnovers per hour in dimethyl sulphoxide was obtained using KOH as the base.

The reductions of nitric and nitrous oxides by carbon monoxide (equations 1—3) have received continuous attention for some time owing to the relevance of these reactions to the control of air pollution.¹ While numerous reports on the heterogeneous catalysis of reactions 1—3 have appeared,¹ the analogous work on homogeneous systems has been limited to the reaction of NO with CO to give N_2O (equation 1).^{2–7} Further reduction of N_2O by CO mediated by a soluble catalyst has not been achieved despite the fact that the reaction is thermodynamically favourable ($\Delta G^\circ -86.21$ kcal; $1\text{ kcal} = 4.184\text{ kJ}$). It is well known that N_2O is a rather inert gas and an extremely poor ligand.^{8–10} The latter property precludes the activation of N_2O by metal complexes through co-ordination. Nevertheless, the deoxygenation of N_2O by several transition-metal complexes has been revealed.^{8,9} In particular, a catalytic oxidation of PPh_3 to Ph_3PO by N_2O using $[(\text{Ph}_3\text{P})_3\text{Co}(\text{H})\text{N}_2]$ has been reported.¹¹ The challenge

to find suitable homogeneous systems for the catalysis of reaction 2 prompted us to undertake the current study. We herein report for the first time several systems which are capable of catalysing the reduction of N_2O and NO to N_2 by CO , and which function at a much lower temperature than the corresponding heterogeneous process.¹

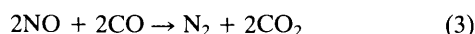
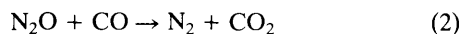
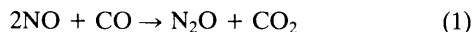
The strong reducing ability of rhodium carbonyl anions and the easy generation of these species from rhodium compounds under CO atmosphere in the presence of base^{12–15} led us to examine the efficacy of rhodium species in the catalysis of reactions 2 and 3. An effective catalyst system was prepared from $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (0.154 mmol), base (2.2 mmol), H_2O (1.8 ml), and solvent (30 ml). The rhodium complex was placed with the solvent in a 335 ml vessel which was evacuated and then charged with CO and N_2O (or NO) to an initial partial pressure of 350 Torr. An approximate 40 Torr of CH_4 was also added as an internal standard for g.c. analysis. The solution

Table 1. Results of the catalytic reduction of N_2O and NO by CO .^a

Entry	Solvent ^e	Base	Time (h)	Gas consumed, ΔP (Torr)			Gas produced, ΔP (Torr)		
				CO	NO	N_2O	N_2O	CO_2	N_2
I ^b	DMSO	KOH^c	2	335		318		0	334
II	DMSO	$\text{Me}_4\text{N}^+\text{OH}^-$	7	369		351		315	352
III	DMF	$\text{Me}_4\text{N}^+\text{OH}^-$	7	276		258		178(262) ^d	296
IV	HMPA	$\text{Me}_4\text{N}^+\text{OH}^-$	7	214		227		111	210
V	EG	$\text{Me}_4\text{N}^+\text{OH}^-$	7	20		23		10	18
VI	DMF	Et_3N^c	7	19		14		14	17
VII	DMF	$(\text{HOC}_2\text{H}_4)_3\text{N}^c$	7	17		15		10	14
VIII	DMF	Et_3N	7	51		59		35	46
IX	DMF	$\text{MeCO}_2\text{K}^{c,f}$	7	221		232		137(209) ^d	214
X ^g	DMF	$\text{Me}_4\text{N}^+\text{OH}^-$	8	184	459		110	165	93
XI ^h	DMF	$\text{Me}_4\text{N}^+\text{OH}^-$	12	227		205		133	217

^a Unless otherwise stated, each catalyst solution was prepared according to the procedure described in the text. Runs I—IX and XI were conducted at $100 \pm 1^\circ\text{C}$ under an initial partial pressure of ca. 350 Torr at 32°C for N_2O and CO . ^b $[\text{Rh}(\text{CO})_4](\text{Ph}_3\text{P})_2\text{N}$, 0.106 mmol; KOH (ground), 1.50 g. ^c No water was added. ^d The amount of CO_2 produced after neutralization with H_2SO_4 . ^e DMSO = dimethyl sulphoxide, DMF = dimethylformamide, HMPA = hexamethylphosphoramide, EG = ethylene glycol. ^f One equivalent of 18-crown-6 was added. ^g Initial partial pressure: NO , 459; CO , 275 Torr at 32°C . ^h $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 0.382 mmol.

was stirred at room temperature for 5 min and the specified amount of base and H₂O were added to the solution through a septum. The system was heated with stirring at 100 °C for ca. 7 h. While quantitative analysis (g.c.) of each gas component was performed according to previous methods,^{5,16} the identities of the products were verified from the g.c.-mass spectroscopic data of these components. Table 1 presents the quantitative data of reaction runs under different conditions.



The results of runs I–IX clearly demonstrate that the N₂O and CO consumed is equal to the N₂ formed within experimental error as the stoichiometry of equation 2 predicts. The discrepancy in CO₂ produced in most runs is a consequence of the absorption of CO₂ by base as shown by the release of a substantial amount of the gas on addition of acid to the catalytic solution at the end of the reaction (runs III and IX). Direct evidence showing that the N₂ formed is from N₂O comes from the use of ¹⁵NNO yielding ¹⁵NN having the same abundance (99.2%) of ¹⁵N label as ¹⁵NNO (99.8%). As indicated by the data in Table 1, the catalytic activity is affected dramatically by the solvent and base employed. The highest activity is observed in DMSO using KOH as the base with a rate of 25.2 turnovers per hour based on N₂ produced. In protic solvent or in amine solution, the activity decreases to less than 1/10 of that in DMSO using Me₄N⁺OH[−] as the base. In the absence of base, the catalyst does not reduce N₂O to N₂ with or without CO present. Under similar conditions, the catalyst systems also catalyse the reduction of NO to N₂ (run X). Monitoring of the gas components by g.c. reveals that NO is first reduced to N₂O and then to N₂. It is noteworthy that ruthenium complexes also catalyse the reduction of N₂O to N₂ (equation 2) under similar conditions albeit with lower activities (run XI).

The rhodium carbonyls observed during the catalysis of reaction 2 in the most active solution, I, were Rh(CO)₄[−] and Rh₄(CO)₁₁^{2−}.† If the gas mixture was removed and replaced

by 1 atm of CO, Rh₄(CO)₁₁^{2−} was converted into Rh(CO)₄[−] in 10 min. The reaction of [Rh(CO)₄](Ph₃P)₂N in DMF with N₂O at ambient temperature, produced 3.74 mol of N₂ and 1.81 mol of CO₂ and consumed 3.92 mol of N₂O per mol of Rh(CO)₄[−] in 30 min. In addition, the use of [Rh(CO)₄](Ph₃P)₂N alone in DMSO for the catalysis of reaction 2 resulted in a very high activity of 51.1 turnovers per hour in the first 10 min at 100 °C. These observations indicate that Rh(CO)₄[−] is most likely the species responsible for N₂O reduction to N₂ during the catalysis.

It appears that the reactivity of N₂O toward Rh(CO)₄[−], coupled with the ready reduction of rhodium carbonyl clusters to Rh(CO)₄[−] by CO in basic solution makes possible the catalysis of reaction 2 by these clusters.

We thank the National Science Council of the Republic of China for support of this work.

Received, 4th November 1985; Com. 1547

References

- 1 E.g., M. Shelef, *Catal. Rev. Sci. Eng.*, 1975, **11**, 1; B. Harrison, M. Wyatt, and K. G. Gough, 'Catalysis,' The Royal Society of Chemistry, London, 1982, vol. 5, p. 147, and references therein.
- 2 S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, and R. H. Walter, *J. Chem. Soc., Chem. Commun.*, 1974, 809.
- 3 J. Reed and R. Eisenberg, *Science*, 1974, **184**, 568.
- 4 S. Bhaduri and B. F. G. Johnson, *Transition Met. Chem.*, 1978, **3**, 156.
- 5 C. D. Meyer and R. Eisenberg, *J. Am. Chem. Soc.*, 1976, **98**, 1364.
- 6 J. A. Kaduk and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3070.
- 7 M. Kubota, K. J. Evas, C. A. Koerntgen, and J. C. Marsters, *J. Am. Chem. Soc.*, 1978, **100**, 342.
- 8 R. G. S. Banks, R. J. Henderson, and J. M. Pratt, *Chem. Commun.*, 1967, 387.
- 9 F. Bottomley, I. J. B. Lin, and M. Mukaida, *J. Am. Chem. Soc.*, 1980, **102**, 5238.
- 10 M. L. H. Green and C. R. Lucas, *J. Chem. Soc., Dalton Trans.*, 1972, 1000.
- 11 A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *J. Am. Chem. Soc.*, 1971, **93**, 371.
- 12 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37.
- 13 S. Martinengo, A. Fumagalli, P. Chini, V. G. Albano, and G. Ciani, *J. Organomet. Chem.*, 1976, **116**, 333.
- 14 V. G. Albano and G. Ciani, *J. Organomet. Chem.*, 1976, **116**, 333.
- 15 P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 21.
- 16 C. H. Cheng and R. Eisenberg, *J. Am. Chem. Soc.*, 1978, **100**, 5968.
- 17 J. L. Vidal and R. C. Schoening, *Inorg. Chem.*, 1982, **21**, 438.

† The i.r. data for Rh(CO)₄[−]: 1900 cm^{−1}; for Rh₄(CO)₁₁^{2−}: 1940, 1810 cm^{−1}. These values are in agreement with the data reported previously (ref. 15, 17, and 13).