Electrocatalytic Reduction of Nitrous Oxide to Dinitrogen at a Mercury Electrode using Ni^{II} Complexes of Macrocyclic Polyamines

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Reduction of N_2O takes place efficiently at a Hg electode to give only N_2 in yields close to 100% in the presence of a small amount of a Ni^{II} complex of [15 or 14]aneN$_4$ {[15 or 14]aneN$_4$ = 1,4,8,12(or 11)-tetra-azacyclopenta(or tetra)decane} in aqueous solution.

Metal complexes of macrocyclic polyamines have received much attention because of their variety of functions.[1] Catalytic activity is one of the most interesting and promising aspects,[2—4] because unusual valence states of central transition metals can be obtained and also structures of complexes are similar to those of active centres of enzymes. In the present experiment, Ni^{II} complexes of macrocyclic polyamines such as [15 or 14]aneN$_4$ have been demonstrated, for the first time, to be efficient catalysts for electrochemical reduction of nitrous oxide, N_2O, in water to give only N_2 with extremely large turnover frequencies and current yields close to 100% at a Hg electrode. The present results are interesting from the viewpoints of (i) development of new techniques for protection of the environment (N_2O is one of the main compounds responsible for the greenhouse effect), (ii) application of metal complexes of macrocyclic polyamines to new catalytic reactions, and (iii) designing artificial catalysts as models of natural N_2O reductases.

Kuwabata et al.[5] have shown in their report on nitrate and nitrite reduction on a Mo–Fe cluster modified electrode that

N_2O was also catalytically reduced to N_2 at the electrode with a 50% current efficiency. Co^{III} and Ni^{II} complexes of [14]aneN$_4$ have also been used as catalysts in the electrochemical reduction of nitrate and nitrite[4] to give hydroxylamine and ammonia. However, reduction of N_2O using such complexes has not yet been given to date.

Macrocyclic polyamines were prepared according to the literature,[6] and their metal complexes were obtained by mixing a metal ion of interest and a macrocyclic polyamine, as a ligand, in ethanol and/or methanol.[6] Cyclic voltammograms were obtained using a Metrohm EA 290 hanging mercury drop electrode (HMDE, ca. 2.2 mm^2). Controlled-potential electrolyses were carried out at a Hg pool electrode (ca. 8 cm^2) under a N_2O atmosphere using a gas-tight divided cell with a glass frit diaphragm. After electrolysis, the gas phase was analysed by GC using columns of 5 Å molecular sieve (for N_2, O_2, and NO) and Porapak PS (for H_2 and N_2O) at 40 °C. The cathode potentials were controlled using a saturated calomel electrode, but potentials in this paper are given with respect to a normal hydrogen electrode (NHE).

Table 1. Typical results of electrocatalytic reduction of N_2O.[a]

Run	Cathode potential E/V vs. NHE	Catalyst concn./μM	Product/ μmol (% current yields)[b] N_2	Turnover frequency[c]/h^{-1}	Electrolysis time[a]/h
		Ni^{II}–[14]aneN$_4$			
1	−1.05	20	272 (105)	161	3.25
2	−1.05	200	252 (97)	112	0.45
3	−1.15	20	240 (93)	1116	0.43
4	−1.15	200	244 (94)	144	0.34
		Ni^{II}–[15]aneN$_4$			
5	−0.95	20	250 (96)	476	1.05
6	−0.95	200	256 (99)	52	0.98
7	−1.05	20	260 (100)	1333	0.39
8	−1.05	200	268 (103)	191	0.28
9	−1.15	20	261 (101)	1933	0.27
		Ni^{II}–[16]andN$_4$			
10	−0.95	200	236 (91)	8	6.28
11	−1.05	200	253 (98)	22	2.30
12	−1.15	200	235 (91)	7	6.83

[a] 25 ml of 0.1 M KCl solution saturated with N_2O (*ca.* 14 mM) was electrolysed by passing 50 coulombs. Average values obtained by several independent experiments are given. [b] Current yields were calculated on the basis of equation (1), two-electron reduction, for the amount of N_2 detected in the gas phase. When N_2 remaining in the solution was taken into account, the total current yields increased by *ca.* 1%. [c] Turnover frequency of the catalyst was estimated by the ratio of the amount of N_2 formed per hour to catalyst used.

Figure 1 shows typical cyclic voltammograms of N_2O in the absence and presence of 50 μM Ni^{II} complexes of [13—16]aneN$_4$ at a HMDE. In the presence of a Ni^{II} complex of [14 or 15]aneN$_4$, a large increase in the reduction current of N_2O was clearly seen, while Ni^{II}–[13]aneN$_4$ showed very poor activity as a catalyst. Voltammograms of the complexes themselves were too small to see on the scale used. Among the complexes tested, Ni^{II}–[15]aneN$_4$ was the best catalyst because of the less negative effective potential region and the larger catalytic current. Interestingly, for Ni^{II}–[15 and 14]aneN$_4$, both the catalytic peak current and the peak potential for N_2O reduction, obtained by cyclic voltammetry, did not change at a catalyst concentration down to ≤3 μM, suggesting that the catalyst adsorbed onto the electrode surface would be sufficient to effect catalysis. For Ni^{II}–[16]aneN$_4$, catalyst concentrations much larger (>500 μM) than those of Ni^{II}–[15 and 14]aneN$_4$ were required to obtain enough catalytic currents for the N_2O reduction. Since potentials where the catalytic current increased were around those at which prepeaks due to adsorption of the complex onto the electrode surface appeared [see Figure 1(f) and (g)], formation of the adsorbed Ni^I species seems to be an important step for the present catalytic reaction. The adsorption of Ni^{II}–[14 or 15]aneN$_4$ onto a Hg electrode in about a monolayer (*ca.* 3 × 10^{-10} mol cm^{-2}) at the potentials studied was also suggested by spectrochemical measurements using a long optical path cell, while Ni^{II}–[16]aneN$_4$ adsorbed much less (at least by one order) than Ni^{II}–[14 or 15]aneN$_4$.

Controlled potential electrolyses gave the following results. (i) In the absence of a catalyst or in the presence of $NiCl_2$ (0.2 mM) with no macrocyclic polyamine as a ligand, there was no significant reduction current of N_2O to carry out the bulk electrolysis at the potentials used. Also, electrolysis at a Ni electrode with no catalyst at potentials more negative than −1.15 V (*vs.* NHE), gave 60—80% yields of N_2 with H_2 evolution. (ii) In the presence of a catalyst the reduction potential of N_2O shifted by more than 0.5 V toward the positive direction. (iii) The reduction of N_2O in the presence
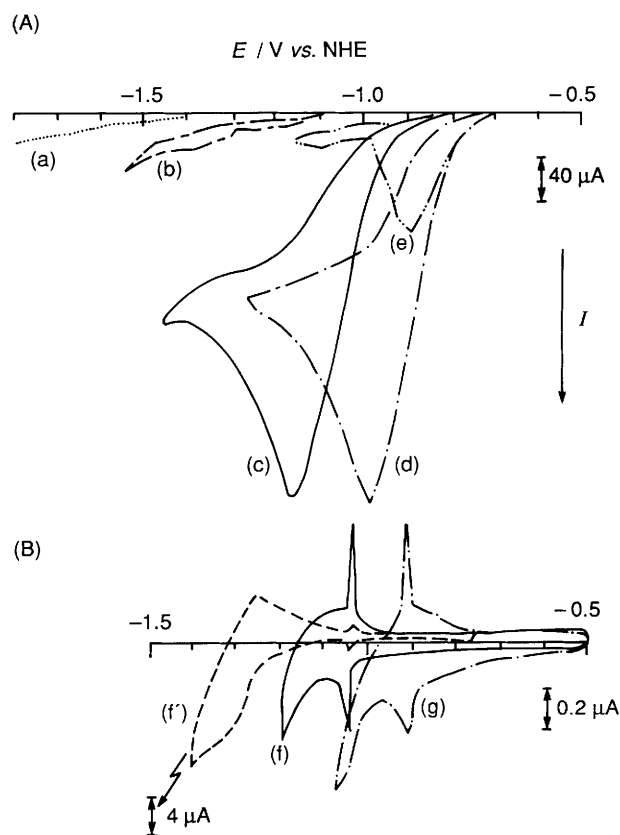
Figure 1. Cyclic voltammograms at a HMDE at 25 °C, (A) in a 0.1 M KCl solution saturated with N_2O in the absence (a) and in presence of 50 μM Ni^{II} complexes of (b) [13]aneN$_4$, (c) [14]aneN$_4$, (d) [15]aneN$_4$, (e) [16]aneN$_4$; (B) those of 1 mM Ni^{II} complexes of (f) and (f′) [14]aneN$_4$ and (g) [15]aneN$_4$ in a 0.1 M KCl solution under a N_2 atmosphere. Scan rate: 0.1 V s^{-1}.

of the catalysts gave N_2 in yields close to 100% (Table 1); no appreciable amount of H_2 or NO was detected. (iv) No decrease in activity of the catalyst was observed during electrolysis for at least several hours, and the turnover frequencies of the catalysts for N_2 formation based on the amounts of the catalysts used were more than $1000 \, h^{-1}$ under the conditions used (Table 1, runs 3, 7, and 9). (v) Without N_2O, the current obtained was too small to do bulk electrolysis and no N_2 was produced. (vi) No significant increase in the electrolysis current was observed when the concentration of the catalyst, Ni^{II}-[15 or 14]aneN$_4$, changed from 0.2 to 2 mM, indicating again that the catalytic reaction takes place at the electrode surface but not in the bulk of the solution. (vii) In the presence of the catalyst, catalytic reduction of N_2O occurred at a glassy carbon electrode but required more negative potentials than at a Hg electrode. A lead amalgam electrode gave similar results to those at the Hg electrode, suggesting that an interaction between the catalyst and Hg may be important. (viii) During electrolysis in 0.1 M KCl solution (pH 5.8), the pH of the solution shifted to become alkaline (pH >12). The overall reaction can be given by equation (1). This is similar to that of the biological reduction of N_2O in the nitrogen cycle.

$$N_2O + 2e + H_2O \rightarrow N_2 + 2OH^- \qquad (1)$$

Although the mechanism is not yet clear, the following aspects may be pointed out. Since no significant change in the spectra of the catalysts (Ni^{II}-[14 and 15]aneN$_4$) in solution was observed on adding N_2O, interaction between the catalyst and N_2O in the solution is negligible; this is in good agreement with the fact that Ni^{II}-[14]aneN$_4$, for example, has a square-planar[7] structure in solution. Reduction and adsorption of the complex at a Hg electrode, however, results in an octahedral structure, where the electrode occupies one axial position. Then, N_2O can co-ordinate at the nitrogen atom as the sixth ligand, followed by electrophilic attack of water at the oxygen of N_2O, *i.e.*, the catalytic reduction.

For the reduction of N_2O, Ni was more effective as the central metal ion of the complexes than, *e.g.*, Co^{III}, Cu^{II}, and Ru^{III}. The structures of the macrocyclic ligands also affected the catalytic behaviour, as can be seen in Figure 1; Ni^{II} complexes of 1,4,8,11-tetramethyltetra-azacyclodecane showed no significant activity as catalysts for the present reaction. This may be due to the differences in the interaction between the catalyst and the electrode and in the stability of intermediates produced during the catalytic reaction.

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