Reduction of Nitrate to give Hydroxylamine at a Mercury Electrode using Cobalt(III)– and Nickel(II)–Cyclams as Catalysts

Isao Taniguchi,* Norihiro Nakashima, and Kazuo Yasukouchi

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University Kurokami, Kumamoto 860, Japan

Electrocatalytic reduction of NO_3^- takes place efficiently in the presence of a small amount of $Co^{III}L-$ or $Ni^{II}-$cyclam (cyclam = 1,4,8,11-tetra-azacyclotetradecane) in aqueous solutions to give NH_2OH selectively at an Hg electrode.

The reduction of nitrogen oxyanions has been one of the most interesting aspects in recent chemistry concerned with the development of new methods for artificial nitrogen fixation and the conversion of pollutants such as NO_x into useful chemicals, and also in bioinorganic chemistry in comparing enzymatic reactions with their model ones. In the present experiment, a Co^{III} complex of 1,4,8,11-tetra-azacyclotetradecane ($Co^{III}-$cyclam) has been demonstrated, for the first time, to be an excellent catalyst for NO_3^- reduction in aqueous solutions to produce NH_2OH selectively at an Hg electrode, while at a Pb electrode, NH_3 was the main product. $Ni^{II}-$cyclam also acted as a catalyst for NO_3^- reduction, although the effective potential region was *ca.* 0.2 V more negative than that of the $Co^{III}-$cyclam. These results suggest that Mo and Fe ions, which appear in naturally-occurring enzymes, such as nitrate and nitrite reductases, are not always essential for developing artificial catalysts for nitrogen fixation.

Recently, cathodic reduction of NO_3^- to give NH_3 using a Mo–Fe cluster-modified glassy carbon electrode[1] has been demonstrated. Sauvage *et al.*[2] and Ruppert[3] suggested in their reports on catalytic reduction of CO_2 using $Ni^{II}-$cyclam at an Hg electrode that $Ni^{II}-$cyclam may also be a catalyst for NO_3^- reduction to give NH_4^+. Also, electrocatalytic reduction of NO_2^- using a water-soluble iron porphyrin[4] and illuminated semiconductor powders[5] has been reported. However, catalysts developed to date for the reduction of nitrogen oxyanions, especially those for NO_3^- reduction, are still limited, and thus it would be useful to find new effective catalysts. $Co^{III}-$cyclam can reduce NO_3^- very rapidly [*e.g.*, a current density of more than 5 mA/cm² was obtained in a 0.1 M

NO_3^- solution even at -1.25 V *vs.* normal hydrogen electrode (n.h.e.) in the presence of only 20 μM or less of the catalyst] to produce NH_2OH with extremely large turnover frequencies (>500 h⁻¹) and higher current yields (*ca.* 90%) than any other catalyst reported so far.

Metal cyclams were prepared as $[Co^{III}-cyclamCl_2]Cl$ and $[Ni^{II}-cyclamCl_2]$ according to the literature.[6] After electrolysis, ammonia and hydroxylamine in the liquid phase were analysed as NH_4^+ and NH_3^+OH, respectively, by h.p.l.c. using a Wescan cation column (269-004) and a conductivity detector (Wescan 213A) with a 4 mM HNO_3 solution as eluant. The other experimental conditions and typical results of the electrocatalytic reduction are given in Table 1. The cathode potentials were controlled using a saturated calomel electrode, but potentials in this paper are given with respect to n.h.e.

Figure 1 shows the cyclic voltammograms of NO_3^- in the absence and presence of 20 μM $Co^{III}L-$ and $Ni^{II}-$cyclam at a hanging mercury drop electrode (h.m.d.e.). A large increase in the reduction current of NO_3^- was clearly observed on adding metal cyclams, indicating the catalytic activity of these metal cyclams; no appreciable voltammograms of metal cyclams themselves at such a low concentration were observed at the current scale used. $Co^{III}-$cyclam is a better catalyst than $Ni^{II}-$cyclam because the effective potential is less negative and the catalytic current is somewhat larger. Interestingly, only very small amounts of these catalysts were required to show catalytic activity; *e.g.*, the peak current for NO_3^- reduction observed by cyclic voltammetry increased to reach a certain value at a concentration of $Co^{III}-$cyclam of *ca.* 5 μM or less, suggesting that $Co^{III}-$cyclam (or its reduced species) adsorbed

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

Run	Cathode	E/V vs. n.h.e.	Catalyst (concn./μM)	Product/μmol (% current yields)[b] NH_2OH	NH_3	Turnover frequency[c]/ h⁻¹	Electrolysis time[a]/h
1	Hg pool[d]	-1.15	$Co^{III}-$cyclam	458 (88)	9 (2)	369	2.48
2		-1.25	(20)	452 (87)	12 (3)	569	1.59
3		-1.55		470 (91)	5 (1)	1237	0.76
4		-1.25	(200)	406 (78)	9 (2)	99	0.82
5		-1.25	$Ni^{II}-$cyclam	350 (68)	7 (2)	170	4.12
6		-1.55	(20)	329 (64)	5 (1)	901	0.73
7		-1.25	(200)	403 (78)	7 (2)	52	1.55
8	Pb plate[d]	-1.25	$Co^{III}-$cyclam (20)	9 (2)	332 (85)	75	8.85
9		-1.25	(200)	28 (5)	334 (86)	25	2.63
10	Pb–Hg[d]	-1.25	$Co^{III}-$cyclam (20)	432 (83)	10 (3)	275	3.14
11		-1.25	(200)	464 (90)	13 (3)	40	2.33

[a] 25 ml of 0.1 M KNO_3 solution was electrolysed using a gas-tight cell. 300 coulombs were passed. [b] Current yields were calculated on the basis that 6 and 8 electrons were consumed in producing NH_2OH and NH_3 molecules, respectively. Total current yield close to 100% was obtained for each run, when NO_2^- remaining in the solution was taken into account. Only trace amounts of H_2 (less than 1% in current efficiency) were detected by g.c. using a gaschropac 54 column. [c] Turnover frequency of the catalyst was estimated by the ratio of the average amount of NH_2OH (runs 1—7, 10, and 11) or NH_3 (runs 8 and 9) formed per hour to that of the catalyst used. [d] Electrode areas were *ca.* 8 cm² for Hg pool and 2 × 2 cm² for Pb and mercury-coated Pb (Pb–Hg) plates.
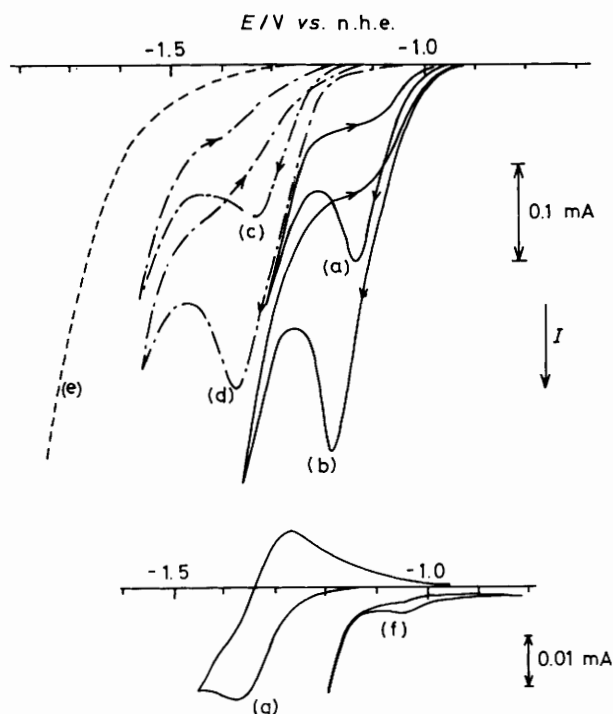
Figure 1. Cyclic voltammograms in a 0.1 M KCl solution at an h.m.d.e. (*ca.* 2.2 mm^2) at 25 °C under an N$_2$ atmosphere of (a) 5 mM NO$_3^-$, 20 μM Co^{III}–cyclam; (b) 10 mM NO$_3^-$, 20 μM Co^{III}–cyclam; (c) 5 mM NO$_3^-$, 20 μM Ni^{II}–cyclam; (d) 10 mM NO$_3^-$, 20 μM Ni^{II}–cyclam; (e) 10 mM NO$_3^-$, no catalyst; (f) 5 mM Co^{III}–cyclam; (g) 5 mM Ni^{II}–cyclam. Scan rate: 0.1 V s^{-1}.

onto the electrode surface would be sufficient to effect catalysis; unfortunately, however, a modified electrode containing pre-adsorbed catalyst has not yet been successfully prepared. The reduction of Co^{III}–cyclam itself showed a redox wave due to the Co^{III}/Co^{II} couple at *ca.* 0.1 V (not shown) and a rather small wave at *ca.* −1.05 V (*vs.* n.h.e.) with a subsequent steep increase in the reduction current (see Figure 1); the small wave is due to further reduction of Co^{II}–cyclam. Since the catalytic reduction of NO$_3^-$ took place at potentials where these metal cyclams can be reduced to their monocations,[7] the formation of Co^L– and Ni^L–cyclams is thought to be an important step in the present reduction process; in the presence of Co^{II} and Ni^{II} ions without cyclam, no catalytic reduction of NO$_3^-$ was observed.

Controlled-potential electrolyses gave the following results. (i) Without catalysts, the observed current was too small at the potentials of interest to carry out the bulk electrolysis. (ii) In the presence of catalysts, even in a small amount, cathodic current increased remarkably and gave reduction products of NO$_3^-$ as shown in Table 1. (iii) The catalysts were re-cycled very rapidly and no appreciable decrease in catalytic activity was observed after electrolysis for several hours; *e.g.*, the turnover frequency for production of NH$_2$OH based on the amount of Co^{III}–cyclam, 20 μM, was more than 500 and 10^3 h^{-1} at −1.25 and −1.55 V *vs.* n.h.e., respectively (see runs 2 and 3), and turnover numbers much larger than 10^3 were easily obtained by electrolysis for a few hours. (iv) Furthermore, at Hg pool and Hg-coated Pb electrodes the main product was NH$_2$OH, while NH$_3$ was obtained preferentially at a Pb electrode (see runs 8 and 9).

At present, the reduction mechanism is not yet fully understood. However, since NO$_2^-$ was detected in all cases

(by u.v. spectroscopy with an absorption maximum at 355 nm) in appreciable amounts in the solution and its concentration increased to remain almost constant at a certain value, while NH$_2$OH was produced almost linearly with the electricity passed during electrolysis of NO$_3^-$ at an Hg electrode, this suggests that NO$_3^-$ is reduced *via* NO$_2^-$ to form further reduced products. Also, NO$_2^-$ was effectively reduced to give NH$_2$OH at an Hg electrode in the presence of these metal cyclams, and NH$_3$ was formed at a Pb electrode. In solution, NO$_3^-$ may either co-ordinate to Co^{III}– and Ni^{II}–cyclams weakly to give outer-sphere complexes or may bind to reduced forms of metal cyclams, since no significant change in the spectra of the Co^{III}– and Ni^{II}–cyclam solutions was observed on adding an excess of nitrate (5 mM metal cyclams + 1 M KNO$_3$); in the solid state, however, the complex [Ni^{II}–cyclam(NO$_3$)$_2$] is known.[8] During electrolysis, the pH-value of the solution shifted to become alkaline, and the overall reaction for NH$_2$OH formation in a KNO$_3$ solution is shown in equation (1).

$$NO_3^- + 5\,H_2O + 6\,e \rightarrow NH_2OH + 7\,OH^- \qquad (1)$$

Both Co^{III}– and Ni^{II}–cyclams were almost ineffective for the reduction of NH$_2$OH to give NH$_3$. However, NH$_2$OH was reduced rather easily to NH$_3$ at a Pb electrode with no catalyst, while at an Hg electrode, reduction of NH$_2$OH was slow under the present experimental conditions; this resulted in the difference in product selectivity observed, depending upon the cathode material.

Among various metal cyclams tested for NO$_3^-$ reduction, cobalt and nickel were much more effective as central metals than Cu^{II}, Zn^{II}, Rh^{III}, Fe^{III}, Au^{III}, Mo^{VI}, and W^{VI}. Also, metal complexes of 1,4,7,11-tetra-azacyclotetradecane (the so-called isocyclam ligand) were less active than the corresponding metal cyclams. These results show that both the structure of the ligand and the central metal play important roles in catalytic activity.

One of the authors (I. T.) acknowledges useful discussions on this subject with Professor J.-P. Sauvage of C.N.R.S. Strasbourg, France.

References

1 S. Kuwabata, S. Uezumu, K. Tanaka, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1986, 135.

2 M. Beley, J.-P. Collin, R. Ruppert, and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1984, 1315.

3 R. Ruppert, Ph.D. Dissertation, University of Louis Pasteur at Strasbourg, 1985.

4 M. H. Barley, K. Takeuchi, W. R. Murphy, Jr., and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 507.

5 M. Halmann and K. Zuckerman, *J. Chem. Soc., Chem. Commun.*, 1986, 455.

6 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102; B. Bosnich, M. L. Tobe, and G. A. Webb, *ibid.*, 1965, **4**, 1109.

7 Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4029; L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438; N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh, and D. Beyerstein, *ibid.*, 1985, **24**, 251.

8 V. J. Thöm, C. C. Fox, J. C. A. Boeyens, and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.