

Electrochemical Conversion of Cyanide into Methylamine and C₁–C₂ Hydrocarbons

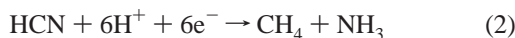
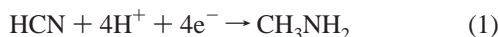
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The reduction of cyanide to form methane, ammonia, and methylamine, which occurs in biological systems catalyzed by molybdenum nitrogenase,¹ the enzyme which catalyzes nitrogen reduction to ammonia, has never been reproduced until now in artificial systems. However, in an attempt to mimic the biological systems, Hughes et al.² succeeded in synthesizing Mo-containing complexes able to coordinate cyanide and to convert it electrochemically but only to the aminocarbonyne ligand (Mo=CNH₂), a supposed intermediate in the HCN reduction by nitrogenase. In fact, despite a considerable amount of work devoted to catalytic activation of cyanide in nonbiological systems, no reports exist on its complete conversion to methane even at high temperatures and at elevated pressures.^{3,4}

Herein we report, for the first time, the electrochemical reduction of cyanide in aqueous solution occurring at nickel, copper, and silver electrodes. In particular, electrolyses of a NaCN solution of pH 6 (0.035 M NaCN, 1 M NaClO₄, 0.2 M phosphate buffer) on a Ni cathode⁵ led to the formation of large amounts of methylamine, ammonia, and methane consistent with reactions 1 and 2.⁶



(1) (a) Hardy, R. W. F.; Knight, E., Jr. *Biochim. Biophys. Acta* **1967**, *139*, 69–90. (b) Kelly, M.; Postgate, J. R.; Richards, R. L. *Biochem. J.* **1967**, *201*, 1c–3c. (c) Lowe, D. J.; Fisher, K.; Thorneley, R. N. F.; Vaughn, S. A.; Burgess, B. K. *Biochemistry* **1989**, *28*, 8460–8466. (d) Li, J.; Burgess, B. K.; Corbin, J. L. *Biochemistry* **1982**, *21*, 4393–4402. (e) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377–1406. (f) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983–3011.

(2) Hughes, D. L.; Mohammed, M. Y.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1399–1400.

(3) (a) Jentz, D.; Mills, P.; Celio, H.; Belyanski, M.; Trenary, M. *J. Chem. Phys.* **1996**, *105*, 3250–3257. (b) Jentz, D.; Celio, H.; Mills, P.; Trenary, M. *Surf. Sci.* **1995**, *341*, 1–8. (c) Guo, X.; Hoffman, A.; Yates, J. T., Jr. *J. Phys. Chem.* **1989**, *93*, 4253–4258. (d) Hagans, P. L.; Chorkendorff, I.; Winkler, A.; Yates, J. T., Jr. *J. Phys. Chem.* **1988**, *92*, 471–476. (e) Lloyd, G.; Hemminger, J. C. *Surf. Sci.* **1987**, *179*, L6–L12. (f) Hwang, S. Y.; Seebauer, E. G.; Schmidt, L. D. *Surf. Sci.* **1987**, *188*, 219–234. (g) Bair, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1985**, *82*, 2280–2294. (h) Yang, H.; Whitten, J. L. *Chem. Phys. Lett.* **1996**, *251*, 20–25. (i) Yang, H.; Whitten, J. L. *J. Phys. Chem.* **1996**, *100*, 5090–5097. (j) Celio, H.; Mills, P.; Jentz, D.; Pae, Y. I.; Trenary, M. *Langmuir* **1998**, *14*, 1379–1383. (k) Bridge, M. E.; Marbrown, R. A.; Lambert, R. M. *Surf. Sci.* **1976**, *57*, 415–419.

(4) Two isolated works (Heard, R. D. H.; Jamieson, J. R.; Solomon, S. J. *Am. Chem. Soc.* **1951**, *73*, 4985–4986. Jones, A. R.; Skraha, W. J. *Science* **1953**, *117*, 252–253) report the reduction of cyanide on a platinum oxide catalyst, in dilute aqueous sulphuric acid, under atmospheric pressure of hydrogen, yielding methylamine. Small amounts of CH₄ and NH₃ were detected during thermal decomposition of K₃Co(CN)₅L (L = CN⁻, NO₂⁻, N₃⁻, NO) complexes (Yuan, J.; Xin, X.; Dai, A. *Thermochim. Acta* **1988**, *130*, 77–85). On the other hand, CH₃NH₂ and NH₃ were formed on boiling alkaline solutions of KCN or K₄[Fe(CN)₆] in the presence of Raney nickel (Tanabe, Y.; Miyantani, J. *Bunseki Kagaku* **1978**, *27*, 123–125).

(5) In this and the following experiments, the cathodic compartment was separated from a Pt anode either by a fine ceramic frit or by a Nafion membrane. Cyanide was added into the solution while keeping the electrode potential at -1 V to avoid cathode dissolution.

(6) HCN being a weak acid, pK_a 9.39 (*Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. VII, pp 208–209), the acidic form is by far the dominant species in a buffered solution of NaCN at pH 6.

(7) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.

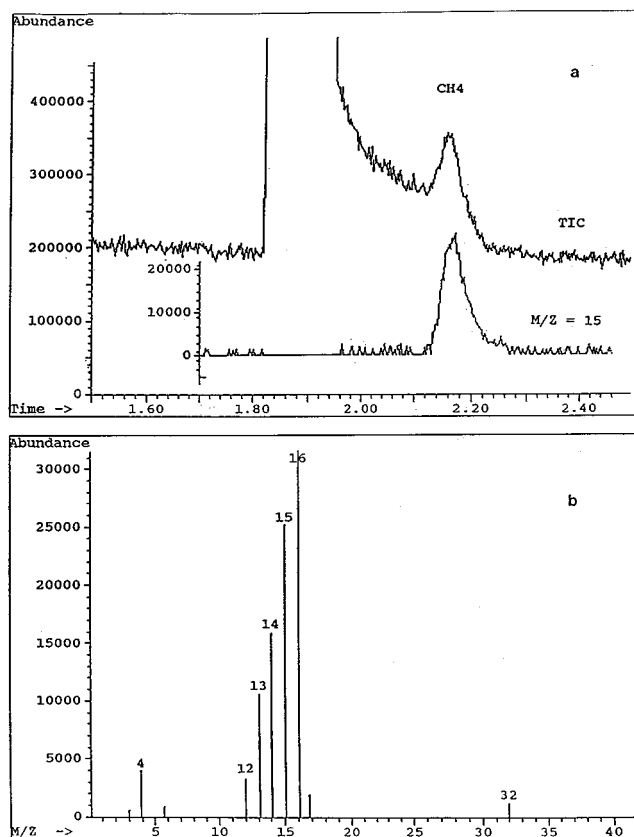


Figure 1. Formation of hydrocarbons during electroreduction of HCN on Ag has been followed by GC-MS. The total ion chromatogram from time 1.5 to 2.5 min is presented in the upper trace and compared to the selected ion-chromatogram of *m/z* 15 (CH₃⁺) in the lower trace, identifying methane at retention time of 2.2 min (a), which is confirmed by the spectra obtained after background subtraction (b).

Note that the final products of cyanide reduction, CH₄ and NH₃, are also reactants in an industrial synthesis of HCN.⁷ The standard redox potential, *E*^o, calculated with Δ*G*^o values⁸ for the gaseous reactants and products of reaction 1, is 0.238 V, while in the case of reaction 2, *E*^o = 0.331 V. These values are much more positive than the observed onset of HCN reduction that (as discussed below) appears to be closely related to the potential at which hydrogen is actually formed at the electrode surface. The highest faradaic efficiency, exceeding 70%, was observed for a Ni cathode polarized at -1.4 V vs AgCl/Ag/Cl⁻, i.e., ca. 1 V below *E*^o for reaction 1, where the amount of CH₃NH₂ formed was ca. 3.7 times larger than that of NH₃.⁹ HPLC analyses of the solutions collected at the end (normally after 1 h) of electrolyses in the cathodic compartment were performed following essentially the method described by Krause et al.¹⁰ Hydrocarbons, including methane and minor amounts of ethylene and ethane, in the effluent gas from the cathodic compartment of the cell were monitored by gas chromatography¹¹ and, in addition, by GC-mass spectrometry (Figure 1). The amount of the reduction products followed the increase of the cathodic current down to -1.4 V and then decreased in the potential region corresponding to the reduction of water. At -1.7 V, the faradaic efficiency dropped to ca. 43%

(8) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Frederikse, H. P. R., Eds.; CRC Press: Boca Raton, 1995.

(9) The faradaic yields were calculated from the detected amounts of CH₃NH₂ and NH₃ according to reactions 1 and 2.

(10) Krause, I.; Bockhardt, A.; Neckermann, H.; Henle, T.; Klostermeyer, H. *J. Chromatogr. A* **1995**, *715*, 67–79.

(11) A Haysep R column and a FID detector were used.

due to increased H₂ evolution and the CH₃NH₂/NH₃ ratio decreased to 2.7. Electrolyses of a NaCN solution of pH 6 performed on Cu and Ag cathodes were markedly less efficient than when a Ni electrode is used. On Cu, the faradaic yield culminated in ca. 28% at -1.7 V with the amount of formed CH₃NH₂ being 5.2 times larger than those of NH₃ and CH₄. On the other hand, Ag cathodes produced almost equal amounts of CH₃NH₂, NH₃, and CH₄ contributing to a total faradaic yield of ca. 10% at -1.3 V. Importantly, closely similar product distribution was obtained when Ag(111) instead of the polycrystalline electrode is used. The same products of cyanide reduction are also formed in alkaline solutions in which CN⁻ ions are practically the only species present.¹² Electrolyses of a 0.035 M NaCN, 1 M NaClO₄ solution of pH 11.9 (adjusted using NaOH) conducted on Ni and Cu at -1.7 V vs AgCl/Ag/Cl⁻ resulted, however, in faradaic yields ca. 4 times lower than those obtained with the solution of pH 6. In contrast, an Ag cathode produced under analogous conditions only trace amounts of CH₃NH₂.

Preliminary experiments showed also cyanogen¹³ (dissolved in 0.2 M phosphate buffer, pH 6.0) to undergo reduction at the Ag electrode in the same potential range as HCN to give mainly ethylene, ethane, and a small amount of methane.

As cyanide reduction actually occurs at Ni, Cu, and Ag bearing a large excess of negative charge, HCN is, in principle, not expected to undergo adsorption at the electrode surface. Thus, surface-enhanced Raman spectroscopic measurements showed HCN present on the Ag surface only at potentials less negative than -0.8 V,¹⁴ i.e., well above the onset of cyanide reduction. On the other hand, HCN in the gas phase interacts weakly with Ag and Cu surfaces, desorbing as the molecular species markedly below the room temperature.^{3j,k} HCN is also partially desorbing from Ni(111) at 271 K; however, a fraction remaining at the surface apparently dissociates, close to 300 K, into H_{ad} and CN_{ad}.^{3d} As the HCN adsorption at the negatively polarized Ni, Cu, and Ag surfaces appears unlikely, it is HCN from the solution that is expected to react with electrochemically formed H_{ad} to give adsorbed formimidoyl radical according to



or, alternatively, aminocarbyne (CNH₂). Ni, Cu, and Ag belong to the class of medium hydrogen overvoltage metals. As the onset potential for cyanide reduction is located in the region where substantial H₂ evolution already occurs, the H_{ad} coverage of all three surfaces is expected to be significant.¹⁵

Although the actual coverage of H_{ad} certainly affects the electrode activity toward cyanide reduction, the nature and stability of reaction intermediates are expected to play an even more important role in such a multielectron process. Both HCNH and CNH₂ have been identified among the products of thermal decomposition of CH₃NH₂ on various metal surfaces and are considered as intermediates of HCN hydrogenation.^{3b,h} CNH₂ and, especially, HCNH are strongly bound to the Ni surface, their calculated adsorption energies on Ni(111) reaching as much as 237 and 369 kJ/mol, respectively.^{13h,16} Bonding of HCNH through both the C and N atoms with the C-N bond oriented parallel to

the Ni surface should favor its further hydrogenation to formaldimine CH₂NH and then to CH₃NH₂



As our attempts to reduce cathodically CH₃NH₂ did not result in the formation of any perceptible amount of CH₄, the 6e⁻ pathway (reaction 2) is most probably initiated by the C-N bond breaking in CH₂NH_{ad} resulting in the formation of reactive carbene species:



Under conditions of important coverage of H_{ad} prevailing on cathodically polarized Ni, Cu, and Ag, the formation of (-CH₃)_{ad} followed by CH₄ evolution is expected to be the major pathway with respect to the recombination of carbene species. The latter process, leading to the formation of C₂H₄ and/or C₂H₆, requires relatively large carbene coverages and is opposed by the presence of coadsorbed hydrogen.¹⁷ Normally, the amount of C₂-hydrocarbons, ethylene and ethane formed in ca. 1:1 ratio during HCN reduction on Ni, Cu, or Ag at potentials more negative than -1.2 V, did not exceed 6% of the total hydrocarbon production.¹⁸

The large extent of cyanide conversion at the Ni electrode contrasts with the apparent lack of activity exhibited by platinum.¹⁹ In fact, only traces of hydrocarbons were detected during electrolyses of NaCN solutions we performed at Pt cathodes and the faradaic yield of CH₃NH₂ did not exceed 1%. Although low hydrogen overvoltage associated with high coverage of chemisorbed H on Pt may be the main reason for this divergent behavior, there are also some important differences in the chemistry of HCN on Ni and Pt surfaces. As mentioned above, HCNH (primary product of HCN hydrogenation) adopts a flat position on Ni,^{3h} which favors further hydrogenation. In contrast, on Pt, a distorted trans -CH=NH species, bound to the surface through the C atom, has been identified.²⁰ It is also noted that two cathode materials exhibiting marked activity toward electroreduction of cyanides, Cu and Ag, are apparently unable to even initiate the reduction of HCN in the gas phase. The latter reactant is in fact desorbed intact from both these surfaces already at low temperatures.^{3j,k} Clearly, interaction of HCN from the solution with the electrochemically generated H atoms at the metal surfaces offers an activation route not available under the gas-phase conditions. This situation presents an interesting analogy with the cathodic reduction of CO₂ at Cu, yielding CH₄ as the principal product,^{21a} for which the involvement of surface atomic hydrogen acting as reductant at various stages of the 8e⁻ process has been suggested.^{21b}

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(12) On the other hand, in acidic solutions (pH < 4) the HCN reduction tends to be suppressed and replaced by hydrogen evolution.

(13) Cyanogen was prepared by reacting CuSO₄ with NaCN according to the procedures described previously (Durrant, P. J.; Durrant, B. *Introduction to Advanced Inorganic Chemistry*, 2nd ed.; Longman: London, 1970; p 613).

(14) Kellogg, D. S.; Pemberton, J. E. *J. Phys. Chem.* **1987**, *91*, 1120-1126.

(15) According to the gas-phase measurements, the coverage of H_{ad} should decrease in the order Ni > Cu > Ag; Lee, G.; Plummer, E. W. *Phys. Rev. B* **1995**, *51*, 7250-7260. In addition, in the case of Ni, hydrides are known to be formed during cathodic H₂ evolution at this metal: Conway, B. E.; Angerstein-Kozłowska, H.; Sattar, M. A.; Tilak, B. V. *J. Electrochem. Soc.* **1983**, *130*, 1825-1836. Bernardini, M.; Comisso, N.; Davolio, G.; Mengoli, G. *J. Electroanal. Chem.* **1998**, *442*, 125-135.

(16) The actual adsorption energies of reaction intermediates are expected to be lower due to the large excess of negative charge at the Ni cathode.

(17) (a) Bent, B. E. *Chem. Rev.* **1996**, *96*, 1361-1390. (b) Zaera, F. *Chem. Rev.* **1995**, *95*, 2651-2693.

(18) Note, however, that acetylene formed, for example, on Ni in the gas phase via dehydrogenation of carbene species (cf. ref 17a) was never detected in our HCN electroreduction experiments.

(19) Also trace amounts of HCN reduction products were collected during tests carried out with a series of other cathode materials: glassy carbon, graphite, and lead.

(20) Levoguer, C. L.; Nix, R. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4799-4807.

(21) (a) Hori, Y.; Kikuchi, K.; Suzuki, S. *Chem. Lett.* **1985**, 1695-1698. (b) DeWulf D. W.; Jin, T.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 1686-1691.