

Electrochemical conversion of dinitrogen to ammonia mediated by a complex of fullerene C₆₀ and γ -cyclodextrin

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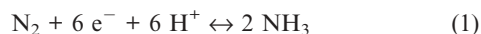
Received (in Cambridge, UK) 23rd January 2007, Accepted 2nd February 2007

First published as an Advance Article on the web 5th March 2007

DOI: 10.1039/b701017f

We report on an electrochemical conversion of N₂ to NH₃ at ambient pressure and 60 °C, which is mediated by reduced C₆₀ inside the molecular cavity of γ -cyclodextrin.

Molecular nano-sized cavities provide a confined reaction environment, which can significantly change the mechanism of chemical processes. This communication reports the reduction of dinitrogen to ammonia in water by reduced fullerene, which is protected by the cavity of γ -cyclodextrin. Gaseous molecular dinitrogen is a highly inert molecule; however nitrogen is an essential element of the metabolism of living organisms. The conversion of N₂ molecule to other nitrogen compounds (oxide, carbides, ammonia, hydrazine *etc.*) is termed the nitrogen fixation. Reduction of dinitrogen to ammonia



proceeds at ambient reaction conditions under catalysis of enzyme nitrogenase,¹ however, man-made synthesis requires rather harsh conditions.² Currently the Haber–Bosch synthesis, yielding an estimated 100 million of tons annually, provides the main supply of ammonia to chemical industry. For almost half a century interest has continued towards discovering various activation modes leading to a catalytic functionalization of nitrogen molecule under less energy demanding conditions. After the discovery of the coordination of dinitrogen to transition metals³ numerous methods performing nitrogen fixation were found.⁴ The hydrogenation of nitrogen is often hampered by a simultaneous evolution of hydrogen. Our previous studies have shown that the presence of surfactants provides a protecting environment to reactive intermediates and improves the conversion efficiency.⁵ Reaction (1) was achieved by several other systems described in the literature. It was accomplished at very negative potential –4 V in LiClO₄ in tetrahydrofuran–ethanol.⁶ Considerably lower overvoltage was sufficient when a polyaniline coated Pt electrode was used at elevated pressure of nitrogen.⁷ Another system based on a Ru cathode produced a small yield of ammonia at 100 °C and ambient pressure.⁸ At Pd electrode⁹ the nitrogen is reduced at 570 °C. The only non-metallic system performing the reaction (1) is based on the photo-excitation of a fullerene–cyclodextrin complex¹⁰ combined with a chemical reduction by means of sodium bisulfite (Na₂S₂O₄). This recent report led us to attempt an electrochemical

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reduction of nitrogen in the presence of water-soluble fullerene– γ -cyclodextrin complex. Free uncomplexed fullerene can be reduced in six consecutive one-electron redox steps yielding very reactive redox states of C₆₀. Insolubility of fullerene in protic solvents prevents attempting proton-coupled reactions, like the nitrogen fixation, mediated by the reduced form of a C₆₀ core. Encapsulation of C₆₀ in the cavity of cyclodextrins (CD) yields a sufficient solubility of the resulting complex in aqueous medium.^{11–13} The preparation of the complex [C₆₀-(γ CD)₂] followed the published procedure.¹¹ The solid violet powder was dissolved in 0.1 M aqueous KCl and the concentration of the complex was determined by UV-vis spectroscopy¹² using the published extinction coefficient 11 600 M⁻¹ cm⁻¹ at 330 nm. Our previous study¹⁴ confirmed that the redox properties of the complex [C₆₀-(γ CD)₂] are retained though the redox potentials are shifted towards more negative values by approximately 750 mV. A shift of the redox potential of a complexed redox form is a well known feature and used for the determination of stability constants.¹⁵ Fig. 1 shows the estimation of five different redox steps of the water soluble complex. The high degree of redox reversibility known for reductions of C₆₀ in aprotic solvents is not seen in the present case. For this reason some of the individual redox steps yield down-out polarographic current–voltage curves, which are not accurate enough for an estimation of the redox potentials. Considerably better potential resolution was achieved

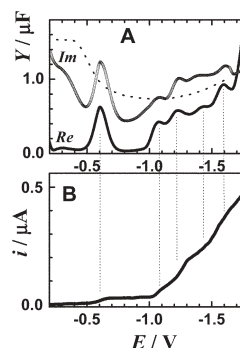


Fig. 1 Five redox steps observed in aqueous 0.27 mM complex of fullerene and γ -cyclodextrin and 0.1 M KCl. (A) The phase-sensitive AC polarogram on static mercury drop electrode measured at frequency 1.6 Hz and amplitude 10 mV (p–p). The dotted line is the imaginary admittance component (the double layer capacitance) of a blank 0.1 M KCl. The real and imaginary admittance components are labeled Re and Im, respectively. (B) Sampled DC polarogram on a mercury drop electrode. The voltage scan rate was 5 mV sec⁻¹.

by using low frequency phase-sensitive AC polarography, which yields admittance maxima at -0.61 V, -1.08 V, -1.22 V, -1.43 V and -1.59 V. The dependence of admittance on applied frequency of voltage perturbation (not shown here) indicates that the first and the third electron transfers are much faster than other redox exchanges. This result brings some doubt on the actual composition of the solution of the complex prepared according to literature data. It is not excluded that the preparative procedure yields besides complex with the stoichiometry of $C_{60} : \gamma\text{CD}$ equal to $1 : 2$ also some fraction of $1 : 1$ complex or even a metastable solution¹⁶ of free C_{60} . We are currently attempting to resolve this problem. The identification of potentials of individual redox steps was necessary for further attempts to reduce N_2 molecule by a preparative electrolysis.

The cyclic voltammetry of 0.3 mM solutions of $C_{60}\text{-}\gamma\text{CD}$ complex under the atmosphere of argon at 60 °C yields a current–voltage curve analogous to one shown in Fig. 1. However, the same experiment performed in solution saturated with gaseous nitrogen yields considerably enhanced current at -1.1 and -1.2 V (Fig. 2). This indicates the presence of a coupled homogeneous reaction involving the reduced form of the complexed C_{60} and dinitrogen. The first reduction peak at -0.6 V is almost unaffected by the presence of nitrogen. Data shown in Fig. 2 suggest that the preparative electrolysis at -1.2 V could yield a product of the reaction between anions of C_{60} and dinitrogen.

The electrolysis setup included a glass cell with the anodic compartment separated by a sintered glass. The working electrode was a mercury pool with area of 4.1 cm², the auxiliary electrode was a Pt net and the reference electrode was the $\text{Ag}|\text{AgCl}|0.1$ M KCl electrode separated by two fritted junctions from the cathodic compartment. Electrolysis was performed using 10 ml of 0.31 mM complex of fullerene- γCD in aqueous 0.1 M KCl. The solution was degassed and thermostated to 60 °C. The potential was set to -1.2 V and controlled by a potentiostat Autolab, model PGSTAT30, which also registered the faradaic current and charge. A stream of nitrogen was purged through the solution during the whole electrolysis. Gas emerging from the cell was passed through a Schlenk tube filled with 30 ml of 0.1 M H_2SO_4 . The initial electrolytic current was approximately 2 mA and monotonically decayed. The charge consumption corresponded to transfer of two electrons per molecule. The electrolysis was terminated when the current dropped to a few percent of the initial value (typically $30\text{--}40$ μA). The Schlenk tube was removed and attached to an evacuated Schlenk tube cooled by liquid nitrogen. After addition of a surplus of KOH to the H_2SO_4 solution both Schlenk tubes were connected. The tube containing the captured ammonia was closed and transferred to a photoacoustic spectrometer.

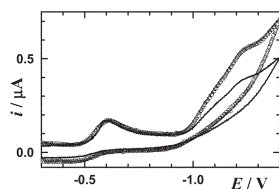


Fig. 2 Cyclic voltammetry of 0.31 mM complex of C_{60} and γ -cyclodextrin in aqueous 0.1 M KCl at 60 °C under the atmosphere of argon (full line) and nitrogen (circles). The voltage scan rate was 62 mV sec^{-1} . Curves show the first voltage scan on a freshly formed mercury drop electrode.

Electrolyzed solution was separately treated by the same procedure (the addition of KOH and capture of ammonia in a cooled Schlenk tube). Ammonia released from the electrolyzed solution was determined by the same way. The electrolyzed solution was dried and nitrogen was searched for in the solid residue by means of electron spectroscopy for chemical analysis (ESCA). The residue contains no traces of nitrogen, which confirms that neither ammonia nor intermediates chemically attack fullerene or cyclodextrin structures.

The photoacoustic spectrometer used the GaSb MID infrared laser¹⁷ as an excitation source. The emitting radiation was tunable in the range 4342 to 4362 cm^{-1} . The setup¹⁸ allows simultaneous measurements of the absorption spectrum using a nitrogen-cooled InSb detector. The calibration of the laser frequency was achieved by measuring highly resolved infrared spectra of NH_3 using a FTIR spectrometer (Bruker, model IFS 120) featuring the resolution of 0.002 cm^{-1} . Fig. 3 shows a spectrum of the captured gas (curve a) from the electrolysis experiment. Its identification as the spectrum of ammonia (compare curve b) is without any doubt. Spectrum of NH_3 proves our expectation that the current enhancement observed in Fig. 2 at negative potentials and under the nitrogen atmosphere is due to the reduction of dinitrogen to ammonia (reaction (1)) mediated by the reduced form of the $C_{60}\text{-}\gamma\text{CD}$ complex. The recovery of ammonia from electrolyzed solution yielded much higher amount than was found in emerging gas. The transfer of ammonia from a solution phase to an evacuated spectroscopic cuvette may involve some losses.

Therefore, an estimation of ammonia yield from comparison of the curves in Fig. 3 is not reliable. We constructed a calibration curve by using the same procedure for release of ammonia from a solution of a known concentration of NH_4Cl . Fig. 4 shows the calibration and an estimate of the ammonia yield. The electrolysis of 3 μmol s of the $C_{60}\text{-}\gamma\text{CD}$ complex produced 30 μmol s of ammonia. Hence the nitrogen fixation is an electrocatalytic process. Termination reactions most likely involve the dissociation of the $C_{60}\text{-}\gamma\text{CD}$ complex caused by binding of electrogenerated ammonia in the cyclodextrin cavity and expelling C_{60} from it. This is supported by finding that a major part of ammonia ($>90\%$) was recovered from the electrolyzed solution compared to the sulfuric acid trap. Furthermore, a dark deposit precipitating after some

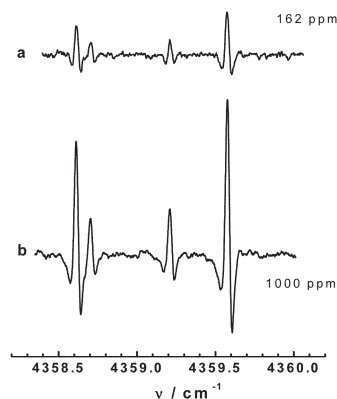


Fig. 3 Photoacoustic detection of ammonia in the gas emerging from the electrochemical cell where the electrolysis at -1.2 V was performed (curve a). Curve b is a spectrum of 1000 ppm of pure ammonia yielding an approximate estimate of ammonia concentration. The intensity is in arbitrary units.

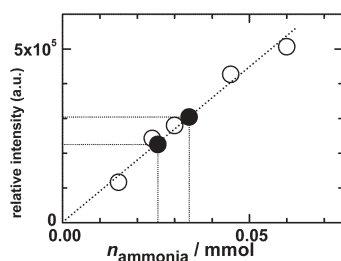


Fig. 4 The calibration curve (hollow circles) is the dependence of the relative intensity of the ammonia line at 4359.6 cm^{-1} on the number of mols released from aqueous solutions of NH_4Cl of known concentration. Full circles represent an estimated yield of ammonia from electrolysis experiments using 3 μmol s of the fullerene- γCD complex.

time from the solution was formed. This deposit contains no nitrogen compounds as confirmed by ESCA.

We searched for a possible formation of hydrazine. For this purpose we used a sensitive spectroscopic detection using 4-(dimethylamino) benzaldehyde (the Ehrlich reagent). The formation of hydrazine was not found, which leads to a conclusion that a dissociative mechanism is operative. The transfer of the first electron to the dinitrogen molecule requires the highest energy, whereas subsequent five electron transfers are progressively less energy demanding.¹⁹ This is caused by an unequal distribution of energy between three bonds of the dinitrogen triple bond. We found that no ammonia is produced for potential more positive than -0.8 V. This finding is in agreement with the calculated⁸ standard redox potential -0.88 V ($\text{Ag}|\text{AgCl}$) for the couple N_2/NH_3 . Our finding that the electrochemical formation of the C_{60} dianion is required for triggering the conversion of dinitrogen to ammonia suggests a plausible mechanism. The highly reactive dianion of C_{60} formed at the electrode surface transfers two electrons to dinitrogen and is again electrochemically reduced. This causes an enhanced voltammetric current seen in the nitrogen atmosphere (see Fig. 2). Subsequent reduction of nitrogen intermediates is much easier and can proceed either by a direct electron uptake from the electrode or by the electron transfer from the dianion of C_{60} complex. We assume that the cycle is terminated by ammonia inclusion in the cyclodextrin cavity. The host-guest interaction of ammonia is promoted by the formation of H-bonds with cyclodextrin OH groups. The formation of ammonia- γCD host-guest complex competes with the dissociation equilibrium of the active C_{60} - γCD complex or just occupies free sites for activation of dinitrogen. Either process would lead to termination of the nitrogen fixation reaction. This is supported by a slow precipitation of a dark solid, the uncomplexed fullerene, observed after the end of the electrolysis. We recall that aqueous solutions of fullerene- γCD complex are sufficiently stable. The system fullerene- γCD described here does not require neither catalytic noble metal electrodes, nor the photoactivation. The mercury electrode, well known for its ideally large overvoltage for the hydrogen evolution reaction, serves in this case only as a source of electrons. The activation is not achieved by a coordination of the N_2 molecule to a transition metal, yet the reaction conditions are mild. Our results extend the previously reported homogeneous nitrogen fixation by Nishibayashi *et al.*¹⁰ in several aspects: (i) the photoactivation is not needed; (ii) the yield of ammonia is catalytic; (iii) a

major part of ammonia is retained in the solution probably bound in the cyclodextrin cavity.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (A400400505 and KJB400400603) and the Ministry of Education (LC510 and COST OC140).

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- 18 The laser was placed in a Thorlab TCLDM9 cold head connected to a temperature control module working in the -20 to 80 °C temperature range. The laser beam was focused by an optical lens into an absorption cell. The photoacoustic resonator was made from a 200 mm long glass tube with a diameter of 5 mm, into which two Knowles EK-3024 microphones were placed in the centre opposite to each other. The external glass jacket was closed on each side by an aluminium flange fitted with CaF_2 windows with a thickness of 2 mm, which were placed in the direction of the beam at the Brewster angle. The spectra were measured using internal laser frequency modulation. An optimal frequency value of 390 Hz for the region around 4350 cm^{-1} was found experimentally. The signal from microphones was fed into a phase-sensitive amplifier (Stanford Research System, model SR530) operating in the second harmonic mode. The demodulated signal was recorded using an AD converter connected to a PC.
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