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The copper catalysed reduction of nitric oxide by ammonia in aqueous solution studied by membrane inlet mass spectrometry

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Abstract

The copper(II)–ammonia–nitric oxide reaction system in aqueous solution was studied by the measurement of dissolved nitric oxide with membrane inlet mass spectrometry. When the reaction was initiated by the addition of ammonia and copper(II) chloride to a saturated solution of nitric oxide, nitric oxide was found to be consumed in a two-stage reaction. Approximately 2 moles nitric oxide per mole copper(II) was consumed during the initial rapid reaction stage. Acidification of the reaction mixture at the end of the rapid reaction caused the reappearance of most of the nitric oxide. Spectrophotometric studies showed that copper(II) ammine complex disappeared during the rapid reaction consuming 2 moles of nitric oxide per mole copper(II). Chemical analysis showed that nitrite was a product of the rapid reaction and membrane inlet mass spectrometry revealed that nitrous oxide was a product of the slow reaction. The rate of the initial rapid reaction decreased with increasing ammonia concentration, whereas the rate of the slow reaction increased with increasing ammonia concentration. We ascribe the rapid reaction to the reversible conversion of copper(II) ammine complex and 2 moles of nitric oxide to copper(I) ammine nitric oxide complex and nitrite. The apparent inhibition of the rapid reaction by ammonia may indicate that nitric oxide competes with ammonia for binding to a vacant site in a copper(II) ammine complex. We ascribe the slow reaction to the irreversible reduction of nitric oxide to nitrous oxide by ammonia catalysed by a copper(I) complex of unknown composition.

Keywords: Nitric oxide; Copper; Membrane inlet mass spectrometry

1. Introduction

In recent years, the study of nitric oxide chemistry has been stimulated by the discoveries of two important functions of nitric oxide, one as an atmospheric pollutant and another as a regulatory agent in living organisms. Impressive numbers of papers related to these two aspects of nitric oxide have appeared. Considering the amount of work which has been done, we are surprised to find that simple reactions of nitric oxide in aqueous solution have received little attention. Many papers may be found on the reduction of nitric oxide by ammonia catalysed by various solid copper containing catalysts, but the copper(II)–ammonia–nitric oxide reaction in homogeneous aqueous solution apparently has been related in only one paper published by

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Oates and Lunsford [1]. They followed the reaction by mass spectrometric analysis of a gas mixture which was circulated through the solution in a closed reactor and they reported copper-catalysed reduction of nitric oxide by ammonia. Catalytic reduction of nitric oxide by ammonia was also reported in a paper on the copper-catalysed reduction of nitric oxide by diethylamine in methanol solution [2]. We have previously studied the homogeneous catalytic reduction of nitric oxide by amines in the presence of cobalt(III) complexes [3]. As the catalytic activity of copper(II) complexes seemed to be higher than that of cobalt(III) complexes, we decided to investigate the copper(II)–ammonia–nitric oxide system in aqueous solution using membrane inlet mass spectrometry (MIMS) for continuous measurement of dissolved nitric oxide. By direct measurement of dissolved nitric oxide, possible errors due to inadequate equilibration of the two phases are avoided. The use of membrane inlet mass spectrometry for the measurement of dissolved nitric oxide has been reported previously by another group but they apparently have not used it for kinetic studies [4]. Although the background signal of the mass spectrometer is low at the main peak of nitric oxide, m/z 30, MIMS is not sensitive enough to measure the naturally occurring nitric oxide in biological systems.

2. Experimental

Measurements of dissolved gases were done both in a closed system where no gas phase was present and in open systems where there was a gas phase of controlled composition above the liquid sample. In both cases, the sample was stirred by a magnetic stirrer. In a measurement in closed system, the reaction rate is determined from the slope of the concentration vs. time curve. In open system measurements, where a gaseous reactant is present at a constant partial pressure in the head space gas, the reaction rate, ν, is determined from the difference between the equilibrium concentration, c_{eq}, and the steady state concentration, c_{ss}, of the gaseous reactant according to the equation $\nu = kV(c_{eq} - c_{ss})$. The constant k is the first-order rate constant for the equilibration of the liquid sample with the gas and V is the volume of the liquid sample [5]. The actual values of k and V in the present experiments were 0.007 s^{-1} and 6 ml, respectively.

The measuring cell for the membrane inlet mass spectrometer (Fig. 1) was a slightly modified version of the one we have described earlier [6]. In order to ensure that the cell could be filled completely with liquid sample without gas bubbles being trapped, the cell was given a conical ceiling ending in a 2-cm-long capillary

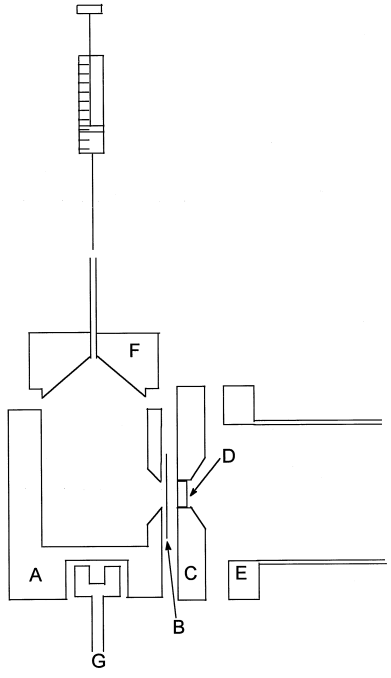

Fig. 1. Sample cell for membrane inlet mass spectrometry, exploded vertical cross section. (A) Block with cylindrical well for sample. Channels for thermostated water not shown. (B) Polymer membrane. (C) Standard vacuum flange with porous disk for membrane support (D) mounted in the centre. (E) End of vacuum chamber where the ion source of the quadrupole mass spectrometer is situated (not shown). (F) Conical lid with capillary tube for injection. (G) Stirring magnet. When the block is clamped against the flange with device not shown, the membrane is in contact with sample on one side and the vacuum of the mass spectrometer on the other side.

tube. The bulk of the sample was protected against entry of gases from the atmosphere by the stagnant liquid in the capillary tube. The cell used for closed system measurements held 4.2 ml and was mounted on a quadrupole mass spectrometer model QGA-2 from ATOMKI (Debrecen, Hungary) which was pumped by an oil diffusion pump. The cell used for open system measurements was similar to the one used for closed system measurements except that its volume was 14 ml. It was mounted on a Monitor quadrupole mass spectrometer from VG Quadrupoles (East Sussex, UK). In both cells, the membrane was a 250-μm-thick sheet of silicone rubber from Siltec, Technical Products (Georgia, USA), and the membrane area was 7 mm^2.

The measurement of dissolved gases by membrane inlet mass spectrometry depends on the diffusion of gases through the membrane from the sample to the vacuum of the mass spectrometer. Corrections for the loss of analyte by diffusion through the membrane must be made when slow processes are monitored, i.e., processes whose half times are of the same order of magnitude as that of the diffusion loss.

Calibration of the dissolved gas measurements was done by recording the signals obtained with stirred, saturated solutions of the gases and using the following table values for the molar concentrations of saturated solutions at 25°C [7]. N_2: 0.629 mM, NO: 1.88 mM, N_2O: 23.5 mM. The three gases were measured at the mass/charge ratios 28, 30 and 44, respectively. Since the measurements were always done in strongly alkaline solutions, there was no interference from carbon dioxide at m/z 44. Beside the main peak at m/z 44 (100%), the mass spectrum of nitrous oxide has peaks of significant magnitudes at m/z 28 (8%) and m/z 30 (11%), giving rise to a correctable interference with the measurements of nitrogen and nitric oxide, respectively. It was not possible to monitor ammonia.

Nitric oxide was generated by adding sulfuric acid to a mixture of sodium nitrite and potassium iodide, purified by bubbling through a sodium hydroxide solution and stored in a Kipp apparatus under water [8]. All vessels and the distilled water employed in the experiments were flushed with argon before use in order to avoid the presence of oxygen. Copper(I) chloride was prepared by boiling a solution of copper(II) chloride with metallic copper powder, filtering off the excess copper and precipitating the product by dilution with deoxygenated water. A 0.1 M solution of copper(I)–ammonia complex was prepared by dissolving copper(I) chloride in 5 M ammonium chloride buffer, pH 9. The Griess–Ilosvay reagent was made by dissolving 0.5 g sulfanilic acid in 150 ml acetic acid solution (30%, w/w) and 0.1 g α-naphthylamine in 20 ml distilled water and poured into 180 ml acetic acid solution (30%, w/w). 0.5 ml of sample was added to 4 ml solution of sulfanilic acid and 4 ml solution of α-naphthylamine, and completed to 50 ml with distilled water in Ar atmosphere. The absorbance was measured to 540 nm.

3. Results

Fig. 2 shows experiments where the measuring cell was first filled with distilled water saturated with nitric oxide. A fixed amount of ammonium buffer and different amounts of a solution of copper(II) chloride were then added with micro syringes. The nitric oxide concentration was monitored by MIMS at m/z 30. It is seen that the addition of copper(II) chloride caused a two-stage fall in the nitric oxide concentration. The two-stage character of the reaction was more pronounced at the lower concentrations of added copper(II) chloride. At low copper concentrations, the amplitude of the initial rapid stage increased with the amount of copper complex added. When the copper concentration was higher than one half of the saturation concentration of nitric oxide, all the nitric oxide was consumed during the rapid reaction. Acidification of the sample by the addition of

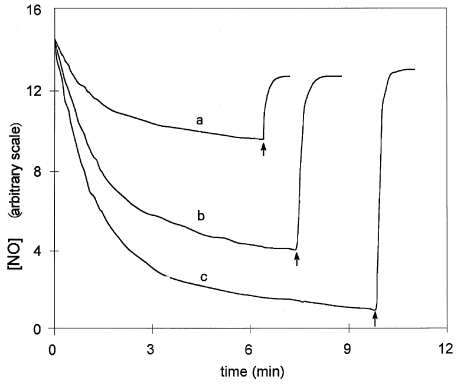

Fig. 2. Reaction between nitric oxide and copper(II) ammonia complex at different initial concentrations followed by mass spectrometric measurement of the nitric oxide concentration as a function of time. The reaction mixture was 4 ml of water saturated with nitric oxide to which (a) 1 μl, (b) 3 μl and (c) 5 μl 1 M copper(II) chloride was added followed by 50 μl of 5 M ammonium chloride buffer pH 9 at time zero. At the arrow the sample was acidified by the addition of 10 μl 10 M sulfuric acid.

sulfuric acid during the slow reaction caused a rapid reappearance of nitric oxide. In Fig. 3, the amount of nitric oxide which had disappeared during the time between the addition of copper and the acidification of the sample and the amount of nitric oxide which reappeared at acidification are plotted as functions of the concentration of copper(II) chloride added. It is seen that the amount of nitric oxide which appeared on acidification was always lower than the amount originally present and at low copper concentrations, it was proportional to the copper concentration. These data indicate that there are at least two processes which consume nitric oxide, one of which is a reversible reaction with copper consuming 2 moles of nitric oxide per mole copper. The reversible process is responsible for the initial rapid phase of the reaction whereas the irreversible loss of nitric oxide is predominant during the slow phase of the reaction. Since nitrite was expected to be a product of the reaction, some samples with excess copper were extracted from the measuring cell after the nitric oxide had disappeared and were analysed for nitrite. We found that the ratio of NO_2^- formed to NO consumed is about 0.5 (0.55).

Periodic scanning of absorption spectra when the reaction was taking place in a closed quartz cuvette revealed that the strong absorption at 620 nm giving rise to the deep blue colour of copper(II) ammine complex disappeared at a rate similar to that of the disappearance of nitric oxide during the rapid reaction phase as observed in the mass spectrometric measurements. At the same time, an absorption peak appeared at 354 nm (Fig. 4). This peak is almost certainly due to nitrite which has an absorption peak at that wavelength. Copper(I) ammine complex has no absorption at 354 nm [5]. As it was observed

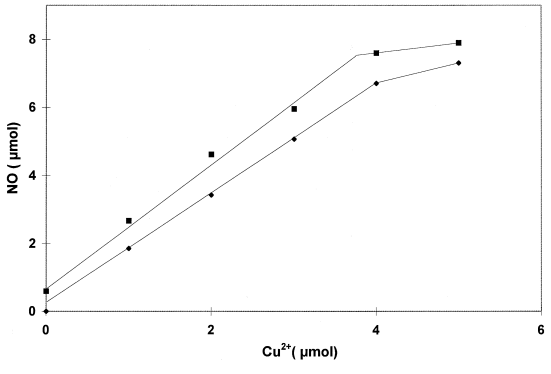

Fig. 3. Nitric oxide consumed (■) in initial rapid reaction and nitric oxide regenerated (◆) on acidification as functions of initial copper(II) concentration. The measurements were performed as in Fig. 2.

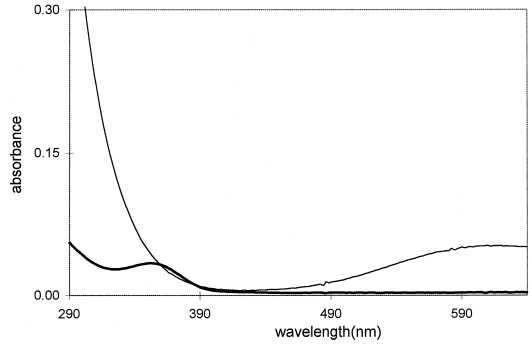

Fig. 4. Absorption spectrum before and after the reaction in the copper–ammonia–nitric oxide system. To a saturated solution of nitric oxide in a stoppered cuvette was added ammonia, and the base line was recorded with the cuvette in the light path. Copper(II) sulfate was then added and the absorption spectrum was scanned after the reaction. The base line spectrum was automatically subtracted.

that an alkaline saturated solution of nitric oxide contained some nitrite, the spectra shown in Fig. 4 were recorded as difference spectra where the absorption spectrum of the saturated nitric oxide solution with ammonia was automatically subtracted. Fig. 5 shows the light absorption at 620 nm of the remaining copper(II) ammine complex after the end of the reaction when different amounts of copper(II) and a fixed amount of ammonia had been added to water saturated with nitric oxide. The points are on a straight line whose intersection with the abscissa indicates the amount of copper (3.7 μmol) which is half of the amount of nitric oxide present (7.9 μmol). This confirms that 2 moles nitric oxide are used per mole copper(II) chloride.

The data presented so far and the bleaching of the deep blue colour of the solution suggested that the copper(II) complex and nitric oxide reacted to form a copper(I) complex and nitrite during the rapid phase. Consequently, a mixture of copper(I) ammine complex and nitrite also should yield nitric oxide on acidification as the reaction mixture did after the nitric oxide had been consumed. We tested this hypothesis by preparing a solution of copper(I) ammine complex to which nitrite was added in the mass spectrometric measuring cell. The mixture was found to generate nitric oxide on acidification. Precise quantification was difficult because it could not be avoided that during the manipulations some of the copper(I) ammine complex reacted with traces of molecular oxygen to form copper(II) ammine complex.

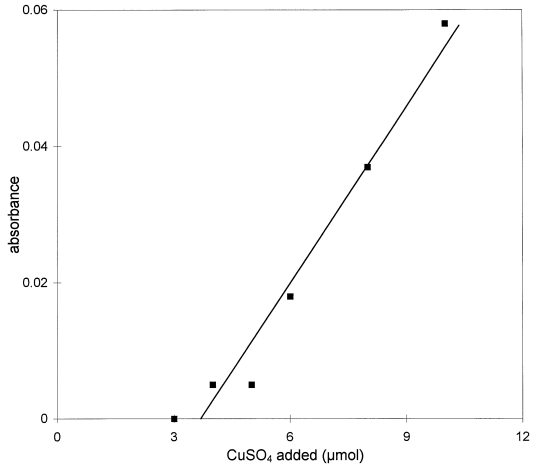

Fig. 5. Titration of nitric oxide with copper(II) sulfate. Different amounts of copper(II) sulfate were added to a solution containing 250 mM ammonia and saturated with nitric oxide in a stoppered cuvette. The light absorption due to copper(II) ammonia complex at 620 nm after the end of the reaction is plotted as a function of the amount of copper(II) added.

When the experiment shown in Fig. 2 was repeated with the addition of copper(I) chloride instead of copper(II) chloride was added to the reaction mixture in the mass spectrometric measuring cell, nitric oxide was consumed at a slower rate than in the experiment with copper(II) chloride and the reaction mixture was found to generate nitric oxide on acidification. The explanation of the latter finding probably is that copper(I) ammine complex binds nitric oxide as a ligand and this is released on acidification.

In order to investigate the slow reaction without the limitations set by the solubility of nitric oxide, we used an open system measuring cell where the stirred reaction mixture was supplied with nitric oxide and ammonia from a head space gas of nitric oxide which had been passed through an ammonia solution. After the sample of distilled water had been freed from atmospheric gases by flushing the head space with argon, the head space gas was changed to nitric oxide spiked with ammonia. When the sample had been equilibrated with nitric oxide and a quasi equilibrium concentration of ammonia had been established, a small amount of copper(II) chloride was added. The result of such an experiment is shown in Fig. 6. It is seen that the addition of copper(II) caused a rapid fall in the nitric oxide concentration followed by an increase to a steady state concentration which was lower than the initial equilibrium concentration. Repeated additions of copper(II) chloride were followed by similar transients, each new steady state concentration of nitric oxide being lower than the previous one. The two-stage character of the reaction is born out in the open system

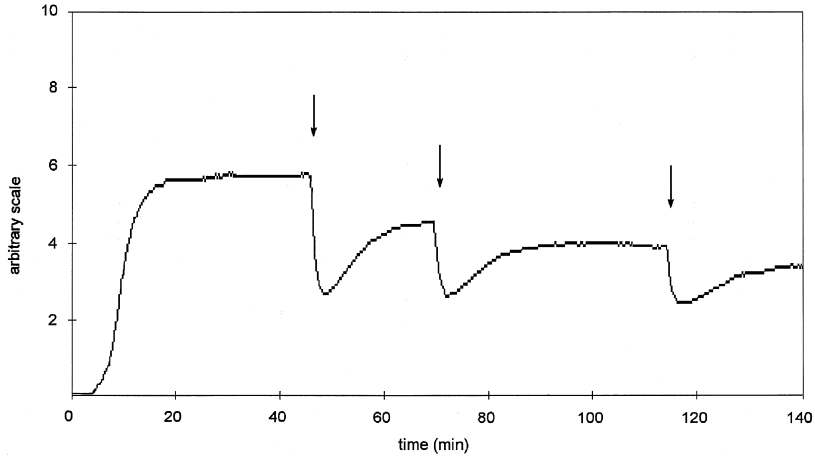

Fig. 6. The copper–ammonium–nitric oxide reaction system monitored (at m/z 30) in open system where nitric oxide and ammonia entered the aqueous sample from a flowing head space gas. The head space gas was a mixture of 20% nitric oxide in argon. Ammonia was added to the head space gas by passing it through a 5% solution of ammonia in water. At the arrows, 5 μl of 1 M copper(II) ammonium chloride was added.

measurements as the initial rapid reaction gives rise to a minimum in the concentration vs. time curve.

Since the flowing head space gas would carry away gaseous reaction products, we performed open system measurements of the type shown in Fig. 6 with the difference that after the equilibration the flow of the head space gas was stopped and the head space was kept under constant pressure from the nitric oxide supply. Copper(II) chloride was then added and nitrogen, nitric oxide and nitrous oxide were monitored in the solution at m/z 28, 30 and 44, respectively. The result of such an experiment is shown in Fig. 7. Again, it is seen that the nitric oxide concentration fell rapidly after the addition of copper(II), passed through a minimum and reached a steady state lower than the equilibrium concentration. Because of the expanded scale, the nitric oxide concentration is only within the scale during the minimum. The mass spectrometric signals corresponding to nitrogen and nitrous oxide both began to increase at approximately constant rates after the addition of copper. Because the mass spectrum of nitrous oxide has a peak at m/z 28 where nitrogen is measured, the nitrogen trace must be corrected for the interference by nitrous oxide. It turns out that the corrected signal at m/z 28 does not indicate a significant production of nitrogen as a product of the slow reaction. The rate of consumption of nitric oxide calculated by the help of the equation and the values of the constants k and V given in Section 2 is 8 μM/s and the rate of formation of nitrous oxide calculated from the slope of the curve is 1 μM/s. The two numbers are not directly comparable because of

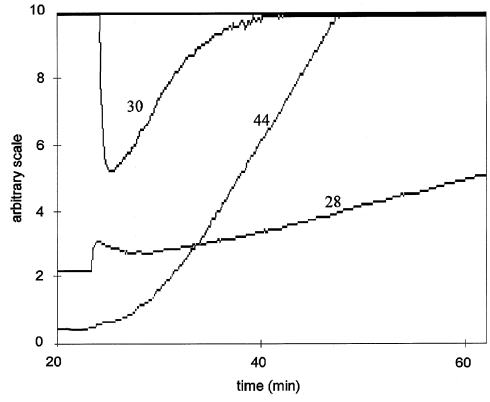

Fig. 7. The copper(II)–ammonia–nitric oxide reaction system monitored (at m/z 30, 28 and 44) in a semi-open system. Experiment similar to that of Fig. 6 except that the flow of the head space gas was interrupted before copper(II) chloride was added. The head space gas was pure nitric oxide to which ammonia had been added by bubbling it through a 10% solution of ammonia in water.

the nitrous oxide partitions between the liquid and the head space gas phase which is not moving. Assuming equilibrium between the two phases with respect to nitrous oxide, we find that twice as much nitrous oxide is present in the head space as in the liquid. If all the nitrous oxide had stayed in the liquid, the rate of formation of nitrous oxide would have been recorded as about 3 μM/s. In similar experiments where the nitric oxide was passed through ammonia solutions of different concentrations resulting in different concentrations of ammonia in the sample, we observed that the rate of the initial fall in nitric oxide concentration decreased with increasing ammonia concentration, whereas the steady state rate of nitric oxide consumption increased with the ammonia concentration.

4. Discussion

Under excess nitric oxide, the reaction between copper(II) ammine complex and nitric oxide is two stages. The rapid and the slow reaction stages are due to different reactions, which we shall discuss separately, beginning with the rapid reaction.

The observations that the copper(II) ammine solution turns colourless as nitric oxide is consumed during the rapid reaction and that nitric oxide is regenerated on acidification suggest that during the initial rapid stage nitric oxide reacts with copper(II) ammine complex to form a copper(I) complex through reversible steps. Spectrophotometric measurements show that 2 moles of nitric oxide are consumed per mole copper(II) and nitrite is a product of the rapid reaction stage. We propose the following equation to describe the reversible transformation.

$$\left[Cu^{II}(NH_3)_n\right]^{2+} + 2NO + 2OH^- \rightleftharpoons \left[Cu^{I}(NH_3)_m NO\right]^{+} + NO_2^- + H_2O + (n-m)NH_3. \quad (1)$$

The reaction mechanism could be that a copper(II)–ammonia–nitric oxide complex is formed which dissociates reversibly into a copper(I) ammine complex and nitrite ion with the free nitrosonium ion as a possible intermediate. The copper(I) ammine complex formed then binds one molecule of nitric oxide.

$$\left[Cu^{II}(NH_3)_n\right]^{2+} + NO \rightleftharpoons \left[Cu^{II}(NH_3)_n NO\right]^{2+}, \quad (2)$$

$$\left[Cu^{II}(NH_3)_n NO\right]^{2+} \rightleftharpoons \left[Cu^{I}(NH_3)_n\right]^{+} + NO^+, \quad (3)$$

$$NO^+ + 2OH^- \rightleftharpoons NO_2^- + H_2O, \quad (4)$$

$$\left[Cu^{I}(NH_3)_n\right]^{+} + NO \rightleftharpoons \left[Cu^{I}(NH_3)_m NO\right]^{+} + (n-m)NH_3. \quad (5)$$

Eqs. (2)–(4) are patterned after equations used to describe the formation and dissociation of copper(II)-halide–nitric oxide complexes in organic solvents [9,10]. Since the formation of such mixed complexes was found to be strongly depressed by traces of water in organic solvent [4], they would not be expected to be formed at all in aqueous solution. We think that the copper(II)–ammonia–nitric oxide complex exists at a low concentration in aqueous solution and its thermodynamically favourable dissociation according to the above equilibria results in an almost complete transformation from copper(II) complex to copper(I) complex. Supporting evidence is that the addition of nitrite to a solution of copper(I) ammine complex results in a mixture that generates nitric oxide on acidification. The formation of a copper(I) complex with nitric oxide as a ligand during the fast reaction is supported by the observation that a reaction mixture, where copper(I) chloride was substituted for copper(II) chloride, released nitric oxide on acidification. The regenerated nitric oxide most likely originates from complex bound nitric oxide.

The apparent inhibition of the rapid reaction by ammonia may indicate that nitric oxide competes with ammonia for binding to the copper(II)

ammonia complex. In terms of the chemical equations above, this would mean that nitric oxide binds to a copper(II) ammonia complex that is not saturated with ammonia ligands. The question of the magnitudes of *n* and *m* calls for further studies. The finding of the reversible process was unexpected and it may have some significance in connection with the formation of nitric oxide in biological contexts. Unfortunately, we cannot easily determine the equilibrium constant because the equilibrium cannot be established unperturbed by the slow reaction.

Following the earlier authors [1], the irreversible loss of nitric oxide associated with the slow reaction would be ascribed to the reduction of nitric oxide by ammonia catalysed by a copper complex. The catalytic nature of the slow reaction was confirmed in the open system measurements where a high steady state rate of the slow reaction and the accumulation of the produced nitrous oxide could be observed. Nitrous oxide was found to be produced in the slow reaction at a rate roughly compatible with the following stoichiometry:

$$8NO + 2NH_3 = 5N_2O + 3H_2O. \quad (6)$$

There was no firm evidence of the formation of nitrogen as a product. As ammonia is difficult to measure by membrane inlet mass spectrometry, we could not detect the consumption of ammonia in the reaction. We do not have sufficient knowledge of the slow reaction to be able to propose a reaction mechanism or the identity of the catalytic complex. Because the rate of the slow reaction increases with the ammonia concentration, the reaction of nitric oxide with the catalytic copper complex probably does not imply binding of nitric oxide in competition with ammonia.

Our work confirms the report by Oates and Lunsford [1] of the reduction of nitric oxide by ammonia catalysed by copper ammine complex in homogeneous aqueous solution but we obtained a different result with respect to reaction products. They found nitrogen and nitrous oxide as reaction product at a ratio of about 2:1. In our experiment, only nitrous oxide and no significant amount of nitrogen were detected. This discrepancy may be due to differences in the conditions. They used a higher temperature and a much higher concentration of ammonia than we did. Since the amount of nitric oxide, which was initially present in their reactor, was not significantly in excess of the amount of copper(II) salt, they should only have been able to observe the rapid phase of the reaction where the consumption of nitric oxide can be accounted for by equilibrium (Eq. (1)). However, as the rate of the rapid reaction decreases and the rate of the slow catalytic reaction increases with the ammonium concentration, the two stages may not be clearly distinguishable under their conditions.

Acknowledgements

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