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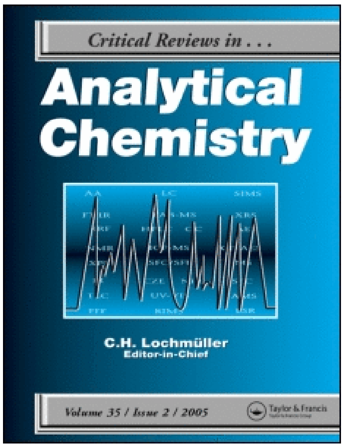

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SOURCES AND MECHANISMS OF NITROUS OXIDE FORMATION

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Introduction. Nitrous oxide is an important byproduct of bacterial nitrification and denitrification, which is a trace component (315 ppb) of the Earth's atmosphere with a long atmospheric lifetime (~120 yrs).[1] The concentration of N_2O has increased by ~10% since 1750, which is thought to arise from several anthropogenic sources. This is significant because N_2O is an important greenhouse gas with about 310 times the global warming potential of CO_2 on a per molecule basis.[2]

Because of its long lifetime N_2O influences stratospheric ozone chemistry. After transport to the stratosphere, N_2O may react with $O(^1D)$ atoms produced from ozone photolysis to generate 2 moles of NO. This is one of the main ways that NO is generated in the stratosphere, and it can cause ozone loss by the catalytic mechanism shown below:

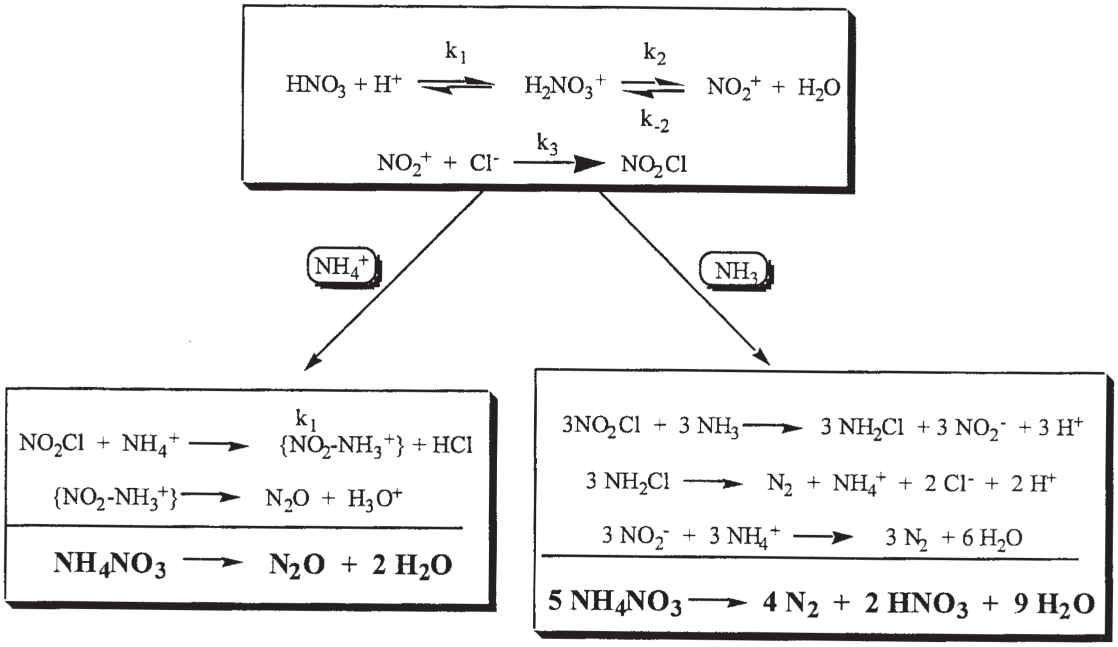
$$NO + O_3 \text{ -----> } NO_2 + O_2$$
$$NO_2 + O \text{ -----> } NO + O_2$$

$$O_3 + O \text{ -----> } 2\ O_2$$

Estimated excess N_2O emissions of ~1 Tg N/yr in the Northern Hemisphere suggested the presence of unknown industrial sources.[3] This was puzzling because nitrous oxide's commercial uses as a dental anesthetic (laughing gas) and a propellant in canned whipping cream were too small to be significant. In 1990, we became aware that N_2O is produced as a byproduct from the manufacture of adipic acid for the synthesis of 6,6-nylon. We showed that oxidation of cyclohexanol/cyclohexanone mixtures with 50% nitric acid charged with VO_3^- and Cu^{2+} catalysts evolved about 1 mole of N_2O gas for each mole of adipic acid isolated. By using the known yearly production of adipic acid we inferred that 0.4-0.6 Tg N/yr are produced as a byproduct of this process. These emissions can account for about *half* the difference seen in N_2O emission rates from the Northern and Southern Hemispheres. Within two months of publishing this article[4] worldwide nylon producers voluntarily committed to a five-year phase out of N_2O emissions. The EPA "Green Nylon" program will help the U.S. meet 10% of its target greenhouse gas emission reduction goals by placing controls on adipic acid manufacturing facilities. This has led to modifications in commercial adipic acid synthesis. The most recent advance has been the BTOP process, which originated at the Boreskov Institute of Catalysis and was recently commercialized by Solutia.[5-7] It captures N_2O from the adipic acid process and uses it for the one-step catalytic oxidation of benzene to produce phenol, which is subsequently oxidized to adipic acid.

Ammonium nitrate is an important fertilizer and over 88 billion lbs are produced each year. It is also an explosive compound, which decomposes at lower temperatures ~220° C to yield N_2O. Much ammonium nitrate is produced by the exothermic neutralization of ammonia and nitric acid in titanium pressure reactors where temperatures approach 180-190° C. Therefore we explored the possible production of nitrous oxide under conditions similar to those used in the commercial process.[8] The decomposition of aqueous ammonium nitrate at elevated temperatures and pressures was examined as a function of chloride, nitrate, and total acidity. Catalysis requiring both chloride and acid was observed in solutions containing 20% (w/w) NH_4NO_3 at 180°C.

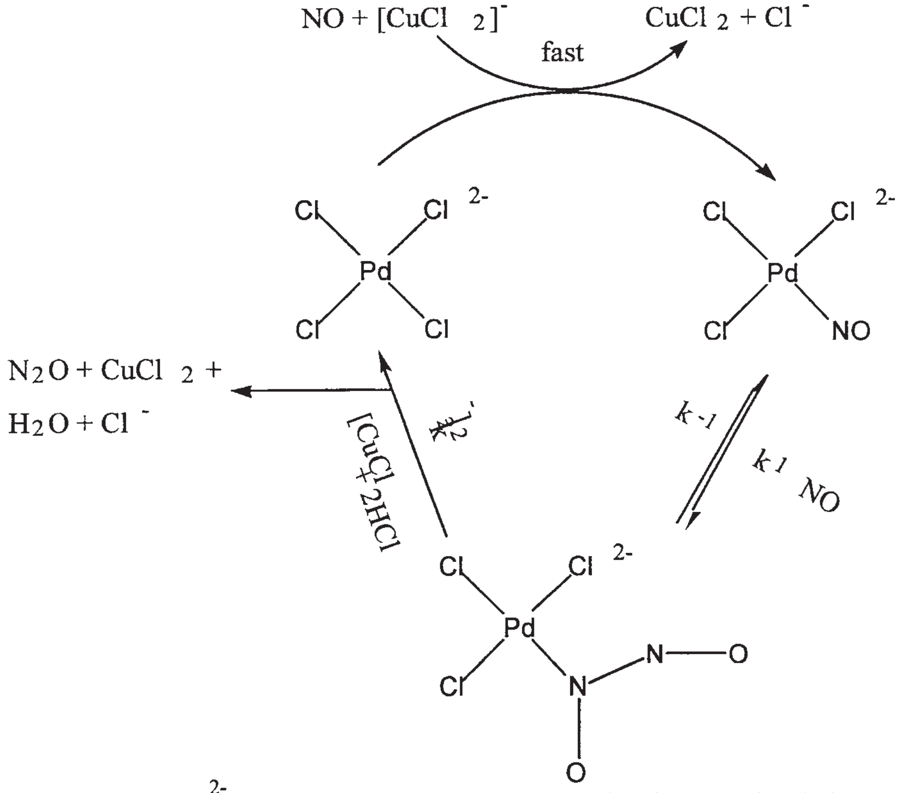
Nitrous oxide and dinitrogen were generated in a 4:1 ratio below 0.2M H^+. Dinitrogen formation correlated with the production of additional acidity by the reaction 5 NH_4NO_3 ---> 4 N_2 + 2 HNO_3 + 9 H_2O. The decomposition reaction's second-order dependence on $[H^+]$ is consistent with the reversible formation of NO_2^+. Incorporation of ^{18}O into the N_2O product, as well as the inverse deuterium isotope effect, support this conclusion. A novel mechanism based on the intermediacy of NO_2Cl is proposed for the chloride catalysis, and contrasted to the radical-based pathways operational in molten NH_4NO_3 decompositions. Isotope labeling experiments using $^{15}NH_4NO_3$ yield $^{15}N{=}N{=}O$ labeled nitrous oxide and the dinitrogen products $^{15}N{\equiv}^{15}N$ and $N{\equiv}^{15}N$ in a 1:3 ratio. Decomposition of $NH_4{}^{15}NO_3$ produces only $N{=}^{15}N{=}O$ and $N{\equiv}^{15}N$. The kinetics and isotope labeling studies agree with the reaction mechanism shown below. Initial reversible formation of NO_2^+ explains the second order proton dependence, inverse deuterium isotope effect, and exchange of ^{18}O with $^{18}OH_2$ solvent. The k_3 step explains the catalytic role of chloride. The branching of the mechanism, with the NO_2Cl/NH_4^+ reaction yielding N_2O and the NO_2Cl/NH_3 reaction producing N_2, explains the linear dependence of the N_2O/N_2 product ratio on the proton concentration.



These results bear on the industrial preparation of NH_4NO_3, and suggest conditions under which nitrous oxide emissions might be important to the global N_2O budget. The high efficiency of chloride catalysis also suggest a plausible mechanism for a 1994 accidental explosion at Terra Industries,[9] as well as the greatest industrial disaster that ever occurred in the U.S. (Texas City, 1947).[10]

On a more fundamental level we have explored catalytic mechanisms that might be important in N_2O forming reactions. Kinetics data were collected for the palladium-catalyzed reduction of nitric oxide (NO) to nitrous oxide (N_2O) with cuprous chloride reductant in 2M hydrochloric acid (2 NO + 2 CuCl + 2 HCl --- $[PdCl_4]^{2-}$ ---> N_2O + 2 $CuCl_2$ + H_2O).[11] The rate-determining step was first order in the palladium concentration and NO partial pressure. The cuprous chloride dependence was first-order below 0.1M; at higher concentrations saturation kinetics were observed. The rate of reaction was independent of H^+ and Cl^- concentrations. The kinetic results were consistent with the initial, reversible attack (k_1/k_{-1}) of free NO on the bound nitrosyl of

$[PdCl_3NO]^{2-}$ yielding $[PdCl_3\,(N_2O_2)]^{2-}$ which is then reduced by Cu(I) (k_2) to generate products and recycle the palladium, as shown in the scheme below.



The $[PdCl_3NO]^{2-}$ ion could be spectroscopically characterized (in D_2O/DCl) by its strong N-O stretching frequency at 1662 cm^{-1}. A k_1 value of $(6.0 \pm 0.4)x10^{-6}$ $(P_{torr})^{-1}$ sec^{-1} at 20°C was calculated, with a $k_1/\,k_2$ ratio of 0.116 ±.004 M. Nitric oxide reduction by Cu(I) is the rate-limiting step in the Pd(II)/Cu(II) Wacker-style catalysis of the CO + 2 NO ----> CO_2 + N_2O reaction. The current mechanism parallels the nitric oxide reductase activity of cytochrome *c* oxidases, which proceed by Cu(I) reduction of a heme bound nitrosyl. Although a 2-electron reduction to a metal nitrido complex has been suggested, we propose that a stepwise NO binding, 1-electron reduction, NO coupling, 1-electron reduction mechanism is a lower energy pathway.[11]

A heterogeneous Pd^0 on activated charcoal catalyst was examined in 3M NaOH.[12] The activity of this catalyst for removing NO from the headspace above the solution was exceptional, and control reactions showed little activity in the filtrate from these solutions. Reaction 1 is catalyzed by a slurry of activated carbon, and further accelerated by palladium-treated activated carbons. Mass balance experiments are consistent with the stoichiometry of reaction 1 in all instances.

$$4\,NO + 2OH^- \text{---->} N_2O + 2\,NO_2^- + H_2O \qquad (1)$$

The rate can be followed conveniently by monitoring the evolution of N_2O, Figure 1, which established true catalytic turnover.

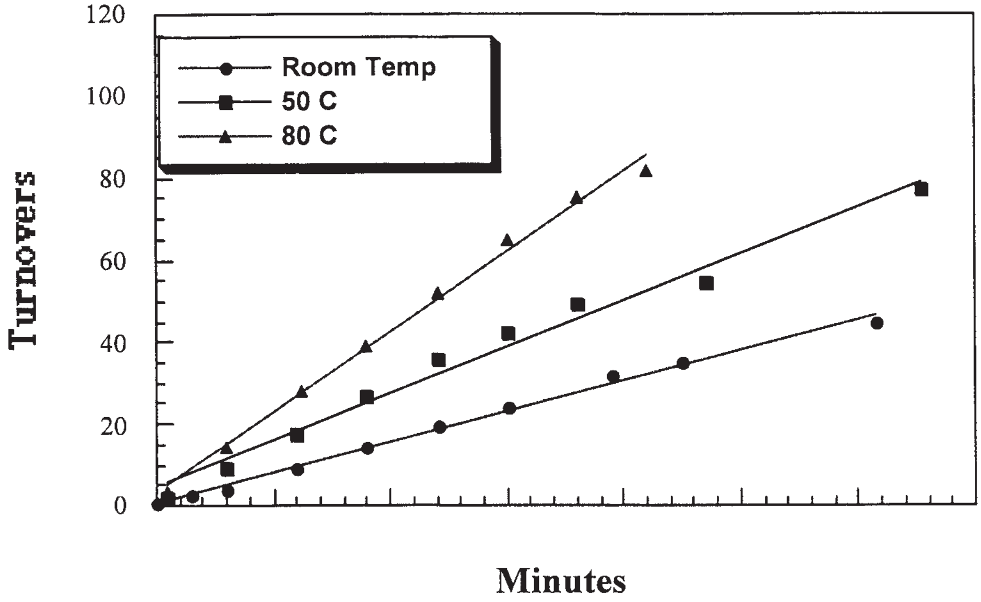
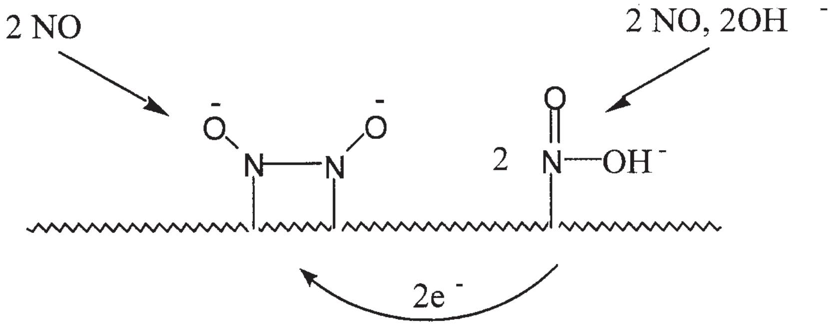


Figure 1. Plot of the moles of N_2O produced per mole of Pd vs. time during the aqueous catalytic disproportionation of NO.

The mechanism postulated is shown below:

Postulated Surface Redox Mechanism



At present the evidence for this mechanism is that the pH dependence of catalysis shows a thermodynamic limitation consistent with $N_2O_2^{2-}$ being a requisite intermediate. Furthermore, formation of N_2O can be blocked by the addition of 1-2% O_2 to the reaction gases. This suggests that surface bound O_2, which is a stronger oxidant than NO dimer, can act as the electron acceptor and the product can be directed entirely to NO_2^- formation. This offers a new catalytic approach for NO scrubbing from exhaust gases. The catalysts are not poisoned by SO_2 and the basic solution simultaneously removes SO_x. Current mechanistic studies focus on defining the surface electrochemistry of bound NO.

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