ISGC 2022

N°870 / OC

TOPIC(s) : Homogenous, heterogenous and biocatalysis / Mechanism investigations

Photocatalytic deoxygenation of nitrogen oxide compounds

AUTHORS

Marianne KJELLBERG / CEA SACLAY, CEA SACLAY, GIF-SUR-YVETTE
Annamaria QUARANTA / CEA SACLAY, CEA SACLAY, GIF-SUR-YVETTE
Emmanuel NICOLAS / CEA SACLAY, CEA SACLAY, GIF-SUR-YVETTE
Lucile ANTHORE-DALION / CNRS, CEA SACLAY, GIF-SUR-YVETTE
Alexia OHLEIER / CEA SACLAY, CEA SACLAY, GIF-SUR-YVETTE
Corresponding author : Thibault CANTAT / thibault.cantat@cea.fr

PURPOSE OF THE ABSTRACT

The accumulation of nitrogen oxides in the environment calls for new pathways to interconvert the various oxidation states of nitrogen, and especially their reduction. However, the large spectrum of reduction potentials covered by nitrogen oxides makes it difficult to find general systems capable of efficiently reducing various N-oxides.

Commonly known as "laughing gas", nitrous oxide N2O is an ozone-depleting substance 298 times more powerful a greenhouse gas than CO2. It accumulates in the atmosphere due to its kinetic stability (average lifetime of 120 years), thus contributing to 6% of anthropogenic greenhouse effect.[1,2] A solution would be the reduction of N2O back to N2, which would close the nitrogen cycle; however, few methods have been proposed due to the low reactivity of N2O. Herein we describe a new pathway to reduce N2O back to nitrogen at room temperature by means of photocatalysis. N2O being isoelectronic with CO2, inspiration came from previous work on the photoreduction of CO2 to CO first disclosed by the group of Jean-Marie Lehn.[3] Remarkably, [Re(bpy)(CO)3Cl] and its derivatives proved successful for the reduction of N2O. With [Re(tBu-bpy)(CO)3Cl], GC monitoring gave out 86% conversion and a maximum TON of 17.[4]

Encouraged by this success, we extended this methodology to the reduction of other N?O bonds, leading to a selective and synthetically applicable photocatalytic version of the deoxygenation of pyridine N-oxides. The mechanism of the N?O bond deoxygenation was studied on this substrate using laser flash photolysis and spectroelectrochemistry. Key steps of the mechanism were identified; those insights enabled to optimize the system by shortening the reaction time from 34 h to 2 h. This unlocked the path to the deoxygenation of a broader scope of compounds, such as quinoline N-oxide derivatives and other heteroaromatic N-oxides.

FIGURES

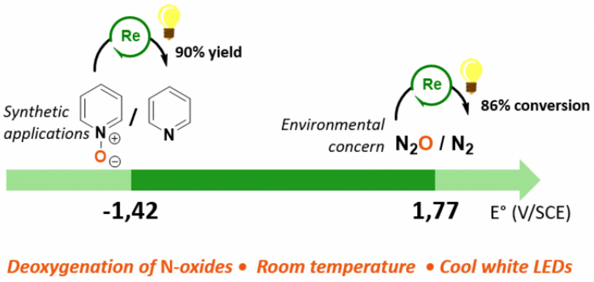

FIGURE 1

Photocatalytic deoxygenation of various N-oxides

Photocatalysts of the type [Re(bpy)(CO)3Cl] proved efficient to deoxygenate N oxide compounds at opposite ends of the redox potential scale.

FIGURE 2

KEYWORDS

nitrous oxide | photocatalysis | mechanism | NOx

BIBLIOGRAPHY

[1] D. Ussiri, R. Lal, Soil Emission of Nitrous Oxide and its Mitigation, 2013, 243-275.
[2] M. Dameris, Angew. Chem. Int. Ed. Engl., 2010, 49, 489-491.
[3] J. Hawecker, J-M. Lehn, R. Ziessel, J. Chem. Soc, Chem. Commun., 1983, 536-538.
[4] M. Kjellberg, A. Ohleier, P. Thuéry, E. Nicolas, L. Anthore-Dalion, T. Cantat, Chem. Sci. 2021, 12, 10266-10272.