5594 *J. Am. Chem. Soc.* **1995,** *117,* 5594−5595

Nitrous Oxide Activation by a Ruthenium Porphyrin

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Received July 18, 1994

Ruthenium porphyrins have received considerable attention due to their potential as catalysts for the oxidation of a variety of organic functional groups.[1] Pathways to high-valent oxoruthenium complexes include the use of organic[1b,2] and inorganic[1d,g,3] oxidants, electrochemical techniques,[1h] and aerobic oxidation.[1a,c,f,2] The latter could be of considerable practical importance for the large-scale catalytic oxygenation of hydrocarbons using ruthenium porphyrins.[1k] We have recently considered nitrous oxide as an alternative oxidant due to its vast availability as a byproduct of the industrial manufacture of nylon and its wider range of process safety *vis à vis* oxygen. Further, N_2O has been implicated as a greenhouse gas and ozone antagonist, which may make current emission practice untenable.[4]

Nitrous oxide is an extremely inert molecule[5] and a very poor ligand.[6] This is surprising given its free energy of formation ($\Delta G° = +24.9$ kcal/mol) and potential oxidizing power.[7] To our knowledge, $[Ru(NH_3)_5(N_2O)]^{2+}$ is the only well-characterized complex containing nitrous oxide.[8] Of the few known reactions of this gas are its deoxygenation by certain transition-metal complexes[5] and the catalytic oxidation of PPh_3 using a cobalt(I) species.[9] Dinitrogen oxide has also been observed to function as a bridging ligand in the preparation of oxo-bridged molecular clusters of Ti, V, and Cr.[6,10] Insertions of N_2O and oxidation at a ligand site are also known.[11] The reduction of nitrous oxide over cobalt porphyrins,[12] polyamine complexes of nickel,[13] transition-metal oxides,[14] and group VIII carbonyl anion[15] catalysts has been reported, as has the oxidation of simple hydrocarbons over supported metals[16] or FeZSM-5 zeolites[17] at elevated temperatures. Our interest in the catalytic oxidation of organic substrates using *trans*-dioxoruthenium(VI) porphyrins[1a−c] has prompted us to investigate the reactivity of nitrous oxide toward these catalysts. We describe here the first example of direct oxygen atom transfer from N_2O to a metalloporphyrin.

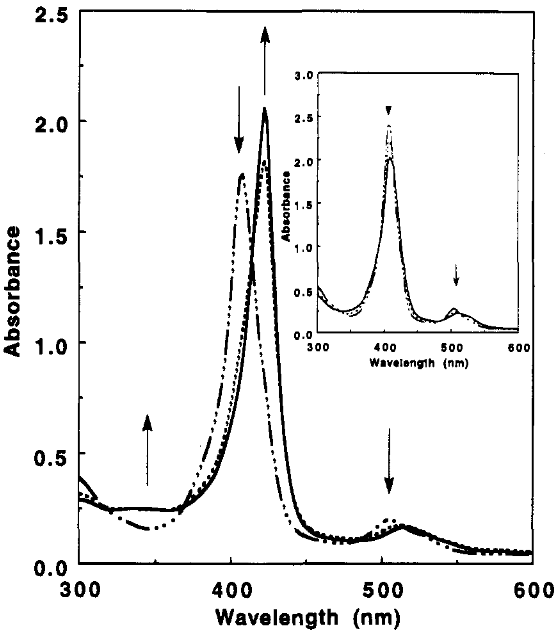

Figure 1. Visible spectral changes of 8.46×10^{-6} M $Ru(TMP)(THF)_2$ (**1**) in toluene at 0 °C upon addition of 6 psi N_2O (time = 0, 8, 20 min). Inset: control reaction using argon at the same time intervals.

When 6 psi N_2O was admitted[18] to a sealed quartz cuvette containing a $\sim 10^{-5}$ M toluene solution of $Ru^{II}(TMP)(THF)_2$[19] (**1**, TMP = dianion of tetramesitylporphyrin), a rapid conversion to $Ru^{VI}(TMP)(O)_2$ (**2**) was observed, as judged by visible spectroscopy (Figure 1)[20] and subsequent TLC separation. This sample of **2** was capable of oxidizing ethyl sulfide to its sulfoxide.[1f] Control experiments using argon resulted in broadening of the visible absorption bands over several minutes. This behavior was also observed when a solution of **1** was allowed to stand under an inert atmosphere, suggesting the cause is dissociation of one or both THF ligands in a noncoordinating solvent such as toluene.

Reaction intermediates preceding the formation of **2** could be observed when $Ru(TMP)(THF)_2$ (**1**) in C_6D_6 ($\sim 10^{-3}$ M) was

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[18] Nitrous oxide (>99.995%) was purchased from Alphagaz and contained <0.8 ppm (Ar + O_2). Further purification via three freeze−pump−thaw cycles had no effect on the observed results.

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[20] $Ru(TMP)(THF)_2$ (toluene): λ_{max} (log ϵ) = 408 (5.32), 504 (4.37), 526 (sh) nm; $Ru(TMP)(O)_2$ (toluene): λ_{max} (log ϵ) = 422 (5.47), 516 (4.20) nm.

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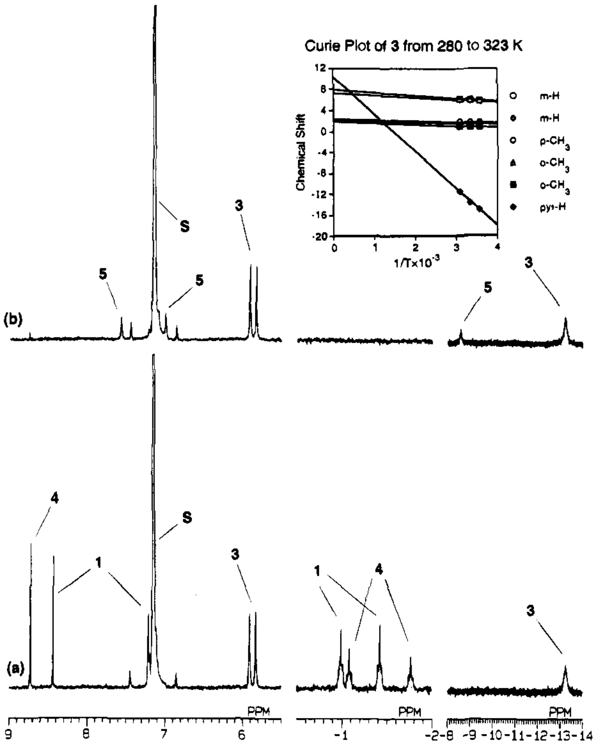


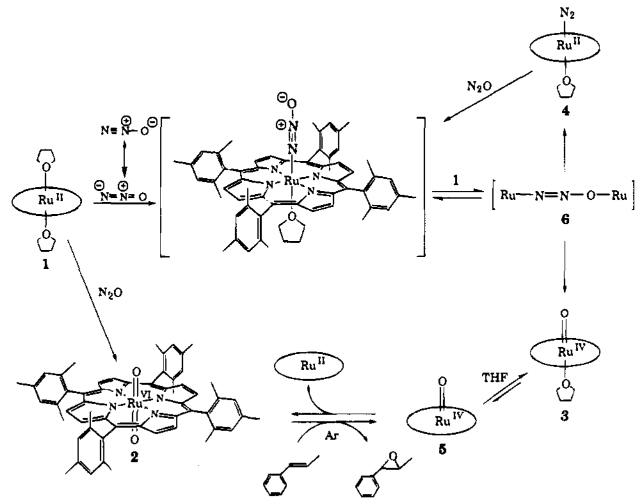
Figure 2. ^{1}H-NMR spectra of $\sim10^{-3}$ M $Ru(TMP)(THF)_2$ (**1**) in C_6D_6 (a) 5 min and (b) 23 h after exposure to 50 psi N_2O. Inset: Curie plot of $Ru(TMP)(O)(THF)$ (**3**) from 280 to 323 K.

vacuum-sealed in an NMR tube under 50 psi N_2O. Resonances corresponding to a new unsymmetrical paramagnetic porphyrin (**3**) and $Ru^{II}(TMP)(THF)(N_2)$[21] (**4**) appeared within 5 min (Figure 2), while after 30 min, compound **3** was the only species present. The broad *o*-methyl and upfield-shifted *β*-pyrrole resonances of **3** and a Curie plot (Figure 2, inset) resemble those of $Ru^{IV}(TMP)(O)$[1c] (**5**) and intimate a similar structure. Solutions of **3** were found to equilibrate to a mixture of **3** and **5** over a period of several hours. When a toluene-d_8 solution of $Ru(TMP)(THF)_2$ ($\sim10^{-4}$ M) was sealed under N_2O, all the starting material disappeared within minutes to afford **3** according to the ^{1}H-NMR and visible (λ_{max} = 414, 524 nm) spectra. When this sample was cooled to −50 °C, two new broad peaks corresponding to 1 equiv of *coordinated* THF appeared, and the resonances due to free THF sharpened dramatically.

This same species **3** was also produced when $Ru^{IV}(TMP)(O)$ (**5**) was generated in the presence of 1.6 equiv of free THF. $Ru^{VI}(TMP)(O)_2$ (**2**) can be efficiently reduced by *trans-β*-methylstyrene to **5** under anaerobic conditions. This olefin and its epoxide do not coordinate appreciably to Ru(TMP). However, in the presence of THF, the Ru(IV) monooxo species was slowly converted into **3**. These results strongly support the formulation of **3** as $Ru^{IV}(TMP)(O)(THF)$, with exchange broadening being responsible for the absence of THF resonances at ambient temperature.

Since the formation of $Ru(TMP)(O)_2$ (**2**) requires the disproportionation[1a] of two molecules of $Ru(TMP)(O)$ (**5**), the reaction could proceed at high dilution while the axially bound THF in **3** effectively blocks the oxo transfer from one ruthenium to another at concentrations of $\sim10^{-3}$ M. This effect could be demonstrated by the reaction of $Ru(TMP)(THF)_2$ (**1**) with N_2O in a dilute toluene solution containing 10% THF (v/v). No oxidation was detected by visible spectroscopy over a period of 30 min. Similar inhibition by added THF and by higher porphyrin concentrations was also observed in the aerobic oxidation of **1**.

Scheme 1



Scheme 1 summarizes the major intermediates observed in the reaction of nitrous oxide with $Ru(TMP)(THF)_2$ (**1**), as well as the independent formation of **3** from the reduction of **2**. The simultaneous appearance of compounds **3** *and* **4** implicates an N_2O-bridged dimer, similar to $[Ru(NH_3)_5N_2ORu(NH_3)_5]^{4+}$,[22] with terminal N-coordination as the initial step. Heterolytic cleavage of the N−O bond in such a bridged dimer (**6**) would lead to the concurrent formation of these two species. Although some interpretations suggest that N_2O is bonded to ruthenium through its oxygen atom in $[Ru(NH_3)_5N_2O]^{2+}$,[8a,23] there is much circumstantial evidence which favors a terminal N-bound structure.[24]

We have demonstrated here that nitrous oxide can be used to oxidize $Ru(TMP)(THF)_2$ directly and efficiently under mild conditions to *trans*-$Ru(TMP)(O)_2$ (**2**). We have also observed two key intermediates which may be useful in elucidating the mechanism of oxygen atom transfer from N_2O. An industrial process which utilizes dinitrogen oxide in the manufacture of oxiranes and alcohols would be of considerable economic and environmental benefit. Toward this goal, continuing research is aimed at developing a ruthenium-promoted catalytic system where nitrous oxide can be used as the sole oxidant.

Acknowledgment. Support of this research by the National Science Foundation (CHE-8706310) is gratefully acknowledged.

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