## 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.<sup>1</sup> Pathways to high-valent oxoru-thenium complexes include the use of organic<sup>1b,2</sup> and inorganic<sup>1d,g,3</sup> oxidants, electrochemical techniques,<sup>1h</sup> and aerobic oxidation.<sup>1a,c,f,2</sup> 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<sub>2</sub>O has been implicated as a greenhouse gas and ozone antagonist, which may make current emission practice untenable.<sup>4</sup>

Nitrous oxide is an extremely inert molecule<sup>5</sup> and a very poor ligand.<sup>6</sup> This is surprising given its free energy of formation  $(\Delta G^{\circ} = +24.9 \text{ kcal/mol})$  and potential oxidizing power.<sup>7</sup> To our knowledge,  $[Ru(NH_3)_5(N_2O)]^{2+}$  is the only well-characterized complex containing nitrous oxide.<sup>8</sup> Of the few known reactions of this gas are its deoxygenation by certain transitionmetal complexes<sup>5</sup> and the catalytic oxidation of PPh<sub>3</sub> using a cobalt(I) species.<sup>9</sup> 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.<sup>6,10</sup> Insertions of N<sub>2</sub>O and oxidation at a ligand site are also known.<sup>11</sup> The reduction of nitrous oxide over cobalt porphyrins,12 polyamine complexes

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Figure 1. Visible spectral changes of  $8.46 \times 10^{-6} \text{ M Ru}(\text{TMP})(\text{THF})_2$ (1) in toluene at 0 °C upon addition of 6 psi N<sub>2</sub>O (time = 0, 8, 20 min). Inset: control reaction using argon at the same time intervals.

of nickel,<sup>13</sup> transition-metal oxides,<sup>14</sup> and group VIII carbonyl anion<sup>15</sup> catalysts has been reported, as has the oxidation of simple hydrocarbons over supported metals<sup>16</sup> or FeZSM-5 zeolites<sup>17</sup> at elevated temperatures. Our interest in the catalytic oxidation of organic substrates using trans-dioxoruthenium(VI) porphyrins<sup>1a-c</sup> 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 N2O to a metalloporphyrin.

When 6 psi  $N_2O$  was admitted<sup>18</sup> to a sealed quartz cuvette containing a  $\sim 10^{-5}$  M toluene solution of Ru<sup>II</sup>(TMP)(THF)<sub>2</sub><sup>19</sup> (1, TMP = dianion of tetramesitylporphyrin), a rapid conversion to  $Ru^{VI}(TMP)(O)_2$  (2) was observed, as judged by visible spectroscopy (Figure 1)<sup>20</sup> and subsequent TLC separation. This sample of 2 was capable of oxidizing ethyl sulfide to its sulfoxide.<sup>1f</sup> 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)<sub>2</sub> (1) in C<sub>6</sub>D<sub>6</sub> ( $\sim 10^{-3}$  M) was

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(20) Ru(TMP)(THF)<sub>2</sub> (toluene):  $\lambda_{max} (\log \epsilon) = 408 (5.32), 504 (4.37), 526 (sh) nm; Ru(TMP)(O)<sub>2</sub> (toluene): <math>\lambda_{max} (\log \epsilon) = 422 (5.47), 516 (4.20)$ 

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Figure 2. <sup>1</sup>H-NMR spectra of  $\sim 10^{-3}$  M Ru(TMP)(THF)<sub>2</sub> (1) in C<sub>6</sub>D<sub>6</sub> (a) 5 min and (b) 23 h after exposure to 50 psi N<sub>2</sub>O. Inset: Curie plot of Ru(TMP)(O)(THF) (3) from 280 to 323 K.

vacuum-sealed in an NMR tube under 50 psi N<sub>2</sub>O. 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  $\beta$ -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  $Ru(TMP)(THF)_2$  (~10<sup>-4</sup> M) was sealed under N<sub>2</sub>O, all the starting material disappeared within minutes to afford 3 according to the <sup>1</sup>H-NMR and visible ( $\lambda_{max} = 414$ , 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<sup>1a</sup> of two molecules of Ru(TMP)(O) (5), the

Scheme 1



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  $\sim 10^{-3}$  M. This effect could be demonstrated by the reaction of Ru(TMP)(THF)<sub>2</sub> (1) with N<sub>2</sub>O 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 summarizes the major intermediates observed in the reaction of nitrous oxide with Ru(TMP)(THF)<sub>2</sub> (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<sub>2</sub>O-bridged dimer, similar to [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>ORu(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>,<sup>22</sup> 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<sub>2</sub>O is bonded to ruthenium through its oxygen atom in [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup>,<sup>8a,23</sup> there is much circumstantial evidence which favors a terminal N-bound structure.<sup>24</sup>

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<sub>2</sub>O. 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.

## JA942315I

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