Supporting Info

for

Kinetics and Thermodynamics of Nitric Oxide Binding to Transition Metal Complexes.

Relationship to Dioxygen Binding

Andreja Bakac*, Oleg Pestovsky, Bridget L. Durfey and Kathleen E. Kristian

Chemistry Department and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Table of contents

Experimental detail pp S3-S5

Table S1. Reagent Concentrations and UV-Vis Data Used in Determinations of \( k_{NO,Co} \) S5
Table S2. Reagent Concentrations and UV-Vis Data Used in Determinations of \( k_{NO,Co} \) S6

Figure S1. An example of a kinetic trace (red) and fit to first-order kinetics (black) for the homolysis of \( L^2(H_2O)Co(NO)^{2+} \) (0.02 mM) in the presence of \( IrCl_6^{2-} \) (0.09 mM) at 38.0°C. Data yield \( k = 0.030 \text{ s}^{-1} \). S6

Figure S2. Plot according to the Eyring equation for the homolysis of \( L^2(H_2O)Co(NO)^{2+}, 0.5 - 1.0 \text{ mM} \), in the presence of excess \( IrCl_6^{2-}, [H^+] = 0.001 - 0.01 \text{ M}, \lambda 487 \text{ nm} (\epsilon = 3920 \text{ M}^{-1} \text{ cm}^{-1}) \). S7

Figure S3. UV-Vis spectra of \( L^1(H_2O)CoNO^{2+} \). S7

Figure S4. Dissociation of \( ^*\text{NO} \) from \( L^1(H_2O)Co(NO)^{2+} \) (0.05 mM) in the presence of 0.12 mM \( IrCl_6^{2-} \) at 35.0°C. Fit (black line) to the first-order rate law is shown on the left, and to \{first + linear\} on the right. The slightly smaller \( k \) in the left figure is caused by the slow decomposition of excess \( IrCl_6^{2-} \) and drifting absorbance at long times. The \{first + linear\} treatment corrects for this secondary reaction. S8

Figure S5. Eyring plot for \( ^*\text{NO} \) dissociation from \( L^1(H_2O)Co(NO)^{2+} \) with \( O_2 \) (red circles) or \( IrCl_6^{2-} \) (blue squares) as scavengers. S9

Figure S6. UV-Vis spectra of \( [L^2(H_2O)Rh(NO)^{2+}] \). S9

Figure S7. Kinetic plot for the dissociation of \( ^*\text{NO} \) from \( L^2(H_2O)Rh(NO)^{2+} \) (1 mM) at S10
650 nm ($\epsilon = 45 \text{ M}^{-1} \text{ cm}^{-1}$) in O$_2$-saturated 0.01 M aqueous HClO$_4$ at 88.0$^0$ C

**Figure S8.** Eyring plot for $^\cdot$NO dissociation from $L^2$(H$_2$O)Rh(NO)$_2^{2+}$ with O$_2$ and air as scavengers.

**Figure S9.** UV -Vis spectrum of 7.8 mM Cr(H$_2$O)$_5$(NO)$_2^{2+}$ in 0.4 M aqueous HClO$_4$

**Figure S10.** Absorbance vs time plot at 449 nm ($\epsilon = 121 \text{ M}^{-1} \text{ cm}^{-1}$) for $^\cdot$NO dissociation from Cr(H$_2$O)$_5$(NO)$_2^{2+}$ (0.9 mM) at 50.0$^0$ C with O$_2$ as scavenger. Data yield $k = 4.70 \times 10^{-6}$ s$^{-1}$.

**Figure S11.** Eyring plot for $^\cdot$NO dissociation from Cr(H$_2$O)$_5$(NO)$_2^{2+}$ with O$_2$/air as scavenger

**Figure S12.** Plots of log $K_{NO}$ and of log $K_{O2}$ vs $E^0$ of MIII/M(II) couples. Data from Table 3.

**Figure S13.** Expanded plot of log $K_{NO}$ vs log $K_{O2}$ for the complexes of cobalt (red), iron (blue), rhodium (black), chromium (green) and Fe(edta)$^{2-}$ (gray). The data point for hydrogen atom is omitted.

**References**
Experimental detail

Cr(H₂O)₅NO²⁺ was prepared in solution from Cr(H₂O)₆²⁺ and 'NO and ion-exchanged on a column of Sephadex C-25 cation exchange resin.² The UV-Vis spectrum matched exactly that reported in the literature.² L¹(H₂O)Co(NO)²⁺ was prepared analogously from L¹Co(H₂O)₂²⁺ and NO, and ion-exchanged. UV-Vis in 0.01 - 0.40 M HClO₄, $\lambda_{\text{max}}$ ($\varepsilon$/M·cm⁻¹): 740 (17.8), 540 (79), 442 (99), 344 (130), 234 (1.01 × 10⁴).

**Preparation of [L²(H₂O)Co(NO)](CF₃SO₃)₂.** To a sample of 42 mg of [L²(H₂O)₂Co](CF₃SO₃)₂ (0.061 mmol) under argon was added 9 mL of deaerated 5 mM CF₃SO₃H. Nitrogen monoxide was bubbled through the solution for several minutes during which time the color changed from pale pink to dark purple. The solution was cooled in ice, and an excess of solid LiCF₃SO₃ was added. In a few minutes, [L²(H₂O)Co(NO)](CF₃SO₃)₂ precipitated and was collected by filtration, washed with ice-cold water, and dried in a dessicator at atmospheric pressure. Attempts at purifying the compound by recrystallization yielded a lower-quality product owing to the high water solubility of the triflate salt and ready dissociation of 'NO in solution and even in the solid state. The sensitivity of 'NO to oxygen prevented us from performing recrystallization in an 'NO atmosphere. Yield: 24 mg (57%, FW 689.58). Anal. calcd. for C₁₈H₃₈CoF₆N₅O₈S₂: C, 31.35; H, 5.55; N, 10.16; S, 9.30. Found: C, 33.10; H, 5.58; N, 10.10; S, 9.80. UV-Vis $\lambda_{\text{max}}$: 531 nm (212 M⁻¹ cm⁻¹), 422 nm (234 M⁻¹ cm⁻¹), 359 nm (472 M⁻¹ cm⁻¹). IR (photoacoustic, solid state): 1547 cm⁻¹, 1662 cm⁻¹.

Fresh samples of solid [L²(H₂O)Co(NO)](CF₃SO₃)₂ for kinetic studies were synthesized every 1-2 weeks. The concentration of L²(H₂O)Co(NO)²⁺ was determined from the visible spectrum, **Figure 1**, prior to each experiment. The rate constants were independent of the age of the solutions.
Gaseous nitrogen monoxide (Matheson) was purified by passage through Ascarite, sodium hydroxide and water. Ammonium hexachloroiridate and sodium hexabromooiridate were purchased from Aldrich and used as received. UV-Vis spectra and the kinetics of 'NO dissociation from the nitrosyl complexes were determined with a Shimadzu 3101 PC spectrophotometer. IR spectra were obtained with a Bio-Rad Digilab FTS-60A FT-IR spectrometer equipped with an MTEC Model 200 photoacoustic cell. The kinetics of NO binding to $L^2(H_2O)Rh(NO)^{2+}$ and to $LCo(H_2O)_2^{2+}$ ($L = L^1$ and $L^2$) were determined by laser flash photolysis. The laser set-up is based on a Lambda Physik Excimer Pro 2 xenon chloride excimer laser and an Applied Photophysics monitoring system described earlier. In-house distilled water was further purified by passage through a Barnstead EASY Pure III system.

**Kinetic studies**

The dissociation of 'NO from $L^2(H_2O)Rh(NO)^{2+}$ and from $Cr(H_2O)_5(NO)^{2+}$ is extremely slow even at the high temperatures employed. Work with $L^2(H_2O)RhNO^{2+}$ is further complicated by its sensitivity to light. To avoid interference from photo-homolysis induced by analyzing spectrophotometer light over long periods of time, the samples were handled and thermostatted in the dark. Several spectra were recorded for kinetic purpose over the course of the reaction. For experiments above 65°C, 3-mL samples in 10-mL thick-walled septum-sealed glass bottles were kept at a constant temperature in an oil bath for the desired amount of time, followed by rapid cooling and recording of the spectrum. The large volume of the gas relative to the solution phase assured that oxygen concentration was always much greater than the concentration of any of the homolysis fragments. There was no measurable loss of solvent during the long heating times. Each experiment was run on three sets of samples that were identical in every respect except that one set was saturated with oxygen, one with air, and one with argon. A large boiling-
water bath was used for the experiments at 100° C. Experiments at ≤65° C utilized 1-cm spectrophotometric cells inside a thermostatted cell compartment of a spectrophotometer. The analyzing beam was blocked except during the recording of the spectra. Data were collected only through the first 20-50% reaction. The final absorbance reading was obtained after completion of the reaction at 100° C. To minimize the potential error caused by slow drifting of the baseline over long times, kinetic calculations utilized the difference between the absorbance at 650 nm (max for L²(H₂O)Rh(NO)²⁺) or 449 nm (Cr(H₂O)₅(NO)²⁺) and 840 nm, where neither complex absorbs.

Because of the limited number of kinetic points for the chromium and rhodium complexes, and extrapolations over long temperature ranges, the precision of the rate constants at 25° C is probably only about ± 50%, even though standard deviations obtained from data fits are much smaller.

**Table S1.** Summary of Experimental Conditions in Kinetic Measurements

<table>
<thead>
<tr>
<th>Complex</th>
<th>Scavengers used</th>
<th>Temperature range°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>L²Co(H₂O)NO²⁺</td>
<td>O₂, IrCl₆²⁻, IrBr₆²⁻</td>
<td>15.9 - 40</td>
</tr>
<tr>
<td>L¹Co(H₂O)NO²⁺</td>
<td>O₂, IrCl₆²⁻</td>
<td>25 - 47.5</td>
</tr>
<tr>
<td>L²Rh(H₂O)NO²⁺</td>
<td>O₂, air</td>
<td>65 - 100</td>
</tr>
<tr>
<td>(H₂O)₅CrNO²⁺</td>
<td>O₂, air</td>
<td>50 - 100</td>
</tr>
</tbody>
</table>
Table S2. Reagent Concentrations and UV-Vis Data Used in Determinations of $k_{\text{NO,Co}}$

<table>
<thead>
<tr>
<th>[Scavenger]$^a$</th>
<th>[$L^2(H_2O)Co(NO)^{2+}]^a$</th>
<th>$\lambda_{\text{mon}}$/ nm$^b$</th>
<th>$\varepsilon$/M⁻¹cm⁻¹$c$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ (0.2 - 1.25)</td>
<td>0.05 - 0.2</td>
<td>531 ($L^2(H_2O)CoNO^{2+}$)</td>
<td>212</td>
<td>This work</td>
</tr>
<tr>
<td>IrCl$_6^{2-}$ (0.1 - 0.45)</td>
<td>0.004 - 0.011</td>
<td>487 (IrCl$_6^{2-}$)</td>
<td>3920</td>
<td>Ref 1</td>
</tr>
<tr>
<td>IrBr$_6^{2-}$ (0.2 - 0.6)</td>
<td>0.004 - 0.015</td>
<td>584 (IrBr$_6^{2-}$)</td>
<td>3870</td>
<td>Ref 5</td>
</tr>
</tbody>
</table>

$^a$ In mM.  $^b$ Wavelength of maximum absorbance for the monitored species listed in parenthesis.

$^c$ Molar absorptivity of the monitored species at $\lambda_{\text{mon}}$.

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Figure S2. Plot according to the Eyring equation for the homolysis of $L^2$(H$_2$O)Co(NO)$_2^+$, 0.5 - 1.0 mM, [H$^+$] = 0.001 - 0.01 M, in the presence of excess IrCl$_6^{2-}$, $\lambda$ 487 nm ($\varepsilon = 3920$ M$^{-1}$ cm$^{-1}$).$^1$

Figure S3. UV-Vis spectra of $L^1$(H$_2$O)CoNO$_2^+$. $\lambda_{max}$ 442 nm ($\varepsilon = 99$ M$^{-1}$ cm$^{-1}$), 540 nm ($\varepsilon = 79$ M$^{-1}$ cm$^{-1}$).
Figure S4. Dissociation of °NO from L¹(H₂O)Co(NO)²⁺ (0.05 mM) in the presence of 0.12 mM IrCl₆²⁻ at 35.0 °C. Fit (black line) to the first-order rate law is shown on the left, and to {first + linear} on the right. The slightly smaller k in the left figure is caused by the slow decomposition of excess IrCl₆²⁻ and drifting absorbance at long times. The {first + linear} treatment properly corrects for this secondary reaction.
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**Figure S6.** UV-Vis spectra of \(L^2(H_2O)Rh(NO)^{2+}\) and \(L^2(H_2O)Rh^{2+}\)
Figure S7. Kinetic plot for the dissociation of •NO from L²(H₂O)Rh(NO)²⁺ (1 mM) at 650 nm ($\epsilon = 45 \text{ M}^{-1} \text{ cm}^{-1}$) in O₂-saturated 0.01 M aqueous HClO₄ at 88.0°C.

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**Figure S11.** Eyring plot for \(^{\text{\textsuperscript{1}}}\text{NO}\) dissociation from \(\text{Cr(H}_2\text{O})_5(\text{NO})^{\text{2+}}\) with \(\text{O}_2/\text{air}\) as scavenger.

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