Some Mechanistic Evidence for an Oxygen Transfer Reaction Accompanied by the Redox-Induced Nitrito-Nitro Linkage Isomerization of Ruthenium Complex Having Nitrosyl, *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ (X = ONO, NO_2)

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An oxygen transfer between the NO and the ONO ligands occurs in *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ when the complex undergoes a redox-induced nitrito-to-nitro linkage isomerization. Such an oxygen transfer does not occur in a thermally-induced linkage isomerization reported previously.

We have reported a nitro-nitrito isomeric pair complex of ruthenium(II) having nitrosyl as a spectator ligand: *cis*-$[Ru(NO)(X)(bpy)_2]^{2+}$ (X = ONO **[1]** and NO_2 **[2]**, bpy = 2,2'-bipyridine).[1] Either the nitrito **[1]** or the nitro **[2]** species undergoes a thermally-induced rearrangement to give the same equilibrium mixture of the nitro and nitrito isomers.[1] A mechanistic investigation allowed us to assume that the thermally-induced rearrangement proceeded by an intramolecular process, without any oxygen transfer reaction.[1] We report here that a redox-induced linkage isomerization occurs also in **[1]**: in contrast to the thermally-induced isomerization, this rearrangement involves an oxygen transfer between the nitrosyl and adjacent nitrito ligands. Such a redox-induced rearrangement does not occur in **[2]** while it undergoes a reduction. Some evidence which stems from the oxygen transfer process is also reported.

The electrochemical behavior of **[1]** is very similar to that of the analogue nitrito complex reported previously, *cis*-$[Ru(NO)(ONO)(bpy)(py)_2]^{2+}$.[1] A CH_3CN solution of **[1]** exhibits two one-electron reduction waves at -0.02 and -0.75 V [vs Ag|$AgNO_3$ (0.01 mol dm^{-3} in CH_3CN)] on a cyclic voltammetry time scale. Such CV observation is common for the reductive process of $\{MNO\}^6$-type nitrosyl complexes:[2,3] usually this class of complexes undergo ligand-based (NO) reduction, from *formally* $(M^{II}\text{-}NO^+)^{3+}$ moiety to $(M^{II}\text{-}NO^-)^+$, *via* the generation of $(M^{II}\text{-}NO\bullet)^{2+}$.[3] Cyclic voltammetry of **[1]** showed a reversible behavior in the first reduction wave, but a controlled potential electrolysis carried out at 25 °C was followed by a rapid linkage isomerization, which gave a one-electron reduction species of **[2]** (n = 0.99 by Coulometry). The one-electron reduction species, *cis*-$[Ru(NO\bullet)(NO_2)(bpy)_2]^+$, was able to convert to **[2]** by an exhaust oxidative electrolysis (n = 0.99). When the reductive exhaust electrolysis is carried out on **[1]** at -40 °C, a one-electron reduction species of **[1]**, *cis*-$[Ru(NO\bullet)(ONO)(bpy)_2]^+$, is generated without any redox-induced linkage isomerization.

In combination with the previous result,[1] the above results can be represented by the following equations (1-3) that illustrate the isomeric behavior of both **[1]** and **[2]** (2,2'-bpy is omitted for clarity):

$$\{Ru(ONO)(NO^+)\}^{2+}\ [1] + e^- \rightarrow \{Ru(ONO)(NO\bullet)\}^+ \quad (1)$$
$$\{Ru(ONO)(NO\bullet)\}^+ \rightarrow \{Ru(NO_2)(NO\bullet)\}^+ \quad (2)$$
$$\{Ru(NO_2)(NO\bullet)\}^+ \rightarrow \{Ru(NO_2)(NO^+)\}^{2+}\ [2] + e^- \quad (3)$$

eq 1: A one-electron reduction of **[1]** at -40 °C.
eq 2: A spontaneous rearrangement at 25 °C.
eq 3: A one-electron oxidation of the reduction species of **[1]** at 25 °C.

As the investigation of *cis*-$[Fe(NO)(NO_2)(S_2CN(Me)_2)_2]$ has shown, an intramolecular oxygen atom transfer occurs in the *cis*-$(NO)(NO_2)$ groups during a thermally-induced nitro-nitrito linkage isomerization.[4] Numerous investigations have also addressed intramolecular oxygen atom transfer from an NO_2 ligand to an adjacent CO ligand, leading to spontaneous CO_2 loss and the formation of nitrosyl complexes.[5] Such oxygen transfer, however, has not been found in the thermally-induced linkage isomerization of **[1]**:[1] a rearrangement process similar to that proposed by Basolo and Hammaker[6] and also by Murmann and Taube[7] is likely to be operating (Figure 1).[1]

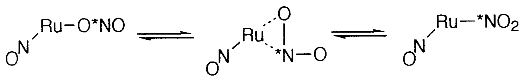

Figure 1. Conversion scheme for the thermally-induced nitro-nitrito linkage isomerization.[1]

The presence of the oxygen transfer between the nitrosyl and adjacent nitrito moieties, *via* the redox-induced linkage isomerization process, was established by the following synthetic experiment: using **[1]** as a starting material of eq 1, we could isolate the redox product **[2]** in eq 3. The same experiment carried out using *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2]^{2+}$ gave a mixture composed of nearly equimolar amounts of *cis*-$[Ru(NO)(^{15}NO_2)$-

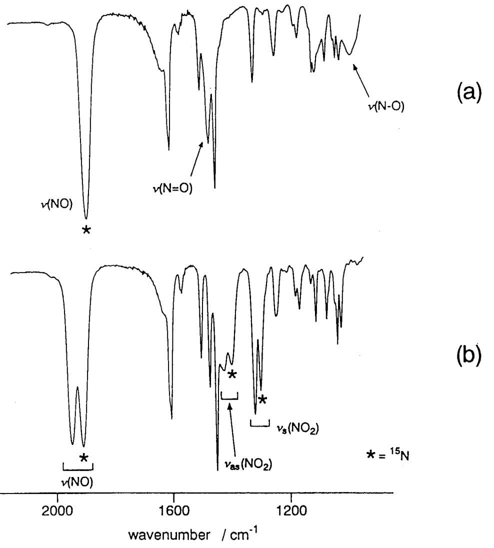

Figure 2. IR spectra. (a) *cis*-$[Ru(^{15}NO)(ONO)(bpy)_2](PF_6)_2$: ν(N=O) overlapped with the band due to 2,2'-bipyridine. (b) Mixture of *cis*-$[Ru(NO)(NO_2)(bpy)_2](PF_6)_2$ containing ^{15}NO or $^{15}NO_2$ moiety.

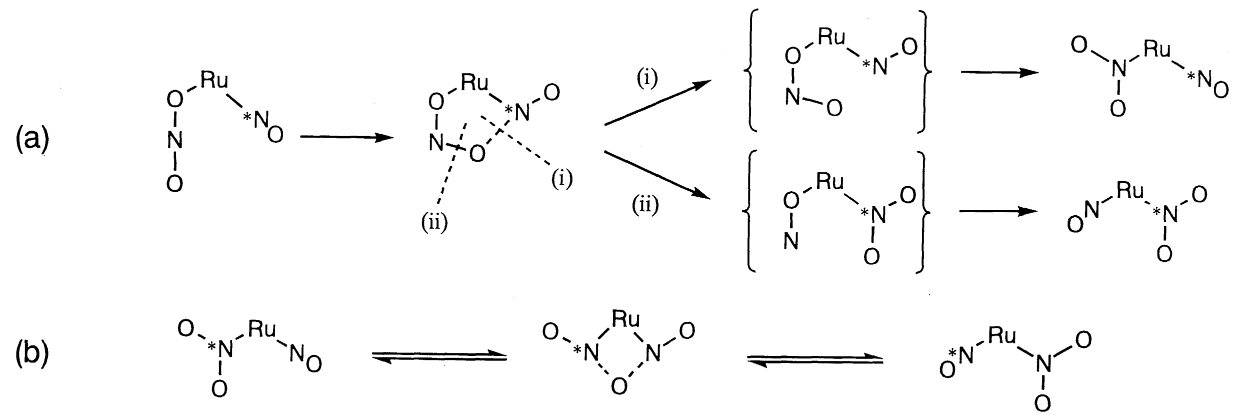

Figure 3. Two possible schemes for the oxygen atom transfer reaction involving {RuNO}^{7}-type nitrosyl complexes (*N = ^{15}N). (a): *cis*-[Ru(*NO•)(ONO)(bpy)$_2$]$^+$ gives *cis*-[Ru(NO•)(*NO$_2$)(bpy)$_2$]$^+$, along with *cis*-[Ru(*NO•)(NO$_2$)(bpy)$_2$]$^+$ (see Figure 1). (b): an interconversion process of *cis*-[Ru(NO•)(^{15}NO$_2$)(bpy)$_2$]$^+$.

(bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{15}NO)(NO$_2$)(bpy)$_2$]$^{2+}$ (Figure 2). If we assume that the rearrangement proceeds without the oxygen transfer reaction, *cis*-[Ru(^{15}NO)(ONO)(bpy)$_2$]$^{2+}$ will give *cis*-[Ru(^{15}NO)(NO$_2$)(bpy)$_2$]$^{2+}$ alone as the redox-induced isomerization product. The generation of equimolar amounts of two isotopomers is suggestive of the processes depicted in Figure 3(a) and/or (b).

Two mechanistic explanations are possible for the present oxygen atom transfer reaction. Figure 3(a) shows the nitrito-to-nitro rearrangement of *cis*-[Ru(^{15}NO•)(ONO)(bpy)$_2$]$^+$,[8] which occurs *via* the formation of an assumed cyclic intermediate species.[9] The assumed intermediate will disintegrate in two ways ((i) and (ii)) to give either *cis*-[Ru(^{15}NO•)(ONO)(bpy)$_2$]$^+$ or *cis*-[Ru(NO•)(^{15}NO$_2$)(bpy)$_2$]$^+$: bond breaking at (i) affords an original species having {Ru(^{15}NO•)(ONO)} moiety, which can undergo a facile rearrangement to give *cis*-[Ru(^{15}NO•)(NO$_2$)(bpy)$_2$]$^+$, without any oxygen transfer.[10] Disintegration at (ii) gives *cis*-[Ru(NO•)(^{15}NO$_2$)(bpy)$_2$]$^+$, *via* the formation process of a transient *O*-bound nitrosyl species.[9]

Another explanation may be possible using Figure 3(b), which involves an equilibrium process between the nitro and the nitrosyl ligands. In this case, the oxygen atom transfer will occur in the isomerized nitro species in eq 2 and/or eq 3, if Feltham's mechanism (Figure 3(b)) is operating. Participations of such oxygen transfer processes in the equilibrium system will be clarified experimentally if *cis*-[Ru(NO)(^{15}NO$_2$)(bpy)$_2$]$^{2+}$ (or *cis*-[Ru(^{15}NO)(NO$_2$)(bpy)$_2$]$^{2+}$) is available. However, efforts so far to prepare these isotopomers were all unsuccessful. Although both *cis*-[Ru(^{15}NO)(^{15}NO$_2$)(bpy)$_2$]$^{2+}$ and *cis*-[Ru(^{15}NO)(O^{15}NO)(bpy)$_2$]$^{2+}$ are available by a known procedure, these were useless for the present purpose.

The present study demonstrated that oxygen abstraction by NO ligand, which results in the formation of NO$_2$ ligand, occurs depending on the formal charge of the nitrosyl ligand: in *cis*-[Ru(NO•)(ONO)(bpy)$_2$]$^+$ ({RuNO}^{7}-type complex), the nitrosyl-to-nitro conversion occurred rapidly at room temperature, while *cis*-[Ru(NO$^+$)(ONO)(bpy)$_2$]$^{2+}$ ({RuNO}^{6}-type complex) did not show such behavior, under the same conditions.[1] Despite much work on the {MNO}^{7}-type nitrosyl complex,[3,11,12] no report has been published yet on the nitrosyl function of (M^{II}-NO•)$^{2+}$ moiety, which accelerates significantly the oxygen transfer reaction in *cis*-(NO)(NO$_2$) groups.

References and Notes

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