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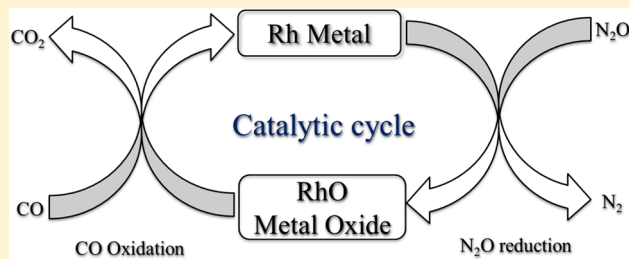
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Computational Study for the Circular Reaction Mechanisms of N₂O with CO Catalyzed by Rh and Rh⁺

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ABSTRACT: On the basis of ab initio calculations, we have examined the circular reaction mechanisms of N₂O with CO catalyzed by doublet and quartet states of Rh and singlet, triplet, and quintet of Rh⁺. For more reliable energetics, the single point calculation with the CCSD(T)/[SDD+6-311G(d)] level was carried out based on the B3LYP/[SDD+6-311G(d)] geometry. Calculations showed that the first half-reaction Rh + N₂O → RhO + N₂ is exothermic by 26.62 and 38.99 kcal/mol with the energy barriers of 3.57 and 4.94 kcal/mol for the doublet and quartet states via O atom abstraction path, whereas the Rh⁺ + N₂O → RhO⁺ + N₂ is exothermic by 3.69, 0.51, and 57.32 kcal/mol for the singlet, triplet, and quintet states via N–O insertion path, respectively. The second half-reaction in the catalyzed reduction of N₂O by CO proceeds by attachment of RhO or RhO⁺ to CO. Both neutral and cationic reactions are highly exothermic. However, the overall cyclic reaction is a multistate step, comprises several different lower-lying electronic states of intermediates and transition states, and results in products of CO₂ + N₂ with a small barrier of 2.81 kcal/mol for the neutral reaction and a negligible barrier for the cationic reaction. The low-lying electronic states for the overall cyclic reaction are predicted to be ⁴Rh + N₂O + CO → ⁴Rh(η¹-ONN) (⁴IM1) → ⁴TS1 → ⁴ORhNN (⁴IM2) → ⁴RhO + N₂ + CO → ⁴OCRhO (⁴IM3) → ²TS2 → ⁴Rh(η¹-OCO) (⁴IM4) → ⁴Rh + N₂ + CO₂ and ³Rh⁺ + N₂O + CO → ³Rh(η¹-ONN)⁺ (³IM1⁺) → ⁵ORhNN⁺ (⁵IM2⁺) → ⁵RhO⁺ + N₂ + CO → ³OCRhO⁺ (³IM3⁺) → ⁵TS2⁺ → ³Rh(η¹-OCO)⁺ (³IM4⁺) → ³Rh⁺ + N₂ + CO₂ for the neutral and cationic reactions, respectively.



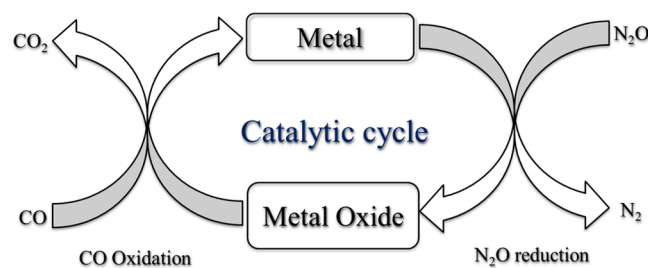
INTRODUCTION

The gas-phase reactions of transition metal atoms and ions with small pollutant molecules (for example, N₂O, NO, NO₂, CO, CO₂, etc.) have received a great deal of attention by the reason for designing novel and more robust catalysts for applying to both fundamental and practical chemical processes, such as the catalytic activation of the N–O bond and the abatement of nitrogen oxides (NO_x).^{1–3} These fields are interesting but complicated due to the nature of transition metal centers (high multiplicities) and a great amount of low-lying metastable electronic states in these reactions. The spin multiplicities of transition metal centers and electronic states of reactive intermediates have been shown to be important factors for studying the reaction mechanisms.^{4–16} Both computational studies^{17–27} and gas-phase experiments^{5,28–38} have been carried out to understand the atomistic level of the reactions related to these fields.

In 1981, Kappes and Staley reported the first cyclic N₂O reduction by CO catalyzed by atomic metal cation in the landmark experiments.³⁹ Henceforward, a great number of theoretical and experimental studies on the reaction of N₂O with 3d transition metals (TMs) and alkaline-earth metals have been reported.^{15,40–49} Böhme et al.^{4,5} combine inductively coupled plasma and selected-ion flow tube (ICP-SIFT) tandem mass spectrometry to study the reduction of N₂O by CO producing N₂ and CO₂ catalyzed by 26 atomic metal cations. Ten of these 26 atomic cations, such as Ca⁺, Sr⁺, Ba⁺, Fe⁺, Ge⁺,

Os⁺, Ir⁺, Pt⁺, Eu⁺, and Yb⁺, are found to be catalytically active. The authors proposed a catalytic cycle reaction of N₂O + CO as depicted in Scheme 1. The reaction mechanisms include two

Scheme 1. Cyclic Reaction of N₂O + CO Catalyzed by Metal



major parts: (i) M + N₂O → MO + N₂, where an oxygen atom of N₂O is abstracted and metal oxide is formed, and (ii) MO + CO → M + CO₂, where oxidation of CO accompanies reduction of metal oxide to generate M and CO₂. However, the detailed reaction mechanism involving various low-lying electronic states of reactants, intermediates, and products is still lacking.

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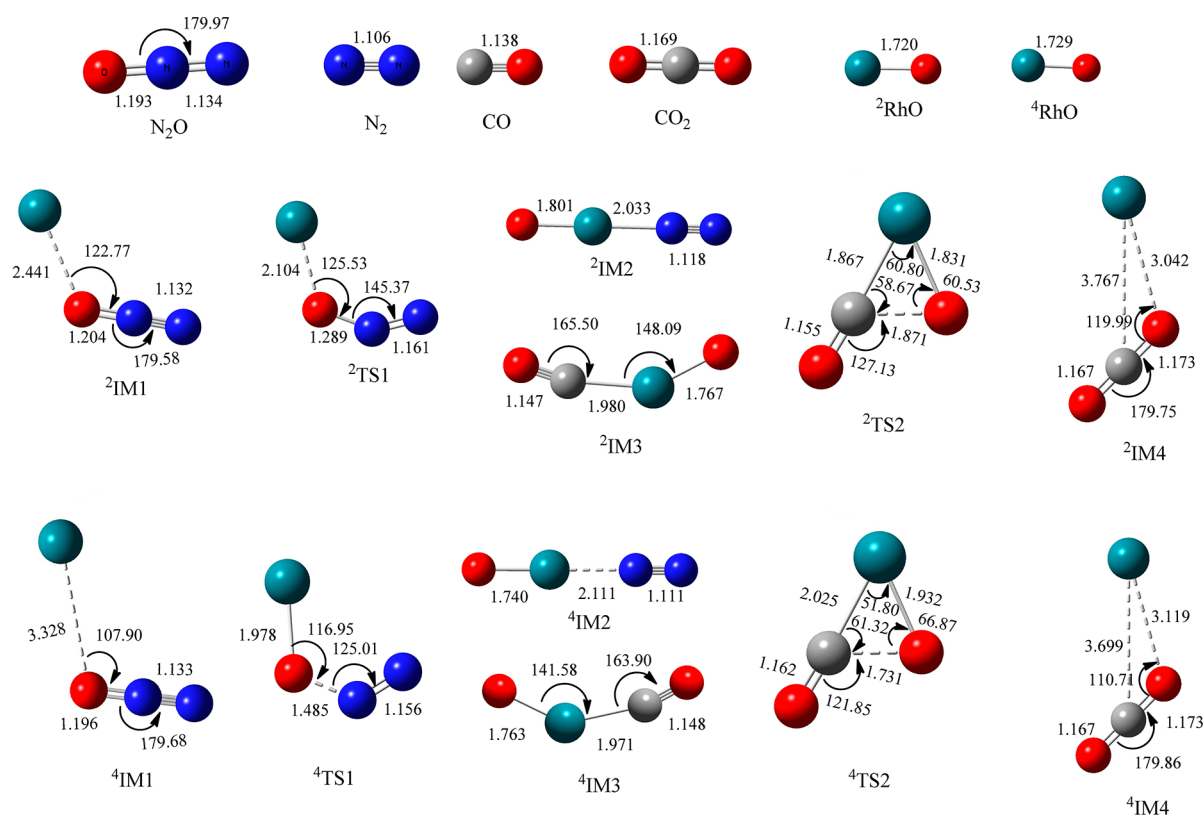


Figure 1. Optimized structures of reactants, intermediates, transition states, and products of the cyclic reaction of Rh + N₂O + CO. Distances are in angstroms, and angles are in degrees.

To provide vital information for explanation of experimental observations and for an exhaustive understanding of complex reaction mechanisms consisting of TM chemistry, state-of-the-art calculations are needed for searching the potential energy surfaces (PESs) of the title reactions on several multiplicity-state processes. In this present study, we attempt to investigate the cyclic reaction mechanisms of N₂O with CO catalyzed by Rh/Rh⁺. Doublet and quartet state surfaces for the reactions of Rh with N₂O and RhO with CO and singlet, triplet, and quintet state surfaces in the case of Rh⁺ system are elucidated since Rh and Rh⁺ chemistry contains various low-lying multiplicity states. It is of importance to understand the role of lower-lying multiplicities of Rh atom and Rh⁺ cation and illustrate the detailed reaction mechanisms from a theoretical point of view.

■ COMPUTATIONAL METHODS

All structures of the stationary states on the potential energy surfaces (PESs) for the reactions of N₂O with CO catalyzed by Rh/Rh⁺ were optimized with the hybrid Becke's three-parameter functional with the nonlocal Lee–Yang–Parr correlation functional (B3LYP) theory^{50,51} by using the Gaussian09 quantum chemical software package.⁵² The Stuttgart/Dresden relativistic effective core potential (ECP)⁵³ connected with triple- ζ SDD basis set for Rh/Rh⁺ and 6-31G(d) basis set for carbon, nitrogen, and oxygen elements designated as B3LYP/[SDD+6-31G(d)] was used. Vibrational frequency calculations were performed to confirm all stationary states on the PESs of the reactions. Minimum structures were found to have no negative eigenvalue, and TS structures were found to have one. The predicted transition states between the corresponding minima were also verified by the intrinsic reaction coordinate (IRC) approach.⁵⁴ Previous studies have

illustrated that the B3LYP functional with triple- ζ SDD basis set gives results well consistent with experiments for optimizing the configurations of transition metal systems.^{17,18,55} To get more accurate energies, we performed the CCSD(T) single point calculations based on the optimized geometries from B3LYP calculations. In addition, we extended the large 6-311G(d) basis sets for carbon, nitrogen, and oxygen elements during the CCSD(T) single point calculations. The CCSD(T) energy was also corrected by the unscaled B3LYP zero-point energy.

One should note that locating the exact crossing points of these lower-lying electronic state PESs would require the computationally demanding methods considering the spin–orbit coupling (SOC) effect. By the reason for technical limitations and significant computational time demands, we did not search for the crossing points of the lower-lying electronic state PESs by the SOC calculations as we did in previous studies.^{17,18} A detailed SOC calculations will be carried out in the future.

■ RESULTS AND DISCUSSION

The electronic ground state of the Rh atom is predicted to be a quartet ⁴F state with the s¹d⁸ electronic configuration while the doublet ²D (d⁹) state is 8.55 kcal/mol slightly higher in energy at the CCSD(T)/[SDD+6-311G(d)] level of theory, which agrees with the experimental value of 9.46 kcal/mol.⁶ The sextet state of Rh is computed to be 81.72 kcal/mol higher than the Rh atom ground state. For Rh⁺ cation, the electronic ground state is the triplet state: its singlet and quintet states are 30.98 and 37.72 kcal/mol higher in energies. In addition, the heat of gas-phase reaction N₂O + CO → N₂ + CO₂ is computed to be −86.08 kcal/mol, which is well consistent with

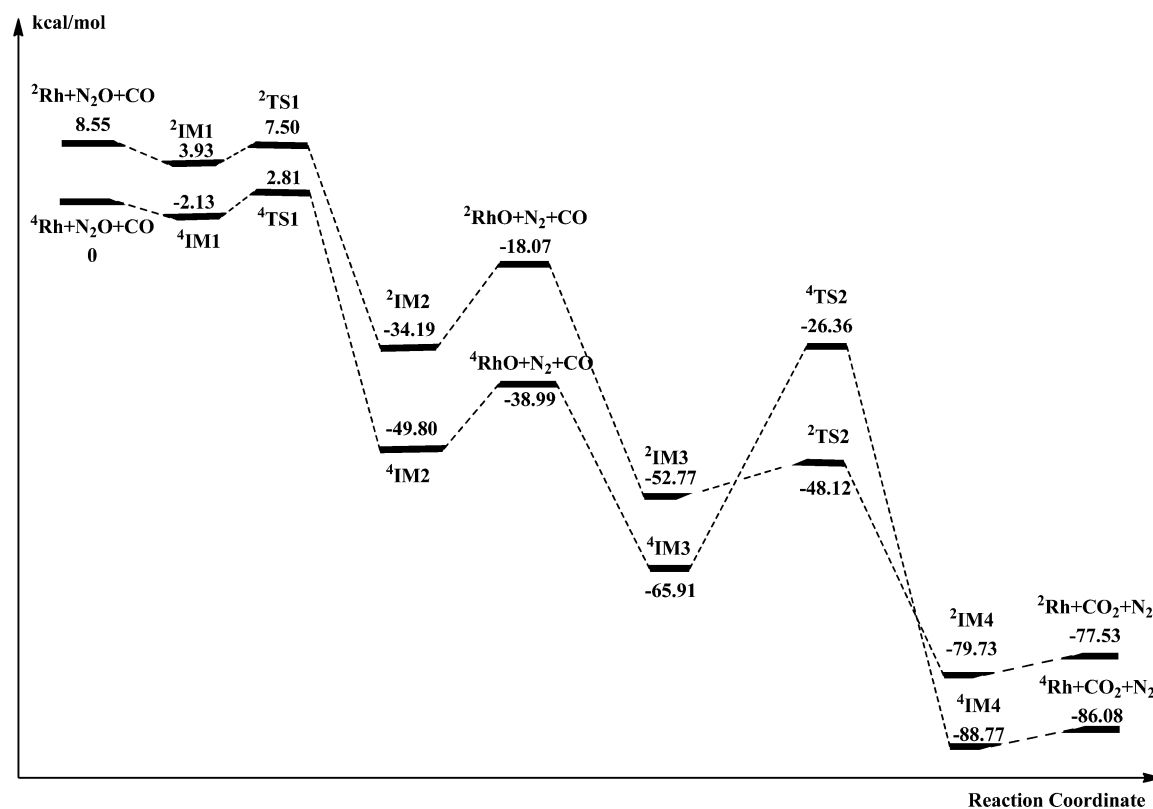


Figure 2. Predicted potential energy profiles of the cyclic reaction of $\text{Rh} + \text{N}_2\text{O} + \text{CO}$ for the doublet and quartet electronic states of Rh atom. The unit of energy is in kcal/mol.

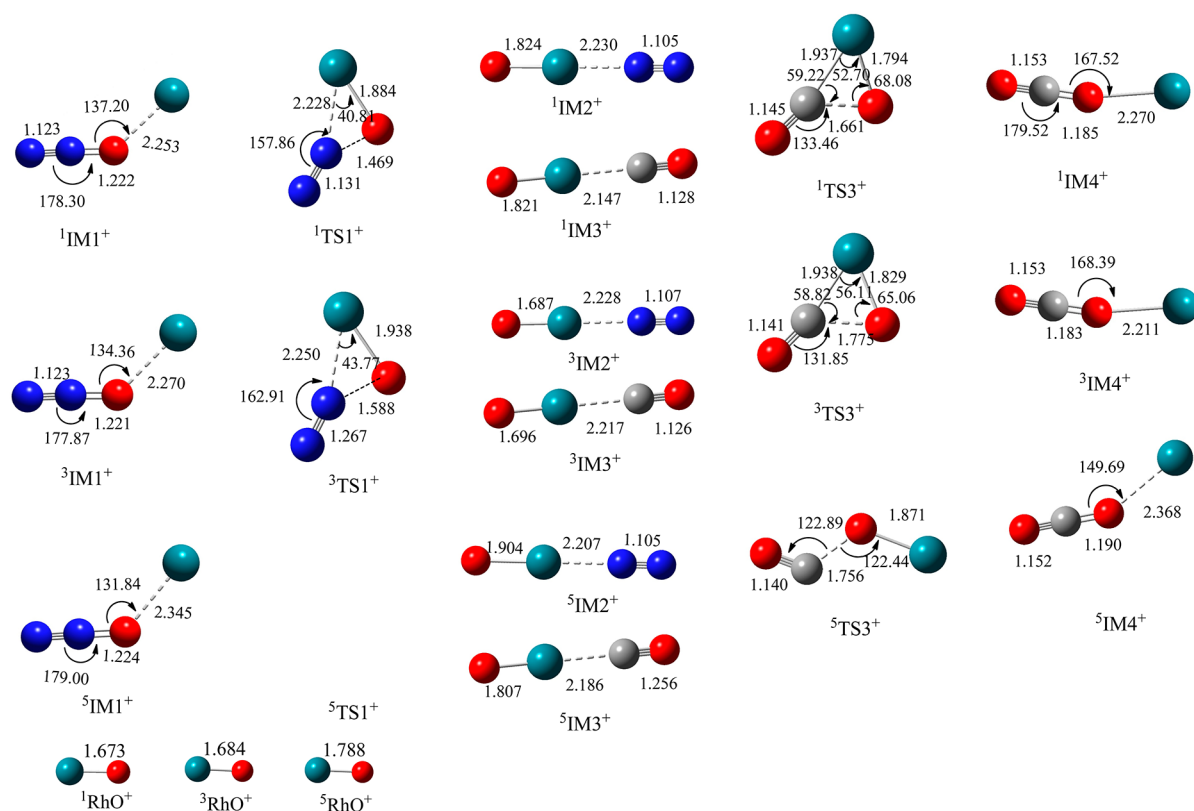


Figure 3. Optimized structures of reactants, intermediates, transition states, and products of the cyclic reaction of $\text{Rh}^+ + \text{N}_2\text{O} + \text{CO}$. Distances are in angstroms, and angles are in degrees.

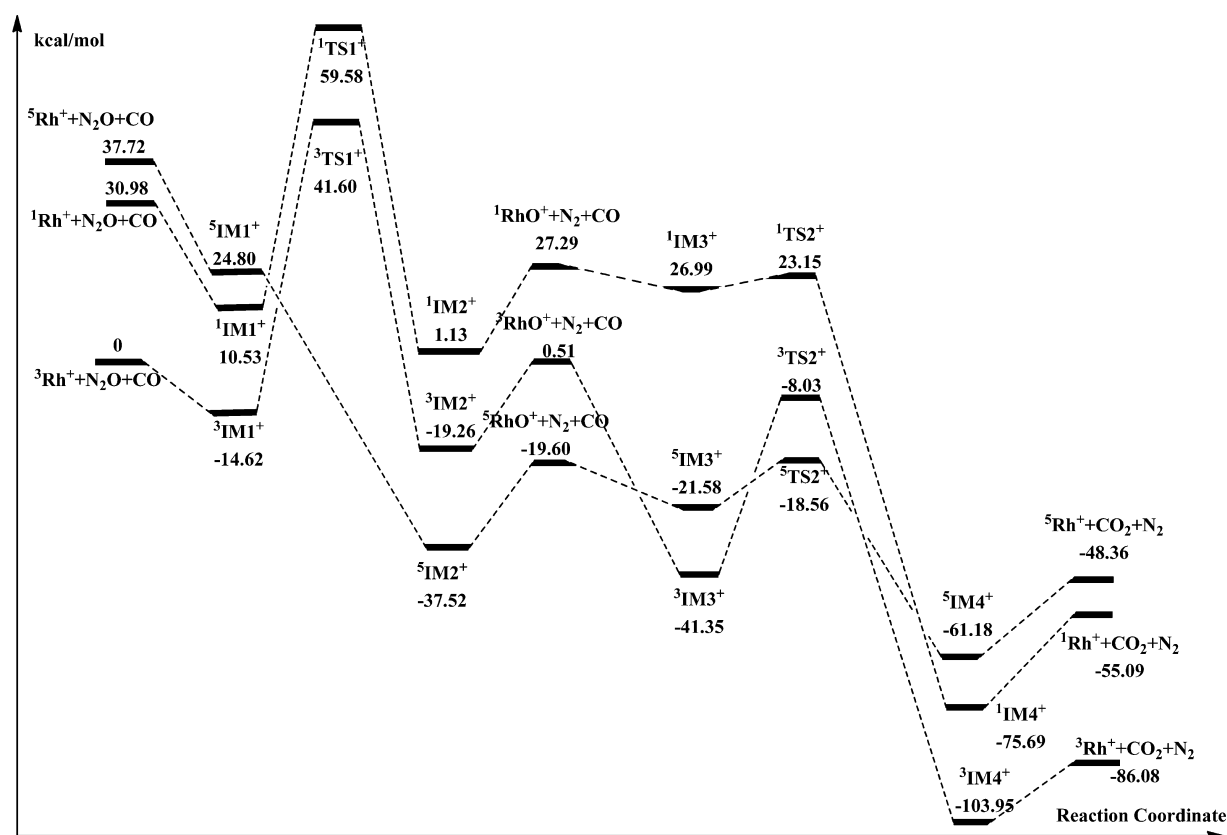


Figure 4. Predicted potential energy profiles of the cyclic reaction of $\text{Rh}^+ + \text{N}_2\text{O} + \text{CO}$ for the singlet, triplet, and quintet electronic states of Rh atom. The unit of energy is in kcal/mol.

the experimental value of 86.38 kcal/mol.⁵ Thus, the computational approach, single point energy calculation CCSD(T)/[SDD+6-311G(d)] with the B3LYP/[SDD+6-311G(d)] structure is suitable to illustrate the cyclic reaction mechanism of N_2O with CO catalyzed by Rh and Rh^+ .

In the following discussion, we map out the PESs of the circular reaction of N_2O with CO catalyzed by the doublet and quartet states of the Rh atom and the singlet, triplet, and quintet states of Rh^+ ion. The optimized configurations of intermediates, transition states, and products of the reaction $\text{Rh} + \text{N}_2\text{O} + \text{CO}$ are depicted in Figure 1. Their energetics is given in Figure 2. Those of the $\text{Rh}^+ + \text{N}_2\text{O} + \text{CO}$ reaction are shown in Figures 3 and 4. To generalize the nomenclature, the notation of $^a\text{S}^b$ (S = species including Rh, intermediates, and products) is used for the species in the PESs. The superscript *a* denotes the electronic state of the species while the superscript *b* represents the oxidation number. For example, $^3\text{RhO}^+$ represents the species in triplet state with one positive charge.

Mechanisms for the Cyclic Reaction of $\text{Rh} + \text{N}_2\text{O} + \text{CO}$

The first step is coordination of N_2O to Rh (doublet and quartet states). The bound complex, $\text{Rh}-\text{N}_2\text{O}$, can have two isomers: $\text{Rh}(\eta^1\text{-ONN})$ where N_2O binds to Rh end-on via its O atom and $\text{Rh}(\eta^1\text{-NNO})$ where N_2O binds to Rh end-on via its N atom as seen in Figure 1. Our calculations showed that the end-on $\text{Rh}(\eta^1\text{-ONN})$ is more stable than the end-on $\text{Rh}(\eta^1\text{-NNO})$. This finding has been demonstrated according to the theoretical results for Rh^+ , Pt^+ , Fe^+ , Ti^+ , and Y^+ transition metal ions.^{56–58} The structures of doublet and quartet states of $\text{Rh}(\eta^1\text{-ONN})$, $^2\text{IM1}$, and $^4\text{IM1}$ are displayed in Figure 1. The doublet ground state of $\text{Rh}(\eta^1\text{-ONN})$, $^2\text{IM1}$, is computed to be 6.06 kcal/mol higher than the quartet state $^4\text{IM1}$, as depicted in

Figure 2. The next step starts from $^2\text{IM1}$ and $^4\text{IM1}$ to form ORhNN intermediates, $^2\text{IM2}$ and $^4\text{IM2}$, via O atom abstraction path by passing transition states, $^2\text{TS1}$ and $^4\text{TS1}$. The $^2\text{IM2}$ and $^4\text{IM2}$ are calculated to be -34.19 and -49.80 kcal/mol in energy relative to the ground state reactants. The energy barriers are 3.57 and 4.94 kcal/mol for doublet and quartet states, respectively. The forming bonds of $^2\text{Rh}-\text{O}$ and $^4\text{Rh}-\text{O}$ in $^2\text{TS1}$ and $^4\text{TS1}$ are predicted to be 2.104 and 1.978 Å. The broken bonds of $^2\text{N}-\text{O}$ and $^4\text{N}-\text{O}$ in $^2\text{TS1}$ and $^4\text{TS1}$ are predicted to be 1.289 and 1.485 Å (see Figure 1). In $^2\text{IM2}$ and $^4\text{IM2}$, the bonds of $^2\text{Rh}-\text{N}$ and $^4\text{Rh}-\text{N}$ are computed to be 2.033 and 2.111 Å, respectively. The products, RhO and N_2 , of the half-reaction of the cyclic reaction form by cleavage of the $\text{Rh}-\text{N}$ bonds in $^2\text{IM2}$ and $^4\text{IM2}$ without any intrinsic barriers. The overall half-reaction $\text{Rh} + \text{N}_2\text{O} + \text{CO} \rightarrow \text{RhO} + \text{N}_2 + \text{CO}$ is exothermic by 26.62 and 38.99 kcal/mol for the doublet and quartet states.

The second half-reaction in the catalyzed reduction of N_2O by CO proceeds by attachment of RhO to CO with the formation of ORhCO intermediate, $^2\text{IM3}$ and $^4\text{IM3}$ without a barrier. The process is exothermic of 34.70 kcal/mol for the doublet state (26.92 kcal/mol for the quartet state). The path occurs from $^2\text{IM3}$ and $^4\text{IM3}$ to produce $\text{Rh}(\eta^1\text{-OCO})$ intermediates, $^2\text{IM4}$ and $^4\text{IM4}$, via O atom transfer from RhO to CO through transition states, $^2\text{TS2}$ and $^4\text{TS2}$. The $^2\text{IM4}$ and $^4\text{IM4}$ are computed to be -79.73 and -88.77 kcal/mol in energy relative to the ground reactants ($^4\text{Rh} + \text{N}_2\text{O} + \text{CO}$), respectively. The energy barriers are predicted to be 4.65 and 39.55 kcal/mol for doublet and quartet states, respectively. The forming bonds of $^2\text{C}-\text{O}$ and $^4\text{C}-\text{O}$ in $^2\text{TS2}$ and $^4\text{TS2}$ are predicted to be 1.871 and 1.731 Å. The broken bonds of $^2\text{Rh}-$

O and $^4\text{Rh}-\text{O}$ are calculated to be 1.831 and 1.932 Å (see Figure 1). In $^2\text{IM4}$ and $^4\text{IM4}$, the bonds of $^2\text{Rh}-\text{O}$ and $^4\text{Rh}-\text{O}$ are computed to be 3.042 and 3.119 Å, respectively. One should note that the energy of the quartet state $^4\text{TS2}$ is 21.76 kcal/mol higher than the doublet state $^2\text{TS2}$. The reaction may take place via the doublet–quartet surface curve crossing via the surface intersection point. Because of the cost and technical limitations, we did not carry out SOC calculations for searching the crossing seam of PESs of the lower-lying electronic states. The final products of the $\text{Rh} + \text{CO}_2 + \text{N}_2$ reaction form from preproduct IM4 and are only slight higher in energy compared to IM4 (2.20 and 2.69 kcal/mol for the doublet and quartet states, respectively). The lower-lying electronic states for the overall reduction reaction mechanism of N_2O with CO catalyzed by Rh is predicted to be $^4\text{Rh} + \text{N}_2\text{O} + \text{CO} \rightarrow ^4\text{Rh}(\eta^1\text{-ONN})^+ (^4\text{IM1}) \rightarrow ^4\text{TS1} \rightarrow ^4\text{ORhNN}^+ (^4\text{IM2}) \rightarrow ^4\text{RhO} + \text{N}_2 + \text{CO} \rightarrow ^4\text{OCRhO}^+ (^4\text{IM3}) \rightarrow ^2\text{TS2} \rightarrow ^4\text{Rh}(\eta^1\text{-OCO})^+ (^4\text{IM4}) \rightarrow ^4\text{Rh} + \text{N}_2 + \text{CO}_2$, which is predicted to be highly exothermic by 86.08 kcal/mol with a small barrier of 2.81 kcal/mol. Compare this value to the uncatalyzed reaction $\text{N}_2\text{O} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2$, where a high energy barrier of 47.23 kcal/mol is required.

Mechanisms for the Cyclic Reaction of $\text{Rh}^+ + \text{N}_2\text{O} + \text{CO}$. Similar to the neutral Rh atom, the first intermediate for the singlet, triplet, and quintet of Rh^+ with N_2O is likely to be the $\text{Rh}(\eta^1\text{-ONN})^+$ complex where N_2O binds to Rh end-on via its O atom. As Fe^+ , Rh^+ , Pt^+ , Ti^+ , and Y^+ transition metal ions,^{56–58} the cationic complex $\text{Rh}(\eta^1\text{-ONN})^+$ is found to be more stable than the $\text{Rh}(\eta^1\text{-NNO})^+$ complex. As illustrated in Figure 4, the triplet ground state of $\text{Rh}(\eta^1\text{-ONN})^+$, $^3\text{IM1}^+$, is computed to be 25.15 and 39.42 kcal/mol more stable than the singlet $^1\text{IM1}^+$ and quintet $^5\text{IM1}^+$ species, respectively. The structures of singlet, triplet, and quintet states of $\text{Rh}(\eta^1\text{-ONN})^+$, $^1\text{IM1}^+$, $^3\text{IM1}^+$, and $^5\text{IM1}^+$ are shown in Figure 3. The Rh–O bond lengths of $^1\text{IM1}^+$, $^3\text{IM1}^+$, and $^5\text{IM1}^+$ are predicted to be 2.253, 2.270, and 2.345 Å. The angles of NNO are slightly reduced to 178.30°, 177.87°, and 179.0° for $^1\text{IM1}^+$, $^3\text{IM1}^+$, and $^5\text{IM1}^+$ from 179.97° of the gas-phase NNO molecule. Different than the neutral Rh atom, the second process starts from singlet and triplet states of $\text{Rh}(\eta^1\text{-ONN})^+$ to form ORhNN^+ intermediates, $^1\text{IM2}^+$ and $^3\text{IM2}^+$, via N–O insertion path by passing transition states, $^1\text{TS1}^+$ and $^3\text{TS1}^+$. It should be noted that we are unable to locate the transition state between $^5\text{IM1}^+$ and $^5\text{IM2}^+$ after a vast search. The quintet state $^5\text{IM2}^+$ may be directly formed without any energy barrier via N–O insertion. The transition states $^1\text{TS1}^+$ and $^3\text{TS1}^+$ are predicted to be 41.60 and 59.58 kcal/mol higher than the ground state of $^3\text{Rh}^+ + \text{N}_2\text{O}$ reactants, respectively. The forming bonds of $^1\text{Rh}^+-\text{N}$ and $^3\text{Rh}^+-\text{N}$ in $^1\text{TS1}^+$ and $^3\text{TS1}^+$ are predicted to be 2.228 and 2.250 Å and the broken bonds of $^1\text{N}-\text{O}$ and $^3\text{N}-\text{O}$ are 1.469 and 1.588 Å as represented in Figure 3. The $^1\text{IM2}^+$, $^3\text{IM2}^+$, and $^5\text{IM2}^+$ are found to be 1.13, –19.26, and –37.52 kcal/mol in energy relative to the ground state reactants. Interestingly, the ground state of ORhNN^+ intermediate is computed to be a quintet state, which is 38.65 and 18.26 kcal/mol lower than the singlet and triplet states, respectively. The RhO^+ and N_2 are produced in the half cyclic reaction by cleavage of the Rh–N bonds in $^1\text{IM2}^+$, $^3\text{IM2}^+$, and $^5\text{IM2}^+$ without any intrinsic barriers. The quintet state RhO^+ is computed to be 46.89 and 20.11 kcal/mol lower than its singlet and triplet states, respectively. As shown in Figure 4, the overall half-reaction $\text{Rh}^+ + \text{N}_2\text{O} + \text{CO} \rightarrow \text{RhO}^+ + \text{N}_2 + \text{CO}$ is exothermic by 3.69,

0.51, and 57.32 kcal/mol for the singlet, triplet, and quintet states.

The second half-reaction in the catalyzed reduction of N_2O by CO takes place by attachment of RhO^+ to CO with the formation of ORhCO^+ intermediate, $^1\text{IM3}^+$, $^3\text{IM3}^+$, and $^5\text{IM3}^+$, without a barrier. The ground state of ORhCO^+ complex is predicted to be a singlet state, which is 68.34 and 19.77 kcal/mol lower than the singlet and quintet states. The next step begins from $^1\text{IM3}^+$, $^3\text{IM3}^+$, and $^5\text{IM3}^+$ and leads to production of $\text{Rh}(\eta^1\text{-OCO})^+$ intermediates, $^1\text{IM4}^+$, $^3\text{IM4}^+$, and $^5\text{IM4}^+$, via O atom transfer from RhO^+ to CO by overcoming transition states, $^1\text{TS2}^+$, $^3\text{TS2}^+$, and $^5\text{TS2}^+$. The Rh–O distances in $^1\text{IM4}^+$, $^3\text{IM4}^+$, and $^5\text{IM4}^+$ are computed to be 2.270, 2.211, and 2.368 Å, respectively. The $^1\text{IM4}^+$, $^3\text{IM4}^+$, and $^5\text{IM4}^+$ are found to be –75.69, –103.95, and –61.18 kcal/mol relative to the ground reactants ($^3\text{Rh}^+ + \text{N}_2\text{O} + \text{CO}$) in energy, respectively. The $^1\text{TS2}^+$, $^3\text{TS2}^+$, and $^5\text{TS2}^+$ are 23.15, –8.03, and –18.15 kcal/mol (see Figure 4) relative to the ground reactants in energy, respectively. The forming C–O bonds in $^1\text{TS2}^+$, $^3\text{TS2}^+$, and $^5\text{TS2}^+$ are predicted to be 1.937, 1.938, and 1.871 Å, and the broken Rh–O bonds are calculated to be 1.661, 1.775, and 1.756 Å (see Figure 3). The final products of $\text{Rh}^+ + \text{CO}_2 + \text{N}_2$ form from preproduct IM4^+ via dissociation of the Rh–O bond without any barrier. The process is endothermic by 20.60, 17.87, and 12.82 kcal/mol for singlet, triplet, and quintet states, respectively. The lower-lying electronic states for the overall reduction reaction of N_2O with CO catalyzed by Rh^+ are predicted to be $^3\text{Rh}^+ + \text{N}_2\text{O} + \text{CO} \rightarrow ^3\text{Rh}(\eta^1\text{-ONN})^+ (^3\text{IM1}^+) \rightarrow ^5\text{ORhNN}^+ (^5\text{IM2}^+) \rightarrow ^5\text{RhO}^+ + \text{N}_2 + \text{CO} \rightarrow ^3\text{OCRhO}^+ (^3\text{IM3}^+) \rightarrow ^5\text{TS2}^+ \rightarrow ^3\text{Rh}(\eta^1\text{-OCO})^+ (^3\text{IM4}^+) \rightarrow ^3\text{Rh}^+ + \text{N}_2 + \text{CO}_2$, which is computed to be highly exothermic by 86.08 kcal/mol without any barrier. Compare to the uncatalyzed reaction $\text{N}_2\text{O} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2$, where a high energy barrier of 47.23 kcal/mol is required.

CONCLUSIONS

The circular reaction mechanisms of N_2O with CO catalyzed by doublet and quartet states of Rh and singlet, triplet, and quintet of Rh^+ have been interpreted at the CCSD(T)/[SDD+6-311G(d)]//B3LYP/[SDD+6-31G(d)] level. The calculation results are summarized as follows:

1. The first half-reaction of $\text{Rh} + \text{N}_2\text{O} \rightarrow \text{RhO} + \text{N}_2$ occurs via O atom abstraction path with the activation barriers of 3.57 and 4.94 kcal/mol and exothermicity of 26.62 and 38.99 kcal/mol for the doublet and quartet states. The second half-reaction in the catalyzed reduction of N_2O by CO proceeds by an oxygen atom transfer from RhO to CO. However, the overall cyclic reaction follows by a multistate procedure, proceeds via several different intermediates and transition states, and results in the reduction of N_2O and oxidation of CO: $^4\text{Rh} + \text{N}_2\text{O} + \text{CO} \rightarrow ^4\text{Rh}(\eta^1\text{-ONN})^+ (^4\text{IM1}) \rightarrow ^4\text{TS1} \rightarrow ^4\text{ORhNN}^+ (^4\text{IM2}) \rightarrow ^4\text{RhO} + \text{N}_2 + \text{CO} \rightarrow ^4\text{OCRhO}^+ (^4\text{IM3}) \rightarrow ^2\text{TS2} \rightarrow ^4\text{Rh}(\eta^1\text{-OCO})^+ (^4\text{IM4}) \rightarrow ^4\text{Rh} + \text{N}_2 + \text{CO}_2$. The overall reaction $\text{Rh} + \text{N}_2\text{O} + \text{CO} \rightarrow \text{Rh} + \text{N}_2 + \text{CO}_2$ is calculated to be 86.08 kcal/mol exothermic, which is well consistent with the experimental value of 86.38 kcal/mol. It requires only 2.81 kcal/mol energy barrier, which lies much lower than that (47.23 kcal/mol) without Rh metal catalyst.

2. For the cationic reaction, the first half-reaction of $\text{Rh}^+ + \text{N}_2\text{O} \rightarrow \text{RhO}^+ + \text{N}_2$ takes place via N–O insertion path with exothermic by 3.69, 0.51, and 57.32 kcal/mol for the singlet, triplet, and quintet states. The second half-reaction in the

catalyzed reduction of N₂O by CO proceeds by attachment of RhO⁺ to CO. The overall cyclic reaction ${}^3\text{Rh}^+ + \text{N}_2\text{O} + \text{CO} \rightarrow {}^3\text{Rh}(\eta^1\text{-ONN})^+ ({}^3\text{IM1}^+) \rightarrow {}^5\text{ORhNN}^+ ({}^5\text{IM2}^+) \rightarrow {}^5\text{RhO}^+ + \text{N}_2 + \text{CO} \rightarrow {}^3\text{OCRhO}^+ ({}^3\text{IM3}^+) \rightarrow {}^5\text{TS2}^+ \rightarrow {}^3\text{Rh}(\eta^1\text{-OCO})^+ ({}^3\text{IM4}^+) \rightarrow {}^3\text{Rh}^+ + \text{N}_2 + \text{CO}_2$ is predicted to be a highly exothermic but barrierless process.

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Notes

The authors declare no competing financial interest.

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