

On the Pt^+ and Rh^+ Catalytic Activity in the Nitrous Oxide Reduction by Carbon Monoxide

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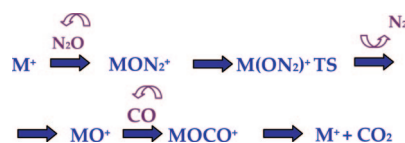
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Abstract: Nitrous oxide activation by CO in the presence of platinum and rhodium monocations was elucidated by density functional methods for ground and first excited states. Platinum and rhodium cations fulfill the thermodynamic request for the oxygen-atom transport that allows the catalytic cycle to be completed, but actually, just the first one meaningfully improves the kinetics of the process. For both catalysts, the reaction pathways show the only activation barrier in correspondence of nitrogen release and monoxide cation formation. The kinetic analysis of the potential energy profile, in agreement with ICP/SIFT MS experimental data, indicates that platinum performs more in the reduction, while the whole process is not sufficiently fast in the case of rhodium ionic catalyst.

Introduction

N_2O is a greenhouse gas that is naturally present in trace amounts in the Earth's atmosphere. The increasing concentration of nitrous oxide drastically influences global warming because it is estimated that each molecule affects Earth's temperature about 300 times more than carbon dioxide. Just recently, its environmental impact was proved. The lack of N_2O elimination processes in the troposphere gives rise to its spread throughout the stratosphere, where it causes the ozone depletion.^{1–3} Moreover, contrary to carbon dioxide emissions, less than 40% of atmospheric nitrous oxide comes from anthropic sources. In recent years, since its environmental dangerousness was proven, N_2O emissions control became the object of study of many research areas, from chemistry to engineering. In addition, the new laws about the acceptable levels of outdoor pollutants boosted the introduction of efficient catalytic methods.⁴ Although the catalytic process by which transition and main group metals catalyze the conversion of N_2O has not yet been completely investigated, it is, however, well-known that transition and main group metal catalysts do perform considerably well and give rise to versatile reaction events under conditions of homogeneous and heterogeneous catalysis.^{5–7} As part of our

Scheme 1. First and Second Part of N_2O Activation Catalytic Cycle ($\text{M} = \text{Rh}, \text{Pt}$)



systematic study^{8,9} about the efficiency of experimentally analyzed^{6,10} metal monocations, the N_2O activation mechanism by carbon monoxide in the presence of Rh^+ and Pt^+ was elucidated by DFT approach. The stepwise process proposed by Kappes and Staley¹¹ is well-known, but just recently, the case of the homogeneous catalysis was considered as a possible reactive event for nitrous oxide conversion. According to mass spectrometry data,⁶ rhodium and platinum monocations can both act as oxygen carriers in the mechanism indicated in the Scheme 1, but Rh^+ does not kinetically improve the process.

Previous studies on a similar subject,^{8,9} have pointed out the influence that in such a type of processes can have the two state reactivity (TSR) phenomenon¹² that consists of the occurrence of crossovers between low- and high-spin energetic profiles. In fact, most of the experimental determinations are based on the catalytic behavior of metal cations only in their ground state. However, often, the participation of metal ions excited states appeared to be of fundamental

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importance to explain the differences in the performance that experiment attributes to the various metal cations and, in some cases, has contributed to better rationalization of some uncertain results because of the difficulty of the experimental measures.⁹ Since the TSR concept originated from theoretical studies of a number of gas-phase reactions of small transition metal cations like Rh⁺ and Pt⁺, we have made it mandatory to take it into account in this investigation.

Computational Strategy

All calculations were carried out using the Gaussian 03 program package.¹³ The hybrid B3LYP functional^{14,15} was adopted in connection with Stuttgart RSC ECP for metals,¹⁶ and 6-311+G(d)¹⁷⁻¹⁹ was used for carbon, nitrogen, and oxygen atoms. All optimizations, carried out without any constraints, were followed by the vibrational analysis at the same theoretical approach to identify the stationary points located on the potential energy surfaces. Zero-point energy correction was added to all the absolute energies. Intrinsic reaction coordinate (IRC) calculation²⁰ was performed to verify the correction of all transition states. In addition, the stability of DFT density function was tested by the Stable calculation method,^{21,22} while the eALTER keyword¹³ ensured that the lowest-energy electronic states were found.

Results and Discussion

As previously mentioned, because of the presence of metal cations as catalysts, particular attention was devoted to the possible occurrence of a two-state reactivity phenomenon.²³⁻²⁶ Therefore, the potential energy surfaces were traced for rhodium and platinum monocations ground and first excited states. The reliability of the stationary points energetic scale is strictly dependent on the exact gap between the two electronic states of the catalyst. Stuttgart RSC pseudopotential correctly reproduces the stability order between Rh⁺ and Pt⁺ most stable excited states.

(a). N₂O Deoxygenation Catalyzed by Rhodium Monocation. In agreement with experimental data,²⁷ the ³F rhodium monocation lowest-energy state is followed by ¹D, and both correspond to the 4d⁸ configuration. According to our calculations, ¹D Rh⁺ resulted higher than ³F by 52.8 kJ/mol, versus an experimental value of 78.2 kJ/mol.²⁷ Although in the case of the rhodium electronic states, the theoretical value of the gap is quite different than the experimental one,²⁷ the reproduction of the spin states' correct order by an adequate basis set is a result rarely obtained by DFT methods.²⁸

B3LYP/Stuttgart results indicate that Pt⁺ ²D (5d⁹)/⁴F (6s¹ 5d⁸) gap corresponds to 77.0 kJ/mol, in good agreement with the estimated value of 73.0 kJ/mol.²⁹

Experimental evidence indicates that both Rh⁺ and Pt⁺ can act as oxygen carriers, where their oxygen affinities (OA) are found to be between the N₂ and CO affinities.⁶ Theoretical values of OA(N₂) and OA(CO) of 167.9 and 528.8 kJ/mol, respectively, were computed in a previous work⁸ by B3LYP/6-311+G(d) theoretical approach and define a range width of 360.8 kJ/mol in which Pt⁺ and Rh⁺ oxygen affinities were estimated to be 254.1 and 227.7 kJ/mol,

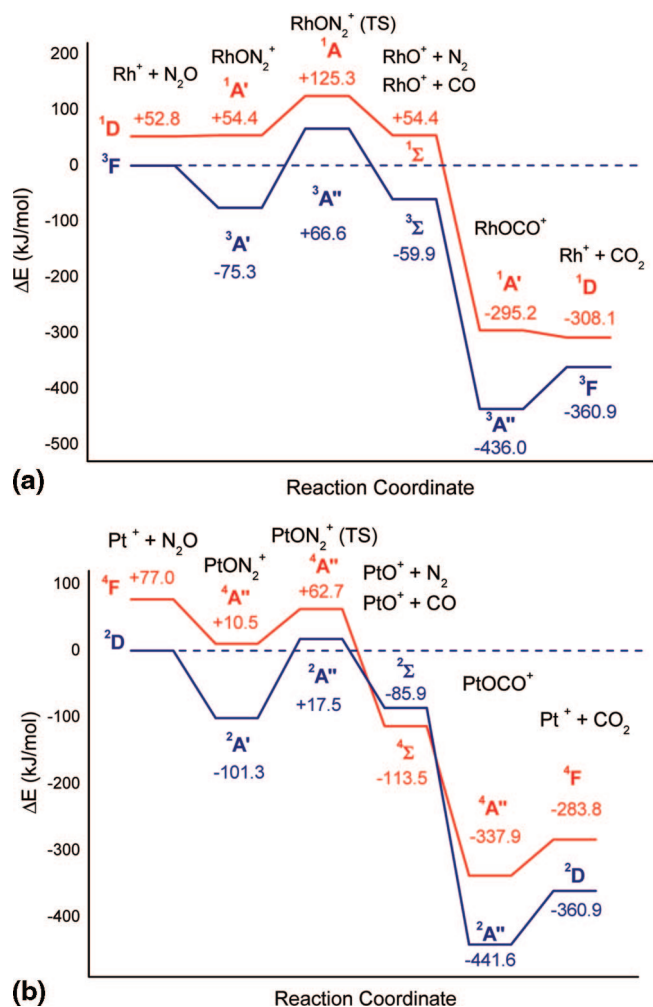


Figure 1. Nitrous oxide activation by carbon monoxide catalyzed by (a) Rh⁺ and (b) Pt⁺.

respectively. As it is often found for DFT calculations, these values are underestimated compared to the experimental data of 322.3 and 291.3 ± 5.9 kJ/mol, correspondingly.³⁰

Thus, the different catalytic activities of the platinum and rhodium monocations, both thermodynamically suitable to the oxygen transport mechanism, evidently have a kinetic origin as the potential energy surfaces (PES) highlight. In Figure 1, N₂O activation PES for both catalysts is reported. In the case of platinum and rhodium, first and second part of the whole process are characterized by the same steps. The interaction between the metal cation and nitrous oxide allows the formation of the oxygen side-bonded adduct MON₂⁺ that, through a transition state, evolves into the MO⁺ species releasing nitrogen. Subsequently, after the introduction of carbon monoxide in the reaction environment, the monoxide cation binds CO by the carbon side, giving rise to MOCO⁺ complex that releases carbon dioxide regenerating the catalyst. As in our previous works on the same deoxygenation catalytic cycle,^{8,9} we verified the coordination compounds to N₂O and CO to be the most stable species. In particular, we found that the metal cations always prefer to bind nitrous oxide by the oxygen side and that MO⁺ species gives rise to an extremely stable compound through the coordination between the cation's oxygen and CO's carbon.

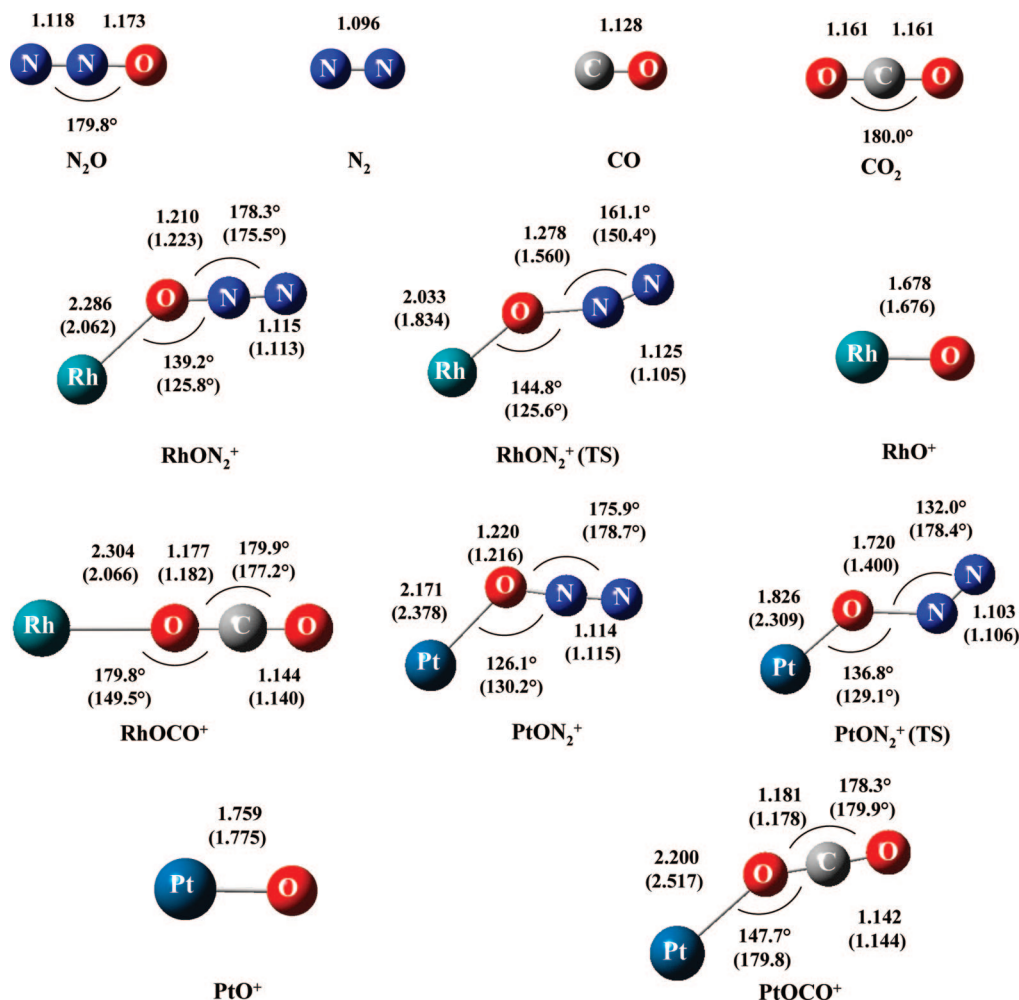


Figure 2. Optimized geometries of rhodium and platinum stationary points in their ground and first excited states. Bond distances are given in angstrom, and angles are given in degrees. Values in parentheses are referred to singlet spin state for rhodium and quartet multiplicity for platinum.

In the case of rhodium, no crossover characterizes triplet and singlet reaction channels because compounds at triplet multiplicity show always a higher stability. Therefore, the process takes place following the ground-state potential energy surface.

Except for the only transition state of the reduction process, all ground-state stationary points lie below the triplet reference reactants. Unlike the first step on singlet PES, the formation of the ³A' RhON₂⁺ complex is a stage exothermic by 75.3 kJ/mol. The only energetic barrier to overcome corresponds to 66.6 kJ/mol and allows the formation of the monoxide cation. It is worthwhile that in a gas-phase experiment, the intermediates do not lose all of their energy. Thus, the relevant barrier is not that of the bottom of the well, but rather that from the reactants.

The released N₂, inert toward the species involved in the process, does not influence the course of reaction. In the saddle point RhON₂⁺(TS), the normal mode relating to the imaginary frequency of 857.6i cm⁻¹ is associated to the O-N stretching corresponding to the breaking of bond. After the introduction of CO, the formation of the ³Σ rhodium monoxide cation, stage exoergonic by 59.9 kJ/mol, is followed by the appearance of the ³A'' RhOCO⁺ adduct. The species, product of the RhO⁺ coordination to CO by its carbon-side, is extremely

stable with respect to the reference reactants, feature that we always have found for MOCO⁺ compounds (M = Fe, Mn, Se, Ge) in our previous studies.^{8,9} In the rhodium coordination compound, both O-C distances of 1.14 and 1.18 Å (see Figure 2 for geometrical details) are very close to free carbon dioxide bond lengths, allowing the release of the catalyst in a barrierless step.

Among the first excited-state species, it is worthwhile that ¹A' RhON₂⁺ complex is almost isoenergetic with the reactants including the metal at the same multiplicity. The adduct gives rise to rhodium monoxide cation by overcoming a barrier of 70.9 kJ/mol. ¹A RhON₂⁺(TS) imaginary frequency equal to 716.8i cm⁻¹ corresponds to O-N bond scission. Carbon monoxide coordination to ¹Σ RhO⁺ leads to the formation of ¹A' RhOCO⁺ compound, 12.9 kJ/mol less stable than the products located on the path at the same multiplicity.

As any interaction characterizes ground and first excited states potential energy surfaces, the reaction mediated by rhodium cation is a single-state reactivity process and takes place along the triplet path. The activation barrier of 66.6 kJ/mol prevents the formation of an adequate quantity of rhodium monoxide cation to complete the catalytic cycle. This is the origin of the impossibility to experimentally detect

RhO⁺ in the reaction environment.⁶ Therefore, this stage of the process compromises Rh⁺ catalytic activity. The remarkable reaction rate improvement induced by platinum was quantified by Bohme and co-workers through the valuation of a first step kinetic constant 10³ higher than rhodium one.⁶

(b). N₂O Deoxygenation Catalyzed by Platinum Monocation. In agreement with this data, the nitrous oxide reaction path in the presence of platinum, illustrated in Figure 1b, shows a very low activation barrier. Doublet and quartet reaction channels show two adjacent spin inversions before and after PtO⁺ appearance, subsequently the only transition state, so that strictly we cannot define the reaction as a two-state reactivity process.¹² Along the doublet reaction path, N₂O coordination to the metal catalyst gives rise to the ²A' PtON₂⁺ species, 101.3 kJ/mol lower than the ground-state reactants. In its excited state, the same compound is 10.5 kJ/mol above the reactants asymptote. The release of nitrogen is preceded by the ²A'' transition state for which the vibrational analysis gave an imaginary frequency of 401.3 cm⁻¹. The ⁴Σ platinum monoxide cation, located at 113.5 kJ/mol below the reactants asymptote is about 27.6 kJ/mol more stable than the doublet species so that, after the ²A'' transition state, the reaction moves temporarily along the excited energetic profile rather than follow the doublet surface. The second crossing allows the catalytic cycle to regain the ground-state reaction channel being the ²A'' PtOCO⁺ strongly favored (of about 103.7 kJ/mol) with respect to the corresponding quartet species.

In the case of quite exothermic deoxygenation processes concerning the nitrous oxide activation mechanism, the spin conservation resulting from the interaction of potential energy surfaces was already mentioned by Schwarz.³¹

The detachment of carbon dioxide from ²A'' PtOCO⁺ compound is a step that is exothermic by 360.9 kJ/mol. The drastic decrease of the N₂O reduction activation barrier, from 199.2 kJ/mol⁸ in the absence of catalyst to 17.5 kJ/mol because of the interaction with Pt⁺, indicates in agreement with experimental data⁶ the excellent performance of platinum monocation.

A glance to the pathways shown in Figure 1 reveals that, as far as the oxide formation is concerned, the reaction profiles for both examined cations are quite similar to that obtained by Bohme and co-workers¹⁰ for the reaction mediated by iron catalyst. However, the second part of the catalytic cycle appears different because of the absence of the OCMO⁺ species and of the next transition state that should evolve into the MOCO⁺ most stable adduct. In our previous study concerning the iron catalytic activity in the reduction of N₂O by CO,⁸ in which we took account some aspects of the problem not investigated previously, we ascertained that the lack of the OCMO⁺ stationary point along the reaction's PES does not influence neither kinetics nor thermodynamic of the process since the energetic profile after the oxide formation lies entirely below the reactants asymptote.

Conclusions

On the basis of an experimental screening about the performances of some atomic cations carried out by Bohme

et al.,⁶ the oxygen transport activation of nitrous oxide by carbon monoxide mediated by Pt⁺ and Rh⁺ was analyzed by B3LYP/Stuttgart RSC ECP/6-311+G(d) on the basis of the mechanism suggested by Kappes and Staley.¹¹ The evaluation of the thermodynamic condition necessary to the achievement of the catalytic cycle, common to both metal cations, was followed by the analysis of the kinetic features of the process. Ground and first excited-state reaction channels were traced to consider possible spin inversions in the activation process. The reliability of our data is demonstrated by the exact ordering of catalysts' spin states. The stepwise mechanism in the case of rhodium catalyst entirely takes place along the triplet ground-state PES. The lowering of the activation barrier with respect to the uncatalyzed process is not enough significant to give rise to a sufficient RhO⁺ production so that, as indicated by experimental evidence, the second and last part of the catalytic cycle cannot easily take place.

In the case of platinum monocation, except for a double spin inversion in correspondence of PtO⁺ formation, the reaction proceeds along the doublet ground-state channel. The global process is therefore characterized by reactants and products in the same multiplicity. According to our analysis and in agreement with experimental evidence, Pt⁺ performs in the catalysis of N₂O reduction as the activation barrier to overcome in the first part of the process is equal to 17.5 kJ/mol.

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