The high covalence of metal-ligand bonds as stability limiting factor: the case of Rh(IX)O_4^+ and Rh(IX)NO_3

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Abstract

Rhodium, a 4d transition metal and a lighter analogue of iridium, is known to exhibit its highest VIth oxidation state in RhF_6 molecule. In this report, the stability and decomposition pathways of two species containing rhodium at a potentially formal +IX oxidation state, $[\text{RhO}_4]^+$ and RhNO_3 , have been investigated theoretically within the framework of the relativistic two-component Hamiltonian calculations. Possible rearrangement into isomers featuring lower formal oxidation numbers has been explored. We found that both species studied are metastable with respect to elimination of O_2 or NO . However, the local minima containing Rh(IX) are protected by sufficient energy barriers on the decomposition pathway, and they could in principle be prepared. The analysis of a broader set of compounds containing group 8 and 9 metals in high formal oxidation states that correspond to the group number showed that, in contrast to a standard trend, the limits of formally attainable oxidation state correlate with high level of covalent bonding character in the complexes studied.

Keywords Oxidation states · Rhodium · Ruthenium · Density functional theory · Relativistic effects · Theory of chemical bonding

Introduction

The classical theory of 2-electron/2-center chemical bonding based on a molecular orbital picture, as taught to the chemistry students, puts accent on proper match of energy and “size” (i.e. spatial decay of electronic density) of atomic orbitals involved in chemical bonding. The better the match of energy and spatial distribution of orbitals (overlap), the stronger the chemical bond. Obviously, in this simplified picture, the homonuclear diatomics best fulfil the criteria which favour strong bonding, albeit heteronuclear systems may still benefit

to a certain degree from an increased Coulombic stabilization, i.e. ionic contribution to bond energy. Take C_2 molecule, with the dissociation energy of 607 kJ/mol. If one now performs “electronegativity perturbation” by substituting one C atom by less electronegative B and another C atom by more electronegative N, the bonding energy is still high (389 kJ/mol), but it markedly decreases as compared with C_2 . A similar trend may be noticed for many other homo- and related heteronuclear systems, with some interesting exceptions [1]. In other words, substantial covalence is often taken as an indication of strength of the chemical bonding.

The theoretical prediction and experimental observation of Ir (XI) oxidation state [2, 3] have raised the questions of kinetic and thermochemical stabilities of transition metal systems with uncommonly high oxidation numbers of a metal (coinciding with the group number). The well-known group 8 complexes are represented by stable yet largely covalent Os(VIII)O_4 and the less stable and highly reactive Ru(VIII)O_4 while related Fe(VIII)O_4 has never been observed but it has been predicted to be metastable [4]. Moving to the right in the periodic table, in group 9, only the observed $[\text{IrO}_4]^+$ cation and the recently predicted neutral molecule IrNO_3 (nitride trioxide) [5] feature genuine nonavalent transition metal center. Similar to Fe(VIII)O_4 , Ir (IX) NO_3 has been predicted to be mildly metastable with respect to $(\eta^2\text{-NO})\text{IrO}_2$ and $(\eta^1\text{-NO})\text{IrO}_2$ but elimination of NO is predicted to be protected

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by considerable barriers thus leaving some hope that Ir(IX)NO₃ might be observed experimentally. The theoretical investigations of other nonavalent elements in group 9 have been rather limited. For rhodium, the highest experimentally observed oxidation state is VI in RhF₆ [6–8]. Rh(IX) has only been studied in [RhO₄]⁺ complex by B3LYP density functional method (DFT), with an effective core potential [2]. It has been found to be thermodynamically unstable, with exothermic energetic effect of oxygen molecule elimination estimated at –133.2 kJ/mol (this work does not provide any information on decomposition channels and kinetic stability). Since standard enthalpy of formation for molecular RuO₄ is ca. 144 kJ/mol smaller than for its osmium analogue [9] (which can be attributed to the smaller relativistic effects and consequently weaker destabilization of valence d orbitals in Ru as compared with Os [10]), similar decrease of the stability of the Rh(IX) complexes as compared with Ir(IX) ones might indeed be expected.

In this work, we look again at [RhO₄]⁺ and for the first time at RhNO₃ to determine energetics and kinetic barriers towards decomposition of both species. Comparison of these systems within a broader set of related Ru, Os and Ir high-valent species allows us to draw more general conclusions about trends of chemical bonding in the entire family.

Methods

The most of our calculations were performed using M06-L density functional which has been well validated for transition metals [11–13]. We have included the relativistic effects using two most popular ways: via Douglass-Kroll-Hess two-component (DKH2) Hamiltonian [14, 15] or utilizing zero-order regular approximation (ZORA) [16–18]. The computations with DKH2 approach were performed with ORCA 4.0.1 program [19], and the results by ZORA were obtained in ADF 2018 [20–22]. In our calculations, we employed Gaussian-type cc-pVTZ-DK (developed in combination with DKH2) [23] and the Slater-type TZ2P (used with ZORA) [24] all-electron basis sets. The calculations performed in both used programs were done without resolution of identity and frozen-core approximation.

Abovementioned calculations based on DFT were used to perform geometry optimizations of stationary point structures (minimum energy ones and transition states (TS)) and relaxed surface scans, i.e. series of constrained geometry optimizations, with stretching or shortening of selected bond distances (reaction paths). For all these structures, optimized as of electronic singlet multiplicity, single-point energies for higher multiplicities (triplet or quintet) were also obtained to find intersections that may appear on our reaction path PESs (potential energy surfaces).

In order to validate DFT predictions and to evaluate adequacy of single-determinant wave function solutions, the single-point CCSD(T) [25, 26] energies with DKH2 Hamiltonian and cc-pVTZ-DK basis set were obtained using ORCA computational package for M06-L/DKH2 and M06-L/ZORA equilibrium geometries (see note [27]). *T*₁ diagnostic parameter [28] values were analysed (see electronic supplementary material, ESI). Recent study about usefulness of this parameter among 4d metal-containing molecules has statistically shown that the criterion of *T*₁ < 0.045 might be used to judge the importance of contribution of the nondynamical correlation in these systems [29].

The bond indices based on definitions by Gopinathan and Jug [30] and Nalewajski and Mrozek [31–33] (the set 2 presented by Michalak et al. [34]) has been employed. All indices were calculated using M06-L/ZORA/TZ2P method. Gopinathan-Jug index (G-J) is equivalent to the covalent two-center part of Nalewajski-Mrozek bond index (N-M), while the latter includes also two-center ionic contributions [30, 34] (for further information about the ratio of [G-J]/[N-M], see ESI). Partial charges were calculated with NBO 6.0 program [35] with mentioned M06-L/DKH2/cc-pVTZ-DK approach.

Results and discussion

Let us begin with two notes. Firstly, both ways of including relativistic effects used by us lead to very similar results, so we will focus here mainly on M06-L/ZORA results, while M06-L/DKH2 ones are available in ESI. Secondly, the CCSD(T)/DKH2 single-point energy calculations qualitatively agree with DFT estimates (see superposition of CCSD(T) and DFT energy values in ESI, Figs. S1, S2). Some disagreement between DFT and CCSD(T) methods appears only in the vicinity of the TS structures, where multireference character of electronic structure appears.

Analysis of the single-reference character of wave function with *T*₁ diagnostic parameter (Fig. 2) shows that local energy minima, such as those containing a metal at high formal oxidation state (Table 1), may be reasonably well described with single-determinant methods. This alone is an indicator that higher multiplicity states in which metal is at lower formal oxidation state do not admix substantially to the local minima of interest, particularly because they are quite distant from them in the space of internal geometry parameters of a molecule (bond lengths and angles). Calculated partial charges of 4d metal atoms are about 22–24% smaller than 5d metal atoms in analogous molecules (22.1%, 22.7% and 23.8% for MO₄, [MO₄]⁺ and MNO₃ respectively, results in ESI, Table S1).

However, in the case of transition states (TSs) and their neighbourhood, single-determinant methods may be insufficient (Fig. 2). This is natural since a transition state is by

Table 1 Calculated bond lengths and valency indices of optimized tetrahedral or quasi-tetrahedral structures of respective systems (A structures presented in Fig. 1). Experimental data for OsO₄ and RuO₄ are from gas phase (ED) [36, 37]; data for CsOsNO₃ are from crystal structure

Molecule	Bond	Bond length (Å)		Bond index (v.u.)			<i>T</i> ₁
		Calc.	Exp.	G-J	N-M	$\frac{[G-J]}{[N-M]}$ (%)	
OsO ₄	Os=O	1.706	1.712 [36]	1.43	1.68	85	0.016
RuO ₄	Ru=O	1.691	1.706 [37]	1.37	1.50	91	0.022
[IrO ₄] ⁺	Ir=O	1.696	—	1.37	1.54	89	0.017
[RhO ₄] ⁺	Rh=O	1.689	—	1.25	1.31	95	0.026
[OsNO ₃] [−]	Os=O	1.748	1.740 [38]	1.24	1.52	82	0.015
	Os≡N	1.685	1.676 [38]	2.01	2.26	89	
IrNO ₃	Ir=O	1.732	—	1.19	1.39	86	0.019
	Ir≡N	1.675	—	1.85	2.03	91	
RhNO ₃	Rh=O	1.725	—	1.08	1.18	92	0.039
	Rh≡N	1.667	—	1.69	1.73	98	

definition a multicenter-bonded hybrid of the substrates and products of the chemical reaction, and a minimum set of two Slater determinants is needed to describe it. Some hope gives us the fact that DFT is less sensitive to the multireference character than wave function-based computations, especially when functionals with small amount of HF exchange are used (such as M06-L one, with 0% HF contribution, applied in this work). Thus, being aware of approximate character of our investigations, sometimes it is a good idea to focus on DFT values rather than CCSD(T) ones. Based on DFT data, we found out that for some TSs, the triplet energies at the geometry of singlet solutions are lower than those of the parent singlets. This obviously reduces the effective energetic barriers on the reaction pathway leading to ³O₂ or ²NO elimination and associated with lowering of central metal ion formal oxidation number (Fig. 1). This means that the energy barriers computed in this work should be treated with the grain of salt, and they are likely smaller than the values discussed.

As expected, RuO₄ was found to be stable with respect to (η²-O₂)MO₂ (minimum marked as C_{OO} in Fig. 1) and (η¹-O₂)MO₂ states (minimum E_{OO}), while rendering the isomerization an “energy uphill” process by 141.5 kJ/mol and 281.0 kJ/mol, respectively. The first of those, which governs energetic stability of the tetrahedral minimum, is, however, smaller than that for OsO₄ of 428 kJ/mol with M06-L/ZORA approach [5] (cf. 380.7 kJ/mol at B3LYP/ECP level [39]). The transition state (B_{OO}) on the pathway of O₂ elimination from ruthenium tetraoxide resembles the transition state in the case of osmium tetraoxide [5, 39], and it corresponds to O–O bond formation during isomerization process: MO₄ ↔ (η²-O₂)MO₂. Recall that the high kinetic stability of tetraoxide complexes with metal on +8 oxidation state is secured in OsO₄ with the huge barrier of 406.3 kJ/mol on singlet PES and the corresponding barrier on the triplet PES of

(XRD) [38]. Interatomic distances and bond indices come from M06-L/ZORA computations, *T*₁ parameter values were calculated at CCSD(T)/DKH2 for M06-L/DKH2 equilibrium structures

334.4 kJ/mol [5] (cf. 394.3 kJ/mol in [39]). The height of isomerisation barrier (on the pathway from A to B_{OO}) for tetrahedral RuO₄ is again smaller but still substantial, i.e. 318.7 kJ/mol and 225.1 kJ/mol on singlet/triplet PES (see Fig. 1a, and Fig. S3a for comparison with M06-L/DKH2 approach).

Having discussed the results for important reference compounds containing group 8 metals, let us now move to group 9, which is our main focus here. Wang et al. found out that isomerization from tetrahedral [IrO₄]⁺ to [(η²-O₂)IrO₂]⁺ is an endoergic process by 40 kJ/mol (B3LYP/ZORA with spin-orbit coupling) or 89 kJ/mol (CCSD(T)/ECP) [3]. The respective barrier of first reaction step has been estimated to 190 kJ/mol [3]. This compares nicely with the values of 91 kJ/mol for isomerization and 198 kJ/mol for energy barrier which we have obtained using M06-L/ZORA method and SARC-ZORA basis set [40] (Fig. S4). In contrast to [IrO₄]⁺, we found (Fig. 1b) that [RhO₄]⁺ is metastable with respect to (η²-O₂)RhO₂ isomer, which is by 71.2 kJ/mol lower in energy.

However, the kinetic stability of [RhO₄]⁺ is secured with the large barrier of 240.2 kJ/mol at singlet PES and still appreciable one of ~87 kJ/mol at triplet PES (as estimated at singlet-triplet PES crossing, see Fig. S5b). Therefore this case is similar to FeO₄ specie (with iron in +VIII formal oxidation state), which is metastable with respect to (η²-O₂)Fe^{VI}O₂ by −44 kJ/mol and yet kinetically protected by a barrier of 174 kJ/mol at CCSD(T)/ECP level [4]. In the same study at DFT (PBE)/ECP method, these two minima are nearly degenerated in terms of energy (0.1 kJ/mol) and a barrier between them equals 121 kJ/mol [4].

The reaction path leading to partial O₂ elimination from the neutral quasi-tetrahedral IrNO₃ molecule has been recently determined to be endoergic by 200.4 kJ/mol, and the NO elimination pathway exoergic by −89 kJ/mol, but the

Fig. 1 Relative energies calculated at M06-L/ZORA level of theory for minimum-energy structures and transition states of singlet multiplicities for RuO_4 (a), $[\text{RhO}_4]^+$ (b) and RhNO_3 (c) systems. Single-point energies of all structures in their electronic triplet configurations (red bars and dashed lines) exhibiting energies lower than singlets are shown. Grey

area highlights energetic barriers around minimum A. Relevant equilibrium structures are visualized above each graph. Two largest displacement vectors of imaginary frequency are presented for each transition state. Energy of minimum A corresponding to the largest formal valence of transition metal has been set to zero

minimum of interest was found to be surrounded by two comparable energy barriers of about 208 kJ/mol [5]. In the case of its rhodium analogue, RhNO_3 , the $(\eta^2\text{-O}_2)\text{RhNO}$ state is lower by -33.8 kJ/mol from the quasi-tetrahedral Rh(IX)NO_3 , and the associated singlet-triplet crossing which creates a barrier is about 35% smaller than for the Ir complex but still quite large (~ 154 kJ/mol, Fig. S5). On the other hand, $(\eta^1\text{-O}_2)\text{RhNO}$ triplet at the geometry of a corresponding singlet is higher in energy than the tetrahedral minimum A (Fig. 1c) by 21.8 kJ/mol. Although in RhNO_3 , the NO reaction path is as exoergic as by -246.3 kJ/mol, the $(\eta^2\text{-NO})\text{RhO}_2$ state (C_{NO}) is much more energetically stable (-193.3 kJ/mol) than RhNO_3 isomer with central atom formally in +9 oxidation state (Fig. 1c). The key energy barrier on the NO elimination pathway which governs kinetic stability of RhNO_3 is large (125.3 kJ/mol) and comparable with that for the O_2 elimination. Concluding this paragraph, one should state that both $[\text{RhO}_4]^+$ and RhNO_3 seem to be sufficiently kinetically stable to be observed in experiment at low temperature.

In the case of both rhodium (+IX) complexes, the T_1 diagnostic increases (up to 0.06, see Fig. 2) while distance between $\text{O}\cdots\text{O}$ and $\text{N}\cdots\text{O}$ ligand decrease, thus indicating a growing multireference character of the wave function even before

the DFT-calculated singlet transition states are reached. That agrees well with obtained singlet-triplet crossings on PES scans Fig. S5. Again, this means that the actual barriers will be smaller than those presented in Fig. 2.

Supplementary information to energetical considerations is provided by systematic coincidence between degree of ionic/covalent character of metal-ligand bonds and energy lowering upon isomerization from high oxidation number state into the next local minimum. The concept of percentage covalent or ionic character of a bond is associated with bond polarization and charge transfer effects and from orbital viewpoint might be attached to probability of simultaneously finding two electrons on atoms A and B. It turns out that nice interpretation is provided based on covalent and ionic valence indices [41]. The covalent valence index, a measure of atom polarization and the amount of charge transfer, might be defined relative to changes in the electron “pairings” in molecule with respect to separated atom/ion limit [41]. The degree of covalence is evaluated through a ratio of bond multiplicity indices [42]:

$$\% \text{ of covalent character} = \frac{b_{\text{G-J}}}{b_{\text{N-M}}}$$

Fig. 2 CCSD(T)/DKH2 relative energy profiles of reactions of dissociations of NO and O₂ ligands from RuO₄ (a), [RhO₄]⁺ (b) and RhNO₃ (c) systems. Equilibrium geometries constituting reaction paths were obtained with M06-L/ZORA method (from Fig. S5). Interatomic distances d(O-O) and d(N-O) stand for the internal reaction coordinates, i.e. O···O and N···O separation, respectively. The *T*₁ diagnostic parameter

values are also placed on the plots. In the case of d(O-O) RhNO₃, increase of multireference character around B_{OO} probably causes abrupt energy dependence. Blue points indicate energies of the stationary point structures from DFT calculations. We found comparable results with M06-L/DKH2 (Figs. S6, S7 in ESI). Energy of minimum A has been set to zero

It is essential that the ionic and covalent valence numbers, used to determine b_{G-J} and b_{N-M} , are defined within the same theoretical framework offering a consistent set. Moreover, diatomic contributions in this method are independent of the atomic reference, as well as not much sensitive to basis set, hence reliable [34, 41]. The G-J index is based on sum of squares of density matrix elements corresponding to pairs of orbitals centered on different atoms, which is conceptually close to classical Lewis representation of covalent interaction as shared electron pairs. The covalent indices are related to exchange part of the two-particle density matrix. The N-M index includes the former covalent as well as the ionic contributions (originating from the Coulomb part of the two-particle density matrix), both affecting the fractional bond character.

The analysis of the ratio of G-J to N-M indices in our systems (Fig. 3) shows that the M=O bonds in tetraoxo-species of Os and Ir have considerable covalent character (85–89%). The analogous species of lighter 4d elements, Ru and Rh, respectively, exhibit even more covalent bonding (91–95%). On the other hand, the Ir=O bonds in IrNO₃ show

similar covalence as Os=O ones in OsO₄ (86–89%) while the Ir≡N bond is more covalent (91%). Again, and as expected,

Fig. 3 The energy of (η²-O₂)MO₂/(η²-O₂)MNO or (η²-NO)MO₂ states with respect to MO₄/MNO₃ in relation to level of covalent bonding in M=O or M≡N determined as the ratio of G-J to M-N bond indices for Ru, Os, Rh and Ir tetraoxide and nitride trioxide complexes. Energies and bond indices calculated at M06-L/ZORA level of theory

moving to the 4d element in this series increases covalence with respect to its 5d counterpart. Thus, the Rh=O bond covalence in RhNO₃ (92%) corresponds to that of the Ru=O in RuO₄ while the Rh≡N bond shows the highest value of all studied here (98%).

The increased covalent character of bonding in the complex causes the decrease of the effective central atom charge thus contributes to the ease of isomerization to the form having formally a lower oxidation number. Indeed, there appears to be general correlation between level of covalent bonding character in M=O or M≡N bonds of tetroxide or nitride trioxide complexes and energetic stability of MO₄ or MNO₃ with respect to (η^2 -O₂)MO₂/(η^2 -O₂) MNO or (η^2 -NO)MO₂ states (Fig. 3).

Conclusions

The geometry, energetics and energy barriers protecting local minima have been computed here for RuO₄, [RhO₄]⁺ and RhNO₃ using DFT calculations and cross-checked using the CCSD(T) method with relativistic two-component Hamiltonians. A tetrahedral rhodium tetroxide cation seems to be truly single-reference metastable minimum on PES though its isomerisation leading to the decrease of the formal oxidation state of a metal has no significant energetic barriers. The quasi-tetrahedral RhNO₃ species seems to exhibit larger barriers against isomerisation (> 120 kJ/mol) but it has a stronger multireference character itself. The energetic and kinetic stability of mentioned molecules containing Rh(IX) is comparable with those of Fe (VIII)O₄ [4]. Because the *T*₁ parameter for Rh system scans is close or exceeds at some points, the limiting value, especially for the NO elimination reaction pathway, the multireference methods [4] should be applied in the future to gain a deeper insight into decomposition pathways and barriers. Nevertheless, our preliminary results suggest that existence of small molecules with Rh in +IX oxidation state is conceivable, especially at very low temperatures.

We also found that high covalence of chemical bonding, as measured by the ratio of G-J to N-M indices (ESI), is associated with high susceptibility of a molecule to reconfigure into an isomer showing lower oxidation state of a transition metal. While this seems to be expected for heteroatomic molecules (an inverse ligand field implies a redox reaction [43]), yet it remains in stark contrast to what is usually observed for homonuclear systems.

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