

Simulation of the isomerization of an anionic hydroxo complex of rhodium(V)

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The molecular ion $\text{Rh}(\text{OH})_6^-$ was simulated, and the occurrence of a great number of isomers with symmetry no higher than C_i was found.

The compounds of rhodium in high oxidation states have long been of interest, since these compounds are widely used, for example, as catalysts for the oxidation of organic compounds.¹ At the same time, information on rhodium(V) and rhodium(VI) compounds has hitherto lacked completeness and reliability.

Within the framework of an experimental and theoretical examination of the oxidation of a hydroxo complex of rhodium, it was of interest to study the $\langle \text{Rh}(\text{OH})_6^- \rangle$ cluster with a closed electron shell using a wide variety of traditional quantum-chemical methods.

The potential energy surfaces (PESs), stationary points and reaction paths were calculated in terms of the second-order Møller–Plesset perturbation theory (MP2). A portion of PES cross-sections was additionally studied taking into account fourth-order perturbation theory corrections. All the calculations were performed with the use of the PC GAMESS program package.^{2,3} A pseudopotential approximation with the parameterisation according to Stevens, Basch and Krauss (SBK)³ with the $(8s8p5d)/[4s4p3d]$ atomic basis sets on the Rh atom⁵ and the $(4s4p)/[2s2p]$ atomic basis sets on the O atom was used. The standard two-exponent $(4s)/[2s]$ basis set on the hydrogen atom was chosen.

The *ab initio* modelling of systems containing transition metals is very difficult to perform because of the strongly correlated *d*-electron motion. We believed that errors in the energies calculated at different points of a PES are close and focused our attention on the general characterization of a potential surface. Note that a search for reactions with low energy barriers does not include the modelling of valence bond breaking. Therefore, the simulations of these processes within the Hartree–Fock approximation do not lead to qualitative errors. For the systems with closed electron shells, such as $\text{Rh}(\text{OH})_6^-$, the HOMO–LUMO gap is rather high because the near-degeneracy effects are quite small. Thus, the Hartree–Fock approach followed by second-order perturbation theory corrections seems appropriate for our modelling. Moreover, the choice of closed shell with zero spin possesses to ignore spin-orbit coupling, which is small for the second-row transition metals.

The number of local minima and transition states, especially taking into account the high symmetry of PESs, is extremely high, so that the result of a search for stationary points crucially depends on the geometry of the initial approximation and on

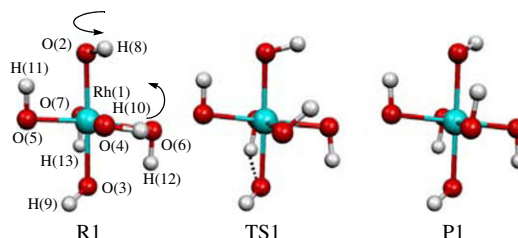


Figure 2 Schematic diagram of the isomerization of the complex $\text{Rh}(\text{OH})_6^-$ (reaction A).

the optimisation algorithm. The search for transition states was performed with the use of restricted and hypersphere optimisation⁶ and a standard quadratic approximation procedure.⁷ The reaction path was calculated using the IRC technique.⁸

It is reasonable to consider the stability of highly symmetrical complex isomers by a comparison with data calculated for the $\text{Rh}(\text{OH})_6$ neutral system. The test vibrational analysis was performed for all of the found stationary points with non-trivial symmetry, and a great number of imaginary frequencies was detected, 6 (C_{4h}) or 10 (S_4 and C_{2h}). The energy of these configurations was higher than the energy of the lower isomer with symmetry C_i by 50–70 kcal mol⁻¹. The closed-shell complex $[\text{Rh}(\text{OH})_6^-]$ is also unstable in high-symmetry configurations, as follows from the occurrence of 11 (C_{4h}) and 4 (C_i) imaginary frequencies. The results obtained are not random because structures with a higher than twofold symmetry axis imply the linear structure of the Rh–O–H fragment, which is inconsistent with the molecular structure of water and the majority of other hydroxides, that is, is contradictory to chemical intuition. It is easy to see that the non-linear structure of the Rh–O–H fragment is primarily responsible for the asymmetric arrangement of hydroxyl groups in both complexes (neutral and negatively charged). The only highly symmetrical (D_3) configuration of the $\text{Rh}(\text{OH})_6^-$ complex, which is responsible for the non-linear structure of Rh–O–H groups, is also characterised by imaginary frequencies.

In addition to this factor, the Jahn–Teller distortion of a highly symmetrical configuration in the $\text{Rh}(\text{OH})_6$ hydroxo complex should be taken into account. However, this factor is not crucial, as can be seen from a comparison with a closed-shell system.

On the other hand, the PES of the complex exhibits a high symmetry, which provides a giant number of $6!6!/2/48$ equiva-

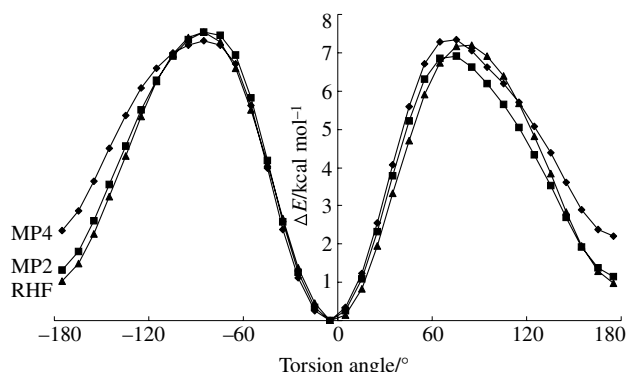


Figure 1 Torsion rotation barriers of hydrogen atoms on restricted optimisation calculated in various approximations.

Table 1 Reaction paths for reactions A and B.

Reaction	Reactive global minimum energy/kcal mol ⁻¹	$\gamma/^\circ$	$180 - \gamma/^\circ$	First hydrogen bond length/Å	Second hydrogen bond length/Å	Number of hydrogen bonds
Barrier A	1.24	—	—	—	—	—
R1	2.69	159.69	20.31	2.07	—	0
P1 (C_i)	1.98	180.00	0	—	—	0
TS1	3.92	168.07	11.93	2.00	—	1
Barrier B	2.98	—	—	—	—	—
R2	1.28	149.83	30.17	1.96	2.01	2
P2	0	143.23	36.77	1.96	1.96	2
TS2	4.51	146.27	33.73	1.96	— (bond ~2.04)	1

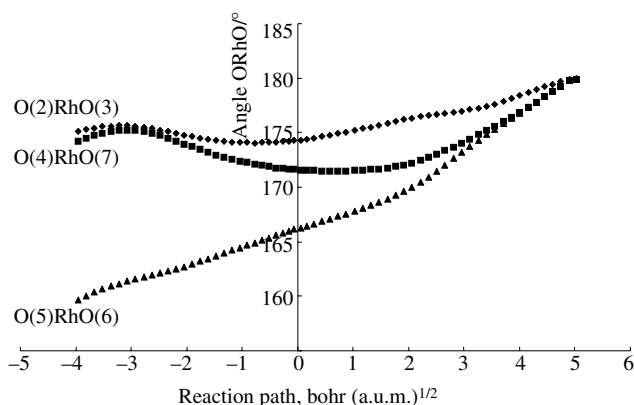


Figure 3 Dependence of the ORhO angle on the reaction path of reaction A.

lent positions for these systems. The absence of a minimum at the symmetrical point of a nuclear configuration directly denotes the occurrence of a great number of equivalent isomers, which are likely separated by not very high energy barriers. We believe that the structure of the complex exhibits a high effective symmetry of the heavy atom skeleton. We interpret the effective symmetry as the continuous migration of hydrogen atoms in the system (high-amplitude vibrations), which provides only small vibrations of oxygen atoms at symmetrical positions (vertices of an octahedron). Undoubtedly, the effect of an aqueous solvent makes a considerable additional contribution to the migration of hydrogens, although we focused our attention on the modelling of the isomerization of a free complex. The molecule of $\text{Rh}(\text{OH})_6^-$, which is a closed-shell system, was chosen as the test object.

Taking into account a great number of reaction paths, including equivalent paths, between the local minima of PESs, we did not attempt to find all the transition states. We only attempted to perform a systematic search for the reactions of hydrogen migration with low activation energies. The migration processes were described based on the internal (torsion) rotation of hydrogen atoms about Rh–O bonds.

We used two different strategies for choosing an initial geometry to find the transition state: restricted and hypersphere optimisations. The search for transition states was finished in accordance with a standard procedure⁴ supplemented with the Hessian calculation at the final point to check the type of the stationary point found.

Restricted optimisation. The potential of internal rotation for one of the hydrogen atoms (in the Rh–O–H fragment) was calculated for the most stable configuration of the energy system over the range 0–360°. To take into account the relaxation of the other geometry parameters, we performed restricted optimisation at each particular torsion angle. Figure 1 illustrates the energy profile, where a change in the H–O–Rh–O torsion angle is taken as the coordinate of reaction. On rotation, hydrogen passes over four oxygens; however, the potential exhibits only two maxima. Both minima and maxima correspond to the positions of hydrogens over oxygen atoms (an angle of 85°), although this seems unusual. A detailed analysis of conformation changes along the reaction path demonstrated that a portion of hydrogens follows the rotating hydrogen in accordance with a pinion mechanism. Thus, passing over oxygen atoms has almost no

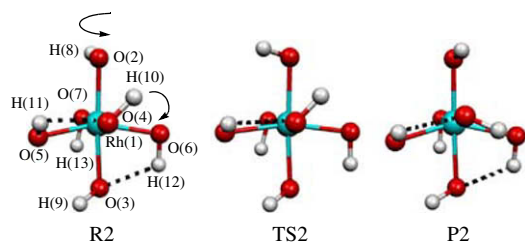


Figure 4 Schematic diagram of the isomerization of the complex $\text{Rh}(\text{OH})_6^-$ (reaction B).

effect on the potential profile, which completely depends on a steric factor, gearing with other hydrogens.

Hydrogen atoms that do not change their positions are hydrogen bonded. Evidently, the strength of a hydrogen bond, which is usually⁸ of the order of 30 kJ mol⁻¹, limits the height of these barriers. Geometry configurations corresponding to potential vertices are a good estimation for the structures of transition states.

Hypersphere optimisation. The migrations of hydrogens with a very high activation energy were studied in accordance with the above procedure. This is associated with inadequate consideration for the collective migration of hydrogen atoms, which can be corrected by the hypersphere optimisation method. The above procedure begins at a minimum point and performs the consecutive minimisation of the energy of the system on the hypersurfaces of 3N-5-dimensional spheres with increasing radii. The resulting set of points represents a fragment of the reaction path and leads to the transition state of the lowest energy. This algorithm requires an extremely high computer power; because of this, we restricted ourselves by passing an initial portion of the reaction path to the point at which the Hessian matrix ceases to be positively-defined. This point has an energy of 4.06 kcal mol⁻¹ with respect to a global minimum. A further search for the transition state was performed using a standard quadratic approximation procedure, and it resulted in a transition state with an energy of 4.5 kcal mol⁻¹ with the only imaginary frequency of 250.6 cm⁻¹.

Simulation of the reaction paths of hydrogen atom migration. We considered reaction paths A and B, which describe the migration of hydrogen atoms and connect different local minima in the PES of the hydroxo complex of rhodium.

The former reaction (A) (Figure 2) is characterised by the lowest energy barrier (1.2 kcal mol⁻¹) between two complex isomers: reactant R1 and product P1. Their energies are 2.69 and 1.98 kcal mol⁻¹, respectively, with respect to the PES global minimum. It is appropriate to evaluate the asymmetry of the oxygen environment and to give changes in the O–Rh–O angles for three opposite pairs of oxygens (which are equal to 180° in an undistorted octahedron).

The initial portion of the reaction path is characterised by the synchronous rotation of H8 and H10 hydrogen atoms with a weak drift of the other torsion parameters. After passing the point of a transition state (TS1) and completing the rotation of 8H and 10H atoms at the reaction path length of ~2 bohr(a.u.m.)^{1/2} H9 atom begins to rotate. In other words, the relative positions of only three hydrogen atoms are considerably changed.

The modification of an oxygen skeleton occurred in accordance with the migration of hydrogen atoms. As can be seen in Figure 3, reactant R1 is characterised by a strong deviation (> 20°) of one of the angles of the 5O–Rh–6O fragment from a linear configuration.

In the course of the given reaction, all the O–Rh–O angles unbend so that the final state exhibited a centre of symmetry (C_i group). Note that the rotation of hydrogen atoms about Rh–O bonds seems to provide an opportunity for unbending the 5O–Rh–6O fragment. A low barrier in this reaction can be explained by the stabilisation of the transition state by a hydrogen bond (2.0034 Å), which is ruptured on going from TS1 to P1. It seems reasonable that the higher stability of a sym-

Table 2 Comparison of the relative energies of system isomers (MP2 calculation) on extending the atomic basis sets.

Reaction	SBKJC ¹⁰	Stuttgart ^{16–19}
Barrier A	1.24	3.51
R1	2.69	2.83
P1 (C_i)	1.98	4.03
TS1	3.92	6.33
Barrier B	2.98	2.84
R2	1.28	2.44
P2 ^a	0	0
TS2	4.51	5.29

^aGeometry of a global minimum.

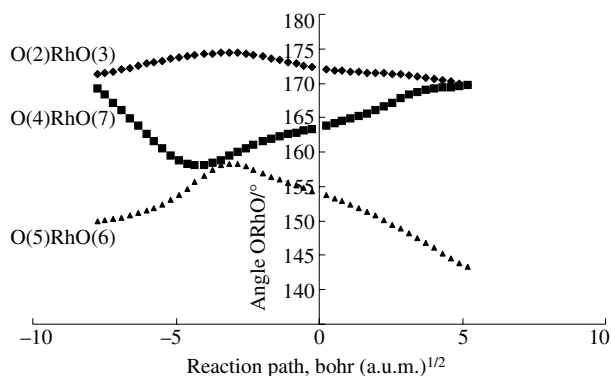


Figure 5 Dependence of the ORhO angle on the reaction path of reaction B.

metrical isomer resulted from a near-octahedral environment of oxygens (Table 1).

Reaction B (Figure 4) describes the isomerization of reactant R2 (1.28 kcal mol⁻¹) through a transition state with an energy of 4.26 kcal mol⁻¹ to an isomer with the lowest energy P2, which corresponds to the global minimum of the PES.

The torsion rotation of hydrogens along the reaction path is reduced to the synchronous rotation of hydrogens 8, 9 and 10 with a weak drift of the other parameters. Reagent R2 is characterised by a stronger deviation (33°) of one of the O–Rh–O angles from linearity. This is due to the fact that two hydrogen atoms form hydrogen bonds with neighbouring oxygens. The lengths of these bonds are equal to 1.96 and 2.01 Å, respectively.

The reaction product is also fixed by hydrogen bonds, so that the distortion of the initial O–Rh–O angle is as high as 37° (Figure 5). Because of the gearing of hydrogens in accordance with a pinion mechanism, one of the O–Rh–O fragments unbends, whereas the other bends so that both of the functions pass through extremums in the same region of the reaction path. Product P2 has two hydrogen bonds with a length of 1.96 Å; this fact can explain the stabilization (this is a global minimum in the PES). In the transition state, the distortion of the oxygen skeleton is different from that in the product (Figure 5), and there is only a single hydrogen bond.

We evaluated the reliability level of the resulting calculations by taking into account electron correlations with the use of greater atomic basis sets and higher order perturbation theories. Thus, we additionally performed test calculations for the total energy at the previously found stationary points. Estimations were made in terms of the Møller–Plesset perturbation theory of second to fourth orders with an atomic basis set containing polarization

functions on all the atoms. For rhodium, the (8s7p6d)/[6s5p3d] atomic basis sets with the Stuttgart RSC ECP parameterisation¹⁰ was taken, which was supplemented with the contracted *f*-function (3*f*)/[1*f*] according to Rakowitz *et al.*¹¹ For oxygen, the (4s,5p)/[2s,3p] set¹² supplemented with two *d*-functions from the oxygen 6-311++G basis sets¹³ was chosen. Table 2 summarises the calculated energies (in kcal mol⁻¹) with respect to the global minimum. A considerable result of the test consists in a change in the conclusion on the most stable isomer in favour of P1. On the other hand, quantitative changes in the energy parameters (barriers and relative energies of isomers) are insignificant. A careful analysis indicates a high contribution of triple excitations to a fourth-order correction and, thereby, a crucial role in a comparison of isomer energies. Nevertheless, the energy distribution of the structures found previously does not indicate a change in the flat character of the PES. We can state that the migration of hydrogen atoms in the test complex is a low-energy process, and it can be qualitatively reproduced with the use of the initial calculation procedure.

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