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ScienceDirect
Mendeleev Commun., 2017, **27**, 144–146
Mendeleev Communications

Quantum-chemical modeling of the oxidation of Au^{III} hydride complexes by hydrogen peroxide

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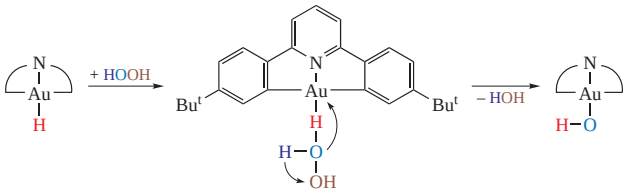
DOI: 10.1016/j.mencom.2017.03.012

According to quantum chemical calculations, the interaction of a thermally stable Au^{III} hydride complex with H_2O_2 leads to the formation of an Au^{III} hydroxyl complex in one stage with a low activation barrier and a significant energy decrease.



Gold-based catalysts are promising to solve the problem of homogeneous oxidation of alkanes RH under mild conditions.[1–3] These reactions include a stage of C–H bond activation, which may lead to the formation of intermediate alkyl-hydride complexes. According to quantum-chemical modeling, such a scenario is approved in some cases.[4–7] A valuable product ROH can be formed at the next step of reductive elimination if the Au–H bond is easily oxidized by hydrogen peroxide. Indeed, gold hydride complexes are well-known key intermediates in homogeneous and heterogeneous catalytic reactions.[8–13] In this work, we studied the reactivity of Au^{III} hydride complexes toward H_2O_2.

Thermally stable gold hydride complex **1** [(C^N^C)*AuH], where (C^N^C)* is a 2,6-bis(4′-*tert*-butylphenyl)pyridine ligand, which was experimentally studied by Rosca *et al.*,[14] was chosen for the quantum-chemical modeling of a reaction with H_2O_2. The calculations were performed using the PBE density functional method[15] with an extended basis set for valence electrons and the relativistic SBK-JC pseudopotentials[16,17] (PBE/SBK approach). In order to take into account more accurately indirect relativistic effects, which are important for the outer-shell electrons of the Au atom, the scalar relativistic approach[18] was also applied using the extended four-component basis (PBE/basis4 approach). In both cases, the Priroda program package[19] was used. The connection of the transition states with minima on potential energy surfaces was confirmed by the calculation of intrinsic reaction coordinates. Thermodynamic functions for the isolated molecules were calculated in a rigid rotor-harmonic oscillator approximation. The atomic charges were obtained by the Hirshfeld method.[20] The standard Gibbs energies of hydration for all optimized structures were calculated by the Gaussian 03 program package[21] using the polarizable continuum model[22] at PBEPBE/SBK approach. DFT methods are well suitable for studies of Au-containing catalyst systems including the participation of intermediate Au^{III} hydride complexes.[23,24]

Figure 1 shows the structure of complex **1** and complexes **2**–**4** formed during the reaction of **1** with H_2O_2. It can be seen that the calculated and experimental[14,25] bond lengths in the coordination center of **1** are in a good agreement. The accuracy of the relativistic pseudopotential approach is comparable to that of the scalar relativistic one. That is why more economical PBE/SBK calculations were used for a detailed study of the properties and reactivity of complex **1**. The calculated stretching vibration frequency and dissociation energy for the Au–H bond are 2189 cm^{-1} and 76.6 kcal mol^{-1}, respectively, which are in a good agreement with the experimental values of 2188 cm^{-1} and 69.6–78.6 kcal mol^{-1}.[14,26] Thus, the PBE/SBK approach adequately describes the structure and properties of the chosen Au^{III} hydride complex.

Table 1 shows the calculated energy characteristics. At the first stage of the reaction of **1** with H_2O_2, prereaction complex **2** was formed: the H_2O_2 molecule forms a hydrogen bond with an H hydride ligand, which possesses a negative charge of –0.06. The fairly short H–H(1) distance (1.921 Å) corresponds to the appreciable formation energy (5.2 kcal mol^{-1}) of **2** relative to free reagents. In the course of further reaction between **1** and H_2O_2, significant electron density transfer from the hydride ligand to the lowest unoccupied molecular orbital of H_2O_2 is observed. As

Table 1 Relative energy ΔE_0 (with zero-point vibration energy correction) and relative standard Gibbs energies in a gas phase ΔG^0_{298} and in aqueous solution ΔG^0_{298}(solv.) for prereaction complex **2**, transition state **3** and product **4** formed in the reaction of **1** with H_2O_2.

Complex	PBE/SBK								PBE/basis4
	ΔE_0/kcal mol^{-1}	ΔG^0_{298}/kcal mol^{-1}	ΔG^0_{298}(solv.)/kcal mol^{-1}	Hirshfeld atomic charge					ΔE_0/kcal mol^{-1}
				Au	H	H(1)	O(1)	O(2)	
1 + H_2O_2	0	0	0	0.16	–0.06	0.16	–0.16	–0.16	0
2	–5.2	4.5	7.2	0.18	–0.06	0.12	–0.15	–0.16	–4.6
3	10.0	19.2	18.6	0.19	0.04	0.15	–0.14	–0.31	11.7
4	–68.2	–58.0	–59.3	0.27	0.12	0.10	–0.28	–0.31	–68.4

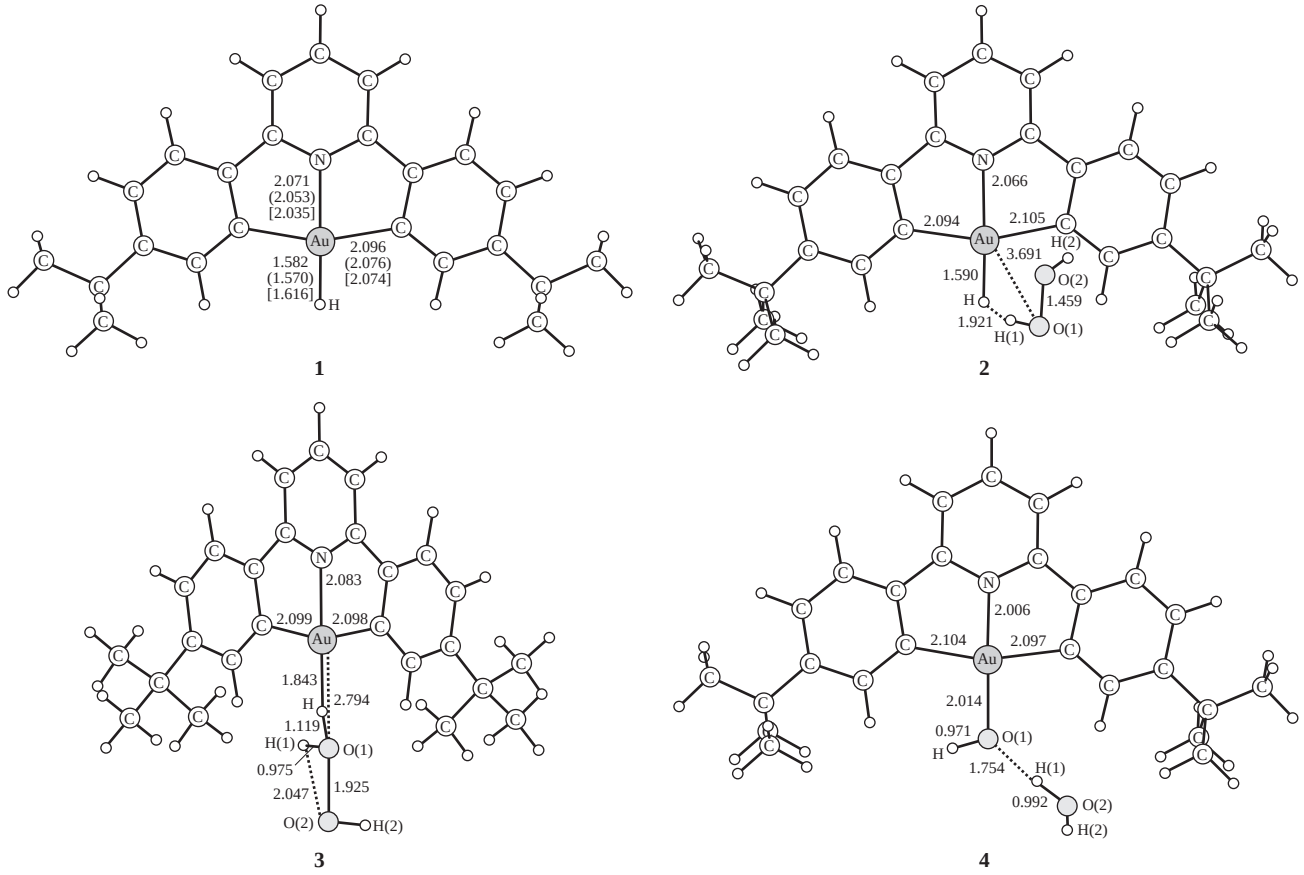


Figure 1 Structures of Au^{III} hydride complex **1**, prereaction complex **2**, transition state **3** and reaction product **4**. The optimized bond lengths at the PBE/SBK level, at the PBE/basis4 level (in parentheses) and the X-ray data from refs. 14, 25 (in brackets) are given in Å.

a result, a negative charge of –0.18 at the H(1)–O(1)–O(2)–H(2) fragment is localized and a short H–O(1) distance of 1.119 Å is formed in transition state **3** (Figure 1), in which there is only one imaginary frequency (296.4i cm^{-1}) that corresponds to vibration with the movement of the O(1) atom as the main. Note that a significant elongation of O(1)–O(2) and Au–H bonds in **3** by 0.466 and 0.261 Å, respectively, takes place, despite a small energy barrier of 10.0 kcal mol^{-1} relative to free reagents is observed. A significant negative charge of –0.31 is centered at the O(2) atom, but the O(1)–H(1) group has a slightly positive charge of 0.01. This charge distribution is favorable for H(1)–O(2) bond formation and O(1)–O(2) bond cleavage. At the same time, the H–O(1) bond is oriented in such a way that a new bond between the O(1) donor atom and the Au atom is formed. Thus, under moving along the reaction coordinate, the following concerted processes are observed: the cleavage of O(1)–O(2) and O(1)–H(1) bonds accompanied by $H(1)^+$ proton transfer to the O(2) atom and by the insertion of the O(1) atom into the Au–H bond. The energy of formation of product **4** relative to free reagents is 68.2 kcal mol^{-1}. The H(1)–O(2)–H(2) water molecule in an outer sphere of **4** has a hydrogen bond (with an energy of 8.9 kcal mol^{-1}) with the O(1)–H hydroxyl group, which is coordinated at the Au center. Table 1 shows minimal differences in the relative energy ΔE_0 for the PBE/SBK and the PBE/basis4 approaches. Changes in the standard Gibbs energy (ΔG^0_{298}) in a gas phase for all elementary stages were calculated. Prereaction complex **2** and transition state **3** have positive ΔG^0_{298} of 4.5 and 19.2 kcal mol^{-1} relative to free reagents, respectively. The account for solvation effects in aqueous solution gives small corrections (Table 1). The free activation energy in water is 18.6 kcal mol^{-1}, which is lower by only 0.6 kcal mol^{-1} than that in a gas phase reaction.

The energy profile of a similar reaction of the $[AuCl_3H]^-$ model hydride complex with H_2O_2, which leads to the formation of the $[AuCl_3OH]^-$ hydroxyl complex and H_2O, was calculated. The energies relative to free reagents for the prereaction complex (in which the H_2O_2 molecule forms a hydrogen bond with the hydride ligand of $[AuCl_3H]^-$), the transition state and the product are –10.6, –1.4 and –57.7 kcal mol^{-1}, respectively. In this case, steric hindrances are absent and the energy barrier relative to the prereaction complex, 9.2 kcal mol^{-1}, is by 6.0 kcal mol^{-1} lower than that in the system with complex **1** (Table 1). The low activation energies in both systems result from the weak steric dependence. It is due to a small deviation of the reaction center Au–H–O(1)–O(2) from linearity in transition states, *e.g.*, in **3** the Au–H–O(1) angle is 140° and the H–O(1)–O(2) angle is 160°. Moreover, since additional coordination bonds with the metal center are not formed in the reaction, the favorable coordination number four of Au^{III} is saved.

Thus, we found an easy transformation of Au^{III} hydride complexes into Au^{III} hydroxyl complexes in aqueous solution by direct one-stage oxidation with H_2O_2 through a molecular mechanism with low activation barriers and a large energy gain. The mechanism has concerted nature when the insertion of a hydrogen atom of H_2O_2 into the O–O bond is coupled with oxygen atom insertion into the Au–H bond. In this case, there is a minimal steric hindrance even in the presence of bulky ligands. Thus, Au^{III} hydrides formed upon the activation of aliphatic C–H bonds are also expected to be oxidized by hydrogen peroxide. The energetically favorable reaction mechanism of the Au–H bond functionalization described in this work is of interest for this class of compounds, and it is of general importance as a route of chemical reactions with a minimal steric hindrance.

All of the calculations were carried out using the facilities of the Joint Supercomputer Center of the Russian Academy of Sciences and of the Computing Center of the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

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Received: 14th July 2016; Com. 16/4996