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Radical decomposition of hydrogen peroxide catalyzed by aqua complexes $[M(H_2O)_n]^{2+}$ (M = Be, Zn, Cd)

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ABSTRACT

The catalytic activity of the aqua complexes $[M(H_2O)_n]^{2+}$ (**1**) (M = Be, $n = 4$; M = Zn, Cd, $n = 6$) toward the radical decomposition of H_2O_2 and generation of the $HO^{\cdot}$ radicals was investigated in detail by theoretical (DFT) methods. It was predicted and then confirmed by preliminary experiments that complexes **1** are able to catalyze this process despite the metals have only one stable non-zero oxidation state and, hence, cannot change it during the reaction as proposed in the classical Fenton chemistry. The mechanism of the H_2O_2 decomposition includes the substitution of a water ligand for H_2O_2, protolysis of the coordinated H_2O_2, second H_2O-for-H_2O_2 substitution, elimination of one ligated water molecule (for Zn and Cd), and the homolytic HO–OH bond cleavage in complexes $[M(H_2O)_p(H_2O_2)(OOH)]^{+}$. The principal factors affecting the $HO^{\cdot}$ formation are lability of the complexes, their acidity, and their ability to activate H_2O_2 toward the homolytic HO–OH bond cleavage. The participation of two H_2O_2 molecules is necessary for an efficient $HO^{\cdot}$ generation. The water substitution steps occur via concerted I_a (Be, Cd) or dissociative D (Zn, Cd) mechanisms.

1. Introduction

Hydrogen peroxide (H_2O_2) is an important ecologically benign oxidant with a broad application in various industrial fields (from waste oxidation and dye decomposition to pulp and paper bleaching and rocketry) and laboratory practice [1]. The O–O bond cleavage in the H_2O_2 molecule occurs relatively easy in the presence of an appropriate catalyst due to the rather low energy of this bond (48.75 ± 0.005 kcal/mol [2]). One of the most historically important systems that facilitate the hydrogen peroxide decomposition is the Fenton reagent ($Fe^{II} + H_2O_2$) [3]. Two general types of the mechanism of the H_2O_2 decomposition in the Fenton reagent were initially proposed, *i.e.* the non-radical type via the formation of the ferryl ion $Fe^{IV}{=}O^{2+}$ [4] and the radical type involving the formation of the $HO^{\cdot}$ and $HOO^{\cdot}$ radicals [5], and even today it is still unclear which mechanism is realized (or predominant) in this system [6–30]. Meanwhile, in the case of the catalytic systems based on other metals, the radical pathway seems to be preferable [31–36].

One of the key steps of the Fenton or Fenton-like reactions involves the change in the metal oxidation state. Therefore, complexes of transition metals that have at least two relatively stable oxidation states (Fe, Co, Cu, Mo, Re, V, Au, etc.) are usually used in these systems, while complexes of metals that have a single stable non-zero oxidation state (SSOS metals), *e.g.* Al, Ga, In, Sc, Y, Be, Mg, Ca, Zn, Cd, some Ln, are not typical for the Fenton-type chemistry and they are often considered as Lewis acids without participating in electron transfer reactions. At the same time, recently, the simple catalytic system $[Al(H_2O)_6]^{3+}/H_2O_2/CH_3CN{+}H_2O$ was found to be rather active for the oxidation of non-activated alkanes [37]. The experimental kinetic data and reaction selectivity parameters indicate that the mechanism of this reaction is the radical one and it includes the formation of highly reactive $HO^{\cdot}$ radicals which then directly oxidize the alkane molecule. Thus, this system behaves as a typical Fenton-like reagent despite Al is a SSOS metal. This was the first example of the homogeneous oxidation of non-activated alkanes with H_2O_2 catalyzed by a non-transition metal complex (although the oxidation of benzylic or allylic C–H bonds [38–40], epoxidation of alkenes [41–52], oxidation of sulfides [53] or heterogeneous oxidation of alkanes [54–75] by peroxides with SSOS or non-transition metals used as catalysts or supports are known).

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Later, some of us proposed and theoretically investigated the mechanism of the $HO^{\cdot}$ radical generation in the system $[Al(H_2O)_6]^{3+}/H_2O_2$ [76] as well as in other systems of the SSOS metals of Group III $[M(H_2O)_n]^{3+}/H_2O_2$ (M = Ga, In, Sc, Y, La) [77]. This mechanism does not require the change in the metal oxidation state and it includes the substitution of a water ligand for hydrogen peroxide, protolysis of the coordinated H_2O_2, the second H_2O-for-H_2O_2 substitution and, finally, the homolytic HO–OH bond cleavage (Scheme 1). It was found that the H_2O_2 molecule is highly activated in complexes $[M(H_2O)_{n-2}(H_2O_2)(OOH)]^{2+}$ toward the homolytic HO–OH bond rupture and the formation of the $HO^{\cdot}$ radicals.

Here, we extend the theoretical study of this mechanism to other SSOS metals, *i.e.* those of Group II (Be, Zn, and Cd). The essential goal of this work is to uncover if the complexes of these bi-charged SSOS metal ions, which are not typical for Fenton chemistry, can also catalyze the homolytic decomposition of H_2O_2 and the formation of the $HO^{\cdot}$ radicals or these species are inactive in this process. The catalytic systems $[M(H_2O)_n]^{2+}/H_2O_2$/solvent ($CH_3CN + H_2O$) (M = Be, Zn, Cd) were selected for this study, and they are similar to those investigated previously by experimental and theoretical methods for the metals of Group III. Details of the plausible mechanism of the $HO^{\cdot}$ generation are discussed and main factors determining the catalytic activity of the aqua complexes are analyzed.

2. Computational details

The full geometry optimization of all structures and transition states (TS) has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang and Parr (B3LYP) [78,79] with the help of the Gaussian-03 [80] program package. The standard basis set 6-311+G(d,p) [81–84] was applied for all atoms, in the case of complexes of Be and Zn, and for non-metal atoms, in the case of complexes of Cd. The Def2-TZVP (7s7p6d1f)/[6s4p3d1f] basis set [85] and corresponding pseudopotentials describing 28 core electrons [86] taken from the EMSL Basis Set Exchange Library [87] were employed for Cd. No symmetry operations have been applied for any of the structures calculated.

Taking into account the importance of the consideration of the second coordination sphere in the calculations of solvent effects for reactions involving highly charged species, one solvent molecule (H_2O or H_2O_2) was included explicitly in the second shell of the calculated structures except intermediates and transition state of the associative mechanism of the water substitutions (consult Tables S1–S3 in Supplementary information for each particular case). In the latter cases, the external solvent molecule was not added to preserve the number of molecules participating in the reaction and, hence, to minimize the error of the entropy estimates. For simplicity, the second-sphere solvent molecules are not shown in the formulae of complexes except the cases when they are important for a better understanding of results.

As indicated in the previous [76,77] and this (see below) works, the combination of the B3LYP functional, the basis sets used and the model with one explicit solvent molecule in the second coordination sphere provide an excellent agreement between the calculated and experimental activation energies of the water substitution reactions – two relevant steps of the calculated mechanism. Additionally, the O–O bond dissociation energy in H_2O_2 calculated at this level of theory (48.7 kcal/mol, the total gas-phase energy scale) is very close to the experimental value of 48.75 ± 0.005 kcal/mol [2].

Restricted approximations for the structures with closed electron shells and unrestricted methods for the structures with open electron shells have been employed. For several structures, instability of wavefunctions was found. In these cases, the following reoptimization of the wavefunctions was carried out to achieve a stable solution using the keyword STABLE(Opt) in Gaussian-03.

The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one imaginary frequency) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis of vectors associated with the imaginary frequency and, in some cases, by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez–Schlegel method [88].

Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries using the polarizable continuum model in the CPCM version [89] with CH_3CN or, in some cases, H_2O as solvents. The entropic term for the CH_3CN solvent (S_s) was calculated according to the procedure described by Wertz [90] and Cooper and Ziegler [91] using the following equations:

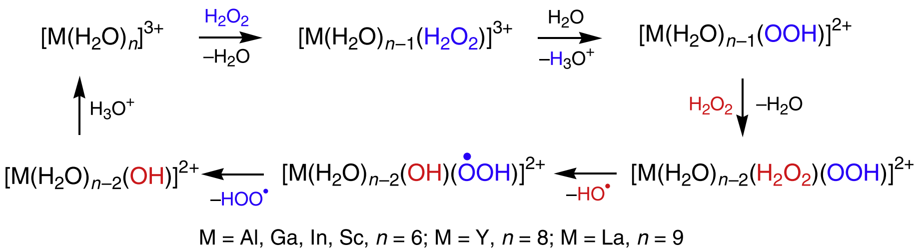
$$\Delta S_1 = R\ln\left(V^{s}_{m,liq}/V_{m,gas}\right) \tag{C1}$$

$$\Delta S_2 = R\ln\left(V^{\circ}_{m}/V^{s}_{m,liq}\right) \tag{C2}$$

$$\alpha = \left[S^{\circ,s}_{liq} - \left(S^{\circ,s}_{gas} + \Delta S_1\right)\right]/\left[S^{\circ,s}_{gas} + \Delta S_1\right] \tag{C3}$$

$$\begin{aligned} S_s &= S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2] \\ &= S_g + [(-12.21\ \text{cal/mol K}) - 0.23(S_g - 12.21\text{cal/mol K}) \\ &\quad + 5.87\ \text{cal/mol K}] \end{aligned} \tag{C4}$$

where S_g = gas-phase entropy of solute, ΔS_{sol} = solvation entropy, $S^{\circ s}_{liq}$, $S^{\circ,s}_{gas}$, and $V^{s}_{m,liq}$ = standard entropies and molar volume of the solvent in liquid or gas phases (149.62 and 245.48 J/mol K and 52.16 mL/mol, respectively, for CH_3CN), $V_{m,gas}$ = molar volume of the ideal gas at 25 °C (24,450 mL/mol), V°_{m} = molar volume of the solution corresponding to the standard conditions (1000 mL/mol).



Scheme 1. Mechanism of the $HO^{\cdot}$ radical generation in the systems $[M(H_2O)_n]^{3+}/H_2O_2$ (M = Al, Ga, In, Sc, Y, La).