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Quantum chemical study of the reactions of Al, AlO and AlOH with H_2O_2

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ABSTRACT

Quantum chemical calculations with the use of hybrid density functional with perturbative second-order correlation and dispersion correction are carried out to study the reactions of Al, AlO and AlOH with the H_2O_2 molecule. The values of energy barriers are estimated by means of extrapolation to the basis set limit. The energetically favorable reaction pathways have been revealed during the examination of the potential energy surfaces. Complex character of the processes under study has been established. It has been found that the initial stages of the considered processes are barrierless. Appropriate rate constants for principal channels of the reactions under study have been estimated by using capture model and canonical variational theory. The Arrhenius approximations for these channels have been proposed for the temperature range $T = 300–4000$ K.

1. Introduction

Nowadays, combustion of metal particles is considered as an effective method of conversion of chemical energy of various inorganic compounds into thermal energy. Combustion of metal particles provides very high temperature of combustion products. Water vapor H_2O and hydrogen peroxide H_2O_2 are strong oxidizers for different metals including aluminum. The reactions of some metals with steam proceed with high energy release and produce rather high temperature of the combustion exhaust. In recent years, a great deal of interest has been expressed to the study of elementary reactions in the Al–H_2O system [1–5], and detailed reaction mechanisms describing the ignition in such systems were built [6–8].

As was shown previously [9–11], the addition of hydrogen peroxide to aluminum–steam mixture can increase the reactivity of the fuel/oxidizer mixture and final temperature in the combustion exhaust. It is worth noting that aluminum–hydrogen peroxide mixture is used in fuel-cells for underwater vehicles [12,13]. However, with the exception of reaction of AlH_2 with H_2O_2 [14,15], until now, there are no kinetic data on the reactions of Al and Al-containing species with H_2O_2 molecule. This fact delays the construction of reaction mechanism for the Al–H_2O–H_2O_2 system, though such mechanisms are strongly needed to predict the ignition delay, burning rate, evolution of species concentrations and to estimate the real energy released during combustion of such mixtures in practical devices. Note that the interaction of laser-ablated Al atoms with H_2O_2 was studied experimentally by Wang and Andrews [16], however only possible products were detected there.

The most abundant active species at the initial stage of Al–H_2O mixture oxidation are Al atoms, AlO and AlOH [8]. These species can react potentially with H_2O_2 and, therefore, upon the absence of experimental data, theoretical study of corresponding potential energy surfaces (PESs), allowing one to determine possible reaction channels and reaction products, is required. The current paper is aimed at the quantum-chemical analysis of the reactions of Al, AlO and AlOH in their ground electronic states with H_2O_2 and the estimation of rate constants of these channels.

2. Methodology

2.1. Investigation of potential energy surfaces

The strategy of the investigation is based on series of quantum chemical computations with the use of density functional theory (DFT). The hybrid density functional with perturbative second-order correlation and empirical dispersion correction B2PLYP-D [17] was chosen to explore the PESs for the doublet $Al(^2P) + H_2O_2(X^1A)$, doublet $AlO(X^2\Sigma^+) + H_2O_2(X^1A)$ and singlet $AlOH(X^1\Sigma^+) + H_2O_2(X^1A)$ systems. It is worth noting that this functional is considered as quite suitable one to determine accurately not only the reaction enthalpy but also the activation barriers of chemical reactions [18–20].

In the present work, the PESs analysis was performed with the use of Dunning's correlation consistent basis set with diffuse functions [21]. The geometry of reactants, transition states and

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possible products of reaction pathways were optimized at the UB2PLYP-D/aug-cc-pvDZ level of theory. The characterization of each stationary point either as a minimum or as a first-order saddle point was conducted by using a vibrational frequency analysis at the same level of theory. A special attention was paid to the calculation of low frequency vibrational modes. So, the structures with minimal vibrational frequency $\nu \leqslant 100\ \text{cm}^{-1}$ were re-optimized with tight convergence criteria: root-mean-square forces within 10^{-5} atomic units and root-mean-square displacements within 4×10^{-5} atomic units.

Numerical computations in this case were carried out with the use of a pruned grid comprising 99 radial shells and 590 angular points per shell. In order to compensate an incomplete treatment of electron correlation as well as the effect of truncated basis set and ignoring the anharmonicity of vibrations, the calculated values of frequency were scaled by a factor of 0.9648 in line with the recommendations of Kesharwani et al. [22]. The Gonzalez–Schlegel intrinsic reaction coordinate (IRC) algorithm [23] in both directions was applied in order to prove the fact that the reactants and products are connected by the transition state along the minimum-energy paths (MEPs) of the reactions.

Additionally, in order to refine the energy of revealed critical points, the pointwise electronic energy calculations were performed with extended basis sets: the Dunning's aug-cc-pv*n*Z basis sets [21] with maximal angular momentum quantum numbers $n = 3, 4$ were applied. Obtained energy values were extrapolated to the basis set limit via the exponentially decaying function [24] as following:

$$E(\infty) = \frac{E_{\text{QZ}} \cdot E_{\text{DZ}} - E_{\text{TZ}} \cdot E_{\text{TZ}}}{E_{\text{DZ}} - 2E_{\text{TZ}} + E_{\text{QZ}}}, \qquad (1)$$

where $E(\infty)$ is the energy estimated at the basis set limit, E_{DZ}, E_{TZ} and E_{QZ} are the energy value calculated by using Dunning's basis set with angular momentum quantum numbers $n = 2$, 3 and 4, respectively. Note that the zero point energy (ZPE) correction, obtained at the UB2PLYP-D/aug-cc-pv∞Z level of theory (sign ∞ indicates an extrapolation of aug-cc-pv*n*Z basis set to the complete basis set), was implemented with the usage of the scaled vibrational frequencies. All quantum chemical calculations were conducted by using Firefly QC program package [25] which is partially based on the GAMESS (US) source code [26]. Visualization of the computational results was performed by using ChemCraft software [27].

For the validation of applied methodology we compared the atomization enthalpies of reactants and possible products for the reactions of H_2O_2 with Al, AlO and AlOH, calculated by using approach of this work, and their values reported in the reference databases [28,29]. Table 1 lists the obtained results. One can see that if the aug-cc-pvDZ ($n = 2$) basis set is used, the mean deviation from reference values mounts to 4.9%. However, applying the extrapolated basis set allows one to improve the accuracy up to 0.5%. Thus, the applied methodology provides the reliable energy values for the systems under study.

Table 1
Atomization enthalpies in kJ/mol for the species involved in the reactions of H_2O_2 with Al, AlO and AlOH, calculated by using the present methodology for different values of maximum angular momentum (n) in the basis set and corresponding reference data [28,29]. The magnitudes of mean deviation of the calculated values of atomization enthalpy from the reference ones are also presented.

Molecule	2*s* + 1	*n* = 2	*n* = 3	*n* = 4	*n* = ∞	Reference data
HO_2	2	679.4	699.6	706.3	709.6	704.0
H_2O_2	1	1025.2	1052.6	1060.4	1063.4	1070.2
AlO	2	467.8	496.5	506.3	511.2	512.3
AlH	1	285.0	293.7	296.1	296.7	298.5
AlOH	1	934.9	966.7	976.4	980.4	977.1
$Al(OH)_2$	2	1654.4	1714.5	1733.0	1740.9	1730.9
$Al(OH)_3$	1	2576.7	2669.4	2696.4	2707.1	2709.7
Mean. dev., %		4.9	1.5	0.6	0.5	

2.2. Calculation of reaction rate constants

As is known, for various types of reactions, different theoretical approaches should be used to estimate the rate constants. So, for the barrierless reactions it is believed that the rate coefficient is controlled by long-range interaction forces between reactants [30,31]. In the present work, the interaction of two polar particles (A and B) was described in accordance with the method of dipole reduced formalism (DRFM) developed by Paul and Warnatz [32]. In line with this approach, the interaction is specified by the effective spherically symmetrical potential

$$\varphi_{\text{eff}}(r) = -\frac{C_6^{\text{eff}}}{r^6}, \quad C_6^{\text{eff}} = C_6^{\text{disp}}\left(1 + \frac{C_6^{\text{ind}}}{C_6^{\text{disp}}} + \frac{C_6^{\text{el}}}{4C_6^{\text{disp}}}\right)^2, \qquad (2)$$

where r is the distance between interacting particles, C_6^{disp}, C_6^{el} and C_6^{ind} are the terms specifying the dispersion interaction, electrostatic interaction of dipoles and polarization interaction. These terms can be written as [33]

$$C_6^{\text{disp}} = \frac{3}{2} E_{\text{at}} a_0^{\frac{3}{2}} \frac{\alpha_{\text{A}}\alpha_{\text{B}}}{\sqrt{\frac{\alpha_{\text{A}}}{N_{\text{A}}}} + \sqrt{\frac{\alpha_{\text{B}}}{N_{\text{B}}}}}, \qquad (3)$$

$$C_6^{\text{el}} = \frac{2}{3k_{\text{b}}T}\mu_{\text{A}}^2\mu_{\text{B}}^2, \qquad (4)$$

$$C_6^{\text{ind}} = \mu_{\text{A}}^2\alpha_{\text{B}} + \mu_{\text{B}}^2\alpha_{\text{A}}. \qquad (5)$$

Here $E_{\text{at}} = 27.211$ eV, a_0 is the Bohr radius, k_{b} is the Boltzmann constant, α_{A} and α_{B} are the static isotropic polarizabilities, N_{A} and N_{B} are the numbers of valence electrons (the number of electrons in the outer sub-shell of particle), μ_{A} and μ_{B} are dipole moments of particles of A and B sorts. The values of polarizability and dipole moment of molecules were estimated at the UB2PLYP-D/aug-cc-pvDZ level of theory.

In line with capture approximation [34,35], the rate constant of bimolecular barrierless reaction between two particles, interacting according to the attractive potential (2), can be expressed as

$$k(T) \cong 1.706\rho(T)\left(\frac{\left(C_6^{\text{eff}}\right)^2 k_{\text{b}}T}{M^3}\right)^{\frac{1}{6}}, \quad \rho(T) = \frac{Q_{\text{e}}^{\text{PES}}(T)}{Q_{\text{e}}^{\text{A}}(T)Q_{\text{e}}^{\text{B}}(T)} \qquad (6)$$

where M is the reduced molecular mass of colliding molecules, Q_{e}^{A}, Q_{e}^{B} and $Q_{\text{e}}^{\text{PES}}$ are the electronic partition functions of reactants (A and B) and the electronic degeneracy of reactive PES, respectively. The factor $\rho(T)$ characterizes the probability that the collision of reactants occurs on the reactive PES.

For the reactions with non-zero activation barrier, when a single potential maximum along the MEP on the electronic PES can be associated with the transition state structure, separating the reactant and product PES regions, the rate constant can be estimated by using the transition state theory [31]. In the present study, both canonical variational theory (CVT) and non-variational conventional transition-state theory (CTST) with the use of Eckart-type tunneling correction were applied in the same manner as in our previous work [36]. So, for the estimation of CTST rate constant, the energy values, calculated at the UB2PLYP-D/aug-cc-pv∞Z level of theory $\left(k_{\infty\text{Z}}^{\text{CTST}}\right)$, were used. In order to evaluate the contribution of variational effects, the projected vibrational frequency analysis along the reaction path [37] was conducted at the UB2PLYP-D/aug-cc-pvDZ level of theory (precisely this level of theory was utilized during the IRC calculations). The values of