Research paper

Binding of oxygen with titanium dioxide on singlet potential energy surface: An *ab initio* investigation

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A B S T R A C T

Ab initio calculations have been carried out to investigate interaction of titanium dioxide TiO_2 with oxygen O_2 in ground triplet and excited singlet states. On a singlet potential energy surface (PES) formation of a stable compound of titanium peroxide TiO_4 is revealed which should appear in reaction of TiO_2 with singlet oxygen without activation barrier. This peroxide is lower in energy than the ground state of two individual molecules $TiO_2 + {}^3O_2$ by 34.6 kcal/mol. Location of conical intersection between triplet and singlet PESs of TiO_2—O_2 is also investigated.

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1. Introduction

Titanium dioxide (TiO_2) based materials are most widely used catalysts in the fields of photocatalytic water splitting and hydrogen production, photoelectrochemistry, dye sensitization and solar energy conversion, and photochemical air and water treatments [1–5]. The results of studies of various aspects of the TiO_2-based photocatalysis are addressed in reviews [1–5]. Oxidative processes on the surface of photocatalyst proceed with participation of oxygen. Interaction of oxygen with a surface of TiO_2 has been a subject of numerous experimental and theoretical studies with brief chronology of these studies given by Henderson [2]. According to this review oxygen O_2 at low temperature can only physisorb to TiO_2 surface if there are no sites with reduced cations. Chemisorption proceeding as dissociative O_2 adsorption takes place only when these surface electronic defects (oxygen vacancies) exist and has activation barrier more than ∼0.7 eV (≈16 kcal/mol) [2]. Here we should notice that in all these studies oxygen participates in its ground triplet electronic state ($X^3\Sigma_g^-$) because population of excited electronic states of O_2 is very low at the low temperature values usually used in these experiments. When a system of TiO_2 and O_2 is treated by radiation formation of excited O_2 molecules in singlet electronic state ($a^1\Delta_g$) takes place. Earlier formation of singlet oxygen ${}^1O_2$ after photoexcitation of dispersed TiO_2 in different solvents containing oxygen was revealed by ESR detection of specific products of ${}^1O_2$ interaction with spin trapping agents [6 and references therein]. Later direct detection of singlet oxygen formation was provided by Nosaka et al. [7] who detected appearance of IR luminescence of ${}^1O_2$ centered at 1.27 μm after irradiation of TiO_2. High quantum yield of ${}^1O_2$ at a level of 12–38% was detected [8]. Singlet oxygen itself is a reactive molecule which can be an agent of oxidative processes [9]. But appearance of singlet oxygen at or near the surface brings also up the question about the possibility of its interaction with TiO_2 giving rise to reactive species. In current paper we investigate possible pathways of the TiO_2 molecule interaction with oxygen O_2 in singlet as well as triplet electronic states with *ab initio* calculations.

2. Details of *ab initio* calculations

All calculations have been carried out with the use of Gaussian 09 package [10]. For calculations of substances of TiO_2—O_2 system the approach MP2/6-311+G(2d,2p) has been applied. First of all optimization of individual ground state TiO_2 and O_2 (electron spin S = 0,1) molecules has been carried out. Than energy of TiO_2 (S = 0)—O_2(S = 0,1) systems has been calculated as a function of distance R_m between the center of mass of O_2 molecule and center of Ti atom of TiO_2 unit.

On a triplet potential energy surface (PES) of TiO_2—O_2 system a bound state corresponding to van der Waals complex was found. The most stable conformation of this complex has been found with optimization of geometry providing minimum of total energy $E_{BSSE}[TiO_2$—$O_2]$ which is the sum of total electronic energy with

basis set superposition error BSSE calculated with counterpoise method [11]. Energy of TiO_2–O_2 binding was calculated via equation $E_{bind,BSSE} = \Delta E_{BSSE} + æ \cdot \Delta ZPE_{BSSE}$. Here $\Delta E_{BSSE} = E_{BSSE}[TiO_2$–$O_2] - E[O_2] - E[TiO_2]$ is difference in energy of complex and individual molecules and $\Delta ZPE_{BSSE} = ZPE_{BSSE}[TiO_2$–$O_2] - ZPE[O_2] - ZPE[TiO_2]$ is difference in zero-point energy (ZPE) of complex and unbound molecules. Factor $æ = \{ZPE[O_2] + ZPE[TiO_2]\}_{exp}/\{ZPE[O_2] + ZPE[TiO_2]\}_{calc} = 1.070$ takes into account difference in calculated vibrational wavenumbers as compared with experimental data for TiO_2 and O_2 molecules.

On a singlet PES the strongly bound state has been revealed. To find the lowest energy point of conical intersection (CI) of singlet and triplet states of TiO_2–O_2 the stepwise procedure of CI geometry optimization has been applied. Below this procedure will be described.

All the calculations have been carried out on the hybrid cluster NKS-30T + GPU [12].

3. Results and discussion

In Fig. 1 the energy diagram of the revealed states of system TiO_2–O_2 is presented. The calculated energy values for the found states are given in Table 1. The structure of these states is presented in Fig. 2. On the triplet surface we reveal only weakly bound state corresponding to van der Waals (vdW) complex $^3(TiO_2$–$O_2)$. Geometry parameters of this complex are given in Table 2. The structure of TiO_2 and O_2 units in vdW complex is very close to that for individual molecules. On the singlet PES we reveal the bound state of TiO_2–O_2 system which indicates formation of chemical compound TiO_4. To the best of our knowledge there was no information about this substance in literature. The structure of TiO_4 shown in Fig. 2 has no elements of symmetry (C_1 group) and contains peroxide O–Ti–O ring. Peroxide ring as a structural element was earlier observed in complex salts containing titanium with the O–O distance equal to 1.45 Å, the Ti–O distances equal to 1.872 and 1.905 Å, and the O–Ti–O angle equal to 45.2° [13]. This fragment in TiO_4 found in our calculations is characterized by the O–O distance equal to 1.416 Å, somewhat longer Ti–O distances being equal to 2.167 and 2.219 Å, and the O–Ti–O angle being equal to 37.7°. Existence of this ring allows us to define TiO_4 as the titanium peroxide. This substance is lower in energy than the ground state of two individual molecules $TiO_2 + {}^3O_2$ by
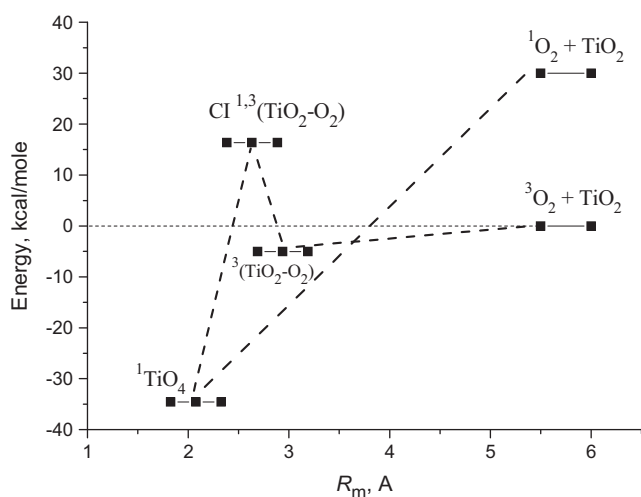
Table 1
Calculated energy parameters for the investigated states of TiO_2–O_2 system.

	vdW complex $^3(TiO_2$–$O_2)$	Titanium peroxide $^1TiO_4$	Conical intersection CI $^{1,3}(TiO_2$–$O_2)$
Energy, kcal/mol[a]	−1.57[b]	−34.6	16.3

[a] Zero of energy corresponds to the energy of a pair of isolated ground state molecules $TiO_2 + 3O_2$.
[b] Value is calculated with BSSE- and ZPE-corrections (see text).

34.6 kcal/mol. This makes peroxide molecule TiO_4 to be stable with respect to dissociation into individual molecules at room temperature.

Here we should also make comments on the energy value for singlet state of system corresponding to a pair of individual molecules $TiO_2 + O_2$. This calculated value is equal to 30.0 kcal/mol and is intermediate between the values of energy 22.5 and 37.5 kcal/mol taken from database [14] for two lowest singlet states of oxygen $a^1\Delta_g$ and $b^1\Sigma_g^+$, respectively. The MP2 approach is a single determinant method. For ground triplet state of O_2 this method is applicable. A single determinant approach for singlet state of individual O_2 molecule provides a wave function which is a mixture of the singlet delta and sigma states [15] and so gives rise to upper intermediate energy value. When singlet O_2 interacts with TiO_2 a loss of symmetry (TiO_4 in Fig. 2 has C_1 group of symmetry) takes place, degeneracy of molecular orbitals disappears and single determinant approach becomes adequate as well.

Principally singlet molecule TiO_4 can be formed from triplet state of TiO_2–O_2 via transition from triplet to singlet PES in the region of their conical intersection (CI). Lower point of this intersection can be used for estimation of an activation barrier height for this transition. Search of this lower point has been provided with approach involving first finding of geometry where singlet and triplet PESs intersect or become very close (within 0.3 kcal/mol) to each other. Then optimization of geometry with conservation of PESs' closeness allows us to find lowest point of CI. As a first point we take configuration of vdW complex in triplet state and calculate energy of singlet state (E_S) which is higher than energy of triplet state (E_T) in this configuration. Then optimization of singlet state results in decreasing of E_S. In this new optimized geometry of S state energy E_T is calculated which is higher than E_T in the starting configuration. So this optimization step makes energy gap between S and T states smaller. Optimization is continued until this gap value becomes less than 0.3 kcal/mol. Further optimization step starts from currently higher state (S or T) with tracing of geometry change for lower lying state. This procedure goes also until the gap will become less than 0.3 kcal/mol and so on. Central point of this small gap at the corresponding value of R_m for each optimization step is shown in Fig. 3. The bars show this energy gap. Each optimization step involved relaxation of all degrees of freedom simultaneously. Finally the optimization allows us to go until a minimum of the conical intersection which is shown in Fig. 3. Further change of geometry in any parameter didn't allow us to go further down. Found lowest point is located at the energy value of 16.3 kcal/mol. This value can be used as an estimate of energy barrier height for reaction of the ground (triplet) state of oxygen with TiO_2 giving rise to TiO_4 molecule.

The role of TiO_4 molecules in photocatalysis should be investigated. Recently Tan et al. [17] carried out synthesis of the oxygen-rich TiO_2 (TiO_2–O_2) with treatment of precursor TiO_2 by hydrogen peroxide H_2O_2. This oxygen-rich catalyst demonstrates unique visible–light photoactivity in reduction of CO_2 to CH_4 [17]. These authors supposed that procedure used results in the formation of an anatase-rutile phase-mixture enriched with interstitial oxygen. So these authors didn't consider possibility of formation of peroxides. We can mention here that earlier observed

Fig. 1. Energy diagram for the states of TiO_2–O_2 system found with *ab initio* calculations. Coordinate R_m corresponds to the distance between the center of mass of O_2 molecule and the Ti atom of TiO_2 unit. Dashed lines are used to visualize the pathways to titanium peroxide from singlet and triplet states of a pair TiO_2–O_2.