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**Author(s)**
Tachikawa, Hiroto; Kawabata, Hiroshi

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Direct Ab-initio MD Study on the Hydrogen Abstraction Reaction of Triplet State Acetone from Methanol Molecule

Hiroto TACHIKAWA* and Hiroshi KAWABATA

Division of Materials Chemistry, Graduate School of Engineering
Hokkaido University, Sapporo 060-8628, JAPAN

Abstract: Solvent re-orientation process of triplet acetone-methanol complex and intermolecular hydrogen atom abstraction reaction on the triplet state energy surface, 
(CH₃)₂C=O (T₁) + CH₃OH → (CH₃)₂C-OH + CH₂OH in gas phase, have been investigated by means of density functional theory (DFT) and direct ab-initio molecular dynamics (MD) methods. The static DFT calculation of hydrogen abstraction reaction at the T₁ state showed that the transition state is 16.4 and 30.9 kcal/mol lower than the energy levels of S₁ and S₂ states, respectively, and 9.2 kcal/mol higher than the bottom of T₁ state. The product state, (CH₃)₂C-OH--CH₂OH, is 8.4 kcal/mol lower in energy than the level of T₁ state. The direct ab-initio MD calculation showed that the product is rapidly formed within 150 fs and the separated products (CH₃)₂C-OH + CH₂OH were formed. The mechanism of reaction dynamics of the triplet acetone-methanol complex was discussed on the basis of theoretical results.

Keywords: triplet acetone, hydrogen abstraction, ab-initio MD, trajectory
1. Introduction

The reactions of triplet state molecule (via triplet state surface) have been important in biochemistry and photochemistry because the molecules at the triplet state have a highly activity as an intermediate. In particular, the carbonyl compounds have usually a long-lifetime, so that several reactions occur via triplet state [1].

For example, Norrish type II reaction is one of the typical reactions of carbonyl compounds at the triplet state (T₁ state) [2,3]. The C=O carbonyl group abstracts a hydrogen atom of methyl group at the T₁ state (1,5-shift). This reaction occurs efficiently as an intramolecular reaction within the carbonyl compound.

Du et al. [4] measured a nanosecond time-resolved resonance Raman (ns-TR3) spectra of the triplet state benzophenone reaction with the 2-propanol hydrogen-donor solvent. The TR3 spectra show that the benzophenone triplet state (nπ*) hydrogen-abstraction reaction with 2-propanol is very fast (about 10 to 20 ns) and forms a diphenylketyl radical and an associated 2-propanol radical partner.

From a theoretical point of view, Chen and Fang [5] calculated that potential energy diagram for the Norrish II reaction of butanol using ab-initio calculation. The activation energy of the 1,5-hydrogen shift in butanal was calculated to be 27.7 kcal/mol from the bottom of T₁ state.

The structural and electronic properties of the triplet state of acetone in aqueous solution model were studied using an effective QM/MM molecular dynamics (MD) approach [6]. In particular, the striking consequences of the electronic transitions of \( n \rightarrow \pi^* \) electron promotion on the acetone structure and on its microsolvation have been analyzed in some detail and compared to the behavior of the acetone ground-state. Moreover, the phosphorescence emission spectrum was calculated on sampled
molecular configuration. They showed a Stokes shift in good agreement with available experimental data.

Muldoon et al. [7] showed that the reaction efficiency via triplet state is significantly higher than the S\textsubscript{1} state because the reaction via S\textsubscript{1} state is branched to both reactive (1,5-hydrogen shift) and non-reactive (return to the S\textsubscript{0} state) products.

Benzophenone, which is a typical C=O carbonyl compound, reacts with alcohol and causes a hydrogen abstraction reaction. It is known that this reaction occurs efficiently on T\textsubscript{1} state. Acetone, one of the simplest C=O carbonyl compounds, also causes an intermolecular hydrogen abstraction reaction. Nau et al. [8] measured rate constants for quenching of excited state acetone by hydrogen donor tributyltin hydride and 2-pripanol using time-resolved spectroscopy. They showed that both singlet- and triplet excited states can abstract a hydrogen atom of the donor molecules.

In the present study, an intermolecular hydrogen abstraction reaction of triplet acetone from a methanol molecule in gas phase is investigated by means of density functional theory (DFT) and direct ab-initio molecular dynamics (MD) methods [9-11] in order to elucidate the reaction mechanism of triplet C=O carbonyl with a methyl group. Also, the solvent re-orientation process of acetone-methanol 1:1 complex before the hydrogen abstraction was investigated. As a model, a hydrogen abstraction reaction on the T\textsubscript{1} state, (CH\textsubscript{3})\textsubscript{2}C=O (T\textsubscript{1}) + CH\textsubscript{3}OH \rightarrow (CH\textsubscript{3})\textsubscript{2}C-OH + CH\textsubscript{2}OH, was examined in this work.

2. Method of calculation

The geometries of the stationary points of the reaction of triplet acetone with a methanol molecule were fully optimized at the B3LYP/6-311++G(d,p) level of theory.
The harmonic vibrational frequency of the complex at the optimized point was calculated to elucidate the stability of the complex.

Direct ab-initio molecular dynamics (MD) calculation was carried out at the B3LYP/6-311++G(d,p) level of theory throughout. The transition state of hydrogen abstraction reaction was fully optimized by the energy gradient method. The trajectories were run from the transition state geometry. The electronic state of the system was monitored during the simulation. We confirmed carefully that the electronic state is kept during the reaction. The solvent re-orientation process of acetone-methanol system was also investigated with the same manner. A trajectory on the T₁ state was run from the optimized structure of acetone-CH₃OH complex at the S₀ state.

The velocities of atoms at the starting point were assumed to zero (i.e. momentum vector of each atom is zero). The equations of motion for \( n \) atoms in a molecule are given by

\[
\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j},
\]

\[
\frac{dP_j}{dt} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j},
\]

where \( j=1-3N \), \( H \) is the classical Hamiltonian, \( Q_j \) is Cartesian coordinate of the \( j \)-th mode and \( P_j \) is conjugated momentum. These equations were numerically solved by the Verlet algorism. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen as 0.10 fs, and a total of 10,000 or 20,000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than \( 10^{-3} \) % throughout at all steps in the trajectory. The momentum of the center of mass and the angular momentum were assumed to zero. More details of the
direct MD calculations are described elsewhere [9-11].

Static ab-initio and DFT calculations were carried out using Gaussian 03 program package [15]. To confirm the stability of the molecules at all stationary points, the harmonic vibrational frequencies were calculated at the B3LYP/6-311++G(d,p) level of theory. All vibrational frequencies obtained were positive except for those of TS, indicating that the stationary points were located at the local minima on the potential energy surface. The excitation energies of acetone-CH₃OH complex were calculated by means of time-dependent (TD) DFT method [16,17]. Ten electronic states were solved. Intrinsic reaction coordinate (IRC) [18-22] of hydrogen abstraction reaction was calculated from the transition state (TS) to both reactant and product directions.

3. Results
A. Energy diagram

The energy diagram of the intermolecular hydrogen atom abstraction reaction of triplet state acetone from a methanol molecule is illustrated in Figure 1. The optimized structures of molecules at the stationary points are illustrated in Figure 2. The value of energy level is calculated at the B3LYP/6-311++G(d,p) level. At an initial state of the reaction, acetone (Ac) binds to the methanol molecule by a hydrogen bond (S₀ state). By photo-irradiation to the complex, the electronic state is vertically changed to the first and second excited states (S₁ and S₂). In case of acetone, intersystem crossing (ISC) from singlet to triplet states occurs efficiently (quantum yield of ISC is 0.53±0.04) [23-25] and the surface is changed to the T₁ state.

The bottom of triplet state (T₁) is 25.6 kcal/mol lower in energy than the vertically excited S₁ state. The point of S₁ state corresponds to the initial state of the hydrogen
abstraction reaction on the T₁ state. The energy level of transition state (TS) of the hydrogen atom abstraction reaction is 9.2 kcal/mol higher than the bottom of T₁ state. The product state (PD) is 34.0 kcal/mol lower than the vertically excited S₁ state. Therefore, the hydrogen abstraction reaction is exothermic in the energetics. The energy level calculation suggests that the solvent re-orientation occurs first, and then the hydrogen abstraction proceeds.

1) S₀ state

Before the photo-irradiation, the complex composed of acetone and methanol molecules is located at the ground state (S₀ state). The optimized geometries at the stationary points along the hydrogen abstraction reaction are given in Figure 2. The hydrogen atom of CH₃OH orients to the carbonyl oxygen of acetone. The binding energy of CH₃OH to acetone is calculated to be 6.3 kcal/mol. The intermolecular distance between hydrogen of CH₃OH and oxygen of C=O carbonyl (i.e. distance of hydrogen bond) is calculated to be 1.923 Å.

2) Excited singlet states (S₁ and S₂)

If the complex is photo-irradiated, the electronic state of acetone-CH₃OH (S₀) is vertically excited to the first and second excited states (S₁ and S₂). The energy differences from S₀ to S₁ and S₂ states are calculated to be 4.52 and 5.15 eV, respectively, at the TD-DFT (B3LYP/6-311++G(d,p) level. These states have singlet nπ* and ππ* excited states denoted by ¹(nπ*) and ¹(ππ*), respectively.
3) T₁ state

In case of acetone, it is known that the intersystem crossing (ISC) occurs rapidly and the electronic state of acetone-CH₃OH (S₁) is efficiently converted to the T₁ state denoted by ³(π∗).

The intermolecular distance r(CO-HO) of acetone-CH₃OH (T₁) is calculated to be 2.027 Å, which is slightly longer than that of the singlet ground state (1.923 Å). The energy level of ³(π∗) triplet state is 25.6 kcal/mol lower than that of the S₁ state.

4) Transition state (TS) and Product state (PD)

Transition state structure of the complex was fully optimized by means of energy gradient method. In the optimized structure, the distances of transferred hydrogen atom from carbonyl oxygen and methyl carbon are R₁=1.336Å and R₂=1.236 Å, respectively. The oxygen-carbon distance is 2.572 Å, which is significantly shorter than that of S₀ state. The activation energy of TS relative to T₁ state is calculated to be 9.2 kcal/mol. The excess energies of TS are 16.4 kcal/mol (vertical excitation to S₁ state) and 30.9 kcal/mol (S₂ state). Imaginary frequency of TS is calculated to be 1087i cm⁻¹. From analysis of vibrational mode, it is assigned that the imaginary frequency of TS is asymmetric stretching mode composed of (HOCH₂---H---O=O).

The energy level of product state (³PD) is -8.4 kcal/mol relative to the T₁ state. The distance between CH₂OH radical and hydroxyl alcohol radical C(CH₃)₂OH is 1.870 Å.

B. Zero point energy dynamics on S₀ state

In an actual complex, the structure fluctuates because of zero-point vibration (ZPV). The results of direct ab-initio MD calculations of the complex with zero-point energy
(ZPE) on the ground state $S_0$ state are illustrated in Figure 3. The ZPE dynamics calculation showed that the potential energy oscillates periodically as a function of time, and the structural conformation of the complex changes markedly over time during the simulation. However, the hydrogen bond is retained during the simulation.

C. Solvent re-orientation dynamics on the T$_1$ surface

First, the solvent re-orientation of CH$_3$OH around the triplet acetone (T$_1$) may occur before the hydrogen abstraction of triplet acetone. In this section, the solvent re-orientation process in gas phase was investigated by means of direct ab-initio MD method. Potential energy of the system is plotted as a function of time in Figure 4. The structure at time zero was assumed to that of $S_0$ state. After the excitation to the T$_1$ state, the energy decreases gradually with a vibrational structure. The intermolecular distance $r$(H--O) is elongated from 1.922 Å (time=0.0 fs) to 2.163 Å (121fs). This bond elongated is caused by a spontaneous weakening of the hydrogen bond after the $S_0$-T$_1$ transition. Also, it was found that the planar structure around a C=O carbonyl of acetone is changed to a bent form. The position of methanol was changed from $n$-orbital of the carbonyl to $\pi$-orbital orientations.

The energy of the system was stabilized to -10.5 kcal/mol after the solvent re-orientation. The time profile of energy vibrates periodically and the solvation structure is gradually changed as a function of time. Thus, the solvent re-orientation takes place spontaneously after the T$_1$ state.

D. Intrinsic reaction coordinates (IRC)

In the IRC calculation, the first, the transition state of hydrogen abstraction reaction
is obtained at the B3LYP/6-311++G(d,p) level. The optimized geometry was illustrated in Figure 2(\(^3\)TS). This structure has an imaginary frequency (1087 cm\(^{-1}\)). The IRC was calculated using normal mode corresponding to the imaginary frequency for the forward and backward directions.

The IRC is plotted in Figure 5 as a function of reaction coordinate (\(s\)). The structures of reactant intermediate (\(^3\)RC'), transition state (\(^3\)TS) and product intermediate (\(^3\)PD') calculated along the IRC are illustrated as insert figures. At \(^3\)RC' (\(s= -1.5\)), the distances R\(_1\) and R\(_2\) are 1.690 and 0.969 Å, respectively. The structure of \(^3\)PD' (\(s= +1.0\)), the distances R\(_1\) and R\(_2\) are 0.984 and 1.609 Å, respectively.

In order to confirm the true transition state connecting between RC and PD states, the geometry optimizations were carried out from the intermediates (\(^3\)RC' and \(^3\)PD') in the IRC. The geometry optimizations from \(^3\)RC' and \(^3\)PD' gave \(^3\)RC and \(^3\)PD, respectively. The results indicate that the transition state (TS) is actually connected between reactant (\(^3\)RC) and product (\(^3\)PD) states in the hydrogen abstraction reaction.

E. Reaction dynamics from transition state (TS)

To elucidate the reaction dynamics of intermolecular hydrogen abstraction of triplet acetone molecule from CH\(_3\)OH, direct ab-initio MD calculation was carried out at the B3LYP/6-311++G(d,p) level. The calculations were started from around TS structure to forward (PD) and backward (RC) directions.

Snapshots and potential energy as a function of time are illustrated in Figure 7. At time zero, the structure is close to that of TS. After the starting the reaction, O-H distance of C(CH\(_3\))\(_2\)OH radical is rapidly shortened (R\(_1\)), indicating that the hydrogen of the O-H group of methanol is abstracted by the carbonyl oxygen C=O. For example, the
O-H distances at time =0 and 24 fs are 1.330 and 0.948 Å, respectively. In addition, the product of CH₂OH radical is gradually leaved from a protonated acetone. The distances of O—C (acetone oxygen and methyl carbon) are 2.648 Å (time=0.0 fs), 2.727 Å (24 fs), 3.126 Å (58 fs) and 4.197 Å (137 fs).

The potential energy (PE) and bond distances of the system are plotted in Figure 7 as a function of time. The PE goes down rapidly within 50 fs, and is minimized at 58 fs. (point e). The lifetime of 3⁴TS is roughly estimated by 90 fs in this trajectory. A complex with a large amplitude mode between OH and alcohol radical is formed as a product. Finally, separated products were formed.

F. Effects of initial structures of the complex at the TS on the dynamics

In the previous section, only one trajectory was discussed as a representative case. In this section, several trajectories initiated at different geometries around TS are compared. A total of ten trajectories were run. The time profiles of potential energies of four trajectories are plotted in Figure 8. All trajectories exhibited the similar energy changes in the reactions. The general results were thus not dependent on the initial structure of TS.

4. Summary

In the present study, first, the solvent re-orientation of methanol molecule around acetone by the photo-irradiation to the triplet state was investigated by means of direct ab-initio MD method. Next, a hydrogen abstraction reaction of acetone from methanol molecule was investigated. The transition state is 9.2 kcal/mol lower than that of S₁ state, and the product state, (CH₃)₂C-OH---OH, is 8.4 kcal/mol lower in energy than that of T₁.
state. The direct DFT-MD calculation showed that the product is rapidly formed within 50 fs and the separated products $(\text{CH}_3)_2\text{C-OH} + \text{CH}_2\text{OH}$ are formed.

We considered only triplet state potential energy surface throughout. Recently, the reaction via singlet excited $S_1$ state has been also observed experimentally. Nau et al. [8] showed that the $S_1$ acetone has a higher reactivity but lower efficiency than the reaction via $T_1$ state. This is attributed to an efficient radiationless deactivation on the $S_1$ state.

To elucidate the overall reaction, in addition to the reaction on the $T_1$ state, reaction dynamics on the $S_1$ and $S_2$ states are also needed. However, it is known that the reaction efficiency (quantum yield) is significantly reduced by addition of the triplet quencher [26]. Hence, the $T_1$ state is correlated strongly to the reaction mechanism. The present work provided one of the theoretical aspects about the reaction dynamics of C=O carbonyl.

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References


Figure captions

Figure 1. Energy diagram of hydrogen abstraction reaction of triplet state acetone from CH$_3$OH. The values were calculated at the B3LYP/6-311++G(d,p) level. $^3$RC, $^3$TS and $^3$PD mean reactant state, transition state, and product state, respectively.

Figure 2. Optimized structures and geometrical parameters of $^3$RC, $^3$TS and $^3$PD. Distances are in Å.

Figure 3. Potential energy (A) and atomic distances ($R_1$ and $R_2$ in Å) of acetone-methanol complex with zero point energy plotted as a function of time, obtained by means of direct ab-initio MD calculation at the B3LYP/6-311++G(d,p) level.

Figure 4. Time profile of potential energy of acetone-methanol system following excitation to the triplet state surface obtained direct ab-initio MD calculation at the B3LYP/6-311++G(d,p) level. Inserted structures show snapshots of acetone (T$_1$)-methanol complex after the triplet state excitation.

Figure 5. Intrinsic reaction coordinate (IRC) for the hydrogen abstraction reaction of triplet state acetone from CH$_3$OH.
Figure 6. Snapshots of hydrogen abstraction reaction of triplet state acetone from CH$_3$OH obtained direct ab-initio MD calculation at the B3LYP/6-311++G(d,p) level.

Figure 7. Time profiles of potential energy and atomic distances of acetone-methanol system. The trajectory was started from near TS of the hydrogen abstraction reaction.

Figure 8. Effects of initial conditions for the trajectories on the hydrogen abstraction dynamics of the acetone (T$_1$)-methanol system. The plot shows the time-dependence of potential energy. Four trajectories from different selected initial structures are shown.
Figure 2

 acetone (Ac)

 3TS

 3RC

 3PD

17
Figure 3.
Figure 4.
Figure 5.
Figure 6.

- **time = 0.0 fs (a)**
- **24 fs (b)**
- **58 fs (c)**
- **137 fs (d)**
Figure 7.
Figure 8.