Theoretical Study on Electron Transfer Matrix Element in Oxidation of α-Amino Carbon-Centered Radical by O_2

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As a successive work of our previous paper,[1] the electron transfer matrix element (V_{rp}) in the oxidation of the simplified model molecule of α-amino carbon-centered radical by O_2 has been investigated with *ab initio* calculation at the level of UHF/6-31++G. Based on the optimized geometries of the reactant and the ion-pair complex obtained previously, the reaction heat and the inner reorganization energy have been obtained by constructing the potential energy curves of reactant and product states considering the solvent effect with the conductor-like screening model (COSMO). The solvent reorganization energy has been estimated using Lippert-Mataga relationship. The calculated results show that the value of V_{rp} is several times larger than that of *RT*, which means that the model reaction is an adiabatic one. Theoretical investigation indicates that the solvent effect on the direct electron transfer (ET) process of oxidation of α-amino carbon-centered radical by oxygen is remarkable.**

Keywords electron transfer, solvent reorganization energy, ET matrix element

Introduction

As known to all, carbon-centered radicals can easily be formed by oxidative damage in biosystems.[2-6] The α-C—H bond dissociation energy (DE) of a series of biological molecules was evaluated through a theoretical study by Armstrong *et al*..[2,7] It was estimated that the DE of α-C—H is about 350 kJ/mol for a glycyl peptide and 330 kJ/mol for neutral glycine. The very low α-C—H bond DE indicates that the formation of carbon-centered radicals can proceed without too large energy barrier. In solution, these radicals can react with oxygen to form peroxyl radicals and subsequently form α-amino acids and superoxide radical anion.[3-6,8]

In general, the oxidation of a neutral molecule or radical by oxidant is essentially a charge separation process. An excitation by light may, but not always, facilitate this kind of processes. Although simple thermal electron transfer (ET) in ionic systems has been extensively investigated, thermal charge separations in neutral systems draw much less attention. As for the formation mechanisms of carbocation and superoxide radical anion, some experimental observations led to a predication that such a reaction takes place either through the formation of a very short-lived peroxyl radical or through direct ET from carbon-centered radicals to oxygen. However, the reaction taking which pathway is not distinguished by experimental investigation.[9,10] Theoretical investigations on charge separation processes in thermal conditions are very few so far, since the charge separation state corresponding to the structure of oppositely charged ionic pair is difficult to obtain from usual SCF treatment for the ground state. In order to ascertain whether such a process is feasible, theoretical calculations were carried out by using Hondo99 package[11] in our previous work.[1] Based on the results obtained in that work,[1] particular attention has been paid to the diabatic potential energy surface, the solvent effect and the ET matrix element in the charge separation process in this work. A main aim of this work is to clarify whether the ET process in the oxidation of α-amino carbon radical is an adiabatic process or a non-adiabatic one

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through the ET matrix element evaluation.

Methodology

In the calculation of rate constant of a thermal ET reaction, Marcus' theory,[12] including both the adiabatic and semi-classical models, has been widely used in this field. For an adiabatic ET,

$$k_{ET} = A\exp[-\Delta G^{\neq}/k_B T] \quad (1)$$

where A, k_B and $\Delta G^{\neq}$ are the frequency factor, the Boltzmann constant and the Gibbs activation free energy, respectively. $\Delta G^{\neq}$ can be expressed as

$$\Delta G^{\neq} = (\Delta G^0 + \lambda)^2/4\lambda \quad (2)$$

where λ stands for the reorganization energy and ΔG^0 the standard Gibbs' free energy of ET. On the other hand, in the case that non-adiabatic transition cannot be ignored, the so-called non-adiabatic model works,[12,13] *i.e.*,

$$k_{ET} = \frac{4\pi^2}{h}V_{rp}^2\left(\frac{1}{4\pi\lambda RT}\right)^{1/2} \cdot \exp[-(\lambda + \Delta G^0)^2/4\lambda RT] \quad (3)$$

where V_{rp} stands for the ET matrix element.

ET reactions in solution are of fundamental significance in chemical and biochemical processes. The reorganization energy λ can be divided into two parts, the inner reorganization energy (IRE) λ_i and the solvent reorganization energy λ_o,[14] *i.e.*,

$$\lambda = \lambda_i + \lambda_o \quad (4)$$

For a self-exchange ET reaction: $B^- + B \rightarrow B + B^-$, it is convenient to employ direct quantum chemical calculation in the IRE evaluation,[15]

$$\lambda_i(B/B^-) = E_0(B^-) - E_1(B^-) + E_1(B) - E_0(B) \quad (5)$$

where the subscripts "0" and "1" refer to the equilibrium geometries of the neutral species and the ionic ones, respectively. For a charge separation process with D representing the electron donor and A the electron acceptor, $D + A \rightarrow D^+ + A^-$, the IRE can be calculated by taking the average value

$$\lambda_i(D/A) = [\lambda_i(D/D^+) + \lambda_i(A/A^-)]/2 \quad (6)$$

Instead of the Marcus' two-sphere model used in our previous work, the Lippert-Mataga relationship[16-18] has been chosen for the estimation of λ_o in this work. The suitability of the Marcus' two-sphere model to the present compact supermolecule is suspectable due to the possible overlap between these two spheres. The Lippert-Mataga relationship reads

$$\lambda_0 = \frac{1}{a_0^3}\left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}\right](\mu_1 - \mu_0)^2 \quad (7)$$

where a_0 is the radius of the cavity, ε_r the static dielectric constant, n the reflective index of the solvent, and μ_0 and μ_1 are the dipole moments of the complex before and after ET, respectively. The correction of λ_o shown in Eq. (7) has been widely employed in both ET and photoexcitation absorption.

A crucial parameter for the calculation of λ_o is the radius of the spherical cavity, a_0. Although much work has been done on this topic in the past decades, the achieved performance has still stayed somewhat unsatisfactory. The following procedure is employed to perform the estimation of the radius of the spherical cavity.

(1) Determining the smallest box (with box parameters l_1, l_2 and l_3) that encloses the solute. This procedure can be easily carried out using Hyperchem package.

(2) Calculating the equivalent cavity volume by

$$V_M = (l_1 + 0.23\ \text{nm})(l_2 + 0.23\ \text{nm})(l_3 + 0.23\ \text{nm}) \quad (8)$$

where 0.23 nm is twice the Van de Waals radius of H atom.

(3) Using Eq. (9) to determine the equivalent cavity radius a_0 of the solute molecule.

$$a_0 = (3V_M/4\pi)^{1/3} \quad (9)$$

This method for estimation of a_0 has been proved reasonable.[19]

It is well known that the ET matrix element (V_{rp}), which couples the initial and final states of the ET process, is of importance in determining whether the reaction

mechanism belongs to a non-adiabatic one or an adiabatic one.[20,21] However, a practical yet reliable approach, which allows the incorporation of structure-dependent electron coupling in simulations of ET reactions in solution, is still a great challenge for quantum chemistry. Up to now, there have been several approaches to evaluating the ET matrix element.[21-23] In this work, the authors take the two-state model and apply the variation principle to this V_{rp} calculation. By using Q to denote the nuclear configuration of the system, a linear coordinate R (R = 0—1) can be defined as,[24]

$$R = (Q - Q_r) / (Q_p - Q_r) \tag{10}$$

where Q_r(or Q_p) denotes the nuclear configuration of the reactant (or product). $R = 0$ corresponds to the reactant geometry and $R = 1$ corresponds to the product one. After the simplification of the multi-dimensional reaction coordinates to the one-dimension problem, those two electron-localized states and their corresponding potential energy surfaces (PES) can be constructed.

In terms of non-adiabatic ET, the Franck-Condon transition may happen between the two diabatic states at the crossing of PES, and the efficiency of electron transfer are determined by the transition probability. From Landau-Zener model,[25,26] the transition probability depends on the splitting energy Δ, which is just twice of the so-called ET matrix element at the crossing of the diabatic PESs. Within two-state framework, through solving the secular equation,

$$\begin{bmatrix} H_{rr} - E & H_{rp} - ES_{rp} \\ H_{pr} - ES_{pr} & H_{pp} - E \end{bmatrix} = 0 \tag{11}$$

we can obtain the expression of ET matrix element as

$$V_{rp} = \Delta/2 = (1 - S_{rp}^2)^{-1} | H_{rp} - S_{rp}(H_{rr} + H_{pp})/2 | \tag{12}$$

with $H_{rp} = \langle \varphi_r | \boldsymbol{H} | \varphi_p \rangle$, $S_{rp} = S_{pr} = \langle \varphi_r | \varphi_p \rangle$. Here $\boldsymbol{H}$ in Eq. (12) is the total electronic Hamiltonian of the system, φ_r and φ_p refer to the electron-localized diabatic wave functions of the initial and the final states, respectively.

Most of the ET reactions take place in solvent environment. In order to give rational illustration of the solvent effect, the exploration of the solvation models attracted much attention in past decades. Up till now, several continuum solvation models have been developed and linked into the popular computational chemistry packages. In the present work, the equilibrium solvation effect in ET is considered with the conductor-like screening model (COSMO).[13,27,28] COSMO treats the solute system of an arbitrary cavity and achieves the solvation energy calculation through self-consistent reaction field method.

Results and discussion

Donor-acceptor complex

In the previous work,[1] the donor-acceptor complex before and after electron transfer has been investigated by using UHFSCF/6-31 + + G * * method associated with COSMO. The geometries of them are shown in Fig. 1.

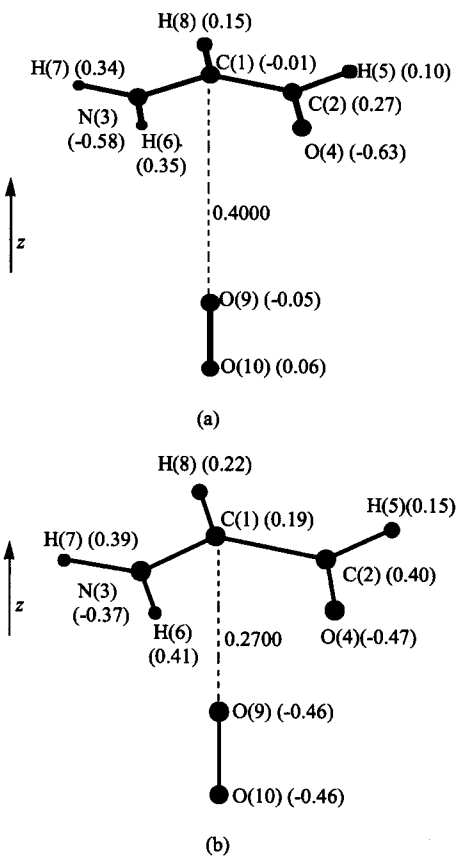

Fig. 1 Stereodigram of complexes [$H_2NCH^{\cdot}CHO\cdots O_2$] (a) and [$H_2NCH^{+}CHO\cdots O_2^{-}$] (b). The net charges condensed on atoms are given in the parentheses. The geometry optimization is carried out at the level of UHFSCF/6-31 + + G * *.

In present work, detailed discussions on the two complexes are performed. For the neutral reactant complex ([D···A]), a usual UHFSCF can easily lead to the normal convergence of the ground doublet state (^{2}A) which possesses the neutral charge distribution on both the donor and the acceptor. While for the charge-separated complex ([$D^+ \cdots A^-$]), with the state of ^{2}A, is somewhat difficulty to acquire. As described in our previous work, an external electric field of 0.03 a.u. (1 a.u. $=5.145 \times 10^{11}$ V/m) in the direction from the acceptor O_2 to the donor has been applied in our work to attain a set of electron-localized molecular orbitals (ELMOs). Using this set of ELMOs to induce the further field-free UHFSCF calculation associated with COSMO, the ion pair (IP) state complex has been obtained.

Why the doublet ^{2}A of the complexes has been employed in our calculations needs a few words for explanation. From the energy comparison, it can be known that, as widely accepted, the ground states of neutral oxygen and its anion are triplet and doublet, respectively. On the other hand, the ground state of $H_2NCH^{\cdot}CHO$ is obviously doublet. The energy calculation of H_2NCH^+CHO shows that the ground state of this cation is singlet. Comparing the geometry parameters of the two moieties in IP complex with those of isolate components, it can be found that the bond parameters only change slightly. In the complexes [$H_2NCH^{\cdot}CHO\cdots O_2$] and [$H_2NCH^+CHO\cdots O_2^-$], there are two most possible multiplicities, doublet and quadruplet. Detailed energy calculation reveals that the former possesses a lower state energy. Therefore, the doublet of the reactant complex and product complex is taken into account in the following calculation.

From the RHFSCF calculation of [$H_2NCH^{\cdot}CHO\cdots O_2$] at its equilibrium geometry ($d_{C(1)—O(9)} = 0.40$ nm) and that of [$H_2NCH^+CHO\cdots O_2^-$] at $d_{C(1)—O(9)} = 0.27$ nm, two sets of MOs of the reactant complex and the charge-separated complex have been attained, and the eigenvalues and the occupation states of some higher energy MOs have been schematically illustrated in Fig. 2.

The configuration of O_2 ($^3\Sigma_g^-$) is known as $KK2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^1 2\pi_g^1$. The isolate O_2 molecule is typically triplet. As far as the case in the reactant complex [$H_2NCH^{\cdot}CHO\cdots O_2$], the triplet appearance of O_2 remains due to the large distance separation between the electron donor and acceptor. MOs 14, 15, 16, 23 and 24 are dominantly contributed from O_2 moiety in complex. MOs 15 and 16 are found π-type and degenerated in energy. Similarly, MOs 23 and 24 are found π^*-type and

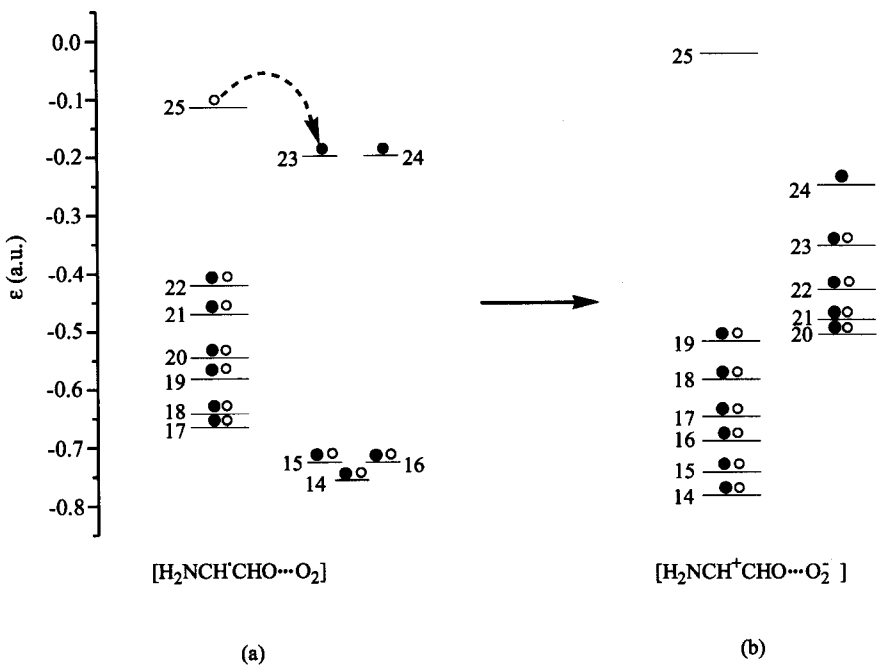

Fig. 2 Eigenvalues of MOs in reactant (a) and product (b) complexes. Left column shows those contributed mainly from $H_2NCH^{\cdot}CHO$ (or H_2NCH^+CHO) and the right column gives those from O_2 (O_2^-) in reactant complex (or product complex).

degenerated also. In the IP state, an electron in MO 25 which is contributed from $H_2NCH^{\cdot}CHO$ moiety, jumps to one of the π^*-type MOs of O_2 moiety, so as to produce an ionic structure of $[H_2NCH^+CHO\cdots O_2^-]$. In this case, the π-type MOs and π^*-type MOs are no longer degenerated. From the MOs of this IP complex, it has been found that the MO sequence is greatly different from that in the reactant state. Although it seems that in reactant state the electron transfer would cause the decrease in energy, for the energy of MO 25 is higher than that of MOs 23 and 24, the repulsion of the paired electrons and the rearrangement of MOs make the total energy of IP state higher than that of the reactant state.

PES *and* ET *matrix element*

By using the linear reaction coordinate definition given in Eq. (10), the two electron-localized states in ET reaction shown in Eq. (13) and their corresponding PESs have been constructed.

$$[H_2NCH^{\cdot}CHO\cdots O_2]=[H_2NCH^+CHO\cdots O_2^-] \quad (13)$$

In order to make a comparison, the PES construction both in the gas-phase and in solution (Fig. 3) has been performed by employing HONDO99 program at the level of UHF/6-31 + + G * *.

Comparison of PES in the gas-phase and in solution makes it clear that the reaction hardly occurs in the gas-phase because there does not exist a crossing point of the PESs in the range of $R = 0$—1 and the reaction heat will be very high if there exists an ET process. On the other hand, the solvent effect on the oxidation reaction is remarkable because it drives the crossing point of PESs to a linear coordinate of $R_c = 1.01$. [Fig. 3(b)]. Once the geometry structure corresponding the crossing point is determined, the calculation of the ET matrix element can be performed. As demonstrated above, the initial guess induced SCF has been used to perform the evaluation of ET matrix element at the crossing. At the level of UHFSCF/6-31 + + G * *, V_{rp} has been obtained 8.8 kJ/mol associated with COSMO. ET integrals of reaction (13) are listed in Table 1. There are two limits in handling with the kinetics of ET: adiabatic and non-adiabatic. It has been widely recognized in the case of $V_{rp} << RT$, the non-adiabatic treatment works, otherwise the adiabatic ET model is a proper one.[21] Since the value of 8.8 kJ/mol is larger than RT which is 2.5 kJ/mol at the temperature of 298 K, the ET reaction (13) should be treated as an adiabatic ET process, and this confirms the rationality using the adiabatic ET model in our previous work.[1]

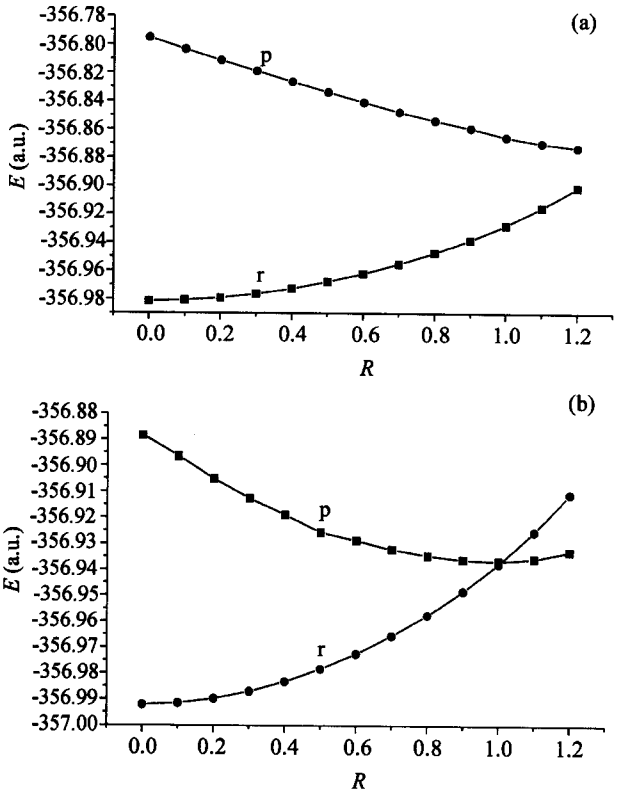

Fig. 3 PESs in the gas-phase (a) and in solution (b). p and r refer to the IP state and the reactant state, respectively. The crossing of PES in the solution case is at $R_c = 1.01$.

Table 1 ET matrix element (V_{rp}) of reaction $[H_2NCH^{\cdot}CHO\cdots O_2]=[H_2NCH^+CHO\cdots O_2^-]$

R_c	S_{rp}	H_{rp} (a.u.)	$\mu_z(r)^a$	$\mu_z(p)^a$	V_{rp} (kJ/mol)
1.01	−0.12852	73.38489	~0	−15.3	8.8

[a] $\mu_z(r)$ and $\mu_z(p)$ are respectively the dipole moment of reactant state and product state at R_c in the direction from C(1) to O(9) (in Debye).

Substituting the estimated cavity radius a_0, 0.3692 nm, of the sphere model at R_c, the λ_o for charge separation process can be estimated by using Lippert-Mataga relationship. The dipole moments of reactant state and product state in the direction from C(1) to O(9) are shown in Table 1. According to Eq. (7), λ_o is estimated

89.7 kJ/mol by taking $\varepsilon_r = 78.5$ and $n^2 = 1.78$ in water. Compared with the value of 112.3 kJ/mol using Marcus' two-sphere model in our previous work,[1] the present value of λ_o is about 20 kJ/mol smaller. In the previous paper, the radii of the donor and the acceptor were estimated 0.326 and 0.205 nm respectively, hence the sum of them is larger than the center-to-center distance of the configuration corresponding to the crossing point, 0.334 nm, by about 0.197 nm. This indicates that there is an overlap between donor sphere and the acceptor sphere. Marcus' two-sphere loses its adequacy in this case. This is just why the authors preferably select the Lippert-Mataga relationship in this work. A judgment on which value is more rational may not be given due to the complicity of this reaction, even though the Lippert-Mataga single-sphere model seems more reasonable.

Conclusion

Detailed energy calculation shows that the doublet complexes formed in the ET reaction possess a lower state energy than the quadruplet ones. From the molecular orbital analysis, it can be found that one electron transfers from the HOMO of α-carbon-centered radical moiety to a π-type MO of O_2 moiety. In the product complex, the energy of MO 25 is higher than that of MOs 23 and 24, so the repulsion of the paired electrons, and the rearrangement of MOs make the total energy of IP state higher than that of the reactant state. In order to study the rate constant of the model reaction, the PESs of the ET reaction have been constructed, and the geometry of ET transition complex has been obtained at the crossing of PESs. The calculation of V_{rp} has been performed based on the geometry of ET transition complex. The value of V_{rp}, 8.8 kJ/mol, shows that the model reaction is an adiabatic one, which verifies the adiabatic assumption in our previous work.[1]

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