

Theoretical Study on Reactivity of Electron Transfer in Model-System of Oxidation of α -Amino Carbon-centered Radical by O_2

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Electron transfer reaction between a simplified model molecule of α -amino carbon-centered radical and O_2 has been studied with *ab initio* calculations at the MP2/6-31 ++ G**/UHF/6-31 ++ G** level. The reactant complex and the ion pair complex have been optimized and employed to perform calculations of the reaction heat and the reorganization energy. Solvent effects have been considered by applying the conductor-like screening model. Theoretical results show that the highly endothermic charge separation process, in which one electron transfers from the α -amino carbon-centered radical to O_2 , so as to form an ion pair complex, is difficult to occur in gas-phase. By applying an external electronic field to prepare the charge-localized molecular orbitals, the charge-separated state has been obtained using the initial-guess-induced self-consistent field technique. The theoretical investigations indicate that the solvent effect in the process of the oxidation of α -amino carbon-centered radical by O_2 is remarkable. From the rate constant estimation, it can be predicted that the oxidation of the model donor molecule by O_2 can proceed, but not very fast. A peroxy radical compound has been found to be a competitive intermediate in the oxidation process.

Keywords α -amino carbon-centered radical, electron transfer, charge-separated complex, solvent effect, rate constant

Introduction

It is widely understood that oxidative damage to proteins exists in physiological processes and pathological disorders.¹ Oxidation of proteins by oxygen leads to the formation of alkyl peroxides and/or hydrogen peroxide, and to peptide cleavage.¹⁻³ A recent theoretical study by

Armstrong *et al.* evaluated the α -C—H bond dissociation energy of a series of glycylic peptides.^{4,5} The very low α -C—H bond dissociation energies for neutral amino acids have been suggested to be due to the effect of the $-NH_2$ and $-CO_2H$ substitutions. Similarly, for a glycylic peptide, the low α -C—H bond dissociation energy has been suggested to be the result of the effect of the $-NH-$ and $-CO-$ substitutions. Therefore, α -amino carbon-centered radicals can be easily formed in physiological processes and pathological disorders. Once formed, in the presence of oxygen, these radicals react with oxygen to form peroxy radicals and subsequently form α -amino acids and superoxide radical anion.⁶⁻¹⁰ But the mechanism of the reaction from the neutral α -amino carbon-centered radicals and oxygen to the carbocation and the superoxide radical anion has not been exactly determined. Some experimental researchers have drawn the conclusion that such a reaction takes place through the formation of a very short-lived peroxy radical first or through direct electron transfer (ET) from the α -amino carbon-centered radical to oxygen (Scheme 1), however, experimental methods are unable to distinguish between the two processes.^{11,12} In this work, the authors focused their investigations on the mechanism shown in path 2 in Scheme 1 by constructing a simple model molecule of α -amino carbon-centered radical.

α -Amino carbon-centered radicals are known to be strong reductants.^{13,14} However, from Scheme 1 one can see that ET reaction between the α -amino carbon-centered radical and O_2 factually involves a charge separation pro-

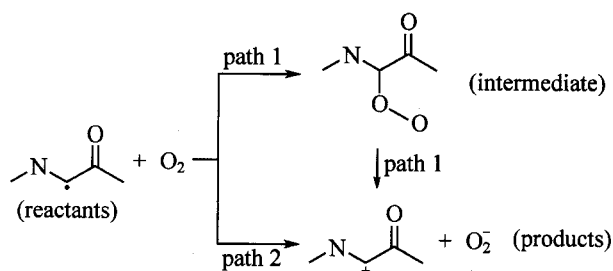
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cess, which usually corresponds to a high reaction free energy. In order to ascertain whether such a process is feasible on the view of the thermal reaction, theoretical calculations have been carried out using Hondo99 package¹⁵ in this work. The reaction heat as well as the inner reorganization energy of the charge separation has been paid attention to by selecting a model donor-acceptor (D-A) system. Based on the energetic calculation, a preliminary kinetic calculation has been done by invoking the Marcus ET theory.¹⁶ Owing to the complicated nature of the real processes in biological systems and the limitation of computation, the authors reduce the sizes of the X and Y subsections of the polymeric backbone on the two sides of X-NHCH' C(O)-Y, and substitute H for both X and Y groups so as to prepare the model molecule and obtain the α -amino carbon-centered radical ($\text{H}_2\text{NCH}'\text{CHO}$). The main aim of this work is to verify if the charge separation process in the complex composed of α -amino carbon-centered radical and oxygen is possible, and what role the solvent molecules may play.

Scheme 1



Computational details and discussion

The geometries of the neutral α -amino carbon-centered radical model molecule ($\text{H}_2\text{NCH}'\text{CHO}$) and the corresponding carbocation radical ($\text{H}_2\text{NCH}^+\text{CHO}$), as well as O_2 ($^3\Sigma_g^-$) and O_2^- ($^2\Pi_g^-$) were optimized at the level of both UHF/6-31++G** and MP2/6-31++G**. $\text{H}_2\text{NCH}^+\text{CHO}$ was found planar with symmetry of C_s because of the sp^2 hybrid orbitals of the central carbon, but the neutral radical departs from the planar geometry somewhat because of the tendency to sp^3 hybrid orbitals of N atom. The frequency analysis has been subsequently performed to ascertain whether the geometries are the stationary ones. Fortunately, the absence of imaginary frequencies confirms that the computed stationary geometries

correspond to the real energy minima. In general, the reaction entropy is usually ignored in a simple ET since there is neither bond formation nor bond cleavage. Thus the difference of free energy ΔG_0 can be expressed as the energy difference of the ground state ET, which approximates to the reaction heat.

Most of the real ET reactions take place in the solvent environment. In order to give a rational illustration of the solvent effect, the exploration of the solvation models attracted much interest in the 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 authors consider the solvent effect in ET with the conductor-like screening model (COSMO),^{15,17,18} which treats with the solute system of arbitrary cavity and achieves the solvation energy calculation through self-consistent reaction field method.

Inner reorganization energy

For a self-exchange ET reaction,



it is convenient to employ direct quantum chemical calculation in the inner reorganization energy (E_{IR}) estimation,¹⁹ that is

$$\lambda_i(\text{B}/\text{B}^-) = E_0(\text{B}^-) - E_1(\text{B}^-) + E_1(\text{B}) - E_0(\text{B}) \quad (1)$$

where the subscript "0" and "1" respectively refer to the equilibrium geometries of the neutral species and the ionic ones. For a charge separation process with D representing the electron donor and A the electron acceptor,

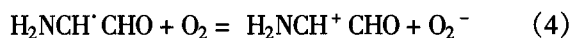


the E_{IR} can be calculated by taking the average value:

$$\lambda_i(\text{D}/\text{A}) = [\lambda_i(\text{D}/\text{D}^+) + \lambda_i(\text{A}/\text{A}^-)]/2 \quad (3)$$

The gas-phase total energies E_0 and E_1 of the donor and the acceptor, as well as their corresponding ions shown in the reaction of path 2 in Scheme 1, were calculated using the spin unrestricted Hatree-Fock self-consistent (UHFSCF) and the Moller-Plesset second order perturbation (MP2) methods. The basis sets used throughout

this work are 6-31 ++ G** (6-31G plus diffuse and polarization functions on all the atoms). The inner reorganization energies of the two self-exchange reactions O_2/O_2^- and H_2NCH^+CHO/H_2NCH^+CHO are presented in Table 1. Since the UHFSCF method is used in open shell species calculations, there exists the spin contaminant, so the MP2 energy after the spin contaminant annihilation is adopted. For the O_2/O_2^- ET couple, the authors performed the MP2/6-31 ++ G** geometry optimization and evaluated E_{IR} . In general, HF calculation gives a too large value of E_{IR} , and MP2 and MCSCF can improve the results.²⁰⁻²² The self-exchange reaction O_2/O_2^- has been theoretically investigated by Morokuma,²³ Bu,^{24,25} and Ebersson.²⁶ In the present work, the authors do not attempt to perform a further discussion on this but only focus on the oxidation of H_2NCH^+CHO by O_2 . For a gas-phase charge separation process,



the MP2 reaction heat, ΔE_0 , was found to be 655.2 kJ/mol, a value extremely high for a real reaction. The E_{IR} for the gas-phase reaction (4), according to Eq. (3) and the corresponding calculation, was 82.2 kJ/mol. A large ΔE_0 indicates that the charge separation process (4) is a highly endothermic one, and an abnormally large activation energy may be estimated by

$$E_a = (\Delta E_0 + \lambda)^2 / 4\lambda \quad (5)$$

Table 1 Total energies (in a. u.) of the species and the inner reorganization energies (in kJ/mol) of the self-exchange of O_2/O_2^- and $H_2NCH^+CHO/H_2NCH^+CHO^a$

Species	E_0	E_1	E_{IR}
H_2NCH^+COH	-207.98194	-207.96133	
H_2NCH^+COH	-207.71587	-207.73021	91.7
O_2	-149.96972	-149.95757	72.6 (104.1, ^b 88.6 ^c)
O_2^-	-149.95671	-149.97221	

^aAll energies were calculated at the level of MP2/6-31 ++ G** in the gas phase. ^bThe *ab initio* value by Ebersson *et al.*²⁶ ^cThe result of classical force-field method.²³

even if the solvent reorganization is excluded. Nevertheless, the Coulomb interaction between the two oppositely charged ions is unable to be considered in the calculation of the isolated species. Thus it can be seen, in the following sections, that the reaction heat considerably decreases in the complex cases by considering the Coulomb interaction.

Encounter complex and charge-separated complex

There must be one or more intermediates formed in the reaction of α -amino carbon-centered radical and O_2 , but what is the intermediate form? To answer this question, the $D\cdots A$ encounter complex and the $D^+\cdots A^-$ ion pair complex were prepared to obtain the reaction heat and the reorganization energy from the viewpoint of intramolecular ET. In physiological processes and pathological disorders, ET reactions between α -amino carbon-centered radicals of glyceryl proteins and O_2 factually take place in the solvent environment. More sophisticated considerations of the solvent environment in biological system are beyond the ability of the authors' present theoretical calculation, so only the water solvent is taken into account. The continuum solvation model (COSMO) was adopted to simulate the solvent effect in ET. Because the product of ET reaction (4) is an ion pair (IP), in aqueous solution, the ion-solvent interaction resulted from the polar water molecules can be expected to stabilize the IP state more than in the gas-phase case, thus the reaction heat ΔE_0 should decrease greatly.

In optimizing the complexes, it is supposed that the O_2 molecule attacks the α -carbon in the perpendicular way (Fig. 1), with the two oxygen atoms and the central carbon in the donor lying on the same line, as shown in Fig. 1. The bond lengths and the bond angles are only given for the heavy atoms. The net charges condensed on atoms are given in the square brackets. The optimization was carried out at the level of UHF/6-31 ++ G**. In the first step, the authors used the optimized isolated species and let the O_2 approach to the donor. Under approximation of perpendicular attack, the point-by-point calculation of the energy profiles was performed by changing the donor-acceptor distance. In order to search the energy minimum where the precursor $D\cdots A$ and the product $D^+\cdots A^-$ reach stabilized geometries, the UHF/6-31 ++ G** method associated with COSMO was used to construct the potential curve based on the geometries of isolated species obtained at the UHF/6-31 ++ G** level. The bond parameters of the fixed fragments are shown in Fig. 1(a). For $D\cdots A$, a usual UHFSCF can easily lead to the normal convergence of the ground state which possesses the neutral charge distribution on both the donor and the acceptor. The potential energy surface is shown in Fig. 2(a). From the perpendicular approach, it can be

found that the energy minimum appears at $d_{C(1)-O(9)} = 0.40$ nm. From the net charges condensed on the atoms given in the square bracket of Fig. 1(a), the two fragments can be found almost completely neutral. $\epsilon_r = 78.5$ for the calculation in aqueous solution was taken.

Unlike the case of the neutral complex, the IP structure $D^+ \cdots A^-$ is somewhat difficult to acquire, since the usual SCF is unable to achieve the charge separation electronic structure. Therefore, some sets of electron-localized molecular orbitals (ELMOs) are needed to induce the SCF calculation. To attain such sets of ELMOs, the authors apply an external electric field of 0.03 a. u. (1 a. u. = 5.145×10^{11} V/m) in the direction from O_2 to the donor, because such a value of external field can give a separation of approximate unit charge. From the gas-phase UHF calculation, a set of molecular orbitals, which yield a charge-separated state, have been obtained. Using this set of ELMOs to induce the further field-free UHF calculation associated with COSMO, a charge-separated state has been obtained without an external electric field. Similar to the neutral complex case, the energy profiles have been constructed with $d_{C(1)-O(9)}$ being the only variable. From Fig. 2(b) it can be seen that the IP complex reaches its minimum total energy at $d_{C(1)-O(9)} = 0.27$ nm.

See Fig. 1 for the diagram of the systems. In the calculation of the total energy, the atoms in O_2 approach to the donor moiety in the perpendicular direction. The separately optimized geometries of the D, D^+ , A, and A^- are fixed and only $d_{C(1)-O(9)}$ varies. COSMO has been taken into consideration for the solvent effect in water ($\epsilon_r = 78.5$). The minimum of energy has been found -356.99214 a. u. at $d_{C(1)-O(9)} = 0.40$ nm for $D \cdots A$

complex, and -356.93642 a. u. at $d_{C(1)-O(9)} = 0.27$ nm for $D^+ \cdots A^-$ complex at the level of UHF/6-31++ G^{**} .

Starting from the geometries of $D \cdots A$ and $D^+ \cdots A^-$ complexes as showed in Fig. 1, the authors have performed full geometry optimizations with COSMO. However, it has been found that the geometries and the total energies are only slightly improved. The total energy is -356.99219 a. u. for $D \cdots A$ and is -356.93762 a. u. for $D^+ \cdots A^-$, and C(1)-O(9)-O(10) bends to 178.8 and 178.1 degrees for $D \cdots A$ and $D^+ \cdots A^-$, respectively. From the results of full geometry optimizations, one can see that the obtained structures of $D \cdots A$ and $D^+ \cdots A^-$ indeed correspond to the local energy minima, and thus the perpendicular approach assumption is reliable. The authors is not preferred to give further description on the fully optimized geometries since it will lead to the loss of the clarity of perpendicular attack. Compared with the $D \cdots A$ complex, it can be found that the distance between the two moieties in $D^+ \cdots A^-$ complex decreases greatly. This can be attributed to the Coulomb interaction between D^+ and A^- . In solution, there are two contrary influencing factors: one is the Coulomb interaction which makes the oppositely charged ions approach to each other, and the other is the dipole-solvent interaction which attempts to make the two ions depart from each other so as to yield a larger dipole moments and thus to obtain a larger equilibrium solvation energy of the system.

After the search for the energy minima of $D \cdots A$ and $D^+ \cdots A^-$ complexes, the MP2 energy calculation at the stable geometries of both was performed. The total energies are listed in Table 2.

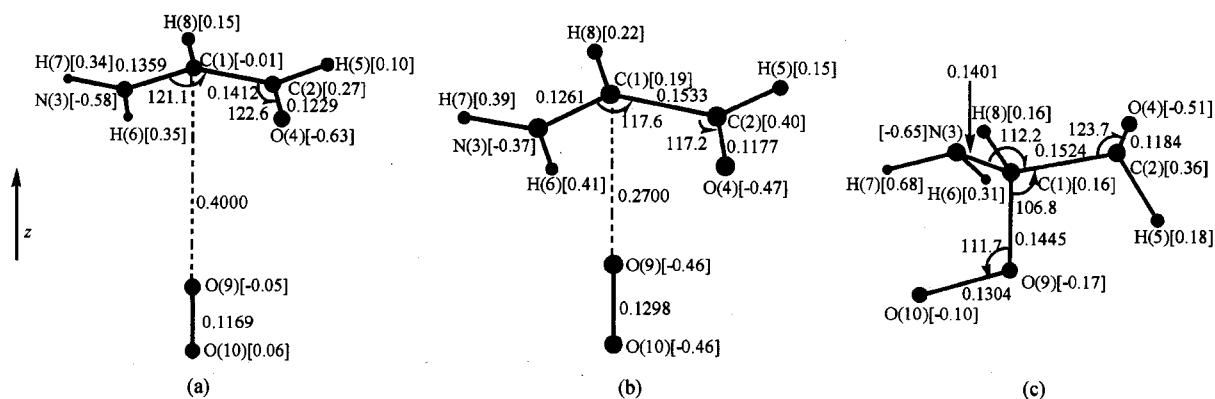


Fig. 1 Skeleton of $D \cdots A$ (a), $D^+ \cdots A^-$ (b) complexes and the peroxy radical compound (c).

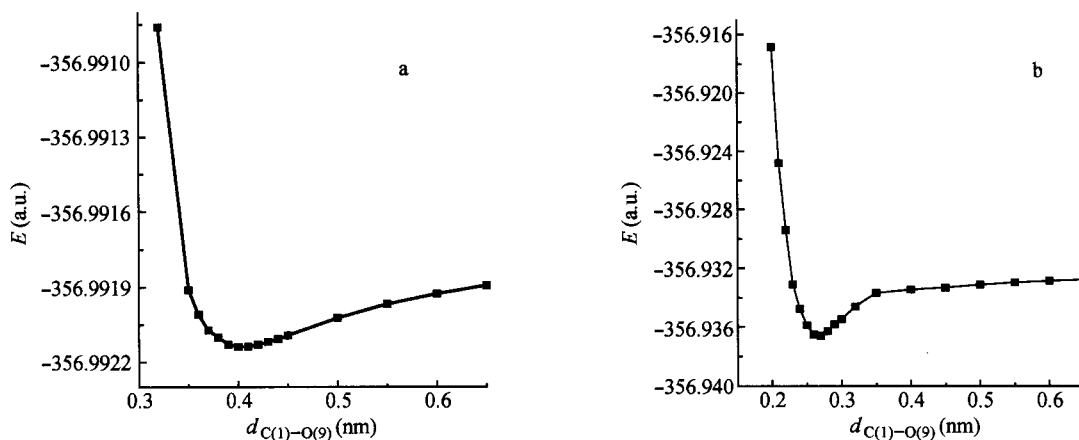


Fig. 2 Energy surface profiles of $D\cdots A$ (a) and $D^+\cdots A^-$ (b) during the approach of O_2 to the donor moiety along the perpendicular direction.

Table 2 Total energies (in a. u.) of $D\cdots A$ and $D^+\cdots A^-$ complexes at the reactant ($d_{O(9)-C(1)} = 0.40$ nm) configuration and the product ($d_{O(9)-C(1)} = 0.27$ nm) configuration^a

	$d_{O(9)-C(1)} = 0.40$ nm		$d_{O(9)-C(1)} = 0.27$ nm		ΔE_0 (kJ/mol)	E_{IR} (kJ/mol)	$d_{O(9)-C(1)} = 0.14$ nm PerORC
	$D\cdots A$	$D^+\cdots A^-$	$D\cdots A$	$D^+\cdots A^-$			
UHF ^b	-356.98127	-356.79301	-356.92784	-356.86441	306.8	163.9	-356.97550
UHF-COS ^c	-356.99214	-356.88840	-356.93775	-356.93642	146.3	134.4	-357.98807
MP2-COS ^d	-357.97692	-357.86840	-357.95859	-357.92399	139.0	97.0	-357.96426
P_{O-O} ^e	0.0	-0.99	0.05	-0.92			-0.27
$P_{C(1)}$ ^f	-0.01	0.26	-0.11	0.19			0.16
D_z ^g	0.0	21.93	0.0	15.44			2.83 ^h

^aSee Fig. 1 for the nuclear configurations. 6-31G++G** basis sets have been used for all the calculations. ^bGas-phase UHFSCF. ^cUHF-SCF associated with COSMO ($\epsilon_r = 78.5$). ^dMP2 associated with COSMO ($\epsilon_r = 78.5$), the spin contaminant has been eliminated. ^eNet charge condensed on the O_2 fragment. ^fNet charge condensed on the central α -carbon. ^gDipole moment along the direction from O_2 to the donor in Debye (*cf.* Fig. 1). ^hThe total dipole moment of the peroxy radical compound.

Beside the complex $D\cdots A$, another less stable peroxy radical compound (PerORC) has been found, in which $O(9)-C(1)$ possesses a much smaller inter-atomic distance than that in $D\cdots A$ and $D^+\cdots A^-$. The diagram is given in Fig. 1(c). The results indicate that the $O(9)-C(1)$ bond length of 0.1445 nm in PerORC is longer than that of the usual C—O single bond, but the $O(10)-O(9)$ bond is intermediate between a single bond and a double bond. The weaker $O(9)-C(1)$ bond interaction implies that the cleavage at this position is relatively easy. The total energy of PerORC is found intermediated between those of $D\cdots A$ and $D^+\cdots A^-$. Unlike the nearly planar structure in $D\cdots A$ and the planar one in $D^+\cdots A^-$, the α -amino carbon-centered radical moiety in PerORC distorts and the $C(1)-O(9)-O(10)$ bends to an angle of 111.6 degrees. From the energy calculation

listed in Table 2, it can be seen that the sequence of stability in aqueous solution is: $D\cdots A > \text{PerORC} > D^+\cdots A^-$.

From the results of theoretical calculations, some discussions can be made on the oxidation of α -amino carbon-centered radical by O_2 . If the ET reaction occurs in the gas-phase, there should be an endothermicity of 306.8 kJ/mol. Such a process can be predicted to be very difficult. It should be noticed again that the energy difference was used to approximate the reaction heat, ignoring the entropy change owing to the negligible change of nuclear rearrangement during ET process. When the polar solvent environment is considered, for example in water, the reaction heat decreases owing to the dipole-solvent interaction. The value of reaction heat becomes 146.3 kJ/mol using the same UHF calculation by applying COSMO,

and 139.0 kJ/mol by using MP2 associated with COSMO. In the calculation of E_{IR} , it has been found that the value of MP2 is smaller than that of HF method, but the existence of solvent does not influence E_{IR} seriously. An average value of the two self-exchange reactions O_2/O_2^- and $\text{H}_2\text{NCH}^-\text{CHO}/\text{H}_2\text{NCH}^+\text{CHO}$ was taken, and a value of 76.8 kJ/mol was obtained (Table 1). Compared with this value, the E_{IR} of the complex case is about 20 kJ/mol higher. This increase mainly results from the variation of the O(9)—C(1) distance during the ET process. From Table 2, it can be seen that the net charge on the O_2 moiety in the charge separation complex is close to -1 , which implies that the treatment reaches good charge separation, but the charge separation at the product geometry ($d = 0.27$ nm) is less satisfactory compared with the case of $d = 0.40$ nm. It seems that the smaller the donor-acceptor distance is, the more difficult the charge localization. In the $\text{D}\cdots\text{A}$ case, the central α -carbon is negligibly charged, but in the IP case, the α -carbon carries a net charge of about 0.2. From Fig. 1, it can be seen that the positive unit charge spreads on the whole donor moiety. Although there exists a dipole moment in the complex, this quantity in the direction from O_2 to the donor is zero in the $\text{D}\cdots\text{A}$ case. On the contrary, the charge separation in the complex results in a large dipole moment in the same direction. It is, of course, understandable that the dipole moment is smaller in the case of $d_{\text{O}(9)\text{—C}(1)} = 0.27$ nm, due to the shorter donor-acceptor distance.

Solvent reorganization energy and rate constant

In order to discuss the rate constant of ET reaction between $\text{H}_2\text{NCH}^-\text{CHO}$ and O_2 , the solvent reorganization energy needs to be calculated. In the present work, the well-known Marcus two-sphere model¹⁶ was used for this purpose, *i. e.*,

$$\lambda_0 = (\Delta e)^2 [1/(2r_a) + 1/(2r_b) - 1/d] (1/\epsilon_\infty - 1/\epsilon_0) \quad (6)$$

where Δe is the charge transferred from the donor to the acceptor, d the distance between the center of the two spheres, r_a and r_b are the radii of the reactants, ϵ_0 and ϵ_∞ the static and optical (square of refractive index) dielectric constants of the solvent respectively. From the

greatest dimension of the optimized geometry and the Van der Waals radius of H atom, the radius of $\text{H}_2\text{NCH}^-\text{CHO}$ is estimated to be 0.326 nm. Similarly, from the distance between two oxygen atoms from the geometry optimization, the radius of O_2 can be estimated to be 0.205 nm by adding the Van der Waals radius of O atom. The average value of the distance from the α -carbon to the center of O(9)—O(10) was used to obtain $d = 0.40$ nm. By taking $\epsilon_\infty = 1.78$ and $\epsilon_0 = 78.3$ in water, $\lambda_0 = 112.3$ kJ/mol was obtained.

Based on Marcus ET theory,¹⁶ the expression of ET rate constant is given by

$$k_{\text{ET}} = A \exp[-\Delta G^*/k_{\text{BT}}] \quad (7)$$

where A and k_{B} are the frequency factor and the Boltzmann constant respectively. As mentioned above, $\Delta G^* = (\Delta E + \lambda)^2/4\lambda$ with $\lambda = \lambda_i + \lambda_0$. For the ET between $\text{H}_2\text{NCH}^-\text{CHO}$ and O_2 , $\Delta E = 139.0$ kJ/mol and $\lambda = 209.3$ kJ/mol were obtained. Thus the reaction activation energy ΔG^* was obtained to be 144.9 kJ/mol. By taking $T = 310$ K and choosing a usual value of $A = 6 \times 10^{12}$ (L/M)/s,²⁷ a rough prediction of $k_{\text{ET}} = 2.297 \times 10^{-12}$ (L/M)/s was given, although a direct experimental evidence for this result has not been found at the present time.

Conclusion

The ET reaction between model system of α -amino carbon-centered radical and O_2 has been investigated in the present work. From the theoretical results, it can be concluded that the step of charge separation explicitly can not process in gas phase, for the abnormally high activation energy barrier predicted. However, the existence of the polar solvents, *e. g.*, water molecules, will greatly increase the feasibility of this process, since solvent effect makes the total energy of the charge separation state decline significantly and thus makes the IP state more stable. Comparing the reaction heat in the gas-phase case with that in aqueous solution from the HF calculation results listed in Table 2, it can be found that the reaction heat of charge separation process varies from 306.8 kJ/mol of the gas-phase case to a value of 146.3 kJ/mol in aqueous solution. The MP2 calculation gives a much smaller E_{IR} than HF calculation. The former is naturally taken as the more reasonable one because the electronic

correlation is partly considered. The result indicates that the solvent effect in the process of oxidation of α -amino carbon-centered radical of glycol proteins by oxygen is remarkable. From the rate constant calculation, the authors can predict that the oxidation of the model donor molecule by oxygen can proceed, but not very fast. The polarity of the solvents can have significant influences on rate constant of the charge separation.

In addition, the intermediate of the possible reaction path 1 shown in Scheme 1 has been also studied. Comparing the energy of PerORC with that of neutral complex $D^{\cdot\cdot}A$, the authors can predict a competition process in which a peroxy radical compound is produced, but the kind of peroxy radical compound is less stable in polar solution at higher temperature.¹¹ Thus the compound cleaves into the corresponding carbocation and the superoxide radical anion as a subsequent step.

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