

Electron Transfer Reaction between M-C₆H₆ and M⁺-C₆H₆ Complexes in the Gas Phase: Density Functional Theory Study

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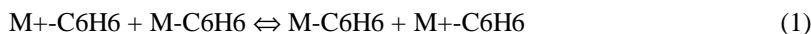
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Abstract: DFT/BLYP method is used to theoretically investigate the electron transfer (ET) reactions between M (Li, Na, Mg)-C₆H₆ and M⁺-C₆H₆ complexes in the gas phase. The geometry optimization of the precursor complexes and the transition state in the process of ET reaction was performed at 6-31G basis set level. The activation energy, the coupling matrix element and the rate constant of the ET reaction are calculated at semi-quantitative level.

Keywords: M-C₆H₆ complex, density functional theory, rate constant.

Significant progress has been made in understanding the nature of the transition state and the paths for electron transfer, especially the influences of environmental factors and the molecular properties on the electron transfer rate. These classical and semi-classical, as well as quantum-mechanical theory, have been very successful in rationalizing several structure-reactivity relationships and in predicting novel features of reactivity. These models established some links between the electron transfer rate and some parameters such as the activation energy or reorganization energy, the electronic transmission factor, the nuclear tunneling factor and others.

In general, for the following type of electron exchange reaction in the gas phase



the dependence of the electron transfer rate (k) on some parameters can be expressed as¹

$$k = \frac{2H_{if}^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2} \cdot \exp(-E_{ad} / RT) \quad (2)$$

Where H_{if} denotes the electron coupling matrix, λ the reorganization energy, and E_{ad} the activation energy. The physical meaning of these parameters in Eq (2) can be conveniently discussed in terms of the energy profiles of **Figure 1**. According to reference [2], the coupling matrix element can be expressed as

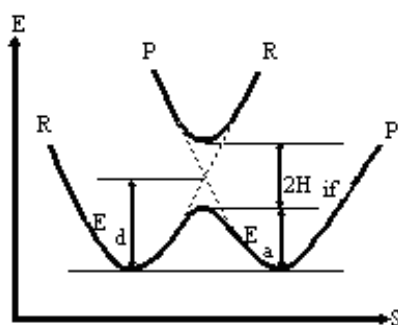
$$H_{if} = E_d - E_{ad} \quad (3)$$

where the adiabatic activation energy (E_{ad}) is easily obtained by subtracting the energy of each encounter complex from the corresponding energy at the activated state, the diabatic activation energy (E_d) can be derived by subtracting the energies of two isolated

species at their own equilibrium geometries from the energy of the crossing point.

In the present paper, the DFT/BLYP method^{3,4} is used to investigate the process of reaction (1) at 6-31G basis set level using the Gaussian-94 program package. We focus on computing the equilibrium geometry of the precursor complex and the transition state. Then three parameters, the coupling matrix element, the activation energy and the reorganization energy for this reaction will be calculated. Finally, according to Eq (2) the electron transfer rate constant can be derived.

Figure 1: Parabolic energy profiles of two diabatic states along the reaction coordinate, displaying the crossing energy E_d and the splitting of the adiabatic states ($2H_{if}$)



Results and Discussion

1. The equilibrium geometry of the complexes in encounter state

The geometrical configuration of the encounter complex influences directly not only the activation energy of reaction but also the electron transfer coupling matrix element and further the electron transfer rate. Thus it is very important to find various possible geometrical configurations for the encounter complex. According to the ET reaction between $M^+-C_6H_6$ and $M-C_6H_6$, three possible structures in encounter state have been considered when two isolated species contact: (a) two species favor the structure of “head to head”, the planes of two benzene molecules retain parallel like the sandwich complexes; (b) two species have the structure of “shoulder to shoulder”, two C_6 axis are parallel; (c) one of the species rotates 90° from the structure of (b). According to the structure of (b) and (c), the geometry optimization was performed. The results show there is no stable position with the distance of the center of two benzene increasing, so the conclusion can be derived that there is no stable equilibrium geometry of these two orientations. Actually, from the analysis of the key orbital of the species $M^+-C_6H_6$ and $M-C_6H_6$, structure (a) is preferred because the overlap between the electron donor orbital (mainly the outer shell s and p_z of M^+ in $M^+-C_6H_6$) and the electron acceptor orbital (mainly the outer shell s and p_z of M in $M-C_6H_6$) will be the largest, then the electron may mainly transfer from M to M^+ . For simplicity, the later discussion will restrict to structure (a). In calculations, we use the following three steps to optimize the precursor complexes: (1) keeping the optimized geometries of $M-C_6H_6$ and $M^+-C_6H_6$, the contacted distance R between two species is optimized; (2) fixing the optimized R and keeping r_+ of the molecular fragment $M^+-C_6H_6$ equal to the optimized

one in isolated state, r_0 of the molecular fragment M-C₆H₆ in the encounter complex is optimized and the result is r_0' ; (3) keeping just optimized R and r_0' , r_+ of the molecular fragment M⁺-C₆H₆ is also optimized, the value is r_+' . Then the geometry of the encounter complex can be defined by three parameters R, r_0' and r_+' .

In order to compare the stabilization of the precursor complex, the bonding energy between acceptor and donor is derived by

$$\Delta E = E_{M-C_6H_6} + E_{M^+-C_6H_6} - E_{ES} \quad (4)$$

where ΔE is the bonding energy of the precursor complexes, E_{ES} is the energy of the encounter complex, $E_{M-C_6H_6}$ and $E_{M^+-C_6H_6}$ are the energy of the M-C₆H₆ and M⁺-C₆H₆ respectively. The larger the values of ΔE are, the more stable the complexes are. **Table** shows the values of structural parameters and ΔE of different system in encounter state. According to Li, Na and Mg systems, the bond length of one M-C₆H₆ fragment is slightly longer than that of isolated M⁺-C₆H₆, while the other M-C₆H₆ fragment has the bond length much shorter than that of the isolated M-C₆H₆ molecule. The distances R are in range from 3.0 to 3.6 Å, which yields the binding energies are about 0.9 ~ 1.5eV and ΔE decreased by the order of Li > Na > Mg. All these results indicate the relatively strong interaction between the acceptor and donor.

Table: The geometrical parameters, relevant energies, coupling matrix elements and rate constants for the reacting system in the encounter complex and transition state

	Li	Na	Mg
Isolated state			
r_0 (Å)	2.6610	3.3785	3.8829
r_+ (Å)	1.9664	2.4344	2.3953
Encounter complex			
R (Å)	3.0711	3.5712	3.07521
r_0' (Å)	2.0972	2.5910	3.1266
r_+' (Å)	2.0972	2.5910	3.1266
ΔE (eV)	1.48	1.05	0.90
Transition complex			
$r_0^*=r_+'$ (Å)	2.3137	2.90645	3.1391
Ea (kJ/mol)	5.7393	2.2529	8.7515
H _{if} (cm ⁻¹)	256.13	626.16	329.11
λ (kJ/mol)	15.0270	9.4113	20.4060
k (/s)	4.27×10^{12}	1.47×10^{14}	1.61×10^9

2. The geometry of the transition state

For the transition state, we define the linear coordinate, then the nuclear configuration parameter of the reacting system can be expressed as¹

$$Q_i = RQ_i^R + (1-R)Q_i^P \quad (5)$$

Where Q_i^R , Q_i^P and Q_i is the *i*th structural parameter of the reactant, product and the reacting system. According to self-exchange model, R=0.5 (the crossing point of two diabatic potential energy surface), then the structural parameter R, r_0^* and r_+^* in description of geometry of the transition state can be obtained using Eq (5). The geometry parameters are also listed in **Table**. The results indicate that at the transition state, r_+^* is longer than r_+ while r_0^* is shorter than r_0 , actually this state is in the preparation for converting into products. The charge distribution on each atom clearly

shows the electron transfer process between $M-C_6H_6$ and $M^+-C_6H_6$. At the transition state, the electron transfer from C_6H_6 and M to $M^+-C_6H_6$ which results in the net charge of C_6H_6 and M increasing, M^+ and C_6H_6 in $M^+-C_6H_6$ decreasing, and yet the electron transference from M to M^+ is dominant since M^+ have large amount of positive charge which is easy to accept the electron from M

3. the calculation of rate constant

According to Eq (2), in order to derive the rate constant of ET reaction of different systems, we must obtain three parameters firstly. E_{ad} and H_{if} can be easily calculated from Eq (3) respectively and the results are also listed in **Table**. From the table, it is observed that the values of E_{ad} decrease by the order of $Mg > Li > Na$; while for H_{if} , the order is $Na > Mg > Li$. The activation energy of these reactions is relatively small, which suggest the ET reaction rate constant should be large. While for the other parameter λ , Hessian matrix method⁵ is used and the results are also listed in **Table**. According to the system of metal-benzene we discussed, the electron prefers to move in the space between benzene molecular plane and the metal rather than delocalize in the benzene molecule⁶. Particularly, when two isolated complexes of $M^+-C_6H_6$ and $M-C_6H_6$ contact *via* the structure of "head to head", the model of the electron transfer should be "through bond" but not "through space"⁷, which makes it easy for the electron to transfer and yield the relatively small reorganization energy. The λ values in **Table** all less than 12.73kcal/mol gives evidence for this conclusion. Then according to Eq (2), the rate constant can be obtained and the results are listed in **Table**. It shows in the table that the rate constants of different reacting system increase by the sequence of $Mg < Li < Na$, which is as same as the order of activation energy and reorganization energy.

In conclusion, the structures and properties of the ET system between $M-C_6H_6$ and $M^+-C_6H_6$ are studied in this paper. Firstly, the geometry optimization of the encounter complex is performed and the results show that there is relatively strong interaction between acceptor and donor. Secondly, we obtain the geometry of transition state using the linear coordinate method. Then in order to derive the rate constant, we discuss the three relevant activation parameters (H_{if} , E_a , λ) of the different reacting system. Finally we obtain the rate constant at semi-quantitative level and the sequence is $Na > Li > Mg$.

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References

1. X. Y. Li, X. J. Xu, F. C. He, *Acta. Chimica. Sinica.*, **1998**, 56, 251.
2. Yuxiang Bu, Conghao Deng, *J. Phys. Chem.* **1996**, 100, 18093, A. Marcus, *J. Phys. Chem.* **1997**, A101, 4072.
3. A. D. Becke, *Phys. Rev.* **1988**, A38, 3098.
4. C. Lee, W. Yang and R. G. Parr, *Phys. Rev.* **1988**, B37, 785.
5. S. Jacobsen, K. V. Mikkelsen and S. U. Pedersen, *J. Phys. Chem.*, **1996**, 100, 7411.
6. K. F. Willey, C. S. Yeh, D. L. Robbins, M. A. Duncan, *J. Phys. Chem.* **1992**, 96, 4769.
7. M. D. Newton, *Chem. Rev.* **1991**, 91, 767.

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