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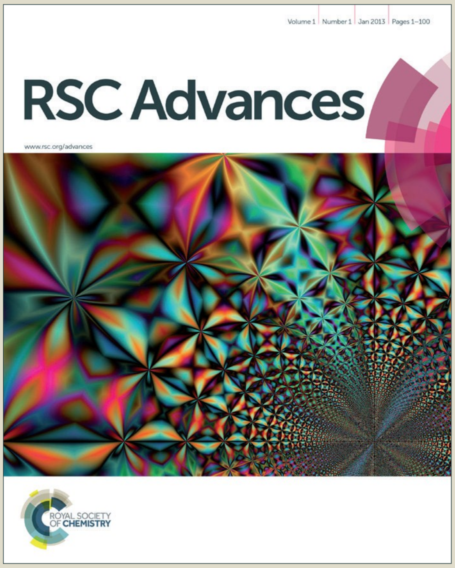

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Excess-electron-induced C-C bond formation in transformation of carbon dioxide

Fang Ma,*[a] Tao Miao,[a] Zhong-Jun Zhou[b] and Hong-Liang Xu[c]

[a] *School of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, China. E-mail:mafangchem@foxmail.com*

[b] *State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun,130023, China.*

[c] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

This work presents a new fixation method of CO_2 through excess-electron-induced C-C bond formation by using quantum chemical method. Because of active $CO_2^{-\bullet}$ with a distinct radical character at the carbon center, two divalent anion complexes $[O_2C-C_6H_6-CO_2]^{2-}$ (**cis-II** and **trans-II**) are obtained via C-C bond formation between the carbon atom of C_6H_6 and the carbon atom of CO_2 in the process of $CO_2^{-\bullet}$ radical attacking on benzene molecule. Further, the transformations of **cis-II** and **trans-II** are predicted. We found that the more favorable transformation is for **cis-II.** It can produce terephthalic and one H_2 molecule via two H-atom elimination with the energy barrier of 35.70 kcal/mol. Further, we found that the formed hydrogen bond complex CO_2-HCN did not reduce the energy barrier, yet it could reduce the energy of the transition state with respect to that of the reactant, due to it dispersing the charge of benzene ring.

1. Introduction

The study of the transformation of carbon dioxide is currently one of the most active research areas in the scientific community,[1-5] since the potentially devastating effects of steadily increased concentration of CO_2 are threatening the sustainable development of our society. Recently, a number of studies have shown that, the use of CO_2 can not only generate useful organic compounds from a nontoxic, abundant, and economical carbon resource,[1-11] but also to a certain extent reduce its atmospheric concentration. However, only a few reaction processes utilize CO_2 as a raw material; because CO_2 is the most oxidized state of carbon and highly stable. Therefore, much effort need to be done regarding the transformation of CO_2.[7,10] In recent years, various strategies of promoting the reactivity of organic materials toward CO_2 have been proposed, especially in the aspect of chemical transformation. First proposal concentrates on coordinating CO_2 to transition-metal complexes,[10-14] where the cleavage of the transformed CO_2 moiety from the metal center hinders catalytic application. Secondly, CO_2 reacts with unsaturated hydrocarbons, for example, the oxidative coupling of CO_2 with olefins and alkynes.[15-29] The third one is regarding insertion of CO_2 into M-X bonds (M=metal, X=C, O and H).[30-41] When a CO_2 molecule inserts into the M-C bond of a compound, a carboxylate species would be formed.[30-35]; By inserting into the M-H bond with suitable catalysts, the synthesis of formic acid from the less toxic and more abundant CO_2 is feasible, and the insertion of CO_2 into M-O bonds results in the formation of carbonate species.[36-41]Another charming reaction strategy is the photocatalytic and electrochemical reduction of CO_2.[42,43] Despite that many papers reported the transformation of CO_2 by various physical and chemical ways, it must be noted that most of reports still go back to the initial concepts of transition metal catalysis proposed by the research groups of Inoue, Musco, Hoberg, Walther and Behr et al. For example, about three decades ago, Hoberg and Walther started examining the oxidative coupling of carbon dioxide (1 bar) and olefins catalyzed by nickel(0) complexes or iron (0) complexes.[44,45] The research groups of Inoue and Musco were the first to report the reaction between carbon dioxide and dienes catalyzed by palladium(0) complexes.[46,47] Behr and co-workers improved the original synthetic procedures of Inoue and Musco by using palladium(II) acetate or acetylacetonate complexes and phosphines in acetonitrile as the solvent, which led to a significant increase in the yield of the lactones.[48] However, a new breakthrough of the transformation of CO_2 has not been developed. Therefore, it is significant that new transformation methods for using CO_2 as a starting material emerge in the nearer future.

Scheme 1. One Potential Reaction Route under an Excess Electron Action.

$$CO_2 \xrightarrow{+e^-} \underset{\text{radical character}}{CO_2^{-\bullet}} \xrightarrow[\text{C-C bond formation}]{\text{H-CR}} [O_2C\text{-}CHR]^{-\bullet} \xrightarrow[\text{dissociating an electron}]{-e^-} \text{product}$$

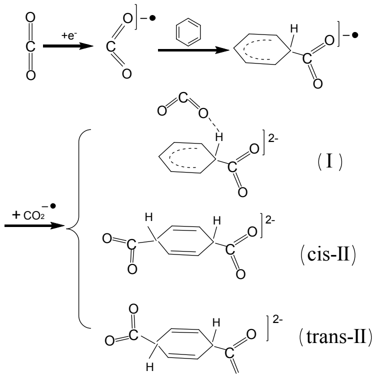
The most prevalent obstacle of CO_2 usage is that it is a weak electrophile. It is difficult to achieve C-C bond formation when reacting with organic molecule. Luckily, the assistance from transition metals may be a good approach to address this problem.[10-43] Herein, we present that free electron assisting provides an alternative approach to achieve the transformation reactions (see Scheme 1). As shown in Scheme 1, firstly, CO_2 captures a free electron to form active $CO_2^{-\bullet}$ with a distinct radical character at the carbon center. Then, the active $CO_2^{-\bullet}$ reacts with an organic molecule H-CR to form intermediate electron-molecule compounds via C-C bond formation. Finally, one product would be obtained through dissociating an electron. In recent years, the chemical reactions via free electron assisting have been widely investigated. For example, upon electron attachment, the van der waals complex of azabenzene and CO_2[49,50] would generate a covalent bond between the nitrogen atom and the carbon atom of CO_2 through an extended π-orbital conjugation over the entire moieties of the complex. Swiderek et al have demonstrated a new strategy to synthesize $C_2H_5NH_2$ from C_2H_4 and NH_3 by low-energy free electrons inducing[51], which relied on the electrostatic attraction caused by the soft ionization of one of the reaction partners. Another important instance was that an excess electron induced hydrogen-bonded complex NH_3•••HCl to form the ionic salt[52], first forming a dipole-bound anion of NH_4Cl, and then a deformed Rydberg radical NH_4, polarized by a chloride anion, Cl^-. For electron impact catalytic reaction, Sajeev' group reported a new elementary reaction mechanism of an electron and a molecule in a metastable compound[53], which strongly relates to bond breaking and bond formation.

Schröder et al. stated that the geometrically bent radical anion of CO_2 constitutes a new type of highly reactive ion, and hence it can be regarded as an activated CO_2 unit.[54] Although in a real gas phase experiment, it is difficult to use $CO_2^{-\bullet}$ as a reactant, due to its low life time, Sajeev and Davis proposed a good strategy that the formation of the weak molecular complex of $[CO_2\bullet HCN]^{-\bullet}$ help the $CO_2^{-\bullet}$ moiety to have long-lived time and permanent reactivity.[55] Beyer' group present that $CO_2^{-\bullet}$ are concurrently solvated and stabilized by the water ligands to form $CO_2^{-\bullet}(H_2O)_n$ [56-59] and performed the reactions with CH_3SSCH_3 to achieve cleavage of the disulfide bond in the gas phase by Fourier transform ion cyclotron resonance mass spectrometry.

It is useful to understand the reaction of active $CO_2^{-\bullet}$ and benzene molecule to investigate other reactions of long-lived $CO_2^{-\bullet}$ in the weak molecular complexes. $CO_2^{-\bullet}$ attacks at C_6H_6, which leads to the formation of a new chemical bond C-C. This is the first step to fix and transform CO_2 by electron impact. Further, because of the attacking from $CO_2^{-\bullet}$, the aromaticity of C_6H_6 ring is broken in electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$. Then, the second $CO_2^{-\bullet}$ would further attach electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ to form the divalent anion complexes **cis-II**, **trans-II** and hydrogen bond complex **I** (see Scheme 2).

In this paper, we investigated that the reaction between $CO_2^{-\bullet}$ and C_6H_6 could form the divalent anion complexes **cis-II**, **trans-II** and hydrogen bond complex **I** via C-C bond formation (see Scheme 2). Further, the transformations of **cis-II** and **trans-II** are predicted, we found that the great possible transformation was that **cis-II** transforms terephthalic and one H_2 molecule via H elimination with the energy barrier of 35.70 kcal/mol. Subsequently, investigations showed that the long-lived $CO_2^{-\bullet}$ moiety in the weak molecular complex of $[CO_2{\bullet}HCN]^{-\bullet}$ also had permanent reactivity to induce C-C bond formation with the energy barrier of 36.35 kcal/mol. Yet we found that it could reduce the energy of the transition state with respect to that of the reactant, due to it dispersing the charge of benzene ring. Therefore, we hope that this work is useful for further theoretical and experimental studies regarding the transformation of CO_2.

Scheme 2. Possible Formed Anion Complexes by $CO_2^{-\bullet}$ Attaching to C_6H_6.



2. Computational Details

All the calculations were performed with the GAUSSIAN 09 programs[60]. The geometrical optimizations of all the intermediates and transition states were performed at the second-order Møller-Plesset perturbation theory (MP2) level with the augmented correlation consistent basis set aug-cc-PVDZ. All studied structures are checked to be closed-shell structures, except for $[C_6H_6\text{-}CO_2]^{-\bullet}$ and $CO_2^{-\bullet}$. Frequency calculations at the same level were performed to confirm each stationary point to be either a minimum or a transition structure (TS). Energy-minimum geometries had only real frequencies, while TS geometries had an imaginary frequency corresponding to the relevant reaction coordinate. In several cases where TS are not easily confirmed by animation of their vibrations, intrinsic reaction coordinate (IRC)[61,62] calculations were performed to confirm the connection of each TS to its corresponding reactant and product. Meanwhile, zero-point energy (ZPE) is also evaluated with a scale factor of 1. Further, high-level (CCSD(t)/aug-cc-PVDZ) energy calculation on the optimized structures is carried out to obtain the single point energy. The charge distributions of complexes were obtained by natural bond orbital (NBO)[63-65] analyses at the MP2/aug-cc-PVDZ level.

3. Results and Discussion

3.1Formation of electron-molecule complex $[C_6H_6\text{-}CO_2]^{-\bullet}$

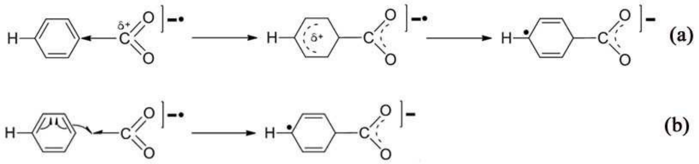
A metastable electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ is obtained in the process of $CO_2^{-\bullet}$ attacking on benzene molecule. The barrier of C-C bond formation is only 7.22 kcal/mol, due to $CO_2^{-\bullet}$ exhibiting radical character. Fig. 1 shows the optimized reactant, TS and product structures. Fig. 2 listed HOMOs of $[C_6H_6\text{-} CO_2]^{-\bullet}$ and **TS**$_{[C6H6\text{-} CO2]-\bullet}$ to roughly illustrate the formation of $[C_6H_6\text{-}CO_2]^{-\bullet}$.

From Fig. 2, the electron density transfers from rich C_6H_6 ring to the C atom with positive charge in $CO_2^{-\bullet}$, meanwhile, the electron density of O atoms in $CO_2^{-\bullet}$ gives a feedback on C_6H_6 ring (see Fig. 2a). Therefore, the coming and going charge transfer enhances the interaction between C_6H_6 and $CO_2^{-\bullet}$. In electron-molecule $[C_6H_6\text{- }CO_2]^{-\bullet}$, the bond length of C1-C2 is 1.618 Å, which is longer than usual C-C bond (~1.55Å). But, the formation of new C1-C2 bond is a key step to fix and transform CO_2. Because the conjugation C_6H_6 ring is destroyed resulting from $CO_2^{-\bullet}$, C_6H_6 ring becomes reactive. The second $CO_2^{-\bullet}$ could be further attached to electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ to form the anion complexes **cis-II** and **trans-II** with no energy barriers (this issue will be discussed in next section).

The geometrical parameters of the optimized reactant, TS and product structures are listed in Fig. 1. In the reactant $CO_2^{-\bullet}$, the bent angle of O-C-O is 136° and the bond lengths of C-O are 1.251 Å. While in the product structure $[C_6H_6\text{-}CO_2]^{-\bullet}$, the bent angle of O-C-O shrinks to 131° and the bond lengths of C-O extend to 1.261 Å.[49,50] This indicates that, the new formed C1-C2 bond further weakened C-O bond and activated C_6H_6 ring. From Fig.1, we found that the 109.7° of C1-C2-C3 bond angle in $TS_{[C6H6\text{-}CO2]^{-\bullet}}$ is much smaller than 135.7° of $[C_6H_6\text{-}CO_2]^{-\bullet}$, this indicates that the process of produced $[C_6H_6\text{-}CO_2]^{-\bullet}$ have a trend of forming extended π-conjugated structure.

Fig. 1 shows that the formation of $[C_6H_6\text{-}CO_2]^{-\bullet}$ may be a reversible reaction. However, the formation C1-C2 bond provide a activation of C_6H_6 ring, the second $CO_2^{-\bullet}$ easily attack C_6H_6 ring to form the divalent anion complexes $[O_2C\text{-}C_6H_6\text{-}CO_2]^{2-}$ (**cis-II** and **trans-II**) with no energy barrier， which can be considered as the combination between two radical ions (see Scheme 3, two possible mechanism of the formation of the radical ion of $[C_6H_6\text{-}CO_2]^{-\bullet}$.). Thus, for the step of the formation of $[C_6H_6\text{-}CO_2]^{-\bullet}$, the shift of the equilibrium is promoted to the product by depleting the $[C_6H_6\text{-}CO_2]^{-\bullet}$ (see Scheme 4).

Scheme 3. The stable radical ions.



Scheme 4. The Shift of the Equilibrium.

$$C_6H_6 + CO_2^{-\bullet} \rightleftharpoons [C_6H_6\text{-}CO_2]^{-\bullet} \xrightarrow[\text{no energy barrier}]{+CO_2^{-\bullet}} [O_2C\text{-}C_6H_6\text{-}CO_2]^{2-}$$

3.2 Fixation of the second $CO_2^{-\bullet}$ to form divalent anion complexes

Due to the activation of C_6H_6, the second $CO_2^{-\bullet}$ can easily fix the electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ to form divalent anion complexes divalent anions $[O_2C\text{-}C_6H_6\text{-}CO_2]^{2-}$ (see Scheme 2). Three possible anion complexes **cis-II**, **trans-II** and hydrogen bond complex **I** are shown in Fig. 3. In divalent anions $[O_2C\text{-}C_6H_6\text{-}CO_2]^{2-}$, the C1-C2 bond is reduced by 0.034~0.047Å, which indicates that the strength of C1-C2 bonds are enhanced. As shown in Fig. 4, the second $CO_2^{-\bullet}$ easily attack C_6H_6

ring to form the divalent anion complexes **cis-II** and **trans-II** with no energy barrier. However, comparing with the reactants, the energies of **cis-II** and **trans-II** only decrease by 1.96 and 2.21 kcal/mol, respectively. However, the formation of hydrogen bond complex **I** is very energetically unfavorable; this formation step is a strong endothermic reaction requiring the energy of 54.00 kcal/mol. Therefore, we concluded that the reaction of the second $CO_2^{-\bullet}$ attacking C_6H_6 ring may follow a producing **cis-II** or **trans-II** pathway, while the former process being energetically more favorable.

Predicting feasible transformation routes is important to study CO_2 transformation. Thus, we calculated the possible transformations of **cis-II** and **trans-II**. Fig. 3 depicts the evolution of the structures, including the reactants, TS and product structures. Although the formation of hydrogen bond complex **I** is unfavorable in energy, we still considered it in order to compare with the transformations of **cis-II** and **trans-II**. (1) Supposing that hydrogen bond complex **I** may transform to $OCOH^-$ and ph-COO^-. In hydrogen bond complex **I**, due to the formation of hydrogen bond, the C2-H1 bond length is lengthened to 1.156 Å, which is longer by 0.042 Å than that in electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ (1.114 Å). This indicates that C2-H1 bond has been activated. In **TS-I**, the C2-H1 bond length is 1.481 Å, and the C2-C1 bond length is shortened to 1.561 Å. Interestingly, the C1-C2-C3 bond angle is approximately thought as the dihedral between two planes of C_6H_6 and $CO_2^{-\bullet}$. It is found that they are 163.2°, 172.6° and 180°, respectively for the reactant, TS and product structure. Those indicate that π_6^6 of C_6H_6 and π_3^5 of $CO_2^{-\bullet}$ become more and more coupled to form an extended π-conjugated network from the reactant to product structure. (2)For the transformation of **tans-II**, the reaction starts with H-transfer from C2 atom to O1 atom to form an intermediate **tans-II-a**. Then, the second H-transfer process occurs to form the product $[HOOC\text{-}ph\text{-}COOH]^{2-}$ (terephthalic acid with two negative charges). As shown in Fig. 3, although the second $CO_2^{-\bullet}$ easily fix on C_6H_6 ring with no energy barrier, C2-H1 bond has not been activated, which is different from hydrogen bond complex **I**. With the evolution of the structures from the reactant to product structure, the C1-C2 and C3-C4 bond lengths become shorter and shorter. In the product $[HOOC\text{-}ph\text{-}COOH]^{2-}$, their bond lengths decrease to 1.400 Å, which would exhibit double bond character. For the change of C1-C2-C3 (C2-C3-C4) bond angle, it is important to understand the formation of the product. It is found that both C1-C2-C3 and C2-C3-C4 bond angles increase with the evolution of the structures, even though C1-C2-C3 (or C2-C3-C4) has a little decrease in transition state structure **TS2-tran-II** (or **TS1-tran-II**). These indicate that an extended π-conjugated network was formed by the couple of one $\pi_6^6$of C_6H_6 and two π_3^5 of $CO2^{-\bullet}$. (3) As shown in Fig. 3, **cis-II** can transform to one $^-OOC\text{-}ph\text{-}COO^-$ and one H_2 molecule, and this plays a significant role in the transformation of CO_2, because it generates not only a useful chemical, but also a clean energy resource H_2. In the transformation of **cis-II**, the reactant **cis-II** with C_{2v} symmetry strengthen the

C1-C2 and C3-C4 bond, they are 1.578 Å, which are shorter than that in electron-molecule compound $[C_6H_6\text{-}CO_2]^{-\bullet}$ (1.618 Å). Like in **tran-II,** C2-H1 bond has not been activated, too. While in **Ts-cis-II**, the C1-C2 and C3-C4 bond of 1.554 Å slight decreases by 0.024 Å. Particularly, the H1-H2 distance is only 1.020 Å, which is much shorter than that in **cis-II** (3.394 Å). Like in **trans-II** and hydrogen bond complex **I**, the change for C1-C2-C3 (C2-C3-C4) bond angle indicates that the forming extended π-conjugated promote the evolution of the structures and stable the product complexes.

The transformation energy profile is presented in Fig. 4. As mentioned above, the formation of hydrogen bond complex **I** is very energetically unfavorable, so we do not discuss its transformation here. For complex **trans-II**, its transformation to the production undergo two transition states **TS1-trans-II** and **TS2-trans-II**. In **TS1-trans-II** (**TS2-trans-II**), the H-transfer process from C2 (C3) to O1 (O2) occurs via a four-membered ring C-H-O-C. However, if the H-transfer process occurs, the energy barriers of **TS1-trans-II** and **TS2-trans-II** are high (47.01 and 59.45 kcal/mol, respectively). They are too high to achieve H-transfer. For **cis-II**, its transformation to the production only undergo one transition state **TS-cis-II** (1635*i* cm^{-1}), which corresponds to the vibration of H elimination with the energy barrier of 35.70 kcal/mol. Comparing to the transformation of **tans-II**, we found that the process of the formation of one H_2 by H elimination is easier than the H-transfer process. In a word, the transformation process of **cis-II** seems to be a more favorable route for the transformation of C_6H_6 and CO_2.

A theoretical analysis of the charge transfer process has been performed. Fig. 5 depicts the charges of benzene skeleton along with the transformation from the reactant to the product. The charges of benzene skeleton increased with regard to **I** and **cis-II,** and decreased with regard to **trans-II**. The decreased charge decreases the stabilities of intermediates and transition states for **trans-II**. In contrast, the increased charge enhances the stabilities of intermediates and transition states for **I** and **cis-II**. Comparing with **TS-I** and **TS-cis-II**, the charges of benzene skeleton in **TS1-trans-II** and **TS2-trans-II** are very negative, and large energy barriers have to be overcome to achieve H transfer. Thus, the H elimination/transfer is easier in **I** and **cis-II**, than in **trans-II**. As Ramos and Fernandes stated,[66] the charge density of the transition structures is more widely distributed than that of reactants, which favors to catalyze the reaction in hydrophobic environments.

3.3 HCN assistance promoting the transformation

Sajeev presented the activated CO_2 moieties in the weak molecular complexes are long-lived and reactive.[55] In this work, we further investigated the reaction for **cis-II** transformation between benzene molecule and the long-lived $CO_2^{-\bullet}$ moiety in the weak molecular complex of $[CO_2\bullet HCN]^{-\bullet}$. Fig. 6 and Fig. 7 depict the process of CO_2 attaching to C_6H_6 and the process of the formation of H_2 under HCN molecule assistance, respectively. First, comparing the process without HCN molecule assistance, the activation energy for the process of CO_2 attaching to C_6H_6 increases by 3.9 kcal/mol from 7.22 to 11.12 kcal/mol, this is because that the weak molecular complex of $CO_2\bullet HCN$ slightly decreases the radical character of the C atom due to the dispersion effect via hydrogen bond interaction. As the same reason, the product $[C_6H_6\text{-}CO_2\text{-}HCN]^-$ has a lower energy of 4.27 kcal/mol than the reactants. In the process of H elimination, we calculated the energy barrier is 36.35 kca/mol, which is very close to 35.70 kcal/mol without HCN molecule assistance. Thus, this shows that the formed hydrogen bond complex CO_2-HCN did not reduce the energy barrier for H elimination process. However, the reduction of the energy of $TS_{[NCH\text{-}2OC\text{-}C6H6\text{-}CO2\text{-}HCN]}{}^{2-}$ (18.57 kcal/mol) with respect to that of the reactant is much larger than TS-cis-II (33.49 kcal/mol) without HCN molecule assistance. This is due to the dispersion effect of HCN via hydrogen bond interaction. From Fig. 8, the NBO charge of benzene skeleton of $TS_{[NCH\text{-}2OC\text{-}C6H6\text{-}CO2\text{-}HCN]}{}^{2-}$ (-0.484 |e|) is lower than -0.52 |e| in TS-cis-II without HCN molecule assistance. Obviously, the NBO charge of benzene skeleton is dispersed to enhance the stability of $TS_{[NCH\text{-}2OC\text{-}C6H6\text{-}CO2\text{-}HCN]}{}^{2-}$. This point may be significant for investigating other relevant reactions

4. Conclusion

In this paper, we have revealed a new fixation method of CO_2 through excess-electron-induced C-C bond formation by using quantum chemical method. Firstly, by excess electron inducing, CO_2 are fixed on benzene molecule to form two divalent anion complexes $[O_2C\text{-}C_6H_6\text{-}CO_2]^{2-}$ (**cis-II** and **trans-II**) via C-C bond formation between the carbon atom of C_6H_6 and the carbon atom of CO_2, due to the distinct radical character at the carbon center of $CO_2^{-\bullet}$. Further, the transformations of **cis-II** and **trans-II** have been predicted. We found that the more favorable transformation of **cis-II** to produce terephthalic and one H_2 molecule via two H-atom elimination with the energy barrier of 35.70 kcal/mol. Further, we found that the long-lived $CO_2^{-\bullet}$ moiety in the weak molecular complex of $[CO_2\bullet HCN]^{-\bullet}$ also had permanent reactivity to induce C-C bond formation, yet it did not reduce the energy barrier. However, it could reduce the energy of the transition state with respect to that of the reactant, due to it dispersing the charge of benzene ring. As we expect, this work may encourage further related research of CO_2 transformation.

Acknowledgments

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Figure Legends

Fig. 1 PES profile for the process of $CO_2^{-\bullet}$ attaching to C_6H_6.

Fig. 2 Coming and going charge transfer form new C-C bond.

Fig. 3 Optimized structures and their geometry parameters. Bond lengths are in angstroms, and angles are in degree.

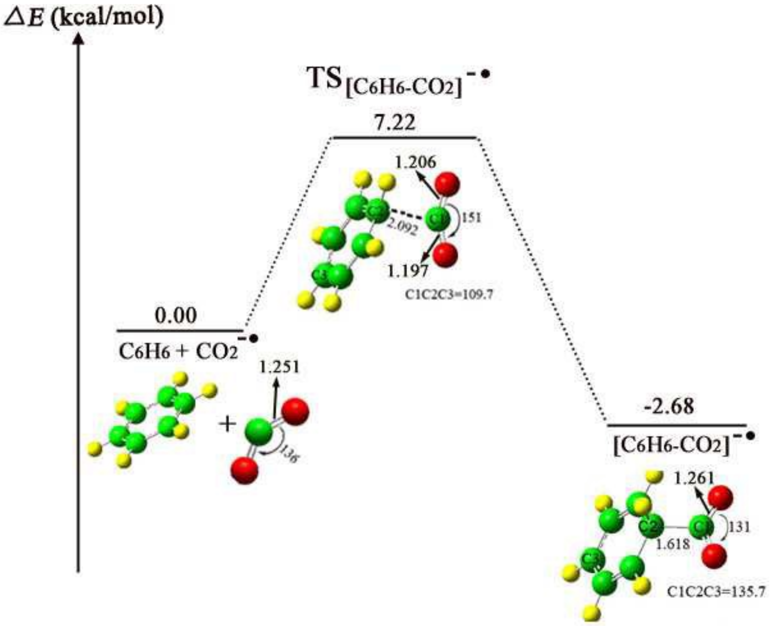
Fig. 4 Energy profiles for the CO_2 transformation reaction.

Fig.5 The charges of benzene skeleton along with the transformation from the reactant to the product.

Fig. 6 PES profile for the process of $CO_2^{-\bullet}$ attaching to C_6H_6 via HCN assistance.

Fig. 7 Energy profiles for the CO_2 transformation reaction via HCN assistance.

Fig. 8 Comparing with the charge of benzene skeleton.



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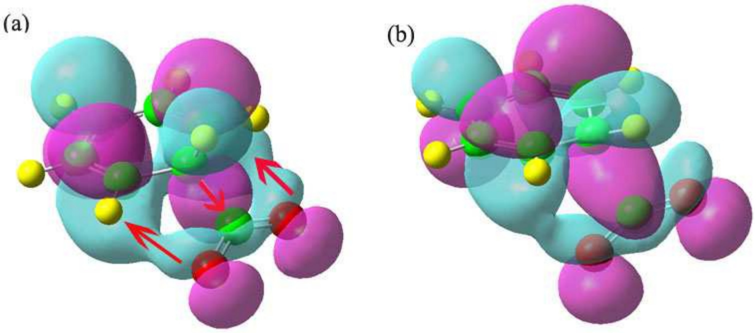
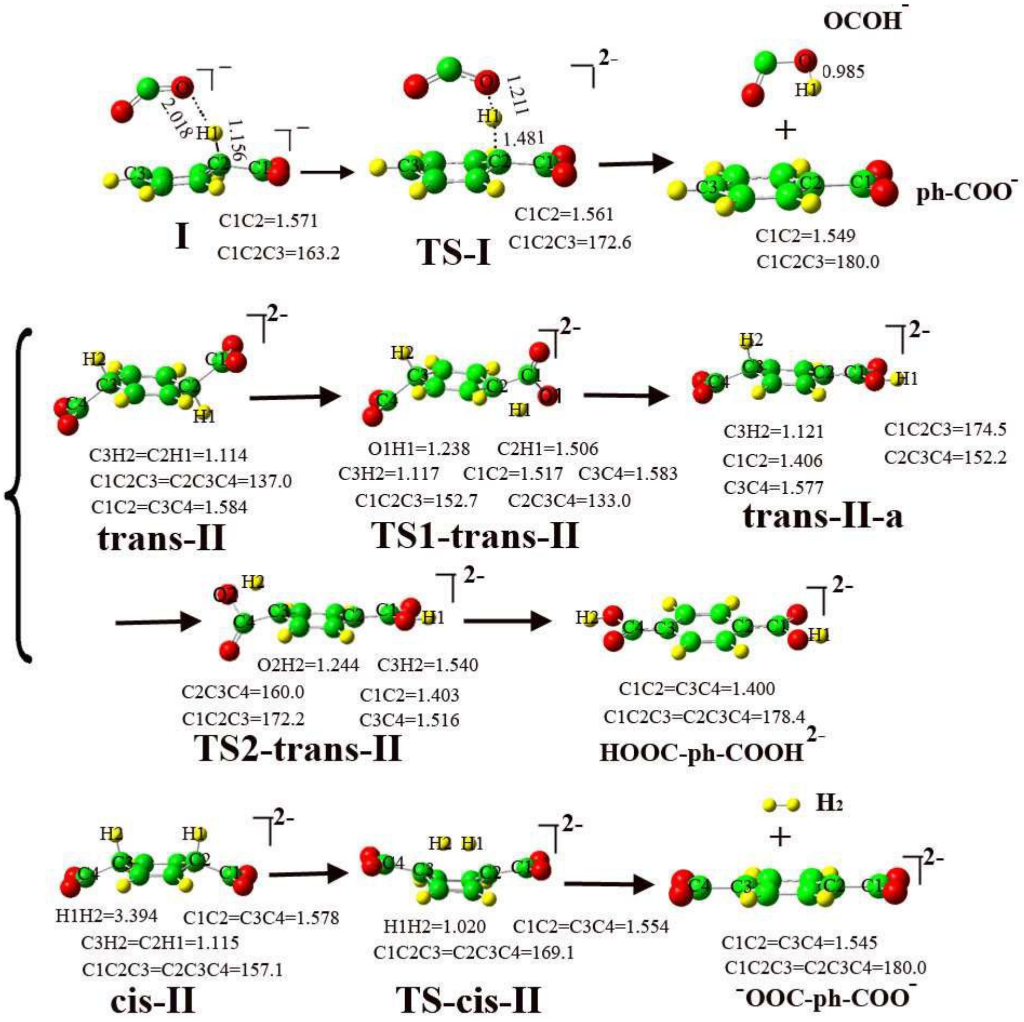


$[C_6H_6\text{-}CO_2]^{-\bullet}$

$TS_{[C_6H_6\text{-}CO_2]^{-\bullet}}$

Fig. 2 HOMOs of $[C_6H_6\text{-}CO_2]^{-\bullet}$ and $TS_{[C6H6\text{-}CO2]-\bullet}$.Coming and going charge transfer form new C-C bond.



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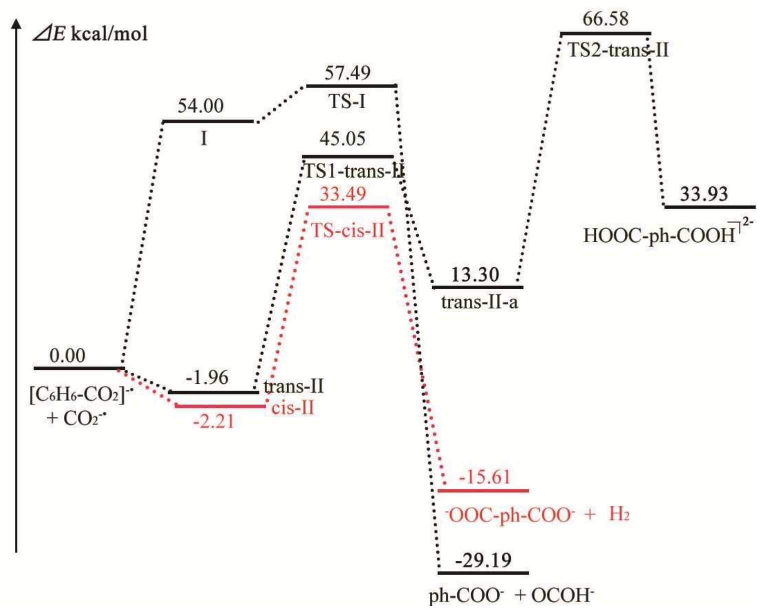

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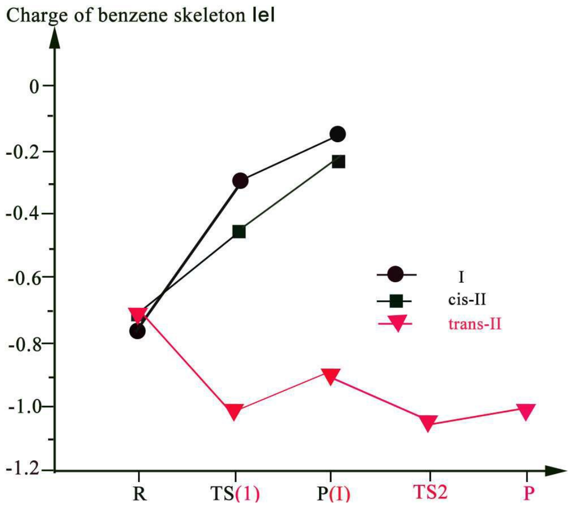

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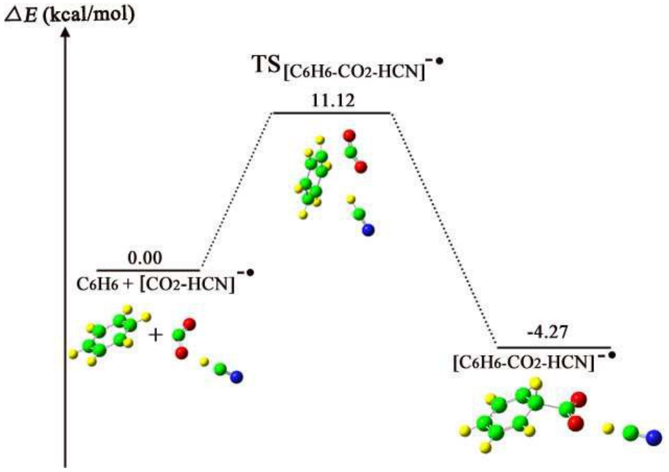

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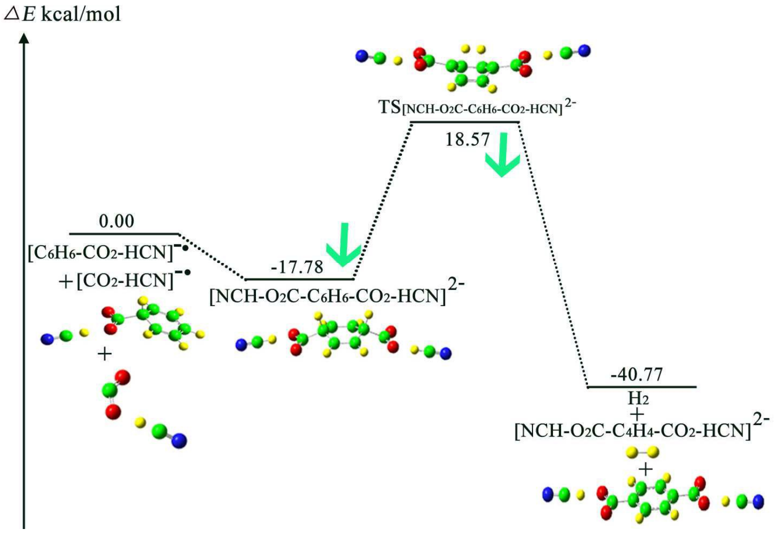
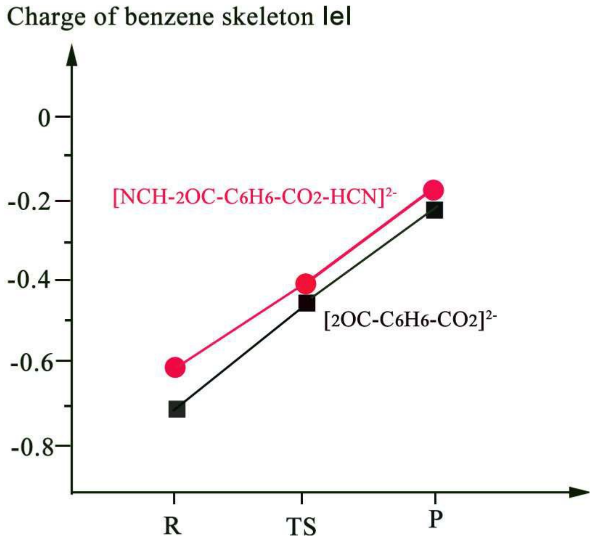


Fig. 7 Energy profiles for the CO_2 transformation reaction via HCN assistance.



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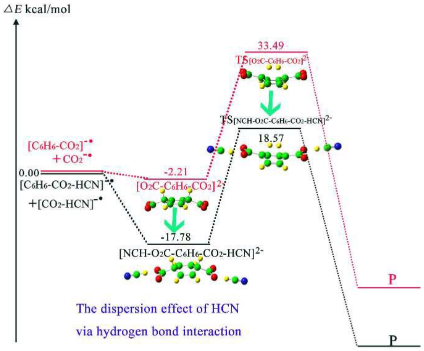
Graphical Abstract



A new fixation method of CO_2 through excess-electron-induced C-C bond formation is presented by using quantum chemical method. For the reaction of CO_2 and C_6H_6, they can produce one H_2 and phthalic acid radical via two H-atom elimination, when the formed hydrogen bond complex disperses the charge of benzene ring.