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Light-Induced Reaction of Benzene with Carbonates

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We found an ultraviolet (UV)-light induced formation of biphenyl and sodium benzoate from benzene and sodium carbonate. The reaction happens in the interface of benzene and aqueous solution at the room temperature. After 5 h of UV-light exposure, 11.4% of initial amount of 4.4 g (5.0 mL) benzene are converted to biphenyl and sodium benzoate, which are distributed in benzene and aqueous solution, respectively. Using density function theory (DFT) and time dependent DFT, we have investigated the mechanism of this light-induced reaction, and found that the sodium carbonate is not only a reactant for the formation of sodium benzoate, but also a catalyst for the formation of biphenyl.

Key words: Benzene, Carbonates, Light-induced reaction, Density function theory calculation, Mechanism

I. INTRODUCTION

Carbonates are widely distributed in nature as inorganic salts, which are formed through environmental chemical reaction of carbon dioxide [1–3]. At present, carbonates are widely used in glass, food and construction industries [4], and in organic synthesis. For example, sodium carbonate and potassium carbonate act as strong bases to catalyze the alkylation of malonate [5] and the deprotonation of L-cyanophenol, respectively [6, 7].

Beller and co-workers reported the synthesis of HCOONa using Na₂CO₃ and MeOH as reactants and ruthenium pincer complexes as homogenous catalysts [8]. There are also some reported organic synthesis reactions between carbon dioxide and aromatic compounds [9–19], including the synthesis of aromatic hydrocarbon. Olah and co-workers reported a heterogeneous catalyst Al₂Cl₆/Al [13]. Nolan and co-workers synthesized homogenous catalysts Cu(NHC)OH (NHC=N-heterocyclic carbene) [15] and Au(NHC)OH [16]. Those catalysts activate the C–H bonds of aromatic compounds and combine with CO₂ for the formation of aromatic carboxylic acids. To the best of our knowledge, the reaction of carbonates and aromatic compounds has not been reported. In this work, we found aqueous

sodium carbonate can react with benzene under UV-light exposure and form biphenyl and sodium benzoate, which are distributed in benzene and aqueous solution, respectively (Fig.1). We also investigated the mechanism of this light-induced reaction using density functional theory (DFT) and time dependent DFT methods [20–22].

II. EXPERIMENTS AND CALCULATION

A. Materials

Materials including sodium carbonate, sodium hydrogen carbonate, cadmium carbonate, magnesium carbonate, benzene, hydrochloric acid, ethyl acetate, were purchased from Shanghai Chemical Reagent Ltd. and of analytically pure grade without further purification,

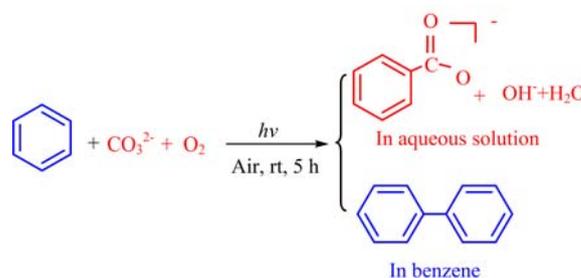


FIG. 1 Light-induced formation of benzoate and biphenyl from benzene and carbonates.

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and carbon dioxide was self-prepared. Deionized water was used throughout this study.

B. Analytical methods

The relative absorption intensity was recorrected by the standard-adding method under UV-Vis absorption intensity using an UV-Vis Absorption Spectroscopy (Hitachi UV-3600). GC was measured on an online gas chromatography (Fuli 9790, China) with FID detector using a SE-30 0.53 mm \times 30 m capillary column using N₂ as carrier gas. GC/MS was measured on a TRACE DSQII (Thermo Fisher). ¹H NMR and ¹³C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz) with CDCl₃ as solvent and recorded in ppm relative to internal tetramethylsilane standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

C. Experimental procedure

Experiments were carried out in a photoreaction apparatus consisting of two parts [29, 30]. The schematic diagram was shown in supplementary materials (Fig.S1). The first part was an annular quartz tube with an empty chamber in which a 375 W medium pressure mercury lamp (Institute of Electric Light Source, Beijing) with a main wavelength of 365 nm was laid. Running water passed through an inner thimble of the annular tube. Owing to continuous cooling, the temperature of the reaction solution was maintained at approximately 30 °C. The second part was an unsealed beaker with a diameter of 10 cm. At the beginning of the experiment, the reaction solution (25 mL), containing 5 g sodium carbonate, 5 mL benzene, and 20 mL deionized water, was put in the unsealed beaker and stirred by a magnetic stirring device. The distance between the light source and the interface of the reaction solution was 11 cm. Before the experiment, the reaction solution had been going through the air for 30 min, and during the experiment, the air was always passed. In order to better disperse two-phase solution prior to exposure of the entire container, the two-phase solution was scattered by ultrasonic oscillation for 20 min. After exposure, the reaction liquid phase samples were extracted, and then characterized using quantitative and qualitative methods. In order to determine the reproducibility of the results, duplicated runs had to be carried out in each condition for averaging the results.

D. Computational method

All DFT and TDDFT calculations were performed using the Gaussian 09 suite of programs [31] for the M06 functional [32] with the 6-31++G(d,p) basis set [33, 34]. All structures were optimized with solvent effect corrections by the method of integral equation

formalism polarizable continuum model (IEFPCM) [35] for water and benzene as the solvent. Thermal corrections were calculated within the harmonic approximation on optimized structures under $T=298.15$ K and $P=1$ atm. Calculating the frequencies for optimized structures and noting the number of imaginary frequencies (IFs) confirmed the nature of intermediates (no IF) and transition states (only one IF). The latter was also confirmed to connect reactants to products by intrinsic reaction coordinate (IRC) calculations. The 3D molecular structures displayed in this work are drawn by using the JIMP2 molecular visualizing and manipulating program [36].

III. RESULTS AND DISCUSSION

A. Characterization of benzoate and biphenyl

Benzoate: ¹H NMR (400 MHz, CDCl₃), δ /ppm 8.143–8.119 (m, 4H), 7.63–7.594 (m, 4H), 7.495–7.456 (m, 3H). ¹³C NMR (100 MHz, CDCl₃), δ 172.5, 133.8, 130.2, 129.3, 128.4.

Biphenyl: ¹H NMR (400 MHz, CDCl₃), δ /ppm 7.607–7.578 (m, 4H), 7.462–7.420 (m, 4H), 7.365–7.332 (m, 2H). ¹³C NMR (100 MHz, CDCl₃), δ 141.22, 128.7, 127.2, 127.1.

B. Light exposure time effect

The initial amounts of 5 g sodium carbonate and 5 mL benzene were mixed in 20 mL deionized water. The relative absorption intensities at different light exposure time in water are shown in Fig.2. The relations between the concentration of sodium benzoate and biphenyl at different UV-light exposure time are shown in Fig.3.

In Fig.2, the six lines from bottom to top are the absorption spectra measured at 0, 1, 2, 3, 4 and 5 h, respectively. As shown in Fig.2(a), the aqueous solution has absorption peaks at 256 and 360 nm, which indicate the formation of new substances after UV-light exposure. As shown in Fig.2(b), the absorptions in the range of 205–220 nm come from benzene. The dramatic increase of the absorption intensities with the increase of exposure time in the range of 240–275 nm indicates the formation of new substances in benzene. In Fig.3, the concentrations of sodium benzoate and biphenyl are 12.2 and 7.4 mmol/L, respectively. Furthermore, we found that the concentrations of benzoates and biphenyl were similar when the fully dissolved carbonates were used, such as potassium carbonate and sodium carbonate. In order to find out possible reactions of benzene and other carbonates under the same condition, we also examined MgCO₃, CdCO₃, and NaHCO₃. The results are shown in Table I.

As shown in Table I, benzene can react with NaHCO₃, but cannot react with insoluble carbonates

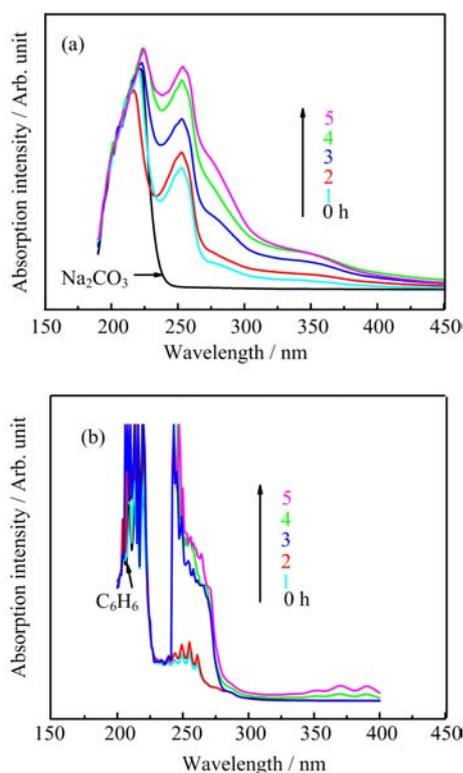


FIG. 2 The relative absorption intensities of (a) aqueous solution and (b) benzene for reaction of sodium carbonate and benzene at different UV-light exposure time.

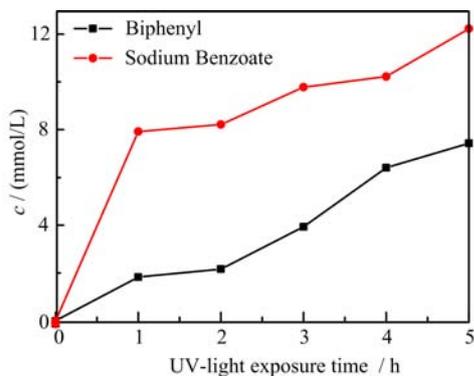


FIG. 3 The relations between the concentrations of sodium benzoate and biphenyl and UV-light exposure time. Determined by GC. The formation of biphenyl or benzoate was not observed without UV-light exposure.

MgCO₃ and CdCO₃. After the same 5 h of UV-light exposure, the concentrations of benzoate anion and biphenyl generated from the reaction of benzene with NaHCO₃ are significantly lower than the product concentrations of the reaction of benzene with Na₂CO₃. We believe this is caused by the incomplete ionization of bicarbonate. Since CO₂ could form CO₃²⁻ in water, we also investigated the reaction of carbon dioxide with benzene at the room temperature and 1 atm pressure.

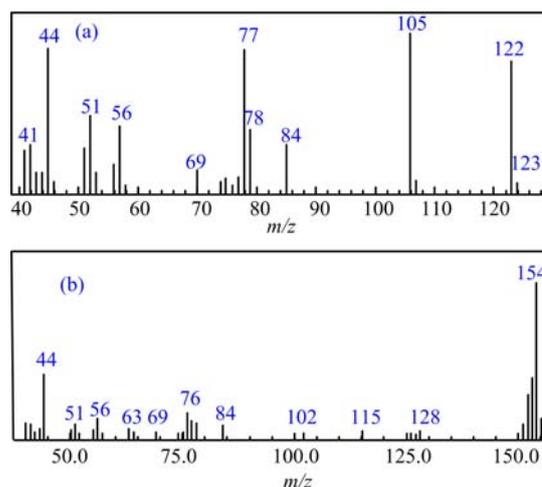


FIG. 4 GC/MS spectra of (a) benzoic acid and (b) biphenyl prepared by light-induced reaction of sodium carbonate and benzene after post-treatment.

TABLE I The reaction results of benzene with different carbonates after 5 h of UV-light exposure, which were determined by GC.

Substance	Product concentration/(mmol/L)	
	Benzoate anion	Biphenyl
Na ₂ CO ₃	12.2	7.4
MgCO ₃		
CdCO ₃		
NaHCO ₃	8.7	2.9
CO ₂	Trace	Trace

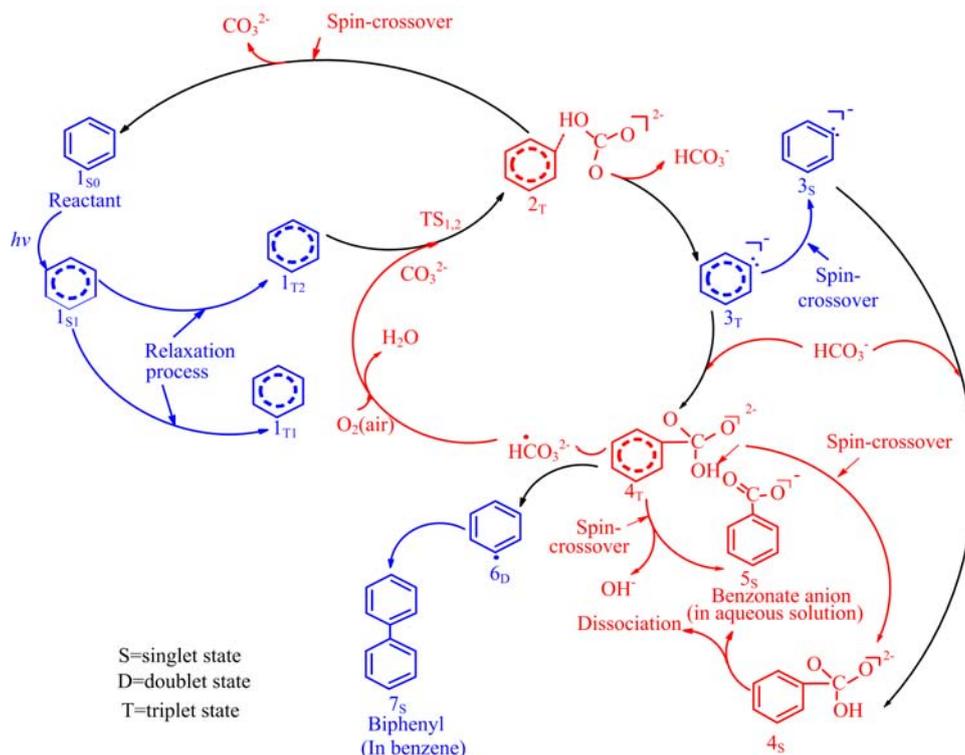
After 5 h of UV-light exposure, we only detected trace amounts of benzoate and biphenyl. Therefore, we believe the carbonate anion is the actual reactant in the reaction.

C. GC/MS analysis

After UV-light exposure, the products were obtained by post-treatment process. In the aqueous solution, diluted hydrochloric acid was added, then, water was extracted with ethyl acetate. Finally, benzoic acid can be obtained through reduced-pressure distillation. In benzene, biphenyl was obtained after separation by reduced-pressure distillation. The GC/MS data of benzoic acid and biphenyl are shown in Fig.4. The NMR measured results of benzoic acid and biphenyl are provided in the supplementary material (Fig.S2–S5).

In Fig.4(a), the m/z of 122, 105, and 77 are benzoic acid, C₆H₅CO⁺ and C₆H₅⁻, respectively. In Fig.4(b), the m/z of 154 and 76 are the biphenyl and C₆H₄⁻. The excess sodium carbonate in water may result in the $m/z=44$ of carbon dioxide in Fig.4.

From the above data, we can conclude that the sodium benzoate is the primary product of the reaction



Scheme 1 Proposed mechanism of the light-induced reaction of benzene and carbonates in aqueous solution (red) and in benzene (blue).

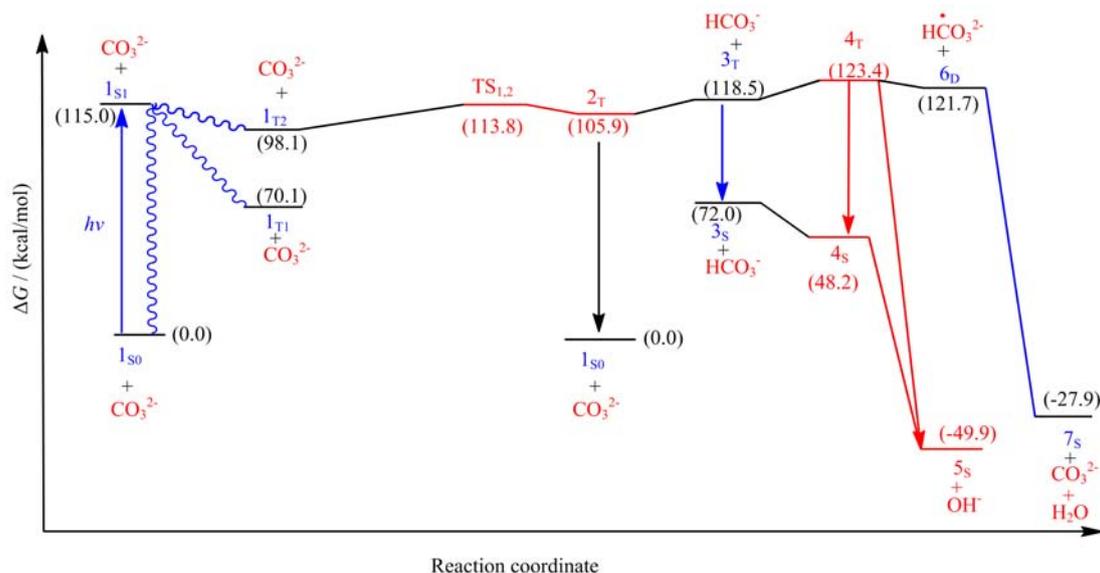


FIG. 5 Free energy profile of light-induced reaction between benzene and carbonates in aqueous solution (red) and in benzene (blue). Free energies of the intermediates, transition state, and product in the reaction are shown in parentheses.

between sodium carbonate and benzene, and biphenyl is possibly formed by combining two benzene radicals.

D. DFT calculations

The proposed mechanism of the light-induced reaction of benzene and carbonates is shown in Scheme 1.

Figure 5 shows the corresponding free energy profile. Figure 6 shows the optimized structures of a key transition state TS_{1,2} and two important intermediates 2_T and 4_T.

At the beginning of the reaction, a benzene molecule is excited to the first excited singlet state 1_{S1}. The sim-

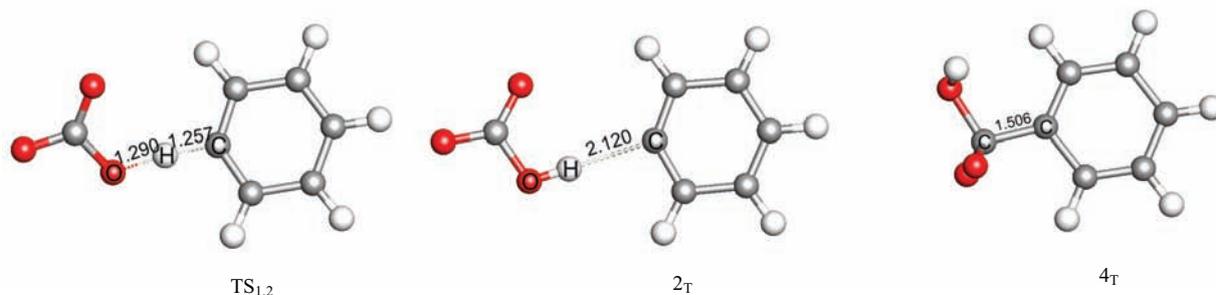


FIG. 6 Optimized structures of $TS_{1,2}$ ($1746i\text{ cm}^{-1}$), 2_T and 4_T . Bond lengths are in Å.

ilar excitation of benzene has been reported [23–28]. The TDDFT results of excited orbitals are shown in supplementary material. Then, the benzene molecule can easily relax to triplet states 1_{T2} and 1_{T1} . In order to form benzoate acid and biphenyl, a C–H bond of benzene must be broken by the carbonate. The lowest transition state for the breaking of a C–H bond is $TS_{1,2}$, in which a proton is transferred from benzene to CO_3^{2-} . $TS_{1,2}$ is 15.7 kcal/mol higher than 1_{T2} and 43.7 kcal/mol higher than 1_{T1} in free energy with a spin multiplicity of three. Such barriers indicate that only the benzene molecule at its second excited state 1_{T2} approaches a carbonate anion in the phase interface of aqueous solution and one transfer a proton to CO_3^{2-} for the formation of intermediate 2_T .

From 2_T , the reaction has various pathways to form the final products with spin-crossovers. 2_T to 1_{S0} and CO_3^{2-} (optimized structures in Fig.6) is 105.9 kcal/mol downhill with the change of spin multiplicity from three to one. Therefore, we believe the ground state 1_{S0} benzene is unable to react with carbonate anion. At the same time, in the phase interface of aqueous solution and benzene, the intermediate 2_T is dissociated to 3_T and HCO_3^- with 12.6 kcal/mol uphill, and then 3_T to 3_S is 46.5 kcal/mol downhill through spin-crossover. Next, HCO_3^- approaches 3_T and 3_S , and forms 4_T and 4_S through electrophilic reaction, respectively. Then, 4_T is dissociated to two radicals, 6_D and $\cdot HCO_3^{2-}$ with 1.7 kcal/mol downhill. Then, 7_S (biphenyl) is formed through the combination of two 6_D radicals. Meanwhile, 4_T and 4_S quickly form 5_S (benzoate anion) through OH^- dissociation, and, $\cdot HCO_3^{2-}$ is oxidized into CO_3^{2-} . Finally, the carbonate anion is regenerated with the formation of biphenyl.

From the above analysis, we can conclude that the low yield of product is due to the low concentration of the excited benzene through relaxation process and the spin-crossover, as well as the quick conversion of 2_T to 2_S . The spin-crossover also affects the reaction pathway. In order to make the reaction proceed continuously, 2_T needs to stay as triplet. Because the barrier is 17.5 kcal/mol uphill from 2_T to 4_T , the pathway $2_T \rightarrow 3_T + HCO_3^- \rightarrow 4_T \rightarrow 6_D$ is thermodynamically less favorable than the pathway

TABLE II Relative free energies of $1_{T2} \rightarrow TS_{1,2}$ and $1_{S0} \rightarrow 4_T$ obtained by using different density functionals.

Functional	$\Delta G / (\text{kcal/mol})$	
	$1_{T2} \rightarrow TS_{1,2}$	$1_{S0} \rightarrow 4_T$
M06	15.7	123.4
B3LYP	13.5	128.1
CAM-B3LYP	15.7	127.4
M06L	7.0	123.0
wb97xd	13.5	127.3
PBE0	9.1	122.5
HSE06	5.8	122.0

$2_T \rightarrow 3_T + HCO_3^- \rightarrow 3_S + HCO_3^- \rightarrow 4_S$. We believe these two pathways are competitive.

E. Evaluation of density functionals

In order to examine the dependence of density functionals of this light-induced reaction, other six well-known or recently developed density functionals, including B3LYP [37, 38], CAM-B3LYP [39], M06L [40], ω B97XD [41], PBE0 [42–44], and HSE06 [45, 46], were selected to calculate the relative free energies of $1_{T2} \rightarrow TS_{1,2}$ and $1_{S0} \rightarrow 4_T$ using the same basis set for the structures optimized by the M06 functional. As shown in Table II, the differences of calculated relative free energies using these six density functionals are less than 10 kcal/mol. For 4_T , the largest difference between the relative energies calculated by using different functionals is less than 5% compared to the relative energies of 4_T . Such a small ratio indicates a weak dependence of density functionals for this light-induced reaction system.

IV. CONCLUSION

In summary, we found benzene can react with carbonates after UV excitation. The DFT method was used to investigate the mechanism of this light-induced reaction. Calculation results indicate that the excited

benzene can react with carbonate anion in the phase interface of benzene and aqueous solution. Both the relaxation process of 1_{S1} and the quick conversion of $2_T \rightarrow 2_S$ result in the low yield of products. Since the final products of benzoic acid and biphenyl are distributed in two phases and are easily separated without complicated post-treatment process, our finding may provide new ways for the production of chemicals without difficult separation process.

Supplementary materials: NMR, free energies and atomic coordinates of all optimized structures, TDDFT calculation results and reaction apparatus are given.

V. ACKNOWLEDGMENTS

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