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High Sensitive Detection of Carbon Dioxide by Pyrimido[1,2-a]benzimidazole derivative: Combining Experimental and Theoretical Studies

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In present paper, a “light-up” chemsensor with a highly specificity for carbon dioxide detection using Pyrimido[1,2-a]benzimidazole derivative (P1H) in liquid media has been developed. The results show that the P1H reacts with carbon dioxide activated by basic ion to form carboxylic acid compound (P1-COOH). These results provide a possible method for carboxylation reactions of P1H using carbon dioxide based on vinyl carbanion as well. The complete reaction mechanism cycle was described by DFT calculation as well.

1. Introduction

With the deterioration of global warming and its secondary induced disasters, researches on greenhouse gases chemistry have caught urgent attention. The capture and utilization of these gases have been greatly promoted in both laboratorial and industrial application for the last decades. Among those researches, the detection, capture and conversion of the abundant, easily available and renewable carbon dioxide as green C1 feedstock have been considered as a sustainable strategy, seeking to balance the industrial development and environmental protection. Because of the inherent kinetic stability, carbon dioxide hardly reacts directly with the organic reactants without being activated by potent catalyst systems. It is well known that the catalyst systems like metal-containing complexes, nitrogen-base (e.g. frustrated amidine and guanidines) and task-specific ionic liquids can activate the carbon dioxide efficiently. Among those catalysts, some special nitrogen-based basic precursors including N-heterocyclic carbenes (NHCs)\(^{8}\), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)\(^{9}\) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)\(^{10,11}\) are able to activate and react with carbon dioxide to form zwitterionic adducts under CO\(_2\) atmosphere. Unfortunately, these base-CO\(_2\) adducts have been proved to be extremely unstable and unobtainable in the presence of ambient moisture. Strict operation condition, such as the water-free and oxygen-free conditions, is necessary for these reactions. For example, direct carboxylation of C-H bond with carbon dioxide is an important reaction in organic synthesis via using CO\(_2\) as the electrophile and other organometallic reagents as nucleophile. Typically, nucleophile such as organolithium, organozinc and organic manganese are universally taken as precursors, and this method is always limited by low catalytic performances, harsh reaction conditions, and restricted substrate scope. Photosynthesis in nature is a process utilized by plants and other organisms to convert light energy to chemical energy via reaction between carbon dioxide and water in mild condition. The key step of photosynthesis is that RuBP enzyme reacts with carbon dioxide which leads to the atmospheric carbon dioxide fixation at its C2 center in the carboxylation reactions(figure 1). The reaction proceeds through several elemental steps, including enolization and deprotonation, yielding the 2,3-enediolate, a carbanion that contains double phosphate ester and is the substrate of carbon dioxide addition(figure 1). These researches indicate that the carbanion hold an efficient capture and activation for carbon dioxide, and transfer carbon dioxide to carboxylic acid compound.

Figure 1. Suggested multistep mechanism for the carboxylation reaction catalyzed by rubisco.
taking inspiration from nature, we report an high effective method for sensitive detection of carbon dioxide using carbamion in mild condition. The results indicate that the PIH can react with carbon dioxide rapidly and sensitively in the presence of excess F- ion to form the carboxylation product. The reaction mechanism was confirmed by its spectroscopic analysis. Furthermore, theoretical calculations provided detailed explanations to the phenomena.

2. Experimental

2.1 Chemicals and reagents

All commercially available reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. Absorption spectrometry was performed using Gold S54T spectrophotometer of Lengguang Company, and fluorescence spectrometry was performed using F-7000 FL Spectrophotometer of Hitachi. Melting points were determined in open capillaries. 1H NMR and 13C NMR spectra were recorded with a Bruker AVANCE 500 spectrometer with use of the deuterated solvent as the lock and TMS as an internal reference. Elemental analysis was performed on Elementar Vario vario EL III. Mass spectra were acquired using a triple quadrupole mass spectrometer (6430 QqQ/LC/MS system; Agilent Technologies, USA) equipped with an internal reference. Tetrabutylammonium salts (F300 suite programs. Geometrical optimization, including transition structure searches were performed by the hybrid density functional B3LYP method and standard 6–311G(d,p) basis set. All reactants and intermediate had no imaginary frequency, and the transition states were ascertained by vibrational analysis with only one imaginary frequency mode. The zero-point energy was calculated by using the vibrational frequencies. In the case of transition states, the vibration was associated with a movement in the direction of the reaction coordinate. Intrinsic reaction coordinate calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products. The solvent effects have been considered using a relatively simple self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM). The solvent used in this calculation is DMF. The values of the relative energies with zero-point energy correction (ΔE0) were calculated and used on the basis of the total energies of the stationary points.

2.2 Synthesis of 3,4-Dichlorocyclobutene-1,2-dione

A mixture of squaric acid (1.14 g, 10 mmol), thionyl dichloride (1.8 ml, 20 mmol) and DMF (200ul) in dry benzene (10 ml) was refluxed for 6 h at 60°C. The solvent was evaporated in vacuo and hexane (20 ml) was added, then the soluble products were separated from gummy precipitates. Concentrating and cooling to give yellow crystalline which was used in the next step without further purification (0.82 g, 5.4mmol), yield 54%.

2.3 Synthesis of PIH

A 2-fold ethanol solution (30ml) of 2-aminobenzimidazole (798mg, 6mmol) was added into fresh 3,4-Dichlorocyclobutene-1,2-dione (750mg, 5mmol) under vigorous stirring, and the mixture was stirred at room temperature for 20min. Then the solvent was removed in vacuo and the residue purified on a column (1% methanol in chloroform as eluent) to give PIH in 41% yield (563mg, 2.08mmol) M.P. 252-253°C. 1H NMR (400 MHz, DMSO-d6) ppm 10.08 (s, 1H), 8.39 (d, J = 8.22 Hz, 1H), 7.94 (d, J = 8.26 Hz, 1H), 7.70-7.46 (m, 2H), 4.49 (q, J = 7.11 Hz, 2H), 1.46-1.32 (m, 3H). 13C-NMR (400 MHz, DMSO-d6), 163.35(1C), 152.60(1C), 147.44(1C), 145.28(1C), 137.23(1C), 127.60(1C), 127.38(1C), 123.23(1C), 120.24(1C), 113.93(1C), 110.99(1C), 63.15(1C), 14.45(1C). Anal. Calcd for PIH: C, 56.64; H, 3.70; N, 15.26. Found: C, 56.60; H, 3.70; N, 15.21.

2.4 Computational detailed

All the theoretical calculations were performed with Gaussian 09 suite programs. Geometrical optimization, including transition structure searches were performed by the hybrid density functional B3LYP methods and standard 6-311G(d,p) basis set. All reactants and intermediate had no imaginary frequency, and the transition states were ascertained by vibrational analysis with only one imaginary frequency mode. The zero-point energy was calculated by using the vibrational frequencies. In the case of transition states, the vibration was associated with a movement in the direction of the reaction coordinate. Intrinsic reaction coordinate calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products. The solvent effects have been considered using a relatively simple self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM). The solvent used in this calculation is DMF. The values of the relative energies with zero-point energy correction (ΔE0) were calculated and used on the basis of the total energies of the stationary points.

3. Results and discussion

At the beginning, a yellow solid PIH with luminescence was synthesized inadvertently by adding an EtOH solution of 2-aminobenzimidazole into fresh squaric acid dichloride under vigorous stirring (Scheme 1). The X-ray crystal structure of PIH is depicted in Figure 2. The whole fused heteroaromatic system is nearly planar except ethoxycarbonyl. The dihedral angle between the pyrimidine ring and ethoxycarbonyl arm is 76.63°. Unexpectedly, the chemical shifts (δ) of the H atom(C8-H) of pyrimidine ring is 125 ppm and 9.72 ppm in DMSO-D6 and CD3CN-d3, which mean that C8-H possesses relative acidity and easily forms a vinyl carbamion intermediate in the presence of base (Figure S1). This special feature emboldened us to build the hypothesis that carbon dioxide conversion can be implemented bases on PIH. This process is similar to imidazolium-based precursors of NHCs.
In order to test this hypothesis, we first investigated the possibilities of the deprotonation of C8-H with different basic anions using UV-vis spectrum in CH$_3$CN. As shown in Figure 3, the absorption intensity of receptor P1H undergoes a significant increasing (from 0.455 to 0.937) and an obvious red shift (from 345 to 390nm) when adding excess basic F$^-$ ion (as the tetrabutylammonium salt, TBAF). And the pale-yellow solution turns into an olivine color. Further examination revealed that P1H exhibited a highly selectivity for the fluoride anion over other anions (Figure S2).

Whereafter, CO$_2$ gas was injected into the CH$_3$CN solution above, a slight downfright was observed at 390nm and the peak appeared at 510nm. It increased with the injection of carbon dioxide and quickly got saturated. The color of the solution was observed to be changed from olivine to red. This means that P1H allows for the sensing of carbon dioxide with high sensitivity. In fact, except for Yoon's group $^{21}$, there are few reports for the optical sensor for carbon dioxide.

For luminescence, the original emission band at 550nm (orange-yellow) of P1H was rapidly quenched in CH$_3$CN with the addition of F$^-$ ion (10 equiv). Consistent with the UV-vis titration results, the emissive intensity of mixtures was dramatically enhanced and broadened with the injection of carbon dioxide gas (Figure 4). The mixtures presented a distinctly orange emission at 520nm. In the same way, addition of poorly basic anion AcO$^-$, Cl$^-$, Br$^-$ and I$^-$, as expected, hardly induced any considerable variations in emission spectroscopies of P1H in CH$_3$CN solution (Figure S3).

Figure 2. ORTEP diagram of compound P1H.
Curiously, one drop deionized H₂O was added in above ¹H NMR titration solution for testing the moisture-sensitive of the P1-COOH. The Figure 5f indicated that the P1-COOH was not very stable in the presence of ambient moisture, and slowly decomposed to afford the initial P1H after 24 hours (Figure 5g and confirmed by TLC). This process is similar to decarboxylation of uridine 5′-monophosphate to give uridine 5′-monophosphate by decarboxylase in organisms.²² 

In practice, because of unstability, we failed to obtain pure P1-COOH adducts by means of fresh column chromatography.

To the best of our knowledge, a tentative mechanism for P1H capturing CO₂ with the addition of excess F⁻ ions in CH₃CN was detailedly illustrated in Scheme 1. Firstly, the adjacent Ha and Hb of P1H are able to coordinate with the additional F⁻ ions by virtue of two strong hydrogen bonds; with addition of excess F⁻ ions, the activated C-Ha bond will be fractured to afford an vinyl carbamion intermediate [P1⁻] and acid molecular HF. Finally, the nucleophilic [P1⁻] will immediately attack CO₂ at the carbonyl to produce the carboxylate P1-COO⁻, which is easily acidized in the case of HF. In order to give an explanation for this reaction mechanism, density functional theory (DFT) calculation was carried out.

The reaction energy profile of carboxylation via CO₂ gas for the P1H in the presence of [Bu₄N]F.
 afford the carboxylate P1-COO$. The step holds an energy barrier of 1.31 kcal mol$^{-1}$ and exothermic heating of 2.15 kcal mol$^{-1}$. The P1-COO$^-$ can easily accept proton from HF with a barrierless process to form P1-COOH. In fact, the P1-COOH is not stable in air at room temperature and able to react with water by decarboxylation reaction and give P1H. The energy barrier and reaction heat of this reaction is 26.74 and -11.76 kcal mol$^{-1}$. The high energy barrier shows that this reaction only can carry out very slowly.

4. Conclusions

In summary, we have developed a biomimetic “light-up” chemosensor with a highly specificity for carbon dioxide detection using Pyrimido[1,2-a]benzimidazole derivative (P1H) in liquid media. On the basis of spectroscopic and theoretical analyses, Pyrimido [1,2-a]benzimidazole tends to capture carbon dioxide to afford carboxylic acid in the presence of excess F$^-$ ion in CH$_3$CN. By combining experimental and computational findings, the method also provides a possible method for carboxylation reactions of P1H using carbon dioxide based on vinyl carbanion. It will pave a practical way to accomplish high sensitive detection of carbon dioxide.

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Notes and references