

Reaction IR Spectroscopy and MCR-ALS Analysis for Investigation of Reaction Mechanisms

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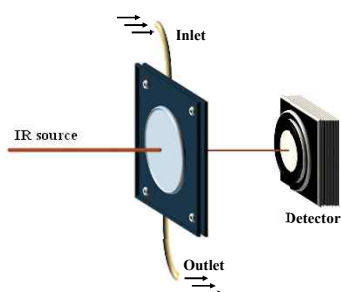
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ABSTRACT

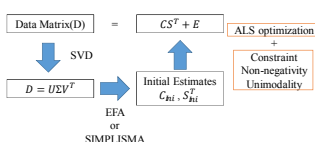
Reaction IR spectroscopy, and Multi Curve Resolution-Alternating Least Square (MCR-ALS) are very useful techniques to define reaction mechanisms with real time. We have developed these techniques, we hope to test the ours. Benzo fused azoles are important building blocks in therapeutically active compounds, natural products, and functional materials. Recently, Prof. Cheon's group in Korea University proposed a cyanide based powerful metal-free catalyst for synthesis of benzoxazole molecules and they asserted that the cyanide attacks the carbon of imine and enables the orbital interaction between σ^* of C-CN and the lone pair on the X-group (Baldwin's 5-exo-tet rule). However, Chen et. al. in Nankai University, argued this mechanism with computational method. They reported the activation energy of this mechanism is too high for the facile preparation of benzoxazole compounds on room temperature. Therefore, we tried IR spectroscopic, computational and MCR-ALS research to verify the mechanisms.

INTRODUCTION

1. Flow type Reaction IR Cell

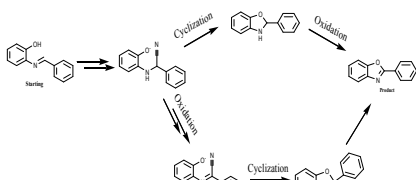


2. MCR-ALS method



SVD : Singular Value Decomposition
EFA : Evolving Factor Analysis
ALS : Alternating Least Square
 $\chi = \xi c$ (ξ : molecular specific coefficient)
 $A = \epsilon bc$ (Beer-Lambert Law)

3. Reaction hypotheses



COMPUTATIONAL METHOD

All the computations reported in this work were carried out using Gaussian 09 program package. All structures were optimized using the M06-2X functional method with 6-31+G(d) basis level. The UM06-2X functional method was used for the molecules that has doublet and triplet spin states structures as oxygen (O_2) molecule, and radical intermediate states. Frequency calculations were implemented at the same functional to confirm the optimized structures but the basis set was used higher level, as 6-311++G(3df,2pd). Solvation model was implemented CPCM model with DMF solvent($\epsilon=36.7$). All the spectroscopic intensity in this work are reported in atomic unit (a.u.), and peak position are scaled by 0.943.

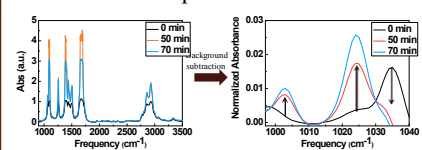
EXPERIMENTAL METHOD

Experiment was performed in the same condition which was performed previously by Y. H. Cho, et. al. in Korea University¹⁾. An open test tube were added a phenolic imine (0.25 mmol; 1.0 equiv) and NaCN (12.2 mg; 0.25 mmol; 100 mol%) were dissolved in DMF (1.0 mL). The reaction mixture was stirred at room temperature in an open flask and monitored by FT-IR every 5 min. The complete termination of the reaction was convinced by the peak of the product in the FT-IR. We tried the MCR-ALS analysis to obtain a time profile of reaction components.

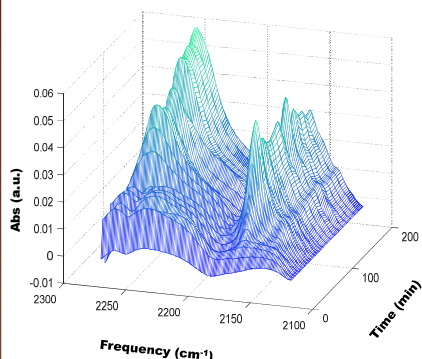
¹⁾ Y. H. Cho, et. al. *Adv. Synth. Catal.*, 2012, 354, 2992-2996

RESULTS

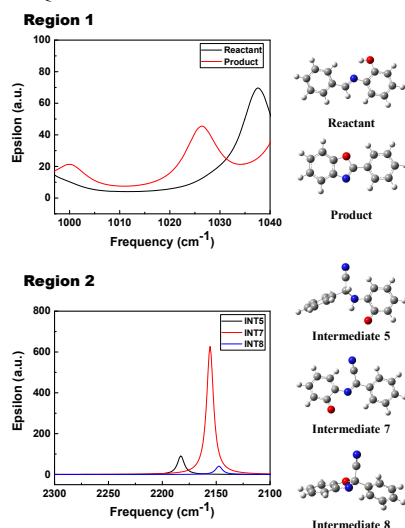
1. Reaction IR Spectra



Vibrational Probe
Region 1: 1000-1040 cm^{-1} reactant and product (aromatic C-H bending modes)
Region 2: 2000-2300 cm^{-1} intermediate molecules (C≡N stretching modes)



2. Quantum Calculations



* Scaling factor: calculated peak position \times 0.943

3. Summary of Calculation

Molecule	Peak Position (cm^{-1})	Vibrational Mode
Reactant	1038	Aromatic C-H bending
Intermediate 5	2183	C≡N stretching
Intermediate 7	2157	C≡N stretching
Intermediate 8	2147	C≡N stretching
Product	1000	Aromatic C-H bending
Product	1026	Aromatic C-H bending

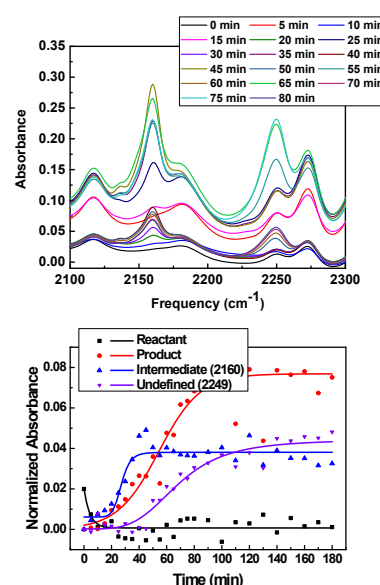
DISCUSSIONS

1. Mode assign of Experimental data

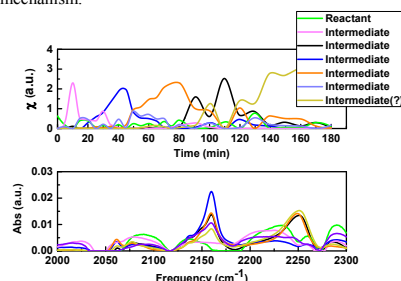
Peak Position (cm^{-1})	Vibrational Mode	Molecule*
1003	Aromatic C-H bending	Product
1024	Aromatic C-H bending	Product
1035	Aromatic C-H bending	Reactant
2150	C≡N stretching	Intermediate 8
2160	C≡N stretching	Intermediate 7
~2200	C≡N stretching	Intermediate 5
2249	C≡N stretching (?)	Undefined

* molecules are estimated.

2. Time profile of Reaction components



Without knowing the shapes of the spectra and the concentration profile, we can decompose the spectroscopic data into the spectra and the concentration profile by using MCR-ALS. Since during the reaction the acquisition of concentration profile is hard, this method will suggest a new way to obtain the concentration information of reaction components. By using this concentration data, we could find the clues to the mechanism.



Conc. & Ack

Conclusion

We could trace the reaction components through above time profile and decomposed IR spectrum. Reaction IR spectroscopy, quantum chemical calculation, and MCR-ALS analysis can provide hints of reaction mechanism.

Acknowledgement

This work was supported by IBS-R023-D1.