APPENDIX A

Conferences and Workshops

1) 5-7 January 2015: The 11th Thai Summer School of Computational Chemistry, at Rajamangala University of Technology Lanna, Nan

2) 21-23 January 2015: Poster presentation at "Pure and Applied Chemistry International Conference (PACCON2015)" at Amari Watergate Hotel, Bangkok

3) 24-27 November 2015: "Molecular Designs for Advanced Materials: Workshop and Conference" at Chiang Mai University, Chiangmai

4) 9-11 February 2016: Oral presentation at "Pure and Applied Chemistry International Conference (PACCON2016)" at BITEC, Bangkok

5) 16-17 November 2016: The 13th Thai Summer School of Computational Chemistry, at Department of Chemistry, Faculty of Science, Chiang Mai University, Chaingmai

6) 16-17 November 2016: Thai-German Mini Symposium on "Functional Organic Materials for Highly Efficient Solar Cells", at Department of Chemistry, Faculty of Science, Chiang Mai University, Chaingmai

APPENDIX B

Publications and Posters

CrossMark

ORIGINAL ARTICLE

TD-DFT Study of Absorption and Emission Spectra of 2-(2′-Aminophenyl)benzothiazole Derivatives in Water

Natthaporn Manojai[1] · Rathawat Daengngern[1] · Khanittha Kerdpol[1] · Nawee Kungwan[1] · Chanisorn Ngaojampa[1]

Abstract Reduction of aromatic azides to amines is an important property of hydrogen sulphide (H_2S) which is useful in fluorescence microscopy and H_2S probing in cells. The aim of this work is to study the substituent effect on the absorption and emission spectra of 2-(2′-aminophenyl)benzothiazole (APBT) in order to design APBT derivatives for the use of H_2S detection. Absorption and emission spectra of APBT derivatives in aqueous environment were calculated using density functional theory (DFT) and time-dependent DFT (TD-DFT) at B3LYP/6-311+G(d,p) level. The computed results favoured the substitution of strong electron-donating group on the phenyl ring opposite to the amino group for their large Stokes' shifts and emission wavelengths of over 600 nm. Also, three designed compounds were suggested as potential candidates for the fluorescent probes. Such generalised guideline learnt from this work can also be useful in further designs of other fluorescent probes of H_2S in water.

Introduction

Intracellular sulfur-containing molecules are involved in many crucial processes in animals and humans. Known biomolecules of the type include glutathione (GSH), cysteine (Cys) and

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homocysteine (Hcy) [1, 2]. Beside these traditional organic examples recent studies also found that the toxic hydrogen sulfide (H_2S) can be produced under cellular regulation and function as a signaling gasotransmitter next to nitric oxide (NO) and carbonmonoxide (CO) [3]. In mammals, H_2S is so far found to be released from lungs, livers, kidneys, pancreases, hearts and brains via the breakdown of Cys and Hcy [4–8]. Imbalance of H_2S quantity in cells could lead to serious physiological malfunctions such as Alzheimer's disease, impaired cognitive ability, gastric mucosal, injury and hypertension [2, 9]. Therefore, the development of H_2S monitoring methods is considered highly important in tackling with these illnesses.

Fluorescent dyeing provides an efficient approach for the H_2S detection. In recent years, several probing strategies for intracellular H_2S have been explored, for instance, copper sulfide precipitation, necleophilic substitutions by H_2S, oxidation of selenoxides and reductions of nitro ($-NO_2$) and azido ($-N_3$) compounds. The last tactic has been actively studied because the azido group can react promptly with H_2S and turn into amino ($-NH_2$) group, while remaining inert against other GSH and other thiols. When attached to a fluorophore the azido group normally turns off the fluorescence due to its ability to quench the excited state of the adjacent fluorophore. Upon the reduction into an amine, the fluorophore suppression terminates and a glow can be observed [1, 2, 10]. So far, several azido fluorogenic probes have been reported, mainly based on well-known fluorophores such as coumarins [11, 12], anthracenes [13], naphthalimide [14], luminol [15] or borondipyrromethene (BODIPY) [16, 17]. However, not every azido dye works well with probing in vivo for a number of challenges. Besides the high sensitivity and fluorescent intensity, the probes are required to have low levels of self-absorption caused by the overlapping of their own absorption and emission bands. Another main challenge is that the probes must emit lights in long wavelengths, preferably in the reddish

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An application of the reaction class transition state theory (RC-TST): Hydrogen abstraction of alkanes by nitrate radical

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Abstract

Kinetics of the hydrogen abstraction reaction of the class alkane + $NO_3{}^\bullet \rightarrow$ alkyl + HNO_3 was studied using reaction class transition state theory (RC-TST) combined with linear energy relationships (LERs). The thermal rate coefficient for the reference reaction of ethane + $NO_3{}^\bullet \rightarrow$ ethyl + HNO_3 was calculated by the canonical variational transition state theory (CVT) incorporating corrections from tunneling using the one dimensional Eckart tunneling approximation. All necessary parameters were derived from the reaction barriers and energies of a representative set of 16 reactions involving a range of alkanes. The outcome rate coefficients from the RC-TST/LER method are far from reproducing the result from the TST/Eckart approach with the differences as large as two orders of magnitude at the temperature range of 200-500 K, and even larger at higher temperature. However, the Arrhenius plots of the rate coefficients from the reaction class method are still in a better agreement with the available experimental results. This still gives a good outlook for the application of calculation results RC-TST/LER method in environmental modelling.

RC-TST

Reaction Class Transition State Theory (RC-TST)

$$k(T) = \kappa(T)\sigma \frac{k_B T}{h} \frac{Q^{\neq}(T)}{\Phi^R(T)} e^{(-\Delta V^*/k_B T)}$$

$$k_t(T) = f(T)\,k_p(T) \qquad f(T) = f_\kappa(T)f_\sigma f_Q(T)f_v(T)$$

$$f_\kappa = \frac{\kappa_t(T)}{\kappa_p(T)} \qquad f_\sigma = \frac{\sigma_t}{\sigma_p}$$

$$f_Q(T) = \left(\frac{Q_t^{\neq}(T)}{\Phi_t^R(T)}\right)\Big/\left(\frac{Q_p^{\neq}(T)}{\Phi_p^R(T)}\right) = \left(\frac{Q_t^{\neq}(T)}{Q_p^{\neq}(T)}\right)\Big/\left(\frac{\Phi_t^R(T)}{\Phi_p^R(T)}\right)$$

Alkane + $NO_3{}^\bullet \rightarrow$ alkyl + HNO_3

Alkane + $NO_3{}^\bullet \rightarrow$ alkyl + HNO_3 Reaction Class

|					
CH_4	+ $NO_3{}^\bullet$	→	HNO_3	+ $\underline{C}H_3{}^\bullet$	Al01
C_2H_6	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3\underline{C}H_2{}^\bullet$	Al02
C_3H_8	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2\underline{C}H_2{}^\bullet$	Al03
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3\underline{C}HCH_3{}^\bullet$	Al04
C_4H_{10}	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2CH_2\underline{C}H_2{}^\bullet$	Al05
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2\underline{C}HCH_3{}^\bullet$	Al06
$CH_3CH(CH_3)CH_3$	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH(CH_3)\underline{C}H_2{}^\bullet$	Al07
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3\underline{C}(CH_3)CH_3{}^\bullet$	Al08
C_5H_{12}	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2CH_2CH_2\underline{C}H_2{}^\bullet$	Al09
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2CH_2\underline{C}HCH_3{}^\bullet$	Al10
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2\underline{C}HCH_2CH_3{}^\bullet$	Al11
$CH_3CH_2CH(CH_3)CH_3$	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2CH(CH_3)\underline{C}H_2{}^\bullet$	Al12
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2\underline{C}(CH_3)CH_3{}^\bullet$	Al13
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3\underline{C}HCH(CH_3)CH_3{}^\bullet$	Al14
	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3CH_2CH(\underline{C}H_2)CH_3{}^\bullet$	Al15
$CH_3C(CH_3)_2CH_3$	+ $NO_3{}^\bullet$	→	HNO_3	+ $CH_3C(CH_3)_2\underline{C}H_2{}^\bullet$	Al16

Principal reaction (Al02)
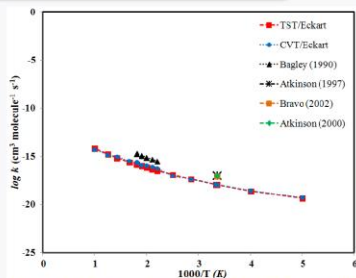
Figure 1. Arrhenius plot of rate coefficients calculated by RC-TST and available experimental data rate coefficients for the reference reaction (Al02).

Determination of Parameters
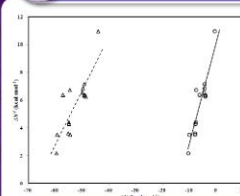
Linear energy relationships (LER) between reaction energy (ΔE) and reaction barrier height ($\Delta V^{\neq}$). ΔE's were calculated at the BH&HLYP/cc-pVTZ (circle symbols and solid line) and AM1 level of theory (Triangle symbols and dashed line).

$$\Delta V^{\neq} = 0.392\Delta E + 26.277 \quad (kcal/mol)$$
(ΔE from AM1 calculations)

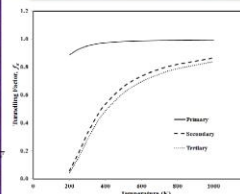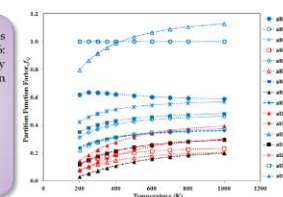$$\Delta V^{\neq} = 0.727\Delta E + 10.162 \quad (kcal/mol)$$
(ΔE from BH&HLYP calculations)

Plot of partition function factors, f_Q as functions of the temperature for Al01-Al16: primary carbon (blue dot line), secondary carbon (red dot line) and tertiary carbon (black dash line).

$f_Q \sim 0.7$ for primary carbon

$f_Q \sim 0.2$ for secondary carbon

$f_Q \sim 0.2$ for tertiary carbon

Plot of tunneling factor , f_κ with temperature for hydrogen abstract reactions on primary carbon (solid line), secondary carbon (dash line) and tertiary carbon (dot line).

$$f_\kappa(T) = 9\times10^{-10}T^3 - 2\times10^{-6}T^2 + 0.0013T + 0.7079$$
$$f_\kappa(T) = 3\times10^{-9}T^3 - 6\times10^{-6}T^2 + 0.0055T - 0.8127$$
$$f_\kappa(T) = 2\times10^{-9}T^3 - 5\times10^{-6}T^2 + 0.0048T - 0.7388$$

Average absolute errors of the total relative rate factor $f(T)$ and its components namely the tunneling(f_κ), partition (f_Q) and potential (f_V) factors as functions of the temperature.
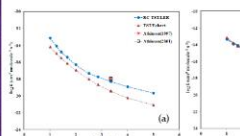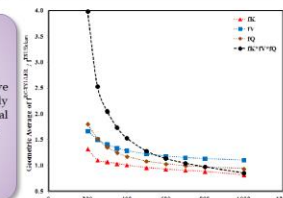

Figure 2. Arrhenius plot of the calculated TST/Eckart thermal rate constants for arbitrary reactions. (a) Al01 (b) Al03 and (c) Al04

Acknowledgements

References

1. T. Piansawan, N. Kungwan, S. Jungsuttiwong, 2013, Comp. Theor. Chem., 1011, 65-74.
2. T.N. Truong, 2000, J. Chem. Phys., 113, 4957-4964.
3. N. Kungwan, T.N. Truong, 2005, J. Phys. Chem. A, 109, 7742-7750.

An Application of the Reaction Class Transition State Theory (RC-TST): Hydrogen Abstraction of Alkanes by Nitrate Radical

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Kinetics of the hydrogen abstraction reaction of the class alkane + $NO_3\cdot \rightarrow$ alkyl + HNO_3 was studied using reaction class transition state theory (RC-TST) combined with linear energy relationships (LERs). The thermal rate coefficient for the reference reaction of ethane + $NO_3\cdot \rightarrow$ ethyl + HNO_3 was calculated by the canonical variational transition state theory (CVT) incorporating corrections from tunneling using the one dimensional Eckart tunneling approximation. All necessary parameters were derived from the reaction barriers and energies of a representative set of 16 reactions involving a range of alkanes. The outcome rate coefficients from the RC-TST/LER method are far from reproducing the result from the TST/Eckart approach with the differences as large as two orders of magnitude at the temperature range of 200-500 K, and even larger at higher temperature. However, the Arrhenius plots of the rate coefficients from the reaction class method are still in a better agreement with the available experimental results. This still gives a good outlook for the application of calculation results RC-TST/LER method in environmental modelling.

Keywords Reaction class transition state theory (RC-TST); Nitrate radical; Hydrogen abstraction Reaction; BH&HLYP

References
1. T. Piansawan, N. Kungwan, S. Jungsuttiwong, 2013, *Comp. Theor. Chem.*, 1011, 65-74.
2. T.N. Truong, 2000, *J. Chem. Phys.*, 113, 4957-4964.
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Publications

1. **Natthaporn Manojai**, Rathawat Daengngern, Khanittha Kerdpol, Nawee Kungwan, Chanisorn Ngaojampa, TD-DFT study of absorption and emission spectra of 2-(2′-Aminophenyl)benzothiazole derivatives in water, *J. Fluoresc*., 27 (2017) 745.

2. **Natthaporn Manojai**, Rathawat Daengngern, Khanittha Kerdpol, Chanisorn Ngaojampa, Nawee Kungwan, Heteroatom effect on photophysical properties of 2-(2'-Hydroxyphenyl)benzimidazole and its derivatives as fluorescent dyes: a TD-DFT study, *Journal of Luminescence*, 2017. *(Accepted)*

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