行政院國家科學委員會專題研究計畫 成果報告

實驗及理論計算小分子醇類於氣相及異相催化分解及氧化反應(3/3)

研究成果報告(完整版)

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執行期間：99年07月01日至100年06月30日
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處理方式：本計畫涉及專利或其他智慧財產權，2年後可公開查詢

中華民國 100年09月09日

中文摘要

交通大學於 97 年 1 月正式成立綠色能源科技中心（CGET, Center for Green Energy Technology），並委以林明璋院士主持，以全力發展本校再生能源之研究。中心的主要研究目標將朝跨領域整合型研究的方向來發展。專注的跨領域研究，將利用最先進的研發技術來從事新型矽薄膜多層光電池、量子光電池、有機光電池及乙醇燃料電池等研究，並配合高階的理論計算來更進一步瞭解這些重要體系的光化學及燃料系統的化學反應及物理特性。

本三年期國科會個人計畫(97 年 7 月 1 日至 100 年 6 月 30 日)，配合 CGET 發展跨領域研究的方向為主軸，和各研究領域的專家學者密切合作，以進行下列重要課題的基礎研究：(1)利用交通大學的衝擊波管做小醇類分子(CH_3OH, C_2H_5OH 及 i-C_3H_7OH)熱分解及燃燒反應機制確立及有關基礎反應化學動力學的研究；(2)小醇分子在固態氧化物表面熱分解及氧化的高階量子計算以供給固態氧化物燃料電池(SOFC)大型模擬的應用。

此報告包含 99 年 7 月 1 日至 100 年 6 月 30 日之研究成果。

關鍵詞：再生小醇分子、熱分解及氧化反應、氧化物燃料電池(SOFC)電極反應

英文摘要

At National Chiao Tung University (NCTU), an interdisciplinary renewable energy research center, CGET (Center for Green Energy Technology), was established in January 2008 with emphasis on studies of a new generation of silicon thin-film solar cells, organic solar cells and ethanol fuel cells. Prof. M. C. Lin of Emory University has assumed the Center's directorship to coordinate the interdisciplinary research program funded by the Ministry of Education through the MOE-ATU Project. He is also in charge of the coordination of the ethanol fuel cell sub-project.

The proposed research support from NSC covers the period of July 1, 2008 – June 30, 2011 for the administration of CGET by the PI as well as for collaborative studies with faculty members at NCTU on high temperature kinetics and mechanisms for small alcohol decomposition and oxidation reactions using a shock tube currently available at NCTU. The measured kinetics for elementary processes related to their decomposition and oxidation at high temperatures such as H + ROH and OH + ROH (R = CH_3, C_2H_5 and i-C_3H_7), as well as the decomposition of RO radicals (CH_3O, C_2H_5O, i-C_3H_7O and their structural isomers, CH_2OH, CH_3CHOH, CH_3CHOCH_3, CH_3COHCH_3 and $CH_3CHOHCH_2$), will be interpreted with high-level *ab initio* molecular orbital and statistical theory calculations.

In addition, the decomposition and oxidation of the alcohols and alkoxyl radicals on solid oxide fuel cell electrode surfaces will be investigated by large-scale quantum chemical calculations to elucidate their decomposition mechanisms and predict their decomposition kinetics based on computed potential energy surfaces.

關鍵詞：Decomposition and oxidation, Small alcohols, Ethanol SOFC, Quantum calculations

目　　錄

報告內容

一、前言

This report covers the period Jul. 1, 2010 – Jun 30, 2011 centering on: 1), Determination of the kinetics and mechanisms for thermal decomposition and oxidation of small alcohols at high temperatures using a shock tube currently available at NCTU. The measured kinetics for elementary processes have been interpreted with high-level *ab initio* molecular orbital and statistical theory calculations; 2), Reactions related to the operation and optimization of ethanol solid oxide fuel cell (SOFC); 3), Management of the Center for Green Energy Technology and the Center for Interdisciplinary Molecular Sciences at NCTU. In the proposed collaborative research, 15 full papers have been completed and submitted for publications with additional 11 papers credited to NSC for works carried out at Emory University but written or edited by the PI during the past year visiting NCTU. Representative cases studied are discussed briefly below. More detailed results can be found in the list of publications covering the reporting period.

二、結果與討論

1. Ab initio chemical kinetics for the $O(^3P)$ + CH_3 reaction: The effect of roaming transition states on the CHO + H_2 formation

The $O(^3P)$ + CH_3 reaction is one of the most influential processes in the combustion of hydrocarbon and bio-fuels. It produces H atom and CH_2O as well as CHO + H_2. The latter product pairs were first detected by Leone and coworkers by time-resolved CO emission with FTIR [1]. The surprising result was reported by Harding and Klippenstein through on-the-flight CPMD calculations to be a reaction which takes place without a transition state [2]. We investigated the kinetics and mechanism of this peculiar reaction at the CCSD/aug-cc-pVTZ, CCSD/aug-cc-pVDZ and B3LYP/6-311+G(3df,2p) levels of theory. The energies of all stationary points have been refined by single-point energy calculations at the CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVTZ level of theory. The predicted PES presented in Fig. 1 shows that both CH_2O + H and CHO + H_2 can be produced by isomerization/decomposition of the excited CH_3O, from which the TS3 → LM1 step is favorable for the CH_2O + H formation and the consecutive well-defined path TS3 → LM1 → TS7 → LM2 → TS4 step leads to the CHO + H_2 products, contrary to the conclusion reached earlier by Harding and Klippenstein that the formation of the latter products occurred without a transition state. The rate constants and the individual product branching ratios predicted with the micro-canonical VTST/RRKM theory according to the CCSD(T) potential energy surface are in good agreement with experimental data as illustrated in Fig. 2 and Fig. 3, respectively.

TS7 and TS4 shown in Fig. 1 are effectively roaming transition states for the formation of CHO + H_2 which are competitive only with the presence of a large amount of energy from the O + CH_3 chemical activation reaction.

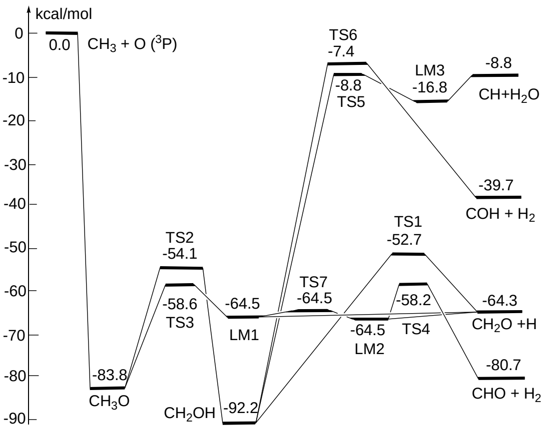

Fig. 1. Schematic energy diagram of the CH_3+O (^{3}P) predicted on the ground electronic doublet state potential energy surface at the CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVTZ level of theory.

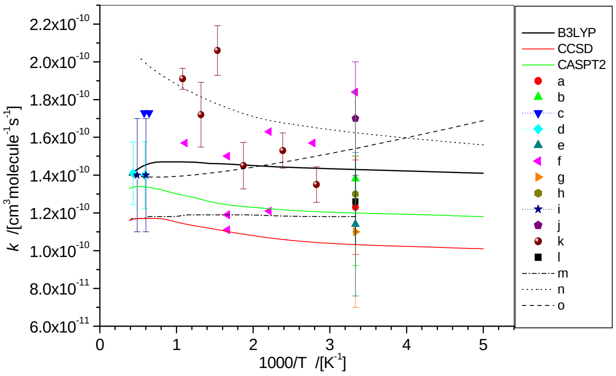

Fig. 2. Predicted total rate constant in the CH_3 + O reaction in the temperature range from 200 to 2600 K, computed with different Morse potentials for the CH_3 + O association process comparing with available data. a. Washida, 1973; b. Washida, 1980; c. Biordi, 1975; d. Bhaskaran, 1980; e. Plumb; 1982; f. Slagle, 1987; g. Zellner, 1988; h. Oser, 199; i. Lim, 1992; j. Fockenberg, 1999; k. Fockenberg, 2002; l. Hack, 2005; m. Dean, 1987; n. Yagi, 2004; o Harding, 2005.

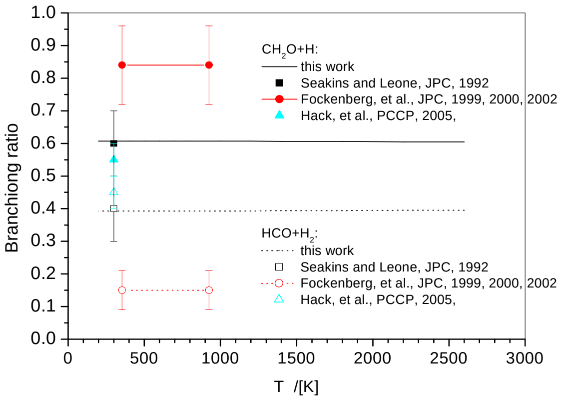

Fig. 3. Individual product rate constants and total rate constant in the CH_3 + O reaction in temperature range from 200 to 2600 K.

2. Kinetics for CH_3O and CH_2OH isomerization/decomposition reactions

Both CH_3O and CH_2OH isomeric radicals play a key role in the decomposition and oxidation of CH_3OH. They are also important intermediates in the combustion of hydrocarbons at the end of the oxidation chain processes. They can be directly formed by reactions such as $CH_3 + O_xH$ and $CH_3 + O_2$. We have studied the ground electronic doublet-state potential energy surface of the $C_1H_3O_1$ system at the CCSD(T)/aug-cc-pVTZ and G2M levels of theory (see Fig. 1). The stationary points were optimized by using the CCSD/aug-cc-pVTZ, CCSD/aug-cc-pVDZ and B3LYP/6-311+G(3df, 2p) methods. The result shows that there are three low energy barrier processes including $CH_2O + H \rightarrow CHO + H_2$, $CH_2O + H \rightarrow CH_2OH$, and $CH_2O + H \rightarrow CH_3O$. For these three reactions computed at the CCSD(T)/aug-cc-pVTZ// CCSD/aug-cc-pVTZ level, the forward potential barriers are predicted to be 6.1, 11.6, and 5.7 kcal/mol, with the corresponding reverse barriers of 22.5, 39.5, and 25.2 kcal/mol, respectively. The heats of formation of CH_2OH and CH_3O are predicted to be -1.2 ± 0.4 and 7.6 ± 0.3 kcal/mol, respectively, using isodesmic reactions. The rate constant for the hydrogen abstraction reaction has been calculated by the canonical variational transition state theory with quantum tunneling and small-curvature corrections to be $k(CH_2O + H \rightarrow CHO + H_2) = 2.28 \times 10^{-19}\ T^{2.65} \exp(-766.5/T)$ cm^{3}molecule^{-1}s^{-1} for the temperature range 200–3000 K. The rate constants for the addition and decomposition reactions have been calculated by the microcanonical RRKM theory with the time-dependent master equation solution of the multiple quantum well system in the temperature range 200 – 3000 K at 1 Torr – 100 atm pressures. The predicted rate constants are in good agreement with most of available data (see Figs. 4 and 5). At 1 atm Ar pressure, the rate constants for the CH_2OH and CH_3O formation can be expressed in units of cm^{3}molecule^{-1}s^{-1} as:

$$k_a^{1atm}(CH_2OH) = 7.00 \times 10^{-10}\ T^{-1.40} \exp(-2612.5/T) \quad (200 - 1000\ K)$$
$$= 3.41 \times 10^{7}\ T^{-6.23} \exp(-7720.3/T) \quad (1000 - 3000\ K)$$
$$k_a^{1atm}(CH_3O) = 2.32 \times 10^{-10}\ T^{-1.22} \exp(-1813.2/T) \quad (200 - 800\ K)$$
$$= 3.10 \times 10^{8}\ T^{-6.79} \exp(-5573.9/T) \quad (800 - 3000\ K)$$

and those for the CH_2OH and CH_3O decomposition reactions can be expressed in unit of s^{-1} as:

$$k_d^{1atm}(CH_2OH) = 4.52 \times 10^{34}\ T^{-7.11} \exp(-22176.3/T) \quad (500 - 3000\ K)$$
$$k_d^{1atm}(CH_3O) = 3.17 \times 10^{24}\ T^{-4.25} \exp(-13104.9/T) \quad (300 - 3000\ K)$$

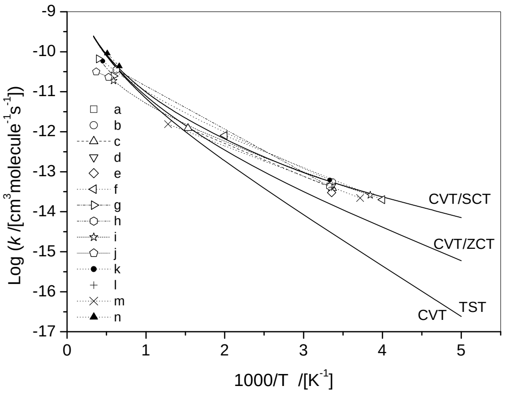

Fig. 4. Rate constants, $k(CH_2O+H)$, of the $CH_2O + H \rightarrow CHO + H_2$.

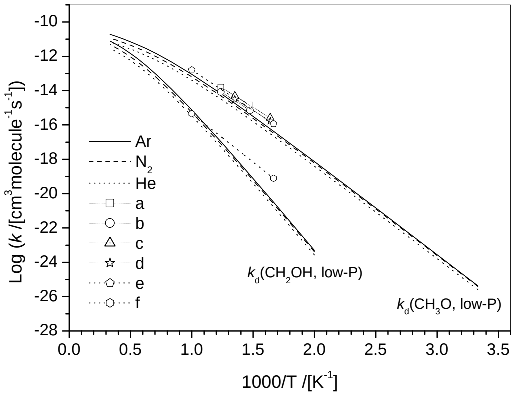

Fig.5. Low pressure rate constants, $k_d^0(CH_2OH)$ and $k_d^0(CH_3O)$, for the decomposition reactions of CH_2OH and CH_3O, comparing with available data in the literature..

3. Thermal decomposition of C_2H_5OH in shock waves under highly diluted conditions

The thermal decomposition of C_2H_5OH highly diluted in Ar (1 and 3 ppm) has been studied by monitoring H atoms using the atomic resonance absorption spectrometry (ARAS) technique behind reflected shock waves over the temperature range 1450 – 1760 K at fixed pressure; 1, 1.45 and 2 atm. The rate constant and the product branching fractions have been determined by analyzing temporal profiles of H atoms; the effect of the secondary reactions on the results has been examined by using a detailed reaction mechanism composed of 103 elementary reactions. The apparent rate constant of ethanol decomposition can be expressed as $k_1/s^{-1} = (5.28 \pm 0.14) \times 10^{10} \exp[-(23530 \pm 980)/T]$ (T = 1450 – 1670 K, P = 1 – 2 atm.) without a detectable pressure dependence within the tested pressure range of this study. Branching fractions for producing CH_3+CH_2OH (1a) and $H_2O+C_2H_4$ (1b) have been examined by a quantitative measurement of H atoms produced in the successive decompositions of the products CH_2OH (1a): the pressure dependence of the branching fraction for channel (1a) is obtained by a linear least-squares analysis of the experimental data and can be expressed as $_{1a} = (0.71\pm0.07) - (826\pm116)/T$, $(0.92\pm0.04) - (1108\pm70)/T$, $(1.02\pm0.10) - (1229\pm168)/T$ for T = 1450 – 1760 K, at P = 0.99, 1.45 and 2.0 atm., respectively; The rate constant obtained in this study is found to be consistent with previous theoretical and experimental results; however, the pressure dependence of the branching fraction obtained in this study is smaller than those of previous theoretical works. Modification of the parameters for the decomposition rate in the fall-off region is suggested to be important to improve the practical modeling of the pyrolysis and combustion of ethanol. These results have been published in J. Phys. Chem. A, 2011, 115, 8086 [3].

4. Ab initio kinetics for the $C_2H_5O_1$ + H reactions

Both CH_3CH_2O and CH_3CHOH are stable but highly reactive intermediates of ethanol decomposition and oxidation reactions. Their reactions with H atoms, key chain carriers in these high temperature processes, generate a number of even more reactive small radicals such as CH_3, CH_3O, CH_2OH and OH. In this project, we have investigated the chemical activation reactions of these two C2-containing radicals with H atoms can be mechanistically presented below for the association/decomposition and direct abstraction processes:

(a) $CH_3CH_2O + H \rightarrow CH_3CH_2OH^* \rightarrow CH_3CH_2OH\ (+M)$ (a1)
$\rightarrow CH_2OH + CH_3$ (a2)
$\rightarrow CH_3CH_2 + OH$ (a3)
$\rightarrow CH_3CHOH + H$ (a4)
$\rightarrow (TS1) \rightarrow CH_2CH_2 + H_2O$ (a5)
$\rightarrow (TS2) \rightarrow LM \rightarrow CH_3CH + H_2O$ (a6)
$\rightarrow (TS3) \rightarrow CHOH + CH_4$ (a7)
$\rightarrow (TS4) \rightarrow CH_3CHO + H_2$ (a8)
$\rightarrow (TS5) \rightarrow CH_2O + CH_4$ (a9)
$\rightarrow (TS7) \rightarrow CH_3CHO + H_2$ (a10)

(b) $CH_3CHOH + H \rightarrow CH_3CH_2OH^* \rightarrow CH_3CH_2OH\ (+M)$ (b1)
$\rightarrow CH_2OH + CH_3$ (b2)
$\rightarrow CH_3CH_2 + OH$ (b3)
$\rightarrow CH_3CH_2O + H$ (b4)
$\rightarrow (TS1) \rightarrow CH_2CH_2 + H_2O$ (b5)
$\rightarrow (TS2) \rightarrow LM \rightarrow CH_3CH + H_2O$ (b6)
$\rightarrow (TS3) \rightarrow CHOH + CH$ (b7)
$\rightarrow (TS4) \rightarrow CH_3CHO + H_2$ (b8)
$\rightarrow (TS5) \rightarrow CH_2 + CH_4$ (b9)
$\rightarrow (TS8) \rightarrow CH_3CHO + H_2$ (b10)
$\rightarrow (TS9) \rightarrow CH_2CHOH + H_2$ (b11)

The various transition states (TSn) and variational transition states for radical-radical production channels are summarized in Fig. 6:

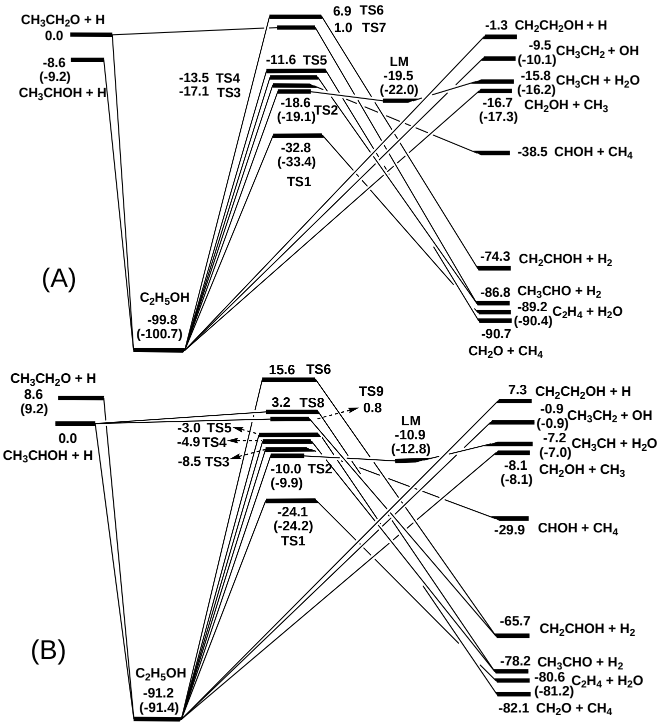

Fig. 6. Schematic diagrams of the potential energy surfaces predicted at the CCSD(T)/6-311+G(3df, 2p)//BH&HLYP /6-311+G(3df, 2p) level of theory with zero-point vibrational energy corrections. (a) CH_3CH_2O + H and (b) CH_3CHOH + H. [E(CH_3CH_2O) = -154.1134354 a.u.; E(CH_3CHOH) = -154.129074 a.u and E(H) = -0.499810 a.u.; E(CH_3CH_2OH) = -154.788661 a.u]. The numbers in parentheses are predicted at the CCSD(T)/6-311+G(3df, 2p)//CCSD/6-311+G(3df, 2p) level of theory with ZPE correction. [E(CH_3CH_2O) = -154.113875 a.u.; E(CH_3CHOH) = -154.1296977 a.u and E(H) = -0.499810 a.u.; E(CH_3CH_2OH) = -154.789264 a.u].

The potential energy surfaces of the two processes have been evaluated at the CCSD(T)/6-311+G(3df, 2p) level of theory with geometric optimization carried out at the BH&HLYP/6-311+G(3df, 2p) level. The direct hydrogen abstraction channels and the indirect association/decomposition channels from the chemically activated ethanol molecule have been considered for both reactions. The rate constants for both reactions have been calculated at 100-3000 K and 10^{-4} Torr-10^{3} atm Ar pressure by micro-canonical VTST/RRKM theory with master equation solution for all accessible product channels. The results show that the major product channel of the CH_3CH_2O + H reaction is CH_3 + CH_2OH (a2) under the atmospheric pressure conditions. Only at high pressure and low temperature, the rate constants for CH_3CH_2OH formation by collisional deactivation (a1) become dominant. For CH_3CHOH + H, there are three major product channels; at high temperatures, CH_3+CH_2OH production (b2) predominates at low pressures ($P <$ 100 Torr), while the formation of CH_3CH_2OH by collisional deactivation (b1) becomes competitive at high pressures and low temperatures (T < 500K). At high temperatures, the direct hydrogen abstraction reaction producing CH_2CHOH + H_2 becomes dominant (b11). Rate constants for all accessible product channels in both systems have been predicted and tabulated for modeling applications. The predicted value for CH_3CHOH + H at 295 K and 1 Torr pressure agrees closely with available experimental data (see Fig. 7). For practical modeling applications, the rate constants for the thermal unimolecular decomposition of ethanol giving key accessible products have been predicted; those for the two major product channels taking place by dehydration and C-C breaking agree closely with available literature data (see Fig. 8); this work has been published in ref. [4]..

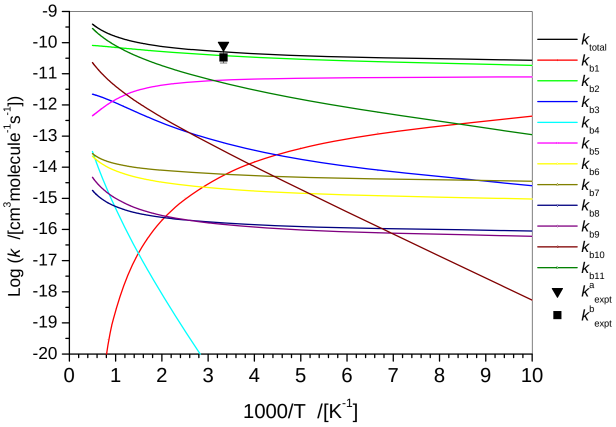

Fig. 7. Predicted braching ratios for the CH_3CHOH + H reaction at 1 Torr, 1 atm, and 100 atm.

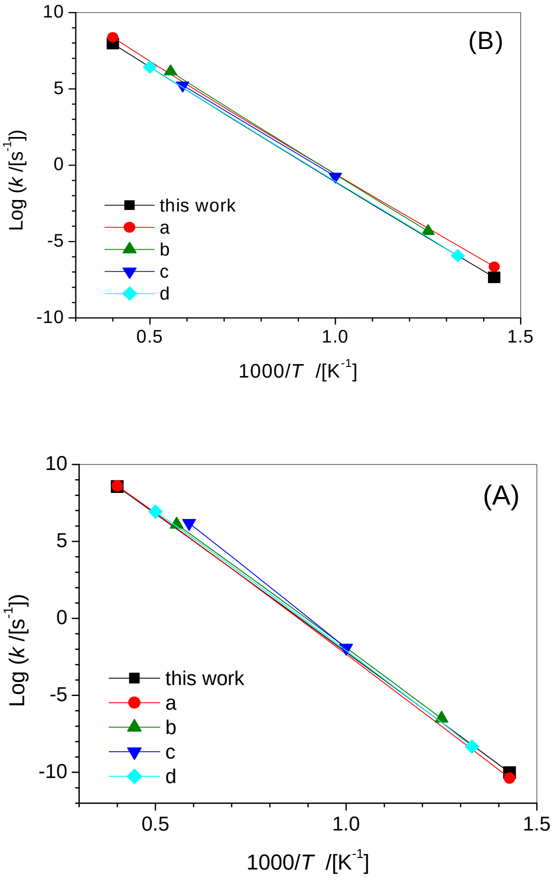

Fig. 8. Comparison of the predicted constants with those in the literature for the decomposition reactions of (A) $CH_3CH_2OH \rightarrow CH_3 + CH_2OH$ and (B) $CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$ at infinite high pressure.

5. Unimolecular decomposition of the $C_3H_7O_1$ isomeric radicals

The $C_3H_7O_1$ radicals, $(CH_3)_2COH$, $(CH_3)_2C(H)O$ and $CH_2CH(OH)CH_3$, are intermediates of n- and iso- propanols, propane and larger hydrocarbon combustion reactions. The kinetics and mechanisms of their unimolecular decomposition and isomerization reactions have not been well characterized. In this work, the mechanisms for the isomerization and decomposition of these radicals have been studied at the CCSD(T) /6-311+G(3df,2p)//B3LYP/6-311+G (3df, 2p) level. The following product channels for these radical isomers are identified as shown in Fig. 9:

$CH_2C(H)OHCH_3 \rightarrow H + CH_2C(OH)CH_3$ (1)
$\rightarrow CH_3 + CH_2C(H)OH$ (2)
$\rightarrow OH + CH_2C(H)CH_3$ (3)
$\rightarrow$ H + Propylene oxide (4)

$(CH_3)_2C(H)O \rightarrow CH_3 + CH_3C(H)O$ (5)
$\rightarrow H + (CH_3)_2CO$ (6)

$(CH_3)_2COH \rightarrow H + (CH_3)_2CO$ (7)
$\rightarrow CH_4 + CH_3CO$ (8)
$\rightarrow H_2O + CH_3CCH_2$ (9)
$(CH_3)_2C(H)O \Leftrightarrow CH_2C(H)OHCH_3$ (10, 11)
$(CH_3)_2C(H)O \Leftrightarrow (CH_3)_2COH$ (12, 13)
$CH_2C(H)OHCH_3 \Leftrightarrow (CH_3)_2COH$ (14, 15)

The rate constants for the low-lying energy channels are evaluated by using The transition-state-theory (TST) and the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Among these radicals, $(CH_3)_2COH$ is the most stable one, $CH_2CH(OH)CH_3$ and $(CH_3)_2COH$ lie above it by 7.8 and 11.3 kcal/mol, respectively. For the $(CH_3)_2CHO$ decomposition, the formation of $CH_3C(H)O$ + CH_3 is the dominant channel with 14.9 kcal/mol barrier; formation of $(CH_3)_2CO$ + H has an 18.4 kcal/mol barrier. Rate constant results show that at 1 atm (N_2), branching ratio of $CH_3C(H)O + CH_3$ is larger than 99% in the temperature range of 298 ~ 3000 K. For the $CH_2CH(OH)CH_3$ decomposition, formation of $CH_2{=}C(H)CH_3$ + OH, $CH_2{=}C(H)OH + CH_3$ needs to overcome 27.0, 30.9 kcal/mol barriers, respectively. For the $(CH_3)_2COH$ decomposition, the lowest energy channel is the formation of $(CH_3)_2CO$ + H with 31.5 kcal/mol barrier. The calculated rates for the formation of $CH_3C(H)O + CH_3$, $(CH_3)_2CO$ + H and $CH_2{=}C(H)CH_3$ + OH are in good agreement with available experimental values. The results by coupling all the channels show that comparing with the low-lying energy processes, the isomerization rates among the isomers can be ignored due to their higher isomerization barriers.

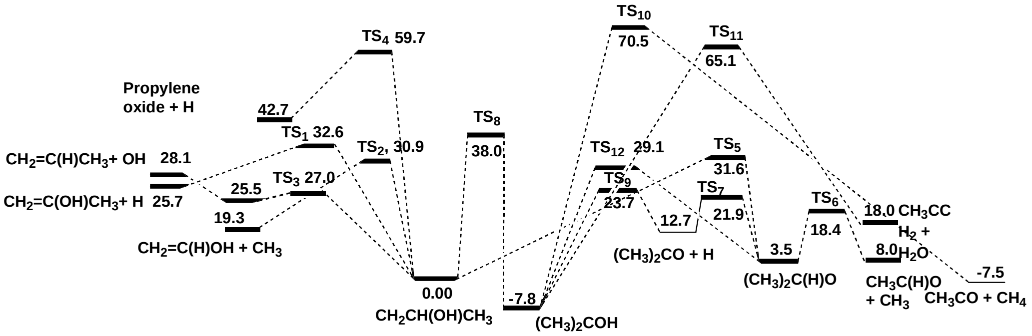

Fig.9. Schematic energy diagram for the dissociation of IPA radicals computed at the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311+G(3df,2p) level.

6. Photo-fragmentation of C_6H_5CHO at 266, 248 and 193 nm

We had reported the preliminary result of this extensive study in our last report; the work resulted from a collaboration with IAMS (C. K. Ni and Y. T. Lee) and NCTU's reaction dynamics laboratory of Y-P Lee employing the multi-mass ion imaging photo-fragmentation machine and step-scan tr-FTIR emission technique, respectively aid by our high-level ab initio MO calculations [5]. We also characterized the potential energies with the CCSD(T)/6-311+G(3df,2p) method and predicted the branching ratios for various channels of dissociation. Upon photolysis at 248 and 266 nm, two major channels for formation of HCO and CO, with relative branching of 0.37: 0.63 and 0.20 : 0.80, respectively, were observed The C_6H_5 + HCO channel has two components with large and small recoil velocities; the rapid component with average translational energy of ~25 kJ mol^{-1} dominates. The C_6H_6 + CO channel has a similar distribution of translational energy for these two components. Secondary dissociation channels C_6H_5CO (from H elimination) → C_6H_5 + CO and C_6H_6 (from CO elimination) → C_6H_5 + H or HCO (from HCO elimination) → CO + H, might also occur. IR emission from internally excited C_6H_5CHO, ν_3 ($v = 1$) of HCO, and levels $v \le 2$, $J \le 43$ of CO was observed; the latter has average rotational energy ~13 kJ mol^{-1} and vibrational energy ~6 kJ mol^{-1}. Upon photolysis at 193 nm, similar distributions of energy were observed, except that the C_6H_5 + HCO channel becomes the only major channel with a branching ratio of 0.82 ± 0.10 and an increased proportion of the slow component; IR emission from levels ν_1 ($v = 1$) and ν_3 ($v = 1$ and 2) of HCO and $v \le 2$, $J \le 43$ of CO were observed; the latter has average energy similar to that observed in photolysis at 248 nm. The observed product yields at different dissociation energies are consistent with statistical-theory predicted results based on the computed singlet and triplet potential energy surfaces given below:

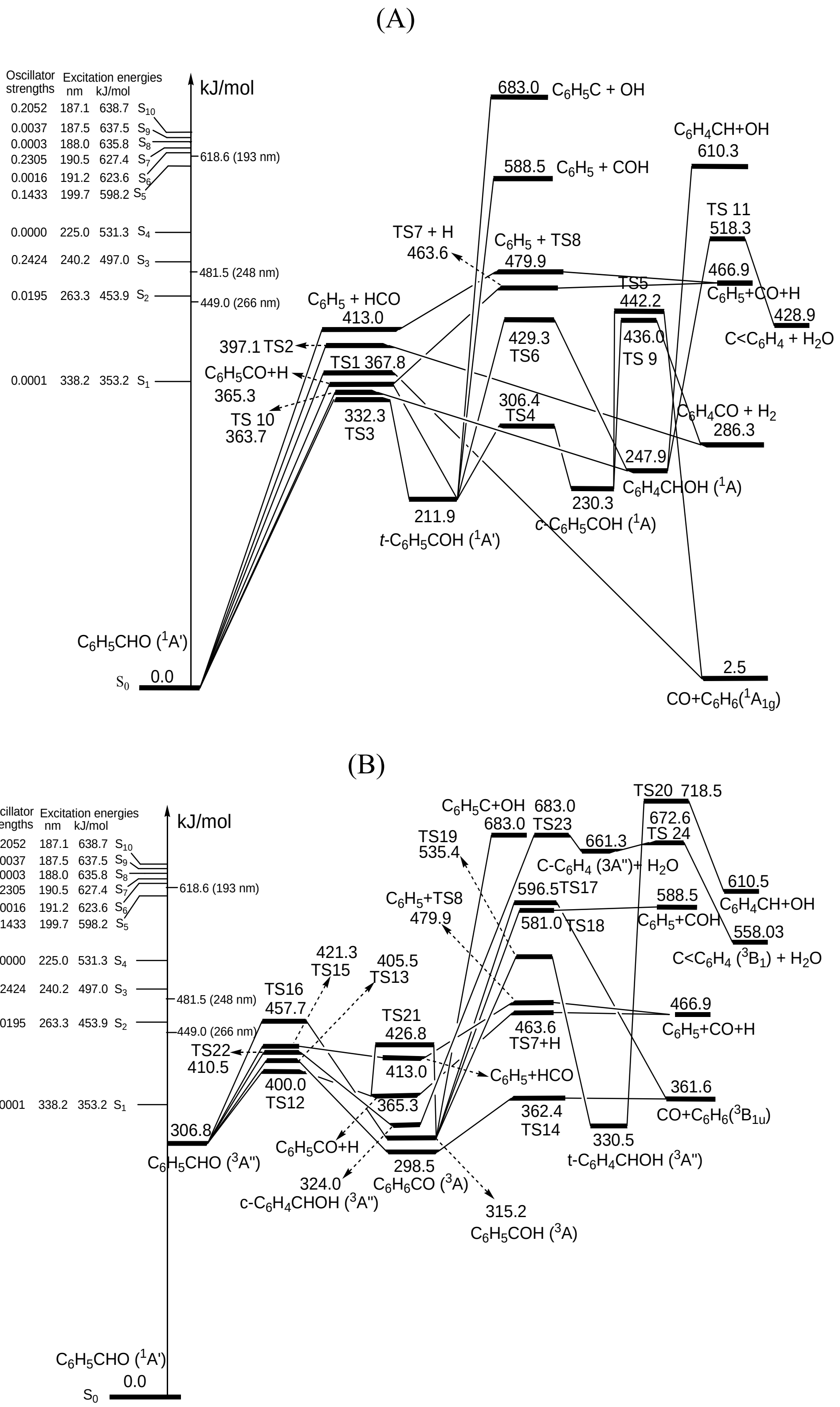

Fig. 10. Singlet (A) and triplet (B) potential energy surfaces of C_6H_5CHO [5].

7. References:

[1]. P. W. Seakins and S. R. Leone, J. Phys. Chem., 1992, 96, 4478

[2]. T. P. Marcy, R. R. Diaz, D. Heard, S. R. Leone, L. B. Harding and S. J. Klippenstein, J. Phys. Chem. A, 2001, 105, 8361.

[3]. Chih-Wei Wu, Hiroyuki Matsui, Niann-Shiah Wang and M. C. Lin, “Shock Tube Study on the Thermal Decomposition of Ethanol”, J. Phys. Chem. A, 2011, 115, 8086-8092.

[4]. Z. F. Xu, Kun Xu and M. C. Lin, “Thermal Decomposition of Ethanol. IV. Ab Initio Chemical Kinetics for Reactions of H Atoms with CH_3CH_2O and CH_3CHOH Radicals”, J. Phys. Chem. A, 2011, 115(15), 3509-3522.

[5]. Arnab Bagchi, Yu-Hsuan Huang, Z. F. Xu, P. Raghunath, Yuan T. Lee, Chi-Kung Ni, M. C. Lin and Yuan-Pern Lee, "Photodissociation dynamics of benzaldehyde (C_6H_5CHO) at 266, 248, and 193 nm", Chemistry--An Asian Journal, accepted.

8. Publications for 2010-2011:

A. Research results on reaction kinetics and dynamics:

[1]. S. Y. Wu, P. Raghunath, J. S. Wu and M. C. Lin*, “Ab initio Chemical Kinetic Study for Reactions of H Atoms with SiH_4 and Si_2H_6: Comparison of Theory and Experiment”, J. Phys. Chem. A, 114(1), 633-639 (2010).

[2]. D. H. Varma, P. Raghunath and M. C. Lin*, “Ab Initio Chemical Kinetics for the Reaction of H atom with Si_3H_8”, J. Phys. Chem. A, 114, 3642-48 (2010).

[3]. Ku-We Lu, Hiroyuki Matsui*, Ching-Liang Huang, P. Raghunath, Niann-Shiah Wang and M. C. Lin, A Shock Tube Study on the Thermal Decomposition of CH_3OH”, J. Phys. Chem. A, 114, 5493-5502 (2010).

[4]. P. Raghunath and M. C. Lin*, “Ab Initio Chemical Kinetics for SiH_3 Reactions with Si_xH_{2x+2} (x=1-4)”, J. Phys. Chem. A, 114, 13353–13361 (2010).

[5]. Keith Freel, J. Park, M. C. Lin and M. C. Heaven*, “Cavity ring-down spectroscopy of the phenyl radical in a pulsed discharge supersonic jet expansion”, Chem. Phys. Lett., 507(4-6), 216-220 (2011).

[6]. Z. F. Xu, Kun Xu and M. C. Lin*, “Thermal Decomposition of Ethanol. IV. Ab Initio Chemical Kinetics for Reactions of H Atoms with CH_3CH_2O and CH_3CHOH Radicals”, J. Phys. Chem. A, 115(15), 3509-3522 (2011).

[7]. Chih-Wei Wu, Hiroyuki Matsui*, Niann-Shiah Wang and M. C. Lin*, “Shock Tube Study on the Thermal Decomposition of Ethanol”, J. Phys. Chem. A, 115, 8086-8092 (2011).

[8]. Arnab Bagchi, Yu-Hsuan Huang, Z. F. Xu, P. Raghunath, Yuan T. Lee, Chi-Kung Ni*, M. C. Lin* and Yuan-Pern Lee*, "Photodissociation dynamics of benzaldehyde (C_6H_5CHO) at 266, 248, and 193 nm", Chemistry--An Asian Journal, accepted.

B. Research results on studies relevant to solar cells and fuel cells:

[1]. YongMan Choi, M. C. Lin and Meilin Liu*, “Rational Design of Novel Cathode Materials in Solid Oxide Fuel Cells using First-Principles Simulations”, J. Power Sources, **195**, 1441-45 (2010)

[2]. Wei-Ta Chen, Kuei-Bo Chen, Ming-Fang Wang, Sheng-Feng Weng, Chi-Shen Lee* and M. C. Lin, “Enhanced Catalytic Activity of $Ce_{1-x}M_xO_2$ (M = Ti, Zr, and Hf) Solid Solution with Controlled Morphologies”, Chem. Comm., 46, 3286-3288 (2010).

[3]. Chih-Wei Wu, Chih-Wei Lu, Y-P Lee, Yu-Jong Wu*, Bing-Ming Cheng and M. C. Lin*, “Blue/Near UV light emission from hybrid InN/TiO_2 nanoparticle films", J. Mater. Chem., 21, 8540-42 (2011).

[4]. Hsin-Tsung Chen*, P. Raghunath and M. C. Lin*, "Computational Investigation of O_2 Reduction and Diffusion on 25% Sr-doped $LaMnO_3$ Cathodes in Solid Oxide Fuel Cells", Langmuir, 27(11), 6787-93 (2011).

[5]. W. F. Huang, P. Raghunath, and M. C. Lin*, "Computational Study on the Reactions of H_2O_2 on TiO_2 Anatase (101) and Rutile (110) Surfaces", J. Comp. Chem., 32(6), 1065-1081 (2011).

[6]. Tsai-Te Wang, P. Raghunath, Yun-Fang Lu, Yu-Chang Liu, Chwei-Huawn Chiou and M. C. Lin*, "Observation of Significant Enhancement in the efficiency of a DSSC by InN Nanoparticles over TiO_2-Nanoparticle Films", Chem. Phys. Lett., 510(1-3), 126-130 (2011).

[7]. Zhe Cheng, Jeng-Han Wang, YongMan Choi, Lei Yang, M. C. Lin and Meilin Liu*, "From Ni-YSZ to Sulfur-Tolerant Anode Materials for SOFCs: Electrochemical Behavior, in situ Characterization, Modeling, and Future Perspectives", Energy and Eviron. Sci., in press.

C. Other publications credited to NSC supports are listed below:

[1]. S. C. Xu and M. C. Lin*, "Ab initio Chemical Kinetics for the NH_2 + HNO_x Reactions: III. Kinetics and Mechanism for NH_2 + $HONO_2$", Int. J. Chem. Kinet., 42(2), 69-78 (2010).

[2]. R. S. Zhu and M. C. Lin*, "An Ab Initio Chemical Kinetic Study on the Reactions of H, OH and Cl with $HOClO_3$", Int. J. Chem. Kinet., 42(4), 253-261 (2010).

[3]. Z. F. Xu and M. C. Lin*, "Computational Studies on Metathetical and Redox Processes of HOCl in the Gas Phase: (II) Reactions with ClO_x ($x = 1-4$)", Phys. Chem. A, 114(2), 833-838 (2010)

[4]. J. Park, Sonya Cates and M. C. Lin*, "Photolytically and Thermally Initiated Reactions of NH_3 with NO_x (x=1,2)", Combust. Sci. Technol., 182, 365-79 (2010).

[5]. S. C. Xu, S. Irle and M. C. Lin*, "Quantum Chemical Prediction of Reaction Pathways and Rate Constants for Reactions of NO and NO_2 with Monovacancy Defects on Grapite (0001) Surfaces", J. Phys. Chem. C, 114, 8375-8382 (2010).

[6]. Z. F. Xu and M. C. Lin*, "Computational Studies on Metathetical and Redox Processes of HOCl in the Gas Phase: (III) Its Self-Reaction and Interactions with HNO_x (x = 1-3)", J. Phys. Chem. A, 114, 5320-26 (2010).

[7]. Z. F. Xu and M. C. Lin*, "Ab Initio Chemical Kinetic Study on Cl + ClO and Related Reverse Processes", J. Phys. Chem. A, 114, 11477-82 (2010).

[8]. R. S. Zhu and M. C. Lin*, "Ab Initio Chemical Kinetic Study on the Reactions of ClO with C_2H_2 and C_2H_4", J. Phys. Chem. A, 114(51), 13395-13401 (2010).

[9]. R. S. Zhu and M. C. Lin*, "Ab Initio Chemical Kinetics for Reactions of ClO with Cl_2O_2 Isomers", J. Chem. Phys., 134(5), 054307/1-054307/6 (2011).

[10]. R. S. Zhu and M. C. Lin*, "Ab initio chemical kinetics for ClO reactions with HO_x, ClO_x and NO_x (x=1, 2): A Review", Comput. Theoret. Chem., 965(2-3), 328-339, (2011).

[11]. R. S. Zhu and M. C. Lin*, "First-Principles Study of Water Effect on the Sublimation of Ammonium Perchlorate", Int. J. Energ. Mater. Chem. Propul., in press.

國科會補助計畫衍生研發成果推廣資料表

日期:2011/09/09

國科會補助計畫	計畫名稱: 實驗及理論計算小分子醇類於氣相及異相催化分解及氧化反應(3/3)
	計畫主持人: 林明璋
	計畫編號: 99-2113-M-009-002- 學門領域: 物理化學

無研發成果推廣資料

99 年度專題研究計畫研究成果彙整表

計畫主持人：林明璋	**計畫編號：**99-2113-M-009-002-

計畫名稱：實驗及理論計算小分子醇類於氣相及異相催化分解及氧化反應(3/3)

成果項目			量化			單位	備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等）
			實際已達成數（被接受或已發表）	預期總達成數(含實際已達成數)	本計畫實際貢獻百分比		
國內	論文著作	期刊論文	0	0	0%	篇	
		研究報告/技術報告	0	0	0%		
		研討會論文	0	0	0%		
		專書	0	0	0%		
	專利	申請中件數	0	0	0%	件	
		已獲得件數	0	0	0%		
	技術移轉	件數	0	0	0%	件	
		權利金	0	0	0%	千元	
	參與計畫人力（本國籍）	碩士生	1	1	100%	人次	
		博士生	2	2	100%		
		博士後研究員	1	1	100%		
		專任助理	1	1	100%		
國外	論文著作	期刊論文	15	5	100%	篇	
		研究報告/技術報告	0	0	0%		
		研討會論文	0	0	0%		
		專書	0	0	0%	章/本	
	專利	申請中件數	0	0	0%	件	
		已獲得件數	0	0	0%		
	技術移轉	件數	0	0	0%	件	
		權利金	0	0	0%	千元	
	參與計畫人力（外國籍）	碩士生	0	0	0%	人次	
		博士生	0	0	0%		
		博士後研究員	0	0	0%		
		專任助理	0	0	0%		

其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)	過去一年重要研究合作之結果包含 1.PEMFC：與原分所陳貴賢教授及台大凝態中心研究取代 Pt/C 陰極材料以及其光化學的理論基礎，此新材料將可作 CO2 還原製作 CH3OH 之應用；2.SOFC：與 Georgia Tech 之 M. Liu 教授合作抗硫之 SOFC 陽極材料，以上與 Fuel Cells 有關結果將於 Energy + Envir. Science 期刊發表；3.photofragmentation dynamics：與美國 Wayne State 大學 Arthur Suits 教授合作有關 Roaming Transition States 新化學動態學研究領域的研究結果，一篇論文已被 Nature (Chem)接受，將於近期發表。

	成果項目	量化	名稱或內容性質簡述
科教處計畫加填項目	測驗工具(含質性與量性)	0	
	課程/模組	0	
	電腦及網路系統或工具	0	
	教材	0	
	舉辦之活動/競賽	0	
	研討會/工作坊	0	
	電子報、網站	0	
	計畫成果推廣之參與（閱聽）人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

■達成目標
□未達成目標（請說明，以 100 字為限）
　□實驗失敗
　□因故實驗中斷
　□其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：■已發表 □未發表之文稿 □撰寫中 □無
專利：□已獲得 □申請中 ■無
技轉：□已技轉 □洽談中 ■無
其他：（以 100 字為限）

本計畫於 2010/07/01-2011/06/30 間共發表 15 篇相關之 SCI 論文，並 Credit 國科會 11 篇與國外大學合作之論文，共計 26 篇論文，除此之外，尚有數篇論正在撰寫中。

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

本研究屬於基礎性，研究課題專注於小醇分子熱分解及氧化的基本化學動力學，配合高階層原始量子計算闡釋其反應機制，研究結果與世界最先進之研究室並駕其驅；與原分所及 Georgia Tech 在 PEMFC, SOFC 及 photofragmentation dynamics 等方面的合作及成果(SCI 論文)均屬頂尖的層次。