FINAL REPORT

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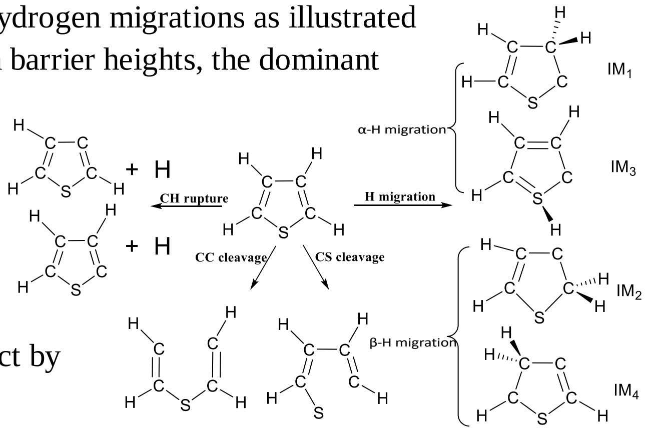
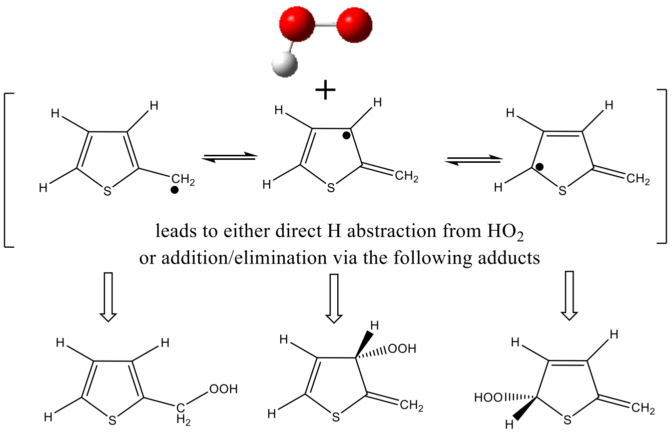
PYROLYSIS MECHANISMS OF THIOPHENE AND METHYLTHIOPHENE IN ASPHALTENES

Using thiophene as a model for asphaltenes, we investigated the pyrolysis mechanism using density functional and *ab initio* quantum chemical techniques. We determined that the pyrolysis process is initiated via four different types of hydrogen migrations as illustrated in the Figure at right. According to the reaction barrier heights, the dominant 1,2-H shift mechanism via IM_1 involves two competitive product channels, namely, C_2H_2 + CH_2CS and CS + CH_3CCH. The minor channels include the formation of CS + CH_2CCH_2, H_2S + C_4H_2, HCS + CH_2CCH, CS + CH_2CHCH, H + C_4H_3S, and HS + C_4H_3. We also investigated the alkyl substitution effect by exploring the pyrolysis pathways of 2-methylthiophene and 3-methylthiophene. The energetics of such systems were very similar to that for unsubstituted thiophene, which suggests that thiophene alkylation may not play a significant role in the pyrolysis of asphaltene compounds. This work was published in the *Journal of Physical Chemistry A* **2011**, *115*, 2882-2891. Barney Ellison (University of Colorado at Boulder) is currently exploring the high temperature decomposition products of thiophene and furan for comparison with our theoretical results.



A MECHANISTIC STUDY OF THE 2-THIENYLMETHYL + HO_2 RADICAL RECOMBINATION REACTION

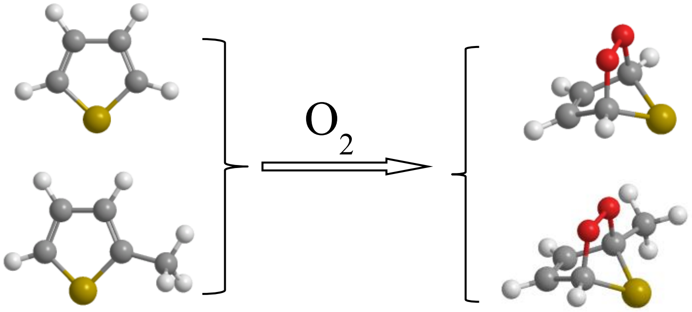
Radical recombination reactions are important in the combustion of fuel oils. Shale oil contains alkylated heteroaromatic species - the simplest example of which is the 2-thienylmethyl radical. The *ab initio* potential energy surface for the reaction of the 2-thienylmethyl radical with the HO_2 radical was examined. Seventeen product channels corresponding to either addition/elimination or direct hydrogen abstraction were characterized. Direct hydrogen abstraction from HO_2 proceeds via a weakly bonded van der Waals complex, which leads to 2-methylthiophene, 2-methylene-2,3-dihydrothiophene or 2-methylene-2,5-dihydrothiophene depending upon the 2-thienylmethyl radical reaction site. The addition pathway for the two radical reactants is barrierless with the formation



of three adducts, as distinguished by HO_2 reaction at three different sites on the 2-thienylmethyl radical. The addition is exothermic by 37 ~ 55 kcal mol^{-1} relative to the entrance channel. These excess energies are available to promote further decomposition or rearrangement of the adducts that lead to nascent products such as H, OH, H_2O and CH_2O. The reaction surfaces are characterized by relatively low barriers (most are lower than 10 kcal mol^{-1}). Based upon a careful analysis of the overall barrier heights and reaction exothermicities, the formation of O_2, OH and H_2O is likely to be an important pathway in the radical recombination reactions of 2-thienylmethyl + HO_2. This work was published in the *Journal of Physical Chemistry A*, **2011**, *115*, 14546-14557.

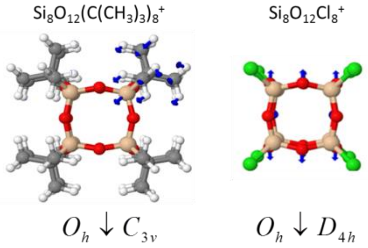
REACTION OF THIOPHENE AND METHYLTHIOPHENE WITH SINGLET AND TRIPLET MOLECULAR OXYGEN

Mechanisms for the reaction of thiophene and 2-methylthiophene with molecular oxygen on both the triplet and singlet potential energy surfaces (PESs) were investigated using *ab initio* methods. Thiophene and 2-methylthiophene where shown to react with O_2 via two types of mechanisms; namely, direct hydrogen abstraction and addition/elimination. The barriers for reaction with triplet oxygen are all significantly large (i.e., > 30 kcal mol^{-1}), which indicates that the direct oxidation of thiophene by ground state oxygen might be important only in high temperature processes. Reaction of thiophene with singlet oxygen via a 2+4 cycloaddition leading to endoperoxides is the most favorable channel. Moreover, it was found that alkylation of the thiophene ring (i.e., methyl-substituted thiophene) is capable of lowering the barrier height for the addition pathway. The implication of the current theoretical results may shed new light on the initiation mechanisms for combustion of asphaltenes. This work was published in the *Journal of Physical Chemistry A*, **2012** *116*, 4934-4946.



JAHN-TELLER STABILIZATION IN POSS CATIONS

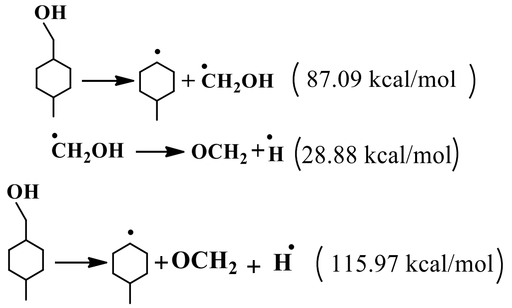
We have a long standing interest in polyoligomeric silsesquioxane (POSS) molecules.[1-2] These molecules have recently been used as advanced surface coatings for photovoltaic devices and have potential as molecular-based energy storage devices as well as magnetically controllable liquid marbles.[3-5] We have been investigating the small molecule encapsulation properties of POSS and discovered some interesting symmetry breaking processes that need to be better understood in order to use POSS in advanced materials. We have investigated this symmetry breaking mechanism in POSS monocations $Si_8O_{12}(C(CH_3)_3)_8^+$ and $Si_8O_{12}Cl_8^+$, using density functional theory (DFT) and group theory. Under O_h symmetry, these ions possess $^2T_{2g}$



and ^2E_g electronic states, respectively, and undergo different symmetry breaking mechanisms. The ground states of $Si_8O_{12}(C(CH_3)_3)_8^+$ and $Si_8O_{12}Cl_8^+$ belong to the C_{3v} and D_{4h} point groups and are characterized by Jahn-Teller stabilization energies of 3959 and 1328 cm^{-1}, respectively, at the B3LYP/def2-SVP level of theory. The symmetry distortion mechanism in $Si_8O_{12}Cl_8^+$ is Jahn-Teller type, whereas in $Si_8O_{12}(C(CH_3)_3)_8^+$ the distortion is a combination of both Jahn-Teller and pseudo-Jahn-Teller effects. The distortion force acting in $Si_8O_{12}(C(CH_3)_3)_8^+$ is mainly localized on one Si-(*tert*-butyl) group while in $Si_8O_{12}Cl_8^+$ it is distributed over the oxygen atoms. The main distortion forces acting on the Si_8O_{12} core arise from the coupling between the electronic state and the vibrational modes; identified as $9t_{2g}+1e_g+3a_{2u}$ for the $Si_8O_{12}(C(CH_3)_3)_8^+$ and $1e_g+2e_g$ for $Si_8O_{12}Cl_8^+$. This work was published in the *Journal of Physical Chemistry A,* **2015**, *119,* 4237-4243.

THERMAL DECOMPOSITION OF (4-METHYLCYCLOHEXANE)METHANOL, $C_8H_{15}OH$. IS THE FORMATION OF FORMALDEHYDE A POSSIBILITY?

On January 9, 2014, (4-methylcyclohexane)methanol (4-MCHM) was inadvertently released into the Elk River in Charleston, West Virginia. Very little is known about the effect of MCHM on human health and initial news reports suggested that MCHM decomposes to formaldehyde. We have investigated the thermal decomposition pathways of 4-MCHM and examined possible formation of formaldehyde using various quantum chemical methods such as B3LYP/6-311++G(d,p), MP2/6-311++G(d,p), CCSD(T)/6-31G(d,p), G3B3, G4, G4MP2 and CBS-QB3. For the reaction, $^{\bullet}CH_2OH \rightarrow CH_2O + H^{\bullet}$, the W1BD theory was also employed. The C-C homolytic bond rupture between the cyclohexane ring and the methanol group in 4-MCHM initiates thermal decomposition of 4-MCHM and requires 87 kcal/mol at the CBS-QB3 level.



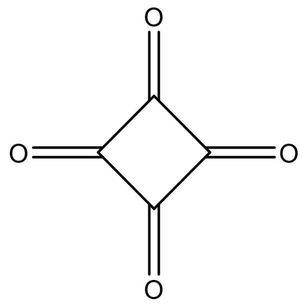
The production of formaldehyde and the methylcylcohexyl radical arising from the decomposition of 4-MCHM is found to be endothermic (ΔH_f = 115 kcal/mol) and is unlikely to occur at ambient temperatures without a specific catalyst. This work has recently been submitted to the *Journal of Physical Chemistry A.*

MULTIREFERENCE CHARACTERIZATION OF THE GROUND AND LOW-LYING VALENCE EXCITED STATES OF DIDEHYDROTHIOPHENE DIRADICALS

High-level multireference theories (MCSCF, MRCISD, MRCISD+Q and MRAQCC at cc-pVDZ and cc-pVTZ levels) were employed to investigate the ground and low-lying excited states of all four didehydrothiophenes (DDThs). We used an active space of 8 eight electrons in eight orbitals

(CAS(8,8) for 2,5DDTh and ten electrons in eight orbitals (CAS(10,8)) for all other isomers. Both state- averaged and single state reference MCSCF wave functions were used for highly symmetrical structures (C_{2V}). These computational methods consistently predict the singlet state as the ground state and with a singlet-triplet (S-T) adiabatic energy gap of 15-23 kcal/mol, indicative of through bond coupling. The 2,3-DDTh isomer possesses the highest S-T splitting energy of 23.5 kcal/mol at the MR-AQCC/cc-pVTZ level of theory. The remaining DDThs have quite similar S-T splitting energies of approximately 16 kcal/mol. A comparison between different multireference methods reveals a competitive performance between MR-AQCC and MR-CISD+Q. The lowest energy isomer is 2,3-DDTh on the basis of the computed total electronic energies (MRAQCC/ccpVtz and MRCISD+Q/ccpVtz) and the CCSD(T)/6-311++G(3df,2p) single point energies of the MRAQCC/ccpVTZ optimized geometries. The 2,3-DDTh isomer has the strongest C-C bond, close to ethyne C-C triple bond. However, an examination of the electronic structure and NBO analysis shows 2,3 and 2,5-DDTh to have the lowest and highest diradical character, respectively. Similar to o-benzyne, the latter can be considered a strained alkyne. In general, the singlet-triplet splitting energies of all didehydrothiophenes are smaller than in the benzynes suggesting them to be more reactive systems. This work has recently been submitted to the *Journal of Physical Chemistry A.*

CYCLOBUTANETETRAONE: AN UNUSUAL CLUSTER OF LOW-LYING ELECTRONIC STATES



Cyclobutane-1,2,3,4-tetraone is a beautifully symmetric, cyclic species that may be regarded as a tetramer of carbon monoxide $(CO)_4$. Identifying the electronic ground state and quantifying the singlet-triplet gaps of this molecule has turned out to be a difficult task for theory. Different approaches predict different ground states and computed energetic spacing have varied by almost 100 kcal/mol! In collaboration with Wes Allen (University of Georgia), we have performed very high level computations on cyclobutanetetraone and found that while the molecule appears to be just another simple, closed-shell molecule it has in fact at least four low-lying electronic states with D_{4h} symmetry.[6] These include a $^1A_{1g}$ state with eight π-electrons, a $^1B_{1u}$ and a $^3B_{1u}$ state with nine π-electrons, and a $^1A_{1g}$ with ten π-electrons. In this work, Mk-MRCCSD and CCSD(T) computations have been completed with a cc-pVQZ basis set resulting in an 8π-$^1A_{1g}$ and 9π-$^3B_{1u}$ ground state, respectively. These states are spread over 5.95 kcal mol^{-1} based upon the focal point approach. A recent photoelectron study[7] of the cyclobutanetetraone anion reported term values of 1.50 ± 0.1 and 3.23 ± 0.1 kcal mol^{-1} for the 8π-$^1A_{1g}$ and the 9π-$^1B_{1u}$ states respectively; however, our computations indicate that the 10π-$^1A_{1g}$ state lies below the 9π-$^1B_{1u}$ state. In contrast, the 9π-$^3B_{1u}$ ground state is predicted to lie 4.34 kcal mol^{-1} below the 8π-$^1A_{1g}$ state, and the 10π-$^1A_{1g}$ state 1.00 kcal mol^{-1} above the 8π-$^1A_{1g}$ state. This work is in preparation for submission to the *Journal of the American Chemical Society*.

STUDENT TRAINING

As a faculty member at a predominately undergraduate institution, my greatest primary contribution is in producing future graduate students who are passionate about pursuing research in physical chemistry and chemical physics and who understand the importance of hard work, focus and outcome oriented research. Since receiving our first DOE award 5 years ago, my research group has published 14 papers in high quality, peer-reviewed journals, summarizing the research of 44 undergraduate student coauthors. Undergraduates as well as post-baccalaureate and post-doctoral fellows have been responsible for more than 250 presentations at regional, national and international chemistry meetings. My research group typically contains 15 – 20 students and is a particularly effective environment for attracting and inspiring women and students from underrepresented groups. They participate in disproportionate numbers: more than 60% of my students are women and in the last five years 40% of my research group has been students of color. I am also proud of my ability to impassion students to pursue graduate work in both applied and fundamental areas. Sixty-seven of my research students have graduated and thirty went on to pursue the Ph.D. in the chemical sciences; some in theoretical groups and some in synthetic or experimental groups. Eighteen former undergraduates are pursuing or have completed the PhD in physical chemistry or chemical physics at: Berkeley (2 students; Geissler lab, Pines lab), Georgia (Schaefer lab), Emory (2 students: Bowman lab, Evangelista lab), Illinois (Hammes-Schiffer lab), Oxford (2 students: Clary lab, Vallence lab), Princeton (2 students: Rabitz lab, Storey lab), Penn (Rappe lab), Cambridge (Glen lab), Cornell (Tester lab), Purdue (Choi lab), Yale (Jorgenson lab), UC-Irvine (Potma lab), Miami (Acevedo lab), Syracuse University (Nafie lab) and VaTech (lab TBA).