Final Technical Report
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Studies of the Chemistry of Oxygenated Fuels with Photoionization Mass Spectrometry

With this report, we wish to communicate the progress and status of Prof. Cool's DOE/BES-funded research activities before his passing on 03/05/2012. Until then his research focused on detailed studies of the complex combustion chemistry of oxygenated, bio-derived fuels. In particular, he studied the flame chemistry of simple methyl and ethyl esters chosen as surrogates for the long-chain esters that are primary constituents of biodiesel fuels. The principal goals of his studies were: (1) show how fuel-specific structural differences including degree of unsaturation, linear *vs.* branched chain structures, and methoxy *vs.* ethoxy functions affect fuel-destruction pathways, (2) understand the chemistry leading to potential increases in the emissions of hazardous air pollutants including aldehydes and ketones inherent in the use of biodiesel fuels, and (3) define the key chemical reaction mechanisms responsible for observed reductions in polycyclic aromatic hydrocarbons and particulate matter when oxygenated fuels are used as replacements for conventional fuels.

In Prof. Cool's experiments, low-pressure flat flames were analyzed using molecular-beam mass spectrometry combined with single-photon ionization by synchrotron-generated vacuum-ultraviolet radiation. His experiments were carried out at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory in collaboration with Dr. Hansen from the Combustion Research Facility at the Sandia National Laboratories and Prof. Kohse-Höinghaus from the University of Bielefeld (Germany). This experimental approach allowed him to gain unprecedented isomer-resolved insights into the combustion chemistry of esters. Prof. Cool also collaborated closely with Dr. Westbrook from the Lawrence Livermore National Laboratory (LLNL) who provided detailed chemical modeling of all flames studied, and Prof. Cool's data helped to further refine and validate the reaction mechanism constantly under development at LLNL

For a first project, Prof. Cool and Dr. Westbrook studied the combustion chemistry and the detailed chemical structures of low-pressure premixed flames of three $C_5H_{10}O_2$ isomers (methyl butanoate, methyl isobutanoate,

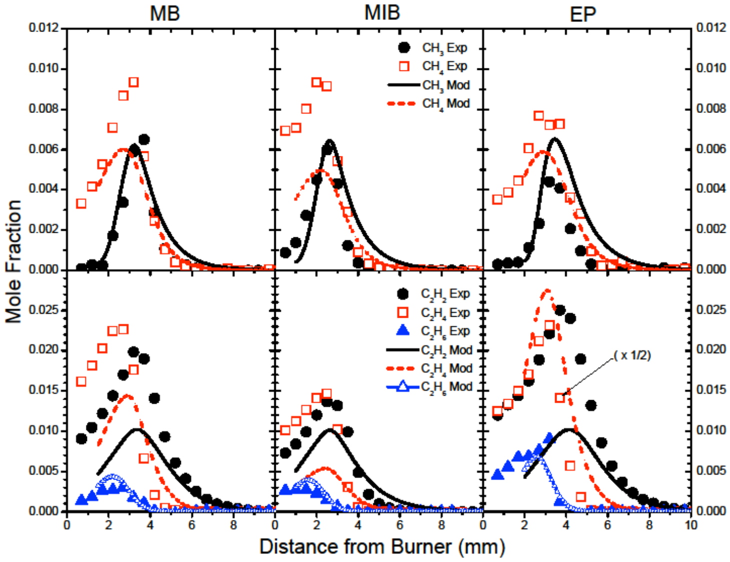

Fig. 1: Comparison of experimental mole fraction profiles with modeling predictions for C_1 and C_2 hydrocarbons in methyl butanoate (MB), methyl isobutanoate (MIB), and ethyl propanoate (EP) flames.

and ethyl propanoate). Despite the simple structures of these small $C_5H_{10}O_2$ esters, they contain structural functional groups that account for fuel-specific effects observed in the combustion of practical biodiesel fuels. The detailed kinetic modeling performed by Dr. Westbrook described how these structural differences are related to molecular structures leading to unique fuel destruction pathways for each of these isomers. The good agreement between experimental and modeling results, which is shown in Fig. 1 for some C_1 and C_2 hydrocarbons, demonstrated that major features of each of these flames can be predicted with reasonable accuracy by building a hierarchical reaction mechanism based on three factors: 1) unimolecular decomposition of the fuel, especially by complex bond fissions; 2) H-atom abstraction reactions followed by β-scission of the resulting radicals leads to nearly all of the observed intermediate species detected experimentally in each flame; 3) the rates of these H-atom abstraction reactions are effectively the same for each distinct type of terminal alkyl radical group (*i.e.,* methoxy, ethoxy, methyl, ethyl, propyl) for ester fuels with comparable structural groups.

To experimentally examine the effect of carbon-carbon (C=C) double bonds on the combustion chemistry of fatty acid esters, Prof. Cool studied the chemical composition of low-pressure premixed laminar flames of a set of four prototypical small esters. Flames of methyl propanate and its isomer ethyl acetate were compared with flame structures of methyl propanate and vinyl acetate flames, respectively. Again, detailed chemical modeling of the flames was provided by Dr. Westbrook. The combined results provided a detailed understanding of the similarities and differences between the combustion of saturated *vs.* unsaturated esters. It became clear that the inclusion of a C=C double bond into an otherwise saturated fuel molecule has a considerable influence on the nature of the reaction pathways that dominate the oxidation of a particular fuel. Specifically, addition of H-atoms and oxygenated species (O, OH, HO_2) to the C=C bonds in methyl propanoate and vinyl acetate led to a larger variety of intermediates than observed in the equivalent flames fueled by methyl propanoate and ethyl acetate. Some of the

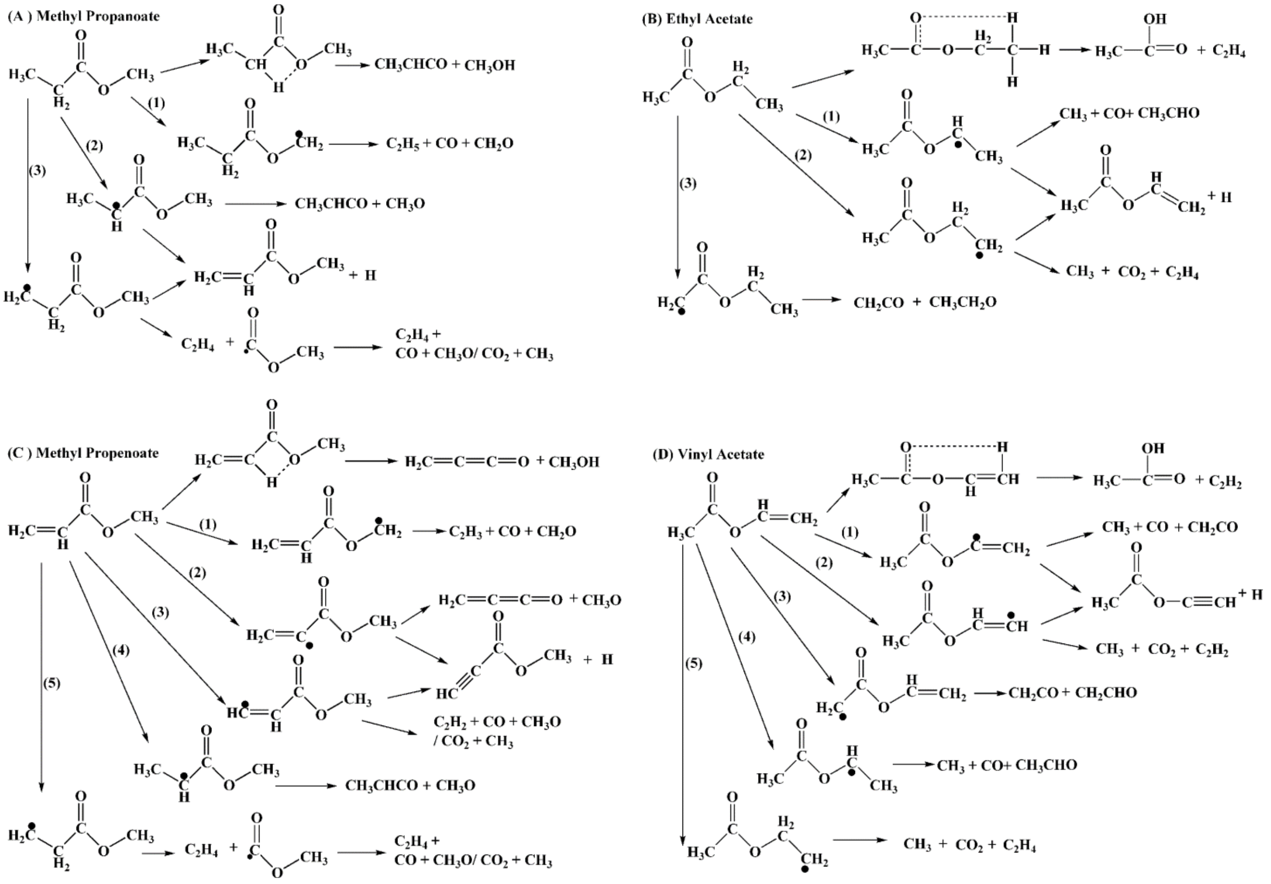

Figure 2: Possible fuel destruction pathways for (a) methyl propanoate, (b) ethyl acetate, (c) methyl propenoate, and (d) vinyl acetate.

early fuel destruction pathways are shown in Fig. 2. In summary, H-additions and unimolecular fuel decomposition reactions were found to play more important roles in flames of unsaturated esters than in the saturated ones. Further studies on the effect of C=C double bonds on the combustion chemistry of small fatty acid esters were reported in last year's International Combustion Symposium in Warsaw, Poland. In this study, which was presented by his former postdoc Bin Yang, Prof. Cool determined the chemical structures of low-pressure premixed laminar flames fueled by methyl crotonate, methyl methacrylate, and ethyl acrylate. Again, the experimental results enabled further refinement and validation of the detailed chemical kinetic reaction mechanism from Dr. Westbrook.

For quantitative determinations of flame species mole fractions, absolute photoionization cross-sections for each species are required. Prof. Cool reported absolute cross sections for near-threshold molecular and dissociative photoionization for several small esters and other species important to combustion processes. The cross-sections for the esters show qualitative features similar to those found for simple alkanes. That is, their total photoionization cross-sections rise gradually from threshold in a quasi-linear fashion, with major contributions from numerous dissociative ionization channels. The parent ion cross-sections rise to plateaus at photon energies coincident with the onset of dissociative photoionization (typically ~0.5-0.8 eV above threshold), which extend to the 11.75 eV limit of the present studies.

To date, Prof. Cool left us with flame-sampled molecular-beam mass spectrometry data on the combustion of dimethoxymethane (DMM), dimethyl carbonate (DMC) and blended DMM/ethane and DMC/ethane flames. A total of nine different flames were established at a carbon-to-oxygen ratio of C/O = 0.5 at 40 mbar. The data has been analyzed by Bin Yang (now Tsinghua University, Beijing, China) and we are awaiting modeling results from Dr. Westbrook. From the experimental data, we learned that the addition of DMM or DMC to the ethane flame showed a strong reduction of soot precursor formation, which is consistent with the lack of the C-C bonds in the oxygenated additives. It is anticipated that details of this study will be published within this year.

Prof. Cool's Publications acknowledging BES Support 2011-present

1. S. Dooley, F. L. Dryer, B. Yang, J. Wang, **T. A. Cool,** T. Kasper, N. Hansen, "An Experimental and Kinetic Modeling Study of Methyl Formate Low-Pressure Flames," *Combust. Flame,* **2011,** 158(4), 732-741.

2. B. Yang, **T. A. Cool,** C. K. Westbrook, N. Hansen, K. Kohse-Höinghaus, "Fuel-Specific Influences on the Composition of Reaction Intermediates in Premixed Flames of Three $C_5H_{10}O_2$ Ester Isomers," *Phys. Chem. Chem. Phys.,* **2011,** 13(15), 7205-7217.

3. B. Yang, C. K. Westbrook, **T. A. Cool,** N. Hansen, K. Kohse-Höinghaus, "The Effect of Carbon-Carbon Double Bonds on the Combustion Chemistry of Small Fatty Acid Esters," *Z. Phys. Chem.,* **2011,** 225(11-12), 1293-1314.

4. T. Kasper, A. Lucassen, A. W. Jasper, W. Li, P. R. Westmoreland, K. Kohse-Höinghaus, B. Yang, J. Wang, **T. A. Cool,** N. Hansen, "Identification of Tetrahydrofuran Reaction Pathways in Premixed Flames," *Z. Phys. Chem.,* **2011,** 225(11-12), 1237-1270.

5. B. Yang, J. Wang, **T. A. Cool,** N. Hansen, S. Skeen, D. L. Osborn , "Absolute Photoionization Cross-Sections of Some Combustion Intermediates," *Int. J. Mass Spectrom.,* **2012,** 309(1), 118-128.

6. C. K. Westbrook, B. Yang, **T. A. Cool,** N. Hansen, K. Kohse-Höinghaus, "Photoionization Mass Spectrometry and Modeling Study of Premixed Flames of Three Unsaturated $C_5H_8O_2$ Esters," *Proc. Combust. Inst.,* **2013,** 34(1), 443-451.