

4C06: A DETAILED CHEMICAL KINETIC REACTION MECHANISM FOR OXIDATION OF FOUR SMALL ALKYL ESTERS IN LAMINAR PREMIXED FLAMES.

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When new mechanisms are presented to the community, experimental research seeks to validate with careful experiments. In case of deviation, there is a tendency to modify some rate constants to achieve good agreement as in the case of methyl butanoate. Sooner rather than later there are several versions of the mechanism. What could be the right manner to optimize mechanisms?

Group additivity methods seem to do quite a good job but there are some key reactions like H-abstraction from fuel molecules which could be much improved by *ab initio* calculations of the bond energies and rate constant parameters. Have you considered doing this for the small methyl esters?

Reply by Charles Westbrook

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The first part of your question addresses a common situation in which an initial reaction mechanism has some good features but also has some rate expressions that could be improved. Then someone else takes that first mechanism and then modifies it, often based on some new experimental validation data. A good example of this sequence is the Fisher et al. paper for methyl butanoate, on which I was a co-author. Gail et al. then improved that mechanism, using some Jet Stirred Reactor data and some laminar flame data, and that revised MB mechanism was called the Gail et al. mechanism. Now, the Walton, Wooldridge and Westbrook paper at the Montreal symposium, using new Rapid Compression Facility and shock tube data, has revised the Gail et al. mechanism and will be called the Walton et al. mechanism. In almost every case, the challenge of each set of authors is to show that the revised mechanism can do a good job of reproducing the experimental results from all of the past mechanisms, in addition to the new experiments, and if that is true, it is really the best overall mechanism for that fuel, with the associated privilege of giving that latest mechanism a respectable name. In cases where none of the papers adequately or completely reproduce all the existing experimental data, then there is debate over which mechanism is best, and the names of those mechanisms can help distinguish which one is being used. Most researchers develop their own revised mechanism, and rarely does anyone follow your suggestion of simply notifying the author of the most recent mechanism. If you, for example, had a new set of MB data but did not have either the skills or tools to develop an improved mechanism, then that would

be an opportunity for you to contact me with your new data, and we would then try to improve our current model.

The group additivity methods I described are intended to be a temporary solution to a situation where the specific reactions in the specific fuel of interest have not been studied via direct kinetics experiments or theoretical techniques. When these additional techniques have been used, we are generally inclined to update our estimates with the new experimental or theoretical rate parameters. Our kinetic modeling suggests that, while these reactions are the main reactions for these fuels, uncertainties in their rates are not particularly large and we are fairly confident that we have rate expressions that are good enough to use in productive modeling calculations.