POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

ANNUAL TECHNICAL PROGRESS REPORT

Dr. Henry F. Schafer
Center for Computational Quantum Chemistry
University of Georgia
Athens, GA 30602

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Henry F. Schaefer III

The research completed spans a rather broad range of chemistry. Taken as a body it conforms well to our goal of three years ago to contribute in a significant way to the fundamental underpinnings of combustion chemistry. The publications resulting from the present DOE grant are listed in Section IV of this proposal. The author has supplied to DOE reprints or preprints of all papers. An additional question dealt with here is whether the science accomplished is consistent with that explicitly proposed three years ago.

The very first chemical problem proposed for study in the 1987 proposal was the reaction of methane with molecular oxygen. The $\text{CH}_4 + \text{O}_2$ research was completed with Tracy Hamilton and published in 1989 in the *Journal of Chemical Physics*. In light of the predictions of our $\text{CH}_4 + \text{O}_2$ studies, the results of the simultaneously proposed research on $\text{C}_2\text{H}_6 + \text{O}_2$ were sufficiently obvious that the explicit examination of the latter reaction proved unnecessary. Like $\text{CH}_4 + \text{O}_2$, the endothermic ethane plus molecular oxygen reaction will surely have a late transition state with a small barrier for the reverse reaction, i.e., $\text{C}_2\text{H}_5 + \text{HO}_2$. RRKM parameters should be readily extrapolated from our $\text{CH}_4 + \text{O}_2$ predictions.

Although we have not yet published our 1987 proposed research on C_2H_7^+ and $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_n$, Richard Remington has sent abundant unpublished results to Yuan Lee's laboratory, and I hope that a full paper will be forthcoming on the first of these topics before the current grant period ends. Unfortunately, higher level theoretical studies are required for $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_n$ prior to publication.

The aluminum atom-unsaturated hydrocarbon systems explicitly targeted for study in the previous proposal have been the subject of three papers with Yaoming Xie in the *Journal of the American Chemical Society* and one in *Chemical Physics Letters*. Many surprising new molecular structures have been discovered, some very low-lying energetically. I am encouraged that a very fundamental understanding of hydrocarbon rearrangements on small metal clusters will emerge from this research. In the current document we propose that the completed studies be extended to aluminum dimer and trimers. The aluminum-hydrocarbon family provides a genuine opportunity to begin to understand heterogeneous catalysis in a truly profound manner.

Another problem explicitly proposed in the 1987 proposal was the infrared spectrum of triplet trimethylenemethane. Chuck Blahous (now an American Physical Society Congressional Fellow in Washington) did a fine piece of work on $C(CH_2)_3$ and it appeared in the January 15, 1990 issue of the *Journal of Chemical Physics*. Trimethylenemethane is anti-aromatic and the work with Blahous confirms long-held suspicions that electron correlation effects are both very important and unconventional. In particular, both the A'_1 and E' carbon-carbon stretching fundamentals are predicted to *increase* when correlation effects are included in a variational manner. We hope that this elusive target (only observed spectroscopically by ESR) will soon succumb to a more detailed identification.

In looking back over the work accomplished during the present grant period, I am particularly happy about our state-of-the-art theoretical studies of the three unimolecular reactions

These are now probably the three best understood photodissociation (this term is

slightly misleading, since virtually all the action occurs on the ground state potential energy hypersurfaces) examples in all of kinetics. Theory has provided valuable assistance to important DOE-supported experimental efforts in all three cases. A fourth important emerging unimolecular reaction

has been the subject of a paper that will appear in late 1990 in the *Journal of Chemical Physics*.

Other papers pertaining to hydrocarbon combustion but not discussed above include our work on bent benzenes, on triplet ketene dissociation, on the structure of methylnitrene, on the *syn* rotational barrier in butane, on the HO_2^+ infrared spectrum, on the rearrangements of neutral vinylidene and its radical cation, on the relative stabilities of the classical and nonclassical vinyl cations, three papers on the carbon clusters C_3 through C_{10} , on the ethylene bromonium and bromoethyl systems, on the unknown tetrazines, as well as our work on some novel larger hydrocarbons.

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