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THEORETICAL STUDIES OF HYDROCARBON COMBUSTION
CHEMISTRY

Annual Progress Report

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Outline of Plans**U. S. Department of Energy Grant DE-FG09-87ER13811****"Theoretical Studies of Hydrocarbon Combustion Chemistry"***Henry F. Schaefer III*

University of Georgia

Six months into this thirty-four month grant, our DOE research is proceeding ahead on schedule. No major changes in the proposed directions are anticipated at the present time. During the second year of the grant period we plan to focus considerable resources on the ethyl radical-oxygen reactions, namely

These reactions are of central importance to combustion and have been studied in several laboratories. Note that for (C) the product may be either ethylene oxide or acetaldehyde. Gutman and coworkers have established from careful experiments that Reaction (A) is exothermic by 35.2 ± 1.5 kcal/mole. Earlier (1980) Baldwin, Pickering, and Walker concluded that the activation energy should be small for the reaction

Westbrook has used a value of 5 kcal/mole for reaction (D) in his modeling of ethane oxidation.

These experimental observations have suggested several potentially fruitful avenues for theoretical inquiry. First, a theoretical study of the infrared and electronic spectra of the ethylperoxyl radical $C_2H_5O_2$ should clarify some of the questions raised by the previous experimental work. For example, not one of the three methyl C-H stretching frequencies has been identified to date.

Three papers concerned primarily with the $C_2H_5 + O_2$ reaction appeared in 1990. Of these the most exhaustive is the joint experimental-theoretical study by Wagner, Slagle, Sarzynski and Gutman. In the autumn of 1989 and summer of this year, Wagner visited the Center for Computational Quantum Chemistry, discussed the current status of the $C_2H_5 + O_2$ problem and emphasized his conviction that there is a wealth of important quantum chemistry waiting to be revealed for the $C_2H_5 + O_2$ reaction. One of the critical assumptions in the 1990 paper by Wagner and coworkers is that rearrangement of the $C_2H_5O_2$ complex *via* a cyclic (five membered ring) transition state leads to formation of $C_2H_4 + HO_2$. Although this proposal is eminently plausible, it and other aspects of Wagner's mechanism for the $C_2H_5 + O_2$ reaction need to be tested *via* reliable *ab initio* methods.

The reliable prediction of activation energies, transition state geometries, and transition state vibrational analyses for the ethyl radical-molecular oxygen reactions (BCD) should make a valuable contribution to physical chemistry. It is not a trivial matter to predict activation energies to ± 3 kcal/mole, but is now feasible using state-of-the-art quantum mechanical methods. We hope that these theoretical studies will in turn stimulate new experimental efforts with respect to fundamental oxidation processes.

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Progress Report May, 1990 - September, 1991
U. S. Department of Energy Grant DE-FG09-87ER13811

Theoretical Studies of Hydrocarbon Combustion Chemistry"

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A. Publications

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B. Theoretical Results for Methylcarbene (CH_3CH).

Geometrical parameters determined at the DZP CISD level for the ground state triplet methylcarbene appear in Figure 1 while those for the lowest lying singlet appear in Figure 2. The triplet state is found to be of C_s symmetry while the singlet is of C_1 symmetry, i.e. the latter contains no elements of point group symmetry. Harmonic vibrational frequencies for both electronic states have also been predicted. The vibrational analyses confirm that both triplet and singlet methylcarbene are potential minima. The predicted vibrational frequencies were also used to determine zero-point vibrational corrections to the energies. These zero-point corrections were simply taken to be the sum of the real harmonic vibrational frequencies divided by two.

The singlet-triplet energy separation determined in this study is of fundamental importance. As expected, the energy separation decreases with an increase in the size of the basis set. The inclusion of Davidson's correction (abbreviated as +Q) further decreases the energy separation. The highest level of theory employed in this work, TZ2P+f CISD+Q/DZP CISD, yields a value for the singlet-triplet energy separation of 6.1 kcal/mol. Inclusion of the zero-point correction to the energy separation further reduces the energy separation by 0.9 kcal/mol, bringing it to 5.2 kcal/mol.

The singlet-triplet energy separation for methylcarbene of 5 kcal/mole is significantly less than that (9 kcal/mole) for the parent methylene molecule. It is anticipated that with a more extensive treatment of electron correlation and an increase in the size of the basis set, the singlet-triplet energy separation will decrease even further, although not below 4 kcal/mol. However, we suggest that the presence of a small singlet-triplet energy separation does not preclude the possibility of the existence of triplet methylcarbene as a stable intermediate or its experimental observation. In this sense methylcarbene should be comparable to methylnitrene (CH_3N), for which the triplet ground state has been well characterized spectroscopically during the past five years.

Figure 1 Optimized geometry for the $^3A''$ ground state of methylcarbene at the DZP/CISD level of theory.

$$\theta_{512} = 96.4^\circ$$

$$\tau_{5123} = 83.5^\circ$$

Figure 2 Optimized geometry for the lowest singlet state (1A) of methylcarbene at the DZP/CISD level of theory.

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