Theoretical study of the gas-phase thermolysis of 3-methyl-1,2,4,5- tetroxane

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Cyclic organic peroxides are a broad and highly sought-after class of peroxide compounds that present high reactivity and even explosive character. The unusually high reactivity of these peroxides can generally be attributed to the rupture of O-O bonds. Cyclic diperoxides are a very interesting series of substituted compounds in which tetroxane is the most prominent member. Gas-phase thermolysis of the simplest substituted member of the series [3-methyl-1,2,4,5-tetroxane or methylformaldehyde diperoxide (MFDP)] has been observed to yield one acetaldehyde, one formaldehyde, and one oxygen molecule as reaction products. DFT at the 6-311+G**level of theory using the BHANDHLYP correlation-exchange functional was applied via the Gaussian09 program to calculate the critical points of the potential energy surface (PES) of this reaction. Equatorial and axial isomers were studied. The singlet state PES of MFDP was calculated, and an open diradical structure was found to be the first intermediate in a stepwise reaction. Two PESs were subsequently obtained: singlet state (S) and triplet state (T) PESs. After that, two alternative stepwise reactions were found to be possible: 1) one in which either an acetaldehyde, or 2) formaldehyde molecule is initially formed. For second one, exothermic reactions were observed for both the S and T PESs. The reaction products include a oxygenmolecule in either S or T state, with the T reaction being the most exothermic. When calculations were performed at the CASSCF(10,10)/6-311+ G**level, spin-orbit coupling permitted S to Tcrossing at the open diradical intermediate stage, a non-adiabatic reaction was observed, and lower activation energies and higher exothermicity were generally seen for the T PES than for the S PES. These results were compared with the corresponding results for tetroxane. The spin-orbit coupling of MFDP and tetroxane yielded identical values, so it appears that

the methyl substituent does not have any effect on this coupling.

3-Methyl-1,2,4,5-tetroxane/methylformaldehyde diperoxide

Cyclic diperoxides

DFT

Equatorial and axial isomers

Gas-phase thermolysis reaction

Potential energy surface

Reaction mechanisms

3 methyl 1,2,4,5 tetroxane

acetaldehyde

formaldehyde

heterocyclic compound

methylformaldehyde diperoxide

oxygen

peroxide

unclassified drug

3-methyl-1,2,4,5-tetroxane

gas

tetraoxane derivative

article

energy

gas

isomer

molecular dynamics

priority journal

temperature

theoretical study

thermolysis

chemical model

chemical structure

chemistry

comparative study

computer simulation

energy transfer

explosion

gas

Acetaldehyde

Computer Simulation

Energy Transfer

Explosions

Formaldehyde

Gases

Models, Chemical

Models, Molecular

Molecular Structure

Oxygen

Temperature

Tetraoxanes