

Computational Modeling of Reactions of Mono- and Di-substituted Carbonyl Oxides

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We investigate the fate of reactive carbonyl oxide intermediates using the methods of computational quantum chemistry. We examine the unimolecular and bimolecular reactions with water of *syn*- and *anti*-acetaldehyde oxide and methyl vinyl ketone oxide using the GAUSSIAN03 software suite. Minima and transition states are first found using the B3LYP level of theory, and are currently being geometrically optimized at the QCISD level, using the very large MG3 basis set where practical. Single-point energies for these optimized structures will be calculated using the MCG3 composite method. *Syn*-acetaldehyde oxide and both methyl vinyl ketone oxides are found to undergo unimolecular, exothermic hydrogen transfers from the methyl group to form unsaturated hydroperoxides with an energetic barrier of $\sim 15 \text{ kcal mol}^{-1}$, which is unaltered by varying substituents opposite the methyl. *Anti*-acetaldehyde oxide exothermically closes to methyl dioxirane with a barrier of $\sim 17 \text{ kcal mol}^{-1}$. All four carbonyl oxides form van der Waals' complexes with water which react to form β -hydroxy hydroperoxides with barriers from ~ 8 to $\sim 16 \text{ kcal mol}^{-1}$. When complete, the highly optimized energies will be used for transition state theory calculations on these reactions.