Chemical reactions were studied using molecular orbital methods. The main objects of the study were location of reaction transition states, the effect of water solvation on the reaction mechanism and, transition state analogs. The RNA hydrolysis, ene reaction and Darzen's reaction were studied. Model systems were used to reduce the computational effort.

For the RNA hydrolysis, the simplest dianionic pentacoordinate oxyphosphorane, PO$_5$H$_2^-$, was used as a model system. The base catalyzed hydrolysis reaction OH$^- +$ H$_2$PO$_4$ $\rightarrow$ [H$_3$PO$_5^2^-$] $\rightarrow$ H$_2$PO$_4^-$ + OH$^-$ was studied. Earlier ab initio calculations indicate that PO$_5$H$_2^-$ exists only as a transition state on gas-phase reaction profile. However, the present HF/3-21+G$^*$ calculations show that it exists as a pentacoordinate intermediate when it is sufficiently hydrated. Since PO$_5$H$_2^-$ is the least stable pentacoordinate oxyphosphorane, these results strongly suggest that any dianionic oxyphosphorane can exist as a pentacoordinate intermediate in aqueous solution.

For the ene reaction, several model systems were studied. The results, with respect to the reactions of formaldehyde and ethylene with propene, indicate that the difference between MP2 and HF level geometry optimizations is almost negligible. However, the inclusion of electron correlation correction has a strong effect on the energetics of the ene reaction. The MP2/6-31G$^*$//HF/3-21G activation energies for the ene reaction between maleic anhydride and propene were quite accurate. The ene reaction of 1-alkenes and maleimide was studied using propene as a representative 1-alkene. MP2/6-31G$^*$//HF/6-31G$^*$ level of accuracy was used for the ab initio reaction modeling. Although the semiempirical AM1 method did not provide accurate reaction energetics, the transition state geometries were found to be in good agreement with the respective HF/6-31G$^*$ structures. The endo transition state of the reaction between 1-butene and maleimide was used as a basis for transition state analog studies. Since the AM1 method provided reliable structural information, the transition state and its putative analogs were optimized using the same method. The comparison between the transition state and the analogs was done using a rigid body field fit.

The Darzen's reaction between benzaldehyde and methyl-1-chloroacetate was studied. A cyclic transition state was optimized at the HF/3-21G$^*$ level and found to have a half-chair conformation. The reaction was exothermic and the activation energy low with respect to the enol form of the ester. The rate limiting step is in consequence of the keto enol tautomerism of the ester. The O-H-O proton migration was found to be simultaneous to the C-C bond formation.