Theoretical Study of $H_2C-X = {}^{3}H_2C + X$ and $H_2Si-X = {}^{1}H_2Si + X$

(X=H, Cl, CH₃, and SiH₃) Bond Breaking Reactions

Figure 1: RO-CCSD, RO-CCL, and U-CCSD(T) errors in mhartree. R is the studied bond distance in angstrom.





* MIX stands for the MINI basis set on the C/Si-Cl bond and 6-311G on the H atoms.

Figure 2. Standard deviation (in mhartree) of the errors of the RO-CCSD, RO-





- 1). $H_2C-H = {}^3H_2C + H$ (MINI)
- 2). $H_2C-H = {}^3H_2C + H$ (6-31G)
- 3). $H_2C-H = {}^{3}H_2C + H [6-31G(d)]$
- 4). $H_2C-Cl = {}^{3}H_2C + Cl (MIX))$
- 5). $H_2C-CH_3 = {}^{3}H_2C + CH_3$ (MINI)
- 6). $H_2C-SiH_3 = {}^{3}H_2C + SiH_3$ (MINI)

- 7). $H_2Si-H = {}^{1}H_2Si + H$ (MINI)
- 8). $H_2Si-H = {}^1H_2Si + H$ (6-31G)
- 9). $H_2Si-H = {}^{1}H_2Si + H [6-31G(d)]$
- 10). $H_2Si-Cl = {}^1H_2Si + Cl (MIX)$
- 11). $H_2Si-CH_3 = {}^1H_2Si + CH_3$ (MINI)
- 12). $H_2Si-SiH_3 = {}^{1}H_2Si + SiH_3$ (MINI)

Conclusions:

The RO-CCL potential energy surfaces agree with the FCI ones within 2 mhartree error for most of the studied bond breaking reactions of open shell species. The largest error is 3.4 mhartree for the $H_2C-H =$ ${}^{3}H_2C + H$ bond breaking reaction with a 6-31G(d) basis set being used. RO-CCL can be used to predict reasonably accurate potential energy surfaces that are needed to calculate reaction rate constants.

The RO-CCL potential energy surfaces match the FCI ones better than the U-CCSD(T) ones. Also the characteristic CC energy error humps appear at longer bond distances on the RO-CCL PES.