Thermodynamic properties of reaction for acid-catalyzed esterification of acetic acid with methanols using X + CH3COOH + (CH3OH)2 as reference reactant species

|  |  |  |  |
| --- | --- | --- | --- |
|  | X=HCl | | Products |
| X3LYP/6-31+G(d) | | 36.93 | 10.84 |
| ΔG\*a | | 135.75 | 128.68 |
| ΔΔG\*solvb | | -130.93 | -129.6 |
| ΔG\*solb | | 5.62 | -0.92 |
| ΔG0sold | | 7.52 | -2.82 |

Values in kcal mol-1

X3LYP/6-31+G(d) = GibbsCPCM ­ SCRFSMD

a Standard state 1 mol L-1 for all species [Relative gas phase free energy of activation]

b Solvation free energy in SMD/X3LYP/6-31+G(d) level [= ΔSCRFSMD ­ (ΔGibbsCPCM ­ ΔSCRFSMD) ­ SCFgas]

c Standard state at 1 mol L-1 for all species

d Standard state at 1 mol L-1for solute and pure solvent for methanol

Thermodynamic properties of reaction and activation for acid-catalyzed esterification of acetic acid in methanol using (CH3OH)2 + CH3C(OH)OH+ as reference reactant species

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Silva  Paper | TSb-3 | Products | Activated HOAc | Products |
| X3LYP/6-31+G(d) | 24.84 | -1.68 | 22.61 | -1.68 |
| ΔG\*a | 20.40 | -8.19 | 20.17 | -11.19 |
| ΔΔG\*solvb | 0.11 | - | 0.71 | 9.33 |
| ΔG\*solb | 20.51 | - | 20.88 | -1.86 |
| ΔG0sold | 22.40 | -4.98 | 22.78 | -3.76 |

Values in kcal mol-1

a Standard state 1 mol L-1 for all species. In order to consider the two possible forms of the CH3OH attack, the ­RTln[CH3OH] = 1.9 kcal mol-1 term was included

b Solvation free energy in SMD/X3LYP/6-31+G(d) level

c Standard state at 1 mol L-1 for all species

d Standard state at 1 mol L-1for solute and pure solvent for methanol

Solvation free energy of some ionic species involved in acid-catalyzed esterification of acetic acid in methanol

|  |  |  |
| --- | --- | --- |
| A+(CH3OH)n | ΔG\*solv(A+) | ΔG\*solv(A+) Silva |
| CH3C(OH)OH+ | -66.12a | -65.22a |
| CH3C(OH)OH+(CH3OH)2 | -75.94b | -75.60b |

Values in kcal mol−1

a Values obtained using continuum solvation model (SMD)

b Values obtained using the hybrid cluster-continuum model