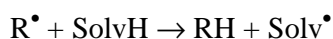
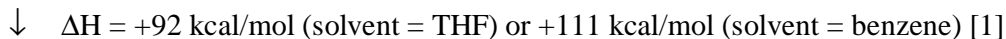
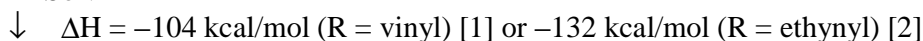
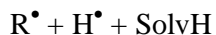


Thermodynamic estimates

1) Hydrogen abstraction from the solvent:



can be decomposed as two elementary steps:

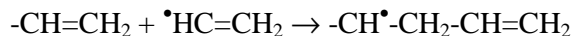


whence the table for ΔH (in kcal/mol):

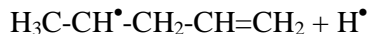
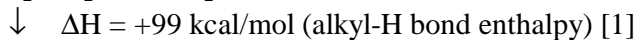
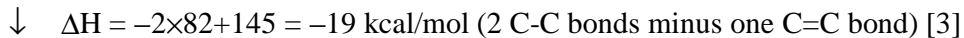
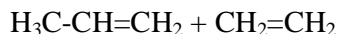
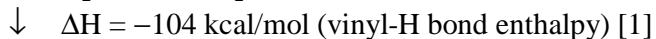
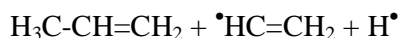
| | vinyl | ethynyl |
|---------|-------|---------|
| THF | -12 | -40 |
| Benzene | +7 | -21 |

2) Addition of R^\bullet on the grafted surface:

For the case of vinyl:

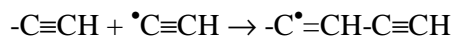


Mimicking the substrate by a methyl group, the reaction can be decomposed into three steps:

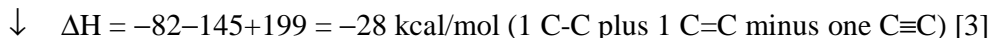
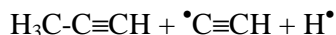


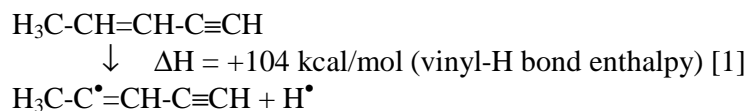
whence a total $\Delta H = -24 \text{ kcal/mol}$.

For the case of ethynyl:



Mimicking the substrate by a methyl group, the reaction can be decomposed into three steps:

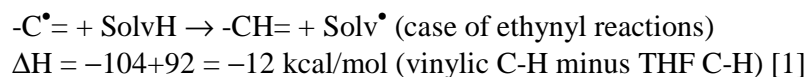
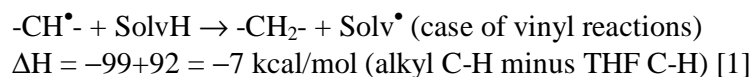




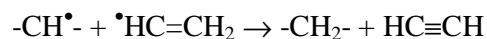
whence a total $\Delta\text{H} = -56 \text{ kcal/mol}$.

3) The rearrangement reactions:

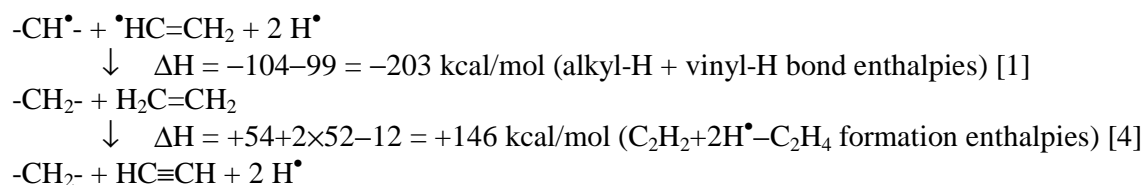
All the reactions of the type $\text{R}_1^\bullet + \text{R}_2^\bullet \rightarrow \text{R}_1\text{R}_2$ are strongly exothermic ($\Delta\text{H} \sim -80$ to -100 kcal/mol [1]) and will not be discussed in more detail. Those involving hydrogen abstraction from the solvent are discussed hereafter (for the case of THF):



The least trivial reaction is now:



It can be decomposed as follows:



whence $\Delta\text{H} = -57 \text{ kcal/mol}$.

References

- [1] Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: Chichester, and Masson: Paris, 1995; pp. 297-299.
- [2] Lide, D. K. *Handbook of Chemistry and Physics, 72th ed.*; CRC Press: Boca Raton, 1991; pp. 9-114 to 9-121.
- [3] Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin: Menlo Park, 1979; p. 77.
- [4] Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Dekker: New York, 1985; pp. 189-200.