Thermodynamic estimates

1) Hydrogen abstraction from the solvent:

$R^{\bullet} + SolvH \rightarrow RH + Solv^{\bullet}$

can be decomposed as two elementary steps:

$R^{\bullet} + H^{\bullet} + SolvH$
↓ ΔH = –104 kcal/mol (R = vinyl) [1] or –132 kcal/mol (R = ethynyl) [2]
$RH + SolvH$
↓ ΔH = +92 kcal/mol (solvent = THF) or +111 kcal/mol (solvent = benzene) [1]
$RH + Solv^{\bullet} + H^{\bullet}$

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:

$-CH=CH_2 + {}^{\bullet}HC=CH_2 \rightarrow -CH^{\bullet}-CH_2-CH=CH_2$

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

$H_3C-CH=CH_2 + {}^{\bullet}HC=CH_2 + H^{\bullet}$
↓ ΔH = –104 kcal/mol (vinyl-H bond enthalpy) [1]
$H_3C-CH=CH_2 + CH_2=CH_2$
↓ ΔH = –2×82+145 = –19 kcal/mol (2 C-C bonds minus one C=C bond) [3]
$H_3C-CH_2-CH_2-CH=CH_2$
↓ ΔH = +99 kcal/mol (alkyl-H bond enthalpy) [1]
$H_3C-CH^{\bullet}-CH_2-CH=CH_2 + H^{\bullet}$

whence a total ΔH = –24 kcal/mol.

For the case of ethynyl:

$-C\equiv CH + {}^{\bullet}C\equiv CH \rightarrow -C^{\bullet}=CH-C\equiv CH$

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

$H_3C-C\equiv CH + {}^{\bullet}C\equiv CH + H^{\bullet}$
↓ ΔH = –132 kcal/mol (ethynyl-H bond enthalpy) [2]
$H_3C-C\equiv CH + HC\equiv CH$
↓ ΔH = –82–145+199 = –28 kcal/mol (1 C-C plus 1 C=C minus one C≡C) [3]

H_3C-CH=CH-C≡CH
↓ ΔH = +104 kcal/mol (vinyl-H bond enthalpy) [1]
H_3C-$C^{\bullet}$=CH-C≡CH + $H^{\bullet}$

whence a total ΔH = –56 kcal/mol.

3) The rearrangement reactions:

All the reactions of the type $R_1^{\bullet} + R_2^{\bullet} \rightarrow R_1R_2$ are strongly exothermic (ΔH~–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):

-$CH^{\bullet}$- + SolvH → -CH_2- + $Solv^{\bullet}$ (case of vinyl reactions)
ΔH = –99+92 = –7 kcal/mol (alkyl C-H minus THF C-H) [1]

-$C^{\bullet}$= + SolvH → -CH= + $Solv^{\bullet}$ (case of ethynyl reactions)
ΔH = –104+92 = –12 kcal/mol (vinylic C-H minus THF C-H) [1]

The least trivial reaction is now:

-$CH^{\bullet}$- + $^{\bullet}HC=CH_2$ → -CH_2- + HC≡CH

It can be decomposed as follows:

-$CH^{\bullet}$- + $^{\bullet}HC=CH_2$ + 2 $H^{\bullet}$
↓ ΔH = –104–99 = –203 kcal/mol (alkyl-H + vinyl-H bond enthalpies) [1]
-CH_2- + $H_2C=CH_2$
↓ ΔH = +54+2×52–12 = +146 kcal/mol (C_2H_2+2$H^{\bullet}$–C_2H_4 formation enthalpies) [4]
-CH_2- + HC≡CH + 2 $H^{\bullet}$

whence ΔH = –57 kcal/mol.

References

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[4] Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Dekker: New York, 1985; pp. 189-200.