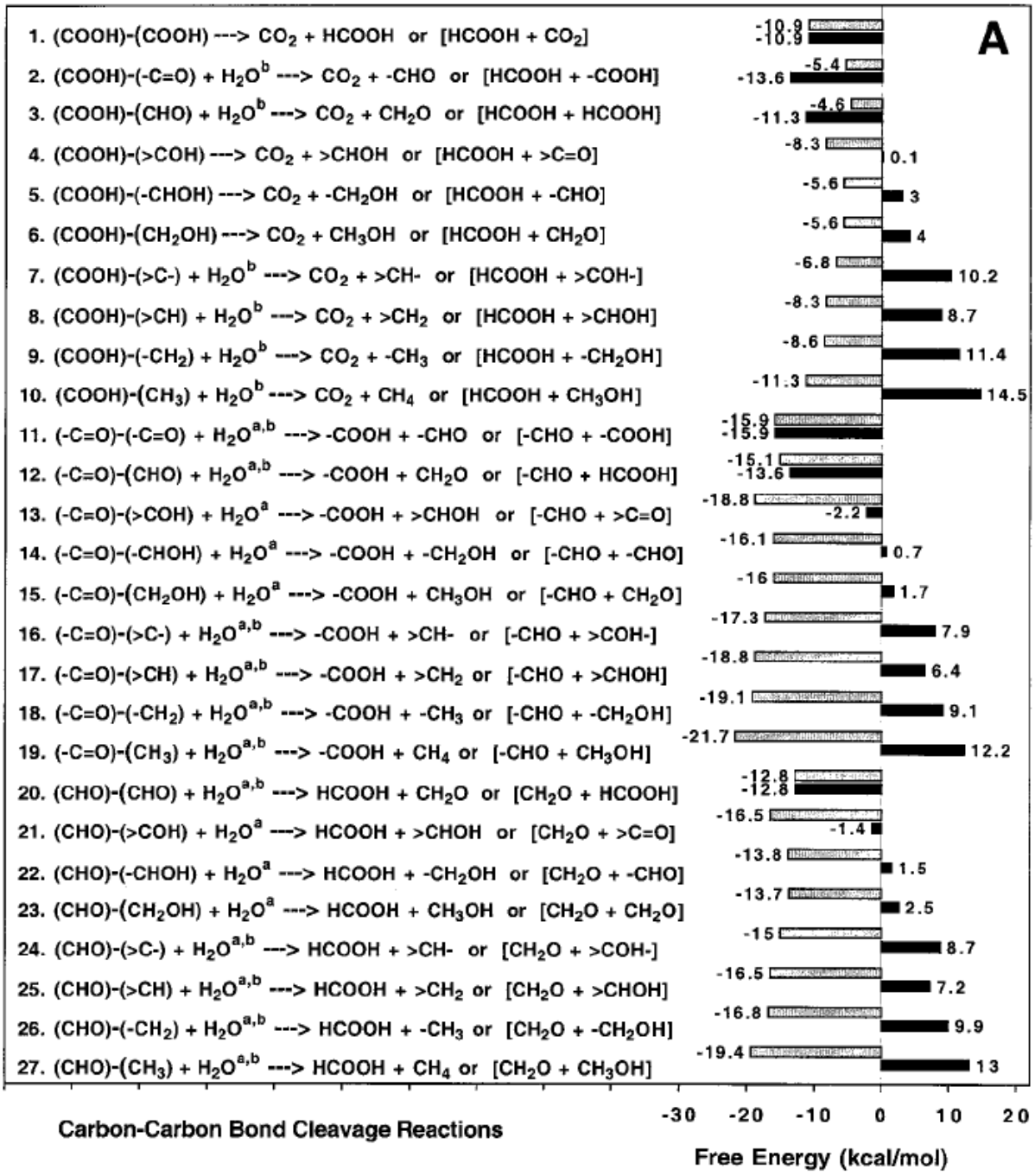
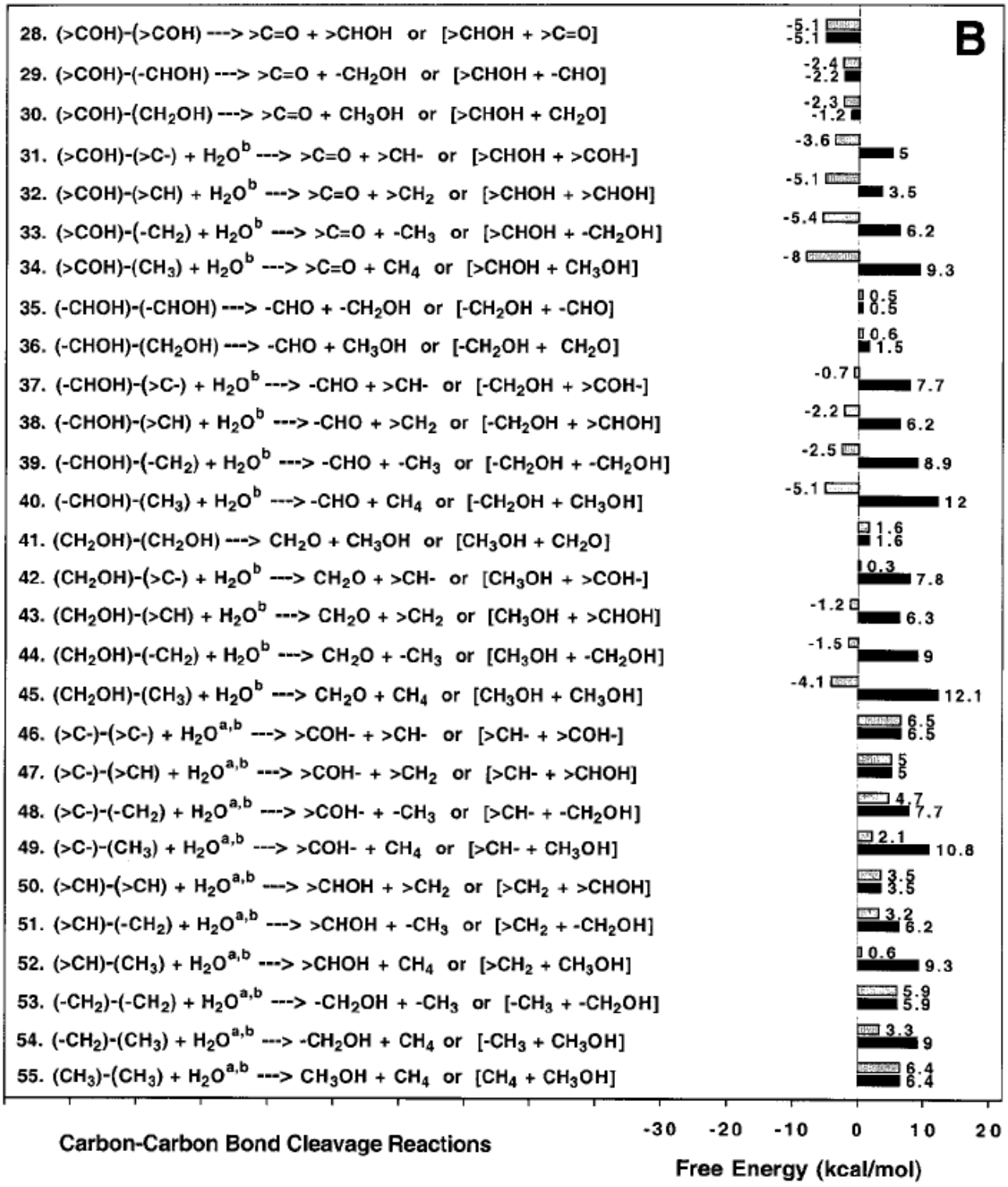
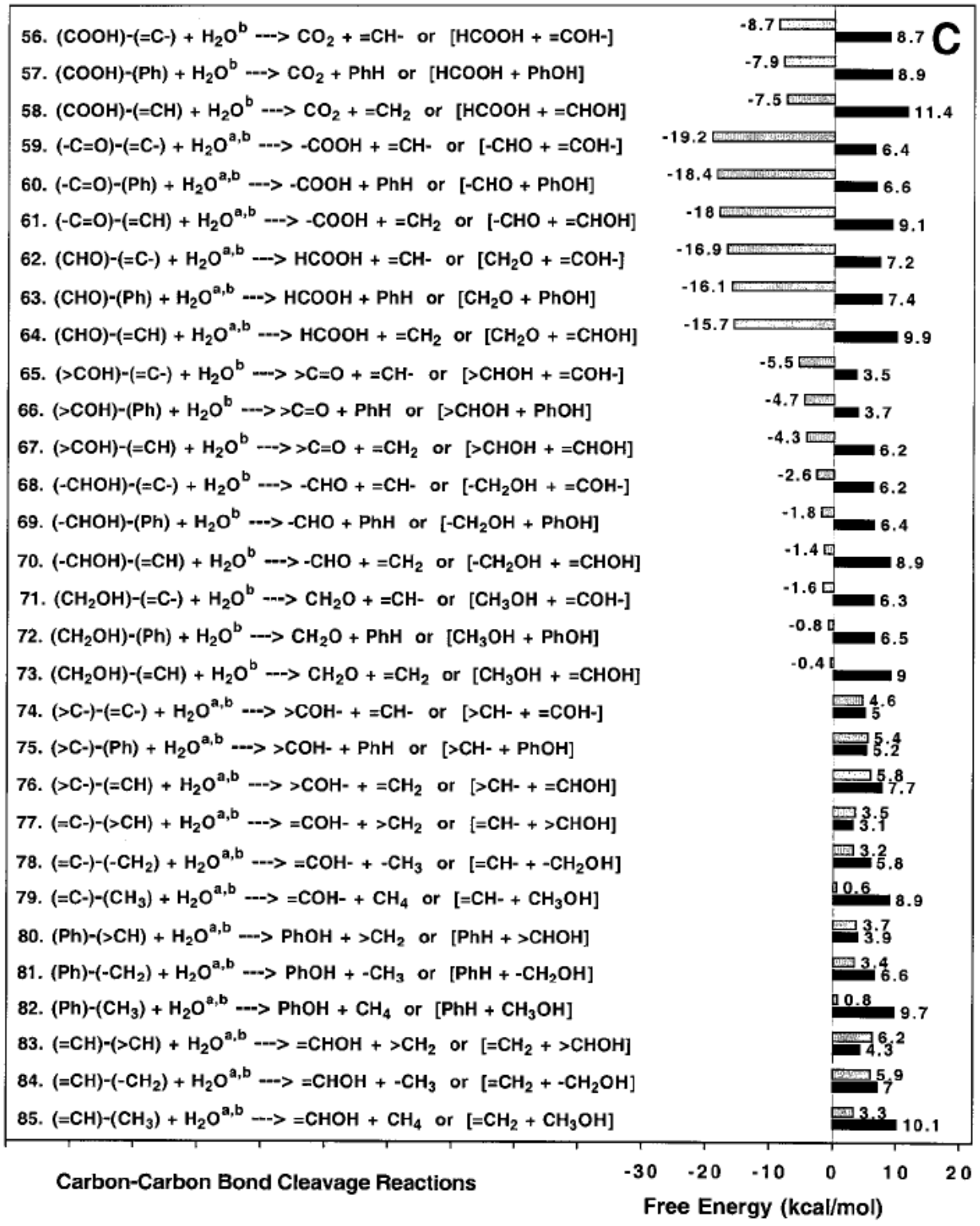


Figure 2. Carbon-carbon bond cleavage reactions and their free energies at 1 mM concentration under mild aqueous conditions (25 °C, pH 7). For each pair of bonded groups the two sets of products of heterolytic cleavage are shown. The first set of unbracketed products have energies represented by the gray bar, and the second set of bracketed products have energies denoted by the black bar. In (A) and (B) single bond cleavage involves groups participating only in C-C single bonds. In (C) single bond cleavage involves one group participating only in C-C single bonds, and one group participating in C-C single bonds and either a C-C double bond or a benzene ring. Superscripts (a) and (b) assign water to first and second cleavage modes, respectively.


B
28. (>COH)-(>COH) ---> >C=O + >CHOH or [>CHOH + >C=O]
29. (>COH)-(-CHOH) ---> >C=O + -CH2OH or [>CHOH + -CHO]
30. (>COH)-(CH2OH) ---> >C=O + CH3OH or [>CHOH + CH2O]
31. (>COH)-(>C-) + H2O[b] ---> >C=O + >CH- or [>CHOH + >COH-]
32. (>COH)-(>CH) + H2O[b] ---> >C=O + >CH2 or [>CHOH + >CHOH]
33. (>COH)-(-CH2) + H2O[b] ---> >C=O + -CH3 or [>CHOH + -CH2OH]
34. (>COH)-(CH3) + H2O[b] ---> >C=O + CH4 or [>CHOH + CH3OH]
35. (-CHOH)-(-CHOH) ---> -CHO + -CH2OH or [-CH2OH + -CHO]
36. (-CHOH)-(CH2OH) ---> -CHO + CH3OH or [-CH2OH + CH2O]
37. (-CHOH)-(>C-) + H2O[b] ---> -CHO + >CH- or [-CH2OH + >COH-]
38. (-CHOH)-(>CH) + H2O[b] ---> -CHO + >CH2 or [-CH2OH + >CHOH]
39. (-CHOH)-(-CH2) + H2O[b] ---> -CHO + -CH3 or [-CH2OH + -CH2OH]
40. (-CHOH)-(CH3) + H2O[b] ---> -CHO + CH4 or [-CH2OH + CH3OH]
41. (CH2OH)-(CH2OH) ---> CH2O + CH3OH or [CH3OH + CH2O]
42. (CH2OH)-(>C-) + H2O[b] ---> CH2O + >CH- or [CH3OH + >COH-]
43. (CH2OH)-(>CH) + H2O[b] ---> CH2O + >CH2 or [CH3OH + >CHOH]
44. (CH2OH)-(-CH2) + H2O[b] ---> CH2O + -CH3 or [CH3OH + -CH2OH]
45. (CH2OH)-(CH3) + H2O[b] ---> CH2O + CH4 or [CH3OH + CH3OH]
46. (>C-)-(>C-) + H2O[a,b] ---> >COH- + >CH- or [>CH- + >COH-]
47. (>C-)-(>CH) + H2O[a,b] ---> >COH- + >CH2 or [>CH- + >CHOH]
48. (>C-)-(-CH2) + H2O[a,b] ---> >COH- + -CH3 or [>CH- + -CH2OH]
49. (>C-)-(CH3) + H2O[a,b] ---> >COH- + CH4 or [>CH- + CH3OH]
50. (>CH)-(>CH) + H2O[a,b] ---> >CHOH + >CH2 or [>CH2 + >CHOH]
51. (>CH)-(-CH2) + H2O[a,b] ---> >CHOH + -CH3 or [>CH2 + -CH2OH]
52. (>CH)-(CH3) + H2O[a,b] ---> >CHOH + CH4 or [>CH2 + CH3OH]
53. (-CH2)-(-CH2) + H2O[a,b] ---> -CH2OH + -CH3 or [-CH3 + -CH2OH]
54. (-CH2)-(CH3) + H2O[a,b] ---> -CH2OH + CH4 or [-CH3 + CH3OH]
55. (CH3)-(CH3) + H2O[a,b] ---> CH3OH + CH4 or [CH4 + CH3OH]
-5.1
-5.1
-2.4
-2.2
-2.3
-1.2
-3.6
5
-5.1
3.5
-5.4
6.2
-8
9.3
0.5
0.5
0.6
1.5
-0.7
7.7
-2.2
6.2
-2.5
8.9
-5.1
12
1.6
1.6
0.3
7.8
-1.2
6.3
-1.5
9
-4.1
12.1
6.5
6.5
5
5
4.7
7.7
2.1
10.8
3.5
3.5
3.2
6.2
0.6
9.3
5.9
5.9
3.3
9
6.4
6.4
-30
-20
-10
0
10
20
Carbon-Carbon Bond Cleavage Reactions
Free Energy (kcal/mol)


56. (COOH)-(=C-) + H2O[b] ---> CO2 + =CH- or [HCOOH + =COH-]
57. (COOH)-(Ph) + H2O[b] ---> CO2 + PhH or [HCOOH + PhOH]
58. (COOH)-(=CH) + H2O[b] ---> CO2 + =CH2 or [HCOOH + =CHOH]
59. (-C=O)-(=C-) + H2O[a,b] ---> -COOH + =CH- or [-CHO + =COH-]
60. (-C=O)-(Ph) + H2O[a,b] ---> -COOH + PhH or [-CHO + PhOH]
61. (-C=O)-(=CH) + H2O[a,b] ---> -COOH + =CH2 or [-CHO + =CHOH]
62. (CHO)-(=C-) + H2O[a,b] ---> HCOOH + =CH- or [CH2O + =COH-]
63. (CHO)-(Ph) + H2O[a,b] ---> HCOOH + PhH or [CH2O + PhOH]
64. (CHO)-(=CH) + H2O[a,b] ---> HCOOH + =CH2 or [CH2O + =CHOH]
65. (>COH)-(=C-) + H2O[b] ---> >C=O + =CH- or [>CHOH + =COH-]
66. (>COH)-(Ph) + H2O[b] ---> >C=O + PhH or [>CHOH + PhOH]
67. (>COH)-(=CH) + H2O[b] ---> >C=O + =CH2 or [>CHOH + =CHOH]
68. (-CHOH)-(=C-) + H2O[b] ---> -CHO + =CH- or [-CH2OH + =COH-]
69. (-CHOH)-(Ph) + H2O[b] ---> -CHO + PhH or [-CH2OH + PhOH]
70. (-CHOH)-(=CH) + H2O[b] ---> -CHO + =CH2 or [-CH2OH + =CHOH]
71. (CH2OH)-(=C-) + H2O[b] ---> CH2O + =CH- or [CH3OH + =COH-]
72. (CH2OH)-(Ph) + H2O[b] ---> CH2O + PhH or [CH3OH + PhOH]
73. (CH2OH)-(=CH) + H2O[b] ---> CH2O + =CH2 or [CH3OH + =CHOH]
74. (>C-)-(=C-) + H2O[a,b] ---> >COH- + =CH- or [>CH- + =COH-]
75. (>C-)-(Ph) + H2O[a,b] ---> >COH- + PhH or [>CH- + PhOH]
76. (>C-)-(=CH) + H2O[a,b] ---> >COH- + =CH2 or [>CH- + =CHOH]
77. (=C-)-(>CH) + H2O[a,b] ---> =COH- + >CH2 or [=CH- + >CHOH]
78. (=C-)-(-CH2) + H2O[a,b] ---> =COH- + -CH3 or [=CH- + -CH2OH]
79. (=C-)-(CH3) + H2O[a,b] ---> =COH- + CH4 or [=CH- + CH3OH]
80. (Ph)-(>CH) + H2O[a,b] ---> PhOH + >CH2 or [PhH + >CHOH]
81. (Ph)-(-CH2) + H2O[a,b] ---> PhOH + -CH3 or [PhH + -CH2OH]
82. (Ph)-(CH3) + H2O[a,b] ---> PhOH + CH4 or [PhH + CH3OH]
83. (=CH)-(>CH) + H2O[a,b] ---> =CHOH + >CH2 or [=CH2 + >CHOH]
84. (=CH)-(-CH2) + H2O[a,b] ---> =CHOH + -CH3 or [=CH2 + -CH2OH]
85. (=CH)-(CH3) + H2O[a,b] ---> =CHOH + CH4 or [=CH2 + CH3OH]
-8.7
8.7
C
-7.9
8.9
-7.5
11.4
-19.2
6.4
-18.4
6.6
-18
9.1
-16.9
7.2
-16.1
7.4
-15.7
9.9
-5.5
3.5
-4.7
3.7
-4.3
6.2
-2.6
6.2
-1.8
6.4
-1.4
8.9
-1.6
6.3
-0.8
6.5
-0.4
9
4.6
5
5.4
5.2
5.8
7.7
3.5
3.1
3.2
5.8
0.6
8.9
3.7
3.9
3.4
6.6
0.8
9.7
6.2
4.3
5.9
7
3.3
10.1
-30
-20
-10
0
10
20
Carbon-Carbon Bond Cleavage Reactions
Free Energy (kcal/mol)