SUPPORTING INFORMATION

FOR

AN INTRINSIC RADICAL STABILITY SCALE FROM THE PERSPECTIVE OF BOND DISSOCIATION ENTHALPIES : A COMPANION TO RADICAL ELECTROPHILICITIES

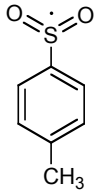
Freija De Vleeschouwer[(1)], Veronique Van Speybroeck[(2)], Michel Waroquier[(2)], Paul Geerlings[(1)], Frank De Proft[(1)*]

[(1)]Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Faculteit Wetenschappen, Pleinlaan 2, 1050 Brussels, Belgium, and [(2)]Center for Molecular Modeling (CMM), Ghent University (UG), Proeftuinstraat 86, 9000 Gent, Belgium

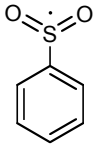
corresponding author: fdeprof@vub.ac.be

Content

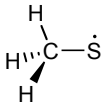
TOSYL



PHENYLSULFONYL

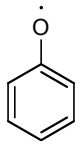


METHYLSULFIDE



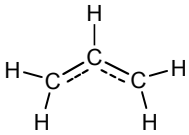
SCH3

PHENOXY



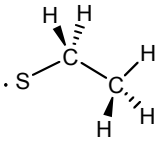
OC6H5

ALLYL



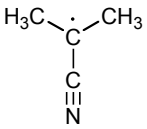
CH2CHCH2

ETHYLSULFIDE



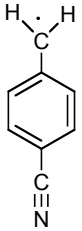
SCH2CH3

2-CYANOPROP-2-YL



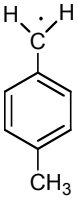
C(CN)(CH3)2

***p*-CYANOBENZYL**



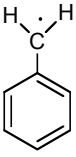
CH2C6H4(CN)

***p*-METHYLBENZYL**



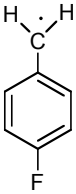
CH2C6H4(CH3)

BENZYL



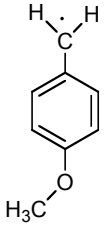
CH2C6H5

***p*-FLUOROBENZYL**



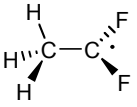
CH2C6H4(F)

***p*-METHOXYBENZYL**



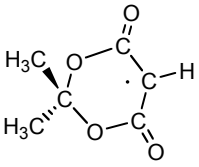
CH2C6H4(OCH3)

1,1-DIFLUOROETHYL

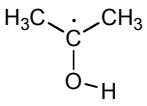


CF2CH3

2,2-DIMETHYL-4,6-DIOXO-1,3-DIOXAN-5-YL

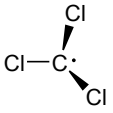


2-HYDROXYPROP-2-YL



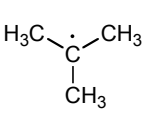
C(OH)(CH3)2

TRICHLOROMETHYL



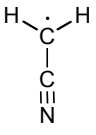
CCl3

***tert*-BUTYL**



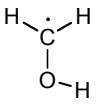
C(CH3)3

CYANOMETHYL



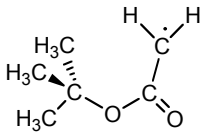
CH2CN

HYDROXYMETHYL



CH2OH

***tert*-BUTOXYCARBONYLMETHYL**



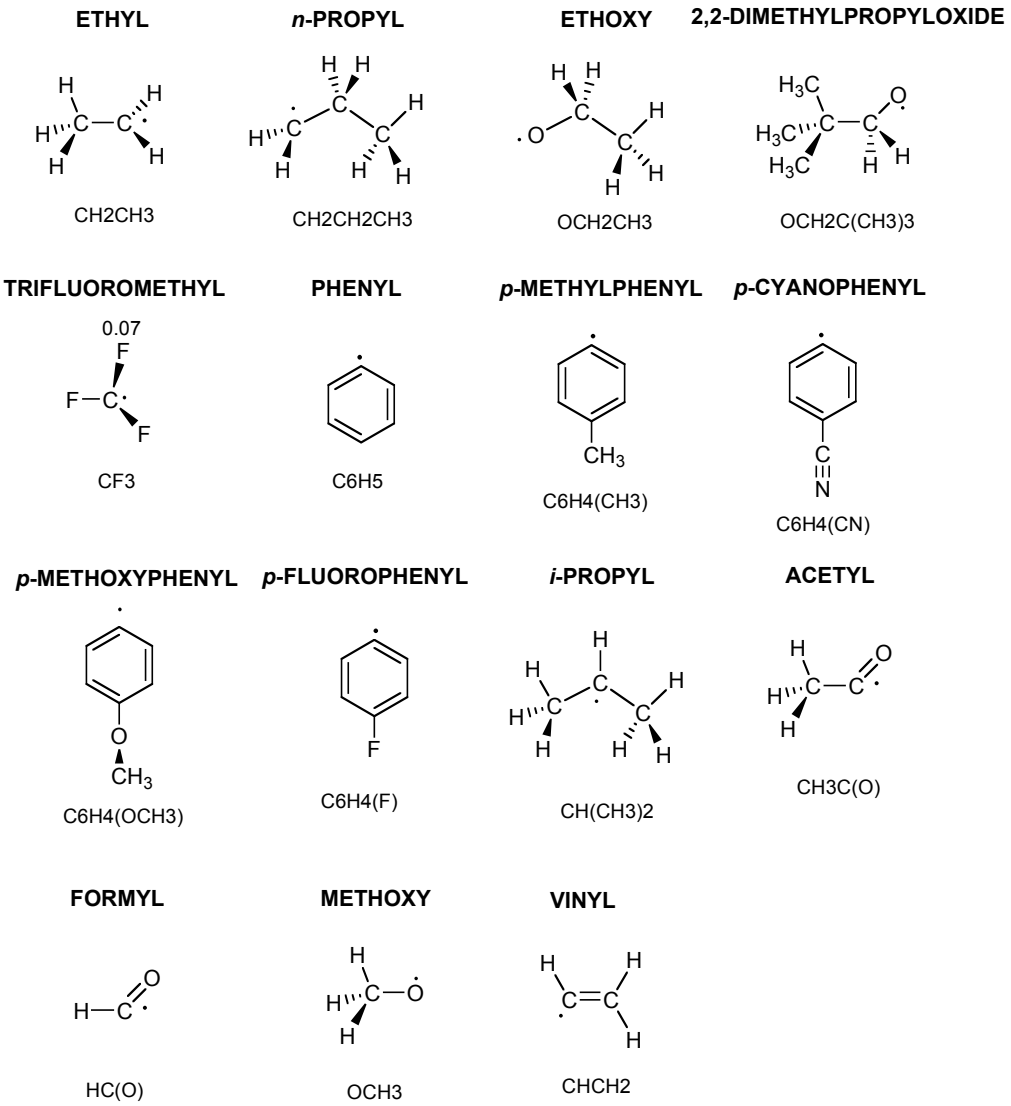


Figure S1: chemical structures of the radicals from the database

Table S1: the experimental and theoretical (i.e. B3LYP, BMK, B3P86, all with basis set 6-311+G) BDEs for the experimental set of 89 radical combinations A and B in kJ mol^{-1}**

A	B	exp	exp. error	B3LYP	BMK	B3P86
Br	H	366.5	0.2[b]	369.4	362.3	385.0
$C(CH_3)_3$	H	403.8	1.7[b]	385.5	398.7	395.8
$C(CN)(CH_3)_2$	H	361.9	8.4[a]	350.9	367.7	361.7
$C(OH)(CH_3)_2$	H	381.0	4.0[a]	375.8	384.8	385.6
C_6H_5	H	472.4	2.5[b]	461.9	467.3	471.9
CCl_3	H	392.5	2.5[a]	381.8	394.6	391.0
CF_2CH_3	H	416.3	10.5[a]	409.7	416.5	419.2
CF_3	H	449.5	[a]	434.7	442.6	444.8
$CH(CH_3)_2$	H	412.5	1.7[b]	396.7	406.8	406.6
$CH_2C_6H_4(CH_3)$	H	368.0	[c]	360.8	371.2	373.4
$CH_2C_6H_4(CN)$	H	363.8	[c]	360.4	371.2	373.0
$CH_2C_6H_4(OCH_3)$	H	364.7	[c]	359.2	369.7	371.9
$CH_2C_6H_5$	H	375.3	2.5[b]	362.5	372.8	375.2
$CH_2CH_2CH_3$	H	423.3	2.1[a]	414.8	422.6	425.9
CH_2CH_3	H	423.0	1.7[b]	411.9	419.6	422.6
CH_2CHCH_2	H	361.9	8.8[a]	351.4	361.3	363.1
CH_2CN	H	392.9	8.4[a]	386.9	399.8	399.3
CH_2OH	H	401.8	1.5[a]	390.5	395.4	400.9
CH_3	H	438.9	0.4[a]	431.2	436.5	442.4
$CH_3C(O)$	H	374.0	1.3[b]	363.1	364.0	375.3
$CHCH_2$	H	463.2	2.9[b]	452.5	458.0	462.7
Cl	H	431.6	0.1[b]	418.9	419.8	436.0
CN	H	527.6	1.7[a]	536.1	549.6	546.5
F	H	570.5	0.0[b]	555.8	553.5	571.8
H	H	436.0	0.0[b]	437.4	426.1	444.9
HC(O)	H	368.6	0.8[b]	360.1	360.9	372.1
NF_2	H	316.7	10.5[a]	298.3	305.3	308.7
NH_2	H	452.7	1.3[a]	438.7	444.6	453.3
NO	H	195.4	0.2[a]	194.7	192.3	206.4
OC_6H_5	H	376.8	12.6[a]	346.9	353.2	363.8
$OCH_2C(CH_3)_3$	H	428.0	6.3[a]	409.4	415.3	424.0
OCH_2CH_3	H	437.7	3.4[a]	412.4	418.0	427.3
OCH_3	H	436.0	3.8[a]	414.0	418.8	428.9
OH	H	497.0	0.4[a]	480.5	483.5	496.8
SCH_2CH_3	H	365.3	[d]	347.9	348.2	361.3
SCH_3	H	365.3	2.5[a]	347.0	346.9	360.4
SH	H	381.6	2.9[a]	368.7	367.7	382.9
C_6H_5	F	532.2	2.9[b]	509.0	523.3	525.8
CF_2CH_3	F	522.2	8.0[a]	495.8	517.4	515.8
$CH(CH_3)_2$	F	462.8	2.1[b]	454.4	471.9	468.9
$CH_2C_6H_5$	F	413.0	2.9[b]	391.8	407.2	407.4
CH_3	F	472.0	[a]	442.9	456.3	458.3
$CH_3C(O)$	F	511.3	3.8[b]	482.2	493.9	503.4
$CHCH_2$	F	515.9	3.3[b]	498.0	512.7	515.4
Br	CH_3	301.7	2.5[b]	284.1	298.7	303.5
$C(CH_3)_3$	CH_3	366.1	1.7[b]	318.1	357.5	337.9
C_6H_5	CH_3	433.0	2.5[b]	401.1	427.6	419.8

CF_3	CH_3	423.4	4.6[a]	401.3	429.8	418.5
$CH(CH_3)_2$	CH_3	370.7	1.7[b]	329.6	363.3	348.3
$CH_2C_6H_5$	CH_3	324.7	2.5[b]	289.9	322.0	310.1
CH_2CH_3	CH_3	372.4	1.7[b]	341.5	370.0	359.2
CH_2CHCH_2	CH_3	320.1	2.1[b]	279.2	310.1	298.2
CH_2CN	CH_3	332.2	8.0[a]	314.9	348.7	334.1
CH_3	CH_3	376.0	2.1[a]	353.7	378.4	371.7
$CH_3C(O)$	CH_3	353.5	1.7[b]	323.2	345.6	343.6
$CHCH_2$	CH_3	424.3	2.9[b]	396.8	421.6	415.2
CN	CH_3	509.6	8.0[a]	510.0	541.0	528.7
HC(O)	CH_3	354.8	0.8[b]	331.0	350.0	350.5
NH_2	CH_3	356.5	1.3[b]	332.0	355.7	351.9
NO	CH_3	167.4	3.3[a]	150.1	165.3	166.9
NO_2	CH_3	254.4	[a]	228.6	256.8	246.1
OH	CH_3	385.3	0.4[b]	360.9	381.6	380.1
SCH_3	CH_3	307.9	3.3[a]	270.7	295.3	291.0
SH	CH_3	312.5	4.2[a]	282.9	306.5	303.3
$C(CH_3)_3$	OCH_3	351.5	4.2[b]	293.5	331.8	314.1
C_6H_5	OCH_3	422.6	4.2[b]	381.1	410.7	402.5
$CH(CH_3)_2$	OCH_3	359.0	2.1[b]	306.4	338.6	325.4
CH_2CH_3	OCH_3	355.6	4.2[b]	314.0	341.8	332.4
CH_3	OCH_3	348.1	3.8[b]	312.0	336.9	330.5
$CH_3C(O)$	OCH_3	418.4	4.2[b]	373.4	400.1	398.1
HC(O)	OCH_3	416.7	3.8[b]	360.3	381.3	383.6
NO	OCH_3	174.9	3.8[a]	146.5	151.5	169.8
NO_2	OCH_3	175.7	4.2[b]	138.7	154.6	161.9
OCH_3	OCH_3	157.3	8.0[a]	113.1	121.3	128.5
$C(CH_3)_3$	OH	400.8	1.7[b]	359.6	391.2	379.3
C_6H_5	OH	470.3	2.5[b]	439.4	463.0	461.0
$CH(CH_3)_2$	OH	399.6	1.7[b]	363.0	390.1	382.1
$CH_2C_6H_5$	OH	345.6	2.9[b]	304.4	328.8	324.3
CH_2CH_3	OH	393.3	1.7[b]	363.7	387.0	382.5
CH_2CHCH_2	OH	335.1	2.5[b]	294.3	319.3	313.7
$CH_3C(O)$	OH	459.8	2.9[b]	428.2	450.1	453.8
Cl	OH	251.0	13.0[a]	196.9	206.1	216.0
HC(O)	OH	458.1	0.8[b]	414.5	432.2	439.1
NO	OH	206.3	[a]	187.4	188.5	211.0
NO_2	OH	206.7	[a]	181.7	193.5	206.2
$OCH_2C(CH_3)_3$	OH	193.7	7.9[a]	140.5	146.7	157.1
OH	OH	213.0	4.0[a]	184.5	187.8	203.3
SH	SH	276.0	8.0[b]	223.1	248.6	244.6
C_6H_5	SH	361.9	8.0[b]	329.8	353.0	352.1

a *CRC Handbook of Chemistry and Physics*, Lide, D. R., Ed.; CRC Press LLC: Florida, 2002.
b Blanksby, S. J.; Ellison, G. B. *Accounts of Chemical Research* **2003**, *36*, 255-263.
c Pratt, D. A.; Wright, J. S.; Ingold, K. U. *Journal of the American Chemical Society* **1999**, *121*, 4877-4882.
d Fu, Y.; Yu, T. Q.; Wang, Y. M.; Liu, L.; Guo, Q. X. *Chinese Journal of Chemistry* **2006**, *24*, 299-306.

Table S2: the BDE of 49 radicals in combination with a set of 8 radicals, calculated with the B3P86/6-311+G method in kJ mol^{-1}**

A	CH_2OH	CH_3	NF_2	H	OCH_3	OH	SH	F
$C(OH)(CH_3)_2$	312.7	335.2	211.8	385.6	325.6	388.7	269.8	485.5
$C(CH_3)_3$	316.8	337.9	211.0	395.8	314.1	379.3	277.1	470.3
CH_2OH	325.6	352.4	219.6	400.9	338.5	391.8	286.7	479.3
$CH(CH_3)_2$	327.9	348.3	217.3	406.6	316.8	382.1	286.4	468.9
NO	149.3	166.9	21.0	206.4	169.8	211.0	128.1	261.6
CH_2CH_3	339.2	359.2	227.5	422.6	332.4	382.5	293.7	465.1
$CH_2CH_2CH_3$	341.9	362.8	232.3	425.9	334.6	384.9	297.0	467.1
$CH_2C_6H_4(OCH_3)$	288.4	307.0	177.0	371.9	273.9	323.7	242.2	408.2
$CH_3C(O)$	331.5	343.6	227.6	375.3	398.1	453.8	304.8	503.4
CF_2CH_3	348.9	384.3	256.4	419.2	376.4	436.2	291.4	515.8
$CH_2C_6H_4(CH_3)$	289.4	308.3	180.3	373.4	274.6	325.2	242.5	407.3
CH_2CHCH_2	277.5	298.2	169.2	363.1	263.4	313.7	230.2	395.2
HC(O)	317.4	350.5	226.9	372.1	383.6	439.1	304.7	501.0
CH_3	352.2	371.7	241.5	442.4	330.5	380.1	303.3	458.3
$CH_2C_6H_5$	290.8	310.1	183.2	375.2	274.6	324.3	243.4	407.4
$CHCH_2$	392.0	415.2	281.3	462.7	394.8	450.3	349.1	515.4
$CH_2C_6H_4(F)$	290.7	310.5	184.1	375.4	277.3	327.6	243.5	407.9
$C_6H_4(CH_3)$	398.1	420.5	295.2	473.4	402.1	460.3	352.9	526.3
$C_6H_4(OCH_3)$	401.7	422.7	296.9	476.7	400.1	458.4	355.0	525.7
C_6H_5	396.6	419.8	294.7	471.9	402.5	461.0	352.1	525.8
CCl_3	325.4	348.7	208.5	391.0	324.0	374.2	239.2	430.7
$C(CN)(CH_3)_2$	279.1	302.9	180.6	361.7	270.1	328.4	227.9	403.6
$C_6H_4(F)$	400.9	424.0	301.2	477.0	402.8	460.3	353.0	525.3
CF_3	383.0	418.5	288.0	444.8	408.9	464.9	309.9	526.7
NF_2	245.8	262.8	81.2	308.7	167.1	213.7	138.6	233.4
$C_6H_4(CN)$	399.6	425.3	306.9	474.6	410.6	467.5	355.8	526.0
NH_2	360.3	351.9	183.2	453.3	218.7	267.8	268.7	291.9
$CH_2C_6H_4(CN)$	284.0	307.9	193.1	373.0	274.7	325.1	237.8	398.9
tert-butoxycarbonylmethyl	320.1	343.5	223.0	407.5	291.4	341.8	262.4	421.8
CH_2CN	309.5	334.1	209.1	399.3	277.9	327.2	245.8	398.7
H	400.9	442.4	320.8	444.9	428.9	496.7	382.9	571.8
OCH_2CH_3	331.4	322.4	119.3	427.3	124.5	163.4	214.1	171.2
NO_2	240.4	246.1	82.8	297.3	161.9	206.2	148.1	235.3
OCH_3	338.5	330.5	120.8	428.9	128.5	165.9	216.1	172.0
$OCH_2C(CH_3)_3$	332.3	324.9	114.5	424.0	118.3	157.1	213.0	164.0
SCH_3	271.5	291.0	160.3	360.4	217.8	272.7	239.8	330.5
SCH_2CH_3	270.4	288.7	161.8	361.3	218.0	273.2	242.1	332.0
OC_6H_5	261.0	256.5	47.3	363.8	44.5	82.1	135.8	84.9
tosyl	229.4	254.9	143.6	278.0	246.8	301.0	188.3	375.7
phenylsulfonyl	229.5	255.5	144.9	278.0	247.1	301.1	188.3	374.7
OH	390.3	380.1	174.8	496.8	165.9	203.3	268.4	196.1
SH	286.7	303.3	173.1	382.9	216.1	268.4	244.5	318.5
2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl	302.0	317.6	215.3	384.9	265.1	319.5	236.5	377.3
Br	294.1	303.5	166.0	385.0	160.8	208.6	227.9	246.2
Cl	341.9	346.7	191.9	436.0	173.6	216.0	247.7	234.5
F	479.3	458.3	221.4	571.8	172.0	196.1	318.5	143.4
CN	484.6	528.7	399.1	546.5	461.8	514.0	430.7	528.6

Table S3: the BDE of 49 radicals in combination with a set of 8 radicals, calculated with model 1 (including the stability and the global electrophilicity) in kJ mol^{-1}

A	CH_2OH	CH_3	NF_2	H	OCH_3	OH	SH	F
$C(OH)(CH_3)_2$	293.8	337.6	213.8	420.4	277.6	342.0	313.2	469.5
$C(CH_3)_3$	296.7	339.4	214.3	420.5	277.6	341.2	312.3	465.7
CH_2OH	303.2	345.0	218.6	424.4	281.4	344.4	315.3	466.0
$CH(CH_3)_2$	306.6	348.3	221.9	427.7	284.7	347.6	318.6	469.1
NO	118.2	157.7	28.4	233.2	89.9	151.3	122.0	266.0
CH_2CH_3	322.1	361.3	231.7	436.4	293.1	354.4	325.0	468.4
$CH_2CH_2CH_3$	328.7	366.7	235.4	439.5	296.1	356.5	327.0	466.6
$CH_2C_6H_4(OCH_3)$	275.6	312.9	180.6	384.4	240.8	300.7	271.1	408.5
$CH_3C(O)$	325.1	361.6	228.4	431.9	288.2	347.6	317.9	453.3
CF_2CH_3	351.0	387.1	253.3	456.6	312.9	372.0	342.3	476.3
$CH_2C_6H_4(CH_3)$	281.7	317.1	182.5	385.5	241.7	300.4	270.6	402.8
CH_2CHCH_2	270.4	305.8	171.1	374.1	230.3	288.9	259.1	391.2
HC(O)	322.5	357.7	222.9	425.8	282.0	340.5	310.6	442.2
CH_3	345.0	379.6	244.1	446.8	302.9	361.0	331.1	461.2
$CH_2C_6H_5$	286.5	320.7	184.6	387.1	243.2	301.0	271.1	399.8
$CHCH_2$	386.0	420.0	283.7	486.1	342.1	399.8	369.9	498.1
$CH_2C_6H_4(F)$	287.8	321.7	185.1	387.4	243.4	301.0	271.0	398.7
$C_6H_4(CH_3)$	401.1	433.2	294.4	496.0	351.8	408.2	378.0	500.7
$C_6H_4(OCH_3)$	403.8	435.8	296.7	498.2	354.0	410.2	380.0	502.1
C_6H_5	400.9	432.7	293.5	494.9	350.7	406.9	376.7	498.5
CCl_3	321.8	352.6	212.0	413.0	268.6	324.1	293.7	412.4
$C(CN)(CH_3)_2$	288.2	318.8	177.9	378.8	234.4	289.7	259.3	377.4
$C_6H_4(F)$	411.6	441.0	298.5	498.8	354.3	408.8	378.3	492.8
CF_3	399.6	427.6	283.3	483.1	338.4	392.0	361.3	471.9
NF_2	218.6	244.1	96.5	295.2	150.2	202.0	171.0	274.2
$C_6H_4(CN)$	423.0	448.4	300.7	499.3	354.3	406.0	375.0	477.9
NH_2	325.4	350.6	202.6	401.1	256.1	307.7	276.7	378.9
$CH_2C_6H_4(CN)$	309.2	334.3	186.2	384.7	239.6	291.1	260.1	362.1
tert-butoxycarbonylmethyl	342.7	367.0	218.0	416.1	271.0	322.0	290.9	390.6
CH_2CN	332.0	355.3	204.8	402.5	257.2	307.5	276.3	373.0
H	424.4	446.8	295.2	492.5	347.1	396.8	365.5	459.6
OCH_2CH_3	277.8	299.4	146.9	343.9	198.4	247.6	216.2	308.2
NO_2	225.6	247.2	94.6	291.6	146.1	195.3	163.8	255.7
OCH_3	281.4	302.9	150.2	347.1	201.6	250.7	219.3	310.9
$OCH_2C(CH_3)_3$	275.3	296.7	143.9	340.8	195.3	244.3	212.8	304.1
SCH_3	292.7	313.0	158.8	355.2	209.6	257.9	226.3	314.5
SCH_2CH_3	293.5	313.7	159.3	355.7	210.0	258.3	226.7	314.5
OC_6H_5	209.8	229.7	74.9	271.1	125.4	173.4	141.8	228.7
tosyl	269.7	288.9	133.2	329.2	183.4	230.9	199.2	284.2
phenylsulfonyl	272.8	290.9	133.8	329.3	183.4	230.1	198.3	280.1
OH	344.4	361.0	202.0	396.8	250.7	296.5	264.4	341.9
SH	315.3	331.1	171.0	365.5	219.3	264.4	232.3	307.4
2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl	362.9	371.5	202.1	393.4	246.3	286.6	253.7	307.8
Br	343.3	343.4	162.8	350.4	202.2	236.6	202.6	231.7
Cl	379.4	377.2	193.6	380.2	231.7	264.6	230.3	252.8
F	466.0	461.2	274.2	459.6	310.9	341.9	307.4	322.2
CN	579.5	571.6	380.6	564.8	415.6	444.5	409.6	415.5

Table S4: the BDE of 49 radicals in combination with a set of 8 radicals, calculated with the final model 2 (including the stability, the global electrophilicity and the local Pauling electronegativity of the radical fragments) in kJ mol^{-1}

A	CH_2OH	CH_3	NF_2	H	OCH_3	OH	SH	F
$C(OH)(CH_3)_2$	311.7	341.7	233.0	402.5	321.8	376.9	281.6	469.5
$C(CH_3)_3$	312.8	342.4	233.0	402.4	321.6	376.5	281.1	467.7
CH_2OH	317.9	347.1	237.2	406.4	325.6	380.1	284.7	470.1
$CH(CH_3)_2$	321.0	350.1	240.2	409.4	328.6	383.1	287.7	473.0
NO	161.2	189.4	69.0	251.2	112.9	166.8	124.2	205.0
CH_2CH_3	332.2	360.3	248.9	417.6	336.7	390.5	294.9	477.1
$CH_2CH_2CH_3$	336.6	364.1	252.0	420.5	339.4	392.9	297.2	477.8
$CH_2C_6H_4(OCH_3)$	282.2	309.4	196.9	365.2	284.1	337.3	241.6	421.2
$CH_3C(O)$	330.4	357.3	244.4	412.5	331.4	384.4	288.6	467.3
CF_2CH_3	355.6	382.2	269.1	437.2	356.0	408.8	313.1	491.2
$CH_2C_6H_4(CH_3)$	285.1	311.5	198.0	366.0	284.8	337.4	241.6	418.9
CH_2CHCH_2	273.8	300.1	186.6	354.5	273.3	326.0	230.2	407.4
HC(O)	325.6	351.9	238.2	406.2	325.0	377.5	281.7	458.7
CH_3	347.1	373.2	259.2	427.0	345.8	398.2	302.4	478.7
$CH_2C_6H_5$	287.9	313.7	199.5	367.3	286.0	338.3	242.5	418.3
$CHCH_2$	387.0	412.8	298.5	466.2	385.0	437.2	341.3	516.9
$CH_2C_6H_4(F)$	288.6	314.3	199.8	367.5	286.2	338.4	242.6	417.9
$C_6H_4(CH_3)$	398.8	423.8	308.4	475.7	394.4	446.0	350.1	523.2
$C_6H_4(OCH_3)$	401.2	426.1	310.6	477.9	396.5	448.1	352.2	525.0
C_6H_5	398.1	422.9	307.4	474.6	393.3	444.8	348.9	521.6
CCl_3	317.2	341.5	225.4	392.4	311.0	362.2	266.2	437.5
$C(CN)(CH_3)_2$	283.2	307.5	191.2	358.2	276.8	327.9	231.9	402.9
$C_6H_4(F)$	404.5	428.2	311.2	478.0	396.5	447.3	351.2	520.7
CF_3	390.1	413.2	295.5	462.0	380.4	430.8	334.7	502.4
NF_2	237.2	259.2	130.8	310.4	171.3	220.9	177.7	240.4
$C_6H_4(CN)$	409.0	430.9	311.6	477.7	395.9	445.5	349.2	513.6
NH_2	343.5	365.3	236.7	416.2	277.1	326.7	283.4	345.7
$CH_2C_6H_4(CN)$	294.6	316.4	197.0	363.0	281.2	330.7	234.4	398.4
tert-butoxycarbonylmethyl	326.8	348.3	228.4	394.3	312.5	361.7	265.4	428.4
CH_2CN	314.3	335.3	214.8	380.4	298.6	347.6	251.2	412.8
H	406.4	427.0	310.4	471.5	432.9	481.6	341.9	589.0
OCH_2CH_3	322.2	342.5	168.1	429.7	163.8	212.3	256.5	178.0
NO_2	237.5	257.8	127.2	306.0	166.7	215.2	171.7	229.5
OCH_3	325.6	345.8	171.3	432.9	166.9	215.4	259.6	180.9
$OCH_2C(CH_3)_3$	319.4	339.6	165.0	426.6	160.6	209.0	253.2	174.3
SCH_3	269.9	289.7	167.5	332.6	250.5	298.6	202.1	360.0
SCH_2CH_3	270.5	290.2	168.0	333.0	251.0	299.0	202.5	360.2
OC_6H_5	251.2	270.7	95.3	356.6	90.6	138.5	182.7	101.9
tosyl	245.0	264.2	141.4	306.3	224.2	271.9	175.3	331.8
phenylsulfonyl	246.2	264.9	141.5	306.1	224.0	271.4	174.8	329.9
OH	380.1	398.2	220.9	481.6	215.4	262.4	306.3	221.3
SH	284.7	302.4	177.7	341.9	259.6	306.3	209.5	361.6
2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl	319.8	334.4	205.5	368.4	285.7	330.3	233.1	376.0
Br	303.3	314.1	177.6	341.5	231.4	273.3	202.8	280.5
Cl	357.1	366.9	212.9	405.5	236.8	278.1	252.9	249.8
F	470.1	478.7	240.4	589.0	180.9	221.3	361.6	97.5
CN	507.6	514.9	376.6	536.2	452.7	492.3	394.2	515.9

Table S5: the difference between the theoretical BDE (with B3P86/6-311+G) and the BDE, calculated with the final model 2 for 49 radicals in combination with a set of 8 radicals in kJ mol^{-1}**

A	CH_2OH	CH_3	NF_2	H	OCH_3	OH	SH	F
$C(OH)(CH_3)_2$	-0.9	6.5	21.1	17.0	-3.8	-11.7	11.8	-16.0
$C(CH_3)_3$	-4.0	4.5	22.1	6.6	7.5	-2.9	4.0	-2.6
CH_2OH	-7.6	-5.3	17.6	5.5	-12.9	-11.6	-2.1	-9.2
$CH(CH_3)_2$	-6.9	1.9	22.9	2.8	11.8	1.0	1.2	4.1
NO	11.9	22.4	48.0	44.8	-56.9	-44.3	-3.8	-56.7
CH_2CH_3	-7.0	1.0	21.4	-5.0	4.3	8.0	1.2	12.0
$CH_2CH_2CH_3$	-5.3	1.3	19.8	-5.4	4.9	8.0	0.2	10.7
$CH_2C_6H_4(OCH_3)$	-6.3	2.4	19.8	-6.7	10.2	13.6	-0.6	13.0
$CH_3C(O)$	-1.1	13.6	16.8	37.2	-66.7	-69.5	-16.2	-36.1
CF_2CH_3	6.7	-2.1	12.6	17.9	-20.4	-27.4	21.7	-24.6
$CH_2C_6H_4(CH_3)$	-4.2	3.2	17.7	-7.4	10.2	12.2	-0.8	11.6
CH_2CHCH_2	-3.7	2.0	17.4	-8.5	9.9	12.3	0.0	12.2
HC(O)	8.2	1.3	11.4	34.1	-58.7	-61.5	-23.0	-42.3
CH_3	-5.1	1.4	17.7	-15.4	15.3	18.1	-0.9	20.5
$CH_2C_6H_5$	-2.9	3.6	16.3	-7.9	11.5	14.0	-0.9	10.8
$CHCH_2$	-4.9	-2.3	17.2	3.5	-9.9	-13.1	-7.8	1.5
$CH_2C_6H_4(F)$	-2.2	3.8	15.7	-7.8	8.9	10.8	-0.9	10.0
$C_6H_4(CH_3)$	0.7	3.3	13.2	2.4	-7.7	-14.3	-2.8	-3.1
$C_6H_4(OCH_3)$	-0.4	3.4	13.7	1.2	-3.6	-10.3	-2.8	-0.8
C_6H_5	1.5	3.1	12.6	2.7	-9.3	-16.2	-3.2	-4.2
CCl_3	-8.2	-7.1	16.8	1.4	-13.0	-12.0	27.1	6.8
$C(CN)(CH_3)_2$	4.1	4.6	10.5	-3.5	6.7	-0.4	4.0	-0.6
$C_6H_4(F)$	3.6	4.3	10.1	1.0	-6.3	-13.0	-1.7	-4.6
CF_3	7.1	-5.3	7.5	17.2	-28.5	-34.1	24.8	-24.3
NF_2	-8.6	-3.6	49.6	1.6	4.1	7.2	39.0	7.0
$C_6H_4(CN)$	9.4	5.6	4.7	3.1	-14.6	-22.0	-6.6	-12.4
NH_2	-16.8	13.4	53.5	-37.0	58.4	58.8	14.7	53.8
$CH_2C_6H_4(CN)$	10.6	8.5	3.9	-10.0	6.5	5.6	-3.4	-0.6
tert-butoxycarbonylmethyl	6.7	4.8	5.4	-13.3	21.1	20.0	3.0	6.5
CH_2CN	4.8	1.2	5.7	-18.8	20.7	20.4	5.4	14.1
H	5.5	-15.4	-10.4	26.6	4.0	-15.1	-41.1	17.2
OCH_2CH_3	-9.2	20.1	48.8	2.4	39.3	48.9	42.4	6.8
NO_2	-2.9	11.7	44.4	8.7	4.8	8.9	23.6	-5.8
OCH_3	-12.9	15.3	50.5	4.0	38.5	49.5	43.5	8.9
$OCH_2C(CH_3)_3$	-12.9	14.7	50.5	2.6	42.3	51.9	40.2	10.3
SCH_3	-1.6	-1.4	7.1	-27.8	32.8	26.0	-37.8	29.5
SCH_2CH_3	0.1	1.4	6.2	-28.3	33.0	25.8	-39.6	28.2
OC_6H_5	-9.8	14.2	48.0	-7.2	46.1	56.4	46.9	17.0
tosyl	15.6	9.3	-2.2	28.3	-22.6	-29.0	-13.0	-43.9
phenylsulfonyl	16.7	9.4	-3.4	28.2	-23.1	-29.6	-13.6	-44.9
OH	-10.1	18.1	46.1	-15.2	49.5	59.1	37.9	25.3
SH	-2.0	-0.9	4.6	-41.1	43.5	37.9	-35.0	43.1
2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl	17.8	16.8	-9.8	-16.5	20.6	10.7	-3.4	-1.3
Br	9.2	10.6	11.6	-43.5	70.5	64.7	-25.2	34.3
Cl	15.2	20.2	21.0	-30.4	63.2	62.1	5.2	15.2
F	-9.2	20.4	19.0	17.2	8.9	25.3	43.1	-45.9
CN	23.0	-13.8	-22.5	-10.3	-9.1	-21.7	-36.5	-12.7