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Homolytic Bond Dissociation Enthalpies of the C−H Bonds Adjacent to Radical Centers

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Homolytic bond dissociation enthalpies (BDEs) at 0 and 298 K of the C−H bonds adjacent to various radical centers have been obtained from ab initio CBS-4 (complete basis set) model calculations and experimental data available in the literature. The BDEs of the C−H bonds adjacent to the radical centers derived from 11 saturated hydrocarbons were found to be 33.5 ± 3 kcal/mol at 298 K. The BDEs of the C−H bonds adjacent to nine allylic and benzylic radical centers were found to be 48 ± 3 kcal/mol at 298 K, but the benzylic C−H BDE of the $PhC\mathit{H}_2CH_2^{\bullet}$ radical was found to be only 29.7 and 30.5 kcal/mol at 0 and 298 K, respectively. The BDEs of the vinylic C−H bonds adjacent to four vinylic radical centers were found to be 35.5 ± 3.5 kcal/mol at 298 K. The BDEs of the vinylic C−H bonds adjacent to three allylic radical centers were found to be 56.5 ± 3 kcal/mol at 298 K. These results suggest that the radical centers weaken the adjacent C−H bond strengths by about 50−70 kcal/mol. The calculated BDEs agree within ±2 kcal/mol with most of the available experimental results. Isomerization enthalpies of butenes and pentenes have been obtained. Substituent effects on BDEs have also been examined.

Introduction

Radicals are the chemical species with unpaired electrons which are common and important reactive intermediates for many chemical,[1] biological,[2] and technological processes.[3] For example, many organic reactions long thought to proceed via polar mechanisms have been reinvestigated and shown to proceed via radical mechanisms.[4]

The quantitative information about the thermodynamic stabilities of radicals is generally obtained from indirect measurements since most radicals are highly reactive and short-lived intermediates, which make the corresponding equilibrium establishment and concentration measurements difficult. The homolytic bond dissociation enthalpy (BDE) of the H−A bond has been widely considered to provide the best reliable quantitative information about the thermodynamic stability of the radical ($A^{\bullet}$) formed by removal of one hydrogen atom.[5] Lots of the BDEs are available in the literature from the gas- or solution-phase experimental measurements.[5,6] The BDE determination is generally based on the application of the appropriate thermodynamic cycles by using the experimentally measurable quantities such as equilibrium constants and redox potentials since BDE is a state function that is independent of the reaction pathway.[7]

On the other hand, the quantitative information about the effect of the radical center on the adjacent C−H bond strength is scarce in the literature.[5d,8,9] This is not surprising since the determination of the C−H BDEs in radicals is expected to be more difficult than those in neutral molecules, primarily due to the extremely high reactivities of the reactant radicals. In the present paper, with the aid of the ab initio CBS-4 (complete basis set) model calculation,[10] we wish to report the BDEs of the C−H bonds adjacent to 28 different radical centers.

Calculations

All of ab initio CBS-4 theoretical calculations were carried out using Gaussian-92 or Gaussian-94.[11] A

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Scheme 1

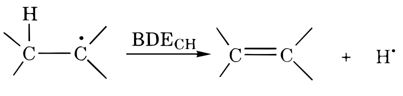

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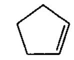
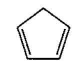
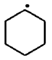
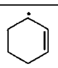
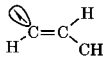
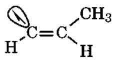
Table 1. Calculated Total Energies, Formation Enthalpies, and Atomization Energies for the Neutral Molecules

Neutral	E_{tol} (0K)[a]	ΔH(0K)[b]	ΔH(298K)[c]	D_0[d]
CH_2=$CHCH_3$	-117.680785	6.53	2.76	-813.21
CH_2=$CHCH_2CH_3$	-156.918424	1.98	-3.46	-1091.00
CH_2=$CHCH(CH_3)_2$	-196.159154	-4.51	-11.50	-1370.73
CH_2=$CHCH_2CH_2CH_3$	-196.157124	-3.23	-10.10	-1369.46
cis-CH_3CH=$CHCH_2CH_3$	-196.158846	-4.31	-11.06	-1370.54
trans-CH_3CH=$CHCH_2CH_3$	-196.160740	-5.50	-12.32	-1371.73
	-194.967423	8.33	2.36	-1254.63
	-193.760726	30.57	26.24	-1129.13
	-234.212462	-0.85	-8.65	-1537.06
	-232.999328	25.42	19.43	-1407.52
	-233.001581	24.00	18.08	-1408.94
$PhCH_2CH_3$	-310.329950	-0.38	-7.68	-1876.54
cis-CH_3CH=CH-CH=CH_2	-194.947462	20.86	15.75	-1242.10
trans-CH_3CH=CH-CH=CH_2	-194.948869	19.98	14.87	-1242.98
$(CH_3)_2C$=CH_2	-156.924915	-2.09	-7.42	-1095.08
CH_2=CH_2	-78.438510	13.98	11.88	-532.51
$PhCH$=CH_2	-309.119527	24.20	18.57	-1748.70
$Ph(CH_3)C$=CH_2	-348.369469	11.93	4.89	-2034.21
$HC\equiv CH$	-77.197684	57.63	57.30	-385.60
CH_2=C=CH_2	-116.447827	45.24	43.28	-671.23
CH_2=C=$CHCH_3$	-155.696245	33.93	30.44	-955.79
CH_2=C=$CHCH_2CH_3$	-194.935068	28.64	23.57	-1234.32
CH_2=CH-CH=CH_2	-155.705613	28.05	34.33	-961.67
CH_2=CH-$CH(CH_3)_2$	-196.159154	-4.51	-11.50	-1370.73
cis-CH_3CH=$CHCH_3$	-156.920689	0.56	-4.72	-1092.42
trans-CH_3CH=$CHCH_3$	-156.923332	-1.10	-6.30	-1094.08
CH_2=$C(CH_3)CH(CH_3)_2$	-235.402099	-12.38	-20.81	-1651.86
$HC\equiv C$-CH_3	-116.449823	43.98	42.03	-672.49
$(CH_3)_2CH$-$CH(CH_3)_2$	-236.617204	-39.89	-50.07	-1782.63
$CH_3CH_2CH_2CH_3$	-158.137115	-27.78	-34.84	-1224.03
CH_2=CH-$C(CH_3)$=CH_2	-194.949766	19.41	14.12	-1243.55
$(CH_3)_2C$=$C(CH_3)_2$	-235.407738	-15.92	-23.91	-1655.39

[a] In Hartree, total energy at 0 K; 1 Hartree = 627.5095 kcal/mol. [b] In kcal/mol; formation enthalpy at 0 K. [c] In kcal/mol; formation enthalpy at 298 K. [d] In kcal/mol; atomization energy at 0 K.

single-point Hartree−Fock calculation with a very large basis set (6-311+G(3d,2f,2df,p)) at the HF/3-21G* optimized geometry followed by correction for electron correlation using MP2 and MP4 (SDQ) calculations with much smaller basis sets and an extrapolation to the complete basis set. The details of the calculations have been discussed in the literature.[10] The CBS-4 method has been used to reproduce bond dissociation enthalpies, proton affinities, electron affinities, and ionization potentials to an accuracy of ±2 kcal/mol for a wide variety of compounds.[10] Examination of the BDEs in Tables 3−6 shows that the calculated C−H BDEs of radicals also agree with most of the experimental results within ±2 kcal/mol.

Table 2. Calculated Total Energies, Formation Enthalpies, and Atomization Energies for the Radicals

Neutral	E_{tol} (0K)[a]	ΔH(0K)[b]	ΔH(298K)[c]	D_0[d]
$C_2H_5^\bullet$	-78.998644	29.98	27.47	-568.14
$CH_3CH_2CH_2^\bullet$	-118.235565	25.89	21.64	-845.48
$CH_3CH(^\bullet)CH_3$	-118.240823	22.59	18.48	-848.78
$(CH_3)_3C^\bullet$	-157.484601	14.19	8.49	-1130.43
	-195.524827	26.05	19.50	-1288.55
	-234.768508	17.71	9.26	-1570.13
CH_2=$CHCH_2^\bullet$	-117.042273	39.71	36.80	-728.40
CH_2=$CHCH(^\bullet)CH_3$	-156.285622	31.58	27.51	-1009.77
CH_2=$CHC(^\bullet)(CH_3)_2$	-195.529101	23.37	17.72	-1291.23
CH_2=$CHCH(^\bullet)CH_2CH_3$	-195.523627	26.80	20.95	-1287.79
cis-CH_3CH=$CHCH(^\bullet)CH_3$	-195.522776	27.34	21.48	-1287.26
trans-CH_3CH=$CHCH(^\bullet)CH_3$	-195.527947	24.09	18.51	-1290.50
	-194.335115	37.62	32.70	-1173.71
	-233.581405	27.65	20.91	-1456.93
$CH_3CH_2CH_2CH_2^\bullet$	-157.473690	21.04	15.26	-1123.58
$PhCH_2CH_2^\bullet$	-309.670130	46.18	40.14	-1778.35
$PhCH_2^\bullet$	-270.449909	39.79	34.91	-1511.49
$PhCH(^\bullet)CH_3$	-309.693871	31.28	25.16	-1793.25
$PhC(^\bullet)(CH_3)_2$	-348.943450	19.24	11.84	-2078.54
$(CH_3)_2CHCH_2^\bullet$	-157.475759	19.74	13.85	-1124.88
CH_2=$CHC(^\bullet)(CH_3)_2$	-195.529101	23.37	17.72	-1291.23
$CH_3CH_2CH(^\bullet)CH_3$	-157.478450	18.05	12.34	-1126.57
$(CH_3)_2CHC(^\bullet)(CH_3)_2$	-235.961888	3.84	-4.93	-1687.27
$PhCH_2CH_2(^\bullet)$	-309.670130	46.18	40.14	-1778.35
CH_2=$CH(^\bullet)$	-77.761396	71.38	70.33	-423.47
CH_2=$C(^\bullet)CH_3$	-117.008877	60.66	58.07	-707.44
	-117.002142	64.89	62.20	-703.21
	-117.002803	64.47	61.78	-703.63
$CH_3CH_2CH(^\bullet)CH_3$	-157.478450	18.05	12.34	-1126.57
$(CH_3)_2CHCH_2(^\bullet)$	-157.476041	19.56	13.69	-1125.06

[a] In Hartree, total energy at 0 K; 1 Hartree = 627.5095 kcal/mol. [b] In kcal/mol; formation enthalpy at 0 K. [c] In kcal/mol; formation enthalpy at 298 K. [d] In kcal/mol; atomization energy at 0 K.

The BDE of the C−H bond adjacent to radical center at 0 and 298 K is readily obtained from eq 1

$$BDE_{CH} = \Delta H(\mathbf{2}) + \Delta H(H^\bullet) - \Delta H(\mathbf{1}) \qquad (1)$$

by using the formation enthalpies (Δ*H*) of the reactant radical (**1**) and product alkene (**2**) together with the formation enthalpy of hydrogen atom [$\Delta H(H^\bullet)$] (51.63 and 52.10 kcal/mol at 0 and 298 K, respectively) as shown in

Scheme 2

$$\mathrm{RCH{=}CH_2 + H_2 \longrightarrow RCH_2\text{-}CH_3} \qquad \Delta H_2 \qquad (2)$$

$$\mathrm{RCH_2\text{-}CH_3 \longrightarrow RCH_2\text{-}CH_2^{\bullet} + H^{\bullet}} \qquad \Delta H_3 \qquad (3)$$

$$\mathrm{H^{\bullet} + H^{\bullet} \longrightarrow H_2} \qquad \Delta H_4 \qquad (4)$$

$$\mathrm{RCH{=}CH_2 + H^{\bullet} \longrightarrow RC\underline{H_2}\text{-}CH_2^{\bullet}} \qquad \Delta H_5 \qquad (5)$$

Scheme 1.[10] The C−H BDE at 0 K could also be obtained from the total energy or atomization energy of the corresponding reactant radical and product alkene.[10] The total energies, formation enthalpies, and atomization energies for the product alkenes and related reactant radicals calculated from the CBS-4 model[10] are summarized in Tables 1 and 2. The calculated C−H BDEs for the radicals derived from 11 saturated and 10 unsaturated hydrocarbons are summarized in Tables 3 and 4, respectively. The vinylic C−H BDEs for vinylic and allylic radicals are summarized in Tables 5 and 6, respectively.

Results and Discussion

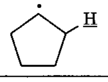
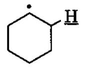
Thermodynamic Cycle for the BDE Determination of the C−H Bonds Adjacent to Radical Centers. To check the calculated BDEs of the C−H bonds adjacent to various radical centers (Tables 3−6), we have designed a thermodynamic cycle (Scheme 2) to determine the experimental BDEs of the C−H bonds adjacent to the related radical centers from the literature hydrogenation enthalpies (ΔH_2) together with the C−H BDEs of the neutrals (ΔH_3) and the H−H BDE of hydrogen ($-\Delta H_4$).

The hydrogenation enthalpy of the alkene (ΔH_2) could be obtained from the formation enthalpies of related alkene and alkane.[12a] The C−H BDEs (ΔH_3) in the neutrals are available in the literature.[5,12b] The H−H BDE of hydrogen molecule ($-\Delta H_4$) is 104.2 kcal/mol at 298 K.[12b] Thus, the BDE ($-\Delta H_5$) of the C−H bond adjacent to the radical center (eq 5 of Scheme 2) can be obtained from eq 6.

$$\Delta H_5 = \Delta H_2 + \Delta H_3 + \Delta H_4 = -\mathrm{BDE_{CH}} \qquad (6)$$

For example, the hydrogenation enthalpy (ΔH_2) of ethylene to ethane is −32.6 kcal/mol,[12a] the C−H BDE (ΔH_3) of $\mathrm{CH_3C}H_3$ is 101.6 kcal/mol.[12a,13] Thus, the C−H BDE of the $\mathrm{C}H_3\mathrm{CH_2^{\bullet}}$ radical equals $-(\Delta H_2 + \Delta H_3 + \Delta H_4) = -(-32.6 + 101.6 - 104.2) = 35.2$ kcal/mol. The BDEs of the vinylic C−H bonds adjacent to the allylic and vinylic radical centers can also be obtained in the same manner. The experimental BDEs of radicals obtained from using eq 6 are all included in the relevant tables for comparison.

Table 3. Homolytic Bond Dissociation Enthalpies (BDEs) of the C−H Bonds (Underlined) Adjacent to the Radical Centers Derived from Saturated Hydrocarbons

substrate	$\mathrm{BDE_{CH}}$(0 K)[a]	$\mathrm{BDE_{CH}}$(298 K)[d]	$\mathrm{BDE_{CH}}$(exp)[e]
$\mathrm{C\underline{H}_3CH_2^{\bullet}}$	35.6	36.3	35.2
$\mathrm{CH_3CH(^{\bullet})C\underline{H}_3}$	35.6	36.4	35.0
$\mathrm{CH_3CH_2CH(^{\bullet})C\underline{H}_3}$	35.6	36.3	34.9
$\mathrm{(CH_3)_2C(^{\bullet})C\underline{H}_3}$	35.4	36.2	34.9
$\mathrm{(CH_3)_2CHC(^{\bullet})(C\underline{H}_3)_2}$	35.4	36.2	33.3
$\mathrm{CH_3C\underline{H}_2CH_2^{\bullet}}$	32.3	33.2	31.9
$\mathrm{CH_3CH_2C\underline{H}_2CH_2^{\bullet}}$	32.6	33.4	32.0
$\mathrm{(CH_3)_2C\underline{H}CH_2^{\bullet}}$	29.8	30.8	29.7
$\mathrm{CH_3C\underline{H}_2CH(^{\bullet})CH_3}$	34.1(*cis*)[b] 32.5 (*trans*)[c]	35.0 (*cis*)[b] 33.5 (*trans*)[c]	33.2 (*cis*)[b] 32.2 (*trans*)[c]
	33.9	35.0	34.0
	33.1	34.2	32.5

[a] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 model. [b] The product is *cis*-2-butene. [c] The product is *trans*-2-butene. [d] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 model. [e] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as obtained by using eq 6; also see the discussion of the text.

BDEs of the C−H Bonds Adjacent to the Radical Centers Derived from Saturated Hydrocarbons. Examination of Table 3 shows that the C−H BDE value of the ethyl ($\mathrm{C}H_3\mathrm{CH_2^{\bullet}}$) radical is 35.6 and 36.5 kcal/mol at 0 and 298 K, respectively, which is in a good agreement with the experimental result of 35.2 kcal/mol at 298 K obtained from eq 6. Berkowitz et al. obtained a similar value of 35 ± 1 kcal/mol for the C−H BDE of the $\mathrm{C}H_3\mathrm{CH_2^{\bullet}}$ radical.[5d] Note that the C−H BDE for the precursor (ethane) is 99.8 and 101.6 kcal/mol at 0 and 298 K, respectively.[13] This indicates that the C−H bond strength has been *weakened* by about *65 kcal/mol* just because of the presence of the adjacent radical center. The tremendous decrease of the C−H bond strength caused by the adjacent radical center is clearly associated with the formation of the stable neutral product ethylene (Scheme 1). Similarly, removal[14] or addition[15] of one electron has also been shown to significantly weaken the C−H bond strengths in various substrates.

The C−H bond strength in neutral alkanes is known to progressively decrease when the C−H bond changes from primary to secondary to tertiary. For example, the C−H BDE value decreases from 101.6 to 99.0 to 97.3 kcal/mol at 298 K for the primary ($\mathrm{CH_3C}H_3$) to secondary ($\mathrm{CH_3C}H_2\mathrm{CH_3}$) to tertiary [$\mathrm{(CH_3)_3C}H$] C−H bond, respectively.[5c,d,12b,13] The progressive BDE decrease could be attributed to a combination of the radical stabilization of the methyl substituent and the radical destabilization of the steric hindrance.[16] Interestingly, the C−H BDEs for the radicals of $\mathrm{C}H_3\mathrm{CH_2^{\bullet}}$, $\mathrm{CH_3CH(^{\bullet})C}H_3$, $\mathrm{CH_3CH_2CH(^{\bullet})C}H_3$, $\mathrm{(CH_3)_2C(^{\bullet})C}H_3$, and $\mathrm{(CH_3)_2CHC(^{\bullet})(C}H_3\mathrm{)_2}$ were found to be essentially constant (36.3 ± 0.1 kcal/mol) at 298 K regardless of the structure of the adjacent radical centers, suggesting that the radical stabilizing effects of the alkyl groups for the reactant radicals have been canceled by their stabilizing effects on the product conjugate π system via hyperconjugation.[17]

On the other hand, the C−H BDEs were found to decrease progressively from 36.5 to 33.2 to 30.8 kcal/mol at 298 K when the C−H bond changes from the primary ($\mathrm{C}H_3\mathrm{CH_2^{\bullet}}$) to secondary ($\mathrm{CH_3C}H_2\mathrm{CH_2^{\bullet}}$) to tertiary [$\mathrm{(CH_3)_2C}H\mathrm{CH_2^{\bullet}}$], even though they are all primary radi-

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Scheme 3

$$R_2C\underline{H}\text{-}CH_2^{\bullet} \longrightarrow R_2C{=}CH_2 + H^{\bullet}$$

$$R = H \text{ or } CH_3$$

cals. Clearly, this is caused by the stabilization of the alkyl groups on the product conjugated π system, whereas the related stabilization on the reactant radicals should be similar since all of them are primary radicals, as shown in Scheme 3. This is also consistent with the observation of Saytzeff elimination rule to form the alkene with more alkyl substitutions.[18]

Removal of one of the methylene hydrogen atoms from the $CH_3CH(^{\bullet})C\mathit{H}_2CH_3$ radical results in formation of *cis*- or *trans*-2-butene, indicating that the two methylene C−H BDEs are dependent on the structures of the product alkene formed. For example, it was found to be 34.1 and 35.1 kcal/mol at 0 and 298 K when *cis*-2-butene was formed; but it is 32.5 and 33.5 kcal/mol at 0 and 298 K when *trans*-2-butene was formed. The slight lower BDE_{CH} value for the process to form the trans-isomer alkene is caused by the relatively higher stability of the trans-isomer than the cis-isomer.[13]

The BDE value of the C−H bond adjacent to the cyclopentyl radical center was found to be 33.9 and 35.0 kcal/mol at 0 and 298 K, respectively, which is very close to that of the $CH_3CH(^{\bullet})C\mathit{H}_2CH_3$ radical when the product alkene is *cis*-2-butene. The BDE value of the C−H bond adjacent to the cyclohexyl radical center is slightly less than that adjacent to the cyclopentyl radical center, presumably due to the more stable cyclohexene than cyclopentene.[12a]

Although hydroxyl ($HO^{\bullet}$) and alkoxyl ($RO^{\bullet}$) radicals readily abstract hydrogen atoms from saturated hydrocarbons,[19] peroxyl radicals ($ROO^{\bullet}$) are known to be not reactive enough to abstract hydrogen atoms from saturated hydrocarbons since the O−H BDEs of hydroperoxides are considerably lower than those of the weakest C−H bonds in saturated hydrocarbons.[5,12b,13,20] Examination of Table 3 shows that the BDEs of the C−H bonds adjacent to the radical centers derived from saturated hydrocarbons are 33.5 ± 3 kcal/mol, suggesting that peroxyl radicals will easily abstract the hydrogen atoms from these radicals. More significantly, the ground-state triplet oxygen ($^3O_2$) from the atmospheric air is even able to abstract the hydrogen atoms adjacent to radical centers since the O−H BDE of the $HOO^{\bullet}$ radical was found to be 42−49 kcal/mol,[13,21] which is considerably higher than the C−H BDEs in radicals (Table 3). In fact, the hydrogen atom abstraction from the β-position of the radical center by oxygen has been proposed to explain the experimental results observed for the autoxidation as shown in Scheme 4.[22]

Scheme 4

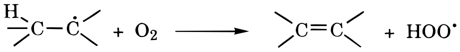
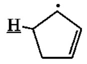
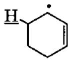
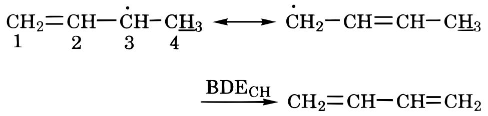


Table 4. Homolytic Bond Dissociation Enthalpies (BDEs) of the C−H Bonds (Underlined) Adjacent to Allylic and Benzylic Radical Centers

substrate	BDE_{CH}(0 K)[a]	BDE_{CH}(298 K)[d]	BDE_{CH}(exp)[e]
$CH_2{=}CHCH(^{\bullet})C\underline{H}_3$	48.1	49.2	47.6
$CH_2{=}CHC(^{\bullet})(C\underline{H}_3)_2$	47.7	48.5	47.5
cis-$CH_3CH{=}CHCH(^{\bullet})C\underline{H}_3$	45.2	46.4	44.2
trans-$CH_3CH{=}CHCH(^{\bullet})C\underline{H}_3$	47.5	48.5	44.6
$CH_2{=}CHCH(^{\bullet})C\underline{H}_2CH_3$	45.7 (*cis*)[b] 44.8 (*trans*)[c]	46.9 (*cis*)[b] 46.0 (*trans*)[c]	45.5 (*cis*)[b] 44.3 (*trans*)[c]
	44.6	45.6	45.8
	49.4	50.6	49.3[f]
$PhCH(^{\bullet})C\underline{H}_3$	44.6	45.5	47.5
$PhC(^{\bullet})(C\underline{H}_3)_2$	44.3	45.2	
$PhC\underline{H}_2CH_2^{\bullet}$	29.7	30.5	32.5

[a] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 model. [b] The product is *cis*-1,3-pentadiene. [c] The product is *trans*-1,3-pentadiene. [d] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 model. [e] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as obtained by using eq 6; also see the discussion of the text. [f] The hydrogenation enthalpy (−26.8 kcal/mol) of 1,3-cyclohexadiene to cyclohexene is taken from ref 25b.

Scheme 5



$$\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{\dot{C}H}{-}\underset{4}{C\underline{H}_3} \longleftrightarrow \dot{C}H_2{-}CH{=}CH{-}C\underline{H}_3 \xrightarrow{BDE_{CH}} CH_2{=}CH{-}CH{=}CH_2 + H^{\bullet}$$

BDEs of the C−H Bonds Adjacent to Allylic and Benzylic Radical Centers. Peroxyl radicals are known to be reactive enough to abstract the substituted allylic and benzylic C−H bonds since the substituted allylic or benzylic C−H BDEs are all smaller than 86 kcal/mol.[13,20] The weaker allylic and benzylic C−H bonds were attributed to the resonance delocalization of the unpaired electron into the conjugated π system.[13,23] The easier loss of the allylic and benzylic hydrogen atom has been shown as one of the major cause for the faster degradation of unsaturated polymers such as rubber than the related saturated polymers.[24]

Examination of Table 4 shows that the BDEs of the C−H bonds adjacent to the allylic and benzylic radical centers are 48 ± 3 kcal/mol, which are about 10−15 kcal/mol higher than those of the C−H bonds adjacent to the radical centers derived from saturated hydrocarbons (Table 3). The higher C−H BDE values for allylic and benzylic radicals could be attributed to the much larger radical stabilization for the reactant radicals than the resonance stabilization for the product dienes as shown in Scheme 5. For example, the radical stabilizations of the conjugated allylic and benzylic π system are about 13−17 kcal/mol,[5c,13,23] whereas the resonance stabilizations of the conjugated dienes are only a few kcal/mol.[25a]

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(18) Reutov, D. A. *Fundamentals of Theoretical Organic Chemistry*; Translated by Katz, T. J.; Appleton-Century-Crofts: New York, 1969; p 173.

(19) Simic, M. G.; Jovanovic, S. V.; Niki, E. *Am. Chem. Soc. Symp. Ser.* **1992**, *500*, 14−32.

(20) Zhu, Q.; Zhang, X.-M.; Fry, A. J. *Polym. Degrad. Stab.* **1997**, *57*, 43 and references therein.

(21) (a) Sawyer, D. T. *J. Phys. Chem.* **1989**, *93*, 7977. (b) Merenyi, G.; Lind, J. *J. Phys. Chem.* **1990**, *94*, 5412. (c) Howard, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 6937.

(22) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row Publishers: New York, 1981; p 715.

(23) (a) Glaser, R.; Choy, G. S.-C. *J. Phys. Chem.* **1994**, *98*, 11379. (b) Wiberg, K. B.; Cheeseman, J. R.; Ochtersk, J. W.; Frisch, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6535. (c) Mo, Y.; Lin, Z.; Wu, W.; Zhang, Q. *J. Phy. Chem.* **1996**, *100*, 6469.

(24) Zhang, X,-M.; Zhu, Q. *J. Org. Chem.* **1997**, *62*, 5934−5938. (b) Zhang, X.-M.; Chen, Q.; Mantzaris, J. *Rubber Chem. Technol.* in press.

(25) Wade, L. G., Jr. *Organic Chemistry*, 2nd ed.; Prentice Hall, New Jersey, 1991; (a) p 630, (b) p 675.

Thus, the net effect is to increase the C−H BDEs of the allylic and benzylic radicals by 10−15 kcal/mol. Introduction of an additional methyl group into the position 1, 3, or 4 of the $CH_2{=}CHCH(^\bullet)CH_3$ radical (Scheme 5) only slightly decreases the BDE of the C−H bond adjacent to the allylic radical center, however.

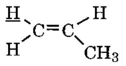
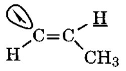
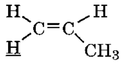
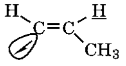
The BDE values of the C−H bonds adjacent to the cyclopentenyl and cyclohexenyl radical centers were also found to be about 10−15 kcal/mol higher than those adjacent to the cyclopentyl and cyclohexyl radical centers. The about 5 kcal/mol higher BDE value for the C−H bond adjacent to the cyclohexenyl than cyclopentenyl radical center is presumably caused by the relatively lower stability of 1,3-cyclohexadiene than 1,3-cyclopentadiene. This statement is supported by the observation that the hydrogenation enthalpy (55.4 kcal/mol[25b]) of 1,3-cyclohexadiene is about 5 kcal/mol larger than that (50.3 kcal/mol[12a]) of 1,3-cyclopentadiene.

The C−H BDE of the $PhCH(^\bullet)CH_3$ radical was found to be 44.8 and 45.5 kcal/mol at 0 and 298 K, respectively, which is about 3−4 kcal/mol less than that of the $CH_2{=}CHCH(^\bullet)CH_3$ radical. The difference agrees very well with the larger radical stabilization effects of the allylic than the benzylic π system.[5c,13] Introduction of an additional methyl group at the benzylic carbon of the $PhCH(^\bullet)CH_3$ radical was found to have negligible effects on the C−H BDE.

Interestingly, the benzylic C−H BDE of the $PhCH_2CH_2^\bullet$ radical was found to be 29.7 and 30.5 kcal/mol at 0 and 298 K, respectively, which is about 15 kcal/mol less than the C−H BDE of the $PhCH(^\bullet)CH_3$ radical. The much lower benzylic C−H BDE of the $PhCH_2CH_2^\bullet$ radical is clearly associated with the separation of the radical center with the aromatic system by a methylene group, which will prevent the resonance delocalization of the unpaired electron of the $PhCH_2CH_2^\bullet$ radical into the aromatic system. The benzylic C−H BDE of the $PhCH_2CH_2^\bullet$ radical is, however, similar to the BDEs of the C−H bonds adjacent to the radical centers derived from saturated hydrocarbons (Table 3).

BDEs of the Vinylic C−H Bonds Adjacent to the Vinylic Radical Centers. The vinylic C−H bonds are stronger than the C−H bonds attached to sp^3 carbon atoms.[5c,d] The vinylic C−H BDE of ethylene ($CH_2{=}CH_2$) was found to be 109.0 and 110.6 kcal/mol at 0 and 298 K, respectively, which agrees very well with the experimental result (110 ± 2 kcal/mol[5c]) (Table 5). The vinylic C−H BDEs of $CH_2{=}CH{-}CH_3$ and $CH_2{=}CH{-}CH_3$ were found to be 111.1 and 107.4 kcal/mol at 298 K, respectively. The BDEs of the vinylic C−H bonds adjacent to vinylic radical centers together with those in related neutrals are summarized in Table 5.

Table 5. Homolytic Bond Dissociation Enthalpies (BDEs) of the Vinylic C−H (Underlined) Bonds Adjacent to Vinylic Radical Centers

substrate	BDE_{CH}(0 K)[a]	BDE_{CH}(298 K)[b]	BDE_{CH}(exp)[c]
$CH_2{=}C\underline{H}_2$	109.0	110.6	110 ± 2[d]
$C\underline{H}_2{=}CH^\bullet$	37.9	39.1	35.6
$CH_2{=}C\underline{H}CH_3$	105.8	107.4	
$C\underline{H}_2{=}C(^\bullet)CH_3$	35.0	36.1	36.2
	110.0	111.5	
	30.7	31.9	32.1
	109.6	111.1	
	31.1	32.3	32.5

[a] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 model. [b] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 model. [c] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as obtained by using eq 6 unless otherwise indicated; also see the discussion of the text. [d] Reference 5c.

Scheme 6

$$C\underline{H}_2{=}\dot{C}H \xrightarrow{BDE_{CH}} CH{\equiv}CH + H^\bullet$$

Scheme 7

$$CH_2{=}C\underline{H}{-}\dot{C}HR \xrightarrow{BDE_{CH}} CH_2{=}C{=}CHR + H^\bullet$$

Table 6. Homolytic Bond Dissociation Enthalpies (BDEs) of the Vinylic C−H Bonds (Underlined) Adjacent to Allylic Radical Ceneters

substrate	BDE_{CH}(0 K)[a]	BDE_{CH}(298 K)[b]	BDE_{CH}(exp)[c]
$CH_2{=}C\underline{H}{-}CH_2^\bullet$	57.2	58.6	58.9
$CH_2{=}C\underline{H}{-}CH(^\bullet)CH_3$	54.0	55.0	60.0
$CH_2{=}C\underline{H}{-}CH(^\bullet)CH_2CH_3$	53.5	54.7	

[a] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 model. [b] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 model. [c] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as obtained by using eq 6; also see the discussion of the text.

Examination of Table 5 shows that the vinylic C−H BDE of the $CH_2{=}CH^\bullet$ radical (Scheme 6) is 37.9 and 39.1 kcal/mol at 0 and 298 K, respectively, indicating that the vinylic radical center ($CH_2{=}CH^\bullet$) *weakens* the adjacent vinylic C−H bond by about *70 kcal/mol.* This explains why it is difficult to experimentally detect the vinylic radical intermediate ($CH_2{=}CH^\bullet$) even at very low temperature, since the vinylic radical readily loses one hydrogen atom to form acetylene, as shown in Scheme 6.[26] The vinylic C−H BDE of the $CH_2{=}C(^\bullet)CH_3$ radical was found to be 35.0 and 36.1 kcal/mol at 0 and 298 K, respectively, which agrees very well with the experimental result (36.2 kcal/mol at 298 K). The difference between the vinylic C−H BDEs for *cis*- and *trans*-$CH(^\bullet){=}CHCH_3$ radicals was found to be negligible.

There appears to be little or no effect of the π electrons on the vinylic C−H bond strength for the vinylic radicals. For example, the vinylic C−H BDE of the $CH_2{=}CH^\bullet$ radical is virtually the same as that of the $CH_3CH_2^\bullet$ radical. This is not unexpected since the π electrons of the double bond system are perpendicular to the p-orbital of the vinylic radical center.

BDEs of the Vinylic C−H Bonds Adjacent to the Allylic Radical Centers. The BDEs of the vinylic C−H bonds adjacent to three different allylic radical centers (Scheme 7) are summarized in Table 6.

Examination of Table 6 shows that the vinylic C−H BDE of the allylic radical ($CH_2{=}CHCH_2^\bullet$) is 57.2 and 58.6 kcal/mol at 0 and 298 K, respectively, which is about 20 kcal/mol higher than the C−H BDE of the propyl ($CH_3CH_2CH_2^\bullet$) radical. The higher vinylic C−H BDE of

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(26) (a) Korolev, V. A.; Nefedov, O. *Adv. Phys. Org. Chem.* **1995**, *30*, 36. (b) Shepherd, R. A.; Doyle, T. J.; Graham, W. R. M. *J. Chem. Phys.* **1988**, *89*, 2738.

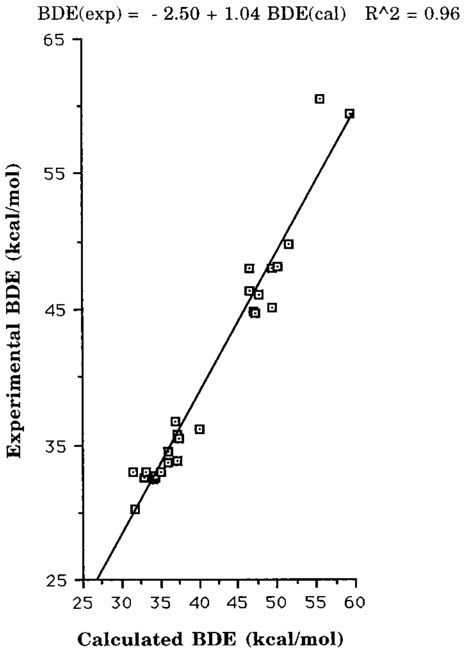

Figure 1. Linear correlation of the calculated BDEs with experimental BDEs.

Table 7. Calculated and Experimental Relative Stabilities of Butenes

Butene	$\Delta H_0{}^a$	$\Delta H_{298}{}^b$	$\Delta H_{exp}{}^c$
CH_2=$CHCH_2CH_3$	3.08	2.84	2.74
cis-CH_3CH=$CHCH_3$	1.66	1.58	1.03
trans-CH_3CH=$CHCH_3$	0	0	0

[a] In kcal/mol; the relative enthalpy at 0 K as calculated from the CBS-4 model. [b] In kcal/mol; relative enthalpy at 298 K as calculated from the CBS-4 model. [c] Obtained from the formation enthalpies at 298 K.[12a]

the allylic radical is clearly associated with the larger radical stabilization of the allylic π system and the lower stabilities of the cumulated double bonds.

The calculated vinylic C−H BDE (58.6 kcal/mol at 298 K) of the $CH_2{=}C\mathit{H}CH_2{}^{\bullet}$ radical agrees very well with the experimental result (58.9 kcal/mol at 298 K) (Table 6). But the calculated vinylic C−H BDE of the $CH_2{=}C\mathit{H}CH(^{\bullet})CH_3$ radical was found to be about 5 kcal/mol less than the experimental result. To check the calculated result, I have calculated the vinylic C−H BDE of the $CH_2{=}C\mathit{H}CH(^{\bullet})CH_2CH_3$ radical to be 53.5 and 54.7 kcal/mol at 0 and 298 K, respectively, which is very close to that of the $CH_2{=}C\mathit{H}CH(^{\bullet})CH_3$ radical. The negligible effect for the introduction of a methyl group seems to agree very well with the essentially same C−H BDEs for the $CH_2{=}CHCH(^{\bullet})C\mathit{H}_3$ and $CH_2{=}CHCH(^{\bullet})C\mathit{H}_2CH_3$ radicals. Therefore, we believe that the difference between the calculated and experimental C−H BDEs for the $CH_2{=}C\mathit{H}CH(^{\bullet})CH_3$ radical is presumably caused by the experimental errors of the related hydrogenation enthalpies.

Table 8. Calculated and Experimental Relative Stabilities of Pentenes

Pentenes	$\Delta H_0{}^a$	$\Delta H_{298}{}^b$	$\Delta H_{exp}{}^c$
CH_2=$CHCH_2CH_2CH_3$	2.27	2.22	2.53
cis-CH_3CH=$CHCH_2CH_3$	1.19	1.26	1.03
trans-CH_3CH=$CHCH_2CH_3$	0	0	0

[a] In kcal/mol; the relative enthalpy 0 K as calculated from the CBS-4 model. [b] In kcal/mol; relative enthalpy at 298 K as calculated from the CBS-4 model. [c] Obtained from the formation enthalpies at 298 K.[12a]

Linear Correlation of the Calculated with Experimental BDEs. The BDEs for neutrals as calculated from the CBS-4 model have been shown to be accurate to ±2 kcal/mol with the best available experimental results.[10] Examination of Tables 3−6 shows that the calculated BDEs of the C−H bonds adjacent to various radical centers also agree within ±2 kcal/mol with the experimentally available results, except for the radicals $(CH_3)_2CHC(^{\bullet})(C\mathit{H}_3)_2$ (2.9 kcal/mol), *cis*-$CH_3CH{=}CHCH(^{\bullet})C\mathit{H}_3$ (2.3 kcal/mol), *trans*-$CH_3CH{=}CHCH(^{\bullet})C\mathit{H}_3$ (3.9 kcal/mol), $CH_2{=}C\mathit{H}CH(^{\bullet})CH_3$ (−5.0 kcal/mol), and $C\mathit{H}_2{=}CH^{\bullet}$ (3.5 kcal/mol). Note that the number in parentheses is the difference between the calculated and experimental BDE values. Nevertheless, a nice linear correlation of the calculated with all available experimental BDEs was obtained with a unit slope and regression coefficient of 0.98 as shown in Figure 1. The good linear correlation provides additional evidence to show that the simple CBS-4 model calculation is accurate and reliable to determine the BDEs of the C−H bonds adjacent to various radical centers.

Hyperconjugation and Isomerization Enthalpies. As mentioned in an earlier section, the methylene C−H BDE value of the $CH_3CH(^{\bullet})C\mathit{H}_2CH_3$ radical is dependent on the product alkene structures. The relative stabilities obtained from the CBS-4 model calculations together with the experimental formation enthalpies[12a] are summarized in Table 7 for three butenes and in Table 8 for three pentenes.

Examination of Tables 7 and 8 shows that the relative stabilities obtained from the CBS-4 model calculations also agree very well with the experimental results (to within ±0.6 kcal/mol). The lesser stabilities of 1-butene and 1-pentene than the corresponding 2-butene and 2-pentene are clearly due to the stabilization of the conjugated π system by the alkyl groups via hyperconjugation since there are two alkyl groups attached to the π bond of 2-butene and 2-pentene, whereas only one alkyl group attached to the π bond of 1-butene and 1-pentene. The higher stabilities of the trans-isomers than the cis-isomers are clearly associated with the lesser steric hindrance in the trans-isomers.

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