Radical Substituent Effects of α-Fluorine and α-Trifluoromethyl Groups

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Homolytic bond dissociation enthalpies (BDEs) of the C−H bonds in 30 fluorinated hydrocarbons have been obtained from ab initio CBS-4 (complete basis set) model calculation at both 0 and 298 K. The calculated C−H BDEs agree with the available literature experimental results within ±2 kcal/mol. Introduction of one or two α-fluorine (α-F) substituent(s) into methane, ethane, or isopropane was found to *weaken* the sp^3 C−H bond strength by 1−4 kcal/mol primarily due to the resonance delocalization of the unpaired electron of the radicals formed by removal of one hydrogen atom. In contrast, introduction of three α-F substituents in trifluoromethane (CHF_3) was found to *strengthen* the sp^3 C−H bond by about 1 kcal/mol. The 4−6 kcal/mol bond-strengthening effects of α-trifluoromethyl groups were attributed exclusively to their inductive effects. The substituent effects of fluorine and trifluoromethyl groups have also been examined on the strength of the ethylene sp^2 C−H bonds and the acetylene sp C−H bonds. The ground-state effects of the polyfluorine substituents on the C−H BDE values have also been discussed.

Introduction

Structure and reactivity relationship is the foundation of the modern physical organic chemistry.[1] The substituent effects derived from Hammett-type linear correlations have been widely used to elucidate and predict the polar reaction mechanisms.[1] In contrast, the substituent effects for radical reactions are relatively less successful because of the extreme difficulty of separating the spin delocalization from the polar effects.[2] The polar effects for most substituents were found to overwhelm their spin delocalization effects in most radical reactions.[3,4] In addition, the agreement between different radical substituent scales is quite poor.[2,4]

Although the radical substituent effects of fluorine and trifluoromethyl (CF_3) groups have been extensively investigated, the results reported in the literature are quite controversy. The $\sigma^{\bullet}$ scale devised from the ESR hyperfine coupling constants of the substituted benzyl-type radicals suggests that both *p*-CF_3 ($\sigma_{p\text{-}CF_3}^{\bullet} = -0.001$) and *p*-F ($\sigma_{p\text{-}F}^{\bullet} = -0.011$) groups are radical destabilizing.[4a,b] Kinetic studies show that the *p*-F group decreases the pyrolysis rate constants of phenylazoethane.[5] The $\sigma_{JJ}^{\bullet}$ scale[6,7] shows that both *p*-CF_3 and *p*-F groups have negligible effects on the radical stabilities. The radical stabilization energies (RSEs) derived from the homolytic bond dissociation enthalpies (BDEs) of phenols and anilines demonstrate that the *p*-F group has negligible effects on the radical stabilities, but the *p*-CF_3 group destabilizes the radicals by 2−5 kcal/mol.[8] On the other hand, the *p*-F substituent was found to increase the rate constants for the azocumene pyrolysis[9] and the NBS bromination of 3-cyanotoluene.[10] Furthermore, the kinetic studies for the *β*-scission of alkoxy radicals show that introduction of one or two α-F substituent(s) stabilizes the methyl radicals, but introduction of three α-F substituents reverses the radical stabilizing nature of one or two α-F substituent(s).[11]

We[12] have employed the ab initio CBS-4 (complete basis set) model calculations[13] to determine the H−A BDEs in neutrals and radicals of various substrates. In the present paper, we extend the studies to examine the radical substituent effects of fluorine and trifluoromethyl groups from the calculated C−H BDEs of various model compounds. The C−H BDEs of few fluorinated ethanes

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have been obtained at the MP2/6-311G(d,p)//MP2/6-31G-(d,p) level.[14]

Calculations

All of the ab initio CBS-4 theoretical calculations were carried out using Gaussian-92 or Gaussian-94:[15] a single-point Hartree−Fock calculation with a very large basis set (6-311+G(3d2f, 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 published previously.[13,16] 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.[12,13,16] Examination of the BDEs in Tables 2−4 shows that the calculated C−H BDEs for the fluorinated compounds also agree with the available experimental results within ±2 kcal/mol. The BDE values derived from different reliable experimental methods usually agree with each other within 2−3 kcal/mol.[17,18]

The BDE of the H−A bond (eq 1) at both 0 and 298 K is readily obtained by using eq 2 from the calculated formation enthalpies (ΔH) of the radicals (A•) and neutral molecules (HA) together with the formation enthalpy of hydrogen atom (51.63 and 52.10 kcal/mol at 0 and 298 K, respectively).[13,16] The BDE of the H−A bond at 0 K could also be obtained from the relative total energies (E_{tol}) or the atomization energies (D_o).[13] The calculated total energies, formation enthalpies, and atomization energies for the neutral molecules and the related radicals are summarized in Table 1. The C−H BDEs were calculated by using the date given in Table 1, and the results are summarized in Tables 2−4. The literature available experimental BDEs are also included in the relevant tables for comparison.

$$\mathrm{HA} \xrightarrow{\mathrm{BDE_{HA}}} \mathrm{A^\bullet} + \mathrm{H^\bullet} \qquad (1)$$

$$\mathrm{BDE_{HA}} = \Delta H_{\mathrm{A}\bullet} + \Delta H_{\mathrm{H}\bullet} - \Delta H_{\mathrm{HA}} \qquad (2)$$

Results and Discussion

Effects of α-F Substituents on sp^3 C−H Bond Strength. Homolytic bond dissociation enthalpy (BDE) of the H−A bond is the energy needed to homolytically cleave the H−A bond to form A• radical and hydrogen atom (H•) (eq 1), indicating that the relative BDE values of the H−A bonds can be used to describe the thermodynamic stabilities of the radicals (A•) formed by removal of one hydrogen atom.[17,18] The calculated sp^3 C−H BDEs for six hydrocarbons with α-fluorine substituents together with the related model compounds are summarized in Table 2.

Comparison of the sp^3 C−H BDEs of fluoromethane (CH_3F) and methane (Table 2) shows that introduction of one α-F substituent weakens the C−H bond strength by 3.4 kcal/mol at 298 K. Introduction of an α-F substituent into ethane was found to decrease the C−H BDE by 3.2 kcal/mol. But the isopropyl C−H BDE of CH_3-$CHFCH_3$ was found to be only 0.7 kcal/mol lower than that of propane. Introduction of a second α-F substituent into 1-fluoroethane (CH_3CH_2F) was found to decrease the α-C−H BDE by another 1.5 kcal/mol, about half of 3.2 kcal/mol decrease in BDE for introduction of the first α-F substituent. Interestingly, the C−H BDE of difluoromethane (CH_2F_2) was found to be exactly identical to that of fluoromethane (CH_3F), indicating that introduction of the second α-F substituent results in *no* additional radical stabilization effects. Most significantly, the sp^3

Table 1. Total Energies, Formation Enthalpies, and Atomization Energies for Neutral Molecules and the Related Radicals As Calculated from the CBS-4 Method

neutral	E_{tol}(0 K)[a]	ΔH(0 K)[b]	ΔH(298 K)[c]	D_o[d]
CH_3F	−139.583 501	−54.76	−56.70	−398.11
$C(\bullet)H_2F$	−138.920 318	−6.10	−6.96	−297.82
CH_2F_2	−238.759 761	−106.03	−107.88	−416.21
$C(\bullet)HF_2$	−238.096 550	−57.35	−58.19	−315.90
CF_3H	−337.947 963	−164.78	−166.48	−441.81
$C(\bullet)F_3$	−337.277 979	−111.85	−112.54	−337.24
CF_3CH_2F	−476.353 034	−215.05	−217.86	−732.16
$CF_3C(\bullet)HF$	−475.688 734	−165.69	−167.39	−631.16
CF_3CHF_2	−575.526 236	−264.40	−266.84	−748.34
$CF_3C(\bullet)F_2$	−574.860 438	−214.09	−215.48	−646.40
CF_3CH_3	−377.200 216	−178.50	−181.70	−728.77
$CF_3C(\bullet)H_2$	−376.529 288	−124.98	−126.98	−623.61
CF_3CHFCF_3	−813.116 073	−371.27	−374.47	−1062.13
$(CF_3)_2C(\bullet)F$	−812.447 738	−319.37	−321.37	−958.60
$CF_3CH_2CF_3$	−713.965 214	−335.94	−339.62	−1059.97
$(CF_3)_2C(\bullet)H$	−713.293 319	−281.81	−284.25	−954.21
$(CF_3)_3CH$	−1050.720 041	−487.00	−491.14	−1384.78
$(CF_3)_3C\bullet$	−1050.035 415	−424.89	−427.65	−1271.03
$CF_3CF_2CF_2H$	−813.103 197	−363.19	−366.33	−1054.05
$CF_3CF_2C(\bullet)F_2$	−812.438 428	−313.53	−315.58	−952.76
$CF_3CH_2CH_3$	−416.438 127	−183.22	−187.93	−1006.73
$CF_3CH(\bullet)CH_3$	−415.774 562	−134.31	−137.68	−906.19
$CF_3CH_2CH_2\bullet$	−415.773 583	−133.70	−137.26	−905.58
$CF_3CH_2CH_2CH_3$	−455.676 680	−188.33	−194.51	−1285.10
$CF_3CH(\bullet)CH_2CH_3$	−455.011 920	−138.68	−143.58	−1183.81
$CF_3CH_2CH(\bullet)CH_3$	−455.016 085	−141.30	−146.17	−1186.42
$CF_3CH_2CH_2CH_2\bullet$	−455.012 292	−138.92	−143.79	−1184.04
$CH_2{=}CH_2$	−78.438 510	13.98	11.88	−532.51
$CH_2{=}CH\bullet$	−77.761 396	71.38	70.33	−423.47
$CH_2{=}CHF$	−177.606 741	−32.24	−34.22	−545.57
$CH_2{=}CF\bullet$	−176.927 355	26.59	25.67	−435.11
$CF_2{=}CFH$	−375.932 073	−117.71	−119.11	−564.71
$CF_2{=}CF\bullet$	−375.243 619	−53.19	−53.46	−448.56
$CF_3CH{=}CH_2$	−415.212 076	−148.84	−151.85	−869.09
cis-$CF_3CH{=}CH\bullet$	−414.530 663	−88.74	−90.68	−757.35
trans-$CF_3CH{=}CH\bullet$	−414.531 112	−89.02	−90.96	−757.63
CH_3CH_2F	−178.826 796	−62.86	−66.52	−679.45
$CH_3CHF\bullet$	−178.167 227	−16.46	−18.98	−581.43
CH_3CHF_2	−278.009 836	−118.38	−121.82	−701.81
$CH_3CF_2\bullet$	−277.347 886	−70.49	−72.84	−602.29
CH_3CHFCH_3	−218.072 852	−72.69	−77.91	−962.53
$CH_3C(\bullet)FCH_3$	−217.415 582	−27.73	−31.72	−865.94
$CF_2{=}CH_2$	−276.781 904	−82.82	−84.63	−562.98
$CF_2{=}CH\bullet$	−276.092 694	−17.82	−18.56	−446.36
$CF_3C(\bullet){=}CH_2$	−414.530 034	−88.34	−90.22	−756.96
$CF_3CF_2CH_3$	−614.779 583	−278.80	−282.73	−1035.99
$CF_3CF_2CH_2\bullet$	−614.109 030	−225.51	−228.17	−931.07
cis-$CHF{=}CH\bullet$	−176.922 292	29.76	28.83	−431.93
trans-$CHF{=}CH\bullet$	−176.922 122	29.87	28.95	−431.82
cis-$CHF{=}CHF$	−276.762 353	−70.55	−72.27	−550.72
cis-$CHF{=}CF\bullet$	−276.079 367	−9.46	−10.09	−437.99
$HC{\equiv}CH$	−77.197 686	57.63	57.30	−385.60
$HC{\equiv}C\bullet$	−76.488 180	135.36	136.13	−256.23
$FC{\equiv}CH$	−176.343 768	25.30	25.15	−384.76
$FC{\equiv}C\bullet$	−175.628 252	106.80	107.98	−251.62
$CF_3C{\equiv}CH$	−413.996 716	−121.17	−122.37	−738.15
$CF_3C{\equiv}C\bullet$	−413.259 181	−25.85	−25.93	−591.20

[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.

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Table 2. Homolytic Bond Dissociation Enthalpies (BDEs) of the C−H Bonds Adjacent to α-F Substituents

substrate	$BDE_{0\ K}$[b]	$BDE_{298\ K}$[c]	$BDE_{298\ K}$ (lit.)
CH_4[a]	103.6	105.2	104.8[d]
CH_3F	100.3	101.8	100 ± 2[e]
CH_2F_2	100.3	101.8	101 ± 2;[e] 103.2[f]
CHF_3	104.6	106.0	106.7 ± 1[e]
CH_3CH_3[a]	99.8	101.6	101.1 ± 0.4[d]
CH_3CH_2F	98.0	99.6	
CH_3CHF_2	99.5	101.1	99.5 ± 2.5[e]
$CH_3CH_2CH_3$[a]	97.1	99.0	98.6 ± 0.4[d]
CH_3CHFCH_3	96.6	98.3	

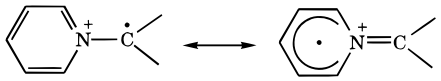
[a] Reference 12a. [b] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 method. [c] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 method. [d] Reference 18a. [e] Reference 18b. [f] Pickard, J. M.; Rodgers *Int. J. Chem. Kinet.* **1983**, *15*, 569.

C−H BDE of CHF_3 was found to be about 5 kcal/mol *higher* than that of CH_2F_2, suggesting that introduction of the third α-F substituent decreases the radical stability by about 5 kcal/mol. Furthermore, the sp^3 C−H BDE of CHF_3 was found to be even about 1 kcal/mol *higher* than that of methane. In other words, introduction of the third α-fluorine substituent completely reverses the radical stabilizing nature of one or two α-F substituents into radical destabilizing. Our calculated results are in remarkable agreement with the experimental observation from the kinetic studies of the *β*-scission of alkoxy radicals.[11]

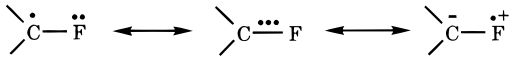
Dual Effects of Substituents on Radical Stabilities. It is well-known that radicals can be destabilized by the inductive effects of electron-withdrawing groups due to the electron deficient nature of radicals, but they can also be stabilized through the resonance delocalization of the unpaired electron. The dual radical (stabilizing and destabilizing) effects of substituents have been recognized both from experiments[19,20] and theoretical calculations.[21] The substituent effects of α-trimethylammonium (α-Me_3N^+) and α-pyridinium (α-$C_5H_5N^+$) groups have been used as examples to demonstrate the dual effects of substituents on radical stabilities.[20] Introduction of an α-Me_3N^+ group was found to *increase* the adjacent C−H BDEs by 2−5 kcal/mol, but introduction of an α-$C_5H_5N^+$ group was found to cause a *decrease* of the adjacent C−H BDEs by 5−10 kcal/mol.[20] The radical destabilizing (or bond strengthening) effects of the α-Me_3N^+ group can be attributed to the inductive effects of the positive charge on nitrogen atom since the resonance delocalization ability of the α-Me_3N^+ group is negligible.[1c,20] In other words, the radical destabilizing effects of the α-Me_3N^+ group reflect exclusively the magnitude of the inductive effects.

The bond weakening effects of the α-$C_5H_5N^+$ group are mainly associated with the resonance delocalization of the unpaired electron into the aromatic ring as shown in Scheme 1. The resonance stabilization overwhelms the radical destabilizing effects caused by the inductive effects of the positive charge on the pyridinium nitrogen atom, which are expected to be close to those of the α-Me_3N^+ group.[20] This conclusion is further supported by the observation that the bond weakening effects of the α-$C_5H_5N^+$ group was found to be ca. 2−5 kcal/mol less than those of α-phenyl group in the same substrates. The relatively smaller radical stabilizing effect of the α-pyridinium than the α-phenyl group was clearly caused by the inductive effects of the positive charge on the α-pyridinium group.[20]

Scheme 1



Scheme 2



The radical stabilizing effects of one or two α-F substituent(s) are no doubt associated with the resonance delocalization of the unpaired electron by formation of the two-center three-electron bond as shown in Scheme 2. This type of radical delocalization has been suggested to account for the enhanced captodative radical stabilization effects.[22] The radical stabilizing effects of one or two α-F substituent(s) are larger than the radical destabilizing effects caused by the inductive effects of the polar C−F bond(s). But the introduction of the third α-F substituent completely reverses the radical stabilizing nature of one or two α-F substituent(s) into radical destabilizing, indicating that the related radical destabilizing effects of the three α-fluorine substituents in the $F_3C^\bullet$ radical are larger than the related radical stabilizing effects.

The geometry of the methyl radical is known to be planar,[23] but the fluoromethyl radicals were found to be pyramidal.[24,25] The nonplanarity of the fluoromethyl radicals was found to increase progressively in the order $^\bullet CH_2F < {}^\bullet CHF_2 < {}^\bullet CF_3$.[24,25] For example, the bisector angles of $^\bullet CH_2F$, $^\bullet CHF_2$, and $^\bullet CF_3$ radicals were found to be 28.8°, 42.4°, and 49.1°, respectively.[21a] The $^\bullet CF_3$ radical was shown to approach even the tetrahedral configuration.[25] The *p*-orbital overlap which is required for the resonance delocalization (Scheme 2) is expected to diminish progressively when the fluoromethyl radicals become increasingly nonplanar with each additional fluorine substituent.[19a,26] In other words, the resonance delocalization of the fluoromethyl radical will not increase progressively, but probably *decrease* with each additional α-fluorine substituent introduced primarily due to the increase of the pyramidal structure.

On the other hand, the inductive effects of the polar C−F bonds should be relatively insensitive to the non-

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Table 3. Homolytic Bond Dissociation Enthalpies (BDEs) of the C−H Bonds Adjacent to α-CF_3 Groups

substrate	$BDE_{0\ K}$[b]	$BDE_{298\ K}$[c]	$BDE_{298\ K}$ (lit.)
CH_3CH_3[a]	99.8	101.6	101.1 ± 0.4[d]
CF_3CH_3	105.2	106.8	106.7 ± 1.1[e]
CF_3CH_2F	101.0	102.6	
CF_3CHF_2	101.9	103.5	102.7 ± 0.5[f]
$CH_3CH_2CH_3$[a]	100.4	102.1	100.4 ± 1[d]
$CH_3CH_2CH_3$[a]	97.1	99.0	98.6 ± 0.5[d]
$CF_3CH_2CH_3$	100.5	102.4	
$CF_3CH_2CH_3$	101.1	102.8	
$CH_3CH_2CH_2CH_3$[a]	100.5	102.2	
$CH_3CH_2CH_2CH_3$[a]	97.5	99.3	98.3 ± 0.5[f]
$CF_3CH_2CH_2CH_3$	101.3	103.0	
$CF_3CH_2CH_2CH_3$	98.7	100.4	
$CF_3CH_2CH_2CH_3$	101.0	102.8	
$(CF_3)_2CH_2$	105.8	107.5	108.1 ± 8[e]
$(CF_3)_2CHF$	103.5	105.2	103.6 ± 1[f]
$CF_3CF_2CHF_2$	101.3	102.9	103.2 ± 2[f]
$(CH_3)_3CH$[a]	95.4	97.3	96.4 ± 1[d]
$(CF_3)_3CH$	113.7	115.5	109 ± 5[g]
$CF_3CF_2CH_3$	104.9	106.7	

[a] Reference 12a. [b] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 method. [c] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 method. [d] Reference 18a. [e] McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112. [f] Reference 18b. [g] Evans, B. S.; Weeks, S. I.; Whittle, E. *J. Chem. Soc. Faraday I* **1983**, *79*, 1471.

planar structure of the fluoromethyl radicals since the inductive effect is essentially caused by the electrostatic interactions.[27] The magnitude of the inductive effects will be proportional to the numbers of the α-fluorine substituents. Thus, the radical destabilizing effects by the inductive effects will increase much faster than the radical stabilization by the resonance delocalization for each additional α-F group. As a result, the fluoromethyl radical stabilities do not increase progressively with each additional α-F substituent. The radical destabilizing effects of the three α-F substituents in the $^{\bullet}CF_3$ radical imply that the inductive effects of the three α-fluorine substituents overpass the related resonance delocalizing effects.

Effects of α-CF_3 Substituents on sp^3 C−H Bond Strength. The calculated sp^3 C−H BDEs for the rest of the fluorinated alkanes and the related model compounds are summarized in Table 3.

Examination of Table 3 shows that the sp^3 C−H BDE of CF_3CH_3 is 105.2 and 106.8 kcal/mol at 0 and 298 K respectively, which is about 5 kcal/mol higher than that of ethane. Also, the sp^3 C−H BDE values of CF_3CH_2-CH_3 and $CF_3CH_2CH_2CH_3$ are 3.4 and 3.8 kcal/mol higher than those of $CH_3CH_2CH_3$ and $CH_3CH_2CH_2CH_3$, respectively, at 298 K. The sp^3 C−H BDE of $CF_3CH_2CF_3$ was found to be 8.5 kcal/mol higher than that of $CH_3CH_2CH_3$, i.e., a 4.3 kcal/mol increase in BDE for each α-CF_3 group. The sp^3 C−H BDE of $(CF_3)_3CH$ was found to be about 18 kcal/mol higher than that of $(CH_3)_3CH$, i.e., about a 6 kcal/mol increase in BDE for each α-CF_3 group. The near constant increase (5 ± 1 kcal/mol) in BDE for each α-CF_3 group indicates that the inductive effects are predominant for the α-CF_3 groups.

The bond strengthening effects of the CF_3 group were found to decrease progressively from 3.8, 1.1, and 0.5 kcal/mol for the α-, *β*-, and *γ*-C−H BDEs of CF_3CH_2-CH_2CH_3, respectively. The progressive decrease in BDE along the α-, *β*-, and *γ*-C−H bond series provides the additional evidence to show that the bond-strengthening effects of the CF_3 group were primarily caused by the inductive effects since the electrostatic interaction diminishes quickly with the increasing distance.[27] Therefore, it is not surprising to find why the fluorination at the *γ*-position ($RCF_2CH_2CH_2^{\bullet}$ radical) has negligible effects on the reactivities of the *n*-alkyl radicals.[28]

Table 4. Homolytic Bond Dissociation Enthalpies (BDEs) of the sp^2 and sp C−H Bonds in Unsaturated Fluorohydrocarbons

substrate	$BDE_{0\ K}$[a]	$BDE_{298\ K}$[b]	$BDE_{298\ K}$ (lit.)
$CH_2{=}CH_2$	109.0	110.6	111.2[c]
cis-$CHF{=}CH_2$	113.6	115.2	
trans-$CHF{=}CH_2$	113.7	115.3	
$CH_2{=}CHF$	110.5	112.0	
cis-$CHF{=}CHF$	112.7	114.3	
$CF_2{=}CHF$	116.2	117.8	112[d]
$CF_2{=}CH_2$	116.6	118.2	112[d]
cis-$CF_3CH{=}CH_2$	111.7	113.3	113[d]
trans-$CF_3CH{=}CH_2$	111.5	113.0	
$CF_3CH{=}CH_2$	112.1	113.7	
$HC{\equiv}C$-*H*	129.4	130.9	132.8[c]
$FC{\equiv}C$-*H*	133.1	134.9	
$CF_3C{\equiv}C$-*H*	147.0	148.5	

[a] In kcal/mol; the homolytic bond dissociation enthalpies at 0 K as calculated from the CBS-4 method. [b] In kcal/mol; the homolytic bond dissociation enthalpies at 298 K as calculated from the CBS-4 method. [c] Reference 18a. [d] Estimated from the recoil tritium abstract measurements.[29]

Comparison of the sp^3 C−H BDEs of CF_3CH_2F and CF_3CHF_2 with that of CF_3CH_3 indicates that introduction of one or two α-F substituent(s) causes a similar decrease of the sp^3 C−H bond strength by about 3−4 kcal/mol as observed for the introduction of one or two fluorine substituent(s) into methane or ethane. The sp^3 C−H BDEs of $CF_3CF_2CHF_2$ and CF_3CHFCF_3 were found to be 2−3 kcal/mol less than those of $CF_3CF_2CH_3$ and CF_3CH_2-CF_3, respectively. The bond weakening effects for introduction of one or two α-F substituent(s) can also be attributed to the resonance delocalization effects by the α-fluorine substituents as shown in Scheme 2.

Homolytic Bond Dissociation Enthalpies of the sp^2 C−H Bonds in Fluoroethylenes. There is a paucity of quantitative information concerning the sp^2 C−H bond strengths for unsaturated fluorohydrocarbons in the literature. As far as we know, there are only four sp^2 C−H BDEs. The sp^2 C−H BDEs of 1,1-difluoroethylene ($CF_2{=}CH_2$), *cis*-1,2-difluoroethylene (*cis*-$CHF{=}CHF$), and 3,3,3-trifluoropropene ($CF_3CH{=}CH_2$) were estimated from the recoil tritium abstraction measurements to be 1, 1, and 2 kcal/mol higher than that of ethylene, respectively.[29] The sp^2 C−H BDE of pentafluorobenzene (C_6HF_5) was found to be about 6 kcal/mol higher than that of benzene.[18b] The calculated sp^2 C−H BDEs for ethylene and propene together with their fluorinated derivatives are all summarized in Table 4.

An inspection of the sp^2 C−H BDEs of $CH_2{=}CHF$ and $CH_2{=}CH_2$ (Table 4) shows that introduction of an α-F substituent causes an *increase* of the sp^2 C−H BDE by about 1.5 kcal/mol. This is opposite to the decrease of the sp^3 C−H BDE for introduction of an α-F substituent (Tables 2 and 3). The sp^3 C−H bond weakening effect was attributed to the resonance delocalization by forma-

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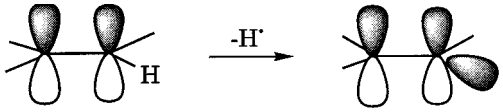
Scheme 3



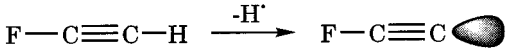
tion of the two-center three-electron bond (Scheme 2), which overwhelms the radical destabilization of the inductive effects by the polar C−F bonds. But the formation of a two-center three-electron bond for the radicals derived from the sp^2 C−H bond cleavage of CH_2=C*H*F is virtually forbidden since the *p*-orbital of the radical formed is perpendicular to the π bond as shown in Scheme 3. Similarly, introduction of an α- or β-CF_3 group was also found to increase the sp^2 C−H BDEs by 2−3 kcal/mol due to the inductive effects of the CF_3 group.

More significantly, even much larger sp^2 C−H bond strengthening effects were found when one or two fluorine substituent(s) were introduced at the β-position than at the α-position. For example, the sp^2 C−H BDEs of *cis*-CHF=CH_2 and *trans*-CHF=CH_2 are about ca. 4.6 kcal/mol higher in energy than that of CH_2=CH_2. The sp^2 C−H BDE of CF_2=CH_2 was found to be 7.6 kcal/mol higher in energy than that of CH_2=CH_2. But introduction of an additional α-F substituent into these β-fluorinated ethylenes was found to slightly *decrease* the sp^2 C−H BDEs. For example, the sp^2 C−H BDEs of CHF=C*H*F and CF_2=C*H*F were found to be slightly less than those of CHF=CH_2 and CF_2=CH_2, respectively. The origin of the slight bond weakening effects for introduction of an α-F substituent into the β-fluorinated ethylenes is less clear. The sp^2 C−H bond weakening effect seems to be caused by the stabilizing interaction of the resulting radical with the α-F substituent.

Homolytic Bond Dissociation Enthalpies of the sp C−H Bonds in Fluoroacetylenes. In this section, we will examine the substituent effects of fluorine and trifluoromethyl groups on the sp C−H bond strength. The calculated sp C−H BDEs of acetylene, fluoroacetylene, and 3,3,3-trifluoro-1-propyne are also summarized in Table 4.

Comparison of the sp C−H BDEs of fluoroacetylene and acetylene shows that introduction of a fluorine substituent at the β-position of acetylene causes an increase of the sp C−H BDE by 4.0 kcal/mol, which is comparable to the sp^2 C−H BDE increase (4.6 kcal/mol) for introduction of a β-fluorine substituent into ethylene. The bond strengthening effects of the β-fluorine substituent can be attributed to the inductive effects of the polar C−F bond since the delocalization of the unpaired electron into the β-fluorine substituent is also forbidden

Scheme 4



due to the perpendicular structure of the *p*-orbitals of the two π bonds as shown in Scheme 4.

It is worth noting that the sp C−H BDE of 3,3,3-trifluoro-1-propyne (CF_3CC*H*) is 18.5 kcal/mol higher than that of acetylene, indicating that introduction of a β-CF_3 group increases the sp C−H bond strength of acetylene by *18.5 kcal/mol!* In other words, the β-CF_3 group destabilizes the related radical stability by 7×10^{14} times! This is much larger than the bond strengthening effects of the CF_3 group ever observed, and it warrants to be checked by experimental measurements.

Ground-State Effects. From the equilibrium acidity and oxidation potential measurements, the benzylic C−H BDEs were found to increase when polyfluorine substituents were introduced into the aromatic rings.[30] The benzylic C−H bond strength increase was believed to be caused by the decrease of the ground-state energies because of the unusual stronger strength of the C−F than the C−H bond.[30]

If the change of the ground-state energy is responsible for the C−H BDE increase, we would expect that the sp^3 C−H BDE of CF_3CF_2C*H*F_2 will be considerably higher in energy than that of CF_3C*H*F_2 since there are more polar C−F bonds in CF_3CF_2C*H*F_2. Similarly, the sp^3 C−H BDE of CF_3CF_2CH_3 must also be higher in energy than that of CF_3CH_3. Examination of Tables 2 and 3 shows that the sp^3 C−H BDE of CF_3CF_2C*H*F_2 is essentially the same as that of CF_3C*H*F_2, and the sp^3 C−H BDE of CF_3CF_2CH_3 is essentially the same as that of CF_3CH_3. These results indicate that the ground-state energy change does not significantly affect the C−H BDEs. In an earlier study,[31] we have provided conclusive evidence to show that the ground-state effects on the BDEs of the nonpolar C−H bonds are negligible. Therefore, we conclude that the benzylic C−H bond strengthening effects caused by introduction of polyfluorine substituents was primarily caused by their inductive effects rather than by the change of the ground-state energy. The identical sp^3 C−H BDEs of CF_3CH_3 and CF_3-CF_2CH_3 also indicate that the inductive effects of the α-CF_3 group are similar to those of the α-CF_2CF_3 group, which is consistent with the results from kinetic studies.[32]

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