A DFT Study on the C−H Bond Dissociation Enthalpies of Haloalkanes: Correlation between the Bond Dissociation Enthalpies and Activation Energies for Hydrogen Abstraction

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The C−H bond dissociation enthalpies of halomethanes were computed from the results of density functional theory (DFT) calculations at the B3LYP level with various basis sets, such as 6-311G(d,p) and 6-311++G(3df,2p). Reasonably accurate C−H bond dissociation enthalpies were obtained even at the B3LYP/6-311G(d,p) level when ROB3LYP method was used for radicals. Applying the same procedure, the C−H bond dissociation enthalpies for a series of haloethanes were also calculated. Good correlation has been observed between the activation energies for the hydrogen abstraction from haloalkanes by OH radical and the corresponding C−H bond dissociation enthalpy values.

Introduction

The importance of haloalkanes in atmospheric chemistry is well-known.[1−3] The chlorofluorocarbons are known to be responsible for the depletion of ozone layer in the stratosphere and greenhouse effects. Understanding of the atmospheric chemistry of halogenated compounds has thus far-reaching implications and become very important.[4] Hydrogen abstraction by OH radical is known to be the major degradation process of alkanes and haloalkanes in the atmosphere.[5] Knowledge of the rate constants for hydrogen abstraction by OH radical thus enables us to estimate the atmospheric lifetime of these compounds. The more the atmospheric lifetime, the more is the efficiency of transport of haloalkanes to the stratosphere. Since it is practically impossible to study experimentally the kinetics of hydrogen abstraction for each potential compounds, finding a relationship between the reactivity and a molecular properties is always useful. Such a relationship can be used to estimate the atmospheric lifetime from the molecular properties representing the trend in reactivity. It can be expected that the reactivity toward the OH radical will vary systematically for a series of homologous compounds. Indeed, bond dissociation enthalpies (BDEs) of the breaking C−H bonds for a series of compounds has been found to be strongly correlated with the observed reactivity trends for hydrogen abstraction from haloalkanes.[6−10]

The reactivity trend and relative rate constants can be estimated from a knowledge of the BDE's of the C−H bond of haloalkanes. The C−H bond energies for the fluoromethanes and chloromethanes were estimated from the experimental data and reported in the literature.[11−13] The same for the bromomethanes has been reported recently.[14] However, the C−H bond energies for most of the mixed halomethanes containing bromine and haloethanes are yet to be determined. Although direct rate constants can be obtained from the experiment or computational study, modeling studies can play an important role considering the large number of relevant chemical species. Accurate estimation of BDE's from experimental as well as theoretical calculations is very difficult. One needs to perform very high level theoretical calculations, such as G2,[15] to obtain BDE's at sufficient accuracy. Unfortunately, however, such high level calculations are computationally too expensive to carry out for larger haloalkanes.

The applicability of the DFT procedures for estimating various thermochemical properties is an area of continuing research interest.[16−19] Bauschlicher made an extensive analysis of the results obtained from the G2 procedure and DFT methods.[16] He found that the performance of B3LYP method is the best among the DFT methods tested. Very recently, DiLabio and co-workers made an analysis on the performance of B3LYP procedure for calculating the bond dissociation energies.[20,21] They observed that reasonably accurate BDEs for the C−H bonds could be obtained by B3LYP procedure when restricted open-shell formalism (ROB3LYP) was used for radicals and the exact energy of hydrogen atom (0.5 au) was taken for calculating the BDE. During the course of this study, another work paying attention to the same problem of computing the BDE of the C−H bond has been appeared in the literature.[22] A computationally efficient methodology has been developed to calculate the C−H and C−X bond dissociation energies for halomethanes. The method requires ab initio calculations at the MP2/cc-pVtz level and then addition of a predetermined correction factor to the MP2/cc-pVtz energies. The correction factor includes the effects of basis set and electron correlation on the BDE. The correction factor was determined by performing higher level calculations, such as MP2/cc-pV5Z and CCSD(T)/cc-pVtz.[22]

There are some advantages in using the DFT procedure. First it is computationally inexpensive compared to the high level ab initio methods based on molecular orbital theory and thus calculations can be performed with a large basis set even for a molecule containing more than 10 halogen atoms. Moreover, DFT methods scale much more favorably with the size of basis set.[23,24] Second, the problem of spin contamination for the open shell systems is almost negligible. In the present study, we have used the DFT based usual B3LYP procedure (where UB3LYP

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method is used for radicals) and the (RO)B3LYP procedure described by DiLabio et al.[20] for estimating BDE's of the C−H bond of halomethanes and haloethanes containing hydrogen atoms at one carbon atom only. As far as we know, there is no theoretical study for the estimation of BDE's for the whole series of halomethanes containing F,Cl and Br atoms. Since experimental BDE's are also not known for many halomethane molecules, the present study can provide useful thermochemical data for the halomethanes and some haloethane molecules. Moreover, the previously observed correlation between the C−H bond energies and hydrogen abstraction rate constants suggests that relative rate constants can be estimated from accurate calculations of bond strengths. The trend in reactivity along a homologous series is discussed in the light of the calculated BDE's of the C−H bonds of haloalkanes.

Computational Methods

Geometries of halomethane molecules (CH_nX_{4-n}, X = F, Cl, Br, and $n = 1-4$) and haloethane series ($CX_3-CH_nY_{3-n}$, X,Y = F,Cl, and $n = 1, 3$) were optimized at the B3LYP level with 6-311G(d,p) basis set. For the open shell radicals, two procedures were used for geometry optimizations. In the first procedure (UB3LYP), the usual unrestricted Hartree−Fock orbitals (UHF) were used to generate the DFT orbitals, whereas in the second procedure (ROB3LYP) restricted open shell Hartree−Fock (ROHF) formalism was used. Geometry optimizations for the halomethane radicals ($CH_{n-1}X_{4-n}$, X = F, Cl, Br, and $n = 1-4$) were carried out at the B3LYP/6-311G(d,p) and (RO)B3LYP/6-311G(d,p) levels, whereas for the haloethane radicals ($CX_3-CH_{n-1}Y_{3-n}$, X,Y = F, Cl, and $n = 1, 3$) only the (RO)B3LYP/6-311G(d,p) method was used for geometry optimizations. Vibrational frequency calculations were performed for each geometry at the same level used for the geometry optimizations. Single-point B3LYP calculations were also carried out by using a larger 6-311++G(3df,2p) basis set. Thermal corrections to the B3LYP/6-311++G(3df,2p) energies for getting the enthalpies were made by using the frequencies and zero-point energies (ZPE) obtained at the B3LYP/6-311G(d,p) level. The enthalpies were estimated from the expression: $H°(298K) = E_o + ZPE + H_{trans} + H_{rot} + H_{vib} + RT$. H_{trans}, H_{rot}, and H_{vib} are the translational, rotational and vibrational contributions, respectively, to the enthalpy, where $H_{trans} = {}^3/_2RT$, $H_{rot} = {}^3/_2RT$ (RT for linear molecule), and H_{vib} can be calculated from the standard formulas.[25] Vibrational frequencies were not scaled since the scale factor prescribed (0.9989)[26] is very close to unity and has hardly any influence on the results obtained. All the calculations were carried out by using the Gaussian-94 suite of programs.[27]

The C−H bond dissociation enthalpies D_o^{298K} were estimated from the direct expression

$$D_o^{298K} = \Delta_f H°(R) + \Delta_f H°(H) - \Delta_f H°(RH) \qquad (1)$$

Where $\Delta_f H°$ (X) are the enthalpies of formation for the species X. Since there is a problem of self-interaction in the DFT procedure,[28] hydrogen atom energy was taken the same as the exact energy of 0.5 au. Similar approach was adopted by DiLabio and co-workers.[20] The BDE values of C−H bonds of halomethanes were evaluated by using both UB3LYP and ROB3LYP results for open shell radicals. The first procedure where B3LYP and UB3LYP methods were used for haloalkane molecules and radicals, respectively, is referred hereafter simply as B3LYP and the second procedure where B3LYP and ROB3LYP methods were used for molecules and radicals, respectively, is referred as (RO)B3LYP.

TABLE 1: Optimized Geometrical Parameters for Four Representative Halomethane Molecules and Four Radicals[a]

parameter	B3LYP[b]	exptl[c]	parameter	UB3LYP[a]	ROB3LYP[a]
CH_4			CH_3		
R(C−H)	1.091	1.090	R(C−H)	1.080	1.080
CH_3F			CH_2F		
R(C−H)	1.093	1.095	R(C−H)	1.082	1.082
R(C−F)	1.389	1.382	R(C−F)	1.343	1.343
θ(H−C−H)	109.8	110.4	θ(H−C−H)	124.7	124.1
			θ(H−C−F)	114.9	114.7
CH_3Cl			CH_2Cl		
R(C−H)	1.087	1.090	R(C−H)	1.077	1.077
R(C−Cl)	1.806	1.785	R(C−Cl)	1.715	1.715
θ(H−C−H)	110.7	110.8	θ(H−C−H)	125.1	124.9
			θ(H−C−Cl)	117.4	117.3
CH_3Br			CH_2Br		
R(C−H)	1.086	1.086	R(C−H)	1.078	1.078
R(C−Br)	1.965	1.933	R(C−Br)	1.864	1.865
θ(H−C−H)	111.2	111.2	θ(H−C−H)	124.8	124.3
			θ(H−C−Br)	117.6	117.2

[a] Bond lengths and angles are in angstrom and degrees, respectively. [b] With 6-311G(d,p) basis set. [c] From ref 29.

TABLE 2: Harmonic Vibrational Frequencies (in cm^{-1}) for CH_3X (X = F,Cl,Br) at the B3LYP/6-311G(d,p) Level and for CH_2X Radicals (X = F, Cl, Br) at the UB3LYP and ROB3LYP Levels with 6-311G(d,p) Basis Set

molecule	B3LYP	exptl[a]	radical	B3LYP	ROB3LYP	exptl[b]
CH_3F	1057	1048	CH_2F	516	573	
	1190	1195		1173	1176	
	1498	1475		1177	1177	
	1484	1471		1472	1473	
	3021	2964		3123	3120	
	3099	2982		3282	3277	
CH_3Cl	707	732	CH_2Cl	144	98	
	1031	1015		823	824	
	1388	1354		1002	1004	
	1479	1454		1412	1414	
	3074	2966		3170	3174	
	3173	3041		3328	3331	
CH_3Br	592	611	CH_2Br	117	211	368
	963	952		691	691	693
	1334	1305		931	935	953
	1475	1445		1382	1384	1356
	3081	2972		3168	3168	
	3188	3056		3328	3326	

[a] From ref 37. [b] From ref 38.

Results and Discussion

A. The C−H bond Dissociation Enthalpies. Table 1 presents optimized geometrical parameters of four representative halomethane molecules along with the corresponding experimental values.[29] The geometrical parameters obtained at the B3LYP/6-311G(d,p) level are quite close to the corresponding experimental values. For the open shell radicals, the difference between the geometrical parameters obtained by using the UB3LYP and ROB3LYP procedures in conjunction with the 6-311G(d,p) basis sets is rather small. Harmonic vibrational frequencies of three representative halomethane molecules and three representative radicals are given in Table 2. It should be pointed out here that the geometry optimizations and frequency calculations of all the halomethane molecules and radicals were also carried out at the B3LYP/6-311++G(3df,2p) level. However, the difference between the geometrical parameters and calculated frequencies at the two levels was found to be very small. Thus, it can be assumed that geometry optimizations and frequency calculations can satisfactorily be performed at the B3LYP/6-311G(d,p) level. The calculated harmonic frequencies are found to be in good agreement with the experimental values

TABLE 3: C−H Bond Dissociation Enthalpies (in kcal/mol) of Five Halomethane Molecules Calculated by Using Various Exchange−Correlation Functional and 6-311G(d,p) Basis Set

molecule	(RO) B3LYP	(RO) B3PW86	(RO) B3PW91	(RO) PW91LYP	exptl[b]
CH_4	106.0	118.9	106.2	102.3	104.9 ± 0.1
CH_3F	100.6	113.3	100.7	95.3	101.3 ± 1
CH_2F_2	100.3	113.1	100.4	94.4	103.2 ± 1
CH_3Cl	100.6	113.1	100.6	95.7	100.1 ± 0.5[c]
CH_2Cl_2	96.9	109.3	96.8	91.6	96.2 ± 0.6[c]
error[a]	1.2	12.4	1.2	5.3	

[a] Average absolute error. [b] Reference 33. [c] Reference 13.

which include anharmonicity in vibration as well. The difference between the calculated frequencies at the UB3LYP and ROB3LYP levels for halomethane radicals is very small.

Before discussing the performance of B3LYP and (RO)-B3LYP procedures for calculating BDE's of the C−H bonds, it may be worthwhile to make a comment on the performance of some other exchange-correlation functionals. We calculated the BDE's of the C−H bonds of five halomethane molecules, such as CH_nX_{4-n} (X = F, Cl and $n = 2-4$) using four different combinations of exchange and correlation functionals, namely B3LYP, B3PW86, B3PW91, and PW91LYP, in conjunction with 6-311G(d,p) basis set. Restricted open shell formalism was used for the radicals. Table 3 shows the BDEs of the C−H bonds obtained from such calculations. The average absolute error for the calculated BDE's was given in the bottom of the table. The error is found to be maximum (12.4 kcal/mol) for the B3PW86 functional. In the case of PW91LYP functional, the error reduces to 5.3 kcal/mol. The best results with an average error of 1.2 kcal/mol were obtained from B3LYP and B3PW91 functionals. Since B3LYP functional is more popular and already used for the calculation of BDE's for a variety of bonds,[20] we prefer to use the same functional in this study.

Table 4 shows the calculated BDE values of the C−H bonds (calculated from the eq 1) for the halomethane molecules. The BDE values were computed by using both B3LYP and (RO)-B3LYP procedures in conjunction with 6-311G(d,p) basis set. To observe the basis set effect, BDEs were also calculated at the (RO)B3LYP level with a larger 6-311++G(3df,2p) basis set. The choice of this basis set stems from the fact that the B3LYP/6-311+G(3df,2p) model calculations predicted heats of formation values with the smallest average absolute deviation.[17] The BDE value of the O−H bond of water is also given in the bottom of the table. It should be mentioned here that the BDE values for the C−H bond of CH_4 and O−H bond of water were also calculated by DiLabio et al.[20] following a variety of procedures based on B3LYP method. The BDE values of the O−H bond of water calculated at the B3LYP and (RO)B3LYP level with 6-311G(d,p) basis set are found to be much lower than the experimental value. The effect of basis set on the BDE of the O−H bond is very strong. The BDE value of the O−H bond increases by nearly 3 kcal/mol with the increase in basis set from the 6-311G(d,p) to 6-311++G(3df,2p). The best result for the BDE of the O−H bond of H_2O is obtained from the (RO)B3LYP method with the larger 6-311++G(3df,2p) basis set. Interestingly, in the case of the C−H bond of halomethanes, reasonably good results are obtained even from the computationally inexpensive B3LYP/6-311G(d,p) method. The BDEs of the C−H bond obtained from the (RO)B3LYP method are higher from the corresponding B3LYP calculated values. The difference between the two values obtained from B3LYP and (RO)B3LYP methods with the 6-311G(d,p) basis set varies from 0.5 to 1 kcal/mol. As expected from the works of DiLabio et al.,[20] The BDE values obtained from the (RO)B3LYP method are found to be in better agreement with the experimental results than that observed for the B3LYP calculated BDE values. The average absolute difference between the experimental and the (RO)B3LYP/6-311G(d,p) calculated BDE values of the C−H bonds is 1.4 kcal/mol. Since in majority of the cases the experimental uncertainty is more than 1 kcal/mol, the (RO)-B3LYP procedure is found to be quite good for estimating the BDEs of the C−H bonds of halomethanes. Moreover, in contrast to the BDE of the O−H bond of water, the effect of increasing the basis set on the calculated BDEs of the C−H bonds is not strong, thus good BDE values are obtained even from the computationally inexpensive (RO)B3LYP/6-311G(d,p) procedure. To understand the reason behind this strikingly different

TABLE 4: C−H Bond Dissociation Enthalpies (kcal/mol) of Halomethanes: Activation Energies (E_{Act}/R in K) for the Hydrogen Abstraction by OH Radical Are Given in the Last Column

molecule	B3LYP (BDE/sb)[f]	(RO)B3LYP BDE/sb[f]	(RO)B3LYP BDE/lb[g]	MP2/cc-pVtz[a]	exptl[b]	E_{act}/R[d]
CH_4	105.1	106.0	105.5	102.8	104.9 ± 0.1	1775 ± 100
CH_3F	99.7	100.6	101.1	99.7	101.3 ± 1	1500 ± 300
CH_2F_2	99.7	100.3	100.7	100.0	103.2 ± 1	1550 ± 200
CHF_3	104.9	105.4	105.3	105.1	106.7 ± 1	2440 ± 200
CH_3Cl	99.6	100.6	99.5	97.7	100.1 ± 0.6[c]	1400 ± 250
CH_2Cl_2	96.0	96.9	95.4	93.8	96.2 ± 0.6[c]	1050 ± 150
$CHCl_3$	93.1	93.9	92.1	93.2	93.8 ± 0.6	900 ± 150
CH_2FCl	98.2	99.0	98.4		100.8 ± 1.3	1270 ± 200
CHF_2Cl	100.5	101.1	100.4		100.7 ± 2	1600 ± 150
$CHFCl_2$	96.8	97.5	96.2		98.9 ± 1.2	1250 ± 150
CH_3Br	100.2	101.2	100.9	98.9	101.6 ± 1	1470 ± 150
CH_2Br_2	96.1	97.0	96.8	96.3	99.7 ± 1.8	900 ± 300
$CHBr_3$	91.7	92.6	92.4	93.2	96.0 ± 1.6	710 ± 200
CH_2FBr	98.1	98.8	98.5			1093[e]
CHF_2Br	98.9	99.5	99.1			1400 ± 200
$CHFBr_2$	94.9	95.6	94.6			665[e]
CH_2ClBr	96.1	97.0	96.2			930 ± 150
$CHCl_2Br$	92.6	93.4	92.2			631[e]
$CHBr_2Cl$	92.2	93.0	92.2			571[e]
CHFClBr	95.8	96.6	95.9			794[e]
HO−H	114.2	115.1	118.4		119.0 ± 1	

[a] BDEs at 0 K, ref 22. [b] Reference 29. [c] Reference 13. [d] Experimental activation energies taken from ref 33. [e] Estimated values taken from ref 35; the error in E_{act}/R was predicted to be around ±150 K. [f] sb: 6-311G(d.p). [g] lb: 6-311++G(3df,2p).

basis set dependence of the BDE's for the O−H bond of H_2O and the C−H bond of halomethane, we examined the change in energy for the H_2O and CH_4 systems with the change in basis set from the 6-311G(d,p) to the 6-311++G(3df,2p). At the B3LYP level, with the increase in basis set the energies of H_2O and CH_4 decreases by 9.96 and 1.90 kcal/mol, respectively. In the case of OH and CH_3 radicals, the energies decrease by 6.97 and 2.53 kcal/mol, respectively, with the increase in basis set. Since H_2O and CH_4 are isoelectronic systems, apparently, availability of more basis functions for CH_4 at a particular level of calculations makes it less basis set dependent than H_2O. The same is true for the isoelectronic OH and CH_3, availability of more basis functions makes the energy of CH_3 radical less basis set dependent than the energy of OH radical. Table 4 shows the BDEs obtained by McGivern et al.[22] at the 0 K for the C−H bonds of CH_3X, CH_2X_2, and CHX_3 (X = F, Cl, Br) molecules. At the 298 K, the BDE values would be higher than those obtained at the 0 K. The BDE values obtained from the (RO)-B3LYP procedure and those obtained by McGivern et al.[22] are quite close to the corresponding experimental values. Only in the case of CH_2Br_2 and $CHBr_3$ the results obtained by McGivern et al. are found to be better than the results obtained from the (RO)B3LYP method. The method proposed by McGivern et al.[22] is based on the addition of a correction factor to the BDE value at MP2/cc-pVtz level. Certainly, their procedure is computationally much more expensive than the (RO)B3LYP/6-311G(d,p) method. Since there is considerable error in the calculated BDE of the O−H bond at the (RO)B3LYP/6-311G-(d,p) level, it is better to use the experimental BDE of the O−H bond of H_2O (119.3 kcal/mol) and (RO)B3LYP/6-311G(d,p) calculated BDEs for calculating the reliable values of heats of reaction for the hydrogen abstraction from haloalkanes by OH radical.

After getting encouraging results for the halomethanes, we extended the study further for calculating the BDE values of the haloethanes containing hydrogen atoms at one carbon atom, such as $CF_3{-}CH_nX_mY_{3n-m}$, $CCl_3{-}CH_nX_mY_{3n-m}$, $CF_2Cl{-}CH_nX_mY_{3n-m}$, $CFCl_2{-}CH_nX_mY_{3n-m}$, where X = F, Y=Cl, n = 1−3 and m = 0−2. Because the results obtained for the halomethane molecules show that the BDE's of the C−H bond can reliably be calculated by using the (RO)B3LYP method, the same procedure was applied for the haloethane series. Geometry optimizations and frequency calculations were carried out for all the 24 molecules (see Table 5) at the B3LYP/6-311G(d,p) level. The ROB3LYP method was used for the haloethyl radicals. To observe whether the trend observed for halomethane series remains the same, single point calculations were also performed by using the larger 6-311++G(3df,2p) basis set. Table 5 displays the BDE values for the hydrogen abstraction reactions between the OH radical and haloethanes and the C−H BDE's obtained from our calculations. Like halomethanes, the BDEs obtained from the smaller and larger basis sets calculations are close for most of the haloethane molecules. Although experimental results are not available for the majority of the cases, it can be expected from our halomethane results that BDEs will be comparable to the exact values. In some cases where experimental results are available, the agreement between those BDE values and our (RO)B3LYP/6-311G(d,p) calculated values is impressive. It is also interesting to note that the BDE's obtained for the C−H bonds of CF_3-$CHCl_2$ and CF_3CHFCl are quite close to those obtained from the computationally much more expensive G2(MP2) method.[30]

B. Reactivity. Long back, Evans and Polanyi[31] suggested that for the exothermic atom transfer reactions the activation energies should correlate well with the exothermicity of the reactions when the central atom remains the same. A change in exothermicity by the amount $\Delta(\Delta H_r)$ should cause a change in activation energy $[\Delta(\Delta E_{act})]$, i.e.,

$$\Delta(\Delta E_{act}) = \alpha\, \Delta(\Delta H_r), \quad \text{where } 0 < \alpha < 1 \qquad (2)$$

Now in the case of hydrogen abstraction reactions between haloalkanes and OH radical [R−H + OH → R + H_2O], the values of $\Delta(\Delta H_r)$ is the same as the change in C−H bond dissociation enthalpies. Thus, a correlation between the change in heats of reaction values and activation energies is the same as observing a correlation between the change in BDE's of the C−H bonds and activation energies for hydrogen abstraction from haloalkanes.

TABLE 5: C−H Bond Dissociation Enthalpies (in kcal/mol) of Haloethane Molecules with General Formula: $CX_3{-}CH_nY_{3-n}$, X,Y = F, Cl, n = 1−3 Calculated by (RO)B3LYP Method Using 6-311G(d,p) [Sb] and 6-311++G(3df,2p) [Lb] Basis Sets: The Activation Energies (E_{Act}/R in K) for the Hydrogen Abstraction Reactions with OH Radical Are Given in the Last Column

	molecule	BDE[sb]	BDE[lb]	exptl[a]	E_{act}/R[c]
1*	$CF_3{-}CH_3$	106.0	105.8	106.7 ± 1.1	2170 ± 150
2*	$CF_3{-}CH_2F$	101.1	101.1		1750 ± 200
3*	$CF_3{-}CHF_2$	102.0	101.7	102.7 ± 0.5	1700 ± 200
4*	$CF_3{-}CH_2Cl$	99.5	98.3	101.8 ± 1.5	1100 ± 300
5*	$CF_3{-}CHCl_2$	95.3	93.6	95.3[b]	900 ± 150
6*	$CF_3{-}CHFCl$	98.9	97.8	99.2[b]	1350 ± 150
7*	$CF_2Cl{-}CH_3$	104.0	103.8		1800 ± 150
8	$CF_2Cl{-}CH_2F$	99.6	100.0		1593[d]
9	$CF_2Cl{-}CHF_2$	100.7	100.4		1657[d]
10*	$CF_2Cl{-}CH_2Cl$	98.6	97.6		1600 ± 400
11*	$CF_2Cl{-}CHCl_2$	93.7	92.1		900 ± 150
12*	$CF_2Cl{-}CHFCl$	97.5	96.4		1280 ± 150
13*	$CFCl_2{-}CH_3$	102.9	102.9		1700 ± 150
14	$CFCl_2{-}CH_2F$	98.9	98.9		1408[d]
15	$CFCl_2{-}CHF_2$	100.9	100.6		1588[d]
16	$CFCl_2{-}CH_2Cl$	97.5	96.7		1291[d]
17	$CFCl_2{-}CHCl_2$	93.7	92.2		827[d]
18*	$CFCl_2{-}CHFCl$	97.3	96.2		1250 ± 150
19*	$CCl_3{-}CH_3$	102.6	102.5		1550 ± 150
20	$CCl_3{-}CH_2F$	98.6	98.7		1264[d]
21	$CCl_3{-}CHF_2$	101.0	100.7		1534[d]
22	$CCl_3{-}CH_2Cl$	97.2	96.2		1147[d]
23	$CCl_3{-}CHCl_2$	94.1	92.5	94.9 ± 1.9	774[d]
24	$CCl_3{-}CHFCl$	97.5	96.4		1103[d]

[a] Reference 29. [b] G2(MP2) values from ref 30. [c] Experimental values from ref 33. [d] Estimated values taken from ref 35, the error in E_{act}/R was predicted to be around ±150 K.

The BDEs of the C−H bonds of the halomethane molecules are thus expected to reflect their reactivity for the hydrogen abstraction reactions. Indeed, correlation between the C−H bond energy and the activation energy for the hydrogen atom abstraction reactions has been observed for many reactions.[8,32] It can be seen from Table 4 that the first fluorine substitution in methane weakens the C−H bond and thus lowers the hydrogen abstraction activation energy (from 3.53 for CH_4 to 2.98 kcal/mol for CH_3F).[33] The second fluorine substitution in methane does not change the bond energy further and thus activation energies for CH_3F and CH_2F_2 are almost similar. The third fluorine substitution brings a dramatic change and the C−H bond energy increases again from 100 kcal/mol for CH_2F_2 to 104.7 kcal/mol for CHF_3. The trend is different for chloromethanes and bromomethanes: successive chlorine or bromine substitution lowers the C−H bond strength and thus increases the reactivity toward the hydrogen abstraction. Very recently, we observed that the first fluorine substitution in methane (from

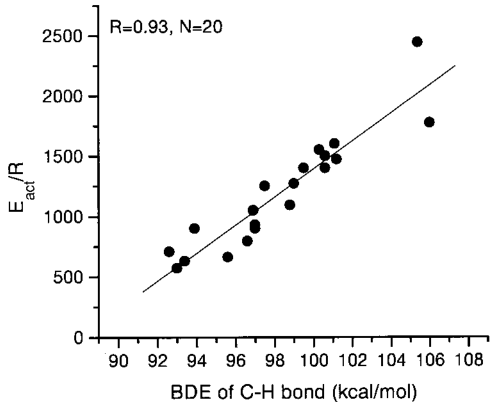

Figure 1. Correlation between the C−H bond dissociation enthalpies (kcal/mol) and the activation energies for hydrogen abstraction reactions between halomethanes (mentioned in Table 4) and the OH radical. The C−H bond dissociation enthalpies were calculated by the (RO)B3LYP procedure with 6-311G(d,p) basis set.

CH_4 to CH_3F) makes the molecule softer.[34] For example, hardness (η) values of CH_4 and CH_3F are 202.0 and 186.6 kcal/mol, respectively, at the B3LYP/6-311G(d,p) level. The second fluorine substitution (CH_2F_2) does not produce any significant change in the hardness value (186.4 kcal/mol). However, CHF_3 molecule is found to be very hard (η = 205.6 kcal/mol). In fact, hardness value of CHF_3 is highest among the halomethane molecules.[34] In the case of chlorine or bromine substitution, the hardness value decreases monotonically with the increase in halogen substitution in methane. This change in hard−soft behavior for the halomethane molecules with increasing halogen substitution probably gives an explanation for the trend of BDE's of the C−H bonds observed for CH_nX_{4-n} series (X = F, Cl, Br and n = 1, 4). In general, replacement of fluorine by chlorine or bromine and replacement of chlorine by bromine lowers the BDE value of the C−H bond. However, for CH_3Br, the C−H BDE is found to be larger than that for CH_3Cl. This explains clearly why the activation energy for the hydrogen abstraction by the OH radical is higher for CH_3Br than that for CH_3Cl.[33] Figure 1 displays the correlation between the BDEs of the C−H bonds and the activation energies for the hydrogen abstraction reactions between halomethanes and the OH radical. The correlation is found to be quite impressive. Only in the case of CHF_3, the activation energy is much higher than that expected from the BDE of the C−H bond. Similar deviation has been observed for CHF_3 when activation energies were correlated with other molecular properties, such as hardness and ionization energy.[34] Since Arrhenius preexponential factors per equivalent C−H bond are nearly constant over a broad range of H atom transfer reactions,[35,36] differences in reactivity primarily result from differing activation energies. Thus, determination of relative rate constants is possible by using the activation energy estimated from the calculated BDE and the above-mentioned correlation equation [eq 2].

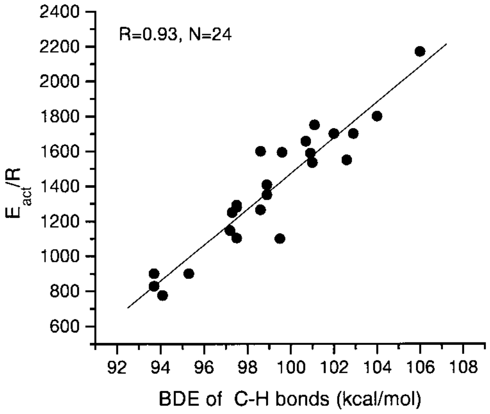

Figure 2. Plot of the C−H bond dissociation enthalpies (kcal/mol) and the activation energies for hydrogen abstraction reactions between haloethanes (mentioned in Table 5) and the OH radical. The C−H bond dissociation enthalpies were calculated by the (RO)B3LYP procedure with 6-311G(d,p) basis set.

The C−H bond energies for the CX_3-CH_3 molecules decreases in the order CF_3-CH_3 > CF_2Cl-CH_3 > $CFCl_2-CH_3$ > CCl_3-CH_3. The activation energies for hydrogen abstraction is also known to decrease in the same order (see Table 5).[33,35] In general, Cl and Br substitution at the hydrogen abstraction site reduces the activation energy, the same trend can be observed from the BDE values as well. The effect of fluorine substitution at the α-position (hydrogen containing carbon atom) on the BDE value of the C−H bond depends on the degree of substitution. The first fluorine substitution reduces the strength of the C−H bond, whereas the second fluorine substitution enhances the C−H bond strength. Figure 2 shows the correlation between the activation energies for hydrogen abstraction and the BDE values of the C−H bonds for the haloethane molecules mentioned in Table 5. It should be pointed out here that out of 24 haloethane molecules studied here, experimental activation energies are known only for 13 compounds (indicated by asterisk in Table 5).[33] The activation energies for the rest 11 molecules are taken from the estimated values of DeMore.[35] A good correlation has been observed once again between the BDE of the C−H bond and activation energy for the hydrogen abstraction. For the CF_3-CH_2Cl and CF_2Cl-CH_2Cl molecules, the activation energies are found to be higher than those expected from the respective heats of reaction values. Interestingly, the error bars in the experimental activation energies for these two molecules are large (0.6 and 0.8 kcal/mol compared to the usual value of 0.3 kcal/mol for the other molecules). Moreover, the activation energy for CF_3-CH_2Cl estimated by DeMore[35] from an empirical formula and the experimental value differs by nearly 1.2 kcal/mol. One can derive a equation from the correlation between the experimental activation energies and the calculated BDE values and then determine the activation energies for the rest of the haloethane molecules using that equation. The estimated values can then be compared with the values predicted by DeMore from his empirical formula. Fitting the BDE values of the C−H bonds at the (RO)B3LYP/6-311G(d,p) level and the experimental activation energies for the 11 haloethane molecules for which experimental values are accurately known (mentioned by asterisk in Table 5 except CF_3-CH_2Cl and CF_2Cl-CH_2Cl), we obtained the following expression: $E_{act} = -16.6 + 0.195D_o^{298K}$, where E_{act} and D_o^{298K} are in kcal/mol. Using this expression and computed BDE values for the C−H bonds, we calculated the activation energies for the rest of the haloethane molecules for which experimental values are unknown. Our estimated values were found to be very close to those predicted by DeMore.[35] The average deviation between the two values was only 0.1 kcal/mol and the maximum deviation was 0.3 kcal/mol, observed for CF_2Cl-CH_2F and CCl_3-CH_3 molecules. Thus, BDE of the C−H bond can be used for the estimation of hydrogen abstraction activation energies for halomethanes and simple haloethanes containing hydrogen atoms at one carbon atom.

Conclusions

The C−H bond dissociation enthalpies for a series of halomethane and haloethane molecules have been determined by using DFT-based B3LYP and (RO)B3LYP procedures. It has been observed that the (RO)B3LYP method in conjunction with the 6-311G(d,p) basis set can provide reliable C−H bond dissociation enthalpies. The BDE's for the C−H bonds of haloalkanes obtained from the (RO)B3LYP/6-311++G(3df,2p) basis set are found to be quite close to those obtained from the smaller 6-311G(d,p) basis set. Since the former basis set is much larger in size, the latter is preferable from the standpoint of computational cost. Thus, (RO)B3LYP/6-311G(d,p) can be a computationally inexpensive method of choice for estimating the C−H bond energies. The results obtained for five halomethane molecules show that, among the DFT functionals, B3LYP and B3PW91 are the best for estimating C−H bond energies. However, there is significant error in the calculated BDE of the O−H bond at the B3LYP level. Thus, for calculating the heats of hydrogen abstraction reactions between haloalkanes and the OH radical, it is better to use the experimental BDE of the O−H bond of H_2O. The C−H bond dissociation enthalpies for a series of haloethanes have also been computed by following the same procedure. Good correlation has been observed between the BDE values of the C−H bonds and the activation energies for hydrogen abstraction reactions. This correlation can be useful for estimating the activation energies and relative rate constants for the compounds for which experimental values are not yet known.

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