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Ab-inito Calculations in Reductive Bond-breaking Reaction of C-X Bond in CH₃X and CH₂X₂ with X = F and Cl

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MP4/6-31+G* level calculations are performed to study the reductive bond-breaking reaction of the C-X bond in halomethanes, CH_3X and CH_2X_2 where X is a fluorine atom or chlorine atom. This type of reaction involves a radical anion, after attaching an extra electron to the halomethane molecule, in which a C-X bond-breaking takes place. Products are a radical and a halogen anion. The equilibrium geometry and bond dissociation energy of the C-X bond thus found are in good agreement with previous theoretical and experimental results. The anomeric effect, electrostatic effect, and radical re-stabilization effect, are investigated to find their influences on bond length and bond dissociation energy in CH_3X and CH_2X_2. Potential energy curves are calculated for the reductive bond-cleavage process, and trends in activation energy for various cases are discussed.

INTRODUCTION

Dissociative electron transfer reaction $RX + e^- \rightarrow R + X^-$ in solution, where R is a carbon-centered radical and X is a halogen, has been extensively studied because of its scientific and environmental relevance.[1-4] From molecular biology to industrial process, it is a powerful synthetic tool to provide alkyl radicals. This kind of reductive bond-breaking reaction between carbon and halogen in aliphatic halides in solution represents an example of the charge transfer process. The most extensive experimental investigation for this type of reaction has been performed by Saveant et al. over the past several years.[1] The gas-phase counterpart of this process, the dissociative electron attachment followed by bond-breaking between carbon and halogen anion, is as follows.

$$RX + e^- \rightarrow [RX]^- \rightarrow R + X^- \qquad (1)$$
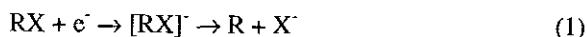
An electron is captured by an isolated molecule (R-X) to form a short-lived negative ion [RX]⁻ which may then dissociate into a stable X⁻ and a radical R. The reaction (1) is of fundamental importance in nucleophilic substitution in the $S_{RN}1$ mechanism[5] where the reaction (1) is followed by a nucleophilic attack on the radical R,

$$Nu^- + R \rightarrow R-Nu^- \qquad (2)$$
$$R-Nu^- + R-X \rightarrow R-Nu + R-X^- \qquad (3)$$
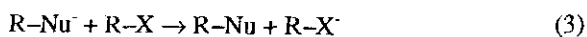
The transfer of a single electron, as in (1), has become rec-ognized as a central step in many organic reactions versus the more traditional two electron process S_N1.[6]

An important mechanistic issue is whether the reaction (1) is concerted or stepwise. In the stepwise case, an anion radical that will eventually dissociate, is formed first as an intermediate. That means the [RX]⁻ anion in reaction (1) is a stable intermediate. In the cases investigated so far, aryl halides undergo stepwise reactions in the gas phase, the matrix, or in polar solvent.[4] On the other hand, in the gas phase, for R as an alkyl group the intermediate [RX]⁻ is unstable with respect to the dissociation of halide anion. That is, alkyl-halides will undergo the concerted mechanism. The production of R and X⁻ is a direct reaction. In fact, the potential energy curve for alkyl C-X bond-breaking is purely repulsive.[1(a),7-9]

The question of $S_{RN}1$ alternatives to the classical S_N reaction is linked to the viability of the electron transfer (ET) reaction (1). This can be studied theoretically by computing the potential surface of the reaction (1). Information about the profiles of the potential energy curves of anion radicals along the reaction coordinate C-X bond length is important for an understanding of the kinetics of the reaction of this type. Up to the present, most quantum chemical calculations for the radical anions of the alkyl halide have been devoted to the study of potential energy curves for CH₃X⁻ (with X = F, Cl, Br, I) in the gas phase.[1(a),7,8] The potential energy curve of C-X bond-breaking in CH₃X⁻ obtained by means of multiconfigurational MCSCF calculations using the complete active space SCF (CAS SCF) method have been reported by Hotokka et al.[7] in 1986 and Benassi et al.[8]

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in 1989. In both studies, a crossing is observed between the curves of the anion and that of the neutral molecule plus a free electron. Whereas in the first of the two studies, the [RX]⁻ energy curve presents a minimum at short C-X distances. This minimum is not found in the second study, with the [RX]⁻ anion curve being purely repulsive. It has been suggested that these types of minima, which appear in the zone where the neutral species is more stable than anionic species, originate in the use of very diffuse orbital functions. This allows the electron to stand so far away from the molecule that, practically speaking, the energy is that of the neutral ground-state system plus a free electron rather than that of a temporary anion radical.[1(a)]

Although the systems CH_3X were studied the most, dihalides are also very interesting for both practical and theoretical reasons. In practical reactions, dichloroalkanes are much more often used as solvent and reagents. Theoretically, dihalides CH_2X_2 present a somewhat different driving force, versus monohalides, due to the generalized anomeric effect[10] existing between X and the dissociating C-X bond. This has never been studied in the context of the ET reaction. The present work is devoted to the calculations for alkyl halides' dissociative electron transfer for the C-X bond in both CH_3X and CH_2X_2 molecules with X = F and Cl. One of the aims of this report to understand the effect of an extra halogen on the activation energy for the reductive bond-breaking reaction for methylhalides. The other purpose is to understand the relation between bond length and the bond dissociation energy of the C-F bond and the C-Cl bond in these molecules.

Structural and energetic effects of substituents on a central carbon atom have been discussed within the context of the negative hyperconjugation (anomeric effect) and electrostatic effects over the past twenty years.[10] Electrostatic effects resulting from electronegative substituents that induce more positive charge on the central carbon atom shorten and strength all bonds attached to the central carbon atom. On the other hand, the anomeric effect based on negative hyperconjugation, which is a stabilizing orbital interaction between the halogen lone pairs donating to the other neighboring σ* orbital, has a net effect of shortening the bond of the donor and lengthening the bond of the acceptor, as well as lowering the energy of the molecule. Recent theoretical work by Chang and Su,[11] using energy decomposition analysis, has shown that both effects are important in the anomeric interaction in methanediol and related systems. In another recent experimental/theoretical study of $CH_2FN(CH_3)_2$, Christen et. al.[12] showed that the hyperconjugation effect has a stronger influence on the C-N bond length than the electrostatic attraction due to the weaker

electronegativity of N. We will consider these two effects in interpreting the variations in the structures and energetics of the fluoromethanes and chloromethanes. And we would like to see how they influence the activation energy of the reductive bond-breaking reactions.

We will discuss the computational methods first, and then present our data and discussions. In the final section, a brief summary of the paper is given.

METHOD

All the calculations used to analyze the reductive bond-breaking reaction of CH_3X and CH_2X_2 (X = F, Cl) were done using unrestricted Hartree-Fock (UHF) formalism. Correlation energy was introduced by using Moller-Plesset perturbation to the fourth order (MP4). Results for all systems were obtained using Hartree-Fock optimized geometry while potential surfaces were calculated at MP4. Since we are interested in comparisons in activation energy and bond dissociation energy among CH_3F, CH_2F_2, CH_3Cl, and CH_2Cl_2 in this work, small errors involved in optimizing geometry at the H-F level should be about the same in the case of CH_3F and CH_2F_2, as for the case of CH_3Cl and CH_2Cl_2. Therefore, for all systems, Hartree-Fock optimized geometry is used. All calculations were performed by using Gaussian 92[13] on an IBM RISC6000-550 workstation.

A word about the choice of MP4 over the multiconfiguration self-consistent field (MCSCF) method should be noted. It is well-known that MCSCF cannot take care of dynamical correlations. But dynamical correlations generally play important roles in fluorine-based compounds[14] because of the high number of valence electrons crowded in a small space. MP4 calculation has the additional advantage of being size-consistent. Since in our system, we do not have the situation of hypervalency or strong degeneracy, we believe an MP4 calculation is more desirable. In fact, in a recent calculation of the potential surface of $Ar-C_2H_2$, the result of MP4 calculation was comparable to the high level CCSD(T) result.[15]

The more difficult task in this paper is to determine the transition state of the C-X bond in the process of bond-breaking. Using the C-X bond length as the reaction coordinate, the optimized geometry at a given C-X bond length was obtained. Then using this geometry, the MP4 energies for the neutral molecule and the corresponding anion were obtained. Repeating the process along the reaction coordinate, when the MP4 energy of the neutral molecule equals that of its corresponding anion, the transition is reached. The transition state is defined as a location where the two di-

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abatic energy curves of neutral molecule and its corresponding anion cross. This is the same definition used by Bertran et al.[1(a)] in their study of C-X bond reductive cleavage. It has been shown in ref(1a) that the resonance interaction between the two diabatic curves at the crossing point is rather weak (about 1 Kcal/mol) for the case of CH_3Cl. This is due to the fact that the orbital overlap between the diffuse antibonding orbital of the anion and the bonding orbit of neutral species is rather small at the transition state. One should note that this is also consistent with the outer-sphere nature of the electron transfer from the donor's point of view. For the purpose of examining the change of charge distribution upon bond cleavage, Natural Bond Orbital (NBO)[16] analysis is performed for energy and charge separation analysis in these complex molecules. And with NBO analysis, one can then evoke the anomeric effect and electrostatic effect to understand the nature of the whole reaction.

The basis set used to perform these calculations is 6-31+G*. It is generally agreed that a semidiffuse function should be added to the basis sets to deal with the diffuse distribution of valence electrons in anions. However, when negative electron affinity is involved for temporary anions, careful attention should be paid in analyzing to which electronic distribution is actually involved. Guerra[17] and Perez et al.[18] have performed ab-initio calculations using diffuse functions for some substituted methane anions recently, and they concluded that the calculation of negative vertical electron affinity (VEA) using a diffuse function without special stabilization techniques[19] may lead to unreliable results. However, the anion concerned in this paper is going to be fragmented, and we are really interested in the adiabatic electron affinity, e.g. the energy difference between equilibrium neutral molecule and the anion at transition state. According to the calculations and analysis of Bertran et al.,[1a] the calculation of the energy of the anion at the transition state is not very sensitive to the semidiffuse basis set because it is no longer metastable toward the loss of the electron. A recent MO calculation[20] of the dissociative radical anion of benzyl chloride employing 6-31G* gives well-behaved repulsive potential curves for the X-Cl reductive bond breakage although temporary radical anions are involved. One can thus expect that the determination of the transition state where one is interested in the relative energy of two bounded systems can be meaningfully accurate even though VEA of the neutral molecule may be inaccurate.[1(a)]

RESULTS AND DISCUSSION

The calculated values of equilibrium geometry and

Table 1. Structure and Energy Characteristics of Molecules CH_3X and CH_2X_2 (X = F, Cl). This Works Refers to the Results Calculated by UMP4/6-31+G*//UHF/6-31+G*, and Experiments Refers to Experimental Data. R_e: Equilibrium Bond Length. BE: Bond Dissociation Energy. Length Unit is Angstrom and Energy Unit is Kcal/mol

		R_e(C-X)	R_e(C-H)	BE(C-X)
CH_3F	this work	1.371	1.081	109.2
	Hopkinson[28]	1.372	1.082	-
	Bertran[1(a)]	1.36	-	105.1
	Hotokka[7]	1.40	-	103.97
	experiments[29]	1.383	1.100	108.03
CH_2F_2	this work	1.342	1.077	117.7
	Hopkinson[28]	1.357	1.079	-
	experiments[30]	1.357	1.093	-
CH_3Cl	this work	1.786	1.078	79.7
	Hopkinson[28]	1.786	1.078	-
	Bertran[1(a)]	1.80	-	79.4
	Hotokka[7]	1.79	-	78.87
	experiments[30]	1.781	1.096	83.5[ref.23]
CH_2Cl_2	this work	1.769	1.074	75.8
	Hopkinson[28]	1.769	1.075	-
	experiments[32]	1.772	1.068	82.8[ref.23]

bond dissociation energy (BE) for C-F bond and C-Cl bond in CH_3F, CH_2F_2, CH_3Cl and CH_2Cl_2 are given in Table 1 along with corresponding experimental data and calculated results in previous works. For CH_3F, the calculated bond energy of 109.15 Kcal/mol agrees with experimental value to within 1 Kcal/mol, better than those reported in Bertran's and Hotokka's results. For CH_3Cl, the resulting BE is comparable with the previous calculations. Table 2 lists the bond lengths of C-F and C-Cl in the transition state and the corresponding activation energies of the reductive bond-breaking reaction. The data from Bertran et al.[1a] and Hotokka et al.[7] for mono-halogenmethane are shown in Table 2 for comparison.

Examining the two tables, some comparisons can be made. First, given a leaving atom (F or Cl), the larger the bond dissociation energy, the larger the activation energy of the corresponding reductive bond-breaking reaction. Second, in the case of C-F bond breaking, di-fluoromethane has a higher activation energy than mono-fluoromethane has. On the other hand, in the case of C-Cl bond breaking, mono-chloromethane has a higher activation energy than di-chloromethane has. The reverse behavior needs an explanation which will be given shortly. Third, the C-Cl bond is longer in CH_3Cl than in CH_2Cl_2, while the trend of bond dissociation energy is in reverse order. This means a longer chemical bond corresponds to a stronger bond which is somewhat counter-intuitive. One would expect the contrary.

The reaction enthalpy of the overall reductive bond-

Table 2. Activation Energies of Reaction (1) in Gas Phase and Elongation of Carbon-Halogen Bond in Transitional Configuration. R_e: Equilibrium Bond Length. R^*: The Bond Length in Transitional Configuration. $\Delta R^*=R^*-R_e$. E_a: Activation Energy. Values of R^*, R_e and ΔR^* are Given in Angstrom and Those of E_a in Kcal/mol

		R_e(C-X)	R^*	ΔR^*	E_a(C-X)
CH_3F	this work	1.371	1.993	0.622	41.7
	Bertran[1(a)]	1.36	1.95	0.59	49.1
	Hotokka[7]	1.40	-	-	54.97
CH_2F_2	this work	1.342	2.066	0.724	52.8
CH_3Cl	this work	1.786	2.269	0.483	25.0
	Bertran[1(a)]	1.80	2.22	0.42	23.5
	Hotokka[7]	1.79	-	-	31.07
CH_2Cl_2	this work	1.769	2.195	0.426	19.0

breaking reaction ΔH is equal to BE(C-X)-EA(X), in which EA(X) is the electron affinity of element X and BE(C-X) is the corresponding bond dissociation energy. For the EA of fluorine, our calculated value of 74.60 Kcal/mol is much better than those of Hotokka (62.4 Kcal/mol) and Bertran (62.6 Kcal/mol) and comparable to the best computed EA(F) of 76.95 Kcal/mol of Kendall et al.,[21] in which a very high level calculation of MRSD-CI with the aug-cc-pVQZ basis set was performed. The final calculated values of reaction enthalpy for flouromethanes are within 3 Kcal/mol accuracy to the experimental ones. For chloromethanes, the deviations should be somewhat bigger. But in this paper, we are mainly concerned with the trends in comparing various

calculated systems. So we believe the level of computation is quite suitable for the purpose.

The transition state will appear as a configuration between reactant (R-X) and product (R+X⁻), so there should be an intimate relation between ΔH and E_a (activation energy) in these reactions. A larger bond dissociation energy will be associated with a larger activation energy among alkyl halides with the same leaving atom. This is indeed reflected in the data in Table 1. The trends are graphically presented in the potential surface curves in Figs. 1 and 2.

One should notice that the nature of bond length and bond dissociation energy are different. The former only concerns the equilibrium state, but the latter involves both the equilibrium state and infinite dissociation state. So there is no definite relation between the two quantities. Using the concept of hyperconjugation and electrostatic effect, one may understand these differences. Substituting one hydrogen atom with one halogen atom in mono-halogen methane introduces more positive charge in the carbon center because of the higher electronegativity of halogen than carbon. That results in a development of positive charge in the carbon atom (-0.10 for CH_3F, 0.55 for CH_2F_2 and an increment 0.65, -0.61 for CH_3Cl and 0.45 for CH_2Cl_2 and an increment 1.16) and produces a larger electrostatic interaction between carbon atom and halogen atom in di-halogen methane. So the bond length of the C-X bond will decrease. On the other hand, according to the anomeric effect, one given halogen atom X_a in di-halogen methane will affect the other C-X_b bond and result in reducing the bond length of the C-X_b
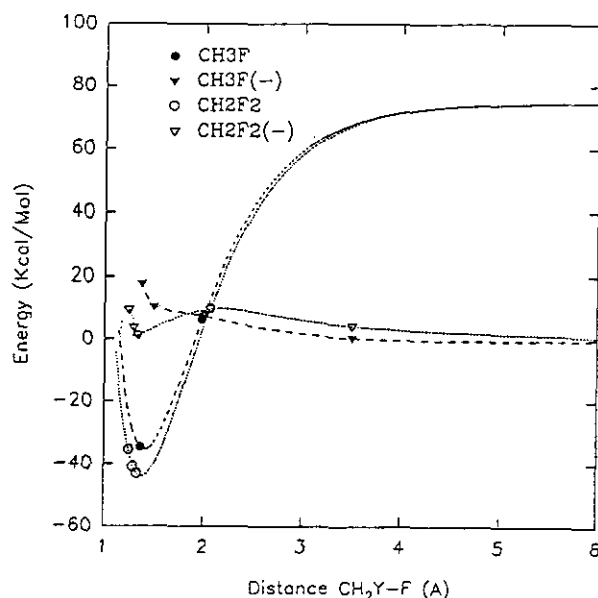

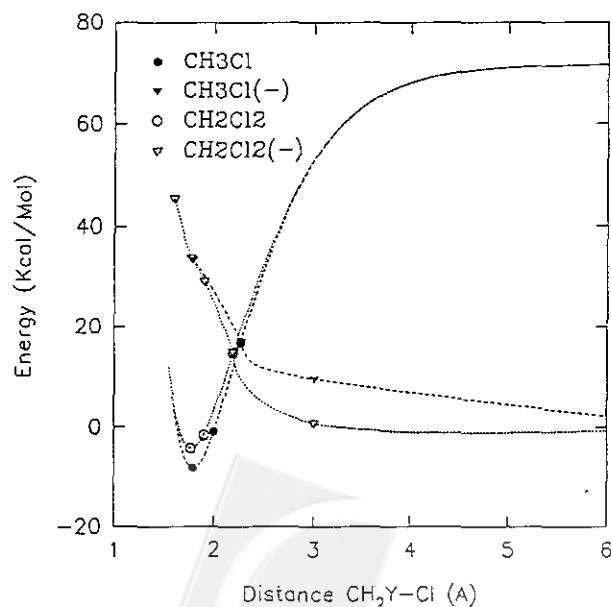Fig. 1. MP4/6-31+G* calculated potential energy curves of CH_3F, CH_2F_2, CH_3F^- and $CH_2F_2^-$.

Fig. 2. MP4/6-31+G* calculated potential energy curves of CH_3Cl, CH_2Cl_2, CH_3Cl^- and $CH_2Cl_2^-$.

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bond and lengthening it in the C-X_a bond. So the negative hyperconjugation effect in bond length of the C-X bond will cancel the other. Hence, as noted previously, increasing the number of halogen substitutes has the effect of decreasing the length of C-halogen bond, and the main effect on bond length is the electrostatic effect.[22,23] It should be noted that for unequal substitutions, such as CH_2XY, both effects should operate in molecular geometry. In fact, in a recent study of halogenated methanols,[22] it was proposed that negative hyperconjugation effect leads to the shortening of C-O bonds mainly.

To interpret the trends in dissociation energy, one has to look into the energies of the departing radicals. Here we will perform an energy analysis for the overall bond dissociation process. The whole process can be separated into two steps as R-X → R + X → R' + X, where R is the structure in equilibrium state and R' represents the structure in the infinite dissociation state. It is obvious that there should be a rearrangement in the structure of R group in the step R → R' which will be accompanied by a change of hybridization of orbitals in the central carbon atom and thus in energy. In a recent work, Lauvergnat et al.[24] used valence bond analysis to investigate the stabilization energy due to rehybridization in the dissociation of X-H bond in a series of molecules. In this paper, we adopt natural bond orbital (NBO) analysis[16] in order to see more clearly the change in energy components during dissociation. The NBO energy analysis, separating SCF energy into localization energy and delocalization energy, is used to analyze the energy change in the process. Localization energy is the energy associated with Lewis bonds. Delocalization energy represents the interaction of Lewis structures with empty or partially filled orbitals. For the molecular fragment CH_3 the step R → R' involves the change of hybridization of C from sp^3 to sp^2, e.g tetrahedral to planar. The localization energy change is -8.4 Kcal/mol but the delocalization energy is positive, 2.6 Kcal/Mol. There is, however, a negative change in delocalization energy in the rearrangement process of molecular fragment CH_2X, -1.9 Kcal/mol for CH_2F and -6.5 Kcal/mol for CH_2Cl. This is significant because the negative change in delocalization energy comes about through the anomeric interaction between the unpaired electron and the C-X bond. The geometrical change of CH_2X leads to the enhancement of the anomeric interaction and stabilization. In fact, the final structure for the radical CH_2X is not planar but pyramidal instead. When taking into account only the change of delocalization energy, one may expect the fluorine case to have a larger gain in it since the first row elements should have stronger anomeric effects than the second-row elements.[25] But for fouromethanes,

there is a smaller change in structure from (CH_2F) to $(CH_2F)'$ because the fluorine atom is smaller. So the molecular fragment CH_2F will obtain less stabilization energy from the rearrangement in structure. Overall, a larger stabilization energy of $(CH_2Cl)'$ means CH_2Cl_2 has a smaller bond dissociation energy for C-Cl bond than CH_3Cl, even though CH_3Cl has a larger bond length in the C-Cl bond. Further details about the NBO analysis of the whole structure change process will be presented in future publications. From the work of Reed et al.,[26] C-F bond dissociation energy increases with increasing fluorine substitution, explained by using the change in delocalization energy for the series of poly-fluoromethane. Although chlorine substitutions cause smaller anomeric effects, the same factor still influences the trend in C-Cl bond dissociation energy in the series of poly-chloromethane, and the trend is consistent with the experimental data.[23]

The energy curve of the reductive bond-breaking reactions of C-F and C-Cl bonds are shown in Figs. 1 and 2. The potential curves of both the neutral and the radical anion species are shown. The neutral species curve is considered to be the energy of the neutral species and a free electron with zero energy. Emphasis is placed near the point of crossing of the potential curves. In fact several points were calculated in the vicinity. But only the data at the crossing points are shown. It is shown that all radical species are unstable toward the dissociation. Reaction (1) is concerted for all the four cases considered here. The crossing points are considered as the transition states of the concerted electron transfer-bond breaking process (1). Further insight can be gained by examining the change of charges of X along the reaction path. This is listed in Table 3. When the fluorine atom acts as the leaving atom, the transition state, with charge closer to -1, is closer to the infinite dissociation state than the chlorine case. On the other hand, the transition state of the chlorine case is closer to the equilibrium state. That means the transition state of C-F breaking is later than C-Cl breaking. Since the chlorine atom is softer than the fluorine atom, it is more easily polarized. As the fluorine or chlorine atom is leaving the carbon center, the positive charge on the carbon atom still has a larger perturbation in chlorine atom, so at transition state, the C-Cl bond still survives somewhat but the C-F bond has broken almost completely. To demonstrate this conclusion further, we have calculated the Laplacian of electron density $\nabla^2\rho$ at the transition state. It is shown in Fig. 3. Solid lines indicate positive values while dashed lines are for negative values of $\nabla^2\rho$. A positive value of $\nabla^2\rho$ in the internuclear region, indicating depletion of electron density, points to the presence of an ionic bond. On the other hand, a negative value of $\nabla^2\rho$ in the

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Table 3. Negative Charge Separations (using Natural Orbital Population) on Leaving Halogen Atoms

	reactant	transition	state	product
X	CH_3X	CH_3X	CH_3X^-	$CH_3 + X^-$
F	-0.45	-0.63	-0.88	-1.00
Cl	-0.11	-0.38	-0.81	-1.00
X	CH_2X_2	CH_2X_2	$CH_2X_2^-$	$CH_2X + X^-$
F	-0.43	-0.70	-0.92	-1.00
Cl	-0.04	-0.30	-0.76	-1.00

internuclear region, indicating contraction of electron density, points to the presence of a covalent bond. We see that at the transition state the covalent C-F bond has broken nearly completely, while the C-Cl bond still persists somewhat.

One would expect that an increase in the number of halogen substitutions would stabilize the radical anions. This trend was reported recently in a semi-empirical calculation.[27] So it is interesting to note that in Figs. 1 and 2, in the small R region, we also see the same trend. But in the large R (above the transition R) the radical anion CH_3F^- has a little less energy than $CH_2F_2^-$ while it is in reverse order for the chloromethanes. Again, this reflects the larger geometry stabilization energy for the chloro case when one chlorine atom is departing.

The potential curves for the radical anions are generally pretty flat from R* to infinity (see Figs. 1 and 2). This
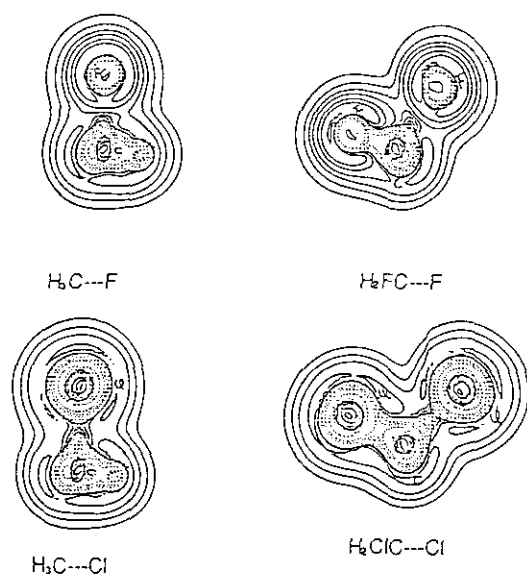

Fig. 3. The Laplacian of electron density at the transition states. Solid lines indicate positive values while dashed lines are for negative values of $\nabla^2\rho$.

reflects the higher negative charge localized on X for the anions. So it would be interesting to examine in more details the charge separation during the reaction. The variation of the charge carried on fluorine and chlorine atoms during the bond-breaking process is shown in Table 3. It demonstrates the points discussed above. A comparison of the charge carried on fluorine and chlorine atoms shows the former (-0.88 for CH_3F and -0.92 for CH_2F_2) is closer to its corresponding anion (the product in the reaction) than the latter (-0.81 for CH_3Cl and -0.76 for CH_2Cl_2). This is consistent with the fact that the transition state is later for the fluorine atom as leaving group. At first sight, one may be surprised to learn that the charge increment of chlorine atom at the transition state is bigger than that of fluorine atoms. One must take into account that the more electronegative fluorine atom can accommodate more electrons in the equilibrium state than the chlorine atom. So the fluorine atom has less space to accept electron density from the extra electron.[1(a)]

SUMMARY

In this work, the activation energies of the reductive bond-breaking of the C-X bond in CH_3X and CH_2X_2 (X = F, Cl) were obtained by using ab-initio calculations. Replacing H with X in CH_3X produces a different effect for the case of X = F and Cl. The additional presence of an extra fluorine atom increases activation energy while the chlorine atom plays a reverse role. This results from the different effects of fluorine and chlorine atoms in bond dissociation energy. Because the chlorine atom is bigger than the fluorine atom, more stabilization energy can be obtained in the case of the chlorine atom after C-X bond-breaking happens in neutral molecules. This leads to a stronger C-Cl bond in monochloromethane. In the case of fluorine substitution, the stronger anomeric interaction between F and the C-F bond leads to the stabilization of diflouromethane. The electron transfer reaction leading to the breaking of the C-X bond can be understood in the crossing of the diabatic potential curves.

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