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Dehydrohalogenation of ethyl halides

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ABSTRACT

Unimolecular decomposition kinetics of selected ethyl halides, phenethyl halides and methoxyphenethyl halides have been investigated using high level computational chemistry methods. The phenethyl halides decompose faster than the ethyl halides due to a more electronegative chlorine atom, induced by the chloroethyl functionality as an electron-withdrawing group. 1-Chloro-2-(methylthio)ethane exhibits faster dehydrochlorination than that of chloroethane/1-chloro-2-methoxyethane, owing to more polarisable C⋯H and C⋯Cl bonds in the transition structures. Calculations suggest that electronic factors rather than anchimeric assistance influence the dehydrochlorination reactions.

In addition to hydrogen abstraction by chlorine atoms, direct elimination of HCl from chlorinated hydrocarbons constitutes a major sink for chlorine present in thermal systems. The elimination of HCl characterises a major pathway of the decomposition of chlorinated hydrocarbons in fires and in municipal waste incinerators (MWI).[1] For instance, chlorinated aliphatic hydrocarbons can undergo unimolecular decomposition to yield HCl and their corresponding alkenes through fission of the C-Cl bonds.[2,3] The experimental work of Chuchani's group reported that the existence of a phenyl group in chlorinated C_2-C_3 aliphatics significantly increases the rate of unimolecular dehydrochlorination reactions.[4-6]

Experimental investigations as well as quantum chemical calculations have shown that the rate of HCl elimination from chloroethane accelerates by an order of magnitude when a phenyl group is substituted on the β carbon of ethyl chloride.[4-7] Researchers have speculated that the phenyl group provides anchimeric assistance through lowering the activation energy of the elimination reaction; i.e., by the involvement of benzene rings in the transition state. As the neighbouring group (in this case phenyl) is supposed to participate in the formation of the transition structure, this effect is also denoted as neighbouring group participation (NGP).

Recent theoretical work by Chuchani's group[8-11] has been aimed toward investigation of the gas phase dehydrochlorination of several substrates. While HCl elimination from some substrates was found to proceed without apparent NGP assistance, the presence of certain functional groups opens up parallel cyclisation pathways. Introducing a methoxy group, as in 2-methoxyphenethyl[10] and methoxyalkyl chlorides,[8] provides a competitive NGP-assisted cyclisation mechanism via five-centred polar transition structures and results in the formation of benzohydrofuran and tetrahydrofuran, respectively. On the other hand, Chuchani's group found that, 1-chloro-2-methoxyethane and 1-chloro-3-methoxypropane do not dehydrochlorinate, but decompose into tetrahydrofuran and chloromethane.[8] Chuchani et al.[9] calculated the rates of dehydrochlorination of 1-chloro-2-(methylthio)ethane (with and without sulfur assistance). Their computed activation energies without NGP by the methylthio group show a reasonable agreement with experimental results. This indicates that certain dehydro-halogenation reactions do not proceed via NGP.

In agreement with the previous theoretical work[8-11] on HCl elimination from selected ethyl chlorides, in the present work, we are unable to find evidence of NGP assistance in the

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geometries of the transition structures pertinent to the direct elimination of HCl. It appears that, the increased rate observed in earlier experiments was only a consequence of the redistribution of electron partial charges, the latter engendered by comparing values of the activation enthalpy values between chloroethane/2-(chloroethyl)benzene and 1-chloro-2-(methylthio)ethane/1-chloro-2-methoxyethane. It was assumed that the +R effect operates together with the anchimeric influence to enhance the rate of dehydrochlorination.[5] The suggestion that the conjugative and +R effects were the only effects that matter agrees with the observation that the effect of the aromatic group participation becomes weak, or of no importance, in the dehydrochlorination reactions of substituted C_5-C_6 alkyl chlorides.[4]

To this end, this contribution reports the results of a theoretical study into the dehydrochlorination of various non-substituted and substituted ethyl halides. While Chuchani's group[4-11] have investigated the HCl/HBr elimination from most of these compounds both experimentally and theoretically, our aim was to elucidate insights into the dependence of dehydrohalogenation on several factors, including the type of neighbouring functional group, its position, and presumed assistance by the phenyl ring. The calculated kinetic and thermodynamic parameters offer mechanistic insights into the effect of neighbouring groups on the rate of HCl elimination during the decomposition of ethyl halides. The results indicate that the electronic factors (i.e., partial electron charges), rather than NGP assistance, dominates the reactivity of the direct dehydrohalogenation.

Methodology

All geometrical optimisations and vibrational frequencies are calculated at the M06-2X/GTlarge//M06-2X/6-311+G(d,p)[12] level of theory as implemented in GAUSSIAN 09[13] software. To provide a benchmark for the accuracy of the M06-2X meta-hybrid DFT functional, reaction and activation energies are also estimated by the CBS-QB3[14] composite chemistry model. The CHEMRATE code serves to perform the kinetic calculations.[15] We thoroughly investigated the effects of pressure and temperature changes on rate constants based on Rice-Ramsperger-Kersel-Marcus (RRKM) theory.[16] The collisional energy transfer is described using an exponential-down model with ΔE_{down}= 800 cm^{-1}. To demonstrate the accuracy of the two theoretical methodologies, we compared calculated standard enthalpy changes for HCl/elimination reactions with the corresponding experimental values.[17]

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The results obtained from CBS-QB3 calculations indicate a better agreement with experimental values as shown in Table 1. A comparison with experimental values based on the kinetic data is presented at the end of the results and discussion section. We, therefore, report the findings of this study based on the values derived at the CBS-QB3 level of theory. We performed intrinsic reaction coordinate (IRC) computations to ensure that the transition state structures link the reactant and products of the investigated reactions. The distribution of partial electronic charges is computed via the atomic polar tensor (APT) formalism.[18]

Results and Discussion

Potential energy surfaces (PES)

Motivated by earlier experimental and theoretical findings, we have investigated the elimination of HCl from eleven distinct compounds, namely, 2-(chloroethyl)benzene (**F1**), 2-(bromoethyl)benzene (**H1**), 1-(2-chloroethyl)-4-methoxybenzene (**J1**), 1-(2-bromooethyl)-4-methoxybenzene (**Q1**), chloroethane (**S1**), bromoethane (**L1**), 1-(2-chloroethyl)-2-methoxybenzene (**A1**), 1-chloro-2-methoxyethane (**E1**), 1-(2-chloroethyl)-2-(methylthio)benzene (**B1**), 1-(2-chloroethyl)-4-(methylthio)benzene (**C1**) and 1-chloro-2-(methylthio)ethane (**D1**). The consideration of these species allows investigating the effect of participation of phenyl, methoxyphenyl, methylthiophenyl, methoxy and methylthio groups on the kinetics and thermochemistry of dehydrohalogenation reactions.

We observed that dehydrochlorination required a lower activation enthalpy in 1-chloro-2-(methylthio)ethane than in 1-chloro-2-methoxyethane (233.0 vs 246.7 kJ/mol), and in 1-(2-chloroethyl)-2-methoxybenzene than in 1-(2-chloroethyl)-2-(methylthio)benzene (232.6 vs 240.7 kJ/mol), and a similar activation enthalpy in 1-(2-chloroethyl)-4-methoxybenzene to that of 1-(2-chloroethyl)-4-(methylthio)benzene (231.7 vs 228.8 kJ/mol). The choice of these compounds enables us to study the effects of (i) CH_3O- and CH_3S- substitution on the β carbon, and (ii) the position of CH_3O- and CH_3S- substitution in $CH_3O-C_6H_4-$ and $CH_3S-C_6H_4-$ on the β carbon in chloroethane on dehalogenation reactions. We also compare dehydrochlorination and dehydrobromination of substituted chloroethane and bromoethane.

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Figure 1 exhibits geometries for all the transition structures (TS), whereas Table 2 summarises the prominent structural parameters. All TS are composed of four-centred geometric structures with atoms Cl1/Br1, C2, C3 and H4 numbered in a clockwise direction for all the optimised reactants, products and transition states. Cl1 or Br1 is attached to C2, and H4 to C3. The increase of the Cl1/Br1-C2 distances in all reactions from 1.798/1.954 Å to 2.502/2.638 Å marks the breaking of the Cl1/Br1-C2 bond in the TS. The shortening of the C2-C3 distances in all the TS highlights a change from sp^3 to sp^2 hybridisation and the formation of a double bond. As shown in Table 2, there is no significant change in the bond length between CH_3O/S and the alpha carbon atom from reactant (R) to TS implying no direct involvement of the methoxy and methylthio neighbouring groups in the geometries of the TS.

Figure 2 displays changes in the activation ($\Delta H^{\ddagger}$) and standard reaction ($\Delta_r H^o$) enthalpies at the CBS level of theory, with Table 3 listing the same quantities calculated at both levels of theory. Subsequent discussion relates to the values derived by the CBS-QB3 method. Ethyl chloride (**S1**) and ethyl bromide (**L1**) undergo a unimolecular decomposition to yield ethene (**S2**), HCl and/or HBr, respectively, with endothermicity of 74.3 and 87.9 kJ/mol. However, 2-(chloroethyl)benzene (**F1**) and 2-(bromoethyl)benzene (**H1**) experience similar dehydrochlorination reactions absorbing smaller amounts of energy; i.e., 58.7 and 70.5 kJ/mol, respectively. Elimination of HCl/HBr from non-substituted ethyl halides **S1** (C_2H_5Cl) and **L1** (C_2H_5Br) requires activation enthalpies $\Delta H^{\ddagger}$ of 244.6 and 240.4 kJ/mol, respectively. In comparison to these non-substituted ethyl halides, the decomposition of 2-(chloroethyl)benzene (**F1**) (C_6H_5-C_2H_4Cl) and 2-(bromoethyl)benzene (**H1**) (C_6H_5-C_2H_4Br) demands lower activation energies of 232.7 vs 225.1 kJ/mol, respectively.

Introducing a methoxy group or methylthio group at the *para* position of the aromatic ring leads to no profound effects on the reaction endothermicity of elimination of HCl (57.2 and 57.8 kJ/mol) or activation enthalpy (231.7 and 228.8 kJ/mol) with respect to unsubstituted phenethyl chloride ($\Delta_r H^o$ = 58.7 kJ/mol and $\Delta H^{\ddagger}$ = 232.7). This contrasts with the experimental findings of Hernandez and Chuchani.[5] However, the $\Delta H^{\ddagger}$ for 1-chloro-2-(methylthio)ethane (233.0 kJ/mol) is significantly lower than that of 1-chloro-2-methoxyethane (246.2 kJ/mol) and chloroethane (244.6 kJ/mol). In addition to these observations, the dehydrochlorination of *ortho*-OCH_3 substituted 2-(chloroethyl)benzene displays a lower $\Delta H^{\ddagger}$ (232.6 kJ/mol) than the dehydrochlorination of *ortho*-SCH_3 substituted

2-(chloroethyl)benzene (240.7 kJ/mol). The fact that $\Delta H^{\ddagger}$ for 1-(2-chloroethyl)-2-methoxybenzene (232.6 kJ/mol) and 1-(2-chloroethyl)-2-(methylthio)benzene (246.7 kJ/mol) exceed those of *para*-methoxy (231.7 kJ/mol) and *para*-methylthio (228.8. kJ/mol) substituted chloroethyl benzenes confirms there is no anchimeric assistance from the methoxy and methylthio groups. It is worth noting that we were unable to locate the transition structures for the dehydrochlorination reactions involving NGP of the sulfur and oxygen atoms in the methoxy and ethylthio benzenes as well as methoxy and ethylthio chlorides. In fact, IRC on the presumed TS with NGP found by Chuchani et al.[9] reveals that their TS corresponds to hydrogen abstraction by Cl and not to HCl elimination.

In analogy to the previously described cyclisation reaction in 1-(2-chloroethyl)-2-methoxybenzene,[10] we found that the methylthio group in 1-(2-chloroethyl)-2-(methylthio)benzene acts to eliminate a chlorine atom via a five-membered cyclic transition state (TS10):
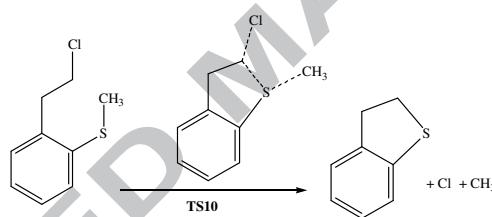
The activation enthalpy of this reaction amounts to 160.3 kJ/mol, lower by a significant 87.4 kJ/mol than the enthalpic barrier for the competing direct HCl elimination reaction (TS9). Our IRC calculations predict that the final products comprise the separated 2,3-dihydrobenzo[*b*]thiophene, a chlorine atom and a methyl radical, with a corresponding reaction enthalpy of 89.2 kJ/mol. Chuchani et al.[10] calculated comparable activation energies for the direct HCl elimination and the cyclisation pathways (219.0 kJ/mol and 230.5 kJ/mol) for case of the 1-(2-chloroethyl)-2-methoxybenzene. It follows that, the *o*-methylthio group induces far more NGP character than the *o*-methoxy group in assisting the cyclisation reaction accompanied by chlorine elimination.

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Electronic partial charges

The theoretical work by Chuchani's group[8-11] applied an analysis of charges based on the natural bond orders (NBO) alongside an examination of bond order to describe changes in the electronic structures along the reaction coordinates of the HCl elimination. Herein, we deploy the methodology of atomic polar tensor-based charges (APT) to elucidate the effect of functional groups on the $\Delta H^{\ddagger}$ values of HCl elimination reactions. We report in Figure 3 the APT-based charges[18] at selected atoms for all the considered molecules. The choice of the APT formalism, to estimate partial atomic charges, stems from the observation that values of the APT derived charges display limited sensitivity to the deployed computational approach and basis sets, unlike the more commonly used Mulliken methodology. Gross et al.[19] have shown that APT-calculated charges produce very similar trends when compared with values obtained using other theoretical approaches such as Mulliken, Bader's and natural population analysis (NPA) methods.

The functionality of C_2H_4Cl as an electron-withdrawing group by induction prompts a transmission of the electron charge density from the π-conjugated system of the phenyl ring. The chlorine atom in 2-(chloroethyl)benzene becomes significantly more electronegative than the chlorine atom in chloromethane (-0.421 *e* versus -0.350 *e*). The calculated APT-charges reveal that the C-Cl and C-H bonds in 2-(chloroethyl)benzene are more polarised than the corresponding bonds in chloroethane. It follows that Cl and H are more prone to leave the chloroethyl side chain in 2-(chloroethyl)benzene in comparison to chloroethane. Hence, HCl elimination from 2-(chloroethyl)benzene is found to occur at a lower $\Delta H^{\ddagger}$ value in comparison to that of a chloroethane molecule (232.7 kJ/mol versus 244.6 kJ/mol). Thus, the effect of the putative anchimeric assistance by the aromatic phenyl nuclei can rather be attributed to the redistribution of the electron density.

Next, we turned our attention to assess the effect of introducing a methoxy group at the *para* and *ortho* positions of 2-(chloroethyl)benzene. The methoxy group constitutes a representative example of an electron-donating group, to the benzene ring, through resonance. Thus, if this electron density transfers to C_2H_4Cl, the chlorine atom would be expected to exhibit more electronegative character in this case. However, as shown in Figure

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3, a marginal increase in chlorine ATP-charges is observed upon introducing a methoxy group at *ortho* (**A1**) and *para* (**J1**) positions, with respect to a non-substituted 2-(chloroethyl)benzene (i.e., 0.002 *e* and 0.042 *e*, respectively). Inspection of the ATP-charges in **A1** and **J1** and comparing them with the corresponding values in the **F1** molecule indicates that excess charges brought by the electron-donating CH_3O group accumulate on the *ortho* and *para* carbons (with respect to the position of the methoxy group). In other words, the electronegativity of the H and Cl atoms in C_2H_4Cl is not enhanced substantially by adding a methoxy group at either *para* or *ortho* positions. This finding accounts for the comparable $\Delta H^{\ddagger}$ values for HCl elimination from **A1**, **J1** and the non-substituted 2-(chloroethyl)benzene (**F1**). The fact that the $\Delta H^{\ddagger}$ value for **A1** exceeds slightly (i.e., 3.4 kJ/mol) that for **Q1**, could be attributed to overlapping in electron charge densities between the two voluminous neighbouring groups (methoxy and chloroethyl).

Figure 4 depicts the ATP-derived charges on all the transition structures. Herein, we analyse in detail the ATP charges on *S1TS* (chloroethane), *E1TS* (1-chloro-2-methoxyethane) and *D1TS* [1-chloro-2-(methylthio)ethane]. The methylthio moiety represents a considerably weaker electron-withdrawing group by induction (the partial charge on the S atom is -0.078 *e*) than the methoxy group (the partial charge on O atom is -0.795 *e*). The latter creates a high partial positive charge on the β carbon atom, which in turn makes the C···H bond less polarisable (the difference in charges between H and β C is -0.311 *e*) with respect to the corresponding bonds in *S1TS* (0.517 *e*) and *D1TS* (0.327 *e*). The larger electronegative character of the Cl atom in *E1TS* (-0.775 *e*) with respect to *S1TS* (-0.741 *e*) seems to counterbalance the less polarisable C···H bond in the former (0.311 *e* in *E1TS* vs 0.517 *e* in *S1TS*). As a result, HCl elimination from chloroethane and 1-chloro-2-methoxyethane is found to occur with very comparable $\Delta H^{\ddagger}$ values (244.6 kJ /mol and 246.7 kJ/mol). Analogously, the more polarisable C···H and C···Cl bonds in *D1TS* (0.327 *e* and -1.182 *e*) collate to yield a notably lower $\Delta H^{\ddagger}$ value (233.0 kcal/mol) for HCl elimination from 1-chloro-2-(methylthio)ethane. Similarly, we found the trend in $\Delta H^{\ddagger}$ values for HBr elimination to be in line with the analysis of electronic partial charges. Lower $\Delta H^{\ddagger}$ values for HBr elimination in comparison with HCl elimination are attributable to weaker C-Br bonds in all the considered molecules.

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Kinetic considerations

Table 4 lists the modified Arrhenius parameters for all the considered reactions at one atmosphere and at the high-pressure limit. Figures 5-7 depict the Arrhenius plots of the selected reactions. Dehydrohalogenation of unsubstituted ethyl halides (**S1** and **L1**) occurs at a rate slower than that of phenyl-substituted ethyl halides (Figures 5 and 6). Positioning of the OCH_3 or SCH_3 group at the *para* site of the benzene ring yields no significant enhancement in the fitted values of the activation energy E_a, Arrhenius factor A, and rate constant k with respect to 2-(chloroethyl)benzene (Figure 7). However, it should be noted that higher AT^n factors for 1-(2-chloroethyl)-2-methoxybenzene seem to counterbalance the higher E_a value in reference to 1-(2-chloroethyl)-4-methoxybenzene (i.e., $\Delta S^{\ddagger}$ for the former at 298.15 K is higher by 6.64 kJ/mol). Hence, slightly higher $k(T)$ values are obtained for 1-(2-chloroethyl)-2-methoxybenzene as shown in Figure 7. The E_a value for 1-chloro-2-(methylthio)ethane (**D1**) is lower than those of 1-chloro-2-methoxyethane (**E1**) and chloroethane (**S1**), in accordance with experimental observations resulting in higher rate constants for CH_3S-substituted ethyl chlorides compared to those of CH_3O-substituted ethyl chlorides and non-substituted ethyl chlorides (Figure 8). The higher Arrhenius factor ensures a more elevated difference in the activation entropy $\Delta S^{\ddagger}$ for *o*-CH_3O- (8.67 kJ/mol) compared to that of *o*-CH_3S- (3.98 kJ/mol).

Table 5 compares the predicted and experimental reaction rate parameters. As shown, our estimated activation energies for the selected reactions remain in relatively good agreement with the corresponding experimentally fitted values. For instance, the rate constant for unimolecular decomposition of ethyl chloride was determined experimentally as 1.79×10^1 s$^-$^{1} at 3.8 atm and 990 K.[20] Our theoretical calculations for the same conditions yield a similar value of 1.0×10^1 s^{-1}. Similarly, the rate of HBr elimination from bromoethane amounts to 1×10^{-4} s^{-1} at 643 K and 0.17 atm,[21] in satisfactory agreement with our theoretical prediction of 1.13×10^{-5} s^{-1}.

Finally, by comparing calculated reaction rate constants for direct HCl elimination and cyclisation reactions in 1-(2-chloroethyl)-2-(methylthio)benzene, it is evident that, placing a

methylthio group at the *ortho* position of a 2-(chloroethyl)benzene hindered dehydrochlorination in favour of the loss of a chlorine atom and subsequent cyclisation.

In conclusion, the unimolecular dehalogenation kinetics of chlorinated and brominated ethanes as well as chlorinated and brominated ethylbenzenes, with and without CH_3O- and CH_3S- substitution, have been compared with those of non-substituted ethyl halides. The phenyl-substituted ethyl halides afford faster elimination reactions than the non-substituted ethyl halides as a consequence of the more polarisable C-H and C-Cl bonds. The distribution of electron partial charges (electronegativity) in a transition structure rather than direct involvement of an adjacent group governs the elimination process of HCl, i.e., there is no evidence of NGP accelerating this elimination process.

Acknowledgement

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Table 1: Comparison of calculated and experimental standard enthalpy change $\Delta_r H^o$ values for two dehydrohalogenation reactions. All values are in kJ/mol at 298.15 K.

Reaction	M06-2X	CBS-QB3	Experimental[15]
$C_2H_5Cl = C_2H_4 + HCl$	80.2	74.3	71.5
$C_2H_5Br = C_2H_4 + HBr$	87.9	87.9	81.4

Table 2. Structural parameters of reactants (R), transition states (TS), and products (P) for the HCl elimination reactions from calculations performed at the CBS theory level.

Reaction		C_6H_5-C	H_3[O/S]-C	Br1/Cl1-C2	C2-C3	C3-H4	H4-Br1/Cl1
				Bond Lengths (Å)			
C_6H_5-C_2H_4Cl→**F2**+HCl	R	1.509	–	1.798	1.525	1.095	2.908
	TS	1.486	–	2.502	1.401	1.258	1.903
	P	1.475	–	–	1.335	–	–
C_6H_5-C_2H_4Br→**F2**+HBr	R	1.515	–	1.954	1.517	1.095	2.935
	TS	1.483	–	2.638	1.401	1.261	2.037
	P	1.475	–	–	1.335	–	–
p-CH_3O-C_6H_4-C_2H_4Cl→**J2**+HCl	R	1.508	1.361	1.799	1.525	1.095	2.906
	TS	1.485	1.356	2.509	1.401	1.251	1.934
	P	1.473	1.358	–	1.336	–	–
p-CH_3O-C_6H_4-C_2H_4Br →**J2**+HBr	R	1.515	1.360	1.956	1.519	1.096	2.917
	TS	1.481	1.356	2.643	1.401	1.254	2.065
	P	1.473	1.358	–	1.336	–	–
p-CH_3S-C_6H_4-C_2H_4Cl →**C2**+HCl	R	1.509	1.821	1.799	1.524	1.092	2.911
	TS	1.482	1.767	2.490	1.399	1.258	1.915
	P	1.473	1.783	–	1.332	–	–
o-CH_3O-C_6H_4-C_2H_4Cl →**A2**+HCl	R	1.507	1.362	1.801	1.523	1.092	2.906
	TS	1.484	1.353	2.502	1.403	1.257	1.940
	P	1.473	1.360	–	1.332	–	–
o-CH_3S-C_6H_4-C_2H_4Cl →**B2**+HCl	R	1.510	1.777	1.799	1.524	1.093	2.893
	TS	1.492	1.774	2.504	1.399	1.279	1.867
	P	–	1.775	–	1.331	–	–
CH_3O-C_2H_4Cl→**E2**+HCl	R	–	1.401	1.794	1.509	1.098	2.867
	TS	–	1.364	2.495	1.394	1.255	1.939
	P	–	1.356	–	1.327	–	–
CH_3S-C_2H_4Cl→**D2**+HCl	R	–	1.819	1.796	1.514	1.092	2.918
	TS	–	1.779	2.486	1.399	1.258	1.843
	P	–	1.672	–	1.329	–	–
C_2H_5Cl→**S2**+HCl	R	–	–	1.800	1.516	1.093	2.948
	TS	–	–	2.539	1.394	1.266	1.837
	P	–	–	–	1.330	–	–
C_2H_5Br→**S2**+HBr	R	–	–	1.954	1.515	1.092	3.064
	TS	–	–	2.709	1.394	1.267	1.974
	P	–	–	–	1.330	–	–

Table 3. Calculated reaction and activation enthalpies at 298.15 K for all the reactions

Reaction	$\Delta H^{\ddagger}$ (kJ/mol)		$\Delta_r H^o$ (kJ/mol)		$\Delta S^{\ddagger}$ (J/mol-K)	
	CBS-QB3	M06-2X	CBS-QB3	M06-2X	CBS-QB3	M06-2X
C_6H_5-$C_2H_4Cl \rightarrow$ **F2**+HCl	232.7	227.9	58.7	57.9	5.30	3.07
C_6H_5-$C_2H_4Br \rightarrow$ **F2**+HBr	225.1	205.8	70.5	58.2	7.29	8.36
p-CH_3O-C_6H_4-$C_2H_4Cl \rightarrow$ **J2**+HCl	231.7	226.6	57.2	58.9	2.03	3.50
p-CH_3O-C_6H_4-$C_2H_4Br \rightarrow$ **J2**+HBr	226.4	222.9	63.6	57.5	9.89	5.73
p-CH_3S-C_6H_4-$C_2H_4Cl \rightarrow$ **C2**+HCl	228.8	228.2	57.8	50.6	22.58	16.11
o-CH_3O-C_6H_4-$C_2H_4Cl \rightarrow$ **A2**+HCl	232.6	232.3	56.4	56.7	8.67	10.00
o-CH_3S-C_6H_4-$C_2H_4Cl \rightarrow$ **B2**+HCl	240.7	242.3	63.5	55.3	3.98	8.97
CH_3O-$C_2H_4Cl \rightarrow$ **E2**+HCl	246.7	243.3	53.0	43.6	10.96	9.15
CH_3S-$C_2H_4Cl \rightarrow$ **D2**+HCl	233.0	229.6	55.3	48.2	48.66	2.17
$C_2H_5Cl \rightarrow$ **S2**+HCl	244.6	240.9	74.3	80.2	6.60	6.59
$C_2H_5Br \rightarrow$ **S2**+HBr	240.4	227.9	87.9	87.9	8.28	7.87

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Table 4. Kinetic parameters for HCl elimination between 300 K and 2000 K
$k=A(T)^n \exp(-E_a/(R \cdot T))^a$

Reaction	Method	At 1 atm			At high pressure		
		$A(s^{-1})$	n	E_a (kJ/mol)	$A(s^{-1})$	n	E_a (kJ/mol)
C_6H_5-C_2H_4Cl →**F2**+HCl	CBS-QB3	4.79×10^{22}	-2.75	245.7	6.06×10^{10}	0.94	228.79
C_6H_5-C_2H_4Br →**F2**+HBr	CBS-QB3	2.77×10^{29}	-4.81	232.4	1.20×10^{11}	0.93	206.68
p-CH_3O-C_6H_4-C_2H_4Cl→**J2**+HCl	CBS-QB3	1.56×10^{16}	-1.02	235.3	8.58×10^{10}	0.63	227.71
p-CH_3O-C_6H_4-C_2H_4Br→**J2**+HBr	CBS-QB3	7.09×10^{26}	-4.06	226.2	1.13×10^{11}	0.89	203.94
p-CH_3S-C_6H_4-C_2H_4Cl→**C2**+HCl	CBS-QB3	1.6×10^{16}	-1.05	238.5	5.06×10^{9}	0.96	229.0
o-CH_3O-C_6H_4-C_2H_4Cl→**A2**+HCl	CBS-QB3	8.59×10^{27}	-4.26	256.9	1.05×10^{11}	0.99	233.19
o-CH_3S-C_6H_4-C_2H_4Cl→**B2**+HCl	CBS-QB3	4.15×10^{25}	-3.50	270.0	5.99×10^{10}	1.06	240.02
o-CH_3S-C_6H_4-C_2H_4Cl→**B3**+Cl + CH_3	CBS-QB3	1.15×10^{25}	-3.19	180.0	4.27×10^{12}	0	160.3.02
CH_3O-C_2H_4Cl →**E2**+HCl	CBS-QB3	5.23×10^{27}	-4.24	267.5	1.07×10^{11}	0.97	244.19
CH_3S-C_2H_4Cl →**D2**+HCl	CBS-QB3	2.07×10^{26}	-3.92	252.5	3.38×10^{10}	1.02	230.39
C_2H_5Cl→**S2**+HCl	CBS-QB3	4.16×10^{27}	-4.27	264.6	4.50×10^{10}	1.05	241.58
C_2H_5Br→**S2**+HBr	CBS-QB3	5.00×10^{29}	-4.91	253.9	5.70×10^{10}	1.03	228.54

$^a A, n$ and Ea denote pre-exponential A-factor, temperature-dependency factor and activation energy, respectively.

Table 5. Arrhenius parameters for HCl elimination fitted to experimental conditions.

Reaction		Experimental conditions		$\log A$ (s^{-1})	E_a (kJ/mol)	T (K)	k (s^{-1})
		T (K)	P (atm)				
$C_2H_5Cl \rightarrow$ **S2**+HCl	Calcd	-	-	13.81	242.1	1000	1.46×10^1
	Expt[19]	990-1200	3.80	13.60	233.4		2.56×10^1
$C_2H_5Br \rightarrow$ **S2**+HBr	Calcd	-	-	13.92	232.31	675	8.76×10^{-5}
	Expt[20]	643-693	0.17	14.06	222.59		6.83×10^{-4}
$C_6H_5\text{-}C_2H_4Cl \rightarrow$ **F2**+HCl	Calcd	-	-	13.89	234.9	700	2.30×10^{-4}
	Expt[5]	684-744	0.20	13.07	220.9		3.85×10^{-4}
$p\text{-}C_8H_8ClOCH_3 \rightarrow$ **J2**+HCl	Calcd	-	-	12.89	231.6	700	4.05×10^{-5}
	Expt[5]	684-744	0.20	13.81	228.4		5.84×10^{-4}

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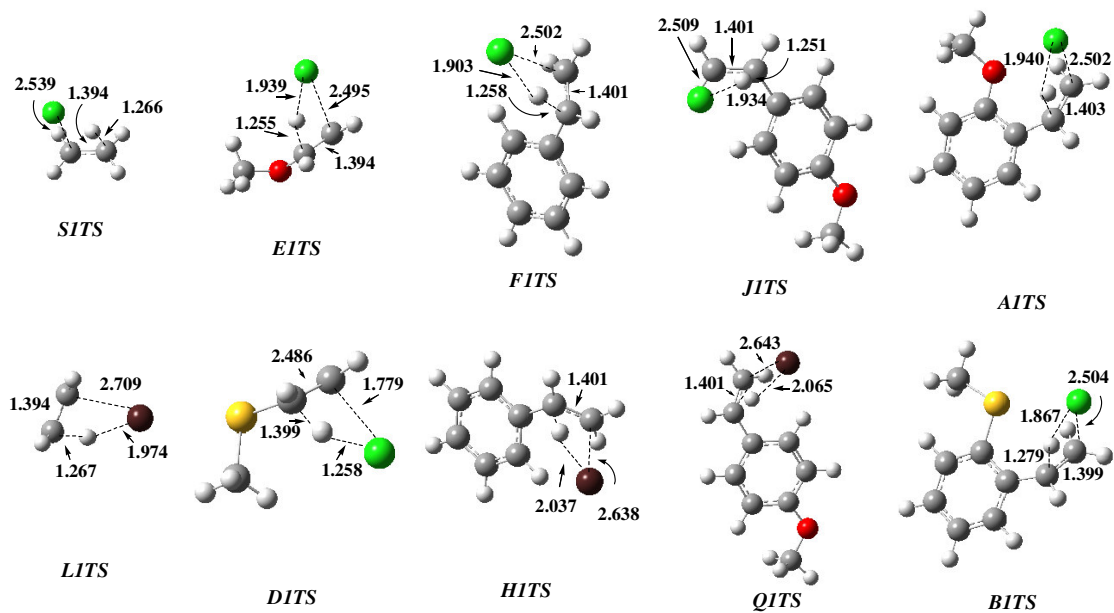
Figure 1. Geometries of the optimised transition structures. Distances are in Å at the M06-2X/6-311+G(d,p) level, obtained at the CBS level of theory.
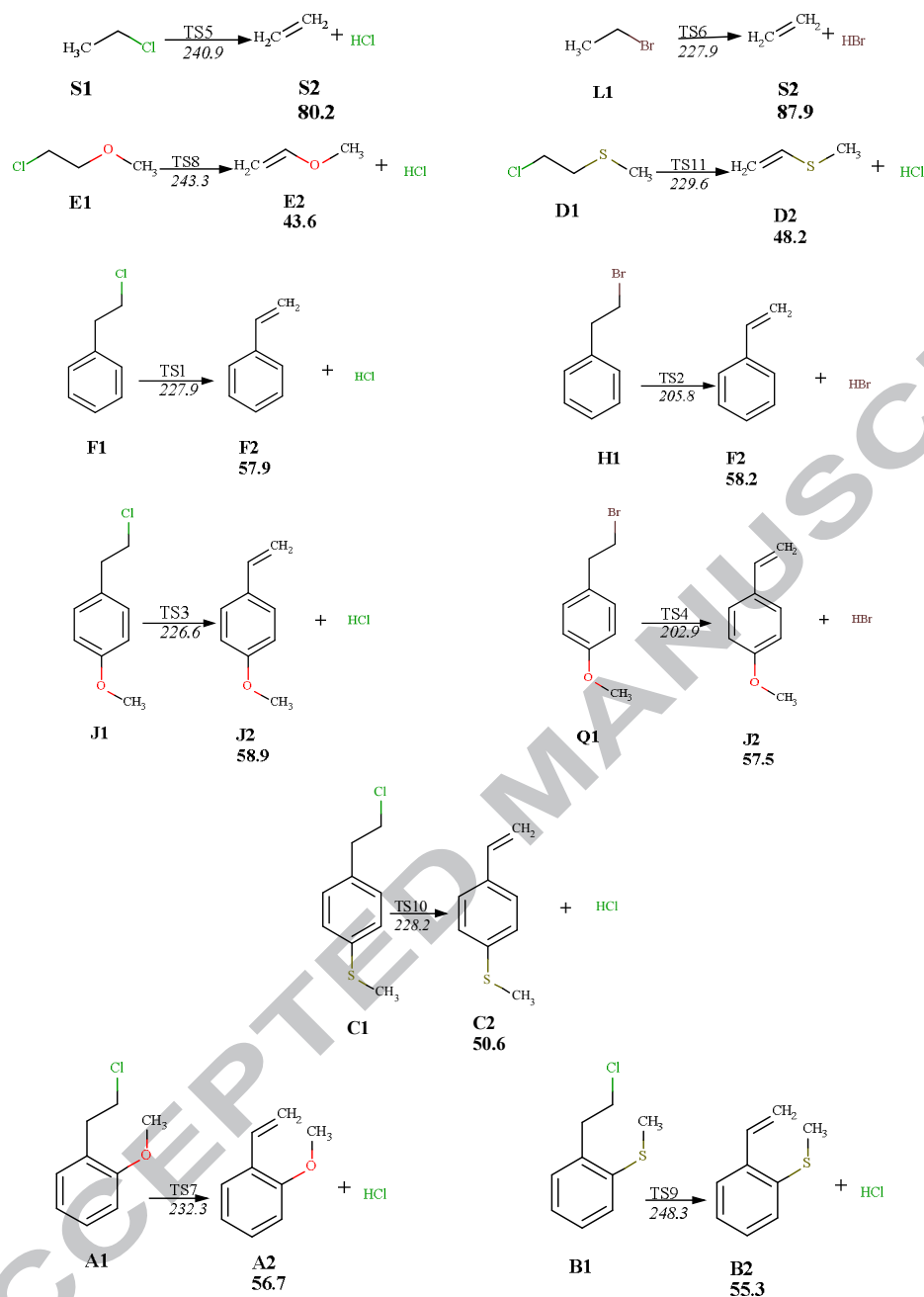
Figure 2. Reaction (in bold) and activation (in italics) energies for the unimolecular decomposition of 2-(chloroethyl)benzene (**F1**), 2-(bromoethyl)benzene (**H1**), 1-(2-chloroethyl)-4-methoxybenzene (**J1**), 1-(2-bromooethyl)-4-methoxybenzene (**Q1**), chloroethane (**S1**), bromoethane (**L1**), 1-(2-chloroethyl)-2-methoxybenzene (**A1**), 1-chloro-2-methoxyethane (**E1**), 1-(2-chloroethyl)-2-(methylthio)benzene (**B1**), 1-(2-chloroethyl)-4-

(methylthio)benzene (**C1**) and 1-chloro-2-(methylthio)ethane (**D1**) in kJ/mol at 298.15 K, obtained at the CBS-QB3 level of theory.
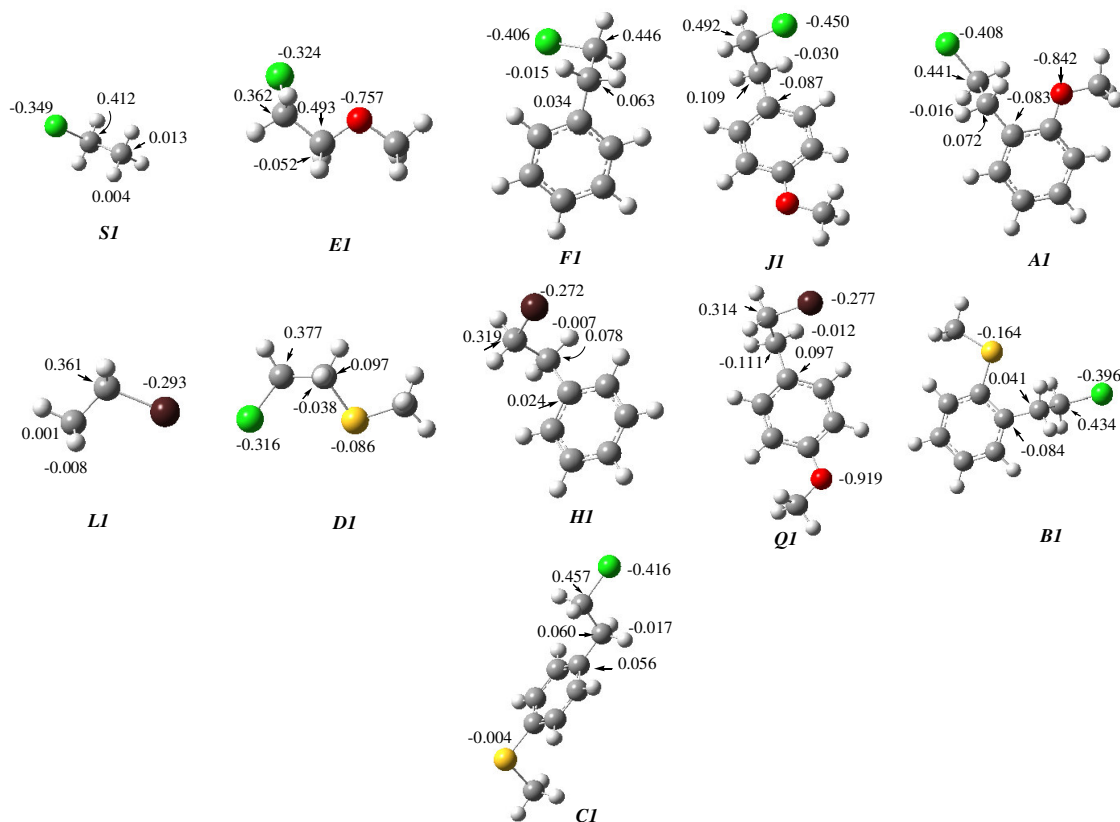
Figure 3. ATP-charges on selected atoms based on the B3LYP/6-311+G(d,p) level of theory. Units are in *e*.
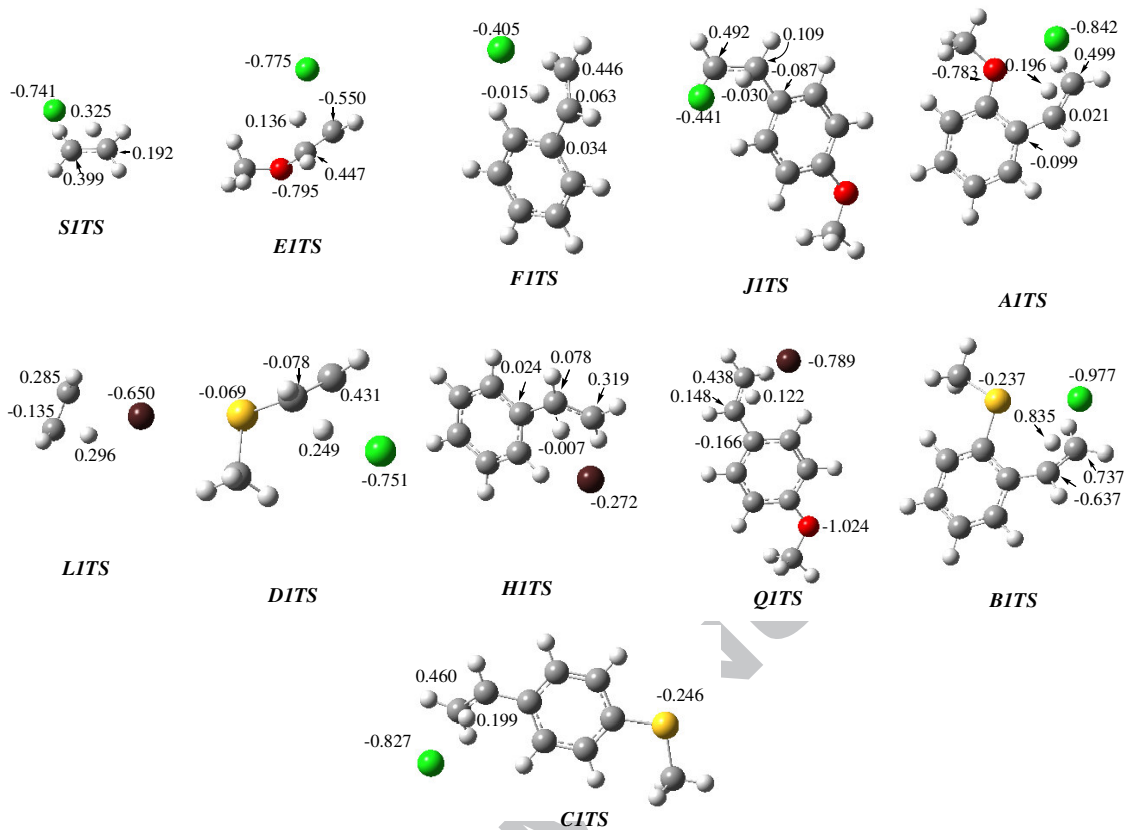
Figure 4. ATP-charges on selected atoms based on the B3LYP/6-311+G(d,p) level of theory. Units are in *e*.
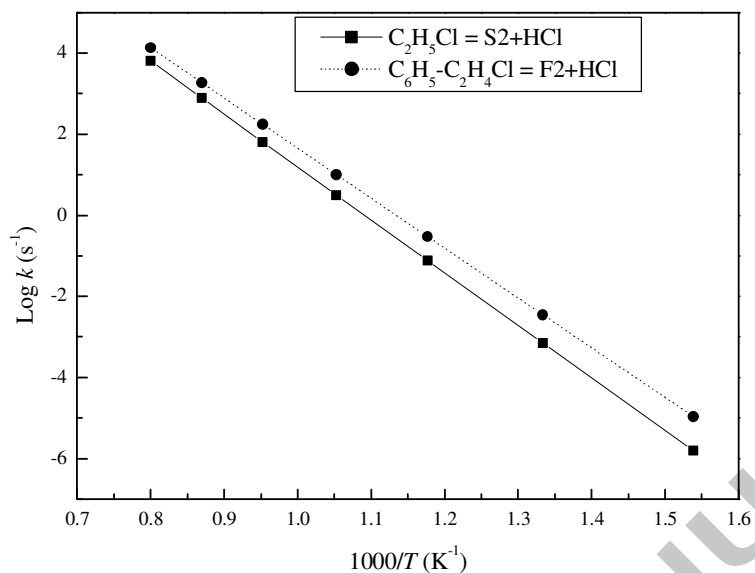
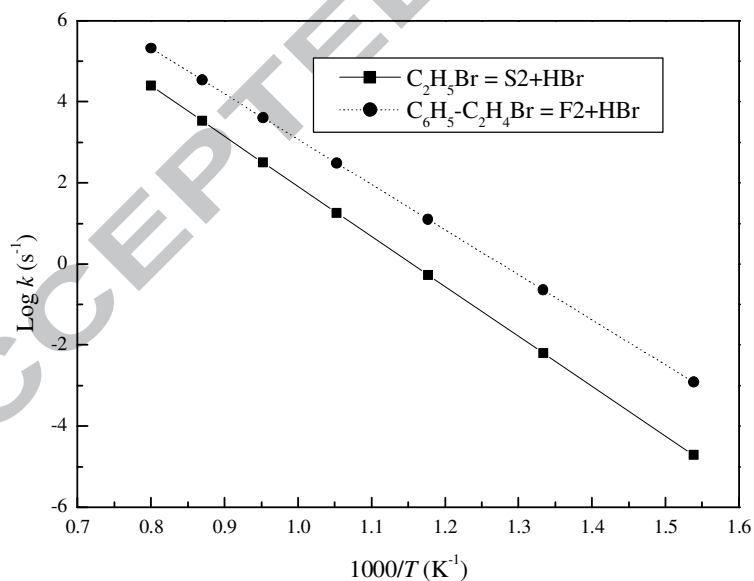**Figure 5.** Arrhenius plots for the elimination of HCl from chloroethane and 2-(chloroethyl)benzene

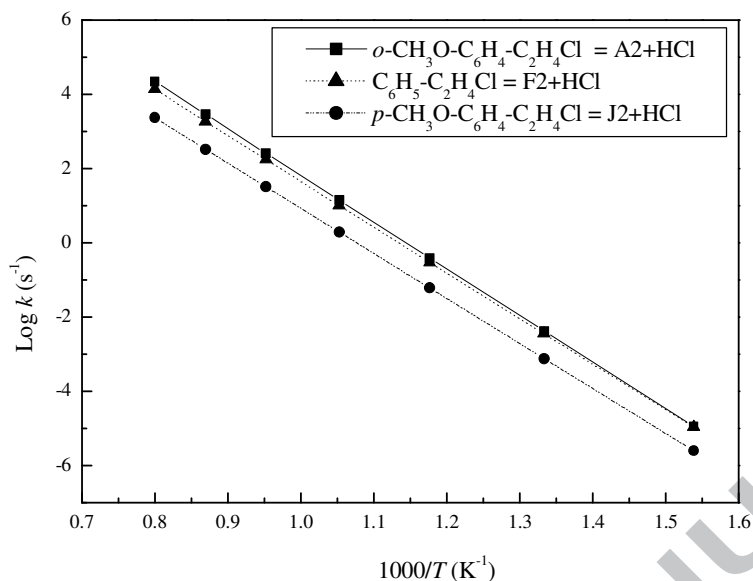**Figure 6.** Arrhenius plots for the elimination of HBr from bromoethane and 2-(bromoethyl)benzene

Figure 7. Arrhenius plots for the elimination of HCl from 1-(2-chloroethyl)-2-methoxybenzene, 1-(2-chloroethyl)-4-methoxybenzene and 2-(chloroethyl)benzene
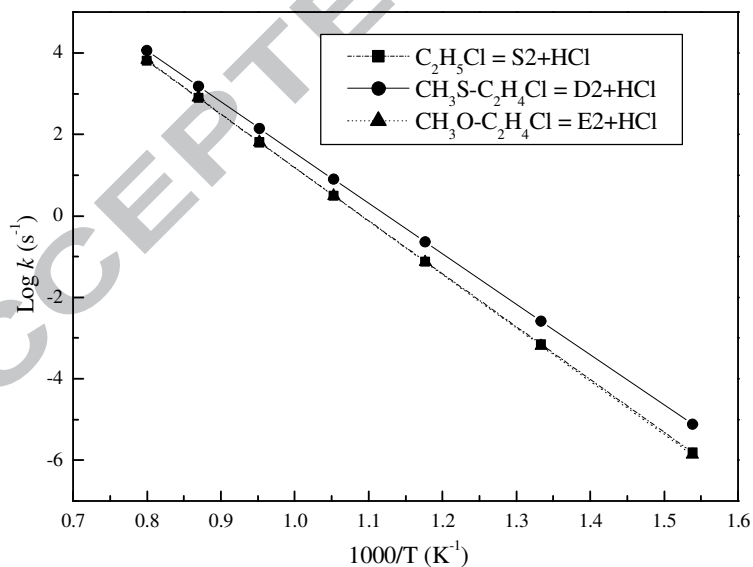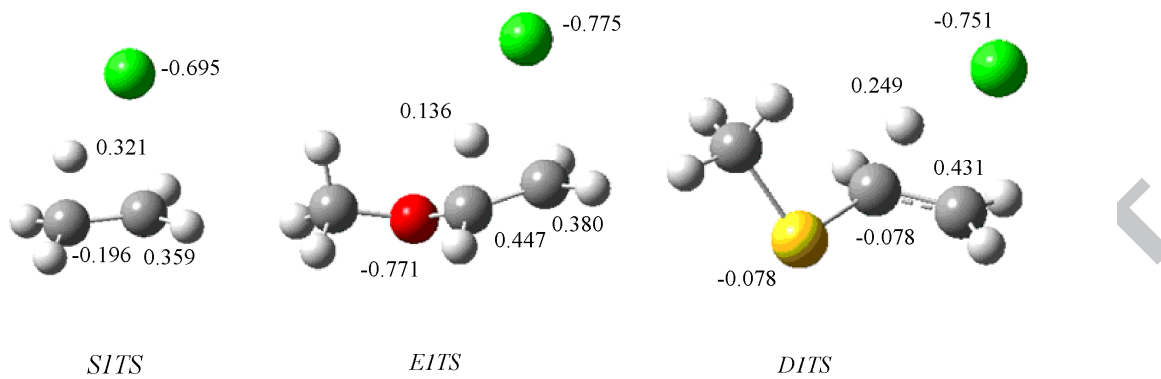

Figure 8. Arrhenius plots for the elimination of HCl from chloroethane, methythiochloroethane and 1-chloro-2-methoxyethane.

SITS   EITS   DITS

Effects of electronic factors on dehydrohalogenation reactivity