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Theoretical Studies of the Nucleophilic Substitution of Halides and Amine at a Sulfonyl Center

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Gas-phase nucleophilic substitution reactions, $F^- + CH_3SO_2F$, $Cl^- + CH_3SO_2Cl$, $Cl^- + CH_3SO_2F$, and $NH_3 + CH_3SO_2Cl$, have been investigated at the B3LYP/6-311+G** and MP2/6-31+G* levels of theory. A very shallow well for the reaction intermediate in a triple-well potential energy surface (PES) was observed for the identity fluoride exchange, but double well PESs were obtained for the other three reactions with three different PES profiles. NBO analyses of the transition states showed substantial charge transfer interactions in all cases which provided a much larger amount of stabilization energy compared with the corresponding species at the carbon center of methyl halides. This difference is primarily caused by the strong electropositive nature of the sulfur center. The F−S−F axial linkage in the distorted TBP type intermediate in the identity fluoride exchange reaction exhibited a weak three-center, four-electron ω-bonding, which is considered to provide stability of the intermediate. All the reactant (RC) and product complexes (PC) have *Cs* symmetry. The symmetry plane bisects angles HCH (of methyl group), OSO (of sulfonyl group), and HNH (of ammonia). Vicinal charge transfer interactions between the two out-of-plane C−H, S−O, and N−H bonds provide extra stabilization to the ion-dipole complexes together with H-bond formation of in-plane H atom with the nucleophile and/or leaving group.

Introduction

The nucleophilic substitution at carbon centers has been extensively studied experimentally as well as theoretically, and the mechanism is well established.[1] The simplest of such reactions involves the gas-phase reaction of halide nucleophiles at a halomethane carbon atom, for which a double-well potential energy surface (PES) applies exhibiting two local minima of ion−molecule complexes connected by a central barrier.[2] When a similar reaction occurs at a carbonyl carbon, a stable intermediate can exist and a triple-well PES may be obtained.[3] Although nucleophilic substitution reactions at sulfur centers are widely explored experimentally,[4] there are few reports on the theoretical studies: Bachrach and co-workers have reported their series of works on the gas-phase nucleophilc substitution at divalent (sulfenyl)[5] and tetravalent (sulfinyl) sulfur.[5d,6] In most cases, substitutions at both sulfenyl and sulfinyl sulfur were found to proceed by an addition−elimination mechanism through an intermediate with a triple-well PES. The geometry of the intermediate was trigonal-bipyramidal (TBP) for sulfenyl substitution, but for sulfinyl substitution a strong distortion from trigonal symmetry was obtained in the TBP structure with the angle between two apical ligands of ca. 150°. Their studies of the reactions of SCl_2 and $SOCl_2$ with chloride anion have also shown stable addition products SCl_3^{7-} and $SOCl_3^{8-}$, respectively. Bickelhaupt and co-workers[9] reported on the nucleophilic substitutions at Si and P centers. They found an interesting change in the mechanism for *chloride exchange* at P, an S_N2@P4 reaction, in the gas phase from a single-well to a triple-well and finally to a double-well PES as the size of substituents R in POR_2Cl is increased from R = H to Cl and to OCH_3, i.e., as the steric demand of the substituents is increased. Ren and co-workers[10] reported on the gas-phase ion pair S_N2 substitutions of lithium halides at simple divalent sulfur centers, CH_3SY (*Y*=F, Cl, Br, I). Lee et al.[11] have studied gas-phase sulfinyl (RSOCl; R = H, CH_3, CN) and sulfonyl (RSO_2Cl; R = H, CH_3, CN) group transfers between halides (F, Cl). The TBP structures of adducts were either a transition state (double-well PES) or an intermediate (triple-well PES) depending on the R and nucleophile (F, Cl). In general, however, sulfinyl transfers were found to proceed by a stepwise mechanism with a triple-well PES, while sulfonyl transfers proceed mostly by a direct displacement mechanism with a double-well PES. Their work involved comparisons of acyl transfer mechanisms at various acyl functional groups (X = Y with X = C, S, P and Y = O, S), and no detailed discussion was given on the mechanistic aspects of sulfinyl and sulfonyl transfers. Recently, Lee[12] has reported on the DFT studies of the aminolysis of methanesulfinyl halides (CH_3SOY; Y = F, Cl) in the gas phase and in water. The results showed that the aminolysis proceeds by an addition−elimination mechanism through a distorted TBP intermediate both in the gas phase and in water. A discrete structural reorganization to a new TBP intermediate was noted when four water molecules are microsolvated to the gas-phase TBP intermediate. In the present study, to extend our works on the mechanism of nucleophilic substitution at sulfur,[12,13] we studied relatively simple halide exchange reactions, reactions (F, F), (Cl, Cl), and (Cl, F), and especially to examine aminolysis mechanism at *sulfonyl* sulfur,[12,13a−c] we examined reaction (N, Cl) using HN_3, theoretically at the (a) B3LYP/6-311+G** and (b) MP2/6-31+G* levels of theory in the gas phase:

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reaction (F,F)

$$F^- + CH_3SO_2F \rightarrow CH_3SO_2F + F^-$$

reaction (Cl,Cl)

$$Cl^- + CH_3SO_2Cl \rightarrow CH_3SO_2Cl + Cl^-$$

reaction (Cl,F)

$$Cl^- + CH_3SO_2F \rightarrow CH_3SO_2Cl + F^-$$

reaction (N,Cl)

$$NH_3 + CH_3SO_2Cl \rightarrow H_3N + CH_3SO_2 + Cl^-$$

The main purpose of this work is to clarify factors determining the mechanistic change involved from addition−elimination for reactions at the sulfenyl and sulfinyl sulfur centers to direct displacement (S_N2) mechanism for reactions at the sulfonyl sulfur center. In addition we are interested in examining the aminolysis mechanism at the sulfonyl center,[12,13a−c] which should also provide a good comparison of reactivity of a neutral nucleophile with that of anionic nucleophiles in the substitution reactions at the sulfonyl center.

Computational Method

All calculations were performed using the GAUSSIAN 03 program package.[14] The optimized geometries, dipole moments, and energies of the reactants (REs), intermediate (INT), transition states (TSs), and products (PRs) were determined at two levels of theory: B3LYP/6-311+G** (**a**) and MP2/6-31+G* (**b**). Natural bond orbital (NBO) analyses[15−17] were performed on the TSs and INT at the **b** level (MP2/6-31+G*). The nature of all structures was confirmed by analytical frequency calculations. The optimized structures of REs, INT, and PRs had all real frequencies, while those of TSs had only one imaginary frequency. Zero-point vibrational energies (ZPEs) were used without scaling. Optimized electronic energies are summarized in Table S1 in the Supporting Information.

Results and Discussion

Reaction (F,F). This reaction was found to proceed via a triple-well PES with an INT surrounded by two TSs. Optimized structures and natural population analysis (NPA) charges[15,18] of reactant complex (RC), INT, and TS determined at the MP2/6-31+G* level are shown in Figure 1. Structurally the two levels (**a** and **b**) of theory provide PES of the same shape and gave similar geometries and charges. We will in the following discuss based on those at the **b** level unless otherwise stated. The incoming nucleophile, F^-, forms an ion−dipole complex (RC, Figure 1, parts a and d) at a relatively long distance away from the reaction center sulfur atom (d_{FS} = 3.800 and 3.707 Å at **a** and **b** levels, respectively). A notable feature of this complex (and likewise of all other RCs and PCs) is that this complex has a *Cs* symmetry with a symmetry plane which bisects HCH angle of the methyl group and OSO angle of the sulfonyl group and comprises all the rest of atoms, i.e., C, S, and both F atoms and the third hydrogen atom of the Me group (Figure 1d). Thus, one hydrogen atom is coplanar with the incoming F^- and a relatively strong hydrogen bond is formed between them as shown in Figure 1a. The substrate molecule retains the original tetrahedral geometry in the complex. The *Cs* symmetry of the RC provides second-order charge transfer stabilizations[16,19] $\Delta E^{(2)} = (-2F_{ij}^2/\delta\varepsilon_{ij}$, where F_{ij} is the Fock matrix element, which is proportional to overlap integral S_{ij} between the two interacting orbitals, and $\delta\varepsilon_{ij}$ is energy gap between two interacting orbitals *i* and j) −10.72 kcal/mol by donor−acceptor interactions between antiperiplanar, out-of-symmetry plane, vicinal bonds, $\sigma_{CH} \rightarrow \sigma^*_{SO}$ and $\sigma_{SO} \rightarrow \sigma^*_{CH}$. The TS (Figure 1b) and intermediate (Figure 1c) have a distorted TBP structure with a nonlinear axial F−S−F linkage (∠FSF = 161.2 and 162.6° for the TS, and 165.7 and 166.3° for the intermediate at **a** and **b** levels, respectively). TS2 is a mirror image of TS1, and the leaving group, F, is further away from S. Dipole moment of the INT (4.588 D) was smaller than that of the TS (7.102 D) reflecting a greater stability due to a more symmetric structure of the INT.

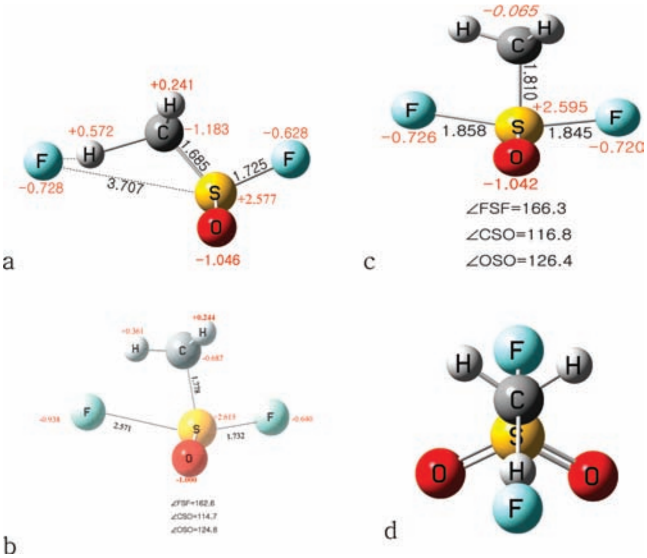

Figure 1. The structures and NPA charges at the MP2/6-31+G* level for reactant complex (a and d), intermediate (c), and TS1 (b) of the (F,F) reaction. Boldface numbers refer to identical atomic charge above and below, while italic numbers refer to the atomic charge with hydrogens summed into the heteroatom. Bond lengths are in angstroms and angles are in degrees. Note that reactant complex, d, has a *Cs* symmetry, and the symmetry plane comprises atoms F, C, S, F, and H (from the Me group), while out-of-plane C−H and S−O bonds are oriented vicinally antiperiplanar to each other. TS2 (not shown) is a mirror image of TS1.

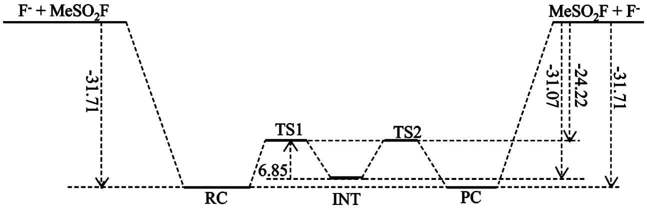

Figure 2. The PES for reaction (F,F) at the MP2/6-31+G* level. The energy differences are in kcal/mol.

The PES for the identity fluoride exchange reaction is presented schematically in Figure 2, and key energy differences relative to the reactants level are summarized in Table 1. We note that the interaction energies (E_{RC}, E_{TS}, and E_{INT}) between F^- and substrate molecule calculated by the DFT method are slightly more stabilizing. The electronic energy difference

TABLE 1: Energies Relative to the Reactants (kcal/mol) for Reactions (F,F), (Cl,Cl), (Cl,F), and (N,Cl) at a and b Levels[a]

reaction	**a** (B3LYP/6-311+G**)	**b** (MP2/6-31+G*)
$F^- + MeSO_2F$		
RC	−40.50	−31.71
TS	−27.71	−24.22
INT	−34.01	−31.07
$Cl^- + MeSO_2Cl$		
RC	−20.32	−18.52
TS	−8.87	−6.91
$Cl^- + MeSO_2F$		
RC	−18.55	−18.08
TS	13.46	18.75
PC	5.02 (−46.44)[b]	3.46 (−36.72)
$NH_3 + MeSO_2Cl$		
RC	−5.59	−7.85
TS	27.51	29.55
PC	−7.54 (−138.33)	−9.54 (−138.92)

[a] Reactants levels in au are for (F,F), −788.44896 (**a**), −786.67335 (**b**); (Cl,Cl), −1509.10172 (**a**), −1506.70385 (**b**); (Cl,F), −1148.75269 (**a**), −1146.72065 (**b**); (N,Cl), −1105.38063 (**a**), −1103.39590 (**b**), respectively. [b] PC levels relative to the products.

between the TS and intermediate is 6.29 and 6.85 kcal/mol at levels **a** and **b**, respectively. The existence of a TBP type intermediate in the (F,F) system can be ascribed to formation of a three-center, four-electron (3c/4e) hyperbond (ω-bond)[16] of the type $[F-S-F]^-$, albeit weak due to its rather strong distortion of the axial triatomic anion linkage ($\angle FSF = 166°$ instead of 180°). This type of ω-bond is characterized by[16] (1) a linear (or near linear) geometry, (2) unusually long bond lengths due to high population of σ^*_{SF} antibonds (the S−F bond length is elongated by ca. 0.2 Å from that of the substrate), (3) equal (or near equal) resonance weightings of $(F_n{:}SF_l) \leftrightarrow (F_l{:}SF_n)$ as evidenced by nearly equal interaction energies of −8.9 ($n_{Fn} \rightarrow \sigma^*_{SFl}$) and −7.3 kcal/mol ($n_{Fl} \rightarrow \sigma^*_{SFn}$) for the INT, and (4) unusually high cationic character of central atom S (ca. +2.6 NPA charges) and anionic character of terminal atoms F (ca. −0.7 NPA charges).

The NBO analysis of the INT showed that the central atom S exhibits a strong d-orbital participation (35.6%) leading to a large valence shell expansion. This leads to a large atomic size of S and large angles between geminal bonds, such as angles between S−C, S−O, and S−F bonds, which result in strong geminal charge transfer delocalization.[16] For example, second-order charge transfer stabilization energies, $\Delta E^{(2)}$ $(=-2F_{ij}/\delta\varepsilon_{ij})$, for *geminal* interactions of $\sigma_{SO} \rightarrow \sigma^*_{SF}$, $\sigma_{SC} \rightarrow \sigma^*_{SF}$, and $\sigma_{SF} \rightarrow \sigma^*_{SF}$ are −140, −114, and −87 kcal/mol, respectively, which are much larger than the reciprocal donor−acceptor *vicinal* charge transfer stabilizations of the type $n_F \rightarrow \sigma^*_{SF}$ of mere 16 kcal/mol. This large charge transfer energy difference in the INT is due mainly to the large difference in the F_{ij} value.[19] For example, F_{ij} values are much larger for geminal interactions, 0.221−0.247 au, than those for the vicinal interactions, 0.059−0.093 au, with little differences in $\delta\varepsilon_{ij}$, ranging from 1.24 to 1.65 au for geminal interactions of the two S−F bonds and vicinal interactions of $n_F \rightarrow \sigma^*_{SF}$. The F_{ij} value of a geminal charge transfer is known to be a maximum at $\angle FSF = 180°$ and becomes larger with greater atomic size.[16] The overlap in the vicinal interactions (and hence F_{ij}) between n_F and σ^*_{SF} is small since F−S−F axial bonds are not quite linear, $\angle FSF = 166°$, as shown above. Thus in the INT of reaction (F,F), geminal charge transfer interactions constitute a major stabilizing factor, but not the vicinal charge transfer stabilizations as we observe for the main group orbital interaction stabilizations in the ordinary organic compounds.[16] We therefore conclude that the existence of INT in the reaction (F,F) can be attributed to the 3c/4e hyperbond formation of F−S−F linkage, in which strong geminal charge transfer interactions provide the majority of stabilization energy as a result of a strong d-orbital participation of the central atom S in the INT. Our NBO analysis of the TS shows that there is no 3c/4e hyperbond (ω-bond) formation due to a stronger distortion ($\angle FSF$ is ca. 4° more distorted than that of the INT) and dissymmetry of the F−S−F linkage (bond lengths of the two S−F axial bonds (1.732 and 2.571 Å) and NPA charges on the two F (−0.938 and −0.640) differ greatly). In the TS d-orbital participation of the central S atom is only 3.75% in the S−F bond so that geminal charge transfer stabilization is not large ($\Delta E^{(2)} = -27.36$ kcal/mol compared with the corresponding value of −341.0 kcal/mol in the INT.). Vicinal charge delocalization of the type $n_O \rightarrow \sigma^*_{SF}$ provides the major stabilization energy ($\Delta E^{(2)} = -131.7$ kcal/mol) in the TS, but $n_F \rightarrow \sigma^*_{SF}$ vicinal interaction provides only −8.70 kcal/mol.

According to the activation strain analysis of Bickelhaupt,[20] activation energy $\Delta E^{\ddagger}$ (=−24.21 kcal/mol) can be expressed as a sum of the activation strain, ΔE_{str} (=6.91 kcal/mol),[21] which is the deformation energy associated with bringing substrate into the geometry of the TS, and the stabilizing TS interaction energy ΔE_{int} (=−30.40 kcal/mol) between the reactants and the activated complex, $\Delta E^{\ddagger} = \Delta E_{str} + \Delta E_{int}$. Therefore, for a nucleophilic displacement reaction with a negative activation energy ($\Delta E^{\ddagger} < 0$) the interaction energy ($\Delta E_{int} < 0$) should be larger numerically than the activation strain ($\Delta E_{str} > 0$). Hence the stabilizing interaction in the TS (or the energy gain mainly by bond formation of the nucleophile)[20d] will have a greater effect on the overall activation energy than the energy required to deform the reactant (or the energy loss mainly due to partial cleavage of the leaving group)[20d] in the TS. Rough comparison of the TS level (−27.71 kcal/mol relative to the reactants at level **a**) with that for identity fluoride exchange at a saturated carbon center, $F^- + CH_3F$ (−2.4 kcal/mol at B3LYP/DZP++ level),[22] indicates that the TS at the sulfonyl center is far more (an order of magnitude more) stabilizing than that at the carbon center. Bickelhaupt[20b,d] pointed out that the barriers correlate only partially with the bond strengths, since $\Delta E^{\ddagger}$ arises as the sum of ΔE_{str} and ΔE_{int}, and it reflects the complex interplay of the mutually counteracting trends in both of these two quantities. Hence, although bond strength of the C−F (bond energy = 116 kcal/mol)[23] is much stronger than that of the S−F bond (bond energy = 68 kcal/mol)[23] the effect of this bond strength difference on $\Delta E^{\ddagger}$ will not be large especially when $\Delta E^{\ddagger}$ is negative since $|\Delta E_{int}| \geq |\Delta E_{str}|$. Thus the higher stability of the sulfonyl TS compared with the saturated carbon TS should be due largely to the highly positive sulfonyl sulfur (NPA charges are +2.605 and −0.106 for S in $MeSO_2F$ and C in MeF, respectively, at level **a**) together with the strong stabilizing effect of hyperbond (ω-bond) formation involving the sulfonyl sulfur in the TS (as well as in the INT).

Reaction (Cl,Cl). Optimized geometries and NPA charges of the reactant complex and TS determined at level **b** are presented in Figure 3. This reaction proceeds through a double-well PES without intermediate formation, Figure 4. The incoming nucleophile Cl^- forms an ion−dipole complex (dipole moment = 9.496 D) at a long distance (4.481 Å) from S with a strong negative charge of −0.945. In this complex the substrate molecule maintains an original tetrahedral geometry with a *Cs* symmetry (Figure 3). The symmetry plane bisects $\angle HCH$ and $\angle OSO$, and comprises all atoms excluding the two out-of-

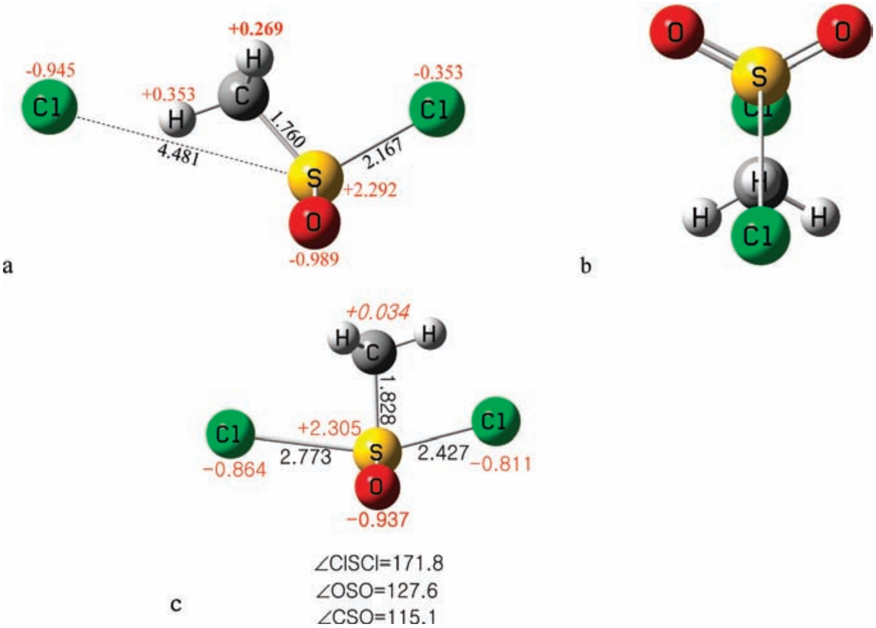

Figure 3. The reactants complex (a) with its side view showing the symmetry plane (b) and TS structure (c) for reaction (Cl,Cl) at the MP2/6-31+G* level. Bond lengths are in angstroms and angles are in degrees. Boldface numbers refer to identical atomic charge above and below, while italic numbers refer to the atomic charge with hydrogens summed into the heteroatoms.

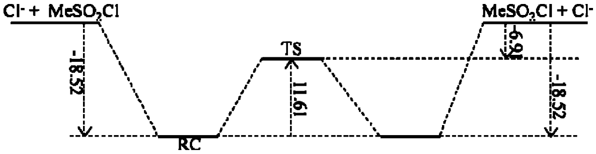

Figure 4. PES for reaction (Cl,Cl) at the MP2/6-31+G* level. Energy differences are in kcal/mol.

plane H and O atoms of the bisected angles. The H-bond between the incoming nucleophile Cl^- and the H atom (+0.354) on the symmetry plane is weaker than the corresponding H-bond (H atom charge = +0.572) observed in the reaction (F,F), since the Cl−S distance (4.481 Å) is much longer than the F−S distance (3.707 Å), even though the negative charge of Cl^- (−0.945) is stronger than that of F^- (−0.728). The *Cs* symmetry structure of the RC provides an extra stabilization of −9.88 kcal/mol as a result of vicinal charge transfer stabilization of $\sigma_{CH} \rightarrow \sigma^*_{SO}$ and $\sigma_{SO} \rightarrow \sigma^*_{CH}$ interactions between the anti-periplanar, out-of-plane C−H and S−O bonds. The TS has a distorted TBP type structure with axial bond angle ∠ClSCl = 171.8°. In the TS the nucleophile Cl^-_n is relatively far away from the S atom so that second-order stabilization by vicinal charge transfer interaction $n_{Cl} \rightarrow \sigma^*_{SCl}$ is relatively weak (−29.62 kcal/mol), which is much smaller than that by vicinal charge transfer $n_O \rightarrow \sigma^*_{SCl}$ of −184.29 kcal/mol. Thus ω-bond formation of the type $[Cl{:}SCl]^- \leftrightarrow [ClS{:}Cl]^-$ is not possible. Furthermore, d-orbital participation of the sulfonyl sulfur is also small (2.40%). Therefore geminal charge transfer interactions of the types $\sigma_{SO} \rightarrow \sigma^*_{SCl}$ and $\sigma_{SC} \rightarrow \sigma^*_{SCl}$ are relatively small (−23.64 kcal/mol). We note that the central barrier hight of reaction (Cl,Cl) is higher than that of reaction (F,F), 11.61 vs 6.85 kcal/mol, but is more symmetric since the reaction (Cl,Cl) is thermoneutral and proceeds by a single step.

We have constructed a hypothetical TBP TS structure optimized with the two S−Cl bond lengths of 2.000 Å each and performed an NBO analysis. The results showed that the Cl−S−Cl axial linkage forms an ω-type bond, $[Cl{:}SCl]^- \leftrightarrow [ClS{:}Cl]^-$, in which there is a strong d-orbital participation (37.26%) with a large geminal charge transfer stabilization (−339.2 kcal/mol) and relatively small $n_{Cl} \rightarrow \sigma^*_{SCl}$ vicinal charge transfer stabilization (−16.15 kcal/mol). These findings are exactly the same characteristic features of the ω- bond found in the INT of the reaction (F,F) discussed above. It seems therefore that in the reaction (Cl,Cl) the bulky nucleophile Cl^- cannot approach the reaction center S near enough to form an ω type bond due largely to steric repulsion of the equatorial ligands, two O and methyl groups, in a TBP structure. This is supported by an NBO analysis of SCl_3^-.[7] The T-shaped pseudo-TBP structure of this compound is stabilized by a 3c/4e hyperbond, ω-bond, $Cl-S-Cl^-$ with one equatorial Cl (and two lone pair electrons). Bond length of the two, equal, axial S−Cl bond was 2.388 Å, while that of an equatorial S−Cl bond was 2.069 Å. On the other hand, an NBO analysis of $SOCl_3^-$[8] showed that this compound has a tetrahedral geometry with ∠ClSCl = 115.6° since formation of an ω-bond of the type $Cl-S-Cl^-$ is not possible in this compound due to the presence of an extra O attached to the central S atom. The three S−Cl bonds have the same length of 2.408 Å each. Thus any one of the three Cl atoms is unable to approach the central S close enough to form an ω-bond due to steric conjestion incurred by an extra O atom. This is in line with the change in the nucleophilic substitution mechanism at P, reported by Bickelhaupt and co-wokers,[9] from a triple PES to a direct displacement as the steric demand of the substituents around P is increased (vide supra). In this respect, the existence of an intermediate in the reaction (F,F) demonstrates that steric crowding is not significant enough to prevent approach of the two F atoms in the formation of the intermediate due to smaller size of the F than Cl atom.

Rough comparison of the TS level relative to the reactants (−8.87 and −6.91 kcal/mol at levels **a** and **b**, respectively) with the corresponding level for the Cl^- + MeCl reaction (−1.31 and −1.52 kcal/mol at the B3LYP/DZP++ [22] and **b** levels,[9c] respectively) illustrates again the strong stabilizing effect (ca. 5−7 times more stabilizing) of the sulfonyl center compared with the saturated carbon center. This is however much smaller

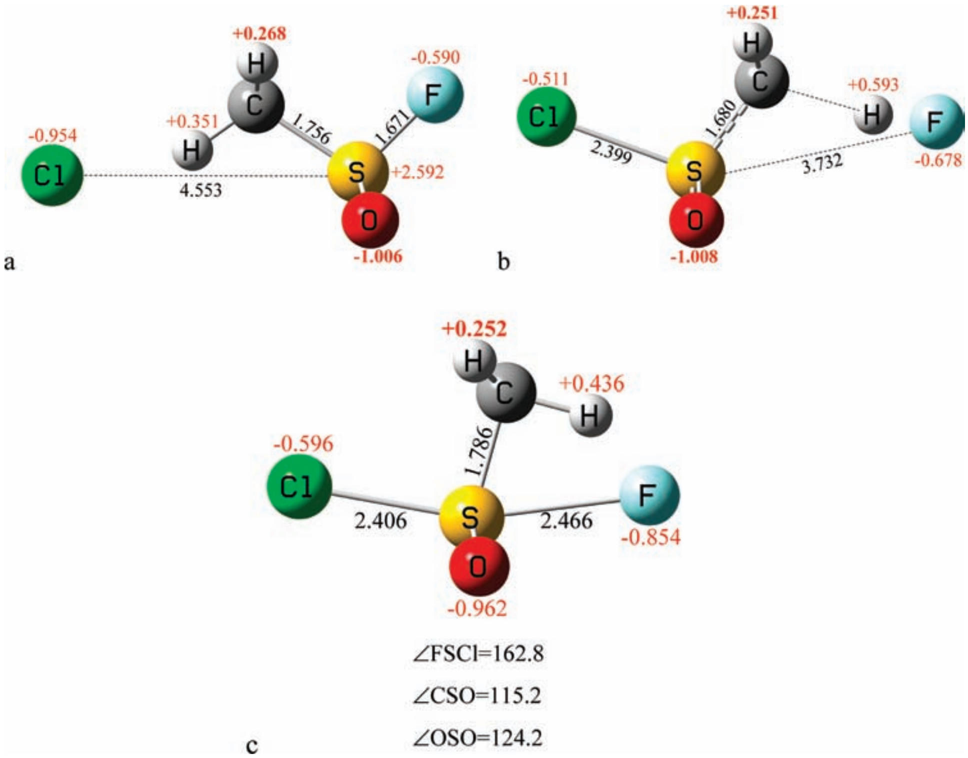

Figure 5. Structures of reactants (a) and products complexes (b) and TS (c) for reaction (Cl,F) at the MP2/6-31+G* level. Boldface numbers refer to identical atomic charge above and below. Bond lengths are in angstroms, and angles are in degrees. The side views that show the symmetry plane in RC and PC are in Figure S1 in Supporting Information.

than that for identity fluoride exchange (ca. 14 times more stabilizing) as a result of an ω-bond formation in the (F,F) reaction.

Reaction (Cl,F). This reaction proceeds via a double-well PES with two different, reactant (RC) and product (PC), ion−dipole complexes separated by a central potential energy barrier which corresponds to a distorted TBP type TS, Figure 5. Here again the two ion−dipole complexes, RC and PC, have *Cs* symmetry. The symmetry plane bisects the two angles, ∠HCH and ∠OSO, and the one remaining methyl hydrogen is coplanar with the incoming Cl^- and departing F^- such that the coplanar H forms a hydrogen bond with Cl^- in the RC and with F^- in the PC. The *Cs* symmetry structure of the RC and PC provides stabilization of −10.72 and −9.48 kcal/mol, respectively, by vicinal charge transfer interactions between antiperiplanar out-of-plane CH and SO bonds. In the TS both bond formation of the nucleophile, Cl^-, and bond cleavage of the leaving group, F^-, are much advanced along the reaction coordinate leading to a late TS. This is in fact consistent with the Hammond postulate,[23,24] since the reaction is highly endothermic (ΔE^0 = 40.22 kcal/mol) and PC (dipole moment = 9.824D) level is considerably higher (by 21.54 kcal/mol) than RC (1.834D) level (−18.08 kcal/mol) so that the high-energy TS (18.75 kcal/mol) resembles the energetically higher PC. This is also in accord with the Bell−Evans−Polanyi (BEP) principle[25,26] which predicts a late TS for an endothermic reaction. The TS being late along the reaction coordinate, bond cleavage of the leaving group, F^-, has progressed to a large extent and carries a strong negative charge (−0.854) which leads to a H-bond with the methyl hydrogen on the symmetry plane (Figure 5). The PES diagram is shown in Figure 6. The level of the TS is higher by 18.75 kcal/mol than that of the reactants, and the PC level is higher by 3.46 kcal/mol than the reactants level and 21.54 kcal/mol higher than the RC level. NBO analyses have shown that the TS has a distorted TBP type (∠ClSF = 162.8°) geometry but the axial linkage, Cl−S−F, does not form a 3c/4e hyperbond (ω-bond) with little d-orbital participation (2.50%) of the central S atom. There is strong vicinal charge transfer interactions of $n_O \rightarrow \sigma^*_{SCl}$ ($\Delta E^{(2)}$ = −184.05 kcal/mol) with relatively weak $n_F \rightarrow \sigma^*_{SCl}$ ($\Delta E^{(2)}$ = −14.68 kcal/mol). As noted above there is a H-bond formation of departing F^- with the coplanar methyl hydrogen, which provides rather strong vicinal charge transfer stabilization by $n_F \rightarrow \sigma^*_{CH}$ ($\Delta E^{(2)}$ = −91.24 kcal/mol).

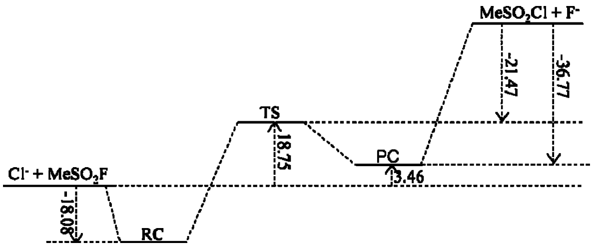

Figure 6. The PES for reaction (Cl,F) at the MP2/6-31+G* level. Energy differences are in kcal/mol.

We note in Figure 5 that the methyl group rotates as the reaction proceeds from RC to TS and to PC. In the RC there is a relatively weak hydrogen bond, HB_a (Cl···H−C), while there is a strong H bond in the PC, HB_b(C−H···F). Detailed analysis of the structures reveals that H−C bonds in the RC rotate 120° clockwise successively as the reaction proceeds from RC to TS and to PC (altogether 240° from RC to PC). The weak HB_a bond in the RC is broken in the activation to the TS, and the strong HB_b bond is formed in the PC. However, the energy required to break the HB_a in the RC is included in the activation energy (36.83 kcal/mol), while the energy released by the HB_b formation in the PC is included in the energy released in PC formation, $E_{PC} - E_{TS}$ (−15.29 kcal/mol). As a result no additional critical points are formed on the PES due to the methyl rotation, as we have confirmed by IRC results.

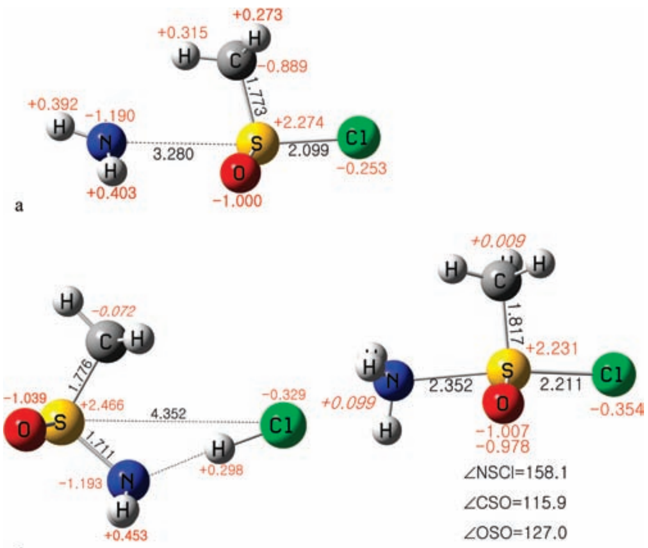

Figure 7. Structures of reactants, a, and products complexes, b, and TS, c, for reaction (N,Cl) at the MP2/6-31+G* level. Bond lengths are in angstroms, and italic numbers refer to the atomic charge with hydrogens summed into the heteroatoms. The side views that show the symmetry plane in RC and PC are in Figure S2 in Supporting Information.

As has been shown above, rough comparison of the sulfonyl transfer reaction ($Cl^- + MeSO_2F$) with the corresponding methyl transfer reaction ($Cl^- + MeF$) indicates that all the complexes and TS are far more stabilized in the sulfonyl transfer; e.g., the RC is −18.55 kcal/mol (at the **a** level) relative to the reactants level for the former but is only −8.27 kcal/mol (at the B3LYP/aug-cc-pVDZ level)[27] for the latter.

Reaction (N,Cl). The RC and PC have *Cs* symmetry and maintain the tetrahedral geometry of the original substrate $MeSO_2Cl$ (Figure 7). The symmetry plane in these complexes bisects three angles, ∠OSO, ∠HCH, and ∠HNH. Thus there are two extra H atoms, one each from CH_3 and NH_3, on this plane and the coplanar H from the ammonia forms a H-bond with the departing Cl^- in the PC. In this case, out-of-plane bonds are three sets, i.e., two C−H, two S−O, and two N−H bonds, and vicinal charge transfer stabilizations, −8.52 kcal/mol and −13.31 kcal/mol in the RC and PC respectively, are provided by interactions between them, $\sigma_{CH} \rightarrow \sigma^*_{SO}$, $\sigma_{NH} \rightarrow \sigma^*_{SO}$, and $\sigma_{NH} \rightarrow \sigma^*_{CH}$. The TS has a distorted pseudo-TBP geometry (∠NSCl = 158.1°) with a relatively lower degree of bond formation and bond cleavage as presented in Figure 7. The PES for this reaction at level **b** is shown in Figure 8. Notable features are that the products ($NH_3^+MeSO_2 + Cl^-$) level is much higher (by 129.37 kcal/mol) than the reactants level, but the PC (dipole moment = 0.860 D) level is lower than the RC (4.091 D) level (by 1.69 kcal/mol) so that the TS is at an early stage in the reaction coordinate resembling the energetically nearer RC in accordance with the Hammond postulate. The NBO analysis shows that the axial N−S−Cl linkage does not form an *ω* bond and d orbital participation of the central S atom is small (2.51%). Thus the main stabilizing interaction in the TS is vicinal charge transfer interactions of the type $n_O \rightarrow \sigma^*_{SCl}$ ($\Delta E^{(2)} = -101.96$ kcal/mol), $n_O \rightarrow \sigma^*_{SO}$ ($\Delta E^{(2)} = -67.93$ kcal/mol) and $n_N \rightarrow \sigma^*_{SCl}$ ($\Delta E^{(2)} = -27.73$ kcal/mol). The activation barrier is relatively high (29.55 kcal/mol) so that gas-phase reaction will be difficult to proceed in the forward direction, but the reverse process will be facile since it is barrierless (−99.82 kcal/mol).

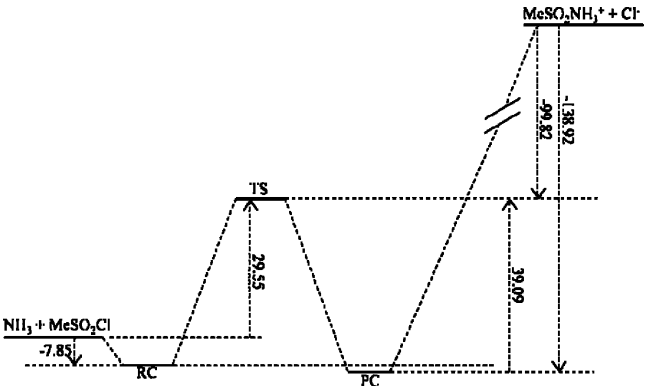

Figure 8. The PES for reaction (N,Cl) at the MP2/6-31+G* level. Energy differences are in kcal/mol.

Comparison of the present aminolysis of sulfonyl chloride, $NH_3 + MeSO_2Cl$, with the corresponding aminolysis of methyl chloride,[28] $NH_3 + MeCl$, shows interesting similarities and differences in the PES profiles. Both reactions proceed via a double-well PES, but in the former the RC and PC (−5.59 and −7.54 kcal/mol, respectively, at the B3LYP/6-311+G** level) are far more stabilizing than those of the latter (−1.2 and +30.5 kcal/mol, respectively, at the B3PW97/6-31+G* level).[27] There is a large difference in the PC level (relative to the reactants); it is lower than that of RC in the former (by 1.95 kcal/mol) but is much higher (by 30.5 kcal/mol) in the latter. However the reaction at the sulfonyl center exhibits very high endothermicity whereas the carbon center reaction is relatively less endothermic (+130.8 vs +33.0 kcal/mol). The fact that the PC is more stabilizing than the RC for the aminolysis of sulfonyl chloride is due to stronger vicinal charge transfer interactions between out-of-plane C−H, N−H, and S−O bonds (13.31 kcal/mol), and also due to a strong H-bond formation of the in-plane (N−)H with the departing Cl^- ion (Figure S3 in Supporting Information).

Summary. Four gas-phase nucleophilic substitution reactions, (F,F), (Cl,Cl), (Cl,F), and (N,Cl) are investigated at the B3LYP/6-31G**, B3LYP/6-311+G**, and MP2/6-31+G* levels of theory in the present work. Only the reaction (F,F) proceeds via a triple-well PES with an intermediate, since highly negative fluoride ligands and strongly electropositive central S atom achieve a strong ionic cooperative three-center resonance coupling forming a 3c/4e hyperbond (an *ω*-bond) in the intermediate. The other three reactions showed three different shapes of double well PES with a TS surrounded by reactant (RC) and product (PC) ion-dipole complexes. All the complexes have *Cs* symmetry with a symmetry plane bisecting the angles HCH (of methyl group), OSO (of sulfonyl group), and HNH (of NH_3). This structure provides extra stabilizations by vicinal charge transfer interactions between out-of-plane C−H, S−O, and N−H bonds that are antiperiplanar to each other, and a hydrogen bond formed between the in-plane H and anionic nucleophile or leaving halide ion. In the aminolysis reaction the PC level is lower than the RC level, and the TS is located at an early position along the reaction coordinate in accordance with the Hammond postulate. This presents a striking contrast to a late TS found in the (Cl,F) reaction where the level of PC is higher than that of RC.

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Supporting Information Available: Cartesian coordinates and electronic energies of all the reactants, product complexes, the intermediate, and transition states investigated, and the side views, Figures S1 and S2, to show symmetry planes of RC and PC for reactions (Cl, F) and (N, Cl). This material is available free of charge via the Internet at http://pubs.acs.org.

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