A G2 Study of SH^+ Exchange Reactions Involving Lone-Pair Donors and Unsaturated Hydrocarbons

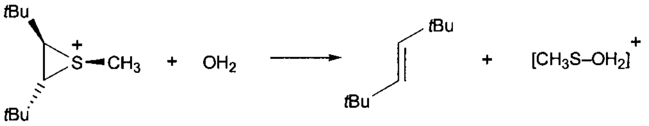
Theis I. Sølling and Leo Radom*[a]

Abstract: The ligand exchange reactions between mono-adducts of the sulfenium ion ($[SH{-}X]^+$) and either unsaturated hydrocarbons or lone-pair donors have been investigated computationally at the G2 level. The mono-adducts react with acetylene or ethylene to form a thiiranium or a thiirenium ion, in most cases without an overall barrier. In the reactions involving lone-pair donors, the original lone-pair donor is expelled from the $[SH{-}X]^+$ mono-adduct with the formation of a new mono-adduct. The reaction proceeds in this case via an intermediate di-adduct. Both the hydrocarbon and the lone-pair donor attack the mono-adduct with the relevant orbitals aligned in a near-collinear fashion, as was also the case for previously investigated reactions involving PH_2^+ and Cl^+. The reaction energies and the binding energies of the intermediate complexes in the exchange reactions are primarily determined by the electronegativities of the lone-pair donors. The thermochemical data can be rationalized within the framework of qualitative molecular orbital theory, and the results are compared with our previous findings for the corresponding reactions involving PH_2^+ and Cl^+.

Keywords: ab initio calculations · donor–acceptor systems · exchange reactions · sulfur heterocycles

Introduction

The intermediacy of thiiranium and thiirenium ions in reactions such as S_N2 and Ad_N-E ring-openings is well established.[1, 2] However, quite apart from being reactive intermediates, thiiranium and thiirenium ions bearing bulky substituents (such as *tert*-butyl or phenyl groups) have been isolated as shelf-stable salts[1, 3] and their chemistry has been investigated both experimentally[4, 5] and theoretically.[6–8] In particular, Modena and co-workers[4] have found that water attacks thiiranium ions at sulfur in an exchange reaction in which *O*-protonated methyl sulfenic acid and an alkene are formed, as shown in Scheme 1.[4]



Scheme 1. Attack by water at sulfur of thiiranium ions.

The reactions of thiiranium ions with disulfides were examined in a recent experimental investigation.[5] The products in this case are a new thiiranium ion and a new disulfide. It was argued that the reaction initially produces an alkene and an adduct between the disulfide and the alkyl sulfenium ion. This adduct can then react with the alkene through two different sulfur atoms, either reforming the original reactants or producing the new thiiranium ion and disulfide. This is exemplified by Scheme 2. On the basis of calculations and an investigation of the reaction kinetics, it was concluded that the reaction is specific with regard to the approach direction of the base.[5]

In recent high-level ab initio investigations, we have examined related exchange reactions involving PH_2^+ and Cl^+ plus a range of bases,[9–13] for which similar reactions have been observed experimentally.[14–16] Our calculations showed that exchange proceeds with little or no barrier in these systems. We found both for the phosphorus and chlorine systems and for exchange reactions involving thiiranium or thiirenium ions and unsaturated hydrocarbons that the base approaches so that the relevant orbitals are aligned in a near-collinear manner (**a**, Scheme 3). On the other hand, Modena et al.[5] concluded that for related sulfur systems the base approaches in a perpendicular manner (**b**, Scheme 3).

These two sets of results are in apparent conflict.[17, 18] In order to explore the possible reasons for this apparent discrepancy, we have embarked on a systematic ab initio investigation of the exchange reactions between unsaturated

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author: G2 total energies (Table S1) and GAUSSIAN archive entries for the MP2(full)/6-31G(d) optimized geometries (Table S2) are available.

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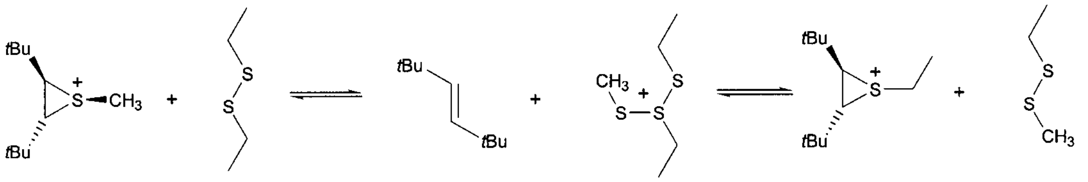
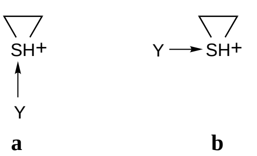


Scheme 2. Reaction of disulfide adduct with the alkene through two different sulfur atoms.



Scheme 3. Approach of the base so that the orbitals are near-collinear (**a**) or perpendicular (**b**).

hydrocarbons and mono-adducts of the sulfenium ion, for example, $[SH{-}SH_2]^+$, to form thiiranium or thiirenium ions.

We have previously found[13, 19] that the exchange processes involving Lewis bases and PH_2^+ or Cl^+ mono-adducts proceed via a di-adduct without the intervention of transition structures. This is exemplified by Scheme 4.

$$H_3N + [Cl{-}NH_3]^+ \longrightarrow [H_3N{-}Cl{-}NH_3]^+ \longrightarrow [H_3N{-}Cl]^+ + NH_3$$

Scheme 4. Example of an exchange reaction that involves a Lewis base and a Cl^+ mono-adduct.

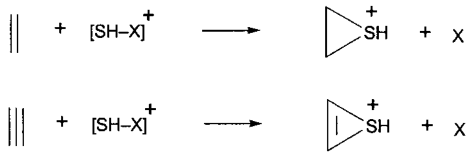
The binding energy of the intermediate di-adduct and the overall reaction energy were found to be closely related to the electronegativity of the involved bases. In the present study, we focus attention on the corresponding sulfur systems in order to investigate whether they behave in a similar manner and use the results to assist with our understanding of the variations encountered in reaction energies and binding energies of the mono- and di-adducts in the series PH_2^+, SH^+, and Cl^+. We note that proton transfer from the mono-adducts represents a plausible alternative pathway to exchange. However a detailed investigation of proton-transfer reactions is beyond the scope of this study and will be presented elsewhere.

Computational Methods

Ab initio molecular orbital calculations[20] were carried out by using a modified form of G2 theory[21] with the GAUSSIAN 94,[22] GAUSSIAN 98,[23] and MOLPRO 96[24] systems of programs. G2 theory corresponds effectively to a QCISD(T)/6-311 + G(3df,2p) single-point calculation on MP2(full)/6-31G(d) optimized geometries, which incorporates scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs), and a so-called higher-level correction. G2 theory was developed by Curtiss et al.[21] with the aim of obtaining thermochemical properties within chemical accuracy (10 kJ mol^{-1}). It has been shown to perform well in the calculation of ionization energies, electron affinities, bond energies, proton affinities, acidities, and reaction barriers.[21, 25] We have employed a slightly modified version of G2 theory to make possible direct comparisons with our previous results for the corresponding chlorine and phosphorus systems.[12, 13, 19] The modification was to use ZPVEs calculated from MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by a factor of 0.9646[26] rather than from scaled HF/6-31G(d) frequencies. The method is formally referred to as G2(ZPE = MP2),[27] but we use the G2 label here for the sake of brevity. The transition structures for the reactions reported in this work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate analysis. Relative energies within the text correspond to G2 values at 0 K unless noted otherwise. The calculated total energies are available as Supporting Information (Table S1), which also includes the MP2(full)/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries (Table S2).

Results and Discussion

Exchange reactions involving unsaturated hydrocarbons and mono-adducts ($[SH{-}X]^+$): We have investigated two series of prototypical exchange reactions between unsaturated hydrocarbons and mono-adducts of the sulfenium ion in order to model the formation of either a thiiranium or a thiirenium ion (Scheme 5), and (in the reverse direction) the exchange reactions in Schemes 1 and 2.



X = NH_3, H_2O, HF, PH_3, H_2S, or HCl

Scheme 5. Prototypical exchange reactions between unsaturated hydrocarbons and mono-adducts of the sulfenium ion.

The species involved in the lowest energy pathway are presented in Figures 1 and 2, in which selected geometrical parameters optimized at MP2(full)/6-31G(d) are included. The relevant thermochemical data are given in Tables 1 and 2.

The reactions between ethylene and a mono-adduct to form a thiiranium ion and a free base are accompanied by a substantial exothermicity in all but one case (Table 1). In the exothermic reactions the reactants initially combine, without a barrier, to form a complex which then dissociates, without a reverse barrier, to products (Figure 3). The reaction is endothermic when phosphine is involved. In this case, ethylene combines with $[SH{-}PH_3]^+$ to form a reactant complex which is connected to a product complex between the thiiranium ion and phosphine via the transition structure (TS) **4** → **5** (Figure 1) at 35.8 kJ mol^{-1} relative to the reactants (11.6 kJ mol^{-1} relative to the products).

For the acetylene systems, two of the investigated reactions are endothermic (Table 2), and there is also an energy barrier between the reactant and product complexes in these cases. The remaining reactions have exothermicities in the range 43.7 to 322.1 kJ mol^{-1}. In the least exothermic reaction (acetylene plus $[SH{-}SH_2]^+$), there is also an intermediate

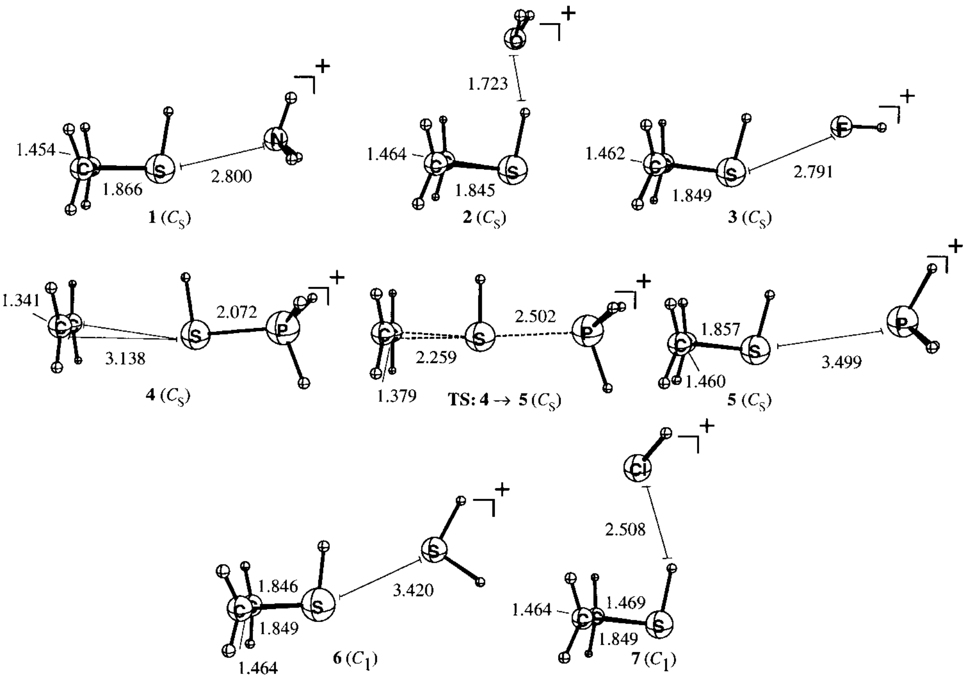


Figure 1. Optimized geometries (MP2(full)/6-31G(d)) of the species involved in the exchange reactions between ethylene and $[SH{-}X]^+$.

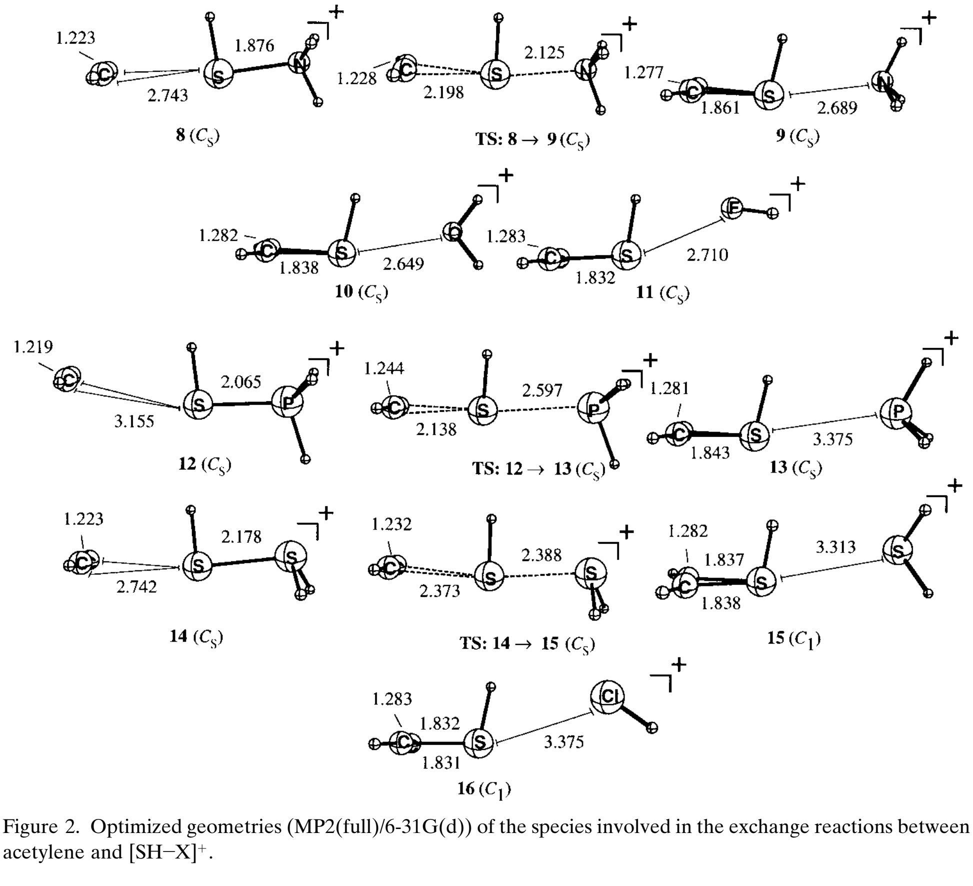


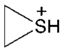
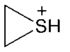
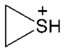
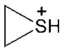
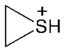
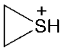
Figure 2. Optimized geometries (MP2(full)/6-31G(d)) of the species involved in the exchange reactions between acetylene and $[SH{-}X]^+$.

barrier, while in the case of the remaining exothermic reactions it disappears. For all the exchange reactions involving acetylene in which there is a central transition structure, it does not impose any additional constraints on the energy which is required for the reaction to occur.

The reaction energies lie between −375.1 and +24.2 kJ mol^{-1} for the reactions involving ethylene. The range is −322.1 to +77.2 kJ mol^{-1} in the case of acetylene. We note that the reaction exothermicities increase as the electronegativity of the donor within the mono-adduct increases (within a row). In addition, the reactions involving first-row donors are less exothermic (or more endothermic) than those involving the corresponding second-row donors. This largely reflects the relative stabilities, which are related to the donor properties of the Lewis base (see below), of the mono-adducts.

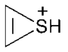
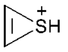
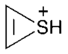
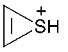
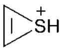
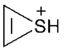
Geometries of complexes and transition structures: The exchange reactions of unsaturated hydrocarbons with mono-adducts of the sulfenium ion generally proceed via an intermediate complex without the intervention of a transition structure. The intermediate generally resembles a product-like complex in which a Lewis base is coordinated to the heterocyclic ion (Figures 1 and 2). It is quite common, as in the present case, that such complexes in exothermic reactions resemble the lower energy side of the well, a behavior that has been referred to as the analogue of Hammond's postulate for complexes.[28] There is a tendency for the coordination direction in the complexes to be distorted from collinearity because of the intervention of a hydrogen-bonding interaction between S–H$^+$ and the Lewis base. For X = H_2O and HCl, this is the key influence in determining the structure (complexes **2** and **7**, Figure 1). In these cases, the structures in which the base is coordinated in a near-collinear manner do not correspond to minima. The complex between HF and the thiiranium ion does exist, however, in two forms, one with the hydrogen-bonded structure and the other with the near-collinear structure (**3**). The latter is formed when the

Table 1. Barriers, reaction energies (ΔE_r), and binding energies of reactant ($\Delta E_{r\text{-comp}}$) and product ($\Delta E_{p\text{-comp}}$) complexes in exchange reactions involving ethylene.[a]

Reaction	$\Delta E_{r\text{-comp}}$[b]	Barrier[c]	$\Delta E_{p\text{-comp}}$[d]	ΔE_r
‖ + $[SH{-}NH_3]^+$ ⟶  + NH_3	[e]	[e]	52.1	−47.7
‖ + $[SH{-}OH_2]^+$ ⟶  + OH_2	[e]	[e]	60.4	−210.0
‖ + $[SH{-}FH]^+$ ⟶  + FH	[e]	[e]	32.2	−375.1
‖ + $[SH{-}PH_3]^+$ ⟶  + PH_3	24.5	35.8	40.1	24.2
‖ + $[SH{-}SH_2]^+$ ⟶  + SH_2	[e]	[e]	25.3	−96.7
‖ + $[SH{-}ClH]^+$ ⟶  + ClH	[e]	[e]	25.9	−259.2

[a] G2 values in kJ mol^{-1} at 0 K. [b] Reactant complex, binding energy relative to reactants. [c] Relative to reactants. [d] Product complex, binding energy relative to products. [e] Reaction proceeds directly from reactants to product complex without a barrier.

Table 2. Barriers, reaction energies (ΔE_r), and binding energies of reactant ($\Delta E_{r\text{-comp}}$) and product ($\Delta E_{p\text{-comp}}$) complexes in exchange reactions involving acetylene.[a]

Reaction	$\Delta E_{r\text{-comp}}$[b]	Barrier[c]	$\Delta E_{p\text{-comp}}$[d]	ΔE_r
⫴ + $[SH{-}NH_3]^+$ ⟶  + NH_3	52.1	−28.6	43.3	5.3
⫴ + $[SH{-}OH_2]^+$ ⟶  + OH_2	[e]	[e]	48.2	−157.1
⫴ + $[SH{-}FH]^+$ ⟶  + FH	[e]	[e]	32.4	−322.1
⫴ + $[SH{-}PH_3]^+$ ⟶  + PH_3	23.8	67.1	31.9	77.2
⫴ + $[SH{-}SH_2]^+$ ⟶  + SH_2	35.9	−28.9	28.5	−43.7
⫴ + $[SH{-}ClH]^+$ ⟶  + ClH	[e]	[e]	19.5	−206.2

[a] G2 values in kJ mol^{-1} at 0 K. [b] Reactant complex, binding energies relative to reactants. [c] Relative to reactants. [d] Product complex, binding energy relative to products. [e] Reaction proceeds directly from reactants to a product complex without a barrier.

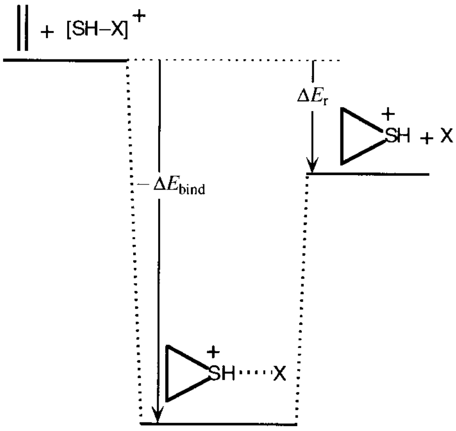
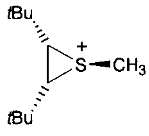


Figure 3. Schematic potential energy profile for the situation in which ethylene and a mono-adduct combine to form a complex which then dissociates to give a thiiranium ion and a free base, with no intermediate barriers.

unsaturated hydrocarbon approaches $[SH{-}FH]^+$. The hydrogen-bonded structure lies 9.6 kJ mol^{-1} higher in energy than **3**. For the three reactions in which there is an intermediate barrier, the transition structures are all quite similar (Figures 1 and 2) with the relevant donor and acceptor orbitals of the unsaturated hydrocarbon, SH^+, and Lewis base arranged in a near-collinear manner.

Comparison of the computational and experimental results for exchange between unsaturated hydrocarbons and mono-adducts: The exchange reactions between H_2O or H_2S and a thiiranium or a thiirenium ion (forming the corresponding mono-adduct and unsaturated hydrocarbon), that is, the reverse of the reactions shown in Scheme 1, proceed without an intermediate energy barrier in addition to the endothermicities, which are quite substantial (43.7 to 210.0 kJ mol^{-1}). Thus, it is quite surprising at first glance that related reactions have been observed to proceed, although with small rate constants, in the condensed phase.[4, 5]

We have considered in the first place whether this apparent disagreement between experiment and the calculations could arise because the systems under theoretical study are poor models for the experimentally investigated reactions between dialkyldisulfides and thiirenium or thiiranium ions with *S*-alkyl substituents and bulky substituents at carbon (the alkyl substitution in the heterocycles being required in order to make the systems sufficiently stable for an experimental study). We have therefore carried out calculations for the reaction between dimethyldisulfide and a thiiranium ion. At the B3-LYP/6-31G(d) level,[29] this reaction is endothermic by only 5.5 kJ mol^{-1}, while at the more reliable (but computationally much more expensive) G2 level the reaction is *exothermic* by 23.9 kJ mol^{-1}. This could be taken to indicate that the experimentally investigated reactions might actually be exothermic. However, the introduction of a methyl group on sulfur in the thiiranium ion and of bulky substituents at carbon work in the opposite direction. For example, the exchange reactions involving dimethyldisulfide and **17**, **18**, or **19** are calculated to be endothermic with B3-LYP/6-31G(d) values[29] of 86.4, 66.7, and 88.4 kJ mol^{-1}, respectively, suggesting G2 values of 57.0, 37.3, and 59.0 kJ mol^{-1}, respectively. These values are smaller than for the parent system.[30] The reduced endothermicities calculated for the dimethyldisulfide reactions could be taken to indicate that the experimental observation of the exchange reactions is no longer in conflict with the calculations.



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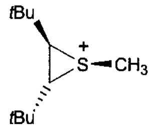

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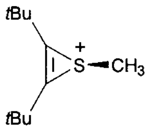

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We have also investigated whether a substantial solvent effect is in play. For example, the bulky substituents could possibly result in a relatively poor solvation of the heterocyclic ions. This would cause the heterocycle/base pair to be destabilized relative to the $[SH{-}X]^+$/hydrocarbon pair and, therefore, result in a decreased endothermicity for exchange. We have employed the polarizable continuum model (PCM) of Tomasi[31] at the B3-LYP/6-31G(d) level as incorporated in GAUSSIAN 98 to model solvation by CH_2Cl_2.[23] Single-point PCM energy calculations on gas-phase B3-LYP/6-31G(d) geometries do not indicate the existence of a substantial solvent effect. For example, for the reaction between dimethyldisulfide and **17**, the reaction energy was found to be reduced only slightly from 86.4 to 81.9 kJ mol^{-1}. This was also the case for the corresponding reactions involving **18** and **19**.

The only remaining apparent conflict with experiment concerns the approach direction of the base to the heterocycle. Modena[5] concluded on the basis of the observed reaction kinetics and from an HF/3-21G(d) natural charge analysis that a perpendicular approach (**b**, Scheme 3) is the appropriate description of the base attack on the heterocycle. On the other hand, the present theoretical results for the transition structures and intermediate complexes seem to indicate that the base preferentially attacks so that the appropriate orbitals are aligned in a near-collinear fashion (**a**, Scheme 3). This was also found to be the case in the exchange reactions involving unsaturated hydrocarbons and thiiranium or thiirenium ions[8] and for the corresponding phosphorus and chlorine systems that we have investigated previously.[12, 13] Modena[17] postulated that the apparent discrepancy with the previous theoretical results[8] could be due to a difference in behavior of σ and π nucleophiles. However, our present results show that the approach directions of σ and π nucleophiles are similar.[18]

The strongest evidence put forward for the perpendicular attack in the analysis of the reaction kinetics appears to be that the rate constants for exchange reactions involving thiiranium ions decrease as the substituents at *both* carbon and sulfur become more bulky.[5] On the other hand, Modena[5] found that the rate constants for exchange involving thiirenium ions are insensitive to whether the thiirenium ion is substituted with two *tert*-butyl groups at the carbons or with one *tert*-butyl group and one adamantyl group, but that the rate constant for exchange is highly sensitive to the bulkiness of the substituent at sulfur.[5] These latter results seem to be more consistent with the near-collinear approach of the Lewis base.

In order to investigate whether the approach directions in solution (CH_2Cl_2) differ from those in the gas phase, we have (again) employed the PCM to model solvation.[31] This procedure has previously been shown to give reliable results for the potential energy profile of S_N2 reactions in solution.[32] The reaction between ammonia and the thiiranium ion was chosen as a model system in the investigation. All our attempts to find a transition structure corresponding to the perpendicular approach direction of Modena led eventually to a collinear transition structure (Figure 4). It is worth noting that the incorporation of solvent introduces a first-order saddle point on the exchange potential energy surface.

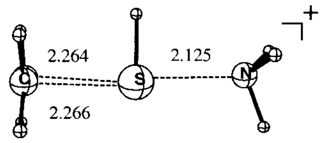

Figure 4. Optimized geometry (B3-LYP/6-31G(d), PCM) of the transition structure for the exchange reaction of the thiiranium ion plus NH_3 in methylene chloride.

The possibility of a front-side attack on the three-membered ring was not considered in the experimental study,[5] even though this mechanism would also seem to be consistent with the experimental result that the rate constant for exchange is sensitive to the size of the substituents at both carbon and sulfur. We find (at the G2 level) that there is indeed a transition structure corresponding to this mode of approach. However, it lies very high in energy. In the case of the reaction between NH_3 and the thiiranium ion, the calculated gas-phase barrier relative to the reactants is 144.0 kJ mol^{-1}. The optimized geometries of the involved transition structure and complexes are presented in Figure 5. It is seen that the product complex yet again is hydrogen bonded, but because of the large proton affinity of ammonia, a complex between the ammonium ion and neutral thiirane is favored in this case. It is noteworthy that we have previously found two pathways for exchange in the reactions involving thiiranium or thiirenium ions and unsaturated hydrocarbons:[8] a high-energy pathway that corresponds to the mode of approach depicted in Figure 5 and the near-collinear lower energy pathway.

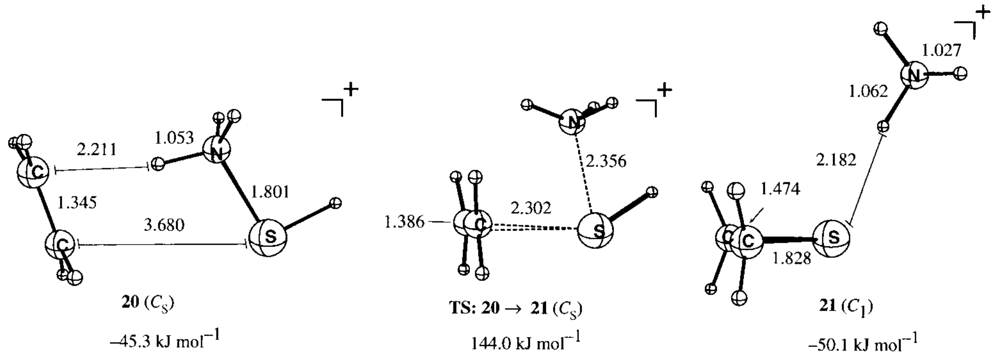

Figure 5. Optimized geometries (MP2(full)/6-31G(d)) of the species involved in the front-side attack of ethylene on $[SH{-}NH_3]^+$. Energies in kJ mol^{-1} (relative to the reactants).

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Exchange reactions involving mono-adducts and lone-pair donors: In order to obtain a better understanding of how the donor properties of the reactant influence the exchange reactions, we have included an investigation of the reactions involving the possible combinations of first- and second-row donors (Y), that is, NH_3, H_2O, HF, PH_3, H_2S, and HCl, and mono-adducts thereof ($[SH{-}X]^+$). The prototypical reaction is shown in Scheme 6.

$$\mathrm{Y} + [\mathrm{SH{-}X}]^+ \longrightarrow [\mathrm{Y{-}SH}]^+ + \mathrm{X}$$

Scheme 6. Reaction involving the possible combinations of first- and second-row donors (Y) and the mono-adducts thereof ($[SH{-}X]^+$).

These reactions are generally found to proceed via an intermediate di-adduct $[Y\text{-}SH\text{-}X]^+$ without the intervention of a transition structure. The only exception to this general reactivity pattern is found in the reaction involving phosphine and its mono-adduct $[SH{-}PH_3]^+$. In this case there are two equivalent asymmetric di-adducts, separated by an intermediate barrier of 26.3 kJ mol^{-1} (relative to the asymmetric di-adducts). Selected geometrical parameters, optimized at MP2(full)/6-31G(d), of the mono- and di-adducts are presented in Tables 3 and 4, while the binding energies and reaction energies are given in Tables 5, 6, 7, and 8.

Table 3. Selected optimized (MP2(full)/6-31G(d)) geometrical parameters of the mono-adducts $[SH{-}X]^+$ formed between SH^+ and a Lewis base.

$[SH{-}X]^+$	$r(S{-}X)$[a]
$[SH{-}NH_3]^+$ (C_s)	1.813
$[SH{-}OH_2]^+$ (C_s)	1.804
$[SH{-}FH]^+$ (C_1)	1.853
$[SH{-}PH_3]^+$ (C_s)	2.054
$[SH{-}SH_2]^+$ (C_s)	2.083
$[SH{-}ClH]^+$ (C_1)	2.108

[a] Bond lengths in Å.

Geometries of di-adducts—relation to the exchange reactions involving unsaturated hydrocarbons: The results for the geometries of the di-adducts between SH^+ and two Lewis bases ($[Y\text{-}SH\text{-}X]^+$) (Table 4) are in line with the results for the transition structures and intermediate complexes involved in the exchange reactions between mono-adducts and unsaturated hydrocarbons. In particular, it is noteworthy that the YSX angles lie in the range 176.0–153.8°. This is consistent with the near-collinear alignment of the relevant orbitals found for the exchange reactions involving SH^+ mono-adducts and unsaturated hydrocarbons in the present study and for the related chlorine and phosphorus exchange reactions involving mono-adducts, lone-pair donors, and unsaturated hydrocarbons investigated previously.[12, 13, 19]

Reaction and binding energies of the di- and mono-adducts: The variations in binding energies with X and Y for the corresponding di-adducts formed from reactions of Y with $[PH_2{-}X]^+$ or $[Cl{-}X]^+$ have been rationalized previously[13, 19]

Table 4. Selected optimized (MP2(full)/6-31G(d)) geometrical parameters of the intermediate di-adducts ($[Y\text{-}SH\text{-}X]^+$) between SH^+ and two Lewis bases (Y and X).

$[Y\text{-}SH\text{-}X]^+$	$r(Y{-}S)$[a]	$r(S{-}X)$[a]	$\measuredangle$YSX[b]
$[H_3N\text{-}SH\text{-}NH_3]^+$ (C_{2v})	2.061	2.061	171.6
$[H_3N\text{-}SH\text{-}OH_2]^+$ (C_s)	1.880	2.302	167.0
$[H_3N\text{-}SH\text{-}FH]^+$ (C_s)	1.829	2.517	162.8
$[H_2O\text{-}SH\text{-}OH_2]^+$ (C_s)	2.002	2.007	171.2
$[H_2O\text{-}SH\text{-}FH]^+$ (C_s)	1.854	2.280	165.1
$[HF\text{-}SH\text{-}FH]^+$ (C_2)	2.008	2.008	169.1
$[H_3P\text{-}SH\text{-}PH_3]^+$ (C_s)[c]	2.074	3.270	172.0
$[H_3P\text{-}SH\text{-}SH_2]^+$ (C_s)	2.066	3.278	164.6
$[H_3P\text{-}SH\text{-}ClH]^+$ (C_s)	2.056	3.369	158.5
$[H_2S\text{-}SH\text{-}SH_2]^+$ (C_s)	2.489	2.385	176.0
$[H_2S\text{-}SH\text{-}ClH]^+$ (C_1)	2.101	3.111	166.1
$[HCl\text{-}SH\text{-}ClH]^+$ (C_2)	2.406	2.406	174.7
$[H_3N\text{-}SH\text{-}PH_3]^+$ (C_s)	2.540	2.107	172.2
$[H_3N\text{-}SH\text{-}SH_2]^+$ (C_s)	1.921	2.700	170.7
$[H_3N\text{-}SH\text{-}ClH]^+$ (C_s)	1.829	3.068	167.8
$[H_2O\text{-}SH\text{-}PH_3]^+$ (C_s)	2.683	2.061	157.9
$[H_2O\text{-}SH\text{-}SH_2]^+$ (C_s)	2.339	2.155	170.0
$[H_2O\text{-}SH\text{-}ClH]^+$ (C_1)	1.889	2.656	170.4
$[HF\text{-}SH\text{-}PH_3]^+$ (C_s)	2.761	2.053	153.8
$[HF\text{-}SH\text{-}SH_2]^+$ (C_s)	2.582	2.095	159.4
$[HF\text{-}SH\text{-}ClH]^+$ (C_1)	2.263	2.188	169.2

[a] Bond lengths in Å. [b] Angles in degrees. [c] Connected to an equivalent C_s structure by a C_{2v} transition structure with $r(S{-}P) = 2.427$ Å, $\measuredangle PSP = 178.7°$.

Table 5. Reaction energies (ΔE_r) for exchange processes involving first-row donors and binding energies (ΔE_{bind}) of the intermediate di-adduct.[a]

Y	$[SH{-}X]^+$	ΔE_{bind}[b]	ΔE_r[c]
NH_3	$[SH{-}NH_3]^+$	100.4	0.0
H_2O		54.7	162.4
HF		29.2	327.4
NH_3	$[SH{-}OH_2]^+$	217.1	− 162.4
H_2O		97.6	0.0
HF		39.4	165.2
NH_3	$[SH{-}FH]^+$	356.6	− 327.4
H_2O		204.4	− 165.0
HF		75.9	0.0

[a] G2 values in kJ mol^{-1} at 0 K. [b] Binding energy of $[Y\text{-}SH\text{-}X]^+$ relative to Y plus $[SH{-}X]^+$. [c] Energy of $[Y{-}SH]^+$ plus X relative to Y plus $[SH{-}X]^+$.

Table 6. Reaction energies (ΔE_r) for exchange processes involving second-row donors and binding energies (ΔE_{bind}) of the intermediate di-adduct.[a]

Y	$[SH{-}X]^+$	ΔE_{bind}[b]	ΔE_r[c]
PH_3	$[SH{-}PH_3]^+$	26.8[d]	0.0
H_2S		24.4	120.9
HCl		16.6	283.0
PH_3	$[SH{-}SH_2]^+$	145.3	− 120.9
H_2S		45.9	0.0
HCl		22.4	162.5
PH_3	$[SH{-}ClH]^+$	300.0	− 283.4
H_2S		184.9	− 162.5
HCl		52.5	0.0

[a] G2 values in kJ mol^{-1} at 0 K. [b] Binding energy of $[Y\text{-}SH\text{-}X]^+$ relative to Y plus $[SH{-}X]^+$. [c] Energy of $[Y{-}SH]^+$ plus X relative to Y plus $[SH{-}X]^+$. [d] Two intermediate complexes are connected by a C_{2v} transition structure at 26.3 kJ mol^{-1} relative to the di-adduct.

Table 7. Reaction energies (ΔE_r) for exchange processes between first-row donors plus mono-adducts of SH^+ and a second-row donor, and binding energies (ΔE_{bind}) of the intermediate di-adduct.[a]

Y	$[SH{-}X]^+$	ΔE_{bind}[b]	ΔE_r[c]
NH_3	$[SH{-}PH_3]^+$	48.6	71.8
H_2O		40.9	234.2
HF		26.8	399.3
NH_3	$[SH{-}SH_2]^+$	98.9	− 49.1
H_2O		44.4	113.3
HF		29.6	278.4
NH_3	$[SH{-}ClH]^+$	234.9	− 211.6
H_2O		97.3	− 49.2
HF		36.7	115.9

[a] G2 values in kJ mol^{-1} at 0 K. [b] Binding energy of $[Y\text{-}SH\text{-}X]^+$ relative to Y plus $[SH{-}X]^+$. [c] Energy of $[Y{-}SH]^+$ plus X relative to Y plus $[SH{-}X]^+$.

Table 8. Reaction energies (ΔE_r) for exchange processes between second-row donors plus mono-adducts of SH^+ and a first-row donor, and binding energies (ΔE_{bind}) of the intermediate di-adduct.[a]

Y	$[SH{-}X]^+$	ΔE_{bind}[b]	ΔE_r[c]
PH_3	$[SH{-}NH_3]^+$	120.5	− 71.8
H_2S		49.8	49.1
HCl		23.3	211.6
PH_3	$[SH{-}OH_2]^+$	275.2	−234.2
H_2S		157.9	− 113.3
HCl		48.1	49.2
PH_3	$[SH{-}FH]^+$	426.1	− 399.3
H_2S		308.0	− 278.4
HCl		152.6	− 115.9

[a] G2 values in kJ mol^{-1} at 0 K. [b] Binding energy of $[Y\text{-}SH\text{-}X]^+$ relative to Y plus $[SH{-}X]^+$. [c] Energy of $[Y{-}SH]^+$ plus X relative to Y plus $[SH{-}X]^+$.

Table 9. Binding energies of mono-adducts formed from a Lewis base and either PH_2^+, SH^+, or Cl^+.[a]

Mono-adduct	ΔE_{bind}	Mono-adduct	ΔE_{bind}	Mono-adduct	ΔE_{bind}
$[PH_2{-}NH_3]^+$ (C_s)	347.4	$[SH{-}NH_3]^+$ (C_s)	466.3	$[Cl{-}NH_3]^+$ (C_{3v})	801.1
$[PH_2{-}OH_2]^+$ (C_1)	230.1	$[SH{-}OH_2]^+$ (C_s)	303.4	$[Cl{-}OH_2]^+$ (C_s)	573.3
$[PH_2{-}FH]^+$ (C_s)	110.3	$[SH{-}FH]^+$ (C_1)	138.8	$[Cl{-}FH]^+$ (C_s)	360.0
$[PH_2{-}PH_3]^+$ (C_s)	340.7	$[SH{-}PH_3]^+$ (C_s)	538.1	$[Cl{-}PH_3]^+$ (C_{3v})	947.0
$[PH_2{-}SH_2]^+$ (C_1)	263.4	$[SH{-}SH_2]^+$ (C_s)	411.1	$[Cl{-}SH_2]^+$ (C_s)	779.5
$[PH_2{-}ClH]^+$ (C_s)	159.2	$[SH{-}ClH]^+$ (C_1)	254.7	$[Cl{-}ClH]^+$ (C_s)	552.3

[a] G2 values in kJ mol^{-1} at 0 K. Binding energies are given relative to the separated cation plus Lewis base. We have used the $^1A_1$ state of PH_2^+, the $^1\Sigma_g$ state of SH^+, and the ^1D state of Cl^+ because we are mainly interested in the interaction between the empty p-orbital on the cation and the lone pair on the base. Binding energies relative to the $^3\Sigma_g$ ground state of SH^+ or the ^3P ground state of Cl^+ would be decreased by 131.2 and 144.3 kJ mol^{-1}, respectively.

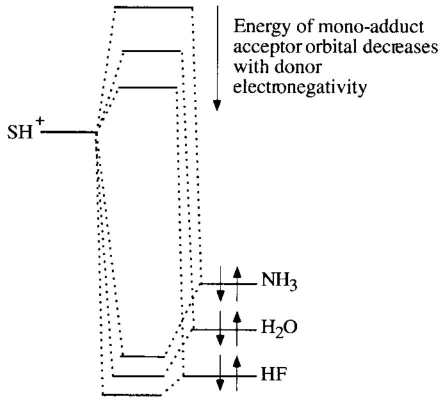

Figure 6. Schematic representation of the interaction of the donor orbitals of Lewis bases with the acceptor orbital of SH^+.

within the framework of qualitative molecular orbital theory.[33] It was noted that the lone-pair (HOMO) energies of the donors decrease along a row and up a column in the periodic table and that the stabilization, which results from the interaction between an acceptor orbital and a donor orbital, is inversely proportional to the energy gap between them.[33, 34] In this manner, it would be expected that the binding energies of the di-adducts formed from a particular mono-adduct and donors from a particular row decrease with the electronegativity of the donor atom, for example, $[H_3N\text{-}SH\text{-}X]^+ > [H_2O\text{-}SH\text{-}X]^+ > [HF\text{-}SH\text{-}X]^+$, and this is indeed observed (Tables 5–8).

The magnitude of the binding energies of the SH^+ mono-adducts (Table 9) can be rationalized in a similar manner. Thus, the binding energies of the mono-adducts formed between SH^+ and donors from a particular row decrease with the electronegativity of the donor atom. Similarly, because the energies of the acceptor orbitals of the mono-adducts decrease (within a row) with the electronegativity of the donor (Figure 6), the binding energies of the di-adducts formed from a particular donor Y and a series of mono-adducts $[SH{-}X]^+$ with bases from a particular row increase with the electronegativity of X.

In addition to the effect of the HOMO–LUMO energy gap, the overlap also influences the strength of the interaction between two orbitals. The overlap effect seems to be most important when weak donors (e.g., HF) or weak acceptors (e.g., $[SH{-}PH_3]^+$) are involved, since the energy gap is large in such cases and results in a smaller contribution from the energy-gap term to the overall binding energy.

The trends in the reaction energies are determined by the relative stabilities of the mono-adducts. This means that when exchange involves donors from a particular row, the reaction proceeds towards the more electronegative donor. The mixed exchange reaction is generally more likely to be exothermic in the direction in which the first-row donor is expelled. The likelihood of observing the di-adduct experimentally is affected by both the reaction and binding energies of the di-adduct. The symmetric di-adducts (e.g., $[NH_3\text{-}SH\text{-}NH_3]^+$) would appear to offer the best prospects for experimental observation.

Comparisons of the exchange reactions involving PH_2^+, SH^+, and Cl^+: The binding energies of the mono-adducts (Table 9) increase in the series $[PH_2{-}X]^+ < [SH{-}X]^+ < [Cl{-}X]^+$, consistent with the better acceptor ability of Cl^+.[35] The sensitivity towards changes in donor abilities increases in the same direction. Variation of X along a row in the periodic table changes the binding energies of $[Cl{-}X]^+$ quite significantly, whereas the change is less pronounced for $[SH{-}X]^+$ and somewhat smaller yet for $[PH_2{-}X]^+$ (Table 9). Again, this can be rationalized in terms of the inverse proportionality of the interaction energy with the energy gap from the donor to the acceptor orbital: since the energy gap is smaller in the case of the Cl^+ systems, there is a larger response from changes in the energy of the donor orbital.

The thermochemistry of the exchange reactions between mono-adducts and Lewis bases follows the trends of the mono-adducts, that is, the chlorine systems give rise to the largest reaction energies, which again is consistent with the large sensitivity towards changes in donor properties for $[Cl{-}X]^+$. The binding energies of Y with $[PH_2{-}X]^+$, $[SH{-}X]^+$, and $[Cl{-}X]^+$ in the di-adducts increase in the order $P < S < Cl$ when first-row donors Y are involved in the exchange reaction.[10, 13] In the case of the second-row donors the trends are less evident, but in most cases the binding energies of the Cl^+ di-adducts are the largest. This indicates that the energies of the acceptor orbitals decrease along the row $[PH_2{-}X]^+ > [SH{-}X]^+ > [Cl{-}X]^+$. Consistent with this, the effect of overlap is found to be the key influence in determining the binding energies of $[Y\text{-}PH_2\text{-}X]^+$, whereas $[Y\text{-}SH\text{-}X]^+$ is less sensitive to overlap and $[Y\text{-}Cl\text{-}X]^+$ even less so.

The reaction energies of the exchange reactions involving mono-adducts and unsaturated hydrocarbons[12, 13] do *not* follow the trends of the mono-adduct binding energies, that is, they do not increase along the row $[PH_2{-}X]^+ < [SH{-}X]^+ < [Cl{-}X]^+$. This is because these reaction energies express the energy of the lone-pair donor/three-membered ring combination relative to the hydrocarbon/mono-adduct combination. Therefore the binding energy of the three-membered ring also has a key influence on the reaction energies. In the case of the exchange reactions between $[PH_2{-}X]^+$ mono-adducts and unsaturated hydrocarbons, an intermediate barrier is found in seven instances;[9] this number reduces to three in the present investigation and in the case of $[Cl{-}X]^+$ there is only an intermediate barrier for a single reaction.[13] This could possibly be due to higher energy demands for the electronic reorganization for the PH_2^+ systems in going from two single bonds in the three-membered ring to a lone pair and a π bond. This expectation is based on the fact that PH_2^+ is a ground-state singlet, whereas SH^+ and Cl^+ are actually ground-state triplets.

Conclusion

Exchange reactions involving mono-adducts of the sulfenium ion and either unsaturated hydrocarbons or Lewis bases proceed in a similar manner to one another and to the previously investigated reactions involving the corresponding chlorine and phosphorus systems. Depending on the reaction energy, exchange for the reactions that involve the unsaturated hydrocarbons proceeds either through a single well or (in the case of the strongly bound mono-adducts leading to endothermic reactions) through a double well.

The transition structures and intermediate complexes generally correspond to a direction of attack on the mono-adduct or three-membered ring such that the relevant orbitals are aligned in a collinear or nearly collinear fashion. This was also the case for the exchange reactions involving PH_2^+ and Cl^+. This result contrasts with the experimental findings of Modena et al.[4, 5] who concluded that the base attacks in a perpendicular manner. This apparent disagreement has been discussed in recent articles.[17, 18] We have addressed the problem further here, but find no evidence for a perpendicular approach direction.

The binding energies of the mono-adducts and intermediate di-adducts and the reaction energies generally increase (in magnitude) in the sequence $PH_2^+ < SH^+ < Cl^+$. This can be rationalized in terms of qualitative molecular orbital theory.

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