Theoretical Studies of the Reactions of Hydrogen Sulfide and Methanethiol with the H, F, and O(^{3}P) Atoms. Possibilities of the Bimolecular Homolytic Substitution (S_H2) Reactions

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Potential energy profiles of the radical substitution reactions of H_2S with some atomic radicals X (X=H, O, F) and of CH_3SH with the hydrogen atom have been investigated by *ab initio* molecular orbital calculations employing the 6-31G** basis sets. All the reactions studied have proved to be elementary reactions with no intermediate adducts involved. At the MRD-CI level using the 6-31G** plus the Rydberg s and p orbitals on sulfur, the activation energies of the homolytic substitution reactions $H_2S+X\rightarrow H+HSX$ are calculated to be 50, 127, and 104 kJ mol^{-1} for X=H, O, and F, respectively, which are uniformly higher than those calculated for the hydrogen abstraction reactions $H_2S+X\rightarrow SH+XH$. For the substitution reaction $CH_3SH+H\rightarrow CH_3+H_2S$, however, the activation energy calculated is as low as 19 kJ mol^{-1}, which is even slightly lower than that for the abstraction $CH_3SH+H\rightarrow CH_3S+H_2$. The predicted prevalence of the homolytic substitution reaction of CH_3SH over the hydrogen abstraction is qualitatively in harmony with observations.

Reactions of organic sulfur compounds are mechanistically intriguing in relation to those of the oxygen homologs. It is known that while the reaction of alcohols with a radical, for example, a hydrogen atom, is exclusively the hydrogen abstraction, not only the abstraction (1a) but the radical substitution (1b) can also take place in the case of thiols.[1,2]

$$\mathrm{RSH + H} \begin{cases} \longrightarrow \mathrm{RS + H_2} & \text{(1a)} \\ \longrightarrow \mathrm{R + H_2S} & \text{(1b)} \end{cases}$$

Pryor and Guard[3] measured the relative rate constants for the reactions of aliphatic disulfides with the phenyl radical in the liquid phase, to suggest that the substitution reaction might proceed by the back-side-attack mechanism similar to the ionic S_N2 reactions.

$$\mathrm{RSSR + Ph \longrightarrow RS + PhSR} \quad (2)$$

The substitution reactions of sulfides with an atom X can formally be divided into the following two categories:

$$\mathrm{RSH + X \rightarrow [R\cdots SH\cdots X]^{\ddagger} \rightarrow R + HSX} \quad (3)$$

$$\mathrm{RSH + X \rightarrow RSH(X) \rightarrow R + HSX} \quad (4)$$

Reaction (3) is a direct substitution, which is in itself an elementary reaction (i.e., bimolecular homolytic substitution, S_H2), while reaction (4) should proceed stepwise (i.e., the addition and the subsequent bond scission). The basic concept underlying the reaction pattern (4) is that an intermediacy of hypervalent adducts might be possible because of the low-lying sulfur d orbitals.

MNDO calculations[5] have predicted that there are stable adducts on both the H_2S+H and CH_3SH+H reactions. They are, however, apparently incompatible with the general features[6] of hypervalent species; namely, (a) the trivalent sulfur compounds (9-S-3)[7] should have the pseudo trigonal bipyramidal structures and (b) the ligands which have a large electronegativity must be present and situated in the apical position to form such structures. For example, the experimental results[8] of ESR spectra have shown that the structure of the SF_3 radical does not have the C_{3v} but the C_{2v} symmetry, even while it has three identical F atoms. Indeed, the *ab initio* SCF and CI calculations of SF_3 and SH_3 explored by Volatron et al.[9] have shown that, while SF_3 is a stable adduct, SH_3 does not have a minimum but is a transition state of the H atoms exchange reaction. In other words, it should correspond to a transition state of the elementary bimolecular reaction (3).

In this paper, we examine the reactions of hydrogen sulfide with the H, O, and F atoms by *ab initio* SCF and MRD-CI computations, paying particular attention to the relative dominance of the abstraction and the substitution. The mechanisms of the reaction CH_3SH+H will also be investigated in a similar manner.

Method of Calculations

All molecular structures, including those for the transition states, were determined by the analytical gradient method.[10] These geometry calculations were first conducted at the 3-21G(*)[11] level. The 3-21G(*) calculations were followed by calculations of the 6-31G**[12] quality. The unrestricted Hartree–Fock (UHF) formalism was availed for all the radical species. The transition states located were verified by the vibrational analyses at the HF/6-31G** level.

All the SCF optimized structures were then subjected to the multi-reference double-excitation configuration interaction (MRD-CI) calculations. The Table MRD-CI program furnished by Buenker[13,14] was used throughout. The configuration-selection and extrapolation routines were followed.[15] The configurations whose contributions $|C_i|^2$ to a state under consideration exceeded 0.3% were selected as reference configurations. The maximal dimension of the con-

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figuration space used was ca. 10000. The extrapolated CI energies ($E_{T\to 0}$) were all subjected to the Langhoff–Davidson corrections,[16] to estimate the full CI limit values.

Two different basis sets were used in the CI calculations. One was the 6-31G** functions, as has been used in the geometry optimizations. The other was the 6-31G** sets augmented with the Rydberg-type s (ζ=0.023) and p (ζ=0.020) functions[17] on sulfur. We will refer to the latter basis sets as Ryd hereafter.

For the sake of comparison, the energies were further computed at the second-order Møller–Plesset perturbation (MP2) as well as the fourth-order perturbation (MP4(SDTQ)) in the single-to-quadruple excitation approximation.[18] All the perturbation calculations were restricted to the valence orbitals only.

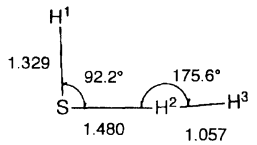
Results

(A)H_2S+H. The H_2S+H system is the simplest prototype of the reaction systems of our present concern. The reaction patterns to be considered here are

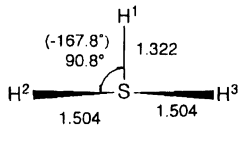
$$H_2S + H \longrightarrow SH + H_2 \quad (5a)$$
$$\longrightarrow H + H_2S \quad (5b)$$

Reaction (5a) is a hydrogen abstraction reaction. Reaction (6b) should be strictly thermoneutral.

The transition state (TS) geometries obtained for these reactions by the UHF/6-31G** method are illustrated in Fig. 1. The transition state (**1**) of the abstraction (reaction (5a)) is planar, with the $<H^3H^2S$ angle being 175.6°. It has one imaginary vibrational frequency ($2280i$ cm^{-1}) in the anti-symmetric stretching mode matching with that of the reaction coordinate. By contrast, in the substitution reaction, the transition state (**2**) is non-planar. It has an almost T-shaped C_s symmetry, as has been demonstrated by Morton et al.[8] using the 4-31G basis sets augmented with polarization and diffuse orbitals on sulfur. Separations of both the incoming (H^3) and outgoing (H^2) atoms from the S atom are relatively large (1.504 Å), while the length of the intact S–H^1 bond remains unaltered (1.322 Å). It should be noted that the T-shaped structure has shown up in the absence of the diffuse functions on sulfur. The imaginary frequency of **2** is calculated to be $1246i$ cm^{-1}.



1 (^{2}A')



2

Fig. 1. Optimized geometries for the transition states of the reactions between H_2S and H. The bond lengths are given in units of Å. The entry given in parentheses indicates the dihedral angle $\phi(H^3SH^1H^2)$. **1**, reaction (5a); **2**, reaction (5b).

The relative energies obtained at various levels of theory are listed in Table 1. At the HF/6-31G** level, the activation energy for the abstraction is $\Delta E^\ddagger$=52 kJ mol^{-1} while that of the substitution is 90 kJ mol^{-1}. As the level of the MP perturbation effect becomes higher, the activation barriers tend to be lowered. At the MP4(SDTQ)/6-31G** level, the activation energies are 31 and 59 kJ mol^{-1}, respectively. The Rydberg-type orbitals on the sulfur atom do not affect the results appreciably. Thus, the abstraction reaction (5b) is predicted to be energetically more favorable than the substitution reaction (5a). At the highest level of the present calculations (CI/Ryd//UHF/6-31G**), the calculated activation barriers $\Delta E^\ddagger$ are 15 and 50 kJ mol^{-1} for the abstraction and the substitution, respectively. When the vibrational zero-point energy corrections at the SCF level are taken into account, the activation energies E_0 come out to be 12 and 51 kJ mol^{-1}, respectively.

(B) H_2S+O(^{3}P). The reaction of H_2S with the ground-state oxygen atom has been a subject of extensive experimental studies by a number of kineticists.[19] Bulk studies[20] have shown that reaction (6a) is the main channel, while the pathway leading to the formation of HSO (reaction (6b)) was estimated to account for only less than 20% of the overall reaction yield. Several groups of workers[21] have investigated the reaction using the molecular beam technique, to conclude that the HSO product scattering favors the backward hemisphere. Moreover, the high translational product energy observed suggests that the reaction (6b) must be a direct process.

$$H_2S + O \longrightarrow SH + OH \quad (6a)$$
$$\longrightarrow H + HSO \quad (6b)$$

As in the case of the H_2S+H reaction, we were unable to locate a stable adduct species. Here again, the substitution reaction (6b) is likely to be an elementary process of the S_H2 type.

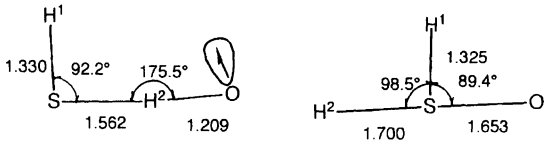
The optimized structures of the transition states for reactions (6a) and (6b) are shown in Fig. 2. For the abstraction reaction (6a) there exist two different transition states. One is the ^{3}A' state while the other, the ^{3}A'' state. Since the total energies little differ from each other, we here deal only with the ^{3}A' state. Thus, the transition state (**3**) of the abstraction is planar, and the O–H^2 and S–H^2 bond lengths are 1.209 and 1.562 Å, respectively. Unlike the H_2S+H system, the transition state (**4**) of the substitution is planar, and the electronic state is ^{3}A''. In the UHF description, one α spin is localized on the O p orbital perpendicular to the symmetry plane, whereas the other exists in the in-plane orbital spread in the direction of the H^2–S–O axis.

We also tried to calculate with different initial geometries to search for other possible optimum geometries. For this purpose, the geometry of singlet sulfox-

Table 1. Total Energies Calculated at Various Levels for the H_2S+H System

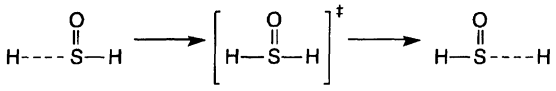
Method	Total energy (hartree)	Relative energies (kJ mol^{-1})[a]		
	E+399 H_2S+H	$\Delta E^{\ddagger}$ **1**(abst.)	$\Delta E^{\ddagger}$ **2**(subst.)	ΔE SH+H_2
HF/6-31G**	−0.17326	52	90	−70
MP2/6-31G**	−0.30826	38	67	−58
MP4(SDTQ)/6-31G**	−0.33195	31	59	−70
CI(full)/6-31G**	−0.32323	14	49	−58
HF/Ryd	−0.17389	51	89	−69
MP2/Ryd	−0.30936	37	66	−58
MP4(SDTQ)/Ryd	−0.33308	29	57	−70
CI(full)/Ryd	−0.32439	15	50	−54

a) Relative to H_2S+H.



3 (^{3}A') **4** (^{3}A")

Fig. 2. Optimized geometries of the transition states of the reactions between H_2S and O(^{3}P). The bond lengths are given in units of Å. **3**, reaction (6a); **4**, reaction (6b).



Scheme 1.

ide, H_2SO was selected for the SCF calculation to optimize the triplet adduct geometries under the C_s restriction. Obtained was merely a C_{2v} symmetric geometry of the transition state corresponding to the exchange of the two hydrogens (Scheme 1).

The activation energies $\Delta E^{\ddagger}$ and the relative energies ΔE of the product systems are listed in Table 2. At the HF/6-31G** level, the calculated activation energy of reaction (6a) is $\Delta E^{\ddagger}$=125 kJ mol^{-1}. By contrast, that of the substitution channel is $\Delta E^{\ddagger}$=221 kJ mol^{-1}. When the correlation is taken into account, both energies decrease. At the highest level (MRD-CI/Ryd) of the present calculations, $\Delta E^{\ddagger}$ for the abstraction and the substitution are 77 and 127 kJ mol^{-1}, respectively. At every level of calculation, the abstraction reaction (6a) is predicted to be more favorable than the substitution reaction (6b), just as in the case of the H_2S+H reactions.

(C) H_2S+F. The reactions which we will examine here are

$$H_2S + F \longrightarrow SH + FH \quad (7a)$$
$$\longrightarrow H + HSF \quad (7b)$$

Reaction (7a) is known as a conventional source for the SH radical beam.[22] Although earlier workers[23] have mentioned the possibility of concurrent occurrence of reaction (7a), it has never been identified yet.

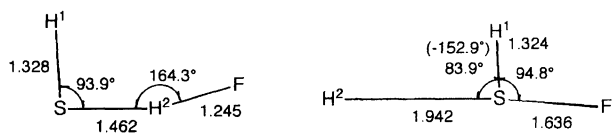
The optimized TS structures obtained are shown in Fig. 3. The geometry of the transition state (**5**) of the abstraction is similar to the planar (C_s) symmetric structures of **1** and **3**. There exists only one imaginary frequency (3092i cm^{-1}) at the UHF/6-31G** level. On the other hand, TS (**6**) for the substitution does not have the C_s symmetry. It has one imaginary frequency, being 937i cm^{-1}. The S–H^2 bond is markedly long, which is as long as 1.942 Å.

The total energies obtained at the various theoretical levels are listed in Table 3. It can be seen in Table 3 that the effects of electron correlation are enormous in the TS (**5**). At the MRD-CI/Ryd level, the activation energy $\Delta E^{\ddagger}$ is calculated to be as low as 2 kJ mol^{-1}. The abstraction reaction (7a) should be by far more favorable than the substitution reaction (7b).

(D) CH_3SH+H. Amano et al.[2] measured the rates of the reactions

$$CH_3SH + H \xrightarrow{k_a} CH_3S + H_2 \quad (8a)$$
$$\xrightarrow{k_b} CH_3 + H_2S \quad (8b)$$

by a discharge flow method at 310—480 K. The Arrhenius rate factors observed for reaction (8a) were A_a= 2.9×10^{13} cm^3 mol^{-1} s^{-1} and E_a=10.9 kJ mol^{-1} while



5 (^{2}A') **6**

Fig. 3. Optimized geometries for the transition states of the reactions between H_2S and F. The bond lengths are given in units of Å. The entry given in parentheses indicates the dihedral angle ϕ(FSH^{1}H^2). **5**, reaction (7a); **6**, reaction (7b).

Table 2. Total Energies Calculated at Various Levels for the H_2S+O System

Method	Total energy (hartree)	Relative energies (kJ mol^{-1})[a]			
	E+473 H_2S+O	$\Delta E^{\ddagger}$ **3**(abst.)	$\Delta E^{\ddagger}$ **4**(subst.)	ΔE SH+OH	ΔE HSO+H
HF/6-31G**	−0.45896	125	221	5	169
MP2/6-31G**	−0.69007	64	97	−38	35
MP4(SDTQ)/6-31G**	−0.72696	62	101	−31	52
CI(full)/6-31G**	−0.71324	77	139	−19	37
HF/Ryd	−0.45959	123	219	6	168
MP2/Ryd	−0.69117	60	94	−38	33
MP4(SDTQ)/Ryd	−0.73082	57	97	−30	50
CI(full)/Ryd	−0.71440	77	127	−18	20

a) Relative to H_2S+O.

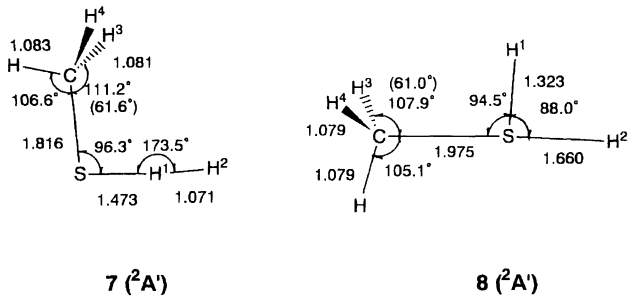
Table 3. Total Energies Calculated at Various Levels for the H_2S+F System

Method	Total energy (hartree)	Relative energies (kJ mol^{-1})[a]			
	E+498 H_2S+F	$\Delta E^{\ddagger}$ **5**(abst.)	$\Delta E^{\ddagger}$ **6**(subst.)	ΔE SH+HF	ΔE HSF+H
HF/6-31G**	−0.03999	85	179	−105	153
MP2/6-31G**	−0.29730	6	57	−183	45
MP4(SDTQ)/6-31G**	−0.33237	7	75	−164	68
CI(full)/6-31G**	−0.31352	3	150	−150	125
HF/Ryd	−0.04062	84	177	−105	153
MP2/Ryd	−0.29840	4	54	−183	44
MP4(SDTQ)/Ryd	−0.33350	5	72	−164	67
CI(full)/Ryd	−0.31468	2	104	−149	123

a) Relative to H_2S+F.

those for reaction (8b) were $A_b=0.69\times10^{13}$ $cm^3\,mol^{-1}\,s^{-1}$ and $E_b=7.0$ kJ mol^{-1}. At 400 K, the rate constant ratio k_a/k_b is nearly unity. The result is of particular interest here since the activation energy for the substitution is lower than that for the abstraction.

Results of the SCF optimizations of the TS structures are shown in Fig. 4. Both the transition states are planar in structure. The TS structure **8** for the substitution reaction is characterized by the remarkably long C–S bond, which is as long as 1.975 Å. The length of the S–H^2 bond associated with the incoming H^2 atom is 1.660 Å.



7 (^{2}A') **8** (^{2}A')

Fig. 4. Optimized geometries for the transition states of the reactions between CH_3SH and H. The bond lengths are given in units of Å. The entries given in parentheses indicate the dihedral angles $\phi(H^3CSH^1)$. **7**, reaction (8a); **8**, reaction (8b).

The relative energies obtained by computations are given in Table 4. At the HF/6-31G** level, the activation energies of abstraction and substitution are 50 and 69 kJ mol^{-1}, respectively. Even at the MP4/6-31G** level, the advantage of abstraction over substitution remains unaltered. Interestingly enough, the CI results are contrary to the SCF and MP results. Thus, the activation energy calculated by the MRD-CI/Ryd procedure for the substitution is clearly *lower* (19 kJ mol^{-1}) than that for the abstraction (32 kJ mol^{-1}). The results of the CI calculations are qualitatively in line with the experimental results reported by Amano et al.[2]

Discussion

As has been demonstrated above, the reactions of H_2S with the atomic species generally seem to favor the hydrogen abstraction pathway (1a). Calculations of the barrier heights thereof are uniformly subject to the electron correlation effects. Probably, the barrier heights calculated by the CI method will be the most reliable.

Recently, Yoshimura et al.[24] investigated reaction (5a) by shock tube experiments on one hand and by theoretical calculations on the other. According to their most elaborated calculation at the PMP4(SDTQ)/6-311G**//MP2/6-31G** level, the activation energy

Table 4. Total Energies Calculated at Various Levels for the CH_3SH+H System

Method	Total energy (hartree)	Relative energies (kJ mol^{-1})[a]			
	E+438 CH_3SH+H	$\Delta E^{\ddagger}$ **7**(abst.)	$\Delta E^{\ddagger}$ **8**(subst.)	ΔE CH_3+H_2	ΔE CH_3+H_2S
HF/6-31G**	−0.20726	50	69	−80	−85
MP2/6-31G**	−0.48587	34	59	−69	−44
MP4(SDTQ)/6-31G**	−0.52601	27	48	−82	−59
MRD-CI/6-31G**	−0.50753	34	12	−91	−86
HF/Ryd	−0.20777	49	68	−80	−85
MP2/Ryd	−0.48690	33	56	−69	−44
MP4(SDTQ)/Ryd	−0.52710	25	45	−82	−59
MRD-CI/Ryd	−0.50764	32	19	−93	−90

a) Relative to CH_3SH+H.

was $E_0=17$ kJ mol^{-1}. However, the theoretical rate constant calculated by using this E_0 value was found to be much lower than the experimental result obtained at $T=293$ K. They noted that the best fit of calculations to experiments was attainable when E_0 was assigned a value of 13 kJ mol^{-1}. The activation energy $E_0=12$ kJ mol^{-1} obtained by our CI+vib calculation agrees reasonably well with the proposed value.

The substitution pathway (1b) deserves special attention, even though it appears to be energetically less favorable than the abstraction pathway (1a). In treating the abstraction reaction in this work, we have used the term "S_H2" for the type of reaction (3) and distinguished it explicitly from the two-step reaction (4) (addition followed by bond scission). The term "S_H2 reaction" has already been used in a review,[25] which treated both the reactions as the S_H2 type. In view of the analogy with the ionic S_N2 (elementary but certainly not stepwise) reaction, however, the term "S_H2" should only be used to mean such an elementary (one-step) reaction as reaction (3).

The reaction system CH_3SH+H is of particular interest, since the barrier height of substitution is shown to be low enough to permit it to compete with the hydrogen abstraction. In fact, the kinetic studies by Amano et al.[2] have shown that the substitution reaction (8b) to form CH_3+H_2S is competitive with the hydrogen abstraction (8a) giving CH_3S+H_2. The activation energies observed in the temperature range 310—480 K were 10.9 and 7.0 kJ mol^{-1} for reactions (8a) and (8b), respectively.

By using the results of MNDO calculations, Amano et al.[2] proposed that the substitution reaction will take place via an initial formation of the metastable intermediate RSH_2. In our calculations, however, such a trivalent adduct could not be found on the potential energy surface of the CH_3SH+H system. Instead, a pathway for the direct S_H2 reaction giving the same product mixtures has been confirmed. Besides, the activation energy obtained for the substitution is found to be clearly lower than that for the abstraction at the CI level. The results corroborate the experimental kinetic results.

Conclusions

The substitution reactions of H_2S and CH_3SH with some atomic radicals (H, O, and F) should all be elementary (S_H2) reactions. In the case of CH_3SH+H, the substitution will even be a lower-barrier process than the abstraction reaction. The result is in line with the experimental results reported by previous workers.

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