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# Atmospheric reaction between the HS radical and chlorine

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## Abstract

The mechanism and the kinetics of the reaction between HS and $Cl_2$ leading to HSCl and Cl were studied theoretically. The effect of the complete basis set limit (CBS) was included by extrapolating the results obtained with cc-pVDZ, cc-pVTZ and cc-pVQZ correlation consistent basis sets functions. At the highest level of calculation, CCSD(T), the calculated rate constant is $1.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The activation Gibbs free energy was calculated to be 7.4 kcal/mol, which is only 0.2 kcal/mol above the value determined experimentally. The enthalpy and Gibbs free energies of the reaction are $-6.9$ and $-6.5$ kcal/mol, respectively. © 2000 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

Sulfur compounds are released into the atmosphere, in reduced and oxidized forms, by means of biogenic and anthropogenic sources [1]. The oxidation of sulfur reduced compounds plays a very important role in atmospheric processes, due to the fact that it leads to the production of $SO_2$, which is oxidized to sulfuric acid in the troposphere. Sulfuric acid forms sulfur aerosol, and it is related to biological climate regulation [2].

Hydrogen sulfide, $H_2S$, is a large source of sulfur in the atmosphere, and it is produced through both aerobic and anaerobic organic decomposition. The major tropospheric process that removes $H_2S$ is the reaction with OH, producing HS and $H_2O$ [3]. It was believed that all the HS generated is oxidized to $SO_2$, in reactions with common tropospheric oxi-

dants such as $O_3$, $NO_2$ and $O_2$, being thus completely consumed in the troposphere [4]. However, volcanic eruptions can inject sulfur compounds in the stratosphere in large amounts, and $H_2S$ seems to be the dominant sulfur species emitted in these situations [5]. In the stratosphere, reaction of HS with $Cl_2$ and/or Cl may be important, leading to a coupling between chlorine and sulfur chemistries. It can also occur in extraterrestrial atmospheres where $H_2S$ is abundant, as that of Venus.

Surprisingly, to the best of our knowledge, very little is known about this reaction, as well the mechanism, and the nature and structure of the products formed [6]. Studies of this type of reactions are certainly very important, since they can significantly contribute to a better understanding of the chlorine and sulfur atmospheric cycles. So far, the only study reported in the literature about the kinetics of the reaction between HS and $Cl_2$ is that of Nesbitt and Leone [7], in which the authors have analyzed a laser-induced chemical chain reaction of the

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Cl$_2$/H$_2$S system. They have obtained an average value of $(1.36 \pm 0.2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the rate constant of the reaction

HS + Cl$_2$ → HSCl + Cl.
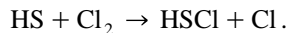
Considering, on one hand, that all methods of study of the HS kinetics are susceptible to errors associated with secondary processes, which can lead to regeneration of the HS radical [3], and, on the other hand, the high performance of present-day theoretical ab initio methods, it is our understanding that theoretical methods can be a valuable aid in the investigation of this kind of reactions, especially for systems of a few atoms. Therefore, our aim in this work is to present a detailed and very accurate investigation of thermodynamical properties and of kinetics data which can help us elucidate the mechanism of the above atmospheric reaction.

## 2. Calculation

Our calculations were performed with the GAUSS-IAN [8] and the MOLPRO [9] packages of programs. The optimizations and harmonical frequency analysis were done at the UMP2/D95(d, p), UCCSD(T)/D95(d, p) and UMP2/cc-pVTZ levels of theory. Besides the reactants, products and the transition state, we have found a weakly bound complex between the reactants. The structures of all stationary points considered in this work are presented in Fig. 1, where the relevant geometrical
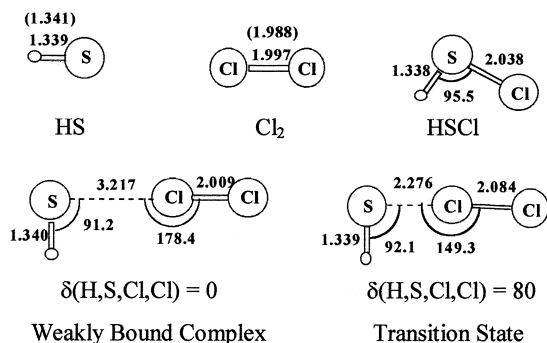


Fig. 1. Geometries and relevant geometrical parameters for the stationary points involved in the reaction between HS and Cl$_2$, at the UMP2/cc-pVTZ level of theory. Available experimental values are given in parentheses [10].

Table 1

Harmonical frequencies calculated for all stationary points obtained at the UMP2/cc-pVTZ level of calculation

Available experimental values are given in parentheses [10]

| HS | Cl$_2$ | Complex | Transition state | HSCl |
|---|---|---|---|---|
| | | 54.7 | 450.0$i$ | |
| | | 58.6 | 153.2 | |
| | | 66.4 | 255.9 | |
| | | 176.6 | 420.0 | |
| | 577.6 (559.7) | 552.9 | 653.9 | 554.9 |
| | | | | 927.7 |
| 2765.1 (2712) | | 2760.4 | 2759.3 | 2753.5 |

parameters are given. In Table 1 are presented the harmonical frequencies calculated. Experimental values are available only for the reactants [10]. Using MP2/cc-pVQZ and CCSD(T)/cc-pVTZ single-point calculations and the additivity approximation [11,12], we have achieved the CCSD(T)/cc-pVQZ level of theory, through the equation

$$E_{\text{CCSD(T)/cc-pVQZ}} = E_{\text{CCSD(T)/co-pVTZ}}$$
$$+ \left( E_{\text{MP2/co-pVQZ}} - E_{\text{MP2/co-pVTZ}} \right). \quad (1)$$

In order to obtain the limit for the basis set completeness, we have performed an MP2/cc-pVDZ single-point calculation, and used the approximation developed and tested by Dunning and co-workers [13,14], which states that the dependence on basis set of several molecular properties, as the stabilization energy, is well represented by a simple exponential function in this form

$$F(n) = A_\infty - B\exp(-cn), \quad (2)$$

where $n$ is the index of the basis set, and $A_\infty$ is the asymptotic limit for the function. The limiting value of this function provides an estimate of the complete basis set (CBS) limit. In our calculation, $n$ ranged from 2 to 4, and the function extrapolated was the energy for every stationary point at the MP2 level. The values for the CCSD(T)/CBS level of calculation were obtained through the following expressions

$$E_{\text{CCSD(T)/CBS}} = E_{\text{CCSD(T)/cc-pVTZ}}$$
$$+ \left( E_{\text{MP2/CBS}} - E_{\text{MP2/cc-pVTZ}} \right). \quad (3)$$

We have also included the effect of the core in the calculation of the electronic energy through an

MP2(full)/cc-pVTZ single-point calculation. Using the additivity approximation again, we have obtained the values for the CCSD(T, full)/CBS levels of calculation as

$$E_{CCSD(T,full)/CBS} = E_{CCSD(T)/CBS}$$
$$+ \left( E_{MP2(full)/cc-pVTZ} - E_{MP2/cc-pVTZ} \right). \qquad (4)$$

Finally, the rate constant for this reaction was calculated using conventional transition state theory (TST) [15], and the possibility of quantum-mechanical tunneling was addressed by means of Wigners' approach, which implies multiplying the TST rate constant by the factor below

$$\Gamma = 1 + \frac{1}{24} \left[ \frac{h\omega}{k_B T} \right]^2, \qquad (5)$$

where $\omega$ stands for the absolute value of the imaginary frequency of the transition state of the reaction.

## 3. Results and discussion

The energy values obtained with all approaches are presented in Table 2. The calculations at the MP2/cc-pVDZ, MP2/cc-pVQZ, CCSD(T)/cc-pVTZ and MP2(full)/cc-pVTZ levels were performed with the geometry optimized at the MP2/cc-pVTZ level. The adjusted values for the CBS limit at the MP2 level are also in Table 2. In

Tables 3 and 4 are the relative energies and the thermodynamical properties, calculated at 298.15 K, for the formation of the weakly bound complex, and for the reaction, respectively. The rate constants calculated at the different levels of theory are also in Table 4, as well as the results for our highest-level calculations, obtained with the CBS limit.

From Table 3, we can see that increasing the size of the basis sets leads to a higher stabilization of the weakly bound complex, whether at the MP2 or at the CCSD(T) level. This behavior can also be observed in Table 4 for the activation energy results. In all cases, the MP2 values overstabilize the species relative to CCSD(T). It can also be noted that the values obtained for the formation of the weakly bound complex and those for the energy of the reaction are very small, showing that the convergence is reached with medium basis set functions as the cc-pVTZ one. For the weakly bound complex, our best value for the stabilization energy is $-2.61$ kcal/mol. All other results differ from this value by $< 1$ kcal/mol. The enthalpy variation is $-2.0$ kcal/mol, and the Gibbs free energy for this species is positive, but of a small value.

For the products of the reaction, a similar behavior is observed. The reaction is spontaneous by $-6.5$ kcal/mol, and exothermic by $-6.9$ kcal/mol. Once again, the values obtained at several levels of calculation do not differ by more than 1 kcal/mol of the

Table 2
Calculated energies (in hartree) and zero-point energies (ZPE, in kcal/mol) for the species studied
The optimizations were performed at the UMP2/D95(d, p), UCCSD(T)/d95(d, p) and UMP2/cc-pVTZ levels

|  | HS | Cl$_2$ | Complex | Transition state | HSCl | Cl |
|---|---|---|---|---|---|---|
| UMP2/D95(d, p) | $-398.17657$ | $-919.17362$ | $-1\,317.35351$ | $-1\,317.33269$ | $-857.81392$ | $-459.55079$ |
| PMP2/D95(d, p) | $-398.17803$ |  | $-1\,317.35502$ | $-1\,317.34360$ |  | $-459.55198$ |
| ZPE | 3.99 | 0.80 | 5.28 | 6.03 | 6.13 | 0.00 |
| UCCSD(T)/d95(d, p) | $-398.19981$ | $-919.20619$ | – | $-1\,317.39702$ | $-857.85114$ | $-459.56868$ |
| ZPE | 3.88 | 0.74 | – | 5.63 | 5.96 | 0.00 |
| UMP2/cc-pVTZ | $-398.25633$ | $-919.37678$ | $-1\,317.63655$ | $-1\,317.62362$ | $-858.00248$ | $-459.64336$ |
| PMP2/cc-pVTZ | $-398.25844$ |  | $-1\,317.63868$ | $-1\,317.63403$ |  | $-459.64524$ |
| ZPE | 3.95 | 0.83 | 5.25 | 6.06 | 6.06 | 0.00 |
| PMP2/cc-pVDZ[a] | $-398.20251$ | $-919.23156$ | $-1\,317.43735$ | $-1\,317.42399$ | $-857.86694$ | $-459.58213$ |
| PMP2/cc-pVQZ[a] | $-398.27614$ | $-919.42453$ | $-1\,317.70471$ | $-1\,317.70221$ | $-858.04688$ | $-459.66599$ |
| PMP2/CBS[b] | $-398.28435$ | $-919.44792$ | $-1\,317.73692$ | $-1\,317.73498$ | $-858.06851$ | $-459.67616$ |
| CCSD(T)/cc-pVTZ[a] | $-398.28706$ | $-919.42647$ | $-1\,317.71619$ | $-1\,317.70987$ | $-858.05402$ | $-459.67181$ |
| PMP2(full)/cc-pVTZ[a] | $-398.29288$ | $-919.44371$ | $-1\,317.74040$ | $-1\,317.73669$ | $-858.07184$ | $-459.67760$ |

[a] Single-point calculations at the UMP2/cc-pVTZ optimized geometry.
[b] Results obtained fitting Eq. (2).

Table 3
Relative energies and thermodynamical values (in kcal/mol) for the weakly bound complex between HS and Cl, at different levels of theory ($T = 298.15$ K)

| | $\Delta E$ | $\Delta E_{ZPE}$ | $\Delta H$ | $\Delta G$ |
|---|---|---|---|---|
| PMP2/D95(d, p) | −2.11 | −1.63 | −1.50 | 3.65 |
| PMP2/cc-pVTZ | −2.17 | −1.70 | −1.56 | 3.55 |
| PMP2(full)/cc-pVTZ | −2.39 | −1.92 | −1.78 | 3.33 |
| CCSD(T)/cc-pVTZ | −1.64 | −1.17 | −1.03 | 4.08 |
| PMP2/cc-pVQZ | −2.53 | −2.06 | −1.92 | 3.19 |
| CCSD(T)/cc-pVQZ[a] | −2.00 | −1.53 | −1.39 | 3.72 |
| PMP2/CBS | −2.92 | −2.46 | −2.32 | 2.80 |
| CCSD(T)/CBS[b] | −2.39 | −1.92 | −1.78 | 3.33 |
| CCSD(T, full)/CBS[c] | −2.61 | −2.14 | −2.00 | 3.11 |

[a] From Eq. (1).
[b] From Eq. (3).
[c] From Eq. (4).

best values for stabilization energies, enthalpies and Gibbs free energies. In their work, Nesbitt and Leone have indicated an $\Delta H$ of −3.6 kcal/mol for this reaction. Since they do not have informed how that value was obtained, we cannot attest for its precision, but we are certain that the value reported in the present investigation is more accurate, due to the fact that we are using a high level of theory.

In the case of the transition state, there is however a significant variation in the electronic and thermodynamical values until the quadruple-zeta basis set.

Since the rate constant varies exponentially with the activation Gibbs free energy, the values of this constant fall over a large interval. The results computed at the limit for the complete basis set present a small variation, showing the importance of the basis set size for this system.

Our best calculation, CCSD(T, full)/CBS// UMP2/cc-pVTZ, produced an activation free energy of 7.47 kcal/mol, which leads to a rate constant of $8.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The imaginary frequency of the transition state is 450 cm$^{-1}$, at the UMP2/cc-pVTZ level. Taking into account Wigners' tunneling correction, the rate constant changes to $1.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and an effective activation free energy of 7.36 kcal/mol is then obtained. This value for the rate constant is slightly smaller than that obtained experimentally, which is $(1.36 \pm 0.2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [7]. This small discrepancy corresponds to a difference of only 0.2 kcal/mol in the activation Gibbs free energy. Considering that we are using a high level of theory and that fact that this reaction is isogyric, this value is certainly a very good result. Also, the influence of secondary reactions could be invoked to explain this small difference, but we think that the agreement is already excellent.

From a broad perspective, the fact that the reaction between HS and Cl$_2$ is predicted to be fast, if

Table 4
Relative energies, thermodynamical values (in kcal/mol), and rate constant ($k$, in cm$^3$ molecule$^{-1}$ s$^{-1}$) for the reaction between HS and Cl$_2$ leading to HSCl and Cl, at different levels of theory ($T = 298.15$ K)

| | Activation | | | | $k$ | Reaction | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta E$ | $\Delta E_{ZPE}$ | $\Delta H$ | $\Delta G$ | | $\Delta E$ | $\Delta E_{ZPE}$ | $\Delta H$ | $\Delta G$ |
| PMP2/D95(d, p) | 5.05 | 6.29 | 5.41 | 13.37 | $4.0 \times 10^{-17}$ | −8.95 | −7.61 | −7.88 | −7.50 |
| CCSD(T)/D95(d, p) | 5.64 | 6.65 | 5.89 | 13.56 | $2.9 \times 10^{-17}$ | −8.67 | −7.33 | −7.59 | −7.20 |
| PMP2/cc-pVTZ | 0.75 | 2.04 | 1.12 | 9.19 | $4.6 \times 10^{-14}$ | −7.84 | −6.57 | −6.82 | −6.46 |
| PMP2(full)/cc-pVTZ | −0.07 | 1.22 | 0.30 | 8.38 | $1.8 \times 10^{-13}$ | −8.06 | −6.79 | −7.04 | −6.68 |
| CCSD(T)/cc-pVTZ | 2.29 | 3.58 | 2.66 | 10.74 | $3.4 \times 10^{-15}$ | −7.72 | −6.44 | −6.70 | −6.33 |
| PMP2/cc-pVQZ | −0.96 | 0.33 | −0.59 | 7.48 | $8.3 \times 10^{-13}$ | −7.66 | −6.38 | −6.64 | −6.27 |
| CCSD(T)/cc-pVQZ[a] | 0.58 | 1.87 | 0.95 | 9.03 | $6.1 \times 10^{-14}$ | −7.53 | −6.25 | −6.51 | −6.14 |
| PMP2/CBS | −1.71 | −0.42 | −1.34 | 6.74 | $2.9 \times 10^{-12}$ | −7.79 | −6.51 | −6.77 | −6.40 |
| CCSD(T)/CBS[b] | −0.16 | 1.13 | 0.21 | 8.28 | $2.1 \times 10^{-13}$ | −7.66 | −6.38 | −6.64 | −6.27 |
| CCSD(T, full)/CBS[c] | −0.98 | 0.31 | 0.61 | 7.47 | $8.5 \times 10^{-13}$ | −7.88 | −6.60 | −6.86 | −6.49 |
| Best value[d] | | | | 7.36 | $1.0 \times 10^{-12}$ | | | | |

[a] From Eq. (1).
[b] From Eq. (3).
[c] From Eq. (4).
[d] CCSD(T, full)/CBS//UMP2/cc-pVTZ with Wigners' correction for tunneling.

the atmospheric conditions are such that the concentrations of the species HS and $Cl_2$ are significant, this reaction will certainly occur, thus contributing to the coupling of the sulfur and chlorine cycles.

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