The Atmospheric Reaction between DMSO and the Chlorine Radical

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The reaction between dimethyl sulfoxide (DMSO) and chlorine was studied theoretically, using ab initio calculation in a high correlated level. A systematic study of reaction paths was conducted to address the role of the $(CH_3)_2SO-Cl$ adduct formation. The channels that lead to $CH_3SOCH_2 + HCl$ and $CH_3SOCl + CH_3$ will be relevant, and the global atmospheric rate constant was determined to be 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}, at 298.15 K and 1 atm. The atmospheric implications of this reaction to DMSO chemistry also are discussed.

Introduction

Dimethyl sulfoxide (DMSO) is a sulfur compound of atmospheric interest, since it has been observed in the marine boundary layer, and in aerosols and rainwater.[1,2] It is found in seawater in higher quantities than dimethyl sulfide (DMS), but its low volatility indicates that the oceans should not be considered significant sources to the atmosphere. So, the main source of DMSO in the atmosphere probably is the reaction of DMS with OH radicals. The addition of OH to DMS produces the adduct $CH_3S(OH)CH_3$, which react with O_2, leading to DMSO.[3−6] Reactions of DMS with halogen oxides may also be an additional source of atmospheric of DMSO.[7]

Despite the importance of DMSO in atmospheric sulfur chemistry, there is a considerable uncertainty concerning its oxidation mechanism. It is believed that DMSO should be removed from the atmosphere through heterogeneous processes like uptake by aerosol and cloud droplets[8] and homogeneous reactions. In the gas phase, DMSO is expected to react with common atmospheric oxidants such as OH, NO_3, O_3, and Cl. The reaction of DMSO with OH has previously been the subject of experimental and theoretical investigations.[4,9−15] In these investigations, this reaction was found to be very fast, with a rate constant of $(6-10) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature. However, the mechanism is still uncertain. Dimethyl sulfone ($CH_3SO_2CH_3$: $DMSO_2$), SO_2 and methanesulfonic acid (CH_3SO_2OH: MSA) have been observed as products in some studies,[4,9,12] but other investigations[10,11,13−15] suggest that the methanesulfinic acid ($CH_3S(O)OH$): MSIA) and CH_3 are produced in high yield.

Regarding the reaction of DMSO with the other oxidants, few results are available for reaction with NO_3 and O_3.[9,12] Nevertheless, although there is no significant source of chlorine in the troposphere, recent investigations have proposed that some natural tropospheric processes could provide a significant chlorine concentration,[16−18] such as this radical could be important in the oxidation of reduced sulfur compounds. In this way, the reaction of DMSO with Cl radical was investigated in four experimental works.[9,12,19,20] Barnes et al.[9] have conducted a reaction chamber study at 298 ± 2 K and 760 Torr, using FTIR absorption spectroscopy for detection of reactants and products. The observed kinetic constant was of $(7.4 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. SO_2 and $DMSO_2$ were the major products, with yields of approximately 42% and 14%, respectively. Their conclusions were that SO_2 was produced in further reactions of CH_3SOCH_2 (hydrogen abstraction channel) and $DMSO_2$ was a product of the further reaction of a DMSO−Cl adduct with O_2 (addition channel). Using the same technique and similar conditions, Falbe-Hansen et al.[12] have determined the rate constant as being $(7.4 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, in excellent agreement with the previous report. However, in this case the yields of SO_2 and $DMSO_2$ were 28 ± 12 and 8 ± 2, respectively. In a discharge flow study of the reaction of DMSO with Cl and ClO radicals, with detection of reactants and products by mass spectrometry, the rate constant measured by Martinez et al.[19] was $(1.7 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, for chlorine reaction. The authors have identified the formation of CH_3SOCl, CH_3 and a DMSO−Cl adduct. No production of HCl was verified. The experiments were conducted from 0.5 to 3.0 Torr of pressure, and no pressure dependence was detected. They concluded that the reaction proceeds through adduct formation and further decomposition involving the cleavage of the C−S bound. Concerning the adduct formation proposed, a weakly bound complex was identified by McKee[21] in a theoretical calculation. In a PMP2/6-31G(d)//UHF/3-21G* calculation, the complex was bound by 7.8 kcal mol^{-1}, and the intermolecular bound is between Cl and S atoms. Very recently, Riffault et al.[20] have conducted a study of the reaction DMSO + Cl by the mass spectrometric discharge flow method, at 298 K. In this investigation, the rate constant was determined as being $(2.05 \pm 0.35) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and HCl and CH_3 were the major products identified, with branching ratios of 0.91 ± 0.15 and 0.10 ± 0.12, respectively. This work was carried out at a pressure of 1 Torr, and no adduct formation was identified.

Although there is reasonable agreement among the four rate constants determined so far for the DMSO + Cl reaction, the divergences found in relation to the products obtained, as well as the increasing interest in accessing the real role of the chlorine in the atmospheric chemistry of the sulfur compounds, led us to investigate this reaction theoretically. The purpose of this work is to conduct a high level ab initio study of the system DMSO−Cl, identifying the reaction mechanism and kinetics, as well as the weakly bound complexes formed. The following reaction channels were analyzed:

$$CH_3S(O)CH_3 + Cl \rightarrow CH_3S(O)CH_2 + HCl \quad (1)$$

$$\rightarrow CH_3SOCl + CH_3 \quad (2)$$

$$\rightarrow CH_3SO + CH_3Cl \quad (3)$$

$$\rightarrow CH_3SCH_3 + ClO \quad (4)$$

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TABLE 1: Absolute Energy Values (in hartree) Calculated for the Species Involved in the Reaction DMSO + Cl[a]

	MP2/6-31G(d,p)	PMP2/cc-pVDZ	PMP2/cc-pVTZ	PMP2/cc-pVQZ	PMP2/CBS	CCSD(T)/6-31G(d,p)	CCSD(T)/CBS[b]	ZPE
DMSO	−552.16002	−552.17364	−552.42913	−552.50889	−552.54508	−552.22075	−552.60581	51.59
Cl	−459.55353	−459.58213	−459.64524	−459.66599	−459.67616	−459.57048	−459.69311	0.00
CH_3SOCH_2	−551.49347	−551.50844	−551.75793	−551.83627	−551.87214	−551.55209	−551.93076	42.40
HCl	−460.20545	−460.23567	−460.30944	−460.33372	−460.34563	−460.22456	−460.36474	4.45
CH_3SOCl	−972.00485	−972.05680	−972.33457	−972.42307	−972.46445	−972.05931	−972.51890	28.03
CH_3	−39.69462	−39.69202	−39.73767	−39.75068	−39.75586	−39.71617	−39.77741	19.27
CH_3SO	−512.38083	−512.40216	−512.60137	−512.66365	−512.69198	−512.42525	−512.73640	26.53
CH_3Cl	−499.37820	−499.40275	−499.52022	−499.55803	−499.57597	−499.41463	−499.61240	24.63
DMS	−477.16935	−477.18786	−477.34071	−477.38833	−477.40988	−477.22730	−477.46783	49.34
ClO	−534.50887	−534.54264	−534.68996	−534.73760	−534.76037	−534.54247	−534.79396	1.22
TS1A	−1011.69805	−1011.74512	−1012.06853	−1012.17125	−1012.21905	−1011.77420	−1012.29521	47.27
TS1B	−1011.69362	−1011.74161	−1012.06404	−1012.16636	−1012.21393	−1011.77029	−1012.29060	46.92
TS1C	−1011.69036	−1011.73752	−1012.06054	−1012.16288	−1012.21034	−1011.76542	−1012.28541	46.68
TS2	−1011.69758	−1011.74690	−1012.07361	−1012.17599	−1012.22272	−1011.77070	−1012.29584	50.15
TS3	−1011.69843	−1011.74578	−1012.06486	−1012.16513	−1012.21108	−1011.77108	−1012.28372	51.31
TS4	−1011.67920	−1011.72762	−1012.03806	−1012.13829	−1012.18609	−1011.75899	−1012.26587	51.33
WBC1	−1011.73385	−1011.77894	−1012.10346	−1012.20669	−1012.25484	−1011.80701	−1012.32800	52.65
WBC2	−1011.72900	−1011.77320	−1012.08923	−1012.19023	−1012.23768	−1011.80694	−1012.31562	52.36
WBC3	−1011.72488	−1011.76900	−1012.08539	−1012.18638	−1012.23372	−1011.80269	−1012.31153	52.08
WBC4	−1011.72432	−1011.76794	−1012.08437	−1012.18517	−1012.23230	−1011.80219	−1012.31018	52.01

[a] Geometry optimizations were conducted at the UMP2/6-31G(d,p) level of theory. [b] Value obtained using eq 1.

Calculations

All calculations were conducted in the Gaussian 98 package of programs.[22] Optimizations and frequency calculations were carried out at the MP2/6-31G(d,p) level of theory. Further calculations with the correlation consistent basis sets cc-pVDZ, cc-pVTZ, cc-pVQZ were done in order to achieve the limit for basis set completeness, using the CBS procedure.[23] A better level of electronic correlation was introduced by means of a CCSD(T)/6-31G(d,p) calculation, and the additivity method,[24,25] according to the following equation:

$$\mathrm{E}_{\mathrm{CCSD(T)/CBS}} = \mathrm{E}_{\mathrm{MP2/CBS}} + (E_{\mathrm{CCSD(T)/6-31G(d,p)}} - \mathrm{E}_{\mathrm{MP2/6-31G(d,p)}}) \quad (5)$$

Here $\mathrm{E}_{\mathrm{MP2/CBS}}$ is the MP2 energy obtained from the CBS procedure, and $E_{\mathrm{CCSD(T)/CBS}}$ is the energy at the CCSD(T) level considering an infinite basis set. This methodology was used before, leading to reliable results.[26,27]

The rate constants were calculated using conventional transition state theory (TST),[28] considering $T = 298.15$ K and a pressure of 1 atm. In this theory, an expression for the thermal rate constant is derived considering the existence of a transition state separating reactants and products, which are in thermodynamical equilibrium. Evaluating the flux through the transition state, i.e., the fraction of activated species that overcome the energy barrier (E_o), the rate constant can be expressed in terms of partition functions as

$$k = \frac{k_B T}{h}\frac{Q^{\ddagger}}{Q_{\mathrm{react}}}e^{-E_o/k_B T}$$

where $Q^{\ddagger}$ and Q_{react} are the partition functions of the transition state and reactants, respectively. Reformulating this in thermodynamical terms will lead to

$$k = \frac{k_B T}{h}\left(\frac{RTc^{o}}{p^{o}}\right)e^{-\Delta G^{o\ddagger}/RT}$$

for a bimolecular reaction. In this equation, c^o is equal to 1 mol L^{-1}, and p^o is 1.013×10^5 N m^{-2}. The term in parentheses is necessary for the conversion to the standard state of 1 mol L^{-1}. Arrhenius parameters, E_a and A, also were calculated for all channels studied. The expressions for these parameters are as follows:

$$E_a = 2RT + \Delta H^{\ddagger} \quad (6)$$

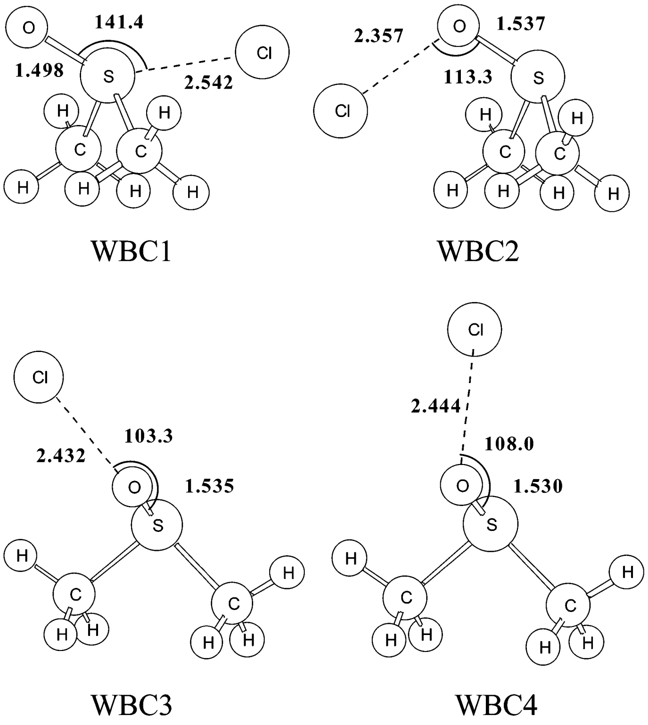
$$A = \frac{k_B T}{h}\left(\frac{RTc^{o}}{p^{o}}\right)e^{[\Delta S^{\ddagger}/R+2]} \quad (7)$$

Note that the values required are temperature and the activation thermodynamical quantities, which are calculated through standard statistical mechanics.

Results and Discussion

In Table 1 are the absolute and zero-point energies calculated for all stationary points found and the values obtained for the CCSD(T)/CBS energies, using the CBS procedure and eq 5. Besides the reactants, transition states, and products, we have studied several possibilities for weakly bound complexes between DMS and Cl, and the stable structures found are represented in Figure 1, along with the more important geometrical parameters. In Figures 2 and 3 are the structures and geometrical parameters for the transition states and reactants and products, respectively. In Table 2 are the relative electronic energies in the more relevant levels of calculation and the thermochemical values for the activation of each channel studied, while the respective values for reaction and complexes are in Table 3. Concerning the methodology used, we can note that increasing the basis set function size stabilizes significantly the transition states in relation to the reactants, while the inclusion of the electronic correlation through the CCSD(T) lead to a small decrease in this value. These results confirm that is necessary to include very extended basis set and a high level of electronic correlation in order to obtain reliable energy values of the barrier to be used in kinetic determinations.

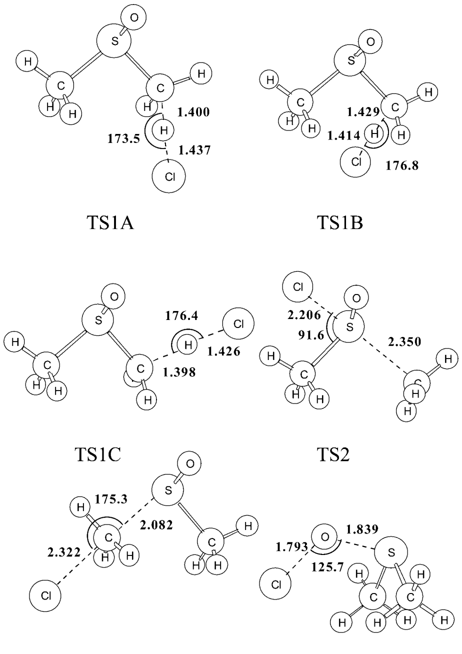
The more stable complex is WBC1, where the intermolecular bond takes place between S and Cl atoms. In our best level of theory, this species is thermodynamically stable, with $\Delta G_r = -10.06$ kcal mol^{-1}, which indicates that it should be considered as an addition complex (adduct) for the DMSO + Cl reaction. We have found three weakly bound complexes resultant of the intermolecular interaction of Cl with O, WBC2, WBC3 and



WBC1 WBC2

WBC3 WBC4

Figure 1. Structures and geometrical parameters for the stable weakly bound complexes between DMSO and Cl, at the UMP2/6-31G(d,p) level of calculation.



TS1A TS1B

TS1C TS2

TS3 TS4

Figure 2. Structures and geometrical parameters for the transition states obtained at the UMP2/6-31G(d,p) level for the reaction between DMSO and chlorine.

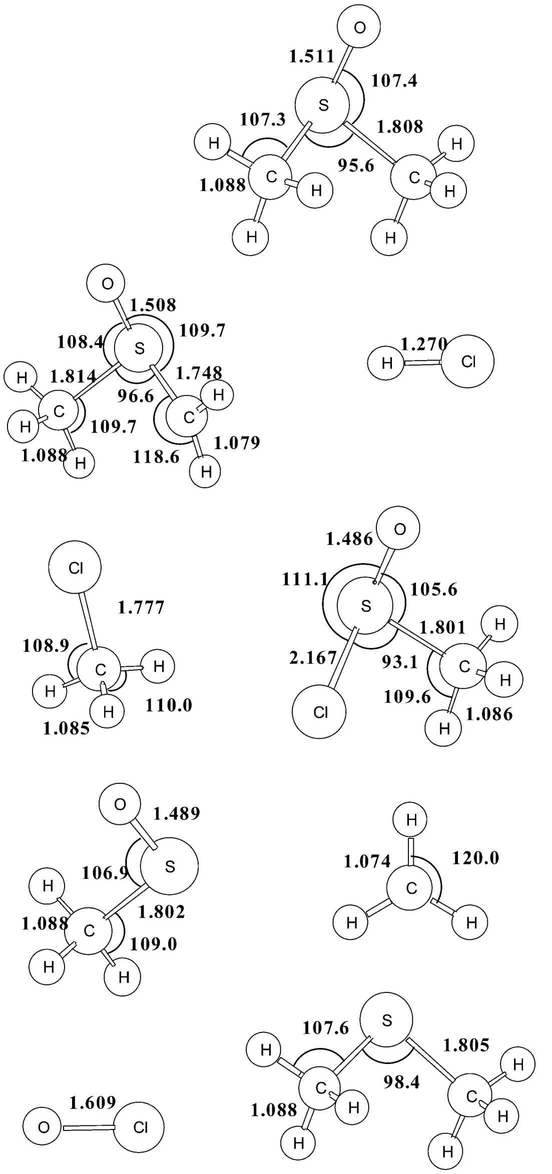


Figure 3. Structures and geometrical parameters for DMSO and the products involved in the reaction of DMSO and Cl, at the UMP2/6-31G(d,p) level.

WBC4. These species have similar structures, the difference staying in the Cl−O−S angle, and they are not very stable. WBC4 is a first-order saddle point, with an imaginary frequency of 14 cm^{-1}, connecting two equivalent structural forms of WBC3. The only previous theoretical calculation regarding this subject has reported a weakly bound complex of same structure as WBC1.[21] However, in our calculation, this species has a smaller intermolecular distance (2.542 Å) and is more stable ($\Delta E_{ZPE} = -17.19$ kcal mol^{-1}) than that found in the previous study, where the intermolecular distance was 2.873 Å and the stabilization energy, only -7.4 kcal mol^{-1}. Since our calculation was conducted at a considerable better level of theory, the present results are more accurate.

Regarding the transition states, the abstraction of each one of the three distinct hydrogens of DMSO by chlorine is considered in channels 1A, 1B, and 1C. The transition states involved are, respectively, TS1A, TS1B and TS1C. In Table 2 we can see that channel 1A has the smaller barrier, with a $\Delta G^{\ddagger}$ of 4.57 kcal mol^{-1}. The activation Gibbs free energies of channels 1B and 1C are higher, 6.95 and 9.77 kcal mol^{-1}, respectively, which indicates that this channel will proceed preferentially by the 1A path. The products will be CH_3SOCH_2 and HCl, and Table 3 shows that it is spontaneous by 4.35 kcal mol^{-1}. In channel 2 occurs the addition of Cl to the sulfur of the DMSO molecule through TS2 structure, breaking the S−C bound and leading to CH_3SOCl plus CH_3 products. The calculated activation Gibbs free energy is 7.02 kcal mol^{-1}, and the reaction Gibbs free energy is -5.63 kcal mol^{-1}. The other transition state studied, TS3, leads to the formation of CH_3SO + CH_3Cl with a high activation Gibbs free energy of 15.49 kcal mol^{-1}. Although the products are very stable, lying -35.84

TABLE 2: Activation Energy and Thermodynamical (Standard State of 1 atm of Pressure) Values (in kcal mol^{-1}) for the Four Channels of the Reaction of Cl with DMSO

channel	$\Delta E_{\mathrm{PMP2/6-31G(d,p)}}$	$\Delta E_{\mathrm{PMP2/CBS}}$	$\Delta E_{\mathrm{CCSD(T)/CBS}}$	ΔE_{ZPE}[a]	$\Delta H^{\ddagger b}$	$\Delta G^{\ddagger b}$
1A	9.73	1.38	2.33	−2.00	−2.52	4.57[c]
1B	12.51	4.59	5.22	0.55	0.11	6.95[c]
1C	14.55	6.84	8.48	3.56	3.19	9.77[c]
2	10.02	−0.93	1.93	0.49	0.31	7.02[c]
3	9.49	6.38	9.54	9.25	8.99	15.49[c]
4	21.55	22.06	20.74	20.47	20.08	27.57

[a] Activation energy, which corresponds to the classical activation energy at the CCSD(T)/CBS level of theory plus the ZPE contribution. [b] Values calculated using the CCSD(T)/CBS energy. [c] Considering the existence of two stereoisomeric transition states.

TABLE 3: Reaction Energy and Thermodynamical (Standard State of 1 atm of Pressure) Values (in kcal mol^{-1}), Obtained for the Weakly Bound Complexes and Products Involved in the Reaction between DMSO and Cl

	$\Delta E_{\mathrm{PMP2/6-31G(d,p)}}$	$\Delta E_{\mathrm{PMP2/CBS}}$	$\Delta E_{\mathrm{CCSD(T)/CBS}}$	ΔE_{ZPE}[a]	ΔH[b]	ΔG[b]
WBC1	−12.74	−21.08	−18.25	−17.19	−17.51	−10.06
WBC2	−9.70	−10.31	−10.48	−9.71	−9.99	−2.72
WBC3	−7.11	−7.83	−7.91	−7.43	−7.53	−1.13
WBC4	−6.76	−6.94	−7.06	−6.64	−7.28	0.62
channel 1	9.18	2.18	2.15	−2.59	−1.90	−4.35
channel 2	8.84	0.58	1.63	−2.66	−1.81	−5.63
channel 3	−28.54	−29.31	−31.30	−31.73	−31.65	−35.84
channel 4	22.17	32.00	23.30	22.26	22.44	19.23

[a] Reaction energy, which corresponds to the classical activation energy at the CCSD(T)/CBS level of theory plus the ZPE contribution. [b] Values calculated using the CCSD(T)/CBS electronic energy.

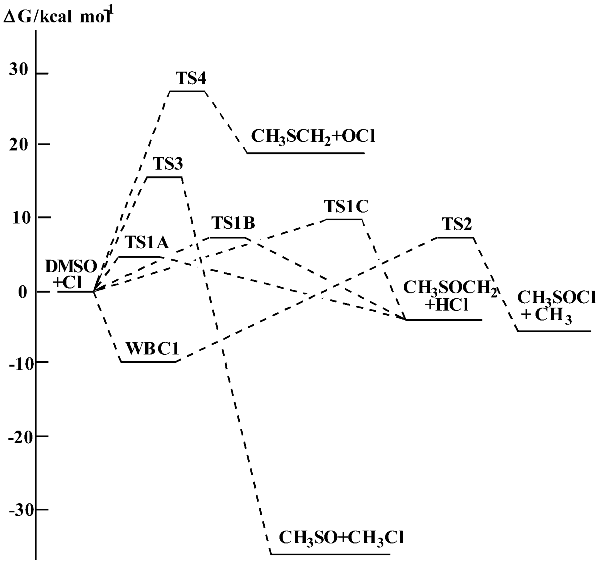


Figure 4. Gibbs free energy diagram for the reaction path of DMSO + Cl reaction.

kcal mol^{-1} below of the reactants, the small reaction rate makes this pathway not viable. Finally, channel 4 leads to a production of CH$_3$SOCH$_3$ and ClO through the transition state TS4, and has the highest activation free energy, 27.57 kcal mol^{-1}. Also, this channel is not spontaneous, and it will not occur in the atmosphere.

The WBC1 adduct is very stable, and its role in this reaction needs to be evaluated. An estimate of the rate constant for its formation by TST is difficult because the variational transition state should occur in a large intermolecular distance, leading to very small harmonic frequencies orthogonal to the reaction path. It would require the use of the flexible transition state theory, which is more difficult to apply. Thus, we have made an estimate of the formation rate constant by simple collision theory. Using a radius of 3.1 Å for the DMSO and 1.8 Å for the Cl, the rate constant will be 3.8×10^{-10} cm^3 molecule^{-1} s^{-1}. With this estimated rate constant and the free energy for the adduct formation, we can evaluate the rate constant for the adduct dissociation as being 4.0×10^2 s^{-1}. This value implies a lifetime of 2.5 ms for this species.

TABLE 4: Rate Constants *k* (in cm^3 molecule^{-1} s^{-1}), Imaginary Frequencies of Each Transition State (in cm^{-1}), and Arrhenius Parameters E_a (in kcal mol^{-1}) and *A* (in cm^3 molecule^{-1} s^{-1}), Calculated for Each Channel Considered in the Reaction DMSO + Cl, at 298.15 K and Pressure of 1 atm

	k	frequency	E_a[a]	A[b]
channel 1A	1.1×10^{-10}	1019.3*i*	−0.74	6.48×10^{-11}
channel 1B	2.0×10^{-12}	1016.7*i*	1.89	9.93×10^{-11}
channel 1C	1.7×10^{-14}	1314.8*i*	5.12	2.63×10^{-10}
channel 2	1.8×10^{-12}	439.8*i*	1.68	3.65×10^{-11}
channel 3	1.1×10^{-18}	1169.8*i*	10.85	2.32×10^{-10}
channel 4	1.6×10^{-27}	1145.1*i*	21.93	4.24×10^{-11}

[a] Calculated using eq 2. [b] Calculated using eq 3.

Figure 4 shows a representative diagram for the Gibbs free energy of all possibilities studied in this work for the reaction between DMSO and Cl. The rate constants determined for channels 1−4 are in Table 4. It is important to say that the rate constant for channel 2 in this table corresponds to going from the reactants directly to the transition state. To justify this procedure and to determine the overall rate constant, consider the kinetic model shown in the scheme below.

$$\mathrm{DMSO + Cl} \xrightarrow{k_1} \mathrm{CH_3SOCH_2 + HCl} \tag{8}$$

$$\mathrm{DMSO + Cl} \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} \mathrm{ADDUCT} \xrightarrow{k_{AD}} \mathrm{CH_3SOCl + CH_3} \tag{9}$$

Reactions through channels 3 and 4 were not considered since the respective rate constants, k_3 and k_4, are very small. Using the steady-state approximation for the adduct, we can obtain the following reaction rate equation:

$$\frac{\mathrm{d[DMSO]}}{\mathrm{d}t} = -\left(k_1 + \frac{k_A k_{AD}}{k_{-A} + k_{AD}}\right)\mathrm{[DMSO][Cl]}$$

Since the activation Gibbs free energy for the adduct decomposition through TS2 is greater than its value for the backward dissociation, which is implied by $k_{-A} \gg k_{AD}$ and the rate constant for the direct reaction through channel 2 (k_2) is given by $k_2 = (k_A k_{AD}/k_{-A})$, we can write the final reaction rate expression:

$$\frac{d[\mathrm{DMSO}]}{dt} = -(k_1 + k_2)[\mathrm{DMSO}][\mathrm{Cl}]$$

Thus, using data from Table 3, the rate constant for the overall reaction observed will be 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}. This approach is suitable in situations where the adduct concentration in the stationary state is lesser or of the same order of the concentration of the reactants.

In the atmosphere, DMSO concentration is about 3 pptv.[29] Using the most optimistic value available in the literature for the atmospheric chlorine concentration in marine areas, 1.3×10^5 molecules cm^{-3},[16] we can estimate the maximum atmospheric concentration of the adduct in equilibrium as being 3×10^3 molecules cm^{-3}. So, the steady state approximation will be suitable and our calculated overall rate constant is applicable in atmospheric conditions. According to our results, in these conditions this reaction will mainly lead to the formation of CH_3SOCH_2 and HCl. Channel 2 will occur in small ratio (2%), and the formation of CH_3SOCl and CH_3 could also be verified. The WBC1 adduct will be formed, but its concentration will not be significant. However, considering its lifetime, it is possible it interacts with an atmospheric oxidant such as O_2, and new reaction pathways can take place. This is a possibility that deserves more investigation in the future.

In the experimental measurements, the reactants concentrations were much higher than those observed in the atmosphere, going from 10^{11} to 10^{13} molecules cm^{-3}. In these conditions, the adduct concentration can be estimated as being 10^{12} molecules cm^{-3}. This amount is on the order of the concentration of the reagents, and this species or its decomposition product could be observed. In these situations, the steady-state approach will not be quantitatively valid, but we believe than it can provide a good estimate of the reaction behavior in these conditions.

Concerning the experimental determinations of the rate constant, in two works[19,20] this reaction was studied using the discharge-flow method and small pressures. The rate constant obtained is about 3.7 times smaller than that determined in the other two experimental investigations, which were conducted in photoreactors and atmospheric pressure.[9,12] It should be indicative of a possible pressure dependence in the rate constant related with the formation and posterior decomposition of the WBC1 adduct. Our results confirm this suggestion, since we have found that the adduct is stable and its formation is a pressure dependent reaction. However, the discrepancies verified in the low-pressure experiments are surprising. Martinez et al. have reported a qualitative detection of an adduct, but not HCl. They also identified the products of channel 2, CH_3 and CH_3SOCl, indicating that they are formed from the decomposition of the adduct, which agrees with our results. The major reaction product identified in the Riffault et al. study was HCl, followed by CH_3, in a proportion of 9 to 1. These findings are in very good agreement with our conclusions; however, the nonobservation of the adduct in this experiment is unexpected.

Nevertheless, our calculations were conducted considering $p = 1$ atm, and our main interest is to understand how this reaction occurs in the atmosphere. In this context, a comparison of our results with those reported in previous works at atmospheric pressure shows that the rate constant obtained in this work is from 1.3 to 2.1 times greater than that determined experimentally. This discrepancy corresponds to a difference of only 0.5 kcal mol^{-1} in the activation Gibbs free energy. This quantity is the uncertainty of the theoretical method. In fact, effects such as the core excitation in the heavy atoms (S and Cl) were not considered, and approximations such as additivity were used, which can justify this difference. Furthermore, under the conditions where the experimental studies were conducted, the concentration of the adduct could be sufficiently high so that the backward reaction (k_{-A}) occurs to a significant extent, where it would lead to a observed reaction rate lesser that the true one.

Regarding the experimental studies conducted at atmospheric pressures, a detailed comparison with the results of this work is not possible, since our study is limited to the first reaction step, and the experimental measurements cover several steps, but a qualitative analysis can be done. The sulfur products identified experimentally for this reaction were SO_2 and $DMSO_2$. Barnes et al.[9] have proposed that SO_2 is obtained from further reactions of CH_3SOCH_2 and that $DMSO_2$ is probably formed by reaction of the adduct with O_2. So, their conclusion is that channel 1 and the adduct formation are the main pathways in this reaction, which is in very good agreement with our findings. Falbe-Hansen et al.'s[12] findings are similar. However, it is important to note that the experimental findings reached only 56 and 36% of the products of sulfur compounds. Our calculation predicts a proportion of 98% for channel 1 and 2% for channel 2. If we consider an error of 0.5 kcal/mol in the theoretical values of $\Delta G^\ddagger$ for k_1 and k_2, which is a reasonable estimate for a calculation of this level, the proportion of channel 1 will range from 92% to 100%, which can indicate that the nonidentified quantity in experimental works should be mainly from decomposition products of the sulfur compound of channel 1, CH_3SOCH_2.

Finally, the atmospheric importance of the DMSO + Cl reaction can be evaluated comparing the lifetime of DMSO with respect to Cl and the main atmospheric oxidants, OH and NO_3. Considering an OH atmospheric concentration of 9.4×10^5 molecules cm^{-3},[30] and the rate constant as being $k_{OH} = 8.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[11] lifetime of DMSO can be determined in 3 h. For NO_3, values are $[NO_3] = 7.4 \times 10^6$ molecules cm^{-3} [31] and $k_{NO3} = 5.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1},[12] which leads to a lifetime of 3 days. For chlorine estimates, it is important to address that its atmospheric concentration deserves some doubt, going from 5×10^3 molecules cm^{-3} [32] to 1.3×10^5 molecules cm^{-3}.[16] Using the rate constant obtained in this work ($k_{Cl} = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), the lifetime will go from 19 days to 17 h. In this way, OH is the main DMSO sink, but the DMSO lifetime in relation to Cl is comparable to the one obtained for NO_3. Since DMSO is mainly produced in marine areas, where the chlorine concentration can reach higher values, we think that this reaction cannot be neglected in the atmospheric chemistry of this compound, at least until a better agreement among the several chlorine atmospheric concentration determinations is reached and the real role of the adduct backward reaction in the experimental measurements is addressed.

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