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Mechanism of the Atmospheric Reaction between the Radical CH_3SCH_2 and O_2

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In this article, the mechanism of the reaction between the atmospheric CH_3SCH_2 radical and O_2 molecule was studied using an ab initio correlated level of theory. We have performed geometry optimizations at the UMP2/6-31G(d) level of theory and used the additivity approximation to obtain the activation energy at the UCCSD(T)/6-311+G(2df,2p) level. The obtained activation energy is −3.31 kcal/mol. The $CH_3SCH_2O_2$ radical has three possible conformations, named P1, P2, and P3. However, the conformer formed in the addition reaction, P1, is not the most stable. The transition states to interconvertion between the three conformers were optimized and the rate constants for these reactions were calculated, as well as the exothermicities of each one. These values allowed us to conclude that, in the equilibrium, the distribution of these conformers will be 71% of P2 and 29% of P1. We have used this distribution to obtain a weight average to the exothermicity of the reaction between the CH_3SCH_2 radical and O_2, which is −26.19 kcal/mol. The heat of formation for the mixture of the two conformers of the $CH_3SCH_2O_2$ radical was also determined as 6.51 kcal/mol. The reaction free energy was calculated as −15.68 kcal/mol, considering that distribution.

Introduction

The natural reduced sulfur compound of greatest interest to atmospheric chemistry is dimethyl sulfide (DMS). It is produced from biodegradation of organosulfur compounds, and it was first detected in the upper levels of the oceans by Lovelock et al.[1] The DMS oxidation in the environment is directly related to the formation of sulfur aerosols, and the presence of these particles in the marine atmosphere has important environmental consequences. Sulfur aerosols are good cloud condensation nuclei (CCN), and it seems that they are responsible for cloud properties such as radiation and reflectance, which are important in the biological climate regulation.[2]

Nowadays, several studies are performed aiming to understand the mechanism and kinetics of the DMS oxidation, searching for the identification of the products and yields. However, some aspects are not understood yet, and a number of steps of important atmospheric reactions involving this species still need to be better described. Experimental studies are performed using modern techniques to generate the radicals involved in the steps of interest, such as pulsed[3,4] or laser[5] flash photolysis, pulsed radiolysis,[6] or discharge flow tube.[7] The appearance of the products or the disappearance of the reactants is monitored by absorption spectroscopy[3−6] in the UV and IR regions or using a photoionization (or quadrupole) mass spectrometer.[7] Nevertheless, the conditions to conduct the experimental measurements may lead to some restrictions and preclude the identification of some intermediates and products. In addition, parallel reactions may occur, interfering in the determination of the rate constants.

On the other hand, ab initio calculations permit the study of the reaction of interest, but a good result depends on the knowledge and investigation of all possible mechanisms. In real conditions, it is a very difficult task. Using high-level ab initio calculation, it is possible to provide the mechanism and kinetics parameters of a reaction-like rate constant and Gibbs free energy with a high degree of confidence. A high level is necessary due to the exponential characteristics of the kinetics laws. Thus, the use of large basis sets and the inclusion of the electronic correlation is essential. The main trouble in the theoretical study of the atmospheric reactions is treating the radical systems in a reliable form, because these systems have unpaired electrons, which require an open-shell methodology. The Unrestricted Hartree−Fock (UHF) methodology permits treatment of it, but it presents a limitation which is the spin contamination, i.e., the contamination of the wave function of the fundamental state by wave functions of excited states of higher multiplicities. This possibility needs to be considered in all unrestricted calculations to ensure the reliability of the result, by means of the spin contamination determination and the projection of the energy to the desired state.

Considering these factors, several atmospheric reactions and species have been studied theoretically.[8,9] In the case of the DMS chemistry, analysis of the geometry of the radicals and adducts has been performed.[10,11] We have also studied the reaction between DMS and Cl atoms,[12] and in that article, we have shown that the production of CH_3SCH_2 and HCl will be dominant in atmospheric conditions, although the formation of the DMS···Cl adduct proceeds very fast. It is due to the fact that, in the reaction of the adduct formation, the equilibrium is displaced to the reactants. The results obtained are in good agreement with the experimental measures available,[5] which show that ab initio calculations can be of valuable aid in the study of this kind of atmospheric reactions. Experimental studies of the DMS reaction with OH and NO_3 radicals also leads to the conclusion that the abstraction product is the leading process.[3,13,14]

Now, we intend to study the following step in the atmospheric fate of the DMS, which is the decomposition of the principal sulfur product of this reaction, CH_3SCH_2. To the best of our knowledge, the methylthiomethyl radical (MTM) has not been observed directly yet, which indicates that it should be very reactive, and there is a consensus that it will react mainly with O_2, which is in abundance in the atmosphere, to produce the

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methylthiylperoxi radical (MTP).[15,16]

$$CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2 \qquad (1)$$

There is an experimental work about this reaction,[6] where Wallington et al. determined the UV absorption spectra of MTM and MTP radicals by the radiolysis of SF_6/CH_3SCH_3 and $SF_6/CH_3SCH_3/O_2$ gas mixtures. And then, the experiment was made on a longer time scale (100−400 μs) and the subsequent decay of the transient UV absorption was monitored as a function of the O_2 concentration to obtain the kinetics of reaction 1. It led to the derivation of values for the lifetime of the MTM radical and for the rate constant of reaction 1. They have obtained that the MTM radical has a short lifetime of 34 ns and the rate constant of reaction 1 is $k_1 = (5.7 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Theoretical studies of the MTM radical were reported by Baker and Dyke,[17] McKee,[10] and Kuhns et al.[18] Baker and Dyke have determined the structure and the vibrational spectrum of this species in order to analyze the results obtained in a photoelectron spectroscopy experiment. Their calculations were at the MP2/6-31G(d,p)//RHF/6-31G(d,p) level of theory. The calculations done by McKee[10] were at the QCISD(T)/6-31G-(2d)//MP2/6-31+G(2d) level, and two different structures were obtained. The lowest energy structure has C_1 symmetry, and a slightly higher energy structure has C_s symmetry. Kuhns et al.[18] have used the G2(MP2) theory to calculate the adiabatic ionization energy of this radical and the enthalpy of formation of the $[CH_3SCH_2]^+$ cation. However, they have considered a structure where the methyl group is rotated about 60° with respect to the CH_2 group, in relation to the minimum energy structure already studied. So, the results do not correspond to the global minimum energy structure for this radical, but a local minimum. Another theoretical study on this system was performed by McKee,[11] but with the aim to determine the exothermicity of reaction 1 and the structure of the product, the MTP radical. The value obtained was 27.3 kcal/mol, but the mechanism was not investigated.

Our objective in this study is to obtain the transition state for this reaction, which will allow us to confirm the experimental findings already presented, and contribute to the knowledge of DMS atmospheric chemistry. In addition, we will perform a conformational analysis of the product, $CH_3SCH_2O_2$, that can be interesting to the further studies of this species.

Calculations

The calculations were performed with the Gaussian package of programs.[19] We have obtained the structure of the reactants, transition states, and the possible conformations of the product. The optimizations of the stationary points were performed at the UMP2/6-31G(d) level, and the analysis of the harmonic frequencies was also performed at this level of theory. All minimum energy structures and transition states were optimized without constraints. Single-point calculations at the UCCSD-(T) level were performed to obtain the electronic correlation in a better level. To include the effect of a larger basis set, we have used the additivity approximation,[20,21] with the UMP2 method and the 6-311+G(2df,2p) basis set. The following expression was used to calculate the energies:

$$E_{\mathrm{UCCSD(T)/6\text{-}311+G(2df,2p)}} = E_{\mathrm{UCCSD(T)/6\text{-}31G(d,p)}} + (E_{\mathrm{PUMP2/6\text{-}311+G(2df,2p)}} - E_{\mathrm{PUMP2/6\text{-}31G(d,p)}})$$

Therefore, our best result is in the UCCSD(T)/6-311+G(2df,2p) level of calculation. The spin contamination was evaluated through the S^2 value, and the projected energies were used to correct the contamination verified at the MP2 level.

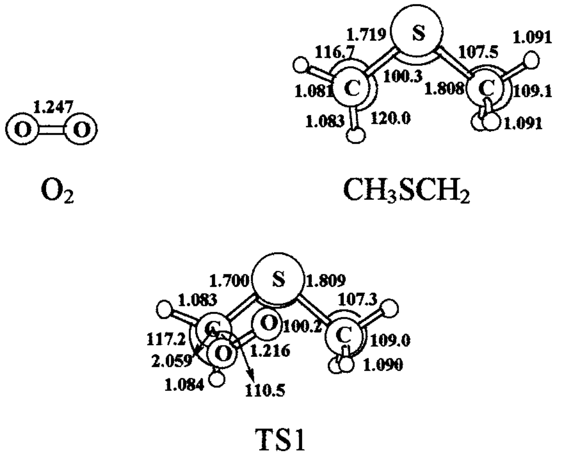

Figure 1. Structures and geometrical parameters obtained at the UMP2/6-31G(d) level of calculation for the reactants and for the transition state involved in reaction 1.

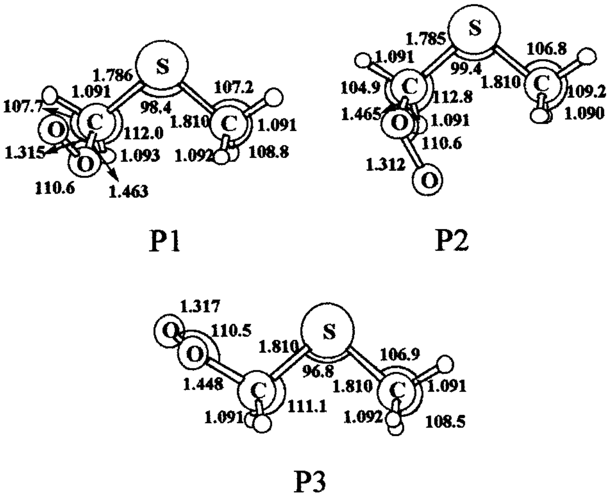

Figure 2. Structures and geometrical parameters obtained at the UMP2/6-31G(d) level of calculation for the three conformers of the $CH_3SCH_2O_2$ radical.

Results

Figure 1 shows the optimized molecular structures obtained for the reactants and the transition state, TS1. In TS1, the oxygen molecule is almost parallel to the S−C bond, which presents a partial double bound character, as was observed in our previous study.[12] Figure 2 shows the molecular structures of the three different conformations obtained for the product, the MTP radical. For structures P1 and P2, the oxygen bonded to the carbon is not in the same plane of the C−S−C atoms. The difference between the P1 and P2 conformers is in the position of the other oxygen. The other conformation is P3, where the oxygen bonded to the carbon is in the same plane of the C−S−C atoms. An IRC calculation of the TS1 species led to the identification of P1 as the first product of the reaction 1. However, P1 is not the most stable conformation for the MTP radical. So, we have found the transition states for interconvertion among the three conformations of MTP, which are shown in Figure 3. TS2 is a transition state for P1 ↔ P2

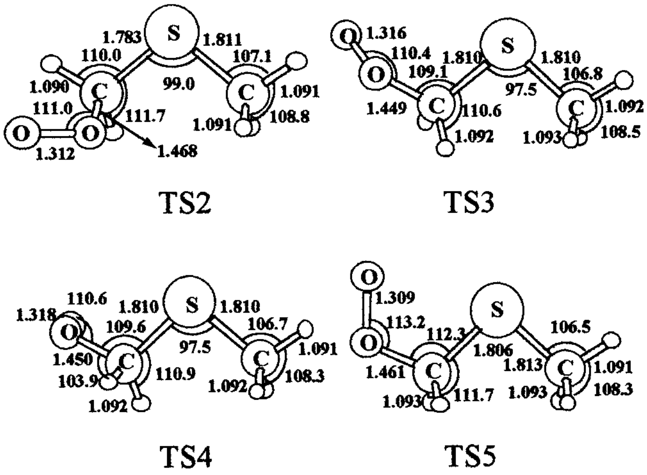

Figure 3. Structures and geometrical parameters obtained at the UMP2/6-31G(d) level of calculation for the four transition states involved in the interconvertion of the conformers of the $CH_3SCH_2O_2$ radical.

interconvertion, TS3 is a transition state for P1 ↔ P3 interconvertion, and TS4 is responsible for P2 ↔ P3 interconvertion. We have found another transition state, which is TS5. It is responsible for interconvertion of two isoenergetic forms of P3.

The values obtained for the energy, zero-point corrections (ZPE), and $\langle S^2 \rangle$ for all stationary points are reported in Table 1. The energy values and the $\langle S^2 \rangle$ values calculated after the correction of the spin contamination through the annihilation method of Löwdin[22] are also presented.

Relative energies with respect to the CH_3SCH_2 and O_2 species were evaluated using different levels of calculation and the relative contribution to the ZPE are presented in Table 2, for all stationary points obtained. In our best level of calculation, UCCSD(T)/6-311+G(2df,2p), the classical activation energy for reaction 1 is −6.34 kcal/mol, and the classical reaction energy is −29.55 kcal/mol to produce P1. The last two rows of Table 2 present the activation and reaction energies, considering the projection (ΔE−P) or not (ΔE). These values are the classical activation and reaction energies plus the zero-point energy correction (ΔZPE). The activation energy of reaction 1 is −3.31 kcal/mol, and the reaction energy is −24.64 kcal/mol in relation to P1 and −25.19 kcal/mol in relation to P2, using the projected values. As it was said before, P2 is the most stable conformation for the MTP radical.

The results obtained for the interconvertion reactions of the three MTP radical conformations are presented in Table 3. The classical activation energy barrier to interconvertion of P1 to P2 passing through TS2 is 0.81 kcal/mol, 4.02 kcal/mol for P1 → P3 interconvertion, and 4.64 kcal/mol for P2 → P3 interconvertion. Table 3 also presents the thermodynamical values, entalphy (H), entropy (S), and Gibbs energy (G). Using these values, we have calculated the activation energy (E_a), the Arrhenius factor (A), and the rate constants (k) for these three reactions by means of the transition state theory (TST).[23] The rate constants obtained for these reactions are 6.18×10^{11} s^{-1}, 2.88×10^{9} s^{-1}, and 3.57×10^{10} s^{-1}, respectively. The P1 → P2 interconvertion has an activation free energy of 1.37 kcal/mol and a reaction free energy of −0.53 kcal/mol. The corresponding values for the other two interconvertion reactions are 4.55 and 3.29 kcal/mol for P1 → P3 interconvertion and 5.30 and 3.82 kcal/mol for P2 → P3 interconvertion, respectively. These values allowed us to calculate the distribution of

TABLE 1: Energy Values (in Hartrees) and $\langle S^2 \rangle$ Values for All Stationary Points Obtained before and after the Correction for the Spin Contamination in Energy (PMP2) and in the Spin Value ($\langle S^2A \rangle$) for the Two Basis Sets Used as well as Zero-Point Energies (in kcal/mol) at the UMP2/6-31G(d) Level of Calculation

	6-31G(d)					6-311+G(2df,2p)			
basis set	MP2	S^2	PMP2	S^2A	ZPE	MP2	S^2	PMP2	S^2A
O_2	−149.949 7318	2.037	−149.955 7668	2.001	2.015	−150.100 8488	2.051	−150.108 4465	2.001
CH_3SCH_2	−476.470 257	0.765	−476.472 5569	0.75	40.111	−476.660 9346	0.771	−476.663 7948	0.75
TS1	−626.403 6054	1.488	−626.431 9051	0.826	45.158	−626.749 7514	1.498	−626.780 2028	0.852
P1	−626.454 4479	0.76	−626.456 8346	0.75	47.040	−626.800 3412	0.763	−626.803 3558	0.75
P2	−626.455 5768	0.761	−626.458 079	0.75	47.131	−626.801 5494	0.764	−626.804 7055	0.75
P3	−626.447 7804	0.76	−626.450 2041	0.75	46.958	−626.793 5471	0.763	−626.796 5909	0.75
TS2	−626.452 7088	0.761	−626.455 1659	0.75	46.866	−626.799 1013	0.764	−626.802 2714	0.75
TS3	−626.447 7605	0.76	−626.450 1978	0.75	46.935	−626.793 5081	0.764	−626.796 5705	0.75
TS4	−626.447 5988	0.76	−626.779 9861	0.75	46.947	−626.793 3366	0.763	−626.796 3346	0.75
TS5	−626.443 9594	0.761	−626.446 444	0.75	46.811	−626.790 2431	0.764	−626.793 3992	0.75

TABLE 2: Relative Energy Values (in kcal/mol) with Respect to the Reactants for the Transition State and Products Involved in the Addition Reaction of O_2 to CH_3SCH_2[e]

	TS1	P1	P2	P3	TS2	TS3	TS4	TS5
				6-31G(d)				
UMP2	10.28	−21.62	−22.33	−17.44	−20.53	−17.43	−17.33	−15.04
PMP2	−2.25	−17.89	−18.67	−13.73	−16.84	−13.73	−13.59	−11.37
ΔZPE	3.03	4.91	5.00	4.83	4.74	4.81	4.82	4.68
UCCSD	−0.29	−27.32	−27.75	−23.41	−25.99	−23.38	−23.36	−20.85
UCCSD(T)	−3.59	−27.92	−28.49	−23.89	−26.57	−23.89	−23.84	−21.56
				6-311+G(2df,2p)				
UMP2	7.55	−24.20	−24.95	−19.93	−23.42	−19.91	−19.80	−17.86
PMP2	−5.00	−19.52	−20.37	−15.28	−18.84	−15.27	−15.12	−13.28
UCCSD(T)[a]	−6.32	−30.50	−31.11	−26.38	−29.46	−26.37	−26.31	−24.38
UCCSD(T)-P[b]	−6.34	−29.55	−30.19	−25.44	−28.57	−25.43	−25.37	−23.47
ΔE[c]	−3.29	−25.59	−26.11	−21.55	−24.72	−21.56	−21.49	−19.70
ΔE-P[d]	−3.31	−24.64	−25.19	−20.61	−23.83	−20.62	−20.55	−18.79

[a] Values obtained using the additivity approximation. [b] Same as in footnote *a* using the projected values. [c] Activation (and reaction) energy, which corresponds to the classical activation (and reaction) energy plus the ZPE contribution. [d] Same as in footnote *c* using the projected values. [e] The optimization was performed at the UMP2/6-31G(d) level of calculation.

TABLE 3: Kinetics (in s^{-1}) and Activation and Reaction (in kcal/mol, Standard State of 1 atm) Thermodynamic Parameters, Calculated for the Interconvertion Reaction of $CH_3CH_2O_2$ for the Three Conformers at the UCCSD(T)/6-311+G(2df,2p) Level, Using the Projected Values (T = 298.15 kcal/mol)

	E	$E + \Delta$ZPE	$\Delta H°$	$\Delta G°$	$-T\Delta S°$	E_a	A	k
TS2[a]	0.98	0.81	0.37	1.37	1.00	0.96	3.12×10^{12}	6.18×10^{11}
P1 → P2	−0.64	−0.55	−0.56	−0.53	0.029			
TS3[a]	4.12	4.02	3.59	4.55	0.96	4.18	3.34×10^{12}	2.88×10^{9}
P1 → P3	4.11	4.03	4.16	3.29	−0.87			
TS4[b]	4.82	4.64	4.18	5.30	1.12	4.77	1.12×10^{14}	3.57×10^{10}
P2 → P3	4.75	4.58	4.72	3.82	−0.90			

[a] Relative energies and thermodynamical values with respect to P1. [b] Relative energies and thermodynamical values with respect to P2.

TABLE 4: Reaction (in kcal/mol, Standard State of 1 atm) Thermodynamic Parameters, Calculated for the Addition Reaction of O_2 to the CH_3SCH_2 at the UCCSD(T)/6-311+G(2df,2p) Level (T = 298.15 kcal/mol)

values	P1	P2
$\Delta H°$	−25.79	−26.35
$-T\Delta S°$	10.84	10.87
$\Delta G°$[a]	−14.95	−15.48
effective $\Delta H°$[b]	−26.19	
effective $\Delta G°$[c]	−15.68	

[a] Considering the existence of two structures in each product which are mirror images. [b] Weight average of the results for P1 and P2 (see text for definition). [c] Considering the distribution of the two conformers in the equilibrium.

these three conformers at equilibrium, using the following equations:

$$\frac{N_2}{N_1} = e^{-\Delta G_{21}/RT}$$

$$\frac{N_3}{N_1} = e^{-\Delta G_{31}/RT}$$

$$N_1 + N_2 + N_3 = 1$$

where N_1, N_2, and N_3 are respectively the amount of P1, P2, and P3 conformers, and ΔG_{21} and ΔG_{31} are the reaction free energies for 1 → 2 and 1 → 3 interconvertions, respectively. We have found that 71% of the product will be in the form of the most stable conformer, P2, while 29% will be in the form of the P1 conformer. Although the rate constant for the P3 conformer formation was found to be very large, $\Delta G°$ is positive, 3.29 kcal/mol, and the conformer P3 will not be present in the equilibrium.

Table 4 presents the reaction thermodynamic results calculated at 298.15 K for reaction 1, such as the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) variations and the reaction Gibbs energies ($\Delta G°$, standard state of 1 atm). The reaction free energies for the two products which will be present in the equilibrium are also shown, as well as the variation of the enthalpy. These values for reaction free energy are −15.71 kcal/mol for the product P1 and −16.24 kcal/mol for the product P2, while the respective values for exothermicities are −25.79 and −26.35 kcal/mol. We can use the calculated proportion of 71% for product P2 and 29% for product P1 to obtain a more accurate value for the exothermicity of this reaction by means of a weight averaged value,

$$\Delta H°_{\mathrm{eff}} = \frac{N_1 \Delta H°_1 + N_2 \Delta H°_2}{(N_1 + N_2)}$$

Thus, the effective enthalpy variation for reaction 1 is −26.19 kcal/mol. An effective reaction free energy also was calculated considering the distribution of the products, and the value obtained is −15.68 kcal/mol. These data are also shown in Table 4.

We have also calculated the $\Delta H_f°$ of the MTP radical at 298.15 K, using the value of the heat of formation of the MTM radical obtained by Jefferson et al.[24] In a temperature-dependent kinetic study of the reaction of hydrogen abstraction of Br from dimethyl sulfide, they have determined that the $\Delta H_f°$ (CH_3SCH_2) is 32.7 kcal/mol. Considering the existence of the two conformers in the equilibrium, we have calculated the heat of formation of the MTP radical as 6.51 kcal/mol.

Discussion

According to our calculations and the experimental measures of Wallington et al., the oxygen molecule can add to the CH_3SCH_2 radical, generating the methylthiylperoxi radical, $CH_3SCH_2O_2$. This adduct can present three spatial conformations near in stability, which can interconvert easily. The conformation of the product that is obtained in the reaction is not the most stable, but it can be interconverted into the most stable through a classical energy barrier of 0.81 kcal/mol.

The value obtained for the activation energy in our best level of calculation is negative, −3.31 kcal/mol. Although this negative value is in qualitative agreement with the experimental findings of a high rate constant for this reaction, the determination of the rate constant would require the use of the variational transition state theory. This approach requires knowledge of the potential energy surface along the reaction path. However, at the UMP2 level, the spin contamination is significant in the dissociative region of the potential energy surface, and thus such treatment would require a higher level of theory which is beyond of our computational resources at the moment.

Considering the three possible conformers of the product, MTP radical, only P3 cannot be formed directly from TS1. Although P2 is the most stable isomer, an IRC calculation showed that the reaction would lead initially to the P1 conformer. The calculated rate constants for interconvertion show that these reactions will occur on the scale of picoseconds. However, the calculation of the reaction free energies for the interconvertion reactions led to results which allowed us to determine that, at equilibrium, there will be 71% of the P2 conformer and 29% of the P1 conformer. These results were used to obtain the exothermicity of reaction 1 as a weight average. In addition, it has led to the calculation of an effective reaction free energy.

In the calculations of McKee, only one conformation for the MTP radical was reported which is a minimum energy structure. The conformation presented is the P2 conformer obtained by us. McKee has also obtained a transition state that is our TS5. McKee's study of the exothermicity of the reaction 1, at the QCISD(T)/6-31+G(2df,p)//MP2/6-31G(d) level of calculation, led to a value of 27.3 kcal/mol. It can be compared with our value for the same product, P2, which is 27.27 kcal/mol at the CCSD(T)/6-311+G(2df,2p)//UMP2/6-31G(d) level of theory without the projection of the energy. It can be seen that the two values are in excellent agreement. However, it is important to remember that the first product for this reaction is P1, and at equilibrium, there will be a mixture of P2 and P1 conformers. Taking these factors into account, the exothermicity of reaction 1 will be 26.19 kcal/mol. The heat of formation calculated by us for the MTP radical is 6.51 kcal/mol, and it can be compared with the result of 5.9 kcal/mol obtained by McKee using an isodesmic reaction and standard heats of formation from the literature. The two values are in good agreement.

Conclusions

In this work, we have studied the reaction between the atmospheric radical CH_3SCH_2 and the O_2 molecule at the UCCSD(T)/6-311+G(2df,2p)//UMP2/6-31G(d) level of theory. According to our results, the mechanism is bimolecular, and we have found a transition state for this reaction. However, the negative activation energy found and the high spin contamination at the transition state precluded us from calculating the rate constant for this reaction at the moment. In addition, we have calculated the exothermicity of this reaction. We found three conformational structures for the MTP radical, and the calculation of the kinetics of the interconvertion shows that the three reactions are very fast. We also determined the distribution of these conformers in the equilibrium as 71% of the conformer P2 and 29% of the conformer P1. These results were used to determine a weight average value of 26.19 kcal/mol for the exothermicity of reaction 1. The reaction free energy was also calculated considering this distribution, and the value obtained is -15.68 kcal/mol. The heat of formation of the product was estimated as 6.51 kcal/mol. These results show that high-level ab initio calculations may be used to identify the mechanism of atmospheric reactions and can provide useful information, such as the mechanism, the structure of the transition state, and the conformational equilibrium of the products.

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