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A quantum chemical calculation of the potential energy surface in the formation of $HOSO_2$ from OH + SO_2

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ABSTRACT

The formation of $HOSO_2$ from OH and SO_2 has been thoroughly investigated using several different methods (MP2=Full, MP2=FC, B3LYP, HF and composite G* methods) and basis sets (6–31G(d,p), 6–31++G(d,p), 6–31++G(2d,2p), 6–31++G(2df,2p) and aug-cc-pVnZ). We have found two different possible transition state structures, one of which is a true transition state since it has a higher energy than the reactants and products (MP2=Full, MP2=FC and HF), while the other is not a true transition state since it has an energy which lies between that of the reactants and products (B3LYP and B3LYP based methods). The transition state structure (from MP2) has a twist angle of the OH fragment relative to the SO bond of the SO_2 fragment of −50.0°, whereas this angle is 26.7° in the product molecule. Examination of the displacement vectors confirms that this is a true transition state structure. The MP2=Full method with a larger basis set (MP2=Full/6–31++G(2df,2p)) predicts the enthalpy of reaction to be −112.8 kJ mol^{-1} which is close to the experimental value of −113.3 ± 6 kJ mol^{-1}, and predicts a rather high barrier of 20.0 kJ mol^{-1}. When the TS structure obtained by the MP2 method is used as the input for calculating the energetics using the QCISD/6–31++G(2df,2p) method, a barrier of 4.1 kJ mol^{-1} is obtained (ZPE corrected). The rate constant calculated from this barrier is 1.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. We conclude that while the MP2 methods correctly predict the TS from a structural point of view, higher level energy corrections are needed for estimation of exact barrier height.

1. Introduction

It is well established that SO_2 is oxidized in the troposphere in a multiple step pathway to sulfuric acid, H_2SO_4, which is the main constituent in acid rain and it contributes to visibility reduction and climate modification (Calvert and Stockwell, 1984; Berresheim et al., 1995). The first step in the process as proposed by Calvert and Stockwell (1984) is the oxidation of SO_2 which is initiated by OH, to form the $HOSO_2$ radical (Calvert et al., 1985, 1978; Margitan, 1984; Stockwell and Calvert, 1983); it is also the rate determining step (Kuo et al., 1991).

$$OH + SO_2 \rightarrow HOSO_2 \quad (1)$$

A lot of attention has been devoted to the kinetics of reaction (1), both experimentally and theoretically (Margitan, 1984; Harris and Wayne, 1975; Castleman and Tang, 1977; Leu, 1982; Martin et al., 1986; Lee et al., 1990; Atkinson et al., 1976; Paraskevopoulos et al., 1983; Davis et al., 1979; Cox and Sheppard, 1980; Izumi et al., 1984; Leung et al., 2001). From a thermodynamic point of view, the presence of a barrier in the transformation potential energy surface (PES) plays a significant role in the kinetics and thus an accurate knowledge of the energetics of the barrier is crucial. The experimental work of Wine et al. (1984), suggests a barrierless PES based on their K_1^{∞} measurement. It should be noted that they report a slight decrease in K_1^{∞} with temperature. On the contrary the experimentally determined K_1^{∞} of Fulle et al. (1999) which was measured over a range of 1–96 bar, increases with increasing temperature, indicating the presence of a barrier in the PES of the OH and SO_2 reaction. The PES of reaction (1) has been explored computationally by Li and McKee (1997), using the G2 level of theory, and by Somnitz (2004) who performed the calculations with the G3X level of theory using the geometry obtained from two model chemistries, viz., UQCISD(T)/6–311G(d,p) and UB3LYP/aug-cc-PVTZ+1 (Augmented triple zeta Dunning correlation consistent basis set enlarged by an additional hard d-function on the sulfur

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atom). The values reported by these authors for the enthalpy of reaction [−109.6 kJ mol^{-1} by Li and McKee (1997) and −109.3 kJ mol^{-1} by Somnitz (2004)] agree well with the experimental enthalpy of the reaction, viz. −113.3 ± 6 kJ mol^{-1} at 298 K (Blitz et al., 2003). Li and McKee (1997) were not able to locate a true transition state (the transition state (TS) was more stable energetically than the reactant), whereas Somnitz (2004) located barriers at 0.5 and 3.0 kJ mol^{-1} higher than the reactant, using UQCISD(T) and UB3LYP geometries respectively, in G3X theory. In recent work, Glowacki et al. (2009) have carried out a relaxed PES scan along the HO−SO_2 bond, using UB3LYP/aug-cc-PVQZ level of theory, and have shown that a barrier of 0.8 kJ mol^{-1} may occur at a separation of ~2.6 Å between the HO and SO_2 units. Their attempt to locate the transition state in this region was also not successful and was attributed to the extremely slight curvature of the PES.

Thus there are conflicting views not only in the experimental data but also in the computational results, as to whether reaction (1) has a barrier, or is barrierless. In this work we have carried out extensive quantum chemical calculations using various methodologies to try and locate a true TS. We have also studied the nature of the orbital interaction in the TS structure and examined the geometry of the TS.

2. Computational methods

All the calculations are carried out using Gaussian 03 (Frisch et al., 2004). Using the optimized geometries, frequency and thermochemistry calculations were carried out at a temperature of 298.15 K and a pressure of 1 atm. For the study we have used four different methods, viz., HF, MP2=FC, MP2=FULL and B3LYP. For the closed shell species, SO_2, the spin restricted approach was employed and for all open shell species, spin unrestricted approaches were used. For the MP2=FC approach only the valence electrons were considered and for the MP2=Full method all the electrons were taken into account during the calculations. For each methodology investigations were carried out in combination with various basis sets. In addition to this we have carried out calculations using various composite methods, namely G1, G2, G2MP2, G3, G3MP2, G3B3 and G3MP2B3 methodologies.

Thermodynamic quantities like, ΔH_R, ΔG_R and the activation barriers (E^a and E^b are the activation energies for forward and reverse reactions) are calculated from the energies of the reactants, product and transition states, using the equations as shown below.

$$\Delta H_R = \Delta H_{PRODUCT} - \Delta H_{REACTANTS} \quad (1)$$

$$\Delta G_R = \Delta G_{PRODUCT} - \Delta G_{REACTANTS} \quad (2)$$

$$\Delta E_R = \Delta E_{PRODUCT} - \Delta E_{REACTANTS} \quad (3)$$

$$E^a = \Delta E_{TS} - \Delta E_{REACTANTS} \quad (4)$$

$$E^b = \Delta E_{TS} - \Delta E_{PRODUCT} \quad (5)$$

We have calculated the rate constants of the OH + SO_2 forward reaction using the transition state theory based RRKM method, implemented in the "Virtual Kinetic Laboratory" software available at Computational Science and Engineering Online (http://cse-online.net/) (Zhang and Truong, 2001).

3. Results and discussion

3.1. Reactants and product

The two reactants in reaction (1) are OH and SO_2 and the product is $HOSO_2$. Both the reactants are neutral in nature with the reactant OH having radical characteristics. The neutral product, $HOSO_2$, is also radical in nature. The methodologies used during minimization were UMP2 for OH and $HOSO_2$, and RMP2 for SO_2. The MP2=Full/6−31++G(2df,2p) optimized structure and geometric parameters of the reactants and product are shown in Fig. 1. The OH radical is in $C_{\infty v}$ symmetry (linear) and has a doublet $^2\Sigma$ state. The O−H bond distance is 0.967 Å. The stable neutral SO_2 is C_{2v} symmetric and is in a singlet $^1A_1$ state. The structure of the SO_2 is planar and bent; the O−S−O angle is 119.4° with S−O bond length of 1.452 Å. Analysis of the vectorial dipole components of both the reactant molecules shows that the dipole vectors of both the molecules have the largest magnitude in the z-direction. For OH, μ_z is −1.81 D, whereas for SO_2, μ_z is +2.13 D. Spin density analysis of the OH shows that, the total spin of the one unpaired α-electron resides on the O-atom. Note that, there is very little spin contamination found in the optimization of the OH radical. Detailed PES analysis of $HOSO_2$ shows that, the molecule is a doublet in the ground state with gauche conformation (state ^2A) and C_1 symmetry (note that, there is very little spin contamination found in the optimization of the $HOSO_2$ radical). This is in agreement with the results of Li and McKee (1997), but the optimized geometric parameters of the molecule differ slightly from their report and the report of Somnitz (2004). The O−S bond that is formed with the approach of the reactant OH towards the SO_2 is important. This bond distance (R_{23}) is found to be 1.618 Å and our value deviates slightly from the values given by Somnitz (2004) [R_{23} = 1.630 Å] and Li and McKee (1997) [R_{23} = 1.650 Å]. Analyzing the D_{1234}, which is 26.7°, the molecule can be assumed to have a gauche type of conformation. Analyzing D_{2345}, it can be seen that, there is a pyramidal type of structural arrangement of the three O-atoms around the S-atom. Analysis of the spin density shows that, the spin density on the OH fragment is largely reduced and the maximum spin density is accumulated on the SO_2 fragment (distributed over the S-atom and O-atoms). This clearly shows almost complete spin

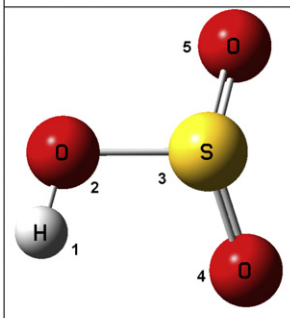
Structure/Formula	Optimized Geometric Parameters
OH	R_{O-H} = 0.967 Å
SO_2	R_{S-O} = 1.452 Å A_{O-S-O} = 119.4°
	R_{12} = 0.970 Å, R_{23} = 1.618 Å, R_{34} = 1.448 Å, R_{35} = 1.439 Å, A_{123} = 107.0°, A_{234} = 108.2°, A_{235} = 105.6°, A_{435} = 124.1°, D_{1234} = 26.7°, D_{1235} = 161.5°, D_{2345} = 124.3°

Fig. 1. MP2=Full/6−31++G(2df,2p) optimized molecular structural parameters of the OH, SO_2 and $HOSO_2$.