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# *Theoretical Investigation of Temperature Effect on the Formation of Sulphuric Acid Rain*

**Koray SAYIN[1], Duran KARAKAŞ**

Cumhuriyet University, Science Faculty, Chemistry Department, 58140 Sivas / Turkey

**Abstract:** The acid rain is a major problem for life and environment. Mainly, acid rain consists from sulfuric acid and nitric acid. There are five successive reaction for the formation of sulfuric acid. All reactions have been investigated experimentally but some properties of them have not been defined clearly. In this study, mechanisms of each reaction were predicted. The temperature effect on activation energy, equilibrium constant and rate constant were investigated for each reaction. The effect of global warming on the formation of sulphuric acid rain was discussed.

***Keywords:*** *Acid rain, Sulfuric acid, Atmospheric reactions, Theoretical study, Global warming*

## 1. Introduction

Acid rain has a special importance since time immemorial and has been recognized as a threat to the environment. Acid rains are influenced from atmospheric acidic pollution [1-3] meteorology [4-6], topographic structure [7-10] and geographic position [11-12]. Acid rain is consisted from some compounds and these compounds spread with human activities such as using car, fossil fuels etc. These compounds are sulphur dioxide ($SO_2$), nitrogen oxides ($NO_x$), ammonia ($NH_3$), carbon monoxide (CO), carbon dioxide ($CO_2$), black carbon (BC) and particulate organic matter (POM) [3, 13-17]. Although these compounds spread with human activities and effect the life of the world such as soil, lakes, plants, animals, buildings and cultural heritages. Composition of acid rain is generally formed from $SO_2$ and $NO_x$. The five-successive reaction for the formation of sulfuric acid was given as following:

$$S + O_2 \rightarrow SO + O \tag{1}$$

$$SO + O_2 \rightarrow SO_2 + O \tag{2}$$

$$HO\cdot + SO_2 + N_2 \rightarrow HOSO_2\cdot + N_2 \tag{3}$$

$$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3 \tag{4}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{5}$$

Different studies for each reaction have been made to determine the rate constant value. For the reaction **(1)**, rate constant (k) is equal to $2.1\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [18]. This value is average of previous reported values [19-23]. It was reported that a small decrease in rate constant was occurred with increasing temperature [23]. As for the reaction **(2)**, different rate constant values were given [24, 25]. The rate constant value is reported as $7.6\times10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [18]. For reaction **(3)**, rate constant values were determined in low and high pressure [26]. The rate constant value is equal to $4.1\times10^{-31}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [18]. OH radical does not react with $SO_2$ in the presence of NO and $O_2$ [27, 28]. But $HOSO_2$ radical forms as a result of reaction **(3)**. After the reaction **(3)**, $HOSO_2$ radical reacts with oxygen gas and transforms to $SO_3$ as a result of reaction **(4)**. The studies on reaction **(4)** have been made to determine the rate constant value [29, 30]. For this reaction rate, constant value was found as $4.1\times10^{-13}$ $cm^3$

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[1] Corresponding Author

e-mail: krysayin@gmail.com and ksayin@cumhuriyet.edu.tr molecule$^{-1}$ s$^{-1}$ at 298 K [18]. As for the reaction **(5)**, rate constant value is less than 6x10$^{-15}$ cm$^{3}$ molecule$^{-1}$ s$^{-1}$ at 298 K [18]. At different temperatures, rate constant values are not known except for reaction **(1)**. In this study, we investigated reaction mechanisms and the temperature effect on the rate constant and the equilibrium constant in the range of 273.15 – 323.15 K for each reaction.

## 2. Computational Method

The input files of the atoms and molecules were prepared with GaussView 5.0.8 [31]. The ground state multiplicity was taken into account for all atoms and molecules. Calculations were made using Gaussian 09 AML64L-Revision-C.01 [32] by the Hartree-Fock (HF) method with 6-311++G(d,p) basis set. 6-311++G(d,p) is the standard and high angular momentum basis set which adds p functions to hydrogen atoms and d functions on heavy atoms. In the first step, the geometries of all reactants and products were fully optimized at the HF/6-311++G(d,p) level. In the second step, the transition states for each reaction were investigated at same level. The transition state (TS) method was used to search for the transition states of all reaction paths [33, 34]. The analyses of vibrational frequencies indicated that optimized structures of reactants and products were at stationary points corresponding to local minima without imaginary frequencies. For transition states, the imaginary frequencies were found. All calculations were performed at 273.15, 283.15, 293.15, 298.15, 303.15, 313.15 and 323.15 K. For each reaction, activation energies ($E_a$), reaction enthalpies ($\Delta H$) and Gibbs free energies ($\Delta G$) were calculated by using Eq. (1), (2) and (3), respectively.

$$E_a = E_{TS} - E_{Reactant} \tag{1}$$

$$\Delta H_{Reaction} = \sum n\Delta H_{Products} - \sum n\Delta H_{Reactants} \tag{2}$$

$$\Delta G_{Reaction} = \sum n\Delta G_{Products} - \sum n\Delta G_{Reactants} \tag{3}$$

Eq. (5), derived from Eq. (4), was used to calculate the equilibrium constants [35].

$$\Delta G^\circ = -RT\ln K \tag{4}$$

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

where $K$ is the equilibrium constant, R is ideal gas constant and T is temperature (K). The rate constants of reactions were calculated with Eq. (7) which is derived from Eq. (6) [35]:

$$\ln k = \frac{-E_a}{RT} + \ln A \tag{6}$$

$$\ln k_1 - \ln k_2 = \left(\frac{Ea_2}{RT_2}\right) - \left(\frac{Ea_1}{RT_1}\right) \tag{7}$$

where $k$ is the rate constant and $A$ is frequency factor.

## 3. Results and Discussion

### 3.1. Reaction Mechanism and Thermo-Chemical Parameters

The mentioned reactions have been investigated experimentally. But there are not theoretical studies about the mechanism of reactions. In this study, theoretical calculations were performed to explain reaction mechanism. The optimized structures of reactants, products, transition states (TS) and imaginary frequencies (IF) were obtained at HF/6-311++G(d,p) level. The results were presented in Fig. 1.

For reaction **(1)**, the optimized structures of reactants and products were obtained. The structure of transition state between reactant and product was investigated and IF value transition state is -1060.9 cm$^{-1}$. Negative frequency is a criterion for determining the transition state. Transition states for each reaction were found in the same way. IF values are -1030.61, -113.61, -1706.97 and -2184.98 cm$^{-1}$ for reaction **(2)**, **(3)**, **(4)** and **(5)**, respectively. The thermo-chemical parameters provide important information about the reactions. selected parameters were listed in Table 1. Activation energies ($E_A$), reaction enthalpies ($\Delta$H) and reaction Gibbs free energies ($\Delta$G) were calculated by using Eq. (1), (2) and (3).

As can be seen from reaction enthalpies, $\Delta$H values for reaction **(1)**, **(2)** and **(5)** are negative. This result means that these reactions are exothermic under the standard conditions. For reaction **(3)** and **(4)**, the $\Delta$H values are zero and positive, respectively. Reaction **(4)** is endothermic. Gibbs free energy values for the reaction **(1)**, **(2)**, **(3)** and **(5)** are negative while $\Delta$G for the reaction **(4)** is positive value. $\Delta$G values for reaction **(3)**, **(4)** and

**(5)** are almost near to zero. According the ΔG values, the direction of reaction **(1)**, **(2)**, **(3)** and **(5)** is spontaneous to product while the direction of reaction **(4)** is spontaneous to reactant under the standard conditions.

**Table 1.** Some calculated thermo-chemical parameters at 298.15 K for reactions

| Reactions | $E_a$ (kJ mol$^{-1}$) | ΔH (kJ mol$^{-1}$) | ΔG (kJ mol$^{-1}$) |
|---|---|---|---|
| **(1)** | 15.34 | -186.14 | -186.20 |
| **(2)** | 25.43 | -141.32 | -156.19 |
| **(3)** | 6.06 | 0.00 | -0.08 |
| **(4)** | 115.711 | 38.57 | 23.10 |
| **(5)** | 141.63 | -106.72 | -3.17 |

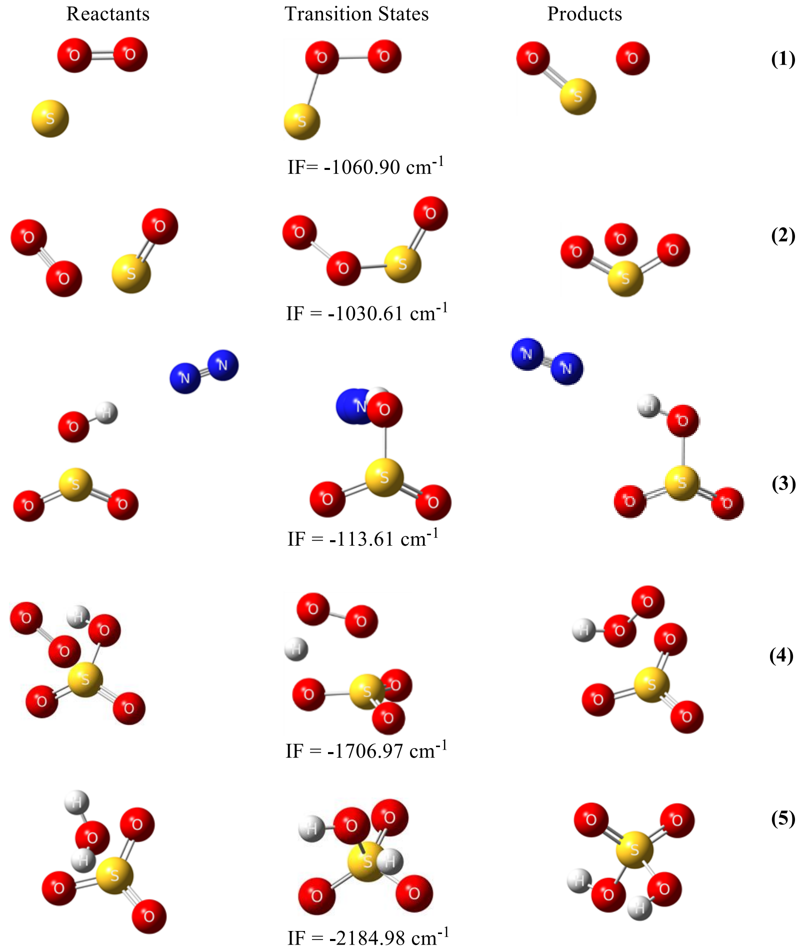

**Fig. 1.** Reaction mechanism of sulphuric acid formation.

### 3.2. The Equilibrium Constants

For all reactions, the temperature effect on the equilibrium constant was not investigated before that. Firstly, the theoretical equilibrium constant was calculated at 298.15 K and 1 atm. After that, the theoretical equilibrium constants at different temperatures were calculated by using the Eq. (5). The equilibrium constant of reactions was presented in Table 2.

According to the Table 2, the equilibrium constants generally decrease with the increasing in temperature. The equilibrium constant values of reaction **(1)** and **(2)** are higher than others. These results show that the directions of reactions are more tendency to products than reaction **(3)**, **(4)** and **(5)**. These reactions are thermodynamically stable. Their equilibrium constant decreases with increasing temperature. According to equilibrium constant of reaction **(1)** and **(2)**, it can be said that all the reactants transform to products. For reaction **(3)**, the equilibrium constant is same value as 1.03 at different temperature. The equilibrium constant of reaction **(4)** increases with increasing temperature. The direction of reaction **(4)** is spontaneous to reactants. For reaction **(5)**, the equilibrium constant decreases with increasing temperature. Tendency to form products decreases with the increasing of temperature. Reaction **(3)** and **(5)** are almost thermodynamically stable while reaction **(4)** is unstable. Reaction **(4)** determines the formation of sulphuric acid because of its lower equilibrium constant. The formation of sulphuric acid increases slightly with increasing temperature. There is a direct correlation between global warming and the formation of sulphuric acid rain.

**Table 2.** The equilibrium constants at different temperatures for each reaction

| Temperature (K) | Reactions | | | | |
|---|---|---|---|---|---|
| | (1) | (2) | (3) | (4) | (5) |
| 273.15 | $4.04\text{x}10^{35}$ | $4.27\text{x}10^{29}$ | 1.03 | $2.16\text{x}10^{-5}$ | 184.9 |
| 283.15 | $2.23\text{x}10^{34}$ | $4.74\text{x}10^{28}$ | 1.03 | $3.93\text{x}10^{-5}$ | 35.17 |
| 293.15 | $1.50\text{x}10^{33}$ | $6.12\text{x}10^{27}$ | 1.03 | $6.87\text{x}10^{-5}$ | 7.49 |
| 303.15 | $1.21\text{x}10^{32}$ | $9.04\text{x}10^{26}$ | 1.03 | $1.16\text{x}10^{-4}$ | 1.77 |
| 313.15 | $1.14\text{x}10^{31}$ | $1.51\text{x}10^{26}$ | 1.03 | $1.89\text{x}10^{-4}$ | 0.46 |
| 323.15 | $1.25\text{x}10^{30}$ | $2.81\text{x}10^{25}$ | 1.03 | $2.99\text{x}10^{-4}$ | 0.13 |

### 3.3. The temperature effect on activation energies and the rate constants

Activation energy is an important parameter for the reactions. For mentioned reactions, activation energies were presented in Table 1 at 298.15 K. The activation energies at different temperature were calculated for each reaction. The temperature effect on activation energies was represented graphically in Fig. 2.

According to Figure 2, activation energies of reaction **(1)**, **(3)** and **(4)** generally decrease with increasing temperature. For reaction **(2)**, there is a fluctuation with the increasing of temperature. Activation energy is higher at 293.15 and 323.15 K while activation energies are mainly equal for other temperatures. The lastly, the activation energy of reaction **(5)** increases properly with the increasing of temperature.

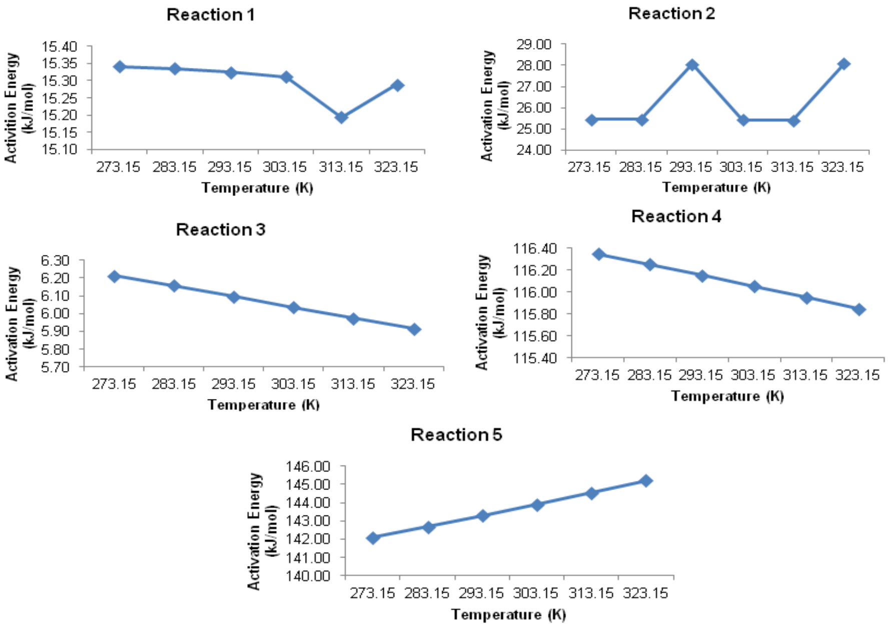

**Figure 2.** Graph of temperature versus activation energy for sulphuric acid formation reactions.

The rate constants at different temperatures were not investigated theoretically before that. At 298.15 K, the experimental rate constants are $2.1\times10^{-17}$, $7.6\times10^{-17}$, $4\times10^{-31}$, $4.3\times10^{-13}$ and $6\times10^{-15}$ for reaction **(1)**, **(2)**, **(3)**, **(4)** and **(5)**, respectively. The rate constants at different temperature were calculated by using Eq. (7). In this equation, $k_1$ is experimental rate constant. Results were listed in Table 3 and rate constants of mentioned reactions generally increase with increasing temperature. These rate constants are small value. Therefore, the mentioned reactions are stable kinetically. Rate determining step is reaction **(3)** according to rate constants. Taken into account the rate constant of reaction **(3)**, it can be said that the formation of sulphuric acid rain increases with global warming.

**Table 3.** Rate constants ($cm^3$ $molecule^{-1}$ $s^{-1}$) at different temperature for each reaction.

| Temperature (K) | Reactions | | | | |
|---|---|---|---|---|---|
| | **(1)** | **(2)** | **(3)** | **(4)** | **(5)** |
| 273.15 | $1.86\times10^{-17}$ | $7.2\times10^{-17}$ | $3.93\times10^{-31}$ | $3.35\times10^{-13}$ | $4.40\times10^{-15}$ |
| 283.15 | $1.89\times10^{-17}$ | $7.4\times10^{-17}$ | $3.96\times10^{-31}$ | $3.72\times10^{-13}$ | $4.90\times10^{-15}$ |
| 293.15 | $1.91\times10^{-17}$ | $7.5\times10^{-17}$ | $3.99\times10^{-31}$ | $4.10\times10^{-13}$ | $5.50\times10^{-15}$ |
| 303.15 | $1.94\times10^{-17}$ | $7.7\times10^{-17}$ | $4.01\times10^{-31}$ | $4.58\times10^{-13}$ | $6.00\times10^{-15}$ |
| 313.15 | $1.96\times10^{-17}$ | $7.8\times10^{-17}$ | $4.03\times10^{-31}$ | $4.90\times10^{-13}$ | $6.60\times10^{-15}$ |
| 323.15 | $1.98\times10^{-17}$ | $7.5\times10^{-17}$ | $4.06\times10^{-31}$ | $5.32\times10^{-13}$ | $7.20\times10^{-15}$ |

## 4. Conclusion

The formation of sulphuric acid, reaction mechanisms, temperature effect on some thermo-chemical parameters which are activation energies, rate constants and equilibrium constants were investigated theoretically. Transition states for each reaction and imaginary frequencies were found. The reaction enhalpies, Gibbs free energies and the activation energies of each reaction were calculated. Equilibrium constant of reaction **(4)** was obtained smaller than other steps. Its value increases with temperature. The results showed that reaction **(4)** was found as thermodynamically unstable. Rate constant of mentioned reactions were calculated and were found to increase with temperature. Rate determining step was found as reaction **(3)**. According to equilibrium and rate constants, formation of sulphuric acid was found to increase with temperature. The results indicated that sulphuric acid rain increases with global warming.

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